Nanostructured titanium dioxide as novel electrodes for water/wastewater treatment

Amir Ahmadi

Follow this and additional works at: https://louis.uah.edu/uah-dissertations

Recommended Citation
https://louis.uah.edu/uah-dissertations/200

This Dissertation is brought to you for free and open access by the UAH Electronic Theses and Dissertations at LOUIS. It has been accepted for inclusion in Dissertations by an authorized administrator of LOUIS.
NANOSTRUCTURED TITANIUM DIOXIDE AS
NOVEL ELECTRODES FOR
WATER/WASTEWATER TREATMENT

by

Amir Ahmadi

A DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in
The Joint Civil Engineering Program of
The University of Alabama in Huntsville
The University of Alabama at Birmingham
to
The School of Graduate Studies
of
The University of Alabama in Huntsville

HUNTSVILLE, ALABAMA

2020
In presenting this dissertation in partial fulfillment of the requirements for a doctoral degree from The University of Alabama in Huntsville, I agree that permission for extensive copying for scholarly purposes may be granted by my advisor or, in his/her absence, by the Chair of the Department or the Dean of the School of Graduate Studies. It is also understood that due to recognition shall be given to me and to The University of Alabama in Huntsville in any scholarly use which may be made of any material in this dissertation.

[Signature]

4/10/2020

(date)
Submitted by Amir Ahmadi in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Civil Engineering and accepted on behalf of the Faculty of the School of Graduates Studies by the dissertation committee.

We, the undersigned members of the Graduate Faculty of The University of Alabama in Huntsville, certify that we have advised and/or supervised the candidate on the work described in this dissertation. We further certify that we have reviewed the dissertation manuscript and approved it in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Civil Engineering.

Tingting Wu
Committee Chair
(Date)

Guangsheng Zhang
(Apr. 11, 2020)

Robert Peters

Ashraf Al-Hamdan
Department Chair

Shankar Mahalingam
College Dean

David Berkowitz
Graduate Dean
ABSTRACT
The School of Graduate Studies
The University of Alabama in Huntsville

Degree Doctor of Philosophy
College/Depart. Engineering / Civil and Environmental Engineering

Name of Candidate Amir Ahmadi

Title Nanostructured titanium dioxide as novel electrodes for water/wastewater treatment

Electrochemical redox processes have emerged as a viable option for water and wastewater treatment as they offer several advantages such as capable of degrading a wide range of contaminants, small footprint, capability to adjust to influent fluctuation, and less waste generation. In electrochemical treatment applications, the electrode material largely determines the efficiency of the treatment processes. However, electrodes commonly used for water treatment may either suffer low reactivity and/or stability (e.g. metal and mixed metal oxides such as SnO₂, PbO₂, IrO₂, RuO₂, and IrO₂/RuO₂ electrodes) or be subject to limited applications due to high cost and the scarcity of the materials (e.g. Pd, Pt, Boron Doped Diamond (BDD), and Au). Therefore, efficient, inexpensive, and stable electrode materials are the key to viable electrochemical treatment systems. Titanium dioxide (TiO₂) have been studied for many environmental applications specifically photocatalysis owing to their outstanding properties such as strong photoreactivity, superhydrophilicity, chemical stability, nontoxicity, and low cost. However, TiO₂ as a semiconductor material has intrinsically low electrical conductivity and electrocatalytic activity. Therefore, the overarching goal of this study was focused on engineered modifications of the main structure parameters including the crystallinity, shape, size, surface structure and defects
to improve the electrochemical functionalities of TiO$_2$ so that different water contaminations can be treated with high efficiency and low energy consumption.

In this Ph.D. study, four specific objectives are pursued to comprehensively evaluate the developed TiO$_2$ nanotube array (NTA) electrodes for different water/wastewater treatment applications so to achieve the overall research goal. The application of electrochemical technology for water/wastewater disinfection studied in chapter II. The most common method of electrochemical disinfection is the use of electro-generated oxidants, such as reactive chlorine species (RCS) and reactive oxygen species (ROS), as disinfectants. TiO$_2$ NTA anode can effectively inactivate *E. coli* by generating RCS and ROS especially hydroxyl radical in different kinds of electrolyte as well as real water samples. In chapters III and IV, the electrochemical oxidation and reduction of water pollutants explored, respectively. Results from electrochemical oxidation (chapter III) demonstrate that Meropenem, a representative recalcitrant antibiotic that is widely present in wastewater, can be effectively removed from environmental matrices (e.g. secondary effluent and RO concentrate) using TiO$_2$ NTA based anode material. Moreover, Co-doping Co/Bi has proved to be a viable approach to enhancing the lifetime and promoting ROS generation of TiO$_2$ NTA electrodes. In chapter IV, Nitrobenzene was successfully removed from synthetic electrolytes through the electrochemical reduction process using TiO$_2$ NTA cathode material with different morphological and crystallographic characteristics. Results indicate that the performance of TiO$_2$ NTA electrodes was enhanced with the \{001\}-exposed facet and increases in the nanotube length and diameter. In all last three chapters, the electrochemical treatment of water pollutants was investigated through either anodic oxidation or cathodic reduction processes, where only half of the cell potential is utilized.
environmental matrices. Compared to the sequential oxidation/reduction process, simultaneous oxidation & reduction with regular polarity switching appeared to be the preferred treatment scheme for environmental matrices with simpler setup and higher energy efficiency. Overall, TiO$_2$ NTA electrode material with excellent anodic and cathode performance for the elimination of different water pollutants, high chemical and electrochemical stability, and the low cost and environmental friendliness can be served as novel electrode materials for different electrochemical water and wastewater treatment applications.

Abstract Approval: Committee Chair

Tingting Wu

Department Chair

Graduate Dean

David Berkowitz
ACKNOWLEDGMENTS

I would like to express my deepest appreciation to my advisor, Dr. Tingting Wu, for her continuous support, patience, encouragement, and advising which enabled me to pursue the degree. Dr. Wu is not only a good advisor but also a good friend who treated me as family during the last four years. This research would not be possible without her support and guidance. Also, I would like to extend my sincerely gratitude to my committee members Prof. Michael D. Anderson, Dr. Ashraf Z. Al-Hamdan, Dr. Guangsheng Zhang at the University of Alabama in Huntsville and Dr. Robert W. Peters from the University of Alabama at Birmingham. I would also like to thank the Alabama Graduate Research Scholars Program (GRSP) from the Alabama EPSCoR for financial support.

I would also like to thank my friend and colleague, Wenwen Yang, for all her help, support and collaboration in the last four years. Also, I would like to thank other group members from Dr. Wu’s group: Thanh chi Vu, Xiankun Chen, Eman Al-Hamdan and Spencer Jones, who I worked with. I would also like to thank Dr. Bernhard Vogler form chemistry department and Dr. Yu Lei form chemical engineering department of UAH for all their help and support.

This dissertation couldn’t have been possible without the support, help and love of my wife, Niloofar, and the unconditional love and prayers of my parents Hossein and Farbia, and my brothers and sister in law, Armin, Ehsan and Gelayol. I am sincerely grateful to them all for being the support and driving force that I needed.
TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................... vii

TABLE OF CONTENTS ........................................................................................................... viii

LIST OF FIGURES ................................................................................................................. xiii

LIST OF TABLES ..................................................................................................................... xxi

LIST OF SYMBOLS ................................................................................................................. xxiii

LIST OF ABBREVIATIONS ....................................................................................................... xxv

LIST OF CHEMICALS .............................................................................................................. xxix

1. CHAPTER I ......................................................................................................................... 1

INTRODUCTION ..................................................................................................................... 1

1.1 Problem Statement and Research Objectives ................................................................. 1

1.2 Background ...................................................................................................................... 3

1.2.1 Overview of electrochemical treatment and mechanism of electro-oxidation and reduction.................................................................................................................. 3

1.2.2 Application of electrochemical oxidation/reduction for water/wastewater treatment ............................................................................................................................... 6

1.2.3 Titanium dioxide nanotube .......................................................................................... 12

1.3 Hypotheses and Research Tasks ..................................................................................... 18

2. CHAPTER II ...................................................................................................................... 21

viii
2.1 Introduction................................................................................................................22
2.2 Materials and Methods...............................................................................................25
  2.2.1 Preparation and characterization of TiO₂ nanotube electrodes ..... 25
  2.2.2 E.coli stock and working solutions ................................................................. 26
  2.2.3 Experimental setup and procedure ................................................................. 27
  2.2.4 Analysis.............................................................................................................. 28
2.3 Results and Discussion .............................................................................................. 29
  2.3.1 Characteristics of the TiO₂ nanotube electrodes ........................................... 29
  2.3.2 Effects of applied current density and NaCl concentrations .............. 31
  2.3.3 Effect of different electrolytes........................................................................ 34
  2.3.4 Generation of reactive oxygen species (ROS) .................................... 38
  2.3.5 Experiments in real water matrices ............................................................... 42
2.4 Conclusion ............................................................................................................... 46
2.5 Supporting information ............................................................................................ 47
3.  CHAPTER III ............................................................................................................... 57
  3.1 Introduction ............................................................................................................. 58
  3.2 Materials and Methods........................................................................................... 60
  3.2.1 Chemicals .......................................................................................................... 60
  3.2.2 Electrode Preparation ..................................................................................... 61
  3.2.3 Electrode characterization .............................................................................. 61
3.2.4 Electrochemical oxidation of Meropenem ........................................ 62
3.2.5 Anodic stability .................................................................................. 62
3.2.6 Analytical methods and identification of intermediate products .. 63

3.3 Results and Discussion .......................................................................... 63
3.3.1 Electrode development and characterization ........................................ 63
3.3.2 Effects of current densities and co-existing ions ............................... 66
3.3.3 Mechanism and transformation products .............................................. 71
3.3.4 Test in environmental matrices ......................................................... 75
3.3.5 Electrode deactivation and lifetime ..................................................... 77

3.4 Conclusion .............................................................................................. 79

3.5 Supporting information .......................................................................... 80

4. CHAPTER IV ............................................................................................. 94

4.1 Introduction ............................................................................................ 95

4.2 Material and Methods ........................................................................... 98
4.2.1 Electrode preparation .......................................................................... 98
4.2.2 Electrode characterization ................................................................... 99
4.2.3 Electrochemical reduction of nitrobenzene ........................................ 100
4.2.4 Analytical methods ........................................................................... 101

4.3 Results and Discussion .......................................................................... 102
4.3.1 Morphology and structure properties ............................................... 102
4.3.2 Electrochemical measurement ........................................... 104
4.3.3 Electrocatalytic reduction of NB ........................................ 107
4.3.4 Effects of applied potential and pH................................. 110
4.3.5 NB degradation mechanism and transformation pathway ...... 111
4.3.6 NB degradation kinetics and the electrode stability ............. 116
4.3.7 Energy consumption and Environmental Implications .......... 118

4.4 Conclusion ............................................................................. 120
4.5 Supporting information ......................................................... 121

5. CHAPTER V ........................................................................... 131
5.1 Introduction ........................................................................... 132
5.2 Materials and Methods ......................................................... 135
  5.2.1 Electrode preparation ....................................................... 135
  5.2.2 Electrode characterization ............................................... 135
  5.2.3 Electrochemical treatment of Meropenem ......................... 135
  5.2.4 Analytical methods ......................................................... 137
5.3 Results and Discussion ......................................................... 137
  5.3.1 Electrode characterization ............................................... 137
  5.3.2 Electrochemical reduction of Meropenem in synthetic electrolyte 137
5.3.3 Electrochemical reduction of Meropenem in environmental matrices 140

5.3.4 Meropenem degradation in coupled anodic/cathodic processes 144

5.3.5 Hybrid electrolysis system 149

5.4 Conclusion 151

5.5 Supporting Information 153

6. CHAPTER VII 166

CONCLUSION AND FUTURE WORKS 166

6.1 Conclusion 166

6.2 Future Works 168
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chapter I</strong></td>
<td></td>
</tr>
<tr>
<td>Figure 1. 1 Direct and indirect mechanisms of electrochemical oxidation/reduction</td>
<td>4</td>
</tr>
<tr>
<td>Figure 1. 2 Photos of TiO₂ NTA electrodes prepared: A) before cathodization; B) after cathodization</td>
<td>17</td>
</tr>
<tr>
<td><strong>Chapter II</strong></td>
<td></td>
</tr>
<tr>
<td>Figure 2. 1 FESEM images of TiO₂ nanotube electrode (a &amp; b: used electrode; c &amp; d: new electrode)</td>
<td>29</td>
</tr>
<tr>
<td>Figure 2. 2 Characteristics of the TiO₂ nanotube electrodes: XRD pattern (A) and XPS spectrum (B)</td>
<td>30</td>
</tr>
<tr>
<td>Figure 2. 3 Cyclic voltammograms (CVs) of the anatase TiO₂ nanotube electrode</td>
<td>31</td>
</tr>
<tr>
<td>Figure 2. 4 Effects of current density (A &amp;B) and NaCl concentration (C &amp;D) on E.Coli reduction and byproduct formation</td>
<td>34</td>
</tr>
<tr>
<td>Figure 2. 5 Effect of different electrolytes on E.coli reduction (A) and oxidizing species generation (B)</td>
<td>36</td>
</tr>
<tr>
<td>Figure 2. 6 E.coli reduction in different concentrations of NaH₂PO₄ (A); Comparison of E.coli reduction in buffered and non-buffered electrolytes (B)</td>
<td>38</td>
</tr>
<tr>
<td>Figure 2. 7 E.coli reduction with TBA/ethanol addition</td>
<td>41</td>
</tr>
<tr>
<td>Figure 2. 8 E.coli reduction in real water matrices</td>
<td>43</td>
</tr>
<tr>
<td>Figure 2. 9 Byproducts formation in real water matrices: chlorate (A); THMs (B)</td>
<td>44</td>
</tr>
<tr>
<td>Figure 2. 10 B-spizizenii reduction in treated surface water</td>
<td>46</td>
</tr>
</tbody>
</table>
Chapter II-Supporting

Figure S2. 1 Effect of washing media on E.coli inactivation ........................................ 52
Figure S2. 2 Schematic diagram of the experiment set-up (A); and Photos of electrodes (B).*Reactor not to scale for illustration purpose, actual effective volume ~20 mL........ 52
Figure S2. 3 XPS spectra of Ti2p and O1s before cathodization (A& B) and after cathodization (C&D)................................................................................................................. 53
Figure S2. 4 •OH formation detected by pCBA reduction .............................................. 53
Figure S2. 5 •O₂⁻ formation detected by NBT reduction ................................................. 54
Figure S2. 6 ¹O₂ formation detected by FFA reduction.................................................... 55
Figure S2. 7 Voltage range at different current density at constant NaCl concentration (1.5 mM NaCl) (A); Different NaCl concentration under constant current density (0.66 mA/cm²) (B); Different electrolytes (1.5 mM) under constant current density (2.63 mA/cm²) (C); Different real water matrices under constant current density (0.88 mA/cm²) (D). ......................................................................................................................... 56

Chapter III

Figure 3. 1 A) Anodic stability of TiO₂ NTA electrodes; B) Comparison of [°OH]ss using different electrodes........................................................................................................... 64
Figure 3. 2 High-resolution XPS spectra of TiO₂ NTA electrodes: A) Ti 2p; B&C) O 1s of TiO₂ NTA and Co/TiO₂ NTA electrodes, respectively. ......................................................... 66
Figure 3. 3 Effects of current density on Meropenem degradation ................................. 68
Figure 3. 4 Effects of co-existing ions on Meropenem removal: A) Chloride; B) Sulfate; C) Bicarbonate ......................................................................................................................... 70
Figure 3.5 Formation of chlorinated organic products in environmental matrices using Co/Bi/TiO$_2$ NTA electrode ................................. 70

Figure 3.6 A&B) Meropenem degradation in the presence and absence of hydroxyl radical and sulfate radical scavengers, respectively; C&D) Generation of oxidizing species in the presence and absence of probe compounds .............................................. 73

Figure 3.7 A) Meropenem removal and TOC mineralization in secondary effluent (SE) and RO concentrate, B) $K_{\text{obs}}$ of Meropenem degradation ............................................. 76

Figure 3.8 A) Anodic stability of Co/Bi/TiO$_2$ NTA electrodes at different current densities, B&B’) SEM image of deactivated Co/Bi/TiO$_2$ NTA electrode ............................................. 79

Chapter III-Supporting

Figure S3.1 Schematic diagram of the experimental setup. .................................................. 84

Figure S3.2 Cyclic voltammetry of different TiO$_2$ NTA electrodes .................................. 84

Figure S3.3 Direct oxidation of BA ................................................................. 85

Figure S3.4 [$\cdot$OH]$_{ss}$ estimated from BA electrocatalytic degradation using Co/Bi/TiO$_2$ NTA electrodes with different metal doping ................................................................. 85

Figure S3.5 A&B) SEM images; C&D) XRD and XPS spectra of Co/Bi/TiO$_2$ NTA electrodes, respectively ......................................................... 86

Figure S3.6 EDX spectra of Co/Bi/TiO$_2$ NTA electrode ............................................. 86

Figure S3.7 XPS spectra of Co/Bi/TiO$_2$ NTA electrode: A) O 1s, B) Ti 2p, C) Co 2p, D) Bi 4f ................................................................. 87

Figure S3.8 pH evolution in different reactor chambers during the experiments: A) anodic chamber, B) cathodic chamber; C) Effects of initial pH on Meropenem degradation .... 87
Figure S3. 9 Meropenem degradation in divided and undivided electrochemical cell using Co/Bi/TiO\textsubscript{2} NTA electrode ........................................................................................................... 88

Figure S3. 10 Chlorinated byproduct formation and Cl\textsuperscript{−} mass balance: A\&C) 60 mg/L Cl\textsuperscript{−}, B\&D) 240 mg/L Cl\textsuperscript{−} ........................................................................................................... 88

Figure S3. 11 Direct oxidation of Meropenem on the Co/Bi/TiO\textsubscript{2} NTA electrode........ 89

Figure S3. 12 Meropenem degradation in the presence and absence of scavengers ....... 89

Figure S3. 13 Direct oxidation of AA, bicarbonate, and TBA .................. 90

Figure S3. 14 Meropenem degradation in the presence and absence of RCS probe compounds .......................................................... 90

Figure S3. 15 LC/MS Spectrum of Meropenem transformation products in the positive EIS mode [M+H]\textsuperscript{+} .......................................................... 91

Figure S3. 16 HPLC/UV Spectra of Meropenem transformation products .............. 91

Figure S3. 17 \textsuperscript{1}H-NMR spectrum of peak # at 500 MHz........................................ 92

Figure S3. 18 HSQCSE spectrum of peak # at 500 MHz; blue peaks corresponding to DSS; red peaks due to sample. .................................................................................. 92

Figure S3. 19 Cobalt leaching from the Co/Bi/TiO\textsubscript{2} NTA electrode in the accelerated lifetime test.................................................................................. 93

Chapter IV

Figure 4. 1 FESEM image: A\&I) \{001\}-TiO\textsubscript{2} NTA-E1 B\&J) TiO\textsubscript{2} NTA-E2, C\&K) TiO\textsubscript{2} NTA L2-E5, D\&L) TiO\textsubscript{2} NTA L3-E4, E\&M) TiO\textsubscript{2} NTA D1-E6, F\&N) TiO\textsubscript{2} NTA D3-E7, G\&O) \{001\}-TiO\textsubscript{2} NTA, H\&P) \{001\}-TiO\textsubscript{2} NTA-E3.............................................. 102
Figure 4. 2 X-ray diffraction patterns of different TiO$_2$ NTAs: A&B) Effect of facets (E1-4), B) Effect of the tube length (E 2, 5, & 4), C) Effect of the tube diameter (E 6, 2, 7).

Figure 4. 3 Electrochemical measurement of TiO$_2$ NTA electrodes: A) Hydrogen Evolution Reaction (HER), B) Tafel Plot, C) NB reduction, D) EIS spectra.

Figure 4. 4 NB reduction using different TiO$_2$ NTA electrodes: A) Effect of facets (E1 & 2), B) Effect of the tube length (E 3, 4, & 5), C) Effect of the tube diameter (E 6, 7, 8).

Figure 4. 5 Effects of applied potential and initial pH on NB reduction using {001}-TiO$_2$ NTA-E3: A) Effects of applied potential, B) Effects of pH.

Figure 4. 6 H* generation using {001}-TiO$_2$ NTA-E3.

Figure 4. 7 A) Effect of TBA on NB reduction using {001}-TiO$_2$ NTA-E3; B) NB transformation products using {001}-TiO$_2$ NTA-E3.

Figure 4. 8 Simplified transformation pathway of NB.

Figure 4. 9 Kinetics modeling NB reduction using {001}-TiO$_2$ NTA-E3: A) $K_{obs}$ of NB and NSB; B) Kinetics modeling of NB and its intermediates degradation.

Figure 4. 10 A) Electrochemical reduction of NB and its intermediates; B) Stability tests of {001}-TiO$_2$ NTA-E3.

Chapter IV-Supporting

Figure S4. 1 Effects of cathodic polarization on NB reduction using {001}-TiO$_2$ NTA-E3.

Figure S4. 2 XRD patterns of carbon paper and palladized carbon.
Figure S4. 3 Hydrogen evolution reaction of TiO$_2$ NTA electrodes: A) Effect of nanotube facets (E1-4), B) Effect of the nanotube length (E2, 4, & 5), C) Effect of the nanotube diameter (E6, 2, & 7) ................................................................. 124

Figure S4. 4 NB reduction on different electrodes; A) E1, B) E2, C) E3, D) E4, E) E5, F) E6, G) E7 ................................................................. 125

Figure S4. 5 Effects of NB concentration on direct reduction on the surface on electrode .......................................................................................... 126

Figure S4. 6 EIS spectra: A) Effect of facets (E1 - 4), B) Effect of the tube length (E 2, 5, & 4), C) Effect of the tube diameter (E 6, 2, &7) ...................................................... 126

Figure S4. 7 Comparison of NB reduction on different electrode ......................... 127

Figure S4. 8 Effects of applied potential and initial pH on NB reduction using TiO$_2$ NTA-E4: A) Effects of applied potential, B) Effects of pH.............................................. 127

Figure S4. 9 Cyclic voltammetry of {001}-TiO$_2$ NTA-E3 at different scan rate........ 128

Figure S4. 10 $H^*$ generation; A) {001}-TiO$_2$ NTA-E3, B) TiO$_2$ NTA-E4 .............. 128

Figure S4. 11 A) NB reduction in the presence of TBA using {001}-TiO$_2$ NTA-E3; B) NB reduction in the presence of TBA using TiO$_2$ NTA-E4.............................................. 129

Figure S4. 12 A) Effect of TBA on NB reduction using TiO$_2$ NTA-E; B) NB transformation products using TiO$_2$ NTA-E4...................................................... 129

Figure S4. 13 Reduction of NSB, PHA and AN on {001}-TiO$_2$ NTA-E3 and TiO$_2$ NTA-E4: A& B & C) {001}-TiO$_2$ NTA-E3; D, E, & F) TiO$_2$ NTA-E4 ......................... 130

Chapter V

Figure 5. 1 A) Effects of applied potential on Meropenem removal; B) $K_{obs}$ of Meropenem degradation........................................................................... 140
Figure 5. 2 Meropenem degradation and TOC mineralization in secondary effluent (SE) and RO concentrate........................................................................................................... 142
Figure 5. 3 Precipitate characterization: A) XRD pattern; B) EDX spectra. .................. 144
Figure 5. 4 Sequential oxidation/reduction treatment scheme for Meropenem degradation in secondary effluent (SE) and RO concentrate......................................................... 146
Figure 5. 5 Simultaneous oxidation & reduction treatment scheme for Meropenem degradation in secondary effluent (SE) and RO concentrate................................. 147
Figure 5. 6 Meropenem degradation in flow-through tests......................................... 151

Chapter V-Supporting

Figure S5. 1 Co/Bi/TiO$_2$ NTA electrode characterization, A&B) SEM image; C) XRD pattern; D) EDX spectra........................................................................................................... 157
Figure S5. 2 XPS spectra of Co/Bi/TiO$_2$ NTA electrode: A) Full scan, B) O 1s, C) Ti 2p, D) Co 2p, E) Bi 4f....................................................................................................................... 158
Figure S5. 3 Meropenem degradation using Co/Bi/TiO$_2$ NTA and carbon cathode..... 159
Figure S5. 4 Effects of co-existing ions on Meropenem removal: A) Chloride, B) Sulfate, C) bicarbonate................................................................................................................. 159
Figure S5. 5 Meropenem reduction mechanism: A) Direct reduction of Meropenem on Co/Bi/TiO$_2$ NTA electrode; B) Performance of TBA on Co/Bi/TiO$_2$ NTA electrode; C) Meropenem degradation in the presence and absence of TBA; D) H$_2$O$_2$ formation during the electrolysis .................................................................................................................. 160
Figure S5. 6 Overall potential in electrochemical oxidation and reduction of Meropenem ................................................................................................................................. 161
Figure S5. 7 LC/MS Spectrum of Meropenem transformation products in the positive EIS mode [M+H]^+: A) Reduction; B) Oxidation................................................................. 161
Figure S5. 8 Meropenem degradation in different water matrices including secondary effluent (SE), RO concentrate (RO), simulated secondary effluent (SSE), simulated RO concentrate (SRO), synthetic electrolyte [30 mM NaClO4] (Syn), synthetic electrolyte with 200 mg/L HCO₃⁻ (Syn with 200 mg/L HCO₃⁻), and synthetic electrolyte with 800 mg/L HCO₃⁻ (Syn with 800 mg/L HCO₃⁻)........................................................................... 162
Figure S5. 9 Photos of A) Pristine Co/Bi/TiO₂ NTA electrode; B) Co/Bi/TiO₂ NTA electrode used in synthetic electrolyte; and C) Co/Bi/TiO₂ NTA electrode used in RO concentrate; SEM images of D) Co/Bi/TiO₂ NTA electrode used in RO concentrate, and E) Precipitates collected from the surface of the used electrode. .................................................. 162
Figure S5. 10 Effects of operational conditions on Meropenem removal in coupled anodic and cathodic processes........................................................................................................ 163
Figure S5. 11 pH evolution during simultaneous oxidation & reduction processes in different environmental matrices: A) RO concentrate, B) SE ................................................. 163
Figure S5. 12 Bipolar stability test of Co/Bi/TiO₂ NTA electrode in simultaneous oxidation & reduction processes........................................................................................................ 164
Figure S5. 13 Deactivated Co/Bi/TiO₂ NTA electrode in bipolar stability tests. ............. 164
Figure S5. 14 Schematic diagram of the Hybrid electrolysis system ............................. 165
Figure S5. 15 TOC mineralization during flow-through tests ................................. 165
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Tables</th>
<th>Page</th>
</tr>
</thead>
</table>

## Chapter I

Table 1. 1 Applications of electrochemical oxidation for water/wastewater treatment ..... 8
Table 1. 2 Applications of electrochemical disinfection for water/wastewater treatment.10
Table 1. 3 Applications of electrochemical reduction for water/wastewater treatment ... 11

## Chapter II

Table 2. 1 H$_2$O$_2$ and O$_3^a$ formation in different electrolytes $^b$ ........................................... 40
Table 2. 2 E.coli reduction in previously electrolyzed electrolytes............................................. 41
Table 2. 3 Comparison of energy consumption using different electrodes for E. coli reduction in real water matrices ........................................................................................................ 45

## Chapter II-Supporting

Table S2. 1 Comparison of E. coli reduction in inert electrolytes using different anodes 50
Table S2. 2 Summary of radical reactions ......................................................................................... 50
Table S2. 3 Characteristics of the real water samples ................................................................. 51
Table S2. 4 Comparison of energy consumption under different conditions $^a$ .................. 51

## Chapter III

Table 3. 1 Characteristics of secondary effluent and RO concentrate used in this study. 76

## Chapter IV

Table 4. 1 Electrode characterization .......................................................................................... 103
Table 4. 2 Energy consumption of NB degradation using different electrodes.............. 120

## Chapter IV-Supporting

xxi
Table S4. 1 Anodization parameters ................................................................. 123

Chapter V

Table 5. 1 Characteristics of secondary effluent and RO concentrate used in this study 142

Chapter V-Supporting

Table S5. 1 Characteristics of simulated secondary effluent and RO concentrate ....... 156
## LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>€</td>
<td>Euro</td>
</tr>
<tr>
<td>$m^2$</td>
<td>Square Meter</td>
</tr>
<tr>
<td>°C</td>
<td>Celsius</td>
</tr>
<tr>
<td>$mL$</td>
<td>Mililiter</td>
</tr>
<tr>
<td>G</td>
<td>Gravity</td>
</tr>
<tr>
<td>$mA$</td>
<td>Miliamper</td>
</tr>
<tr>
<td>$cm^2$</td>
<td>Square Centimeter</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>$kg$</td>
<td>Kilogram</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>$min$</td>
<td>Minutes</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar</td>
</tr>
<tr>
<td>$mM$</td>
<td>Milimolar</td>
</tr>
<tr>
<td>$\log$</td>
<td>Logarithm</td>
</tr>
<tr>
<td>$\mu g$</td>
<td>Microgram</td>
</tr>
<tr>
<td>$\mu L$</td>
<td>Microliter</td>
</tr>
<tr>
<td>$\mu M$</td>
<td>Micromolar</td>
</tr>
<tr>
<td>$k$</td>
<td>Reaction Constant Rate</td>
</tr>
<tr>
<td>$W$</td>
<td>Watt</td>
</tr>
<tr>
<td>$h$</td>
<td>Hour</td>
</tr>
<tr>
<td>$m^3$</td>
<td>Cubic meter</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>$A$</td>
<td>Current</td>
</tr>
<tr>
<td>$v$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$EE/O$</td>
<td>Energy Consumption per Order</td>
</tr>
<tr>
<td>$%$</td>
<td>Percentage</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Degree</td>
</tr>
<tr>
<td>$$</td>
<td>USD Dollar</td>
</tr>
<tr>
<td>$T$</td>
<td>Anodic Lifetime</td>
</tr>
<tr>
<td>$nm$</td>
<td>Nanometer</td>
</tr>
<tr>
<td>$J$</td>
<td>Joule</td>
</tr>
<tr>
<td>$m$</td>
<td>Meter</td>
</tr>
<tr>
<td>$E$</td>
<td>Potential</td>
</tr>
<tr>
<td>$Hz$</td>
<td>Hertz</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Ohm</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday</td>
</tr>
<tr>
<td>$dec$</td>
<td>Decade</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$Wt%$</td>
<td>Weight Percentage</td>
</tr>
</tbody>
</table>
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>Tin (IV) Oxide</td>
</tr>
<tr>
<td>PbO₂</td>
<td>Lead (IV) Oxide</td>
</tr>
<tr>
<td>IrO₂</td>
<td>Iridium (IV) Oxide</td>
</tr>
<tr>
<td>RuO₂</td>
<td>Ruthenium (IV) Oxide</td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
</tr>
<tr>
<td>BDD</td>
<td>Boron-doped Diamond</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium Dioxide</td>
</tr>
<tr>
<td>NTA</td>
<td>Nanotube Array</td>
</tr>
<tr>
<td>RCS</td>
<td>Reactive Chlorine Species</td>
</tr>
<tr>
<td>ROS</td>
<td>Reactive Oxygen Species</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen Evolution Reaction</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
<td>MO</td>
<td>Metal Oxide</td>
</tr>
<tr>
<td>ATO</td>
<td>Antimony-doped Tin Oxide</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular Activated Carbon</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphonel A</td>
</tr>
<tr>
<td>DSA</td>
<td>Dimensionally Stable Anodes</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>CFU</td>
<td>Colony-Formin Unit</td>
</tr>
<tr>
<td>TCAA</td>
<td>Trichloroacetic Acid</td>
</tr>
<tr>
<td>DCAA</td>
<td>Dichloroacetic Acid</td>
</tr>
<tr>
<td>DBAA</td>
<td>Dibromoacetic Acid</td>
</tr>
<tr>
<td>OEP</td>
<td>Oxygen Evolution Potential</td>
</tr>
<tr>
<td>E.coli</td>
<td>Escherichia coli</td>
</tr>
<tr>
<td>THMs</td>
<td>Trihalomethanes</td>
</tr>
<tr>
<td>MMO</td>
<td>Mixed Metal Oxide</td>
</tr>
<tr>
<td>WTP</td>
<td>Water Treatment Plant</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltametry</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>LTB</td>
<td>Lauryl Tryptose Broth</td>
</tr>
<tr>
<td>LC/MS</td>
<td>Liquid chromatography–Mass spectrometry</td>
</tr>
<tr>
<td>2D-NMR</td>
<td>Two-Dimensional Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Effluent</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride</td>
</tr>
<tr>
<td>DAD</td>
<td>Diode Array Detector</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>PROETHEE</td>
<td>Preference Ranking Organization Method for Enrichment Evaluations</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>Ov</td>
<td>Oxygen Vacancy</td>
</tr>
<tr>
<td>HAAs</td>
<td>Haloacetic acids</td>
</tr>
<tr>
<td>HANs</td>
<td>Haloacetonitriles</td>
</tr>
<tr>
<td>HAs</td>
<td>Haloacetaldehydes</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray ionization</td>
</tr>
<tr>
<td>HSQC</td>
<td>Heteronuclear Single Quantum Coherence</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>US</td>
<td>United States</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedence Spectroscopy</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
</tr>
<tr>
<td>ECAS</td>
<td>Electrochemical Active Surface Area</td>
</tr>
<tr>
<td>Hg/HgO</td>
<td>Mercury/Mercury Oxide</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography–Mass Spectrometry</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific Surface Area</td>
</tr>
</tbody>
</table>
SCE  Saturated Calomel Electrode
LIST OF CHEMICALS

Cl₂ Chlorine
HOCl Hypochlorous Acid
OCl⁻ Hypochlorite
‘OH Hydroxyl Radical
O₃ Ozone
H₂O₂ Hydrogen Peroxide
‘O₂⁻ Superoxide Anion
H* Atomic Hydrogen
CO₂ Carbon Dioxide
H₂ Molecular Hydrogen
‘Cl Chlorine Radical
HF Hydrofluoric Acid
NaOH Sodium Hydroxide
NH₄F Ammonium fluoride
DMSO Dimethyl sulfoxide
NaCl Sodium Chloride
Na₂SO₄ Sodium sulfate
Na₂HPO₄ Disodium phosphate
NaNO₃ Sodium Nitrate
NaHCO₃ Sodium bicarbonate
ClO₃⁻ Chlorate
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>Tantalum</td>
</tr>
<tr>
<td>Nb</td>
<td>Niobium</td>
</tr>
<tr>
<td>W</td>
<td>Tungsten</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>ClO₂⁻</td>
<td>Chlorite</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>Monopotassium phosphate</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>Dipotassium phosphate</td>
</tr>
<tr>
<td>FFA</td>
<td>Free fatty acid</td>
</tr>
<tr>
<td>pCBA</td>
<td>4-Chlorobenzoic acid</td>
</tr>
<tr>
<td>S₂O₈²⁻</td>
<td>Peroxydisulfate</td>
</tr>
<tr>
<td>C₂O₆²⁻</td>
<td>Peroxodicarbonate</td>
</tr>
<tr>
<td>P₂O₈⁴⁻</td>
<td>Peroxodiphosphate</td>
</tr>
<tr>
<td>P₂O₈²⁻</td>
<td>Peroxodiphosphate</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Sulfate Radical</td>
</tr>
<tr>
<td>TBA</td>
<td>Tert-butyl Alcohol</td>
</tr>
<tr>
<td>NBT</td>
<td>Nitro Blue Tetrazolium</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Bi</td>
<td>Bismuth</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Sulfate</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Bicarbonate</td>
</tr>
<tr>
<td>H₂</td>
<td>Molecular Hydrogen</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>Perchlorate</td>
</tr>
</tbody>
</table>

xxx
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>Benzoic Acid</td>
</tr>
<tr>
<td>AA</td>
<td>Allyl Alcohol</td>
</tr>
<tr>
<td>DSS</td>
<td>Sodium Trimethylsilylpropanesulfonate</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>USD</td>
<td>US Dollar</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickle</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>NB</td>
<td>Nitrobenzene</td>
</tr>
<tr>
<td>NSB</td>
<td>Nitrosobenzene</td>
</tr>
<tr>
<td>AZ</td>
<td>Azobenzene</td>
</tr>
<tr>
<td>PHA</td>
<td>N-phenylhydroxylamine</td>
</tr>
<tr>
<td>AN</td>
<td>Aniline</td>
</tr>
<tr>
<td>F</td>
<td>Flouride</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

1.1 Problem Statement and Research Objectives

Efficient removal of recalcitrant compounds and pathogens from water/wastewater is a challenging task and calls for novel technologies [1–4]. Electrochemical methods have the advantages of environmental compatibility, high efficiency, mild reaction conditions, simple operation, and capability to adjust to influent fluctuations, and thus represent an attractive approach for the treatment of different pollutants in water [2,5–10]. However, one major concern that hinders the wide application of electrochemical technologies is the electrode material which largely determines the efficiency of the treatment processes [11–13]. Common electrodes often suffer from low reactivity and/or stability (e.g. metal and mixed metal oxides such as SnO₂, PbO₂, IrO₂, RuO₂, and IrO₂/RuO₂ electrodes) or be subject to limited applications due to the high cost and the scarcity of the materials (e.g. Pd, Pt, Boron-doped Diamond (BDD), and Au) [14–18]. Therefore, effective, inexpensive, and stable electrode materials are the key to the development of viable electrochemical water/wastewater treatment systems.

The overarching goal of this research is to develop and further evaluate nanostructured titanium dioxide (TiO₂) based electrodes for different electrochemical
water/wastewater treatment applications. In particular, anodic titanium dioxide nanotube arrays (TiO$_2$ NTAs) are selected as the nanostructured platform. TiO$_2$ NTAs have been studied for various environmental applications, especially photocatalysis owing to their outstanding properties such as strong photoreactivity, chemical stability, easy fabrication, tunable nanostructures, low-cost, and nontoxicity, etc. [19–22]. More importantly, the advantages of the nanotube structure such as high surface area, well-controlled dimensions, and 1-D directional electron transport pathway make it preferable over other nanostructures for electrochemical water/wastewater treatment [21,23,24]. Moreover, facile doping approaches (e.g. cathodic self-doping or dip-doping of other metal species) can further improve the stability and performance of the electrodes [25,26]. In this research, the TiO$_2$ NTA electrodes are prepared via a simple anodization procedure where the nanotube arrays are directly grown on the surface of bulk Ti substrate, thus increasing the conductivity and avoiding secondary separation of nanomaterials from treated water.

In this Ph.D. study, four specific objectives are pursued to comprehensively evaluate the developed TiO$_2$ NTA electrodes for different water/wastewater treatment applications so to achieve the overall research goal. Two main processes, i.e., oxidation and reduction, generally contribute to the destruction of water contaminants or the inactivation of pathogens. Hence, the TiO$_2$ NTA-based electrodes are first developed and examined in two oxidation processes: electro-disinfection of water/wastewater with *Escherichia coli* as an indicator microorganism (Objective 1/Chapter II) and electrochemical oxidation of emerging contaminants (antibiotics: Meropenem) in environmental matrices (Objective 2/Chapter III). Chapter IV (Objective 3) reports on one of the first studies employing TiO$_2$ NTA as the cathode for electrochemical reduction
of water pollutants with nitrobenzene as the model compound. After the anodic oxidation and cathodic reduction performance of TiO$_2$ NTA electrodes are investigated in chapters II-IV, the combination of these two processes are studied in Chapter V (Objective 4), where the anode and cathode processes are coupled and the treatment scheme is optimized to achieve high energy efficiency. Finally, the global conclusions and future research are presented in Chapter VI.

1.2 Background

1.2.1 Overview of electrochemical treatment and mechanism of electro-oxidation and reduction

Electrochemical methods have been used since the early 1960s for the treatment of water/wastewater containing metallic, organic, and inorganic pollutants [2,5–10]. The main electrochemical water treatment processes include electrochemical oxidation, electrochemical reduction, electrocoagulation, electro disinfection, electro flotation (EF), and electro dialysis (ED) [2]. These processes can be used as independent treatment units or in combination with other technologies (e.g., chemical, physical, and biological) as pretreatment/post treatment/main treatment step [7–9,27–30]. In addition, electrochemical treatment can be applied for colored and turbid waters, which cannot be treated by UV and photocatalytic degradation method [31–34].

Water/wastewater treatment by electrochemical methods is based on conducting the electrolysis process in electrolytic cell. In the electrolysis process, an external source of electrical energy is required to generate and maintain a proper potential to occur the non-spontaneous chemical reaction at the surface of anode or cathode, which are placed into an electrochemical cell. The electrochemical process is considered to be a very powerful tool
for the destruction of resistant organic compounds or inactivation of pathogens. Generally, these contaminants can be treated via either direct and/or indirect mechanisms (Figure 1.1) [35].

![Diagram of Electrochemical Oxidation/Reduction Mechanisms]

Figure 1.1 Direct and indirect mechanisms of electrochemical oxidation/reduction

**Direct Mechanism:**

As shown in Figure 1.1, in direct mechanism (or direct electron transfer to the electrode), the pollutants are destroyed after adsorption on the electrode surface without the involvement of any substances other than the electrons [35]. For example, Gattrell and Kirk investigated on the treatment of phenol with platinum and peroxidized platinum electrode using cyclic voltammetry and chronoamperometry. Their results demonstrated that phenol can be irreversibly adsorbed on metallic platinum and quickly oxidized by transferring electrons with electrode surface [36].

**Indirect Mechanism:**
The indirect mechanism relies on the generation of different electroactive species during the electrolysis (Figure 1.1), which are then involved in the decontamination processes [9]. Reactive species commonly found in electrochemical processes include strong oxidants such as reactive chlorine species (RCS, e.g., Cl₂, HOCl, OCl⁻) and reactive oxygen species (ROS, e.g., ′OH, O₃, H₂O₂, ′O₂⁻), or reductants such as atomic hydrogen (H*) [11,37–40]. For example, ROS can be generated through the activation of water molecules, which is achieved by water dissociative adsorption below oxygen evolution reactions (OER) potential or by water electrolytic discharge above OER potential. Hydroxyl radical (′OH) is the second strongest oxidant known after fluorine, with a high standard potential (E⁰ = 2.80 V vs. SHE) that helps achieve the complete combustion of organic compounds [41]. It may be generated from the electrolysis of water using either active anodes (e.g., iridium oxide (IrO₂), ruthenium oxide (RuO₂)) or non-active anodes (e.g. BDD). The water molecules discharge at the surface of anode to form adsorbed ′OH (Reaction 1).

\[ M + H₂O \rightarrow M(′OH) + H^+ + e^- \] [R1]

At active anodes, the interaction between hydroxyl radicals and electrode surface is strong, in thus the adsorbed ′OH may associate with the oxygen which already presents on the surface of anode and form the higher oxidized species (Reaction 2). Therefore, at the surface of the anode, two states of active species can be presented as physical sorbed active oxygen (adsorbed hydroxyl radicals) and chemisorbed active oxygen (oxygen in the oxide lattice), which may contribute in the oxidation of the pollutants (Reaction 3) [9,42].

\[ M(′OH) \rightarrow MO + H^+ + e^- \] [R2]
\[ MO + R \rightarrow M + RO \] [R3]
On the other hand, the interaction between the adsorbed hydroxyl radical and the surface of non-active anodes is weak. Therefore, the oxidation of organics occurred via direct interaction of hydroxyl radicals with organic pollutants and produce CO$_2$ and water (Reaction 4) [9,42].

$$M (\cdot \text{OH}) + R \rightarrow M + m\text{CO}_2 + n\text{H}_2\text{O} + H^+ + e^-$$  \[\text{R4}\]

In electrochemical reduction processes, atomic hydrogen (H*) is one of the most common reductive species. H* is generated directly from the electrolysis of water where water is discharged to hydrogen and hydroxide ions followed by atomic hydrogen recombination by either electrochemical or catalytic mechanism [9]. H* may be formed as absorbed (H*abs) or adsorbed (H*ads) atomic hydrogen depending on the cathode materials. Also, extensive amounts of H* adsorbed on the surface of the cathode or absorbed into the crystal lattice of the cathode material may evolve into a molecular hydrogen (H$_2$) which is often considered as side reactions during electro-reduction for water pollutants [9,40]. The production of these reactive agents largely depends on the electrode materials.

1.2.2 Application of electrochemical oxidation/reduction for water/wastewater treatment

Electrochemical oxidation/reduction has been applied successfully to degrade different pollutants in various waste streams and disinfect water and wastewater [5,9,13,19,26,39,43–45]. In these applications, different electrode materials have been used. For example, in electrochemical oxidation, anodes made of antimony-doped tin oxide (ATO), PbO$_2$, and boron-doped diamond (BDD) are known as non-active anodes and favor the formation of free hydroxyl radical [46,47]. In contrast, dimensionally stable Pt, IrO$_2$,
RuO₂ anodes create surface-bound hydroxyl radical, which mediates the facile formation of RCS [2]. In terms of electrochemical reduction, novel metals and bimetals (Pd, Pt, and Ag) are considered as candidates for cathode materials [26,48].

Electrochemical oxidation

Electrochemical oxidation or “anodic oxidation” is a process in which the pollutants or pathogens are destroyed or inactivated at the surface of anode or react with strong oxidants such as RCS or ROS generated during the electrolysis [5,49]. During the last two decades, research works have been focusing on efficient oxidation of various pollutants on different electrodes, improvement of the electrocatalytic activity and electrochemical stability of electrode materials, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutants degradation [5,8,31,43,49,50]. Table 1.1 summarizes representative applications of electrochemical oxidation for water and wastewater treatment.
Table 1. Applications of electrochemical oxidation for water/wastewater treatment

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Application</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/PbO₂</td>
<td>Industrial park wastewater (COD removal, disinfection)</td>
<td>63.57% COD removal, 100% disinfection</td>
<td>[50]</td>
</tr>
<tr>
<td>Ti/RuO₂</td>
<td>Petroleum industry wastewater (COD removal)</td>
<td>96% COD removal</td>
<td>[18]</td>
</tr>
<tr>
<td>Ti/RuO₂–IrO₂</td>
<td>Dye wastewater (Acid red 3R)</td>
<td>77.2% decolorized efficiency in 100 min</td>
<td>[31]</td>
</tr>
<tr>
<td>Ti/Pt</td>
<td>Raw industrial effluent</td>
<td>96% decolorized efficiency in 30 min</td>
<td>[51]</td>
</tr>
<tr>
<td>Sb–SnO₂</td>
<td>Cibacron Marine FG azo dye</td>
<td>100% decolorized</td>
<td>[52]</td>
</tr>
<tr>
<td>BDD</td>
<td>Synthetic wastewater (Phenol degradation and products formation)</td>
<td>100% phenol removal, ~55% TOC mineralization</td>
<td>[53]</td>
</tr>
<tr>
<td>BDD</td>
<td>Industrial wastewater (Pharmaceutical wastewater)</td>
<td>100% COD removal</td>
<td>[54]</td>
</tr>
<tr>
<td>BDD</td>
<td>Secondary effluent (several pharmaceuticals, and pesticides)</td>
<td>100% DOC and COD removal</td>
<td>[55]</td>
</tr>
<tr>
<td>Stainless steel anode, and Al particles</td>
<td>Tap water (Humic acid removal)</td>
<td>~ 80% DOC removal</td>
<td>[56]</td>
</tr>
<tr>
<td>Graphite and Fe₂O₃/y-Al₂O₃ particle electrodes</td>
<td>Synthetic wastewater (Phenacetin (PNT) removal)</td>
<td>~95% PNT, and 70% COD removal</td>
<td>[35]</td>
</tr>
<tr>
<td>TiO₂–SiO₂/GAC</td>
<td>Dye wastewater (Acid orange 7 (AO7))</td>
<td>~80% AO7 and 55% COD removal</td>
<td>[34]</td>
</tr>
<tr>
<td>TiO₂ single crystals</td>
<td>Raw wastewater (Bisphonenol A (BPA) and landfill leachate)</td>
<td>~100 % BPA degradation, ~80% COD removal</td>
<td>[57]</td>
</tr>
<tr>
<td>TiO₂–NTs/SnO₂–Sb/PbO₂</td>
<td>Synthetic wastewater (Nitrobenzene degradation)</td>
<td>100% COD, Nitrobenzene removal, 95% TOC mineralization</td>
<td>[58]</td>
</tr>
<tr>
<td>TiO₂ NTs</td>
<td>Human wastewater (COD removal)</td>
<td>90% COD removal with 62 kWh/kg COD energy consumption</td>
<td>[38]</td>
</tr>
<tr>
<td>TiO₂ NTs/Co</td>
<td>Latrine wastewater (NH₄⁺ and COD removal)</td>
<td>100% NH₄⁺ and 90% COD removal</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Another application of electrochemical oxidation processes in water/wastewater treatment is electrochemical disinfection [11,59]. It is based on anodic generation of strong...
oxidants during water electrolysis. Similar to conventional chemical disinfection, electrochemical disinfection can be used for the removal and deactivation of a wide spectrum of microorganisms from water/wastewater and often it is more efficient than chemical disinfection. The most common and effective oxidants for microorganism deactivation are RCS and ROS \([27,59,60]\). When chloride is naturally present (e.g., seawater, toilet wastewater) or artificially added, RCS such as free chlorine (Cl\(_2\), HOCl, ClO\(^-\)) and chlorine radical species (Cl\(^-\), Cl\(_2^-\)) are generated and recognized as primary disinfectants. In addition, ROS including hydroxyl radicals ([OH]), hydrogen peroxide ([H\(_2\)O\(_2\)]), ozone ([O\(_3\)]), and superoxide anion radicals ([O\(_2^-\)]) generated during electrochemical water splitting can enhance the overall disinfection efficiency [9,27]. Several applications of electrochemical disinfection for water/wastewater treatment are listed in Table 1.2.
Table 1. Applications of electrochemical disinfection for water/wastewater treatment

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Application</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO₂/graphite</td>
<td>Diluted artificial wastewater</td>
<td>100% disinfection efficiency in 10 min</td>
<td>[17]</td>
</tr>
<tr>
<td>BDD</td>
<td>Secondary effluent <em>(E. coli)</em></td>
<td>~96% disinfection efficiency in 60 min</td>
<td>[46]</td>
</tr>
<tr>
<td>BDD</td>
<td>Synthetic wastewater <em>(M. aeruginosa)</em></td>
<td>80% disinfection efficiency</td>
<td>[61]</td>
</tr>
<tr>
<td>BDD</td>
<td>Synthetic wastewater <em>(E. coli)</em></td>
<td>99% disinfection efficiency in 0.8, 1.2, and 10 hours for chloride, sulfate, and phosphate electrolyte, respectively.</td>
<td>[62]</td>
</tr>
<tr>
<td>DSA</td>
<td>Artificial wastewater</td>
<td>98.9% disinfection efficiency</td>
<td>[60]</td>
</tr>
<tr>
<td>Sb/Sn/W-oxide</td>
<td>Synthetic wastewater (bacteria-laden)</td>
<td>100% disinfection efficiency</td>
<td>[63]</td>
</tr>
<tr>
<td>Ru-Ir/Ti</td>
<td>Secondary effluent <em>(E. coli)</em></td>
<td>3 Log CFU* reduction (initial 10³ CFU/mL)</td>
<td>[64]</td>
</tr>
<tr>
<td>Ti/IrO₂</td>
<td>Surface water <em>(Heterotrophic bacteria)</em></td>
<td>3 Log CFU reduction (initial 10³ CFU/mL)</td>
<td>[65]</td>
</tr>
<tr>
<td>BiOx/TiO₂</td>
<td>Toilet wastewater <em>(E. coli)</em></td>
<td>5 Log CFU reduction (initial 10³ CFU/mL)</td>
<td>[27]</td>
</tr>
<tr>
<td>TiO₂ NTs</td>
<td>Synthetic and real wastewater <em>(E. coli)</em></td>
<td>7.5 Log CFU reduction in 5 min for synthetic water (NaCl electrolyte); 7.5, 6, and 5 log CFU reduction in 40 min for treated surface water, WTP intake water, and secondary effluent (initial 10⁷ CFU/mL)</td>
<td>[19]</td>
</tr>
</tbody>
</table>

*CFU: Colony-Forming Unit

Electrochemical reduction

Electrochemical reduction is a chemical reaction involving the gain of one or more electrons by an atom or a molecule at the cathode during the passage of direct electric current through the electrochemical system (anode, cathode, and an electrolyte). Similar to electrochemical oxidation, electrochemical reduction can occur either directly through the
direct accepting of electrons by molecules and ions or indirectly through the mediated reactions with electrochemically generated species at the cathode such as H$_2$O$_2$ and H$^*$ [40,66,67]. Different applications of electrochemical reduction system for treating water/wastewater are tabulated in Table 1.3.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Application</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene/Cu</td>
<td>Synthetic wastewater (TCAA reduction)</td>
<td>~95% TCAA dechlorination,</td>
<td>[67]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Synthetic wastewater (Bromate reduction)</td>
<td>100% bromate removal</td>
<td>[68]</td>
</tr>
<tr>
<td>Pd/GAC</td>
<td>Synthetic wastewater (Haloacetic acid (DCAA-TCAA-DBAA) removal)</td>
<td>70%, 90%, and 100% removal for DCAA, TCAA, and DBAA, respectively</td>
<td>[48]</td>
</tr>
<tr>
<td>Pd/rGO/carbon fiber</td>
<td>Synthetic wastewater (Bromate reduction)</td>
<td>98.7% bromate removal</td>
<td>[28]</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>Synthetic wastewater (Nitrobenzene (NB) reduction)</td>
<td>~95% NB reduction</td>
<td>[69]</td>
</tr>
<tr>
<td>Graphite</td>
<td>Synthetic wastewater (Nitrophenol reduction)</td>
<td>~97% nitrophenol degradation</td>
<td>[70]</td>
</tr>
<tr>
<td>Polypyrrole/Cu (PPy-Cu)</td>
<td>Synthetic wastewater (Nitrate reduction)</td>
<td>~50% nitrate reduction</td>
<td>[71]</td>
</tr>
<tr>
<td>Cu/Zn</td>
<td>Synthetic wastewater (Nitrate reduction)</td>
<td>~80% nitrate removal</td>
<td>[72]</td>
</tr>
<tr>
<td>Pt</td>
<td>Synthetic wastewater (p-nitrophenol (PNP) reduction)</td>
<td>100% PNP degradation and 100% COD removal</td>
<td>[73]</td>
</tr>
<tr>
<td>Pd/PPy–SLS/TiO$_2$ NTs</td>
<td>Synthetic wastewater (2,4-dichlorophenol reduction)</td>
<td>~96% dechlorination of 2,4-DCP</td>
<td>[74]</td>
</tr>
<tr>
<td>Nitrogen-doped diamond (NDD)</td>
<td>Synthetic wastewater (Nitrobenzene (NB and aniline (AN)) reduction)</td>
<td>96.5% and 88.4% removal for NB and AN, respectively</td>
<td>[75]</td>
</tr>
<tr>
<td>Ni-PVC</td>
<td>Synthetic wastewater (Reactive Black 5 (RB5))</td>
<td>100% decolorized efficiency in 20, and 180 min at 1 and 3V potential</td>
<td>[32]</td>
</tr>
<tr>
<td>TiO$_2$ NTs</td>
<td>Synthetic wastewater (hexavalent chromium (Cr(VI)) reduction)</td>
<td>97% Cr(VI) reduction</td>
<td>[44]</td>
</tr>
<tr>
<td>Pd-Ti/TiO$_2$ NTs</td>
<td>Groundwater (Trichloroethylene (TCE) reduction)</td>
<td>91% TCE removal efficiency</td>
<td>[26]</td>
</tr>
<tr>
<td>TiO$_2$ single crystals</td>
<td>Synthetic wastewater (Nitrobenzene reduction)</td>
<td>~97% NB removal</td>
<td>[39]</td>
</tr>
</tbody>
</table>
In general, the selection of electrode material can largely determine the efficiency of electrochemical treatment processes. For example, the boron doped diamond (BDD) and antimony doped tin oxide (ATO) have been reported to produce *OH with high current efficiency compared with Ti/RuO$_2$, Ti/IrO$_2$, Ti/Pt–IrO$_2$, and Pt while IrO$_2$ and IrO$_2$/RuO$_2$ anodes generate free chlorine more efficiently than BDD and Pt. Novel metals and bimetals (Pd, Pt, and Ag) are considered good materials for H*generation when they are used as cathode [2,5,10,18,40]. However, electrodes commonly used for water treatment may either suffer from low reactivity and/or stability (e.g. metal and mixed metal oxides such as SnO$_2$, PbO$_2$, IrO$_2$, RuO$_2$, and IrO$_2$/RuO$_2$ electrodes) or be subject to limited applications due to high cost and the scarcity of the materials (e.g. Pd, Pt, BDD, and Au) [14–18].

There are several key parameters, including physical/chemical stability, suitable physical form, electrical conductivity, product selectivity, and cost/lifetime, for the selection of a good electrode material.

1.2.3 Titanium dioxide nanotube

As cost-effectiveness is always a main concern in selecting electrode materials, titanium dioxide (TiO$_2$) materials have undergone several studies considering its economic feasibility. TiO$_2$ is one of the most important semiconductor metal oxides with various physical and chemical properties including strong photoreactivity, superhydrophilicity, chemical stability, nontoxicity, and low cost, which make it applicable for many environmental applications especially photocatalysis activities [20,34,76]. However, in contrast to the widely-explored photocatalytic activities, the low conductivity and poor electroactivity hinders the application of TiO$_2$ as an efficient electrode material.
The nanostructured TiO\(_2\) materials (e.g. nano-particles, -wires, -needles, -belts and -tubes) provide a unique combination of the physico-chemical properties of TiO\(_2\) with a nanoscale geometry which may improve the electrocatalytic properties of TiO\(_2\) material [22,79,80]. The properties of TiO\(_2\) nanostructured materials are classified in terms of their crystallinity, purity, structure, chemical composition, size- and/or shape-distribution, dimensionality, and defect centers, which may be modified by changing the parameters using various synthetic methods [81,82].

Among different nanostructures, the TiO\(_2\) nanotube is particularly appealing due to its specific advantages including high surface area, well-controlled dimensions, and 1-D directional electron transport pathway [22,78,83,84]. There are three general approaches to synthesize TiO\(_2\) nanotube: chemical (template) synthesis, alkaline hydrothermal method, and electrochemical approaches [19–21,85–88].

Chemical (template) synthesis

For template synthesis, in order to construct materials with similar properties, different methods including reactive deposition or dissolution have been used [89,90]. The preparation of TiO\(_2\) nanotube by chemical templating usually involves controlled sol-gel hydrolysis of solutions of titanium-containing compounds in the presence of templating agents, followed by polymerization of TiO\(_2\) in the self-assembled template molecules or deposition of TiO\(_2\) nanotube onto the surface of the template aggregates. [20,91]. For example, in TiO\(_2\) sol-gel process, the alkyl group was removed from the precursor at hydrolysis step (Reaction 5). Then, Oxygen Bridge was formed via condensation within titanium metal (Reaction 6&7). Finally, the thin films of TiO\(_2\) which was formed via Reaction 8 can be deposited on substrates by dip-coating or spin-coating [81].
\[
\begin{align*}
\text{Ti} [\text{OCH} (\text{CH}_3)_2]_n + \text{H}_2\text{O} & \rightarrow \text{Ti} [\text{OCH} (\text{CH}_3)_2]_{n-1} (\text{OH}) + \text{CH} (\text{CH}_3)_2 (\text{OH}) & \text{[R5]} \\
\text{Ti} (\text{OH}) + \text{Ti} (\text{OH}) & \rightarrow \text{Ti-O-Ti} + \text{H}_2\text{O} & \text{[R6]} \\
\text{Ti} [\text{OCH} (\text{CH}_3)_2] + \text{Ti} (\text{OH}) & \rightarrow \text{Ti-O-Ti} + \text{CH} (\text{CH}_3)_2 (\text{OH}) & \text{[R7]} \\
\text{Ti} [\text{OCH} (\text{CH}_3)_2]^4 + 2\text{H}_2\text{O} & \rightarrow \text{TiO}_2 + 4\text{CH} (\text{CH}_3)_2 (\text{OH}) & \text{[R8]}
\end{align*}
\]

However, chemical synthesis approaches may bear several disadvantages. The template material needs to be destroyed after synthesis in most cases, leading to an increase in the cost of materials. Also as for all surface-finishing techniques, it is also important to maintain a high level of surface cleanliness to ensure good adhesion between the substrate and the surface coating [20]. Moreover, the tubes may be destroyed during the fabrication process [77].

Alkaline hydrothermal method

Hydrothermal method is conducted without the use of sacrificial templates, by treatment of raw TiO\textsubscript{2} material with concentrated NaOH solution as the solvent in a batch reactor at elevated temperature or pressure [20,81]. The hydrothermally synthesized TiO\textsubscript{2} nanotubes are expected to have a regular chemical composition, be perfect in shape and have no morphological defects, which may be helpful for some applications. The main disadvantage of this method is the limited control of the nanotube dimension, shape, and crystallinity [82].

Electrochemical approaches

The self-organized TiO\textsubscript{2} nanotube arrays can be obtained by a simple electrochemical anodization of bulk Ti substrate under a specific set of environmental conditions (e.g., electrolyte, voltage, temperature, anodization time) [19]. The nanotubes are oriented in the same direction perpendicular to the surface of the substrate, forming a
continuous film. One end of the nanotubes is always open while the other end, which is in contact with the substrate, is always closed. Different electrolytes including aqueous electrolytes (HF/H2O, KF/NaF/H2O, NH4F/CH3COOH and NH4F/H3PO4, etc.) and nonaqueous electrolytes (fluorinated dimethyl sulfoxide (DMSO)/ethanol, NH4F/glycerol, NH4F/ethylene glycol, etc.) have been used to prepare nanotube arrays [21,79,81,92]. The growing of TiO2 NTA can be explained as follows [21]:

(i) Under an anodic potential, stable compact oxide layer of TiO2 is formed on the surface of the Ti metal (Reaction 9):

\[ \text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}^+ + 2\text{e}^- \]  

[R9]

(ii) Fluoride ions in the electrolyte are responsible for the chemical dissolution of the metal oxide layer (TiO2) and pores are formed on the oxide–electrolyte interface to produce soluble [TiF6]2− complex. This complexation may occur with Ti4+ ions that are ejected at the oxide–electrolyte interface (after migration through the oxide film) or via chemical attack of the formed TiO2 by F− (Reaction 10&11):

\[ \text{Ti}^{4+} + 6\text{F}^- \rightarrow [\text{TiF}_6]^{2-} \]  

[R10]

\[ \text{TiO}_2 + 4\text{H}^+ + 6\text{F}^- \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \]  

[R11]

(iii) When the chemical dissolution and oxidation processes achieve a steady state condition TiO2 nanotubes will be formed.

Among these three methods described above, the electrochemical method is selected in this study because this approach leads to the direct growth of nanotubes on the Ti substrate and enables the control of the morphological features of tube structures at nano-scales. Actually, electrochemical anodization allows the formation of a dense and defined nanotube layer attached to bulk Ti materials of any shape, avoiding secondary
separation of fine materials with treated water. This may represent a big advantage in water/wastewater treatment applications, especially in flow-through reactors.

However, TiO$_2$ NTA as a semiconductor material still has intrinsically low electrical conductivity and electrocatalytic activity [38,92]. So far, many research efforts have been made to enhance the conductivity and electrochemical activity of the TiO$_2$ nanotube material, among which self-doping via electrochemical hydrogenation/cathodic polarization can be considered as the simplest approach [92–94] (Figure 1.2). Cathodic polarization can cause a partial reduction of the Ti$^{4+}$ in the lattice to Ti$^{3+}$, which helps electrons to accumulate in the semiconductor film. At the same time, charge compensation is accomplished by proton intercalation (Ti$^{4+}$ +e$^-$ +H$^+$ → Ti$^{3+}$H$^+$) [95]. It should be noted that TiO$_2$ is well known to undergo a color change (usually black or dark blue) when a sufficiently negative potential is applied. This electrochromism is reversible and the dark color may vanish quickly upon the removal of the electrical field [96]. The switching time depends on the solid-state diffusion/migration of H$^+$ into and out of the lattice [21]. However, the TiO$_2$ nanotube activated via this approach has shown irreversible electrochromism, probably because the unique structure and surface properties of TiO$_2$ nanotube lead to stronger bonds (i.e. H-O), deeper migration of H$^+$ into the lattice, or formation of oxygen vacancies [92,93].
The stability/lifetime of TiO$_2$ NTAs as anode materials is also a concern, which was reported in the range of few minutes to several hours at different current densities [38,92,97]. Although many efforts have been employed to overcome this limitation, the complicated procedures have restricted the application of TiO$_2$ NTA as electrode material for electrochemical generation of oxidants or reductants [98,99]. Yang et al. (2018) successfully extended the active lifetime of TiO$_2$ NTA anodes by depositing cobalt into the nanotube (4 hr for TiO$_2$ NTA versus no deactivation after 200 hr for Co-doped TiO$_2$ NTA) [25]. However, cobalt deposition may lower the oxygen evolution potential (OEP) of the electrode, which may adversely affect the electrochemical oxidation of target compounds as oxygen revolution due to water splitting acts as a side reaction and reduces the current efficiency. Therefore, research efforts are still needed to further improve the electrochemical functionalities of TiO$_2$ NTAs particularly for water/wastewater treatment applications, which is also the focus of this Ph.D. study, as outlined below.
1.3 Hypotheses and Research Tasks

Chapter II: Inactivation of *E. coli* using a Novel TiO$_2$ Nanotube Electrode

Here we hypothesize that TiO$_2$ NTA electrodes can generate various oxidizing species such as RCS and ROS, which can act as disinfectants for water and wastewater disinfection. In order to test this hypothesis, inactivation of *Escherichia coli* (*E. coli*) as an indicator microorganism is examined using TiO$_2$ NTA and stainless steel as the anode and the cathode, respectively. Formation of oxidizing species largely depends on the type of electrolyte. For example, the most common oxidizing species generated in chlorine electrolytes is active chlorine (e.g., Cl$_2$, Cl$^*$, HClO, and ClO$^-$) while oxygen species (e.g., *OH, H$_2$O$_2$, O$_3$, O$_2^-$, 1O$_2$) or sulfate radicals may be generated in non-chlorine electrolytes. Therefore, inactivation of *E.coli* is studied in different electrolytes (e.g., NaCl, Na$_2$SO$_4$, Na$_2$HPO$_4$, NaNO$_3$, and NaHCO$_3$) where the log reduction of *E.coli* is monitored. The hypothesis is further supported by confirming the production of oxidizing species using probe compounds. Finally, the good disinfection performance of TiO$_2$ NTA electrode in real water matrices is also demonstrated.

Chapter III: Removal of Antibiotics from Environmental Matrices by Electrochemical Oxidation

A general hypothesis of this study is that antibiotics can be effectively removed from environmental matrices using TiO$_2$ NTA based electrodes with enhanced stabilities. To examine this hypothesis, TiO$_2$ NTA electrode is first modified by co-doping cobalt (Co) and bismuth (Bi) so as to enhance the anode stability/lifetime and ROS (e.g. *OH) generation. Meropenem is selected as a model antibiotic in this study and the optimum experimental condition is determined in synthetic electrolytes through a series of
electrochemical oxidation experiments under different operational conditions (e.g., current density and the presence of different ions). Furthermore, the degradation kinetics, transformation products and the reaction mechanism are studied using probe compounds and various electrochemical measurements. The electrochemical oxidation of Meropenem is also evaluated in environmental matrices (e.g., secondary effluent and RO concentrate generated from water reuse). Finally, the electrode stability is investigated to predict the anodic lifetime of Co/Bi/TiO$_2$ NTA electrode.

Chapters IV: Electrocatalytic Reduction of Nitrobenzene using TiO$_2$ Nanotube Electrodes with Different Morphologies: Kinetics, Mechanism, and Degradation Pathways

The hypothesis is that TiO$_2$ NTA electrodes can be used for electrocatalytic reduction of water pollutants and the performance can be affected by the nanotube morphology. In this study, TiO$_2$ NTA electrodes with different morphologies and exposed facets are first synthesized by manipulating a suite of anodization parameters and applying a post-anodization treatment. Nitrobenzene is selected as a model pollutant of industrial wastewater. In order to test the hypothesis, electrochemical reduction of nitrobenzene is evaluated using TiO$_2$ NTA electrodes with different morphologies under same experimental conditions. Electrochemical measurements are conducted to further explain the different behaviors of these electrodes for nitrobenzene reduction. Based on the results of electrodes with different morphologies, a TiO$_2$ NTA electrode with optimum morphology is prepared for electrochemical reduction of nitrobenzene and the effects of operating parameters, reduction pathway and mechanism, degradation kinetics, and energy consumption are further investigated.
Chapter V: Towards Full Cell Potential Utilization during Water Purification Using Co/Bi/TiO₂ Nanotube Electrodes

The hypothesis of this study is that the electrochemical elimination of emerging contaminants from water can be enhanced by coupling anodic oxidation and cathodic reduction processes. In order to test this hypothesis, Meropenem was selected as a representative recalcitrant antibiotic and a newly-developed Co and Bi co-doped TiO₂ nanotube array (Co/Bi/TiO₂ NTA) electrode was employed as both anode and cathode. Here the electrochemical reduction of meropenem is first conducted in synthetic electrolyte and real water matrices, then compare with those of the oxidation study (Chapter III). Further, the elimination of Meropenem is examined in different coupled treatment schemes (e.g., sequential and simultaneous oxidation and reduction processes) to utilize the full cell potential for Meropenem degradation and take advantages of the “self-regeneration” characteristic of TiO₂ NTA based electrodes through cathodic polarization. Finally, the hybrid treatment scheme with continuous flow rate is tested as a possible practical application for treating organic pollutants from environmental matrices.

In the last chapter, Chapter VII, conclusions and recommendations are given based on the results obtained in this Ph.D. study. Future research directions are also suggested.
CHAPTER II

Inactivation of E. coli using a Novel TiO₂ Nanotube Electrode


Abstract

The performance of electrochemical processes highly depends on the electrodes and development of cost-effective anode materials plays an important role in supporting future adoption of electrochemical technologies for environmental applications. In this study, novel TiO₂ nanotube anodes were fabricated via a simple electrochemical method and tested for inactivation of a model microbial contaminant E. coli, using a filter-press type cell with stainless steel as the cathodes. Effects of current density applied (0.66 ~ 2.63 mA/cm²), electrolyte concentration (0.3 mM~3 mM NaCl), and different electrolytes (NaCl, Na₂SO₄, Na₂HPO₄, NaNO₃, and NaHCO₃) on E. coli inactivation were investigated. Electrochemically generated oxidizing species were measured as free chlorine and production of reactive oxygen species (ROS) were examined using probe compounds. Reactive chlorine species were formed mainly via a •OH-mediated pathway and found to be the dominant species responsible for E. coli inactivation in the presence of Cl⁻. Higher E. coli reduction efficiency was obtained in inert electrolytes using TiO₂ nanotube anodes compared with other electrodes reported in the literature, which can be ascribed to the formation of ROS such as •OH and H₂O₂ and possibly electrolyte-specific oxidants such as sulfate and phosphate radicals. Furthermore, it has been demonstrated that the novel TiO₂ nanotube anode can effectively achieve 5~7.5 log reduction of E. coli with low
byproducts formation (e.g. ClO₃⁻, THMs) and energy consumption (0.1 ~ 0.19 kWh/m³ for 4 log reduction) in real water matrices.

2.1 Introduction

In water/wastewater treatment, disinfection represents the last barrier against microbial contaminants and plays a crucial role in the production of safe drinking water and protection of receiving water bodies. Chlorine disinfection, ozonation, and ultraviolet irradiation have been widely-used method in water and wastewater industries [100–102]. In particular, electrochemical disinfection has been developed and attracted increasing interests as electrochemical technology offers several advantages such as capacity to adjust to influent fluctuations, less waste generation, and easy integration with other treatment units. Moreover, it may find applications in decentralized treatment due to its simplicity, amenability to automation, compact instrumentation, and ease of operation [103,104].

Electro-disinfection has been reported to be able to inactivate a wide spectrum of microorganisms via several mechanisms and electrogeneration of disinfectants is considered to be the most useful and environmentally-sound system in terms of energy consumption [27,46,104–108]. Reactive species that are commonly found in these processes include active chlorine species (e.g. Cl₂, HOCl, OCl⁻) and reactive oxygen species (ROS, e.g. •OH, O₃, H₂O₂, •O₂⁻) [11,27,109]. Efficiency of production of these agents largely depends on the anode material. For example, antimony doped tin oxide and boron doped diamond (BDD) have been reported to produce •OH with high current efficiency compared with Ti/RuO₂, Ti/IrO₂, Ti/Pt–IrO₂, and Pt [2,105,110] while IrO₂ and IrO₂/RuO₂ anodes generate free chlorine more efficiently than that of BDD and Pt under
comparable conditions [111,112]. BDD has been extensively studied due to its distinct features such as extreme stability under anodic polarization, high oxygen overpotential, high activity toward organics oxidation, but substrates onto which the film can be successfully deposited are either expensive (Ta, Nb, W) or suffer a poor mechanical strength (Si) [103,104]. Moreover, the major methods for manufacturing doped diamond materials are limited to small-scale production [112] and the high cost (12,000 ~18,000 €/m²) may impede its large scale application [113]. Another commonly used electrodes, mixed metal oxides (MMO), have limited oxidizing ability and may be subject to a short lifetime when polarities are regularly switched to prevent cathode fouling [46,114]. Also the coating procedure requires expensive metal precursors [115]. Therefore, explorative research on cost-effective anode materials is needed to support future adoption of electrochemical technologies for environmental applications.

Ti-based material is one of the most studied materials and possesses some outstanding properties such as good conductivity, non-toxicity, environmental friendliness, corrosion-resistance, and high biocompatibility [116]. In particular, Ti-based nanostructures have attracted great research interests in recent years. For example, TiO₂ nanotube can be synthesized by simple electrochemical anodization using metallic Ti as the substrate. This one-dimensional nanostructure provides a unique combination of the highly functional features of TiO₂ with a regular and controllable nanoscale geometry. However, TiO₂ as a semiconductor has intrinsic low electric conductivity and electrocatalytic activities [93,117]. Therefore, many research efforts (e.g. doping and coating) have been made to overcome the limited conductivity and electrochemical activity of the pristine TiO₂ nanotube, among which electrochemical hydrogenation/cathodic
polarization may be considered as the simplest approach [93,94,115]. Cathodic polarization has been reported to cause a partial reduction of the Ti$^{4+}$ in the lattice to Ti$^{3+}$, which helps electrons to accumulate in the semiconductor film. At the same time charge compensation is accomplished by proton intercalation (Ti$^{4+} + e^- + H^+ \rightarrow Ti^{3+}H^+$) [95]. It should be noted that TiO$_2$ is well known to undergo a color change (usually black or dark blue) when a sufficiently negative potential is applied. This electrochromism is reversible and the dark color may vanish quickly upon the removal of the electrical field [96]. Surprisingly, the TiO$_2$ nanotube activated via this approach has shown irreversible electrochromism [93,115], probably because the unique structure and surface properties of TiO$_2$ nanotube lead to stronger bonds (i.e. H-O), deeper migration of H$^+$ into the lattice, or formation of oxygen vacancies.

There are very limited studies on applications of such TiO$_2$ nanotube electrodes for water/wastewater treatment reported in the literature. Chang et al. investigated the electrochemical oxidation of salicylic acid at electrochemically reduced TiO$_2$ nanotube [118]. Very recently, Yang and Hoffman tested potential applications of blue-black TiO$_2$ nanotube electrodes for human wastewater treatment [119]. In this study, we investigate the inactivation of *Escherichia coli* (*E. coli*) as an indicator microorganism by TiO$_2$ nanotube electrodes prepared via a simple electrochemical procedure (anodization followed by cathodic polarization). Experiments were conducted in different synthetic electrolyte solutions as well as water treatment plant (WTP) intake water, treated surface water before disinfection, and secondary effluent before disinfection. Formation of organic and inorganic byproducts were examined. Generation and role of ROS in different electrolytes were investigated using probe compounds. Energy cost using TiO$_2$ nanotube
electrodes for the electrodisinfection of real water matrices was estimated and compared with those in the literature. In addition, inactivation of *B-spizizenii* in treated surface water was also tested.

### 2.2 Materials and Methods

#### 2.2.1 Preparation and characterization of TiO$_2$ nanotube electrodes

TiO$_2$ nanotube electrodes were prepared using an electrochemical method reported previously [115]. Briefly, titanium foil (Gallium Source, 99.6% purity, 0.1 mm thick) was cleaned by ultrasonication in acetone for 10 minutes and then anodized in an ethylene glycol electrolyte containing H$_2$O (2.5 wt %) and NH$_4$F (0.2 wt%) for 16 hours under a constant voltage of 45V. A platinum mesh was used as the cathode. The electrode was washed with ethanol to remove remnants from the surface, then annealed in a furnace at 450°C for 1 hour with a heating rate of 2°C/min under atmospheric conditions to enhance crystallinity of the anodic TiO$_2$ nanotube [120]. The final electrochemical hydrogenation was completed by cathodizing the TiO$_2$ nanotube electrode in a phosphate buffer solution under constant current (0.017 A/cm$^2$) for 90s. The surface characterization of the TiO$_2$ nanotube were collected on a Rigaku MiniFlex 600 powder X-ray diffractometer operated at 40 kV and 15 mA. 2 theta data from 20º to 80º were obtained at scanning speed of 0.5 degree/min. The surface composition the TiO$_2$ nanotube before and after cathodization was examined using XPS (Kratos Analytical AXIS 165). Surface morphology of the TiO$_2$ nanotube electrodes (as prepared and used) was characterized by Tescan Lyra FIB-FESEM. The electrochemical properties of the TiO$_2$ nanotube were analyzed with cyclic voltametry (CV) tests using a research potentiostat (Bio-Logic, SP150).
2.2.2 *E. coli* stock and working solutions

*E. coli* stock solution was prepared following the EPA standard method 1103.1 [121]. First, *E. coli* stock culture was prepared by inseminating a Tryptic Soy Agar with *Escherichia coli* ATCC#11775, which was then incubated at 35 ± 3°C for 20 ± 4 hours. 0.5 mL of sterile single strength Lauryl Tryptose Broth (LTB-HACH 216315) was dissolved into 49.5 ml of sterile phosphate buffer saline to prepare 1% solution of LTB. To prepare *E. coli* stock solution, a small amount of *E. coli* growth from the stock culture was added to the 50 mL 1% LTB solution and incubated at 35 ± 3°C for 20 ± 4 hours. This stock solution should contain approximately $10^7$-$10^8$ *E. coli* colony forming units (CFU) per mL. In order to prepare the working solution for each experiment, 35 ~ 45 mL stock solution was centrifuged at 1380×G for 10 minutes, then washed with sterile de-ionized (DI) water and centrifuged for 5 min twice. Finally the concentrated *E. coli* was spiked and well dispersed into 200 mL of sterile working electrolyte. This working solution normally contained $10^5$-$10^7$ CFU/mL. It should be noted that sterilized DI water was used for cell washing to avoid introduction of ions other than the electrolyte used in the experiment for the purpose of investigating the effects of different electrolytes as described below. In order to check if *E. coli* has been pre-stressed and become more vulnerable to disinfection treatment due to DI washing, a comparison experiment where the cells were washed with normal saline solution (0.9% NaCl) was conducted at the lowest current density (0.66 mA/cm²) applied in this study. As shown in Figure S2.1, the *E. coli* reduction profiles in both experiments were similar and no significant “shocking effect” was observed.
2.2.3 Experimental setup and procedure

A laboratory filter pressed reactor (Figure S2.2A) was used in this study. The reactor consisted of 4 stainless steel foil cathodes (2 cm × 1.9 cm, 0.1 mm thickness), 3 TiO₂ nanotube anodes (2 cm × 1.9 cm), and inlet and outlet plates with flow distribution, which created a plug flow pattern in the reactor. Cathodes and anodes were arranged alternatively with electrode spacing of 1.6 mm, and total effective area of 22.8 cm². During the experiments, the reactor was connected to a DC power supply (BK Precision 9111) and the working solution was continuously stir-mixed and pumped through the electrochemical reactor at a flow rate of 100 mL/min via a chemical metering pump. Samples were taken at pre-determined intervals and measured for inorganic chlorine species (ClO₂⁻, ClO₃⁻ etc.), free chlorine, and *E.coli*. 0.5 mL of 0.6 g/L Na₂S₂O₃ was added to the sample to quench the oxidizing species (except for free chlorine measurement). *E.coli* inactivation using the TiO₂ nanotube electrode was investigated in different electrolytes (NaCl, Na₂SO₄, NaH₂PO₄, NaNO₃, and NaHCO₃) prepared in a buffered solution (2.5 mM K₂HPO₄ + 2.5 mM KH₂PO₄) unless noted otherwise, as well as real water samples including intake water, treated surface water before disinfection, and secondary effluent before disinfection taken from local treatment plants. *E.coli* was spiked into the real water samples to increase the initial microorganism level for performance evaluation. Inactivation of *E.coli* after different contact time was also tested in previously electrolyzed solutions to examine the disinfecting effects of the oxidants residue. Moreover, re-growth experiments were conducted to examine if bacterial repair or regrowth can occur after treatment. First, 1.5 mM NaCl (200 mL) containing ~ 10⁷ CFU/mL *E. coli* was electrolyzed for 20 min at 1.32 and 2.63 mA/cm², respectively. Cells were then harvested from 90 mL of the electrolyzed
solution by centrifugation at 1380×G for 20 min and then re-suspended in different sterile solutions, i.e. DI water, normal saline solution (9 g/L NaCl) and treated surface water. These solutions as well as the rest of the electrolyzed solution were kept at 25°C for 24 hrs and then *E. coli* was measured again. As for production of ROS, formation of trace amount of ozone and hydrogen peroxide during electrolysis was monitored. Furthermore, a scavenger method was used to detect the generation of radical ROS (see Supporting Information for experimental details).

2.2.4 Analysis

*E. coli* concentration was determined using membrane filtration via EPA standard method 1103.1 [121]. The detection limit is one CFU/volume filtered. Inorganic chlorine species were measured by ion chromatography (Thermo Dionex ICS-1600 with Dionex Ionpac™ AS23 analytical 4x250 mm column, eluent 4.5mM Na₂CO₃ and 0.8mM NaHCO₃ with 1 mL/min flow rate). THMs was measured with Parker THM Analyzer (PH-THM-1000). Global oxidizing species were quantified as free chlorine using N,N-diethyl-p-phenylenediamine (DPD) method (Hach method 8021, 0.02~2 mg/L). O₃ concentration was measured using Indigo Ozone Reagent AccuVac Ampul (Hach method 8311, 0.01~1.5 mg/L). H₂O₂ concentration was determined using a colorimetric method reported previously (1~120 × 10⁻⁶ M) [122]. FFA, *p*CBA concentrations were measured by HPLC with a diode array detector (Hitachi Primade; 100 x 4.60 mm Kinetex 2.6u C18 100A column). The mobile phase was 50% methanol and 50% water at 1mL/min for FFA and 70% methanol and 30% 20mM phosphoric acid at 0.6 mL/min for *p*CBA. A UV-vis spectrophotometer (Hach DR 6000) was used to measure Nitro BT absorbance at a wavelength of 530nm.
2.3 Results and Discussion

2.3.1 Characteristics of the TiO$_2$ nanotube electrodes

FESEM images were taken to determine the size of TiO$_2$ nanotubes on the surface of electrode. As can be seen from Figure 2.1, the TiO$_2$ nanotube is ~13µm long with a diameter of ~ 60 nm.

![FESEM images of TiO$_2$ nanotube electrode (a & b: used electrode; c & d: new electrode)](image)

Figure 2.1 FESEM images of TiO$_2$ nanotube electrode (a & b: used electrode; c & d: new electrode)

The XRD patterns of TiO$_2$ nanotube after different preparation steps are shown in Figure 2.2A. Annealing has significantly improved crystallinity. The peak intensities increase after cathodization and the positions are in good agreement with the anatase TiO$_2$
Figure 2.2B shows the XPS spectra of the electrodes before and after cathodic polarization. For the sample before cathodization, one peak was found for O 1s at 529.9 eV and two peaks centered at ~464.3 and ~458.6 eV for Ti2p which corresponded to the characteristic Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) peaks of Ti\(^{4+}\), respectively [123,124]. After cathodization, Ti 2p peaks become broader and skewed, indicating the presence of Ti\(^{3+}\) [124,125]. Figure S2.3 shows XPS spectra with deconvolution. As can be seen, two peaks at binding energy of 458.30 eV and 460.05 eV, corresponding to Ti\(^{3+}\)2p\(_{3/2}\) and Ti\(^{3+}\)2p\(_{1/2}\) respectively [126], appear after cathodization. Furthermore, a peak at binding energy of 531.3 eV which represents hydroxyl group/non lattice oxygen is observed in O 1s spectra, demonstrating the oxygen deficiency.

Figure 2. 2 Characteristics of the TiO\(_2\) nanotube electrodes: XRD pattern (A) and XPS spectrum (B).
CVs of the anatase TiO$_2$ (after annealing) are shown in Figure 2.3 Before cathodic polarization (cycle 1), the electrode showed the semiconducting character of the anatase TiO$_2$ nanotube with very low current density. During the cathodic polarization (negative potential) the color of anatase TiO$_2$ nanotube turned to blue by reduction of Ti$^{4+}$ combined with H$^+$ intercalation [96]. At the end of the first CV cycle, the color of anatase TiO$_2$ nanotube remained blue, exhibiting irreversible electrochromism. Similar CVs were obtained from cycle 2 to cycle 10, indicating the stability of the electrodes.

![Cyclic voltammograms (CVs) of the anatase TiO$_2$ nanotube electrode](image)

**Figure 2.3** Cyclic voltammograms (CVs) of the anatase TiO$_2$ nanotube electrode [scan rate: 40mV/s within -2.0 ~ +3.0V: 0 v → 3v → -2v → 0 v; 0.5M KH$_2$PO$_4$ electrolyte with NaOH at pH 7.2].

### 2.3.2 Effects of applied current density and NaCl concentrations

As shown in Figure 2.4A, 6 ~ 7.5 log reduction was achieved after 20 min treatment as the current density varied from 0.66 to 2.63 mA/cm$^2$ in 1.5 mM buffered NaCl solution. In fact no viable bacterial was detected after 5 min electrolysis at current density of 1.32 and 2.63 mA/cm$^2$ indicating a high disinfecting efficiency in NaCl electrolyte. The preliminary experiments also confirmed that there was no inactivation of *E. coli* when no current was applied (data not shown). The most common germicidal species generated in
electrolytes containing Cl\(^{-}\) is active chlorine (Cl\(_2\), HClO, and ClO\(^{-}\)) although other oxidants (e.g. O\(_3\), H\(_2\)O\(_2\)) may also be produced [27,46]. The global oxidizing species were quantified as free Cl\(_2\) shown in Figure 2.4A&C. As expected, higher current density resulted in higher oxidants production and consequently more efficient *E. coli* inactivation, but not in proportion possibly due to side reactions such as water electrolysis and byproducts formation. Figure 2.4C shows the level of *E. coli* inactivation at constant current density (0.66 mA/cm\(^2\)) but different NaCl concentrations. A higher Cl\(^{-}\) concentration led to a faster inactivation although at least 6 log reduction was achieved after 20 min even in 0.3 mM NaCl. All these results indicate that the TiO\(_2\) nanotube electrodes can facilitate very efficient electrochlorination processes for water disinfection. Furthermore, ~7 log reductions were achieved after 20 min electrolysis and no *E. coli* regrowth or reactivation was detected in both regrowth experiments, confirming the persistence of bacterial inactivation in various medium environments. However, one of the major concerns of electrodisinfection involving active chlorine is the formation of chlorination byproducts [127]. Therefore, chlorine inorganic anions (ClO\(_2^{-}\) and ClO\(_3^{-}\)) were monitored during the electrolysis of NaCl electrolyte. As shown in Figure 2.4B&D, formation of chlorate increased with both current density and Cl\(^{-}\) concentration. No chlorite was detected. Within the pH range throughout the experiments (7.03 ± 0.03), chlorate may be formed by electrochemical oxidation of the hypochlorite at the anode [128]:

\[
\begin{align*}
2\text{Cl}^{-} & \rightarrow \text{Cl}_2 + 2e \quad (1) \\
2\text{Cl}_2 + \text{H}_2\text{O} & \rightarrow \text{HClO} + \text{Cl}^{-} + \text{H}^{+} \quad (2) \\
6\text{ClO}^{-} + 3\text{H}_2\text{O} & \rightarrow 2\text{ClO}_3^{-} + 6\text{H}^{+} + 4\text{Cl}^{-} + 1.5\text{O}_2 + 6e \quad (3)
\end{align*}
\]
Chlorate is considered toxic as it can irreversibly weaken the blood’s ability to carry oxygen by interrupting red blood cell membranes. Therefore, WHO recommended the safe concentration of chlorate in drinking water to be 0.7 mg/L [129]. Chloride is one of the ions that are most commonly present in natural waters with concentrations usually in the range of 4 ~ 26 mg/L (0.1 ~ 0.7 mM) in groundwater and 8 ~ 100 mg/L (0.2 ~ 2.8 mM) in surface water in the U.S [130]. Within this concentration range, the results here indicate that effective disinfection can be achieved with chlorate formation being controlled at a safe level. Nonetheless, as generation of ClO$_3^-$ increases with both Cl$^-$ concentration and current density, the applied electric charge should be carefully controlled to prevent excess chlorate formation when Cl$^-$ concentration is high in the source water. In addition, it was reported that ClO$_4^-$ can be generated at BDD anodes as a result of ClO$_3^-$ oxidation by •OH, especially at high current densities (> 60 mA/cm$^2$) [128,131]. However, ClO$_4^-$ formation is unlikely under the experimental conditions in this study because: (1) much lower current densities were applied, (2) •OH generating capacity of TiO$_2$ nanotube electrodes is lower than that of BDD [115], and (3) no reduction of chlorate concentration was observed.
2.3.3 Effect of different electrolytes

Inactivation of E. coli using TiO\textsubscript{2} nanotube electrodes was also investigated in electrolytes other than NaCl. As shown in Figure 2.5A, 2~3 log reduction was achieved in non-chloride electrolytes after 20 min electrolysis, in contrast to 7 log reduction in NaCl at the same current density and electrolyte concentration. Electrochemical inactivation of pathogens may occur through either direct oxidation in contact with the electrodes or indirect oxidation via anodic production of active oxidizing species. In this study, both NaCl concentrations and different electrolytes can affect the E. coli inactivation, indicating that indirect oxidation was predominant [132]. NaCl electrolyte was more effective than...
others because of the formation of active chlorine spices such as Cl\(_2\), HOCl, and OCl\(^-\), i.e. the mechanism of electro-chlorination. Inactivation of E. coli in electrolytes other than NaCl can be ascribed to the generation of ROS (e.g. O\(_3\), H\(_2\)O\(_2\), •OH) and/or other electrolyte-specific oxidants (e.g. S\(_2\)O\(_8^{2-}\), C\(_2\)O\(_6^{2-}\), P\(_2\)O\(_8^{4-}\)) \([11,105,109,133]\). Table S2.1 summarizes the E. coli inactivation in inert electrolytes using different electrodes reported in the literature. For example, phosphate is often used as an inert electrolyte to investigate the ROS generation at different electrodes \([11,105,109,134]\). As can be seen in Figure 2.5A, TiO\(_2\) electrodes used in this study exhibited a similar/higher inactivation efficiency in the phosphate electrolyte, but with much lower current density and shorter electrolysis time compared with those reported previously (Table S2.1). For Na\(_2\)SO\(_4\), NaNO\(_3\), and NaHCO\(_3\), similar E. coli inactivation profiles (2~3 log reduction in 20 min) were observed in this study. The role of persulfate for E. coli reduction in sulfate electrolyte was investigated at different electrodes as summarized in Table S2.1. Similarly, the production of C\(_2\)O\(_6^{2-}\), P\(_2\)O\(_8^{4-}\) was also reported to be important in the chlorine-free electrochemical disinfection process \([11]\).
As all the electrolytes were prepared in phosphate buffered solution here, it is necessary to examine if the buffer solution plays any significant role before further investigation on the active species in chlorine-free electrolytes. Therefore, experiments of E. coli inactivation were conducted in phosphate buffered solution without any other electrolyte (0 mM in Figure 2.6A), with different phosphate concentrations (0.75~3 mM in Figure 2.6A), and non-buffered Na$_2$SO$_4$, NaNO$_3$, NaHCO$_3$ solutions with the same conductivities as the corresponding buffered ones (Figure 2.6B). As shown in Figure 2.6A, ~1 log reduction was achieved in the phosphate buffered solution, which increased to ~3 with 3 mM phosphate addition. Hence the concentration of phosphate seems to have certain
effect on E. coli inactivation. Furthermore, lower reduction was observed in non-buffered NaNO₃ solution compared with the buffered one. All these results imply the possible production of P-related oxidizing species (e.g. P₂O₆⁴⁻, HPO₄²⁻ or PO₄³⁻). Lower inactivation was also obtained in non-buffered NaHCO₃ solution, indicating C₂O₆²⁻, even if formed, is unlikely to play an important role in E. coli inactivation. The reduction in E. coli removal in non-buffered NaNO₃ and NaHCO₃ may either because of the lack of P-oxidants or due to the •OH scavenging by HCO₃⁻ (discussed in the next section). On the other hand, it is speculated that S₂O₈²⁻ and/or SO₄•⁻ may be formed and contribute to electrodisinfection here as a slightly higher reduction was observed in the non-buffered sulfate solution. In spite of the evidence of production of electrolyte-specific oxidants, the principal mechanism for E. coli inactivation in non-chloride electrolyte is still unclear because generation of ROS is yet to be investigated.
Figure 2. 6 E.coli reduction in different concentrations of NaH₂PO₄ (A); Comparison of E.coli reduction in buffered and non-buffered electrolytes (B). [Current density: 2.63 mA/cm²; A: NaH₂PO₄ concentration: 0 ~ 3 mM in buffered solution; B: Electrolyte in buffered solution: 1.5 mM; electrolyte in non-buffered solution: 5 mM Na₂SO₄, 9 mM NaNO₃ and 10 mM NaHCO₃, all with the same conductivity as the corresponding buffered ones].

2.3.4 Generation of reactive oxygen species (ROS)

ROS such as •OH, O₃, H₂O₂ may be generated during electrolysis directly from the oxidation of water molecules. To determine the ROS generation, first the •OH production was examined by the degradation of a •OH probe compound pCBA as shown in Figure S2.4. Similar pCBA degradation rate was observed in all electrolytes. In order to further investigate the effect of •OH on E.coli inactivation, another commonly-used scavenger,
tert-butyl alcohol (TBA) was added into each electrolyte and \textit{E.coli} reductions were monitored over time and compared with those without TBA addition. Preliminary experiments confirmed no lethal effects on \textit{E. coli} caused by the addition of alcohols (TBA and ethanol). It was found that the addition of TBA significantly inhibited the inactivation in all electrolytes, indicating the important role of •OH in electrochemical disinfection using these TiO$_2$ nanotube electrodes (Figure 2.7). Specifically, the lower reduction resulting from the TBA addition in NaCl implies the formation of active chlorine species may be via a •OH mediated pathway in addition to direct oxidation of Cl$^-$ described in Eq. (1). Furthermore, ethanol was also added to Na$_2$SO$_4$ electrolyte to explore the possible formation and role of SO$_4$$^{2-}$ in the sulfate electrolyte. Figure 2.7 shows that compared with ethanol, addition of TBA caused more severe inhibition of \textit{E.coli} reduction after 20 min electrolysis. The reaction rate constants of ethanol/•OH and ethanol/SO$_4$$^{2-}$ are 1.7 $\times$ 10$^9$ M$^{-1}$ S$^{-1}$ and 1.6 $\times$ 10$^7$ M$^{-1}$ S$^{-1}$ respectively [135], while those of TBA are 6.0 $\times$ 10$^8$ M$^{-1}$ S$^{-1}$ and 4.0 $\times$ 10$^5$ M$^{-1}$ S$^{-1}$ respectively [136]. As ethanol can react quickly with both •OH and SO$_4$$^{2-}$, a similar inhibition effect should be observed with TBA and ethanol addition if no SO$_4$$^{2-}$ is formed. Hence, it is indicated that SO$_4$$^{2-}$ was possibly generated but played a less important role in \textit{E.coli} inactivation than that of •OH in the sulfate electrolyte. These results are also consistent with those shown in Figure 2.6, i.e. higher reduction in the non-buffered sulfate solution due to the formation of sulfate-related oxidants.

As can be seen in Figure 2.7, addition of TBA or ethanol did not completely halt \textit{E.coli} reduction indicating that other oxidants may also be generated during the electrolysis as consequent reactions of •OH (Eq. 1–6 in Table S2.2) and contribute to electrochemical disinfection. Production of O$_3$ and H$_2$O$_2$ during electrolysis was examined and the results
are shown in Table 2.1. Neither O\textsubscript{3} nor H\textsubscript{2}O\textsubscript{2} was detected above the detection limits in NaCl electrolyte probably due to the higher electrocatalytic activity of the electrode material toward Cl\textsuperscript{−} ions. H\textsubscript{2}O\textsubscript{2} was detected in all electrolytes except NaCl with concentrations increasing with the electrolysis time, while no O\textsubscript{3} was detected possibly due to the detection limit of the analysis method (0.01 mg/L). In order to examine the disinfecting capability of the trace amount of H\textsubscript{2}O\textsubscript{2}, O\textsubscript{3}, (if any) and/or other non-radical oxidants, inactivation of \textit{E. coli} was tested in different electrolytes that had been previously electrolyzed. Here, electrolysis was first carried out for 20 min and then stopped. \textit{E. coli} was added into the electrolyzed solutions and measured after 5 and 20 min contact time. As shown in Table 2.2, no viable \textit{E. coli} (6 log reduction) was detected in NaCl after 5 min contact due to the presence of residual active chlorine species in the previously electrolyzed solution. 35 ~ 64\% reductions were achieved in other electrolytes after 20 min contact. These results demonstrate that a certain extent of continuing disinfection can be expected in the water being previously electrolyzed by the TiO\textsubscript{2} nanotube anode but may not be significant except in NaCl electrolyte. The formation of other reactive oxygen species was found not significant and the results are detailed in the Supporting Information.

<table>
<thead>
<tr>
<th>Electrolysis time (min)</th>
<th>NaCl</th>
<th>Na\textsubscript{2}SO\textsubscript{4}</th>
<th>NaH\textsubscript{2}PO\textsubscript{4}</th>
<th>NaNO\textsubscript{3}</th>
<th>NaHCO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>ND\textsuperscript{c}</td>
<td>0.056</td>
<td>0.137</td>
<td>0.158</td>
<td>0.112</td>
</tr>
<tr>
<td>20</td>
<td>ND</td>
<td>0.216</td>
<td>0.259</td>
<td>0.279</td>
<td>0.296</td>
</tr>
</tbody>
</table>

\textsuperscript{a} No ozone was detected in all the electrolytes (detection limit: 0.01 mg/L); \textsuperscript{b} Electrolyte concentration: 1.5 mM; current density applied: 2.63 mA/cm\textsuperscript{2}. \textsuperscript{c} Detection limit: 0.034 mg/L.
Figure 2. 7 E.coli reduction with TBA/ethanol addition. [Electrolyte concentration: 1.5 mM; current density: 2.63 mA/cm²; concentration of TBA and ethanol: 30 mM].

Table 2. 2 E.coli reduction in previously electrolyzed electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxidizing species as Cl₂ (mg/L)</td>
<td>Oxidizing species as Cl₂ (mg/L)</td>
<td>E.coli reduction (%)</td>
<td>Oxidizing species as Cl₂ (mg/L)</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.28</td>
<td>0.10</td>
<td>99.9999</td>
<td>0.06</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.10</td>
<td>0.08</td>
<td>25.29</td>
<td>0.02</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td>0.08</td>
<td>0.08</td>
<td>---</td>
<td>0.03</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.08</td>
<td>0.08</td>
<td>22.86</td>
<td>0.03</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.08</td>
<td>0.06</td>
<td>---</td>
<td>0.04</td>
</tr>
</tbody>
</table>

According to the above analysis, generation of ROS especially •OH seems to be the critical step for electrochemical inactivation of E.coli using TiO₂ nanotube anode in all electrolytes including NaCl. An electron tunneling mechanism was proposed to explain the enhanced electrochemical activity of TiO₂ nanotube electrode after cathodic polarization.²⁸
Briefly, a space charge layer will be produced at the solid water surface at a sufficient potential for •OH generation. The width of space charge layer (d_sc) for TiO_2 nanotube electrode before cathodic polarization is too large for electron penetration, while cathodization may shorten d_sc and increase the electron tunneling probability. When a sufficient potential is applied, TiO_2 nanotube electrode is excited and electron is transferred from valance band to conduction band (Eq. 4) [50]. Also water can be split into H_2 and OH^- at the cathode (Eq. 5) [137]. The electrode surface may adsorb OH^- or H_2O and subsequently generate •OH (Eq. 6 & Eq. 7) [50].

\[
≡\text{Ti}-\text{OH} \rightarrow ≡\text{Ti}-\text{OH}(e^- + h^+)
\]

(4)

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-
\]

(5)

\[
≡\text{Ti}-\text{OH}(e^- + h^+) + \text{OH}^- \rightarrow ≡\text{Ti}-\text{OH}[\text{’OH}]_{\text{ad}+\text{free}}
\]

(6)

\[
≡\text{Ti}-\text{OH}(e^- + h^+) + \text{H}_2\text{O} \rightarrow ≡\text{Ti}-\text{OH}[\text{’OH}]_{\text{ad}+\text{free}} + \text{H}^+ + e^-
\]

(7)

2.3.5 Experiments in real water matrices

Inactivation of E.coli was also tested in real water matrices including WTP intake water, treated surface water before disinfection, and secondary effluent before disinfection. The major characteristics of the water matrices are summarized in Table S2.3. E.coli culture was added into the real water samples to increase the initial concentration. Electrochemical disinfection experiments were conducted for 40 min under current density of 0.88 mA/cm^2. E.coli reductions as well as the oxidizing species generated versus the electrolysis time in different water matrices are shown in Figure 2.8, 5 ~7.5 log removal was achieved in the real water samples after 40 min electrolysis. It can also be noted that the efficiency of E. coli inactivation followed the order of treated surface water > WTP.
intake water > secondary effluent. This may be explained by the increasing organic matters in the matrices which can consume the oxidizing species generated.

Figure 2. 8 E.coli reduction in real water matrices. [Current density: 0.88 mA/cm²; voltage: 5 ~ 6.5 V; Initial E.coli: 1~5×10⁷ CFU/mL after E.coli spike; Log reduction: solid symbol; Oxidizing species: open symbol].

Formation of disinfection byproducts was also examined and the results are shown in Figure 2.9. As expected, higher ClO₃⁻ concentration was found in the secondary effluent due to the high Cl⁻ concentration. However, it’s worth noting that the ClO₃⁻ concentration was much lower after 20 min treatment but >5 log reduction was already achieved for intake water and treated surface water, and ~4 log reduction for secondary effluent. Given that the real water samples usually contain much less E. coli (Table S2.3), even shorter electrolysis time should be adequate for disinfecting purposes. Hence formation of ClO₃⁻ is expected to be controlled at a low level. Evaluation of chlorinated organics formation such as trihalomethanes (THMs) is shown in Figure 2.9B. Less than 14 µg/L THMs were detected in all water samples after 40 min treatment, which is much lower than the EPA standard of 80 µg/L [53]. Furthermore, electrochemical disinfection using this TiO₂ nanotube anode generated less THMs than that of chemical chlorination process employed in the water treatment plant, which is usually 30~40µg/L according to personal
communications with the plant operator. The energy consumption of 4 log reduction of *E.coli* in real water matrices using TiO$_2$ nanotube electrodes was estimated to be 0.1 ~ 0.19 kWh/m$^3$ (See Table S2.4 for equation). As shown in Table 2.3, these values are relatively low compared with those reported in the literature to achieve similar *E. coli* log removal using other electrodes in real water matrices.

Figure 2. 9 Byproducts formation in real water matrices: chlorate (A); THMs (B). [Current density: 0.88 mA/cm$^2$].
Table 2. 3 Comparison of energy consumption using different electrodes for E. coli reduction in real water matrices

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Matrices</th>
<th>E. coli Log reduction</th>
<th>Energy consumption (kWh/m³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSA</td>
<td>Wastewater treatment plant effluent</td>
<td>2</td>
<td>0.047</td>
<td>[131]</td>
</tr>
<tr>
<td>BDD</td>
<td>Secondary effluent</td>
<td>4</td>
<td>0.66</td>
<td>[46]</td>
</tr>
<tr>
<td>BDD</td>
<td>Secondary effluent</td>
<td>5</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.4</td>
<td>0.63</td>
<td>[138]</td>
</tr>
<tr>
<td></td>
<td>Drinking water</td>
<td>5</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.4</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>BDD</td>
<td>Biologically treated sewage</td>
<td>4</td>
<td>2-2.6</td>
<td>[139]</td>
</tr>
<tr>
<td>platinum clad niobium</td>
<td>Slow sand filtered water</td>
<td>2</td>
<td>2</td>
<td>[140]</td>
</tr>
<tr>
<td>Ti/PbO₂</td>
<td>Industrial wastewater</td>
<td>4</td>
<td>4.12</td>
<td>[141]</td>
</tr>
<tr>
<td>Tin oxide</td>
<td>Secondary clarifier</td>
<td>4</td>
<td>0.4-1.6</td>
<td>[110]</td>
</tr>
<tr>
<td>TiO₂ nanotube</td>
<td>WTP intake water</td>
<td></td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treated surface water before disinfection</td>
<td>4</td>
<td>0.1</td>
<td>This Study</td>
</tr>
<tr>
<td></td>
<td>Secondary effluent before disinfection</td>
<td></td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>

E. coli. is one of the most commonly used model microorganisms in electrodisinfection studies reported in the literature, which facilitates comparisons between different electrodes. However, a significant amount of other microorganisms are present in water and need to be removed to ensure safe drinking water supply. Here, we selected B-spizizenii as the surrogate for Cryptosporidium, a well-known chorine resistant protozoa, and tested its reduction in treated surface using this novel TiO₂ nanotube electrode (experimental details are available in Supporting Information). As can be seen in Figure 2.10, ~ 0.9 log reduction was achieved after 40 min treatment at 0.88 mA/cm² and tripling the current density increased the log reduction to ~1.5. The much lower efficiency compared with that of E coli. can be ascribed to the low level ROS generated and the fact
that the electrogenerated RCS are not effective against *B-spizizenii*. While increasing the current density applied may result in higher reduction, high energy cost as well as concerns with byproduct formation may render this approach uncompetitive with others. On the other hand, cysts can be effectively removed in sand filtration (e.g. 2~3 log removal credits for *Giardia* [142]) and requirements for additional removal in the disinfection process vary depending on raw water quality. In general, although thorough investigation of other microorganisms’ removal is out of the scope of current study, future studies with other microbes are needed to fully demonstrate the efficacy of the treatment.

Figure 2. 10 *B-spizizenii* reduction in treated surface water [Initial *B-spizizenii*: 1~5×10⁵ cells/mL; log reduction: solid symbol; oxidizing species: open symbol].

### 2.4 Conclusion

In this study, a novel TiO₂ nanotube anode was prepared using a simple electrochemical procedure (electrochemical anodization followed by cathodization) and further tested for *E. coli* reduction in both synthetic electrolytes and real water matrices. Results indicated that the TiO₂ nanotube electrodes can effectively inactivate *E. coli* with low byproducts formation (e.g. ClO₃⁻, THMs) and energy consumption. Specific conclusions include:
• The efficiency of *E. coli* reduction increased with the applied current density and Cl\(^-\) concentration in NaCl electrolyte as more active chlorine species were formed;

• Chlorate was detected as the inorganic byproduct in NaCl electrolyte and the concentration was determined by the electric charge applied as well as the Cl\(^-\) concentration;

• 2–3 log reduction was achieved in non-chloride electrolytes (Na\(_2\)SO\(_4\), NaH\(_2\)PO\(_4\), NaNO\(_3\), NaHCO\(_3\)) after 20 min electrolysis at current density of 2.63 mA/cm\(^2\), which was similar/higher than other electrodes reported previously;

• Generation of ROS especially •OH was found to be the critical step for electrochemical inactivation of *E. coli* using TiO\(_2\) nanotube anode in all electrolytes including NaCl;

• 5 ~7.5 log removal was achieved in the real water samples after 40 min electrolysis with low byproducts formation; and

• The energy consumption of 4 log reduction of *E. coli* in real water matrices using TiO\(_2\) nanotube electrodes was estimated to be 0.1 ~ 0.19 kWh/m\(^3\), which are relatively low compared with those reported in the literature using other electrodes in similar matrices. Future studies with other microbes are needed to fully demonstrate the efficacy of electrodisinfection using this novel electrode.

### 2.5 Supporting information

**Scavenger method for ROS detection:**

Nitro blue tetrazolium salt (NBT) was used to detect the possible formation of superoxide anion (\(•O_2^-\)) and generation of singlet oxygen (\(^1\)O\(_2\)) was monitored by the loss of Furfuryl Alcohol (FFA) [143]. Sodium azide (NaN\(_3\)) was also added in selected runs as
a $^1O_2$ scavenger [144]. Tert-butyl alcohol (TBA) and 4-chlorobenzoic acid ($p$CBA) were used to detect the generation of hydroxyl radicals ($^\cdot$OH) [136,145]. Moreover, it was reported that alcohols with an $\alpha$ hydrogen such as ethanol can rapidly react with both $^\cdot$OH and $SO_4^{\text{-}}$, but alcohol without an $\alpha$ hydrogen such as TBA only reacts rapidly with $^\cdot$OH. Therefore, ethanol was also used in $Na_2SO_4$ electrolyte to examine the generation of $SO_4^{\text{-}}$ [136].

The possible formation of $^\cdot$O_2$ was tested using NBT salt (NBT$^{2+}$) which can be reduced by $^\cdot$O_2$ and form a purple monoformazan product [143]. Preliminary experiments confirmed that negligible changes in absorbance occurred without current applied (data not shown). Greater absorbance was detected in all electrolytes which further increased with time (Figure S5). However, it has to be pointed out that NBT may also be reduced electrochemically [146]. In order to further confirm whether $^\cdot$O_2$ was generated, both TBA and NBT were added into different electrolytes. The purpose of TBA addition was to inhibit the generation of $^\cdot$OH and consequently the $^\cdot$O_2$ formation (Table S2). As shown in Figure S5, similar or even higher absorbance were observed with the TBA addition. These results imply that the NBT reduction should be mainly caused by electrochemical reduction and $^\cdot$O_2$ generation was insignificant (if any) under the experimental conditions here. In addition, singlet oxygen ($^1O_2$) may be formed via several chemical formation pathways, although some may have not been unequivocally proven scientifically (Eq. 8–11 in Table S2). Generation of $^1O_2$ was examined during electrolysis experiments with FFA as the probe compound. NBT and NaN$_3$ were also added along with FFA, serving as the $^\cdot$O_2$ (precursors for $^1O_2$ formation, Table S2) and $^1O_2$ scavengers respectively in selected runs. As shown in Figure S6, reduction rates of FFA with addition of different probe
compounds were similar, which implies that like •O₂⁻ the formation of \(^1\)O₂ does not seem to be significant in this study.

**B-spizizenii experiments**

*B-spizizenii* stock culture was prepared by inseminating a Tryptic Soy Agar with *B*-spizizenii (ATCC 6633), which was then incubated at 37°C for 24 hours. 0.5 mL of sterile single strength Lauryl Tryptose Broth (LTB-HACH 216315) was dissolved into 49.5 ml of sterile phosphate buffer saline to prepare 1% solution of LTB. To prepare *B*-spizizenii stock solution, a small amount of *B*-spizizenii growth from the stock culture was added to the 50 mL 1% LTB solution and aerated at 37°C for 24 hours. This stock solution should contain approximately \(10^8\)-\(10^9\) *B*-spizizenii cells per mL. In order to prepare the working solution, 20µL of the stock solution was added to 200 mL treated surface water and mixed vigorously. This working solution normally contained \(10^4\)-\(10^5\) cells/mL. During the disinfection experiments, the working solution was continuously mixed and pumped through the reactor at a flow rate of 100 mL/min and samples were taken at different interval time and measured for oxidizing species as a free chlorine, and *B*-spizizenii using standard spread plating techniques.
Table S2. 1 Comparison of E. coli reduction in inert electrolytes using different anodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>E. coli log reduction</th>
<th>Experimental conditions</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>≤3</td>
<td>0.2 M KH$_2$PO$_4$, 33 mA/cm$^2$, 120 min electrolysis</td>
<td>---</td>
<td>[109]</td>
</tr>
<tr>
<td>Pt</td>
<td>~1</td>
<td>0.2 M KH$_2$PO$_4$, 100 mA/cm$^2$, 180 min electrolysis</td>
<td>---</td>
<td>[105]</td>
</tr>
<tr>
<td>Ti/TiO$_2$-RuO$_2$</td>
<td>insignificant</td>
<td>Different electrolytes: [0.01 M Na$_2$SO$_4$-0.1 M NaNO$_3$], &gt; 30 mA/cm$^2$, 33 s electrolysis</td>
<td>Short-lived intermediate electrochemical products were believed to be the major killing function; persulfate production did not appear to have any major role</td>
<td>[147]</td>
</tr>
<tr>
<td>BDD</td>
<td>&lt; 0.5</td>
<td>0.2 M Na$_2$SO$_4$, 5 mA/cm$^2$, 20 min electrolysis</td>
<td>Inactivation rate increased with increasing Na$_2$SO$_4$ concentrations and faster in Na$_2$SO$_4$ than in NaH$_2$PO$_4$ or NaNO$_3$</td>
<td>[133]</td>
</tr>
<tr>
<td>BDD</td>
<td>~2.5</td>
<td>0.2 M Na$_2$SO$_4$, 5 mA/cm$^2$, 120 min electrolysis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table S2. 2 Summary of radical reactions

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>•OH → •O + H$^+$ + e$^-$</td>
<td>[37]</td>
</tr>
<tr>
<td>2</td>
<td>•O + O$_2$ → O$_3$</td>
<td>[37]</td>
</tr>
<tr>
<td>3</td>
<td>•OH + •OH → H$_2$O$_2$</td>
<td>[37]</td>
</tr>
<tr>
<td>4</td>
<td>•OH + O$_3$ → HO$_2^+$ + O$_2$</td>
<td>[37]</td>
</tr>
<tr>
<td>5</td>
<td>•OH + H$_2$O$_2$ → HO$_2^*$ + H$_2$O</td>
<td>[37]</td>
</tr>
<tr>
<td>6</td>
<td>HO$_2^<em>$ ↔ •O$_2^</em>$ + H$^+$</td>
<td>[37]</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$O$_2$ + HO$_2^*$ → ^1O$_2$ + H$_2$O + OH$^-$</td>
<td>[148]</td>
</tr>
<tr>
<td>8</td>
<td>•O$_2^<em>$ + •O$_2^</em>$ + 2H$^+$ → ^1O$_2$ + H$_2$O$_2$</td>
<td>[148]</td>
</tr>
<tr>
<td>9</td>
<td>•OH + •O$_2^*$ → ^1O$_2$ + OH$^-$</td>
<td>[148]</td>
</tr>
<tr>
<td>10</td>
<td>H$_2$O$_2$ + •O$_2^*$ → ^1O$_2$ + •OH + OH$^-$</td>
<td>[148]</td>
</tr>
<tr>
<td>11</td>
<td>H$_2$O$_2$ + OCl$^-$ → ^1O$_2$ + H$_2$O + Cl$^-$</td>
<td>[149]</td>
</tr>
</tbody>
</table>
Table S2. 3 Characteristics of the real water samples

<table>
<thead>
<tr>
<th>Parameters</th>
<th>WTP intake</th>
<th>Treated surface water before disinfection</th>
<th>Secondary effluent before disinfection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>2.9</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>pH</td>
<td>7.3</td>
<td>6.5</td>
<td>7.1</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>9.6</td>
<td>9.2</td>
<td>8.2</td>
</tr>
<tr>
<td>Conductivity (µs/cm)</td>
<td>206</td>
<td>234</td>
<td>561</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>103</td>
<td>113</td>
<td>281</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>0.3</td>
<td>0.1</td>
<td>11.1</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>0.09</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>11.2</td>
<td>11.7</td>
<td>50.9</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>13.5</td>
<td>19.4</td>
<td>16.6</td>
</tr>
<tr>
<td>NO₃⁻ (mg/L)</td>
<td>4.5</td>
<td>4.1</td>
<td>4.9</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>8</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>NPOC⁹ (mg/L)</td>
<td>1.7</td>
<td>1.1</td>
<td>3.2</td>
</tr>
<tr>
<td>E.coli (CFU/100mL)</td>
<td>205</td>
<td>N.A.⁹²</td>
<td>1300~1500</td>
</tr>
</tbody>
</table>

⁹ Non-Purgeable Organic Carbon. ² No E. coli was detected in the sampled water possibly because chlorine was added before coagulation in the treatment plant.

Table S2. 4 Comparison of energy consumption under different conditions

<table>
<thead>
<tr>
<th>Effect of applied current density (1.5 mM NaCl)</th>
<th>Current density (mA/cm²)</th>
<th>Energy Consumption (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density (mA/cm²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.66</td>
<td>0.110</td>
<td></td>
</tr>
<tr>
<td>1.32</td>
<td>0.246</td>
<td></td>
</tr>
<tr>
<td>2.63</td>
<td>0.549</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effect of NaCl Concentration (0.66 mA/cm²)</th>
<th>Energy Consumption (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.109</td>
</tr>
<tr>
<td>1.5</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>0.118</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effect of different electrolytes (Concentrating of electrolyte: 1.5 Mm, 2.63 mA/cm²)</th>
<th>Energy Consumption (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.549</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.597</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td>0.608</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.684</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.618</td>
</tr>
</tbody>
</table>

² All electrolytes prepared in buffer solution: 2.5 mM KH₂PO₄ + 2.5 mM K₂HPO₄; electrolysis time: 20 min (see Figure 4 & 5 for log reduction).

Energy consumption (kWh/m³) = (Current (A) × Voltage (V) × Time (h)) / Volume (m³) × 1000
Figure S2. 1 Effect of washing media on *E.coli* inactivation [Electrolyte concentration: 1.5 mM NaCl; current density: 0.66 mA/cm²; saline solution concentration: 9 g/L NaCl].

Figure S2. 2 Schematic diagram of the experiment set-up (A); and Photos of electrodes (B). *Reactor not to scale for illustration purpose, actual effective volume ~20 mL.*
Figure S2. 3 XPS spectra of Ti2p and O1s before cathodization (A& B) and after cathodization (C&D).

![XPS Spectra](image)

Figure S2. 4 •OH formation detected by pCBA reduction. [Electrolyte concentration: 1.5 mM; pCBA: 0.25 mM; current density: 2.63 mA/cm²].

![pCBA Concentration](image)
Figure S2. $\text{•O}_2^-$ formation detected by NBT reduction. [Electrolyte concentration: 1.5 mM; NBT: 0.2 mM; TBA: 30 mM; current density: 2.63 mA/cm$^2$].
Figure S2. 6¹O₂ formation detected by FFA reduction. [Electrolyte concentration: 1.5 mM; FFA: 0.2 mM; NBT: 0.2 mM; NaN₃: 10 mM; current density: 2.63 mA/cm²].
Figure S2. 7 Voltage range at different current density at constant NaCl concentration (1.5 mM NaCl) (A); Different NaCl concentration under constant current density (0.66 mA/cm$^2$) (B); Different electrolytes (1.5 mM) under constant current density (2.63 mA/cm$^2$) (C); Different real water matrices under constant current density (0.88 mA/cm$^2$) (D).
CHAPTER III

Removal of Meropenem from environmental matrices by electrochemical oxidation


Abstract

Degradation of Meropenem via electrochemical oxidation was investigated for the first time. TiO$_2$ nanotube array (TiO$_2$ NTA) was modified by co-doping cobalt and bismuth (Co/Bi/TiO$_2$ NTA) to enhance the anode stability/lifetime and the generation of reactive oxygen species (ROS, e.g. •OH). A series of anodic oxidation tests were carried out to study the effects of operating parameters, including current density (4 ~12 mA/cm$^2$) and presence of different ions (Cl$^-$, HCO$_3^-$, and SO$_4^{2-}$), on the degradation of Meropenem. With an applied current density of 10 mA/cm$^2$ and an initial concentration of 500 µg L$^{-1}$, ~94% of Meropenem was removed in 15 min. The presence of Cl$^-$ and SO$_4^{2-}$ accelerated Meropenem degradation, while HCO$_3^-$ suppressed the removal. The transformation products were also investigated using 2D-NMR and LC/MS, where C$_7$N$_2$O$_2$H$_{12}$ was identified as one of the main intermediates. Results from CV measurements and scavenger tests indicated that both direct degradation and indirect reaction via the formation of ROS contributed to Meropenem removal. Electrochemical oxidation of Meropenem (500 µg/L) was also evaluated in environmental matrices, where ~77% removal ($E_{EO}$ 6.988 kWh/m$^3$) with ~56% TOC mineralization and ~73% removal ($E_{EO}$ 9.026 kWh/m$^3$) with ~55% TOC mineralization were achieved in RO concentrate (10mA/cm$^2$) and secondary effluent (4mA/cm$^2$), respectively. According to the accelerated lifetime tests’ results, the lifetime of Co/Bi /TiO$_2$ NTA anode under 40, 20, 10, and 5 mA/cm$^2$ can be estimated to be 1,337,
5,873, 25,806, and 113,383 hours, respectively, demonstrating the great potential of Co/Bi/TiO₂ NTA as a stable and cost-effective anode material for the removal of recalcitrant organic pollutants from environmental matrices.

### 3.1 Introduction

Antibiotics are widely used in both humans and animals for treating bacterial infection (therapeutic usage). The main adverse effect caused by the presence of antibiotics in the environment is the development of genes and bacteria that are resistant to antibiotics, thereby reducing the therapeutic capacity of antibiotics to prevent and treat diseases [150]. Antibiotics may enter the municipal sewage in many ways: from the production of active pharmaceutical ingredients, through the excretion of residues after usage, or through discarding unused medicines [151–153], resulting in concentrations typically ranged from 0.5 to 3 µg/L for various antibiotics [154,155]. Many antibiotics (e.g. Trimethoprim, Tetracycline, Lactam, Meropenem, etc.) [13,47,156–158] are resistant to biological treatment, leading to partial removal in wastewater treatment plants (WWTPs) and release into the environment through secondary effluent [155,159]. As a result, drinking water sources impacted by secondary effluent may have a concentration of pharmaceuticals around 0.1 µg/L, which poses a potential risk to human health as well [155,160]. On the other hand, reverse osmosis (RO) has been increasingly used to reclaim secondary effluent for various water reuse applications (e.g., direct/indirect potable reuse, industrial process, and aquifer recharge) to meet the increasing demand for clean water.[161–166] However, the RO process also produces a highly concentrated effluent, which may contain organic
and inorganic contaminants, pathogens, and trace organics, and requires proper
treatment/disposal [167–169]. Given the high conductivity of this concentrate stream,
electrochemical oxidation has appeared to be an attractive option owing to the high
efficiency, mild reaction conditions, easy operation, and environmental compatibility
[168,170–172], whereas efficient, inexpensive, and stable electrode materials are the key
to viable electrochemical treatment systems.

Titanium dioxide nanotube array (TiO$_2$ NTA) electrode possesses many
advantageous properties such as chemical stability, myriad of areas, low-cost, and
nontoxicity, which makes it suitable for different water and wastewater treatment
applications [19,21,22,38,115,173]. Electrochemical hydrogenation/cathodic polarization
or reduction with H$_2$ have proved to be effective in overcoming the intrinsic low electrical
conductivity and electrocatalytic activities TiO$_2$ as a semiconductor [25,92,119]. In spite
of all these advantages, one main concern that hinders the practical application is the
electrode lifetime of TiO$_2$ NTA, which was reported in the range of a few minutes to several
hours at different current densities [38,97,115]. In order to overcome this limitation, Yang
et al. (2018) doped Co into the TiO$_2$ nanotube structure and successfully extended the
anode lifetime from a few hours to > 200 hr [174]. However, the presence of cobalt can
lower the oxygen evolution potential (OEP) of the TiO$_2$ NTA electrode, which may
adversely affect the electrochemical oxidation of target compounds as oxygen evolution
due to water splitting acts as a side reaction. Bismuth (Bi) has been used to improve the
generation of hydroxyl radical (’OH) on anode materials in several studies, [175–177]
which can promote the pollutant oxidation via indirect reaction pathways. Hence,
modification of TiO$_2$ NTA by co-doping cobalt and bismuth (Co/Bi) can be an effective
approach to simultaneously enhance the anode stability/lifetime and the ROS (e.g. 'OH) generation.

In this study, electrochemical oxidation of Meropenem as a model antibiotic was evaluated in secondary effluent and RO concentrate stream generated from water reuse for the first time. Meropenem is a widely-used carbapenem broad-spectrum third-generation antibiotic, but is much less studied compared with other antibiotics such as Lactam, Sulfonamide, and Tetracycline [169,178]. Further, Meropenem is recalcitrant to biological degradation and can pass through conventional wastewater treatment processes [76,179]. Herein, we developed Co/Bi co-doped TiO$_2$ NTA as a new cost-effective anode material for water purification applications. A series of anodic oxidation tests were first carried out in a synthetic electrolyte to study the effects of operating conditions including current density and presence of different ions on the degradation of Meropenem. Then the electrochemical oxidation of Meropenem in environmental matrices (RO concentrate and secondary effluent/SE) was evaluated. The reaction mechanism, degradation kinetics, intermediate products, and electrode stability were also investigated. To our knowledge, this paper represents the first attempt to study electrochemical oxidation and the transformation of Meropenem in water/wastewater treatment.

3.2 Materials and Methods

3.2.1 Chemicals

Chemicals used in this study are described in Text S3.1.
3.2.2 Electrode Preparation

Self-organized TiO$_2$ NTA electrode was obtained by a simple electrochemical anodization of Ti substrate (Text S3.2) [19,115]. Dip-coating method was used to prepare the cobalt/bismuth loaded TiO$_2$ NTA (Co/Bi/TiO$_2$ NTA) electrode. The TiO$_2$ NTA electrode was dipped into a 60 mL aqueous solution containing 125 mM cobalt (Cobalt (II) Nitrate hexahydrate) and 10~75 mM bismuth (Bismuth (III) nitrate pentahydrate) for 1 min and pulled up at the rate of 1 cm min$^{-1}$, followed by drying at room temperature. The doping process was repeated three times. Then the Co/Bi-doped electrode was annealed in a stream of 5% H$_2$/Ar at 450 °C for 1 hour with a heating rate of 2 °C min$^{-1}$. After cooled down naturally, the calcined Co/Bi/TiO$_2$ NTA was cathodized in a 100 mM phosphate buffer solution under a constant current (17 mA/cm$^2$) for 90s to further improve the electrochemical reactivity. The prepared electrodes were tested for anodic stability and hydroxyl radical generation (Text S3.3). In addition, un-doped TiO$_2$ NTA (TiO$_2$ NTA), cobalt-doped TiO$_2$ NTA (Co/TiO$_2$ NTA), and bismuth-doped TiO$_2$ NTA (Bi/TiO$_2$ NTA) were also prepared and tested as the control electrodes.

3.2.3 Electrode characterization

The surface morphology of Co/Bi/TiO$_2$ NTA was characterized using a field emission scanning electron (FESEM, JEOL FE 7000). X-Ray diffraction (XRD) patterns were collected on a Rigaku MiniFlex 600 from 2° to 90° of 20. Surface composition of electrode including X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) was examined using Thermo Scientific ESCALAB 250Xi and JEOL 7000 FE SEM equipped with EDX, respectively. Cyclic voltammetry measurements (CV) were
performed on a potentiostat (Bio-Logic, SP150) in a three-electrode single-compartment cell with Pt as the counter electrode and Ag/AgCl (3 M) as the reference electrode.

3.2.4 Electrochemical oxidation of Meropenem

The electrochemical oxidation of Meropenem was conducted in a two-compartment electrolytic cell divided by a proton exchange membrane (Figure S3.1). The spacing between the working and counter electrodes was kept at 1 cm. The effective surface area of the working electrode was 6 cm². 80 mL of 30 mM NaClO₄ solution containing 500 µg L⁻¹ Meropenem was used as the working electrolyte with pH adjustment or addition of co-existing ions as needed. During the experiments, 1 mL solution was sampled at different time intervals and immediately measured for Meropenem concentration. Electrochemical oxidation of Meropenem was also evaluated in secondary effluent (SE) and RO concentrate generated from secondary effluent. The SE sample was collected from a local WWTP and the RO concentrate was generated using a lab-scale RO skid (AMPAC USA-APRO-LP36) with SE as the feed flow. The recovery rate was controlled at ~75%. Meropenem was then spiked into SE or RO concentrate to obtain an initial concentration of 500 µg L⁻¹, which is higher than that in environmental matrices for the ease and accuracy of analytical analysis. Error bars indicate standard deviations from two duplicate experiments.

3.2.5 Anodic stability

The accelerated lifetime tests were conducted at different applied current densities (40, 120, and 200 mA/cm²) in 30 mM NaClO₄ electrolyte. The electrolyte was replaced
with fresh electrolyte every 12 h. The used electrolyte was also collected, acidified by strong acid, and then analyzed for metal ion concentrations.

3.2.6 Analytical methods and identification of intermediate products

Details of the analytical methods are provided in Text S3.4. Briefly, concentration of Meropenem was measured using a high performance liquid chromatography (HPLC-Agilent 1100 series) with a diode array detector (DAD) and a HPLC/MS (DionEX UltiMate 3000- LTQ Orbitrap XL) in positive electrospray ionization (ESI) mode. Further, HPLC/MS and two-dimensional $^1$H-$^{13}$C NMR (Varian Unity Inova 500 MHz 2D-NMR, Darmstadt, Germany) were used to identify the transformation products of Meropenem. Concentrations of ions (Cl$^-$, SO$_4^{2-}$, ClO$_3^-$, NO$_3^-$, PO$_4^{3-}$ and ClO$_4^-$) were measured by an ion chromatography (Thermo Dionex ICS-1600 upgraded with the RFIC system). Global oxidizing species were quantified as free chlorine using N,N-diethyl-p-phenylenediamine (DPD) method (Hach method 8021). Concentrations of metal ions were analyzed using ICP-MS (ICP-MS Thermo X-Series II, XO 472, Thermo Fisher Scientific). Total organic carbon (TOC) was measured with TOC-LCPH (Shimadzu).

3.3 Results and Discussion

3.3.1 Electrode development and characterization

As shown in the inset of Figure 3.1A, the TiO$_2$ NTA electrodes calcined in air (TiO$_2$ NTA-Air) and in H$_2$ (TiO$_2$ NTA-H$_2$) were deactivated in ~8 and ~15 h respectively, as indicated by a sharp increase in the anodic potential in accelerated lifetime tests. Although deposition of Co into the nanotube may extend the anodic lifetime of TiO$_2$ NTA electrode
via tuning of the concentration and stability of surficial oxygen vacancies ($O_\text{v}$) [174], Co/TiO$_2$ NTA has a lower oxygen evolution potential (OEP) ($\sim$2.2 V vs Ag/AgCl for TiO$_2$ NTA and $\sim$1.7 V vs Ag/AgCl for Co/TiO$_2$ NTA; Figure S3.2), which may lead to increased oxygen evolution as a side reaction and decreased current efficiencies for organic oxidation [176,180]. To compensate this detrimental effect, Bi was introduced into the nanostructure as an electrocatalyst for •OH generation [175–177]. As can be seen in Figure 3.1B, while [•OH]$_{ss}$ was reduced by ~53% with Co/TiO$_2$ NTA as compared to TiO$_2$ NTA, co-doping with Bi greatly promoted the production of •OH. Doping solutions with different Bi concentrations (10–75 mM) were used to determine the optimal synthesis procedure and 60 mM was selected based on the [•OH]$_{ss}$ results (Figure S3.4). As shown in Figure 3.1A, the prepared Co/Bi/TiO$_2$ NTA exhibited a high anodic stability where no sign of deactivation was observed in more than 300 h under a constant current density of 40 mA/cm$^2$.

Figure 3. 1 A) Anodic stability of TiO$_2$ NTA electrodes; B) Comparison of [•OH]$_{ss}$ using different electrodes [Experimental conditions: A) 30 mM NaClO$_4$, 40 mA/cm$^2$; B) 1 mM BA+30 mM NaClO$_4$, 10 mA/cm$^2$; Ag/AgCl (3M NaCl) reference electrode].
The SEM images of the cross-section and the top view of Co/Bi/TiO₂ NTA are shown in Figures S3.5A&B, respectively. It can be seen that Co and Bi were doped successfully onto the TiO₂ NTA electrode and the metal loading was determined to be 7.55 ± 0.26 and 23.69 ± 1.18 µg/cm² for Co and Bi respectively using ICP/MS. The XRD patterns of TiO₂ NTA and Co/Bi/TiO₂ NTA are shown in Figure S3.5C. Most diffraction peaks of the samples can be ascribed to the anatase-phase TiO₂ (JCPDS No. 21-1272) with the preferential {101} exposed facets [19,115]. The {101} exposed facets are sensitive to the nanotube surface modification, as the (101) and (004) crystal planes are affected after metal loading. Co doping did not change the TiO₂ crystal phase, but the diffraction intensity of (101) and (004) planes were decreased and increased, respectively, which is consistent with the previous study [174]. Moreover, the peaks at 28.3 and 32.5 degrees refer to bismuth oxide [181]. The EDX analysis confirms the presence of Co and Bi on the surface of nanotube arrays with a weight percentage of 0.54% and 0.41%, respectively (Figure S3.6). The discrepancy between ICP and EDX analysis may be explained by the penetration depth of electron beam in EDX analysis into the sample surface (1-2 µm). In contrast, the intense acid treatment for the ICP/MS measurement should have dissolve all Co/Bi ions loaded in the sample. The full XPS survey spectrum of Co/Bi/TiO₂ NTA sample indicates the presence of Ti, O, Bi, and Co in the structure of nanotube arrays (Figure S3.5D). The deconvolution of high-resolution O 1s, Ti 2p, Bi 4f, and Co 2p spectra was described in Text S3.5 and Figure S3.7. As reported previously, the Co doping may increase and stabilize the oxygen vacancy (Oₓ⁻) of the TiO₂ NTA electrode, leading to a higher stability [25]. Moreover, as shown in Figure 3.2, a decreased binding energy of Ti 2P₃/₂ was observed after Bi doping, indicating the presence of lower Ti oxidation state such
as Ti$^{3+}$ [25,182,183]. Ti$^{3+}$ states can serve as the crucial reactive sites for many reactions such as generation of •OH, an important active species for water purification [19,173,184]. Bi has also been reported to be an effective electrocatalyst for the generation of oxidizing species in aqueous solutions [175,182,185]. All these may explain the enhanced •OH production of Co/Bi/TiO$_2$ NTA than Co/TiO$_2$ NTA, while the high overpotential for oxygen evolution may contribute to the high •OH generation with TiO$_2$ NTA.

![High-resolution XPS spectra of TiO$_2$ NTA electrodes: A) Ti 2p; B&C) O 1s of TiO$_2$ NTA and Co/TiO$_2$ NTA electrodes, respectively.](image)

**Figure 3.** High-resolution XPS spectra of TiO$_2$ NTA electrodes: A) Ti 2p; B&C) O 1s of TiO$_2$ NTA and Co/TiO$_2$ NTA electrodes, respectively.

3.3.2 Effects of current densities and co-existing ions

The efficiency of electrochemical oxidation of organic contaminants is generally dictated by an anode’s capability of transferring electrons and generating ROS such as •OH, both of which are affected by the applied current density. Here, we examined the oxidation of Meropenem using the Co/Bi/TiO$_2$ NTA electrode under different current densities (Figure 3.3). As expected, Meropenem degradation was improved as the current density increased, with a removal efficiency of 68%, 82%, 94%, and 100% at the current density of 4, 7, 10, and 12 mA/cm$^2$ after 15 minutes’ electrolysis, respectively. With the increase
of current density, more electrons took part into the oxidation process, which can accelerate the degradation of Meropenem. While it can speed up the Meropenem removal, a high current density may lead to low current efficiency and high energy consumption due to the side reactions such as oxygen evolution. Therefore, 10 mA/cm$^2$ was selected as the operating current density in following studies. In addition, as metallic ion leaching during electrolysis may be a concern for the Co/Bi/TiO$_2$ NTA electrode, we monitored the concentrations of Co and Bi ions in the electrolyte after electrolysis. It was found that at an electrode area/solution volume ratio of 7.5 m$^{-1}$, concentrations of Co and Bi were as low as 1.65 ± 0.07 and 1.62 ± 0.03 µg/L, respectively after 15 mins electrolysis at 10 mA/cm$^2$, which corresponded to 0.0225 ± 0.0009 and 0.0217 ± 0.0005 µg/cm$^2$, demonstrating the high chemical stability of the Co/Bi/TiO$_2$ NTA electrode. In addition, effects of initial pH on Meropenem degradation and the pH evolution during the electrolysis in the two-compartment electrochemical cell are shown in Figure S3.8 and Text S3.6. Due to the slow migration of proton ($H^+$) generated from the electrolysis of water across the cation exchange membrane in the divided cell, the effects of initial pH on Meropenem degradation was overwhelmed easily. Therefore, the pH effect may be better explored in an undivided cell. It is also worth mentioning that the effluent from the anode chamber of a membrane-assisted electrochemical cell can be highly acidic, which may require post treatment before discharge. In this sense, an undivided cell may be preferred for practical applications. Here we selected a divided cell to eliminate the cathode reactions and focus on electrochemical oxidation of Meropenem degradation. Nonetheless, efficient Meropenem oxidation was also confirmed at neutral pH in an undivided cell (Figure S3.9).
Figure 3. Effects of current density on Meropenem degradation [Experimental conditions: pH=7; background electrolyte: 30 mM NaClO₄; Ag/AgCl (3M NaCl) reference electrode].

In environmental matrices, various background ions may exist at concentrations several magnitudes higher than that of the target compound. Here chloride (Cl⁻), sulfate (SO₄²⁻), and bicarbonate (HCO₃⁻), which are commonly present in secondary effluent at levels of several tens to hundreds mg/L [172,186,187], were selected to assess the impact of co-existing anions on Meropenem degradation (Figures 3.4A-C). As shown in Figure 3.4A, addition of chloride promoted Meropenem oxidation, where complete removal was achieved in ~8 and ~12 minutes in the presence of 240 and 60 mg/L Cl⁻, respectively. In order to investigate the formation of reactive chlorine species RCS), global oxidizing species (e.g. Cl₂, HOCl/OCl⁻, Cl⁻) were quantified as free Cl₂ and the results are shown in Figures S3.10A&B. A higher Cl⁻ concentration led to more oxidants production and consequently higher Meropenem removal (Figure 3.4A). Furthermore, when Cl⁻ is present, both inorganic and organic chlorinated byproducts may form during electrochemical oxidation of organic pollutants [19,188,189]. Hence, the possible inorganic chlorinated byproducts (e.g. ClO₃⁻ and ClO₄⁻) were monitored during the electrolysis of Meropenem.
in the presence of Cl\(^-\) (Figures S3.10A&B). While no perchlorate was detected, chlorate was generated during the oxidation of Meropenem and the generation increased with the increase of chloride concentration. In order to probe the formation of organic chlorinated products, we examined the Cl mass balance throughout the run. Here, 1.5 mM Na\(_2\)S\(_3\)O\(_2\) was added to the samples taken at different time intervals to quench the residual active chlorine species, and then the samples were analyzed for chloride and chlorate. As shown in Figures S3.10C&D, the total Cl mass remained relatively constant during the experiments, indicating the formation of organic chlorinated byproducts (if any) should be very low. As the above test was conducted in the synthetic electrolyte with no bulk organics, we further examined the Cl mass balance in SE and RO concentrate, where the chloride concentration was monitored right after the run as well as after 1~3 days (i.e. so free chlorine may decompose to chloride). As shown in Figure 3.5, the chloride concentration remained constant after 24 hrs, indicating ~5% of Cl may be involved in the formation of chlorinated organic products. The common chlorinated byproducts such as dichloromethane, trichloromethane, tetrachloromethane, and 1,2-dichloroethane may consist of ~1% of total Cl as reported previously [127]. Moreover, the low pH in anodic chamber may inhibit the formation of THMs and HAAs due to the hydrolysis of other chlorinated byproducts like haloacetonitriles (HANs) and haloacetaldehydes (HAs) [170,190].
The Meropenem removal was slightly enhanced in the presence of sulfate (Figure 3.4B), which may be ascribed to the formation of sulfate radicals ($SO_4^{2-}$) that contribute to Meropenem degradation. In contrast, the Meropenem oxidation was suppressed in the presence of bicarbonate ions ($HCO_3^{-}$) (Figure 3.4C). The removal efficiency decreased to 76% and 66% when the concentration of bicarbonate increased from 200 to 800 mg/L, respectively. Here, the bicarbonate may compete with Meropenem for $^\cdot$OH via the reaction
•OH + HCO$^-$→H$^+$_2O + CO$^-$$_3$.[191] It may also adsorb on the electrode surface or participate in side reactions, thus lowering the current efficiency [192].

### 3.3.3 Mechanism and transformation products

In general, electrochemical oxidation of water pollutants may proceed via direct electron transfer or indirect oxidation via the generation of oxidizing species such as ROS, RCS, etc. In order to examine the direct oxidation mechanism, CV tests were conducted in the presence and absence of Meropenem. As shown in Figure S3.11, the oxidation peak started from 1.25 ~ 1.63 V vs. Ag/AgCl as well as the current increase at 2V vs. Ag/AgCl indicates direct oxidation of Meropenem at the Co/Bi/TiO$_2$ NTA anode.

The possible indirect mechanism for Meropenem oxidation in real wastewater were investigated in three electrolytes, including control (NaClO$_4$), sulfate (NaClO$_4$ + SO$_4^{2-}$), and chloride (NaClO$_4$ + Cl$^-$). First, the contribution of •OH to Meropenem oxidation was examined in NaClO$_4$ electrolyte using benzoic acid (BA) as a •OH probe compound ($k_{\text{BA, •OH}}$=5.9×10$^9$ M$^{-1}$ s$^{-1}$) [193], whose electrochemical stability was previously confirmed (Figure S3.3). As shown in Figure 3.6A, the removal of Meropenem decreased with the addition of BA, which indicates •OH plays a role in Meropenem degradation. Since ~80% of Meropenem was still removed in the presence of BA, direct oxidation should be the dominant pathway for the oxidation of Meropenem. To explore the possible formation and role of SO$_4^{2-}$ in Meropenem degradation, ethanol was used as a scavenger ($k_{\text{ethanol, sulfate radical}}$=1.6×10$^7$ M$^{-1}$ s$^{-1}$) [194]. Since ethanol can also react quickly with •OH (1.8×10$^9$ M$^{-1}$ s$^{-1}$) [195], a similar inhibition effect should be observed with BA and ethanol addition if no SO$_4^{2-}$ is formed. Figure 3.6B shows that compared with only adding BA, the removal
efficiency slightly decreased when both ethanol and BA were added. A similar trend was observed for a lower concentration of sulfate under the same experimental conditions (Figure S3.12). These results indicate that \( \text{SO}_4^{2-} \) was possibly generated during the electrolysis when sulfate was present and contributed to Meropenem degradation to certain extent. This is also consistent with the results of Figure 3.4B. The addition of \( \text{Cl}^- \) noticeably enhanced the degradation of Meropenem (Figure 3.4A), which can be ascribed to the formation and contribution of RCS. Chlorine radical (Cl') and hypohalous acid (HOCI/OCl-) are the most important RCS, which may be generated at potentials that are suitable for electrochemical water treatment [2,196–198]. Moreover, Cl' may adsorb on the electrode surface lattice oxygen group, i.e. \( \text{Cl'}_{\text{ads}} \) [196,199,200], which is not stable and participates in reactions at very high constant rates (\(10^8-10^{10} \text{ M}^{-1} \text{ S}^{-1}\)) [201]. Here, allyl alcohol (AA) was first used to scavenge the effects of Cl'/ Cl'_{\text{ads}} (\(k_{\text{AA,Cl'}/\text{Cl'}_{\text{ads}}} \approx 6x10^8 \text{ M}^{-1} \text{ S}^{-1}\)) and HOCI (\(k_{\text{AA,HOCI}} \approx 1x10^{-1} \text{ M}^{-1} \text{ S}^{-1}\)) on Meropenem degradation [196,200]. The electrochemical stability of AA was examined and confirmed in CV tests (Figure S3.13). As shown in Figure 3.6C, Cl' and HOCI formation as oxidizing species were inhibited completely in the presence of 100 mM AA. The formation of Cl' was also confirmed with the addition of benzoic acid (BA) (\(k_{\text{BA,Cl'}/\text{Cl'}_{\text{ads}}} \approx 1.8x10^{10} \text{ M}^{-1} \text{ S}^{-1}\)) as a free chlorine resistant probe compound [202]. As can be seen in Figure 3.6D, the generation of oxidizing species was mostly inhibited with the addition of BA. Such difference in the formation of oxidizing species with the addition of AA and BA can also imply the formation of HOCI during the electrolysis as BA reacts with Cl• much faster than HOCI. In addition to the formation of oxidizing species, the effect of RCS on Meropenem degradation was also confirmed (Figure S3.14).
Figure 3. 6 A&B) Meropenem degradation in the presence and absence of hydroxyl radical and sulfate radical scavengers, respectively; C&D) Generation of oxidizing species in the presence and absence of probe compounds [Experimental conditions: 10 mA/cm², pH=7, A) 1 mM BA, B) 100 mM ethanol & 1 mM BA, C) 100 mM AA, D) 10 mM BA; background electrolyte: ~30 mM Na₂SO₄ (electrolyte conductivity was equal to 30 mM NaClO₄); Ag/AgCl (3M NaCl) reference electrode].

This study is one of the first attempts to identify the transformation products of Meropenem in water/wastewater treatment. Here we employed HPLC-UV, MS and 2D-NMR spectroscopy to obtain structure information of the intermediates. Figure S3.15 shows the spectrum of the sample after electrochemical oxidation treatment using ESI (+) mode with a mass range of 55-400 amu, which demonstrates that intermediates with m/z of 226.60, 185.74, 157.02, 144.88, 104.70, and 63.83 (molecular weights of 225, 184, 156,
143, 103, and 62 g/mol, respectively) were formed. In an effort to obtain the chemical structures of these intermediates, we conducted electrochemical experiments with a high Meropenem concentration (50 mg/L) and attempted to isolate and collect samples of each peak in the HPLC-UV spectra that represent individual intermediates (Figure S3.16); after collection of material an attempt was made to determine the chemical structure of these peaks by means of 2D-NMR spectroscopy. Despite larger amounts of starting material we were only able to isolate enough material for one major peak (i.e. peak at 5.35 min shown in Figure S3.16) in small quantities. The $^1$H NMR scan illustrating signals of this compound at different chemical shifts is shown in Figure S3.17. Signals at ~0.6, 1.8, and 2.9 ppm represent signals of the reference standard, sodium trimethylsilylpropanesulfonate (DSS), that was added at a concentration of 1 mMol to the sample. Signals in the range of 1.1~1.5 and 2.0~2.2 ppm refer to alkane (CH-CR$_3$) and amid (RC=ONR'R'') groups, respectively. The additional signals in the range of 3.3~3.9 ppm are evidence of an alkyl group located next to a nitrogen. As obvious from the $^1$H-NMR spectrum we were only able to isolate minute amounts of compound. Thus, the only way to possibly obtain carbon NMR data was a HSQC NMR experiment (Figure S3.18). Based on the MS-information we were able to determine the formula to be C$_7$N$_2$O$_2$H$_{12}$ (156 g/mol), in addition the $^1$H and $^{13}$C information collected strongly suggests a fragment identified as N,N-dimethyl-4-oxopyrrolidine-2-carboxamide, an oxidation product of Meropenem, as depicted in Figures S3.15 &16 along with Meropenem.
3.3.4 Test in environmental matrices

The electrochemical oxidation of Meropenem was also tested in real water matrices, including secondary effluent (SE) and RO concentrate generated from SE as described previously. The main characteristics of SE and RO concentrate are summarized in Table 3.1. The concentration of Meropenem in SE was found to be ~7 µg L\(^{-1}\), indicating the prevalence of this contaminant in environmental matrices. To facilitate the study of treatment evaluation and analytical analysis, Meropenem was spiked into the water samples to obtain an initial concentration of 500 µg L\(^{-1}\). Two different current densities (4 and 10 mA/cm\(^2\)) were used for electrochemical oxidation of RO concentrate, while only 10 mA/cm\(^2\) was used for secondary effluent due to the low conductivity of secondary effluent. Meropenem degradation and TOC mineralization in real water matrices are shown in Figure 3.7A. Approximate 73% of Meropenem was removed in secondary effluent after 40 minutes’ electrolysis at 4mA/cm\(^2\), while 46 and 77% removal were achieved in RO concentrate at 4 and 10 mA/cm\(^2\), respectively. Higher current density led to higher TOC mineralization as well. As shown in the inset of Figure 3.7A, ~55% and ~37% TOC reduction were achieved in SE and in RO concentrate at 4 mA/cm\(^2\), respectively, which reached ~56% when the current density increased to 10 mA/cm\(^2\) in RO concentrate. Furthermore, the pseudo-1\(^{st}\) kinetics of Meropenem degradation in synthetic electrolyte and real matrices are compared (Figure 3.7B), where the rate constant of \(k\) was determined to be 0.033 ± 0.003 min\(^{-1}\) in SE and 0.015 ± 0.004 min\(^{-1}\) in RO concentrate at 4 mA/cm\(^2\), which was about 2.37 times higher (0.035 ± 0.007 min\(^{-1}\)) in RO concentrate at 10 mA/cm\(^2\). In contrast, a much faster kinetics was obtained in the synthetic electrolyte (0.164 ± 0.009 min\(^{-1}\) at 10 mA/cm\(^2\)). Such difference may be ascribed to the electrolyte conductivity,
competition (e.g. dissolved organic matters) and inhibition (e.g. bicarbonate) effects exerted by different chemical species in the complex environmental matrices.

Table 3.1 Characteristics of secondary effluent and RO concentrate used in this study.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Secondary effluent</th>
<th>RO concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meropenem (µg/L)</strong></td>
<td>6.74 ± 1.60</td>
<td>26.98 ± 6.42</td>
</tr>
<tr>
<td>Na⁺ (mg L⁻¹)</td>
<td>26.52 ± 1.57</td>
<td>177.79 ± 6.35</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>2.70 ± 0.25</td>
<td>8.78 ± 2.61</td>
</tr>
<tr>
<td>K⁺ (mg L⁻¹)</td>
<td>11.78 ± 2.57</td>
<td>29.65 ± 6.19</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>43.89 ± 3.00</td>
<td>165.16 ± 35.93</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>9.05 ± 0.11</td>
<td>43.49 ± 1.92</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>0.7 ± 0.07</td>
<td>3.02 ± 0.11</td>
</tr>
<tr>
<td>HCO₃⁻ (mg/L)</td>
<td>161.04 ± 0.88</td>
<td>756.88 ± 5.62</td>
</tr>
<tr>
<td>NO₃⁻ (mg/L)</td>
<td>4.7 ± 0.4</td>
<td>20.68 ± 0.87</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>11.02 ± 0.98</td>
<td>49.09 ± 3.21</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>3.43 ± 0.67</td>
<td>13.88 ± 1.67</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.47 ± 0.12</td>
<td>0.83 ± 0.09</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>382 ± 4</td>
<td>1508 ± 12.37</td>
</tr>
</tbody>
</table>

Figure 3.7 A) Meropenem removal and TOC mineralization in secondary effluent (SE) and RO concentrate, B) Kₐ of Meropenem degradation [Background electrolyte in control: 30 mM NaClO₄, Ag/AgCl (3M NaCl) reference electrode].

The energy consumption (Eₜₒ) of Meropenem oxidation (Text S3.7) was found to be 0.813, 9.026, and 6.988 kWh/m³ for synthetic electrolyte, SE, and RO concentrate, respectively. Using the current average industrial electrical energy price of $0.07 per kWh.
in United States (U.S. Energy Information Administration-Sep.2019) [203], the costs of energy consumed per m$^3$ of treated wastewater were calculated as $0.06, 0.63, and 0.49 for synthetic electrolyte, SE, and RO concentrate, respectively.

### 3.3.5 Electrode deactivation and lifetime

The electrode life is another practical aspect that needs to be considered for electrochemical treatment. As shown in Figure 3.8A, the Co/Bi/TiO$_2$ NTA electrode has an anodic lifetime of 43h and 128h at the elevated current density of 200 mA/cm$^2$ and 120 mA/cm$^2$, respectively. The deactivation of the electrode may be caused by the gradual dissolution of the doped Co or the destruction of the TiO$_2$ NTA structure during long-time electrolysis at high current densities, if either occurs before the eventual oxidation of Ti$^{3+}$/oxygen vacancies which we think should be the ultimate cause for the loss of electroactivities of TiO$_2$ NTA based anode. To this end, we first examined the residual Co on the deactivated electrode (200 mA/cm$^2$) and found ~37% Co was still present. In addition, we monitored Co dissolution during the accelerated lifetime test at 40 mA/cm$^2$. The time-dependent Co leaching as well as the corresponding anodic potential was illustrated in Figure S3.19. It can be seen that the high current density caused ~40% of cobalt loss during the first 24 hours (after which the dissolution was much lower indicating the initial loss may mostly result from loosely-bonded metal species on the surface), whereas the anodic potential did not increase noticeably and no sign of deactivation was observed in more than 300 hrs (Figure 3.1A). Also, about ~44% Co remained on the electrode at the end of the test (320 hrs). Based on these results, we conclude that the gradual loss of Co is unlikely to be the main mechanism of deactivation under the
conditions tested here. We further examined the integrity of the nanotube structure of the deactivated electrode. Compared to the well-aligned nanotube array in the pristine electrode (Figure S3.5B), broken and cluttered nanotubes are present in the deactivated one (Figure 3.8B&B`). The nanotube structure provides beneficial features of directional charge transport and high efficiency of charge separation, which is considered to be critical for the dramatic enhancement of the electroactivity of TiO$_2$ as a semiconductor [21,204]. Therefore, the mechanical strength of the nanostructure could be the limiting factor that determines the electrode life particularly under high current densities. It should also be emphasized the apparent high loss of Cobalt was observed at elevated currents in the accelerated tests with majority occurred during the first 24 hours, whereas low metal leaching was detected under normal operating conditions as reported in the previous section. Moreover, the electrode may be pre-treated by anodization to remove the loosely-bounded metal dopant if needed. Based on the results of accelerated lifetime tests (Text S3.8), the anodic lifetime at the current density of 40, 20, 10, and 5 mA/cm$^2$ is estimated to be 1,337, 5,873, 25,806, and 113,383 hours, respectively. The long electrode lifetime under current densities relevant to water treatment is beneficial for practical applications of the Co/Bi/TiO$_2$ NTA anode.
Figure 3. 8 A) Anodic stability of Co/Bi/TiO$_2$ NTA electrodes at different current densities, B&B'') SEM image of deactivated Co/Bi/TiO$_2$ NTA electrode [Experimental condition: 30 mM NaClO$_4$, Ag/AgCl (3M NaCl) reference electrode].

3.4 Conclusion

This study has demonstrated that Meropenem, a representative recalcitrant antibiotic that is widely present in wastewater, can be effectively removed from environmental matrices by electrochemical oxidation. Co-doping Co/Bi has proved to be a viable approach to enhancing the lifetime and promoting ROS generation of TiO$_2$ NTA electrodes as a cost-effective anode material for environmental applications. Depending on the treatment requirements and specific applications, anodic oxidation of persistent organic pollutants using Co/Bi/TiO$_2$ NTA electrodes may either be employed as a pre or post-treatment for biological processes or a standalone process. This study also indicates that TiO$_2$ NTA prepared via a facile anodization method can serve as a nanostructured platform where targeted modification or functionalization can be applied. This may be further explored for other environmentally relevant applications. Lastly, more research efforts are needed to fully understand the transformation and fate of Meropenem during wastewater treatment.
3.5 Supporting information

Text S3.1

Meropenem trihydrate was purchased from TCI (Tokyo Chemical Industry, Japan); Benzoic acid (BA), bismuth (III) nitrate pentahydrate, and ammonium fluoride were obtained from Alfa Aesar (Massachusetts, USA); Allyl Alcohole was purchased from Sigma-Aldrich (St. Louis, USA). Other reagents were obtained from Fisher Scientific. All chemicals are of analytical grade and were used without further purification.

Text S3.2

Titanium foil (0.1 mm, 99.6%) was cleaned by sonication in acetone and ethanol for 10 minutes, respectively, followed by rinsing in deionized (DI) water and drying under ambient atmosphere. Then, Ti foil was anodized in an ethylene glycol (EG) electrolyte containing H$_2$O (2.5 wt%) and NH$_4$F (0.2 wt%) for 16 hours under a constant voltage of 45 V at room temperature. Subsequently, the as-formed TiO$_2$ NTA layer is anodized under 60 V for 5 minutes in fluoride free electrolyte (5% H$_3$PO$_4$ in EG solution) to enhance the physical stability of nanotube layer. A platinum mesh was used as the cathode in the anodization processes. After anodization, the electrode was washed with ethanol to remove remnants from the surface, and then dried naturally at room temperature.
Text S3.3

As shown in eqs. 1-2, the quasi steady-state concentration of \( \cdot OH \) \([\cdot OH]_{ss}\) during the electrolysis was estimated based on the pseudo first order rate constant of benzoic acid (BA) decay \( (K_{BA}) \) in background electrolyte \( (30 \text{ mM NaClO}_4) \) [119]. The electrochemical behavior of BA on the surface of TiO\(_2\) NTA-based electrodes was investigated using CV measurements (Figure S3).

\[
\frac{d[BA]}{dt} = k_{BA,OH} [BA][\cdot OH] = k_{BA}[BA]
\]
\[
[\cdot OH]_{ss} = \frac{k_{BA}}{k_{BA,OH}}
\]

Text S3.4

The concentration of Meropenem was measured using a high performance liquid chromatography (HPLC-Agilent 1100 series) with a diode array detector (DAD) at 290 nm with a Hypersil Gold 100 x 2.1 mm C18 column. The mobile phase was acetonitrile/KH\(_2\)PO\(_4\) \((20:80, \text{ vol:vol\%})\) with a flow rate of 0.2 mL/min. The benzoic acid concentration was determined using the same HPLC column at a wavelength of 210 nm with a mobile phase of 30:70, vol:vol\% of methano:water. Concentrations of ions \( (\text{Cl}^-, \text{SO}_4^{2-}, \text{ClO}_3^{-}, \text{NO}_3^{-}, \text{PO}_4^{3-} \text{ and ClO}_4^-) \) were measured by an ion chromatography (Thermo Dionex ICS-1600 upgraded with the RFIC system) using an IonPac AS 19 anion-exchange column \((4 \times 250 \text{ mm})\), where the gradient elution was: 0→5 min \((10 \text{ mM KOH})\), 5→10 min \((10→18 \text{ mM KOH})\) and the flow rate was 1.0 ml/min.

Text S3.5

The peak at 530.06 eV is attributed to the O 1s, which is fitted with two peaks at 529.78 (Ti-O) and 531.28 eV(surface O-H) [126]. The Ti 2p spectra shows two peaks at
464.48 and 458.54 eV, which correspond to the Ti 2p\textsubscript{1/2} and Ti 2p\textsubscript{3/2}, respectively. These two peaks can be deconvoluted into two sets of peaks. One refers to the Ti\textsuperscript{3+}, which is located at 458.58 and 463.76 eV, and the other applies to the Ti\textsuperscript{4+} with binding energy at 464.58 and 458.68 eV [126]. The Co 2p pattern shows two peaks at 786.28 and 780.58 eV, which were deconvoluted into three peaks centered at 786.18, 781.88, and 780.48 eV. The peaks located at 781.88 and 780.48 eV are attributed to Co\textsuperscript{2+} and Co\textsuperscript{3+}, respectively [205]. The peaks at the binding energy of 163.98 and 158.68 eV are assigned to the Bi 4f\textsubscript{7/2} and Bi 4f\textsubscript{5/2}, respectively [185].

Text S3.6

Effects of initial pH on Meropenem degradation and the pH evolution during the electrolysis in different reactor chambers are shown in Figure S8C, respectively. While a slightly better Meropenem removal was observed at pH 8 in the first 5 minutes than pH 7 or 5, overall initial pH exhibited minimum effects during the treatment. As shown in Figure S8A, pH in the anodic chamber dropped to ~3 within 2~3 min regardless of the initial value. High pH at the beginning of experiment may facilitate OH\textsuperscript{-} adsorption on the electrode surface and assist the oxidation of Meropenem via boosting •OH generation [19,206].

Text S3.7

Energy consumption is an important concern for practical applications of electrochemical treatment. In this study, the $E_{EO}$ value was calculated using eq. 3 and data from the batch experiments [207].

$$E_{EO} = \frac{AXIUXt}{1000V \times \log\left(\frac{C_0}{C}\right)}$$  \hspace{1cm} eq. 3
where $E_{EO}$ is the electric energy consumed to degrade the concentration of Meropenem by one order of magnitude in 1 m$^3$ wastewater (kWh/m$^3$), $A$ is the surface area (cm$^2$), $I$ is the applied current density (A/cm$^2$), $U$ is the average overall potential (V), $V$ is the volume of wastewater (m$^3$), $t$ is the time of electrolysis (hr), and $C$ is the concentration of Meropenem (μg/L).

**Text S3.8**

An empirical equation (eq. 4) was used to estimate the anodic lifetime of Co/Bi/TiO$_2$ NTA electrode [208,209].

$$T_1 \times i_1^n = T_2 \times i_2^n$$  \hspace{1cm} \text{eq. 4}

where, $T$ is anodic lifetime of electrode at a constant current density ($i$) and $n$ is a coefficient which can be calibrated with experimental data at different current densities. Here $n = 2.135$ was obtained based on the electrode lifetime at 120 and 200 mA/cm$^2$. 
Figure S3. 1 Schematic diagram of the experimental setup.

1- Working Electrode (TiO$_2$ NTA/Co/Bi-6cm$^2$)  
2- Counter Electrode (Pt)  
3- Reference Electrode (Ag/AgCl-3M NaCl)  
4- Potentiostat  
5- Stir Plate  
6- Magnetic Stir Bar  
7- Cation Exchange Membrane (Nafion-117)  
8- Computer

Figure S3. 2 Cyclic voltammetry of different TiO$_2$ NTA electrodes [Experimental conditions: 100 mA NaClO$_4$, Ag/AgCl (3 M NaCl) reference electrode].
Figure S3. 3 Direct oxidation of BA [Experimental conditions: 1 mM BA, 100 mA NaClO₄, Ag/AgCl (3 M NaCl) reference electrode].

Figure S3. 4 [•OH]ₜₛ estimated from BA electrocatalytic degradation using Co/Bi/TiO₂ NTA electrodes with different metal doping [Experimental conditions: 1 mM BA+100 mM NaClO₄, Ag/AgCl (3M NaCl) reference electrode].
Figure S3. 5 A&B) SEM images; C&D) XRD and XPS spectra of Co/Bi/TiO$_2$ NTA electrodes, respectively.

Figure S3. 6 EDX spectra of Co/Bi/TiO$_2$ NTA electrode.
Figure S3. 7 XPS spectra of Co/Bi/TiO$_2$ NTA electrode: A) O 1s, B) Ti 2p, C) Co 2p, D) Bi 4f.

Figure S3. 8 pH evolution in different reactor chambers during the experiments: A) anodic chamber, B) cathodic chamber; C) Effects of initial pH on Meropenem degradation [Experimental conditions: 10 mA/cm$^2$, Ag/AgCl (3M NaCl) reference electrode].
Figure S3. 9 Meropenem degradation in divided and undivided electrochemical cell using Co/Bi/TiO$_2$ NTA electrode [Experimental condition: working electrode: Co/Bi/TiO$_2$ NTA; counter electrode: Pt; applied current density: 10mA/cm$^2$; pH:7; background electrolyte: 30 mM NaClO$_4$; Ag/AgCl (3M NaCl) reference electrode].

Figure S3. 10 Chlorinated byproduct formation and Cl mass balance: A&C) 60 mg/L Cl$^-$, B&D) 240 mg/L Cl$^-$ [Experimental conditions: 10 mA/cm$^2$, pH 7, 30 mM Na$_2$SO$_4$, Ag/AgCl (3M NaCl) as the reference electrode in A&B, Hg/HgO (20% KOH) as the reference electrode in C&D].
Figure S3. 11 Direct oxidation of Meropenem on the Co/Bi/TiO$_2$ NTA electrode [Experimental conditions: 5mg/L Meropenem, background electrolyte: 5 mM NaClO$_4$, Ag/AgCl (3 M NaCl) reference electrode].

Figure S3. 12 Meropenem degradation in the presence and absence of scavengers [[Experimental conditions: 100 mg/L SO$_4^{2-}$, 100 mM ethanol, 1 mM BA, 10 mA/cm$^2$, pH 7, Ag/AgCl (3M NaCl) reference electrode]].
Figure S3. 13 Direct oxidation of AA, bicarbonate, and TBA [Experimental conditions: 100 mM NaClO₄ A) 100 mM AA, B) 50 mA HCO₃⁻, C) 100 mM TBA Ag/AgCl (3 M NaCl) reference electrode].

Figure S3. 14 Meropenem degradation in the presence and absence of RCS probe compounds [Experimental conditions: A)100 mM AA, B) 10 mM BA; Ag/AgCl (3M NaCl) reference electrode].
Figure S3. 15 LC/MS Spectrum of Meropenem transformation products in the positive EIS mode \([\text{M+H}]^+\).

Figure S3. 16 HPLC/UV Spectra of Meropenem transformation products [Experimental conditions: \(\text{pH}=7\), 10 mA/cm\(^2\), Ag/AgCl, 15 mins electrolysis (3M NaCl) reference electrode].
Figure S3. 17 $^1$H-NMR spectrum of peak # at 500 MHz

Figure S3. 18 HSQCSE spectrum of peak # at 500 MHz; blue peaks corresponding to DSS; red peaks due to sample.
Figure S3. Cobalt leaching from the Co/Bi/TiO$_2$ NTA electrode in the accelerated lifetime test. [Experimental conditions: 30 mM NaClO$_4$, 40 mA/cm$^2$, Ag/AgCl (3M NaCl) reference electrode].
CHAPTER IV

Electrocatalytic reduction of nitrobenzene using TiO₂ nanotube electrodes with different morphologies: kinetics, mechanism, and degradation pathways


Abstract

Here we report on one of the first studies utilizing self-doped TiO₂ nanotube arrays (NTAs) for electrocatalytic reduction of water pollutants with nitrobenzene (NB) as the model compound. In particular, we focused on the effects of morphological and crystallographic characteristics on the electrochemical reactivity of TiO₂ NTAs towards the target pollutant. The TiO₂ NTAs with different morphologies and exposed facets were synthesized by tuning a suite of anodization parameters and applying a post-anodization treatment. A series of electrochemical reduction tests using TiO₂ NTAs as the cathode were carried out to investigate the effects of nanotube morphologies and operating conditions. Results indicate that the {001}-exposed facet, longer nanotube length, and larger nanotube diameter are the structural and morphological features that can lead to enhanced performance of TiO₂ NTA electrodes. With the applied cathode potential of −1.20 V/SCE and an initial concentration of 300 mg/L, > 95% NB can be efficiently degraded at the energy consumption of 2.07 kWh/m³ (E/E₀), 7.67 kWh/kg (NB), and 30 kWh/kg (C), all of which are much lower than those of electrochemical oxidation processes. The good stability of the TiO₂ NTA cathode was also demonstrated in 10 cyclic runs. Furthermore, CV measurements and scavenger tests were employed to study the reaction mechanism. It was found that both the direct reduction and surface adsorbed H⁺ contributed to NB
degradation. The NB transformation pathway and degradation kinetics of NB and the intermediate products were also investigated. Results obtained from this study suggest that the self-doped TiO$_2$ NTA is a promising cost-effective electrode material for electrocatalytic reduction of water pollutants with high efficiency and stability.

4.1 Introduction

Nitrobenzene (NB) is an important raw material in many manufacturing processes and hence can exist at high levels (100~300 mg/L) in industrial wastewater [210–213]. It has been reported that ca. 8600 tons of NB are released into the aquatic environment annually [214]. NB is a pollutant that poses a serious threat to human health and ecosystem due to its persistence and high toxicity [215,216]. It is classified as a B2 carcinogen and listed as one of the priority pollutants by USEPA [217]. Because of its harm to human and the environment, US and China issued the maximum acceptable NB concentrations of 17 and 20 µg/L in a water body respectively [217,218]. However, treatment of wastewater containing NB can be difficult due to its stable structure and chemical properties. The presence of nitro group (-NO$_2$) reduces the electron cloud density of the ring, making it resistant to chemical oxidation and aerobic biological degradation [219]. Among various treatment technologies that have been developed for NB treatment [58,220–223], electrochemical methods have appeared to be an attractive option to tackle this refractory pollutant ascribed to the high efficiency, mild reaction conditions, easy operation, and environmental compatibility [58,223]. In particular, electrochemical reduction can be a more cost-effective approach as the electron-withdrawing nitryl moiety renders the molecule easier to be reduced than to be oxidized. Moreover, while a high degree of
mineralization may be achieved (but at a high energy cost), the stability/lifetime of the electrodes is often a concern for electro-oxidation of NB [58]. The efficiency of electrochemical reduction processes largely depends on the properties of cathode material [224]. However, commonly-used cathodes for pollutant reduction may either suffer low reactivity and/or stability (e.g. Fe, Cu, and Ni) or be subject to limited applications due to the high cost and scarcity of the materials (e.g. Pd, Pt, and Au) [15,225–227].

TiO$_2$, is one of the most important semiconductor metal oxides and possesses some advantageous properties such as high stability, non-toxicity, low cost, and photoactivities, which makes it suitable for water and wastewater treatment applications. However, in contrast to the widely-explored photocatalytic activities, the low conductivity and poor electroactivity hinders the application of TiO$_2$ as an efficient electrode material [21]. Both experimental and theoretical evidence have indicated that nanoarchitectured metal oxides may exhibit new material behavior [228]. As dimensions diminish to the nanoscale, not only the surface area increases significantly but also the electronic properties improve considerably. TiO$_2$ nanotube can be formed on metallic Ti substrates by a simple electrochemical anodization method and represents a controllable 1D nanostructure with beneficial features of directional charge transport and high efficiency of charge separation [229]. The functional capacity can be further enhanced via engineered modifications of the main structure parameters. For example, surface defects (e.g. Ti$^{3+}$ states or O$^{2-}$ vacancies) can serve as the crucial reactive sites for many reactions such as generation of atomic hydrogen (H*) and/or hydroxyl radical (∙OH), both of which are important active species for water purification [230,231]. These defects can be
introduced into TiO$_2$ nanotube much more easily (e.g. cathodization/electrochemical self-doping) than in bulk materials because of the high density of interface sites where defect formation energies are reduced [232]. Moreover, TiO$_2$ crystals may be synthesized with tailored facets that have higher surface free energies (e.g. 0.90 J m$^{-2}$ for {001} > 0.53 J m$^{-2}$ for {100} > 0.44 J m$^{-2}$ for {101}) [233,234]. TiO$_2$ nanostructures with highly exposed {001} facets exhibited higher photocatalytic activity for the degradation of aquatic and air pollutants [235–237]. TiO$_2$ single crystals with dominant {001} facets also showed good electrochemical reactivity towards refractory water contaminants [57,223].

While TiO$_2$ nanotube arrays (NTAs) based materials have been evaluated as the cathode in several studies for water/wastewater relevant applications [44,238–240], the TiO$_2$ NTAs were either doped with other elements [239,240] or were used microbial fuel cells [238]. To the best of our knowledge, pristine TiO$_2$ NTAs haven’t been employed for cathodic reduction of organic pollutants. On the other hand, unlike anodic oxidation which may gradually deactivate the self-doped TiO$_2$ NTA due to surface passivation [184], cathodic reduction can be expected to maintain the electrode high reactivity ascribed to the “de facto regeneration” through cathodic polarization. Moreover, although the effects of nanotube morphologies on the photocatalytic activity have been reported [241,242], there is no study that investigated the morphology effect on the electrocatalytic reactivity of TiO$_2$ nanotube relevant to water and wastewater treatment. Here, we report on one of the first studies employing self-doped TiO$_2$ NTAs as the cathode for electrochemical reduction of organic pollutants with nitrobenzene as the model compound. The TiO$_2$ NTA with different morphologies and exposed facets were synthesized by manipulating a suite of anodization parameters and applying a post-anodization treatment. The
performance of NB reduction using different TiO$_2$ NTA electrodes were examined and compared with that of the benchmark Pd electrode. The effects of morphology and operating conditions, reduction pathway and mechanism, degradation kinetics, and energy consumption were also investigated. Results indicate that the self-doped TiO$_2$ NTA is a promising cost-effective electrode material for electrocatalytic reduction of water pollutants with high efficiency and stability.

4.2 Material and Methods

4.2.1 Electrode preparation

The well-established electrochemical anodization procedure was used to prepare TiO$_2$ NTA electrodes [115,243]. Briefly, titanium foil (0.10 mm, 99.6%) was cleaned by sonication in acetone and ethanol for 10 minutes, respectively, followed by rinsing in deionized (DI) water and drying under ambient atmosphere. Anodization process was carried out in a two-electrode configuration system with a platinum mesh as the cathode. Clean titanium foil was anodized in electrolyte containing ethylene glycol (EG), water, and ammonium fluoride (NH$_4$F) under a constant potential (45 V) at room temperature (22±1°C). The nanotube length and diameter were controlled by changing the anodization time and fluoride concentrations as detailed in Table S4.1. Subsequently, the as-formed TiO$_2$ NTA layer was anodized under 60 V for 5 minutes in fluoride free electrolyte (5% H$_3$PO$_4$ in ethylene glycol (EG) solution) to enhance the physical stability of TiO$_2$ NTA layer to the Ti substrate [244]. The TiO$_2$ NTA with exposed {001} facets was prepared following a post-anodization treatment using 30 mM NaF solution (pH 3.5) as reported previously [236]. After anodization, the electrode was washed with ethanol to remove
remnants from the surface, and then annealed in a furnace at 450 °C for 1 hour with a heating rate of 2 °C min\(^{-1}\) under atmospheric conditions. Calcination can enhance crystallinity of the anodic TiO\(_2\) nanotube and also remove adsorbed carbon and fluoride ion from the electrode surface. Lastly, self-doping of the TiO\(_2\) NTA was achieved by cathodizing the electrode in a 100 mM phosphate buffer solution under constant current (17 mA/cm\(^2\)) for 90s. As discussed previously, cathodic polarization can introduce reactive sites and thus increase the electroactivity of TiO\(_2\) NTAs (Figure S4.1). Here the TiO\(_2\) NTA electrode was used as the cathode and it may actually get “polarized” during cathodic reduction of NB gradually. In order to obtain an electrode with high electrocatalytic reactivities and ensure uniform initial conditions, we cathodized (self-doped) all electrode after calcination. In addition, palladized carbon paper (Pd/C) and titanium foil (Ti) were used as the control electrodes. Pd/C electrode was prepared by electrodeposition of palladium on the surface on carbon paper (0.18 mm, AvCarb P50T) at a constant current of 2.50 mA/cm\(^2\) in 1.80 mM K\(_2\)PdCl\(_6\) electrolyte for ~4 hours [225].

4.2.2 Electrode characterization

The morphology of TiO\(_2\) NTA was characterized using a field emission scanning electron (FESEM, JEOL FE 7000). X-Ray diffraction (XRD) patterns were collected on a Rigaku MiniFlex 600 from 2° to 90° of 2θ. The specific surface area (SSA – multi BET method) of the electrodes was determined by nitrogen adsorption at 77 K using Quantachrome autosorb iQ-MP/XR. All electrochemical measurements (cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), hydrogen evolution reaction (HER), and electro-active surface area) were performed on a potentiostat (Bio-
Logic, SP150) in a three-electrode system where Pt and Ag/AgCl (3 M) were used as the counter and the reference electrodes, respectively. CV measurements were performed in the presence and absence of NB and its intermediates in 5 mM Na₂SO₄ at a scan rate of 25 mV/s. EIS was recorded in an aqueous solution consisting of 50 mM K₃Fe(CN)₆ + 350 mM K₄Fe(CN)₆ + 1 M KCl at open-circuit potential by applying an AC voltage amplitude of 5 mV within the frequency range of 30K to 0.01 Hz. Electrochemical active surface area (ECAS) of TiO₂ NTA electrodes were calculated from double-layer capacitance using CV analysis in 10 mM K₃Fe(CN)₆ + 0.50 M KCl electrolyte at different scan rates [174].

Electrochemical hydrogen evolution reaction (HER) was measured using linear sweep voltammetry at a scan rate of 1 mV/s in N₂-purged 0.50 M KOH electrolytes. The Tafel plots (log \( j_s \) vs. E), were calculated from the corresponding HER curves.

4.2.3 Electrochemical reduction of nitrobenzene

Electrocatalytic reduction of NB was conducted in a three-electrode single compartment cell with TiO₂ NTA electrode as the working electrode, Pt mesh as the counter electrode, and Hg/HgO (20% KOH) as the reference electrode. The spacing between the working and counter electrodes was kept at 1cm. The effective surface area of the working electrode was 6 cm². 80 mL of 100 mM Na₂SO₄ solution containing 300 mg L⁻¹ NB was used as the working solution without pH adjustment (pH ~5.20). The applied potential was controlled using a potentiostat (Bio-Logic, SP150). During the experiments, 1 mL solution was sampled at different time intervals and immediately measured for nitrobenzene (NB), nitrosobenzene (NSB), azobenzene (AZ), N-phenylhydroxylamine (PHA), and aniline (AN) concentrations. The effects of initial pH (3 ~ 10) and applied
potential over the range of (−0.40 ~ −1.50 V versus SCE) were examined on selected electrodes as well. For comparison, cathodic reduction experiments using Ti foil, carbon paper (C), and Pd/C were also conducted under the same conditions. As persulfate may be electrochemically generated by the anodic oxidation of HSO$_4^−$ at a high potential or current density [245,246], stability of the background electrolyte was tested by electrolyzing 80 mL of 100 mM Na$_2$SO$_4$ at -1.20 V vs SCE for 2 hours. Results indicate there was no persulfate generated under our experimental conditions (data not shown; detection limit 1µM). Moreover, CV tests and scavenger studies were performed to explore the mechanism of NB reduction, where t-BuOH (TBA) was used as a specific scavenger of atomic hydrogen (H*). Error bars indicate standard deviations from two duplication experiments.

4.2.4 Analytical methods

GC-MS (Agilent, Model 6890 GC, with Model 5973 MS detector) was used to identify the transformation products of NB degradation. The concentrations of NB, NSB, and AN were measured at 210 nm using a high performance liquid chromatography (HPLC-Agilent 1100 series) with a Hypersil Gold 100 x 2.1 mm C18 column and a diode array detector (DAD). The mobile phase was methanol/water (30:70, vol:vol%) with a flow rate of 0.175 mL/min. PHA concentration was measured using the same column with a mobile phase of methanol/water (60:40 vol:vol%) at 254 nm. AZ concentration was determined using GC-MS [247]. Total organic carbon (TOC) was measured using TOC-LCPH (Shimadzu).
4.3 Results and Discussion

4.3.1 Morphology and structure properties

FESEM images of the TiO$_2$ NTAs prepared under different conditions are shown in Figure 4.1. As can be seen, TiO$_2$ NTAs with different lengths and diameters were successfully grown on the Ti foil substrate by varying the anodization parameters (Table S4.1). The nanotube length and diameter were controlled within the ranges of 2~3, 6~7, and 11~12 μm, and 20~40, 50~70, and 90~120 nm, respectively (Table 4.1).

![FESEM image: A&I) {001}-TiO$_2$ NTA-E1 B&J) TiO$_2$ NTA-E2, C&K) TiO$_2$ NTA L2-E5, D&L) TiO$_2$ NTA L3-E4, E&M) TiO$_2$ NTA D1-E6, F&N) TiO$_2$ NTA D3-E7, G&O) {001}-TiO$_2$ NTA, H&P) {001}-TiO$_2$ NTA-E3 [Scale bars for diameter and length are 100 nm and 1μm respectively for all electrodes].](image)

Figure 4. 1 FESEM image: A&I) {001}-TiO$_2$ NTA-E1 B&J) TiO$_2$ NTA-E2, C&K) TiO$_2$ NTA L2-E5, D&L) TiO$_2$ NTA L3-E4, E&M) TiO$_2$ NTA D1-E6, F&N) TiO$_2$ NTA D3-E7, G&O) {001}-TiO$_2$ NTA, H&P) {001}-TiO$_2$ NTA-E3 [Scale bars for diameter and length are 100 nm and 1μm respectively for all electrodes].
Table 4.1 Electrode characterization

<table>
<thead>
<tr>
<th>Control Parameters</th>
<th>Electrode</th>
<th>Characterization</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Length (µm)</td>
<td>Diameter (nm)</td>
<td>Specific surface area (m²/m²)</td>
<td>Rct (EIS) (Ω/cm²)</td>
<td>Electro active surface area (mF/cm²)</td>
</tr>
<tr>
<td>Facet</td>
<td>[001]-TiO₂ NTA-E1</td>
<td>2-3</td>
<td>50-70</td>
<td>2972</td>
<td>1.86 ± 0.04</td>
<td>11.20</td>
</tr>
<tr>
<td></td>
<td>TiO₂ NTA-E2</td>
<td>2-3</td>
<td>50-70</td>
<td>3444</td>
<td>2.78 ± 0.07</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td>[001]-TiO₂ NTA-E3</td>
<td>11-12</td>
<td>50-70</td>
<td>4411</td>
<td>1.75 ± 0.08</td>
<td>33.20</td>
</tr>
<tr>
<td></td>
<td>TiO₂ NTA-E4</td>
<td>11-12</td>
<td>50-70</td>
<td>4336</td>
<td>2.10 ± 0.06</td>
<td>29.70</td>
</tr>
<tr>
<td>Length</td>
<td>TiO₂ NTA L1-E2</td>
<td>2-3</td>
<td>50-70</td>
<td>3444</td>
<td>2.78 ± 0.07</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td>TiO₂ NTA L2-E5</td>
<td>6-7</td>
<td>50-70</td>
<td>3961</td>
<td>2.45 ± 0.05</td>
<td>19.10</td>
</tr>
<tr>
<td></td>
<td>TiO₂ NTA L3-E4</td>
<td>11-12</td>
<td>50-70</td>
<td>4336</td>
<td>2.10 ± 0.06</td>
<td>29.70</td>
</tr>
<tr>
<td>Diameter</td>
<td>TiO₂ NTA D1-E6</td>
<td>2-3</td>
<td>20-40</td>
<td>3714</td>
<td>4.97 ± 0.04</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>TiO₂ NTA D2-E2</td>
<td>2-3</td>
<td>50-70</td>
<td>3444</td>
<td>2.78 ± 0.07</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td>TiO₂ NTA D3-E7</td>
<td>2-3</td>
<td>90-120</td>
<td>3080</td>
<td>6.17 ± 0.04</td>
<td>8.90</td>
</tr>
<tr>
<td>Control</td>
<td>Ti foil</td>
<td>----</td>
<td>----</td>
<td>220</td>
<td>3.06 ± 0.05</td>
<td>0.90</td>
</tr>
</tbody>
</table>

* [BET specific surface area (m²/g)*electrode mass (g)] / electrode surface area

The XRD patterns of the TiO₂ NTAs with different morphologies are illustrated in Figure 4.2. All peaks are in good agreement with the standard patterns of anatase-phase TiO₂ (JCPDS No. 21-1272) [243]. The {001}-TiO₂ NTA shows a higher (004) diffraction peak at 37.8° and a lower (101) diffraction peak at 25.3° compared to TiO₂ NTAs (Figures 4.2A&B). This high intensity ratio of I(004)/I(101) indicates that the crystal growth of the nanotube was preferentially oriented along the [001] direction and parallel to the longitudinal direction of the tubes. This orientation implies the enhanced percentage of exposed {001} facet.[236,248,249]. The intensity of (101) diffraction peak increased gradually with the increase of the anodization time (Figure 4.2C), which was consistent with the relation of nanotube length and anodizing time [250]. Moreover, the nanotube diameter was tuned mainly by changing the F⁻ concentration in the electrolyte (Table S4.1), which may also influence the intensity of TiO₂ diffraction peaks (Figure 4.2D), especially for the (004) peak as F⁻ can reduce the surface energy of {001} facets and is commonly used as the capping reagent for the preparation of TiO₂ nanocrystals with {001} facets.
[235,236]. The XRD pattern of the Pd/C is shown in Figure S4.2, confirming that Pd was successfully deposited on the carbon paper. The specific surface area of TiO$_2$ NTA electrodes was determined by the BET analysis. The NTAs increased the specific surface area (SSA) by a factor of 14~20 as compared with that of the Ti foil (Table 4.1). In addition, the SSA increased with increasing nanotube lengths and decreasing nanotube diameters, as expected from simple geometry calculation.

![Figure 4. X-ray diffraction patterns of different TiO$_2$ NTAs: A&B) Effect of facets (E1-4), B) Effect of the tube length (E 2, 5, & 4), C) Effect of the tube diameter (E 6, 2, 7).](image)

4.3.2 Electrochemical measurement

The electrochemical characterization of the TiO$_2$ NTA electrodes was conducted by HER, CV, and EIS measurements. As shown in Figures 4.3A & S3 and Table 4.1, the
{001} facet, longer nanotube, and larger diameter may lower the activation energy for H₂ evolution (i.e. more positive HER potentials) and improve the HER activity. This is consistent with the Tafel slope results (Figure 4.3B & Table 4.1). The Tafel slopes for the TiO₂ NTA electrodes with {001} facets are lower than those with {101} facets, which suggests a higher HER activity [251–253]. Also the Tafel slopes determined in this study were lower than those of TiO₂ nanocrystals reported previously [223]. In general, TiO₂ NTA electrodes exhibited a high HER overpotential (<-1.30 V/SCE), a property favors cathodic reduction of water pollutants. CV tests were carried out on different electrodes with and without NB (Figure 4.3C). The reduction peak representing NB degradation started ~ -0.69 V/SCE and ~ -0.50 V/SCE on the electrodes of TiO₂ NTA-E4 and {001}-TiO₂ NTA-E3, respectively, which means NB can be reduced on these electrodes at potentials much more positive than where HER occurred. The NB reduction peaks were in the range of -0.55 ~ -0.95 V/SCE for all the TiO₂ NTA electrodes (Figure S4.4) and were more pronounced on shorter nanotubes due to the lower double-layer capacitance. The electrochemical impedance analysis was conducted to determine the charge transfer resistance of the electrochemical system using different TiO₂ NTA electrodes. The experimental data was fitted with an equivalent circuit illustrated in Figure 4.3D (Text S4.1; Figure S4.6) and the fitting parameters for all electrodes are presented in Table 4.1. As shown in Figures 4.3D & S4.6, all the response spectra of EIS share similar shape and variation tendencies. The semicircle at high frequency presents the Rₑ in the equivalent circuit which refers to the conductivity at the interface between TiO₂ nanotube and electrolyte [254,255]. The small diameters of the semicircular (i.e. low Rₑ values in Table 4.1) indicate fast transfer of the interfacial charge to the electron donor–acceptors [256].
Furthermore, the \{001\} facet exposed nanotube with longer length might decrease the resistance of nanotube and transfer electron easier. The electrochemically active surface area (ECSA) of the electrodes was examined using CV tests to evaluate the double-layer capacitance of each electrode (Table 4.1). While the trend of ECSAs of different TiO$_2$ NTAs is generally consistent with that of SSAs, it’s interesting to note the effect of exposed facets especially at shorter tube lengths. For example, the SSA of E2 (3444 m$^2$/m$^2$) is $\sim$16\% higher than that of E1 (2972 m$^2$/m$^2$), but the ECSA of E1 (11.20 mF/cm$^2$) is more than double that of E2 (4.70 mF/cm$^2$). If we take a closer look at the characteristics of E6, E2, and E7, it further confirms that I (004)/I (101) had appreciable influences on the ECSA (Table 4.1 and Figure 4.2D). As the nanotube became longer, the facet effect somewhat weakened, indicating the dominant role of SSA under such circumstances. Nonetheless, these results imply that \{001\} facets may provide more electrochemical active sites and consequently improve the electrode performance.
4.3.3 Electro catalytic reduction of NB

The electro catalytic reduction of NB was evaluated on TiO$_2$ NTA electrodes with different morphologies as well as three control electrodes, i.e. titanium foil (Ti), carbon paper (C), and the palladized carbon paper (Pd/C) (Figure 4.4). As demonstrated in Figure 4.4A, the {001}-TiO$_2$ NTA-E1 exhibited enhanced performance with faster degradation rates compared to those of Ti and the TiO$_2$ NTA-E2, ascribed to the higher electroactive surface area. It can also be found from Figure 4.4B that the longer the tube length, the higher and faster the NB reduction. The TiO$_2$ NTA-E4 even outperformed the Pd/C slightly.

---

**Figure 4.** Electrochemical measurement of TiO$_2$ NTA electrodes: A) Hydrogen Evolution Reaction (HER), B) Tafel Plot, C) NB reduction, D) EIS spectra [Hg/HgO (20% KOH) was used as the reference electrode in the experiments A&B, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments C&D].
These results indicate that the nanotube length played a significant role in determining the electrode performance. Increasing the length greatly improved the electrocatalytic activity of the TiO$_2$ NTAs due to the higher electroactive surface area and better electron transferring, which may enhance the direct reduction of NB [257]. Moreover, more efficient NB removal was achieved using the electrodes with larger diameters (Figure 4.4C). However, in order to elucidate the true effect of nanotube diameters, the influence of exposed facets should also be considered here as discussed previously for ECSA. As shown in Figure 4.4C, TiO$_2$ NTA-E2 performed better than TiO$_2$ NTA-E6, whereas the ECSA and I (004)/I (101) of TiO$_2$ NTA-E6 was higher. This result indicates larger diameters favor NB reduction, which is also supported by the performance of TiO$_2$ NTA-E7. We also compared the NB reduction using {001}-TiO$_2$ NTA-E1, TiO$_2$ NTA D1-E6, and TiO$_2$ NTA D3-E7, all of which bore similar lengths but different diameters. As can be seen in Figure S4.7A, NB reduction followed the order TiO$_2$ NTA D3-E7 > {001}-TiO$_2$ NTA-E1 > TiO$_2$ NTA D3-E6, further confirming the beneficial effects of larger diameters on the electrochemical reduction of NB. The possible explanation is that the larger pore size of TiO$_2$ nanotube enhanced the intercalation of NB molecules into the nanotube and increased the degradation rate.
Figure 4. 4 NB reduction using different TiO$_2$ NTA electrodes: A) Effect of facets (E1 & 2), B) Effect of the tube length (E 3, 4, & 5), C) Effect of the tube diameter (E 6, 7, 8) [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na$_2$SO$_4$, Applied potential: -1.20 V vs SCE, pH not adjusted ~5.20, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].

Based on the results and discussion above, we may conclude that the {001}-exposed facet, longer nanotube length, and larger nanotube diameter are the structural and morphological characteristics that can lead to enhanced performance of TiO$_2$ NTA electrodes. Therefore, we attempted to prepare electrodes bearing all these advantageous
features. However, it was found that the stable growth of nanotube was limited to 7~ 8 µm with larger diameters (90 ~ 100 nm) due to the strong chemical etching and poor adhesion caused by the high content of F⁻ in the electrolyte, where longer anodization time resulted in peeling off of the TiO₂ NTA layer from the Ti substrate during anodization or calcination. Moreover, {001}-TiO₂ NTA (7µm L -100 nm D) exhibited similar electroactivities toward NB reduction as TiO₂ NTA-E4 (12µm L -60 nm D) (Figure S4.7B). Therefore, TiO₂ NTA-E4 and {001}-TiO₂ NTA-E3 with 11~12 µm tube lengths and 50~70 nm diameters were selected for further investigation in this study.

4.3.4 Effects of applied potential and pH

The electrochemical reduction of NB at different cathode potentials was investigated on {001}-TiO₂ NTA-E3 and TiO₂ NTA-E4. Approximate 17% of NB was removed in 2 hrs at -0.40 V/SCE using {001}-TiO₂ NTA-E3, while the removal efficiency reached > 95% at -1.20V/SCE and -1.50V/SCE under otherwise identical conditions (Figure 4.5A). As NB reduction started at ~ -0.50 V/SCE (Figure 4.3C) electro-assisted adsorption could account for NB removal at the applied potential of -0.40 V/SCE and NB can be degraded via direct reduction at -0.70 V/SCE. When the potential was more negative, NB may also be reduced indirectly via electrochemically-generated reducing species (e.g. H⁺; Figure 4.6, to be discussed later) although the current efficiency may decrease due to the side reaction of H₂ evolution. Owing to the possible involvement of H⁺ in NB reduction, the effect of pH on NB elimination was examined by adjusting the initial pH from 3 to 10. As can be seen in Figure 4.5B, faster NB reduction was achieved at lower pH for {001}-TiO₂ NTA (E3). H⁺ may compete with positively-charged NB for electroadsorption on the
cathode surface. It can also enhance the side reaction of H\textsubscript{2} evolution. However, contrary to these possible competition and inhibition effects, the results shown in Figure 4.5B indicate that H\textsuperscript{+} might assist the reduction of NB such as boosting the generation of H\textsuperscript{-} on electrode surface, which was promoted by the high H\textsuperscript{+} concentration in acidic solutions [75,258,259]. Moreover, the applied potential and initial pH generally exhibited similar effects on NB reduction using TiO\textsubscript{2} NTA-E4 (Figures S4.8A&B).

![Figure 4. 5 Effects of applied potential and initial pH on NB reduction using \{001\}-TiO\textsubscript{2} NTA-E3: A) Effects of applied potential, B) Effects of pH [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na\textsubscript{2}SO\textsubscript{4}, pH was not adjusted in A, -1.20V vs SCE for B, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].]

4.3.5 NB degradation mechanism and transformation pathway

In general, electrochemical reduction of water pollutants may proceed via direct electron transfer or indirect reduction via generation of reductive species such as H\textsuperscript{*}. Direct reduction can occur by electron tunneling or by the formation of a chemisorption complex of the target compound on the cathode [260], while H\textsuperscript{*} involved in indirect reduction may be generated from electrolysis of H\textsubscript{2}O/H\textsuperscript{+} by certain electrodes [223,261]. In order to examine the possible generation of reductive H species, we conducted CV tests with
different starting potentials to investigate the H* evolution on {001}-TiO$_2$ NTA-E3 and TiO$_2$ NTA-E4. As shown in Figure 4.6, there are two coupled cathodic and anodic peaks, labeled as C1/A1 and C2/A2 respectively, and one anodic peak (A3). These anodic peaks may represent the electron deep traps located in TiO$_2$ material. Trapping/detrapping involves symmetric anodic and cathodic current peaks and the peak position would be affected by the potential scan rate [96,262,263]. However, this was not observed in our CV tests (Figure S4.9). Also, there is no cathodic peak for anodic peak A3. Hence these anodic peaks shouldn’t be related to the deep traps in TiO$_2$ material. On the other hand, the pattern of these anodic and cathodic peaks has been reported during H$_2$ evolution using Pd and Pt electrode material [264,265]. Therefore, the two coupled cathodic and anodic peaks (C1/A1 and C2/A2) are assigned to absorbed atomic hydrogen (H$^*_\text{abs}$) and adsorbed atomic hydrogen (H$^*_\text{ads}$), respectively [264,266]. Since the H$_2$ evolution (HER potential) starts from the potential close to the peak A3, the third anodic peak may correspond to the oxidation of H$_2$. Generation of H$^*_\text{abs}$ and H$^*_\text{ads}$ at cathodic potentials lower than that for H$_2$ evolution on noble metals such as Pt or Pd is well known [264,265], but the high cost of these materials may limit large scale applications for water purification. The findings of this study can provide a cost-effective alternative to the expensive precious metals for such applications. It’s also worth noting that the H* evolution peaks were weaker on TiO$_2$ NTA-E4, implying a stronger H* chemical storage capacity of {001} facets (Figure S4.10A&B). These results are also consistent with the pH effect on NB reduction which was less significant for TiO$_2$ NTA-E4 compared with {001}-TiO$_2$ NTA-E3 (Figure S4.8B) as well as the NB reduction experiments where {001}-TiO$_2$ NTA-E3 performed better (Figure S4.7B).
Figure 4. 6 H\(^*\) generation using \{001\}-TiO\(_2\) NTA-E3 [Experimental conditions: N\(_2\)-Saturated 100 mM Na\(_2\)SO\(_4\), scan rate: 25 mV/s, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].

We further studied the NB reduction mechanism on TiO\(_2\) NTA electrodes employing TBA as the H\(^*\) scavenger [223,267]. The electrochemical behavior of TBA was first investigated in CV tests. The peak reduction in the range of -0.10 ~ -0.25 V/SEC, which represented H\(^*\) \textit{ads} evolution, confirmed the scavenging effects of TBA on H\(^*\) (Figures S4.11A & B). Next, different concentrations of TBA was added into the working solution during bulk electrolysis of NB. As shown in Figure 4.7A, NB reduction rate declined with increasing concentrations of TBA, where the efficiency decreased significantly as the TBA concentration increased from 0 to 0.20 M and remained relatively constant with further TBA increase. These results demonstrate the important role of H\(^*\)-mediate mechanism for NB reduction using \{001\}-TiO\(_2\) NTA-E3. On the other hand, even in the presence of 0.3 M TBA, ~70% NB was removed after 2 hrs. Therefore, both direct and indirect mechanisms are responsible for NB reduction here. Similar results were obtained on TiO\(_2\) NTA-E4 (Figure S4.12A). The high electroactive surface area, together with the good conductivity and the beneficial nanotube structure for electron transfer, can
contribute to the direct reduction of NB on TiO$_2$ NTAs. Moreover, it’s well documented in the literature that electrochemical self-doping can generate surface defects (e.g. Ti$^{3+}$ or O vacancies/OVs) on TiO$_2$ NTAs [21,184,223,231,234,243]. These defects are the reactive sites for dissociative adsorption of H$_2$O/H$^+$ leading to the generation of surface adsorbed H*. In particular, the high energy {001} facets with more OVVs than {101} facets can further promote H* generation [57,268]. Furthermore, the unique 1D nanotube structure, enhanced electric conductivity, and decreased charge transfer resistance can facilitate quick in situ regeneration of these defective sites through cathodization for continuous electrocatalytic reduction of NB.

The intermediate products of NB reduction were identified using GC/MS to investigate the transformation pathway. It was reported that the intermediates depended on pH and the electrode material [75,269]. As shown in Figures 4.7B and S4.12B, the transformation products detected included nitrosobenzene (NSB), aniline (AN), and azobenzen (AZ), with the first two being the dominant intermediates. Another intermediate commonly detected in other studies [75,219,223], N-phenylhydroxylamine (PHA), was not detected here. The mass balance of carbon was calculated based on the concentrations of NB and its intermediates as well as TOC measurement. In addition, CV tests on the intermediate products were also conducted. NSB reduction started at -0.40 ~ -0.50V, resulting in a new peak between -0.60 ~ -1.20 V (Figure S4.13A& D). Given the CV results of PHA and AN (Figures S4.13B & E and S4.13C & F), we concluded this broad peak should represent the reduction of NSB to AN. Based on the results of intermediates identification and NSB CV tests, the reduction peak that started to appear at ~ -0.50 V in Figure 4.3C may represent the reaction of NB → NSB → AN. Therefore, the main
transformation pathway of NB reduction can be summarized as follows (Figure 4.8): NB was reduced to NSB via 2 electrons transfer, which could be further reduced to AN with another 4 electrons transfer. Moreover, given the concentration profiles of NSB and AN during the runs (Figure 4.7B), it’s also possible that NB was reduced to AN directly via 6 electrons transfer \[270\]. The small amount of AZ may be produced as a side product of the subsequent chemical reactions rather than electrochemical reactions \[271\]. Eventually the transformation products can be mineralized.

![Figure 4.7 A) Effect of TBA on NB reduction using \{001\}-TiO\textsubscript{2} NTA-E3; B) NB transformation products using \{001\}-TiO\textsubscript{2} NTA-E3 [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na\textsubscript{2}SO\textsubscript{4}, pH was not adjusted, -1.20V vs SCE, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].

![Figure 4.8 Simplified transformation pathway of NB.](image-url)
4.3.6 NB degradation kinetics and the electrode stability

The degradation kinetics of NB as well as its intermediates using \( \{001\}-\text{TiO}_2 \) NTA-E3 were investigated at -1.2 V/SCE. Here the NSB concentration profile was divided into “generation” and “reduction” two stages. As shown in Figure 4.9A, both NB reduction and NSB generation/reduction can fit well with pseudo-1\(^{st}\) order kinetic models. However, the profile of AN concentrations didn’t follow a 1\(^{st}\) order reaction nor 0 or 2\(^{nd}\) order reactions, indicating a more complex model is needed to describe the time-dependent changes of AN. Although photocatalytic/photoelectrocatalytic degradation of NB has been reported with high efficiency [221,272–274], the observed reaction constant rate \((K_{obs})\) of this study was faster than photocatalytic activity using the \( \text{TiO}_2 \) NTA based materials [221,274]. Very recently, Zhang et al. (2019) reported the photocatalytic/photoelectrocatalytic degradation of NB using Au/TiO\(_2\) nanotube arrays and about 50.9% and 68.7% degradation was achieved after 2hrs reaction for photocatalytic and photoelectrocatalytic, respectively [273].

According to the discussion in 3.5, we propose a simplified NB transformation scheme including sequential reduction of NB $\rightarrow$ NSB $\rightarrow$ AN and direct reduction of NB $\rightarrow$ AN (Figure 4.8). As ~35% TOC was removed in 2 hrs, further reduction of AN was also considered. Pseudo-1\(^{st}\) order reactions were assumed for each step of transformation. As illustrated in Figure 4.9B, the kinetic equations derived (Text S4.2) fit the experimental data well. The reaction rate constant of NB $\rightarrow$ NSB \((k_1)\) is $0.0143 \pm 0.0005$ min\(^{-1}\), while the rate constants of NB $\rightarrow$ AN \((k_2)\) and NSB $\rightarrow$ AN \((k_3)\) are $0.0157 \pm 0.0003$ and $0.0394 \pm 0.0004$ min\(^{-1}\), respectively. These results indicate that reduction of NB to NSB and to AN may occur at comparable rates, but reduction of NSB to AN proceeded much faster which is also consistent with the results of CV tests on NSB (Figure S4.9A). Reduction of AN
occurred much more slowly with a rate constant ($k_4$) of $0.003 \pm 0.0001 \text{ min}^{-1}$. The transformation of the NB reduction intermediates was further evaluated in an 8 hrs’ run (Figure 4.10A). NB and NSB disappeared between 2~3 hrs while the AN concentration peaked at ~3 hrs and then started to decline. Furthermore, the current was stabilized at ~ -8 mA after 3 hrs (~ -50 mA at the beginning) and ~75% mineralization was achieved in 8 hrs.

In addition to electrochemical reactivities toward target pollutants, stability is also of great importance in evaluating an electrode material. Here we examined the performance of {001}-TiO$_2$ NTA-E3 electrode in 10 cyclic runs. As shown in Figure 4.10B, the NB reduction profile remained the same and the reaction rate constant of $k_{obs}$ was kept at 0.0249 ± 0.0003 min$^{-1}$ during the 10 cyclic tests, demonstrating the very good stability of self-doped TiO$_2$ NTA cathodes.

Figure 4. 9 Kinetics modeling NB reduction using {001}-TiO$_2$ NTA-E3: A) $k_{obs}$ of NB and NSB; B) Kinetics modeling of NB and its intermediates degradation [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na$_2$SO$_4$, -1.20 V vs SCE, pH not adjusted ~5.20, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].
Figure 4. 10 A) Electrochemical reduction of NB and its intermediates; B) Stability tests of \{001\}-TiO$_2$ NTA-E3 [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na$_2$SO$_4$, -1.20 V vs SCE, pH not adjusted ~5.20, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].

4.3.7 Energy consumption and Environmental Implications

Energy consumption is an important factor that affects the feasibility of practical applications in electrochemical treatment. In this study, we estimated the energy consumption of \{001\}-TiO$_2$ NTA-E3 for NB reduction using two figures of merit: energy per order (E$_{E/O}$) [275] and energy per kilogram (kg) reduction. As listed in Table 4.2, E$_{E/O}$ of NB reduction was calculated to be 2.07 kWh/m$^3$. Moreover, the energy consumption for 1 kg of NB reduction and 1 kg of TOC removal was estimated as 7.67 kWh and 30 kWh, respectively. Although there are numerous reports on electrochemical treatment of NB in the literature, very limited studies provided enough information for estimation of energy consumption [58,269,275], which are summarized in Table 4.2 along with the main experimental conditions. The energy consumption of NB electrochemical reduction using \{001\}-TiO$_2$ NTA electrodes was much lower than those of the electrochemical oxidation processes with different electrodes. Sun et al reported a sequential NB reduction/oxidation
process using graphite electrodes for in situ soil remediation [269]. The much lower $E_{O/E}$ can be attributed to the vastly different initial concentrations (e.g. 12.3 mg/L vs. 300 mg/L) as well as much faster degradation kinetics at lower initial concentrations [223,269,276,277]. As shown in Figure 4.4, TiO$_2$ NTA electrodes outperformed the carbon electrode at the same initial NB concentration. It’s also worth mentioning that the electrode area per treated volume of this study was the lowest in Table 4.2, which further demonstrates the superiority of [001]-TiO$_2$ NTA electrodes. Moreover, NB can be selectively reduced to AN which is much less toxic and easier to be oxidized or biologically treated [218,219,223]. The results of the 8 h-run also indicate the feasibility of mineralization at relatively low energy consumption. Therefore, depending on the treatment requirements and specific applications, electrochemical reduction of NB using self-doped TiO$_2$ NTAs may either be employed as pre-treatment for oxidation/biological processes or a stand-alone process. In addition, catalytic hydrogenation of NB to produce valuable chemicals such as AN is also an important industrial process [278,279]. Self-doped TiO$_2$ NTAs may find potential applications in this aspect as well. We also demonstrated that the reactivities of TiO$_2$ NTAs towards target pollutants can be regulated by finely tuning the morphology and crystallography of the nanostructures, which may be further explored for other environmentally relevant applications. In summary, the low cost and environmental friendliness of Ti/TiO$_2$, the facile synthesis procedure, the high efficiency and excellent stability, and the low energy consumption, all make self-doped TiO$_2$ NTAs promising cathode materials for electrocatalytic reduction of water/wastewater pollutants and in other related fields.
Table 4. 2 Energy consumption of NB degradation using different electrodes.

<table>
<thead>
<tr>
<th>Electrochemical technology</th>
<th>Experimental conditions</th>
<th>Energy consumption</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>Initial Concentration (mg/L)</td>
<td>Electrolyte /Volume (m²/m³)</td>
<td>kWh/ kg(C)</td>
</tr>
<tr>
<td>Oxidation</td>
<td>DSA</td>
<td>100.00</td>
<td>100 mM Na₂SO₄</td>
</tr>
<tr>
<td>TiO₂ NTs/SnO₂-Sb/PbO₂</td>
<td>240.00</td>
<td>50mM Na₂SO₄</td>
<td>12.50</td>
</tr>
<tr>
<td>Sequential Reduction &amp; Oxidation</td>
<td>Graphite Electrodes</td>
<td>12.30</td>
<td>20 mM NaH₂PO₄</td>
</tr>
<tr>
<td>Reduction</td>
<td>{001} - TiO₂ NTA</td>
<td>300.00</td>
<td>100 mM Na₂SO₄</td>
</tr>
</tbody>
</table>

* $E_{E/O}$ (kWh/m³) = $\frac{I \times U \times t}{V \times \log (\frac{C_0}{C})}$; I (A) and U (V) are the recorded current and overall potential, respectively, V is the volume of the solution (m³), C₀ is the initial concentration, C is the final concentration, and t is the time (hr).

* Energy consumption was calculated for 80 % of NB degradation using ultrasound enhanced electrochemical system.

4.4 Conclusion

This study investigated the effects of morphological and crystallographic characteristics on the electrocatalytic reactivity of TiO₂ NTAs towards NB degradation. Results indicated that the performance of TiO₂ NTA electrodes was enhanced with the {001}-exposed facet and increases in the nanotube length and diameter. These can be attributed to the increase in the electroactive surface area and better electron transferring, as well as the improved H* storage capacity in the defected nanostructures which was revealed during CV scans. The unique nanotube structure and the enhanced electric conductivity and decreased charge transfer resistance can facilitate both direct reduction and in situ regeneration of the reactive sites for continuous electrocatalytic degradation of NB. The main transformation pathway of NB reduction can be simplified as sequential reduction of NB → NSB → AN and direct reduction of NB → AN. Further mineralization can also be achieved with extended treatment time. The concentration profiles of NB and
its transformation products were successfully described in the kinetic models derived in this study. The high removal efficiency together with low energy consumption, excellent stability, and the low cost and environmental friendliness of Ti/TiO$_2$ makes the self-doped TiO$_2$ NTAs promising cathode materials for electrocatalytic reduction of water/wastewater pollutants.

4.5 Supporting information

Text S4.1: EIS

Electrochemical impedance analyses of NTA electrodes were performed in a three-electrode system with Pt mesh and a Ag/AgCl as the counter electrode and reference electrode, respectively. The EIS equivalent circuit model ($R_s + C_{dl}/R_{ct}$) was used to model the TiO$_2$ NTA electrodes, where the $R_s$ described the total resistance of the electrolyte, the capacitor $C_{dl}$ and the resistor $R_{ct}$ were related to the formation of the double charge layer capacitance at the electrode/solution interface and the charge transfer resistance, respectively [280,281]. As can be seen in the equivalent circuit, the charge-storage mechanism is modelled considering two different processes: diffusion control and capacitance response.

Text S4.2: Degradation kinetics of NB and its intermediates

A pseudo-1$^{\text{st}}$ order kinetics model expressed in eq. 1 was used to evaluate the rate constant ($k_{\text{obs}}$) of the reactions:

$$\ln[C_t] = -kt + \ln[C_0]$$

**eq. 1**
where \( t \) is the reaction time (min), \( k \) is the reaction rate constant (min\(^{-1}\)), and \( C_t \) and \( C_0 \) are the target compound concentrations (mg/L) at times of \( t = t \) and \( t = 0 \), respectively.

Assuming 1\(^{st}\) -order reaction for each transformation shown in Figure 8, the concentrations of NB and its intermediates can be obtained as follows:

\[
R_{NB} = \frac{d_{NB}}{dt} = -(k_1 + k_2)C_{NB} \quad \text{eq. 2}
\]

\[
R_{NSB} = \frac{d_{NSB}}{dt} = (k_1)C_{NB} - (k_3)C_{NSB} \quad \text{eq. 3}
\]

\[
R_{AN} = \frac{d_{AN}}{dt} = (k_2)C_{NB} + (k_3)C_{NSB} - (k_4)C_{AN} \quad \text{eq. 4}
\]

Furthermore, at \( t=0 \), \( C_{NB} = C_{0NB} \) and \( C_{NSB} = C_{AN} = C_{other\ products} = 0 \), by solving equations 2~4 we get:

\[
C_{NB} = C_{0NB} * \exp(-(k_1 + k_2) * t) \quad \text{eq. 5}
\]

\[
C_{NSB} = C_{0NB} * \frac{k_1}{k_3 - k_1 - k_2} \left[ \exp(-(k_1 + k_2) * t) - (\exp(-(k_3) * t)) \right] \quad \text{eq. 6}
\]

\[
C_{AN} = \left[ \frac{C_{0NB} * k_2}{k_4 - k_1 - k_2} \exp(-(k_1 + k_2) * t) \right] + \left[ \frac{C_{0NB} * k_1 * k_3}{k_4 - k_1 - k_2} \frac{\exp(-(k_1 + k_2) * t)}{k_4 - k_1 - k_2} \right] - \left[ \frac{C_{0NB} * k_1 * k_3}{k_4 - k_2} \frac{\exp(-(k_3) * t)}{k_4 - k_2} \right] \quad \text{eq. 7}
\]

The experimental data were fit with these equations (5~7) using MATLAB to obtain the reaction rate constants (\( k_1\) -\( k_4\)).
Table S4. 1 Anodization parameters

<table>
<thead>
<tr>
<th>Control Parameters</th>
<th>Electrode</th>
<th>Length (µm)</th>
<th>Diameter (nm)</th>
<th>Time (hr)</th>
<th>Voltage (V)</th>
<th>Water content (wt%)</th>
<th>F concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Facet</strong></td>
<td>{001}-TiO$_2$ NTA-E1</td>
<td>2-3</td>
<td>50-70</td>
<td>1</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ NTA-E2</td>
<td>2-3</td>
<td>50-70</td>
<td>1</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>{001}-TiO$_2$ NTA-E3</td>
<td>11-12</td>
<td>50-70</td>
<td>16</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ NTA-E4</td>
<td>11-12</td>
<td>50-70</td>
<td>16</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td><strong>Length</strong></td>
<td>TiO$_2$ NTA L1-E2</td>
<td>2-3</td>
<td>50-70</td>
<td>1</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ NTA L2-E5</td>
<td>6-7</td>
<td>50-70</td>
<td>4</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ NTA L3-E4</td>
<td>11-12</td>
<td>50-70</td>
<td>16</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td><strong>Diameter</strong></td>
<td>TiO$_2$ NTA D1-E6</td>
<td>2-3</td>
<td>20-40</td>
<td>4</td>
<td>45</td>
<td>2.50</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ NTA D2-E2</td>
<td>2-3</td>
<td>50-70</td>
<td>1</td>
<td>45</td>
<td>2.50</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ NTA D3-E7</td>
<td>2-3</td>
<td>90-120</td>
<td>0.33</td>
<td>45</td>
<td>2.50</td>
<td>150</td>
</tr>
</tbody>
</table>

Figure S4. 1 Effects of cathodic polarization on NB reduction using {001}-TiO$_2$ NTA-E3 [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na$_2$SO$_4$, applied potential: -1.20 V vs SCE, pH not adjusted ~5.20, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].
Figure S4. 2 XRD patterns of carbon paper and palladized carbon.

Figure S4. 3 Hydrogen evolution reaction of TiO$_2$ NTA electrodes: A) Effect of nanotube facets (E1-4), B) Effect of the nanotube length (E2, 4, & 5), C) Effect of the nanotube diameter (E6, 2, & 7) [Experimental conditions: electrolyte: N$_2$-Saturated 0.50 M KOH, scan rate: 1 mV/s, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].
Figure S4. NB reduction on different electrodes; A) E1, B) E2, C) E3, D) E4, E) E5, F) E6, G) E7 [Experimental conditions: 50 mg/L NB (when added), electrolyte: N₂-Saturated 5 mM Na₂SO₄, scan rate: 25 mV/s, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].
Figure S4. 5 Effects of NB concentration on direct reduction on the surface on electrode [5 mM Na₂SO₄ electrolyte, 25mV/s, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].

Figure S4. 6 EIS spectra: A) Effect of facets (E1 - 4), B) Effect of the tube length (E 2, 5, & 4), C) Effect of the tube diameter (E 6, 2, & 7) [Experimental conditions: 50 mM K₃Fe(CN)₆ + 350 mM K₄Fe(CN)₆ + 1 M KCl, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].
Figure S4. 7 Comparison of NB reduction on different electrode [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na$_2$SO$_4$, pH was not adjusted, -1.20V vs SCE, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].

Figure S4. 8 Effects of applied potential and initial pH on NB reduction using TiO$_2$ NTA-E4: A) Effects of applied potential, B) Effects of pH [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na$_2$SO$_4$, pH was not adjusted in A, -1.20V vs SCE for B, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].
Figure S4. 9 Cyclic voltammetry of {001}-TiO$_2$ NTA-E3 at different scan rate [N$_2$-Saturated 100 mM Na$_2$SO$_4$ electrolyte, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].

Figure S4. 10 H* generation; A){001}-TiO$_2$ NTA-E3, B) TiO$_2$ NTA-E4 [Experimental conditions: N$_2$-Saturated 100 mM Na$_2$SO$_4$, 25 mV/s, scan rate: 25 mV/s, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].
Figure S4. 11 A) NB reduction in the presence of TBA using {001}-TiO$_2$ NTA-E3; B) NB reduction in the presence of TBA using TiO$_2$ NTA-E4 [Experimental conditions: C&D: 1 mM TBA (when added), 10 mM Na$_2$SO$_4$, scan rate: 25 mV/s, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].

Figure S4. 12 A) Effect of TBA on NB reduction using TiO$_2$ NTA-E; B) NB transformation products using TiO$_2$ NTA-E4 [Experimental conditions: 80 mL electrolyte, 300 mg/L NB, 100 mM Na$_2$SO$_4$, pH was not adjusted, -1.20V vs SCE, Hg/HgO (20% KOH) was used as the reference electrode in the experiments].
Figure S4. 13 Reduction of NSB, PHA and AN on {001}-TiO$_2$ NTA-E3 and TiO$_2$ NTA-E4: A& B & C) {001}-TiO$_2$ NTA-E3; D, E, & F) TiO$_2$ NTA-E4 [Experimental conditions: NSB/PHA/AN: 50 mg/L (when added), 5 mM Na$_2$SO$_4$, Ag/AgCl (3M NaCl) was used as the reference electrode in the experiments].
CHAPTER V

Towards Full Potential Utilization during Water Purification Using Co/Bi/TiO$_2$ Nanotube Electrodes


Abstract

Most studies on electrochemical treatment for water purification have focused on either anodic oxidation or cathodic reduction where only partial of the cell potential is utilized. Here we report on a research effort towards full cell potential utilization during the elimination of organic pollutants under environmentally relevant conditions. Meropenem was selected as a representative recalcitrant antibiotic and a newly-developed Co and Bi co-doped TiO$_2$ nanotube array (Co/Bi/TiO$_2$ NTA) electrode was employed as both anode and cathode. While electrochemical reduction of meropenem appeared to be much more energy efficient (0.042kWh/m$^3$) than electrochemical oxidation (0.813kWh/m$^3$) in synthetic electrolyte, the degradation was significantly inhibited in environmental matrices (secondary effluent/SE and RO concentrate) due to the competition and/or inhibition effects of other species present in the matrices as well as electrode fouling, where calcium carbonate and magnesium oxide were identified to be main foulants. The elimination of Meropenem was then examined in coupled treatment schemes (e.g. sequential and simultaneous), taking advantages of the “self-regeneration” characteristic of TiO$_2$ NTA based electrodes through cathodic polarization. While a simultaneous oxidation & reduction with regular polarity switching seems to be a preferred treatment scheme especially for challenging matrices such as RO concentrate, the bipolar stability of
the nanostructured electrode (~280 switches) may limit the electrode lifetime. A hybrid electrolysis system coupling anodic oxidation of organic pollutants and cathodic hydrogen generation as a renewable energy source was also tested in a flow-through reactor, where consistent and steady treatment performance was demonstrated for a period of 3 days. We think the results obtained from this study have underlined the importance of matrix characteristics on the design and selection of electrochemical treatment processes. It also provides insights into future development of coupled anodic and cathodic processes for water purification.

5.1 Introduction

Electrochemical redox processes have emerged as a viable option for water purification as they offer several advantages such as capable of degrading a wide range of contaminants, small footprint, capability to adjust to influent fluctuation, and less waste generation. [2,282–284]. So far most of the studies in this respect focus on the degradation of selected model compounds or bulk chemical oxygen demand (COD) through either anodic oxidation or cathodic reduction processes, where only half of the cell potential is utilized for pollutant removal, resulting in a low energy efficiency [26,27,44,173,284–287].

Several coupled strategies combining both anodic oxidation and cathodic reduction (sequentially or simultaneously) have also been proposed to take advantages of the synergistic action of each electrode [269,287–289]. Such combination has the potential to utilize the full potential of the cell, increase the current efficiency, and possibly decrease the energy consumption [286,289–292]. For example, del Río et al. studied the electrochemical degradation of C.I. Reactive Orange 4 under different treatment conditions.
10%, 75%, and 94% of COD removal was achieved in electrochemical reduction, anodic oxidation, and coupled anodic oxidation and cathodic reduction, respectively. In addition, higher mineralization was obtained in the coupled process, where both azo group and aromatic structures, which are often stable against the oxidation process, were degraded [286]. Scialdone et al. proposed an electrochemical treatment scheme for de-halogenation of hydrocarbons via cathodic reduction with the simultaneous or sequential oxidation of the de-halogenated byproducts under the anodic oxidation. Results indicate that the higher decontamination and better current efficiency were attained in a simultaneous treatment scheme than the sequential anodic oxidation and cathodic reduction. However, to the best of our knowledge, these studies were only carried out in synthetic electrolytes without the complicated background species present in environmental matrices. In fact, these background species may cause electrode fouling (particularly the cathode) [283,293,294], which can decrease the efficiency of the coupled treatment scheme. Another strategy to put the full cell potential into use is to combine the anodic oxidation with generation of hydrogen gas (H₂) as a potential renewable energy source at the cathode [295,296]. For example, Choi et al. degraded methyl blue (MB) in a hybrid electrolysis system coupled with molecular hydrogen generation, where the electrochemical oxidation of MB took place on the anode side and the hydrogen production from electrochemical water splitting occurred simultaneously on the cathode side. Key prerequisites for successfully realizing such “coupling” are that the anode possesses a high and electro reactivity towards water pollutants while the cathode should have a good water splitting capability [287].

Titanium dioxide nanotube arrays (TiO₂ NTA) with the advantageous properties such as chemical stability, nontoxicity, and low cost have been investigated as an emerging
electrode material for water and wastewater treatment [26,38,173,243]. In particular, in our previous study a Co/Bi co-doped TiO$_2$ NTA electrode (Co/Bi/TiO$_2$ NTA) with high anodic stability and oxidant generating capability has been developed and employed for anodic oxidation of Meropenem, a widely used but less studied parental carbapenem antibiotic, in environmental matrices (e.g. secondary effluent/SE and reverse osmosis/RO concentrate generated from wastewater reuse) [297]. A unique property of TiO$_2$ NTA based electrodes is that the electroreactivity can be significantly enhanced via a simple cathodic polarization process, through which the partial reduction of Ti$^{4+}$ in the lattice to Ti$^{3+}$ can increase the mobility of charge carriers associated with the Ti$^{3+}$ impurities [38,115,243]. This property, together with the good anodic and cathodic reactivity towards water pollutants as well as the H$_2$ evolution capability demonstrated in previous studies [38,173,243,295,296,298], renders TiO$_2$ NTA a promising electrode material to be utilized in coupled electrochemical systems, where the electrode reactivity can possibly be in situ “regenerated” by regularly switching the polarity.

Herein, we report on our study to achieve the full cell potential utilization during electrochemical treatment of Meropenem in environmental matrices using Co/Bi/TiO$_2$ NTA electrodes. Building on our previous study on electrochemical oxidation of Meropenem with Co/Bi/TiO$_2$ NTA [297], in this study we first investigated electrochemical reduction of Meropenem in both synthetic electrolyte and environmental matrices (i.e. SE and RO concentrate). The following research effort focused on evaluation of different coupled anode and cathode processes to achieve an overall high energy efficiency and practical applicability. This study systematically investigated the coupled anodic and cathodic processes utilizing novel TiO$_2$ NTA based electrodes under
environmentally relevant conditions, which can provide insights and guidelines for the future development of cost-effective electrochemical water/wastewater treatment applications.

5.2 Materials and Methods

5.2.1 Electrode preparation

Co/Bi/TiO₂ NTA electrodes was prepared by an electrochemical anodization process followed by a dip-coating method (Text S5.1) [297].

5.2.2 Electrode characterization

The surface micro-morphology and chemical composition of the TiO₂ NTA/Co/Bi electrode were evaluated using a field emission scanning electron (FESEM, JEOL FE 7000) equipped with an energy dispersive X-ray analyzer (EDX). The crystallographic information of the electrode and precipitates were collected from 2° to 90° of 2θ using Rigaku MiniFlex 600. The electrochemical techniques including cyclic voltammetry and bipolar stability tests were performed on a potentiostat (Bio-Logic, SP150) in a three-electrode system with Pt as a counter electrode and Ag/AgCl (3 M NaCl) as a reference electrode.

5.2.3 Electrochemical treatment of Meropenem

Electrochemical reduction of Meropenem was carried out in a divided electrolytic cell (Nafion N-117 membrane) with Co/Bi/TiO₂ NTA as the working electrode, Pt mesh as the counter electrode, and Hg/HgO (20% KOH) as the reference electrode. The
effective surface area of the electrode was 6 cm$^2$ and the electrode spacing was ~1 cm. 80 mL of 30 mM NaClO$_4$ solution containing 500 µg L$^{-1}$ Meropenem was used as the working electrolyte with pH adjustment (pH ~7.00). During the experiments, 0.5 mL solution was sampled at different time intervals and immediately measured for Meropenem concentration. The effects of operating conditions including applied potential (-0.8 ~ -1.4 V vs SCE) and co-existing of different ions (chloride, sulfate, and bicarbonate) on the reduction of Meropenem were also investigated in synthetic electrolyte. Afterwards, the electrochemical reduction of Meropenem was examined in real water matrices including secondary effluent (SE) and reverse osmosis (RO) concentrate generated from secondary effluent (~75% recovery) (Table 5.1). It is worth mentioning that the Meropenem concentration in the SE was much lower than that in our previous study (~ 7 µg/L) [297], although the samples were collected from the same treatment plant, indicating the seasonal variation. Following these studies, the degradation of Meropenem in real water matrices was evaluated in coupled anodic and cathodic processes using Co/Bi/TiO$_2$ NTA as both anode and cathode electrodes, where sequential and simultaneous oxidation and reduction processes were investigated in a divided and an undivided electrolytic cell, respectively. Lastly, a hybrid continuous-flow electrolysis setup integrating anodic pollutant oxidation and cathodic H$_2$ generation using Co/Bi/TiO$_2$ NTA electrodes was examined in RO concentrate to investigate the feasibility of practical applications. The error bars in the figures represent standard deviations from duplicate experiments.
5.2.4 Analytical methods

The concentration of Meropenem, ions, and TOC were measured using a high-performance liquid chromatography (HPLC-Agilent 1100 series), ion chromatography (Thermo Dionex ICS-1600), and TOC-LCPH (Shimadzu), respectively. Moreover, the HPLC/MS/MS (DionEX UltiMate 3000-LTQ Orbitrap XL) in positive electrospray ionization (ESI) mode was used to identify the transformation products. Details of the analytical methods are provided in Text S5.2.

5.3 Results and Discussion

5.3.1 Electrode characterization

The characterization of the Co/Bi/TiO$_2$ NTA electrode was evaluated and reported previously (Text S5.3 and Figure S5.1&2) [297]. Briefly, Co and Bi were successfully doped onto the well-aligned and uniform nanotubes with ~70 nm and ~13 µm diameter and length, respectively.

5.3.2 Electrochemical reduction of Meropenem in synthetic electrolyte

The effects of applied potential on Meropenem degradation was investigated between -0.8--1.4 V/SCE. As can be observed from Figure 5.1A, a more negative potential resulted in a higher removal. After 15 min of electrolysis, 80%, 87%, 93%, and 95% of Meropenem was removed at -0.8, -1.0, -1.2, and -1.4V/SCE, respectively. As a potential beyond -1.2 V/SCE did not lead to much enhanced Meropenem removal, -1.2V/SCE was selected as the operating potential in the following study in synthetic electrolyte. In addition, Co/Bi/TiO$_2$ NTA electrode outperformed the common carbon electrode under the
same treatment conditions (Figure S5.3), confirming the good cathodic reactivity of Co/Bi/TiO$_2$ NTA towards water pollutants. This may be ascribed to the surface defects (e.g. Ti$^{3+}$ states or O$^{2-}$ vacancies) on TiO$_2$ NTA, which can serve as the crucial reactive sites for many reactions such as generation of atomic hydrogen (H*) [173]. Moreover, the effects of anions commonly present in environmental matrices on electro-reduction of Meropenem was evaluated by adding chloride (Cl$^-$), sulfate (SO$_4^{2-}$), or bicarbonate (HCO$_3^-$) into the electrolyte. As shown in Figure S5.4, while chloride and sulfate exhibited no effect on Meropenem degradation, the presence of bicarbonate ions suppressed Meropenem reduction by 10%~15% depending on the bicarbonate concentration, due to the competition between bicarbonate ions and Meropenem for the reactive species (e.g. H*) generated during the electrolysis [299–301].

In general, water pollutants may be degraded in an electrochemical reduction cell via direct electron transfer or indirect mechanism through the generation of reactive species such as H$_2$O$_2$ and H* [260]. The reaction mechanisms of electrochemical reduction of water contaminants (e.g. nitrobenzene) on TiO$_2$ NTA electrodes have been studied in detail [173]. Here, we have also investigated the reaction pathway of electro-reduction of Meropenem through a series of CV tests and scavenging tests and found that while direct electron transfer was the dominant mechanism, atomic H* and H$_2$O$_2$ formed during the electrolysis also contributed to the removal of Meropenem (Text S5.4, Figure S5.5).

Compared to the electrochemical oxidation using the same electrode [297], the electrochemical reduction of Meropenem seems to proceed in a much more energy-efficient way. As shown in Figure 5.1B, the observed reaction constant ($k_{obs}$) of Meropenem reduction was higher than oxidation, even with a much lower applied current.
density (average current density $\sim 1\text{mA/cm}^2$ at -1.2V/SCE), resulting in an energy consumption (EE/O) (Text S5.5 and Figure S5.6) of 0.042 kWh/m$^3$ for electrochemical reduction of Meropenem, which is $\sim 18$ times lower than that of electrochemical oxidation (0.813 kWh/m$^3$). The faster degradation of Meropenem via electro-reduction may be explained by the presence of some functional groups that can be reduced much faster than being oxidized. For example, the carboxyl group (COOH) may be reduced very easily to the hydroxymethyl group (CH$_2$-OH). Here we also examined the transformation products of Meropenem during electrochemical reduction. Compared with those of electrochemical oxidation, fewer intermediates were generated (Figure S5.7). After electrochemical reduction, several signals with m/z of 370.41, 266.95, 157.10, and 144.98 (molecular weights of 369, 265, 156, and 143 g/mol, respectively) were detected (Figure S5.7A), while signals with m/z of 226.60, 185.74, 157.02, 144.88, 104.70, and 63.83 (molecular weights of 225, 184, 156, 143, 103, and 62 g/mol, respectively) were observed after electrochemical oxidation (Figure S5.7B). Moreover, the intermediate with a molecular weight of 156 g/mol determined to be N,N-dimethyl-4-oxopyrrolidine-2-carboxamide (C$_7$N$_2$O$_2$H$_{12}$) in our previous study [297] was formed in both processes. In addition to the reductive reactivity towards Meropenem, the possible leaching of metallic ions (Co and Bi) from the Co/Bi/TiO$_2$ NTA electrode during electrochemical reduction was examined as well. With an electrode area/solution volume ratio of 7.5 m$^{-1}$, 0.295 ± 0.071 µg/L (0.049 ± 0.012 µg/cm$^2$) Co and 0.605 ± 0.217 µg/L (0.100 ± 0.036 µg/cm$^2$) Bi were detected after 15 min treatment, demonstrating the strong bonding between the dopant and the TiO$_2$ NTA substrate. We also compared the Meropenem removal efficiency through either electrochemical oxidation or reduction with other advanced oxidation processes (AOPs)
that have been tested for Meropenem treatment. Meropenem has been treated via photocatalytic ozonation, photo-Fenton oxidation, and photochemical degradation, where much slower degradation kinetics than that of electrochemical oxidation or reduction was reported [178,302,303].

Figure 5.1 A) Effects of applied potential on Meropenem removal; B) $K_{\text{obs}}$ of Meropenem degradation [Experimental conditions: pH=7; background electrolyte: 30 mM NaClO$_4$; B) Oxidation: 10 mA/cm$^2$, Reduction: -1.2 V/SCE (~1 mA/cm$^2$). Reference electrode: Oxidation: Ag/AgCl (3M NaCl), Reduction: Hg/HgO (20% KOH)].

5.3.3 Electrochemical reduction of Meropenem in environmental matrices

Since the Co/Bi/TiO$_2$ NTA electrode showed promising performance in the synthetic electrolyte, we further investigated the electrochemical reduction of Meropenem in environmental matrices of secondary effluent (SE) and RO concentrate (Table 5.1). The real water samples were spiked with 20 mg L$^{-1}$ Meropenem stock solution to obtain an initial concentration of 500 µg L$^{-1}$. Due to the lower conductivity of environmental matrices, -1.6V/SCE was applied so to achieve the same current density as that in the synthetic electrolyte (~1mA/cm$^2$) in SE. As shown in Figure 5.2, in contrast to ~95 % removal
achieved in synthetic electrolyte after 15 min electrolysis, only ~ 44% of Meropenem was removed in SE after 40 min treatment. Furthermore, only 20% Meropenem removal was obtained in RO concentrate with an even higher current density (~4mA/cm²) than that in SE and synthetic electrolyte, highlighting the importance of the matrix effect. In SE or RO concentrate, competition and/or inhibition effects of co-existing species may result in a decreased removal efficiency of the target compound. For example, the removal of Meropenem was inhibited to certain extent in the presence of bicarbonate (Figure S5.4C). The bulk organic matters present in SE and RO (i.e. TOC) can also compete for the active sites and reactive species, leading to an inferior performance. To this end, we tested Meropenem degradation in simulated solutions containing major inorganic species identified in SE and RO concentrate but without bulk organics (Table S5.1). As demonstrated in Figure S5.8, much higher removal was observed in the simulated solutions than that in SE or RO concentrate, confirming the competitive effects caused by other organics in the matrix. However, a closer examination of Figure S5.8 may also indicate suppression mechanisms other than the competition and inhibition effects discussed above. For example, the efficiency in synthetic electrolyte with HCO₃⁻ addition was higher than that in the simulated solutions even at a similar or even lower current density. In fact, electrode fouling exerted by different chemical species in the complex environmental matrices can be a serious concern for practical applications of electrochemical reduction processes. Fouling of electrodes may occur when different compounds precipitate on the electrode surface, covering the active sites and thus decreasing the performance [304–306].
Table 5.1 Characteristics of secondary effluent and RO concentrate used in this study.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Secondary effluent</th>
<th>RO concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meropenem (µg/L)</td>
<td>0.88 ± 0.57</td>
<td>2.83 ± 1.61</td>
</tr>
<tr>
<td>Na⁺ (mg L⁻¹)</td>
<td>40.62 ± 1.31</td>
<td>127.75 ± 4.46</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>7.32 ± 0.16</td>
<td>31.62 ± 1.36</td>
</tr>
<tr>
<td>K⁺ (mg L⁻¹)</td>
<td>10.90 ± 0.56</td>
<td>31.30 ± 1.52</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>44.38 ± 1.29</td>
<td>175.76 ± 8.72</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>16.27 ± 1.55</td>
<td>71.02 ± 5.38</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>0.81 ± 0.27</td>
<td>3.37 ± 0.43</td>
</tr>
<tr>
<td>HCO₃⁻ (mg/L)</td>
<td>86.35 ± 3.57</td>
<td>391.19 ± 10.79</td>
</tr>
<tr>
<td>NO₃⁻ (mg/L)</td>
<td>6.31 ± 0.84</td>
<td>23.26 ± 1.59</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>17.58 ± 2.73</td>
<td>75.17 ± 5.82</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>5.03 ± 1.37</td>
<td>21.96 ± 2.18</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.89 ± 0.13</td>
<td>0.73 ± 0.09</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>403 ± 7</td>
<td>1792 ± 20</td>
</tr>
</tbody>
</table>

Figure 5.2 Meropenem degradation and TOC mineralization in secondary effluent (SE) and RO concentrate [Experimental condition: applied potential: -1.6 V vs SCE; Current density: ~1 and ~3.5 mA/cm² for SE and RO concentrate, respectively; Hg/HgO (20% KOH) reference electrode].

During the electrolysis of aqueous solution, pH in proximity of the cathode rises quickly due to water reduction, whereas a high pH usually means a high thermodynamic driving force for precipitation [306]. In this study, white precipitates were formed on the electrode surface when it was used in SE or RO concentrate, where the sphere-shaped particles are one of the typical morphologies of calcium carbonate (Figure S5.9) [307].
Further analysis of the precipitate XRD spectra indicates a good match with the standard diffraction peaks of calcium carbonate (JCPDS:5-586) [306] and magnesium oxide (JCPDS:45-0946) [308] (Figure 5.3A). EDX spectrum also displays a strong calcium signal with 24.11 wt %, while magnesium and phosphate account for 4.40% and 0.62%, respectively (Figure 5.3B). Hence CaCO$_3$ and MgO are the main constituents of the precipitates. Calcium phosphate may also be formed but at a much lower amount due to the low concentration of phosphate in the matrices. These results are consistent with other studies reported in the literature [293,305,306]. In addition to solution chemistry, some physio-chemical properties of the electrode can also influence cathode fouling. Here, the TiO$_2$ nanotube surface is superhydrophilic with high free energy, causing the precipitate ions to spread on the electrode surface and to infiltrate into the nanotubes. The nanotube structure also provides roughness that can serve as the center for the growth of the precipitate crystals [293,294,309]. On the other hand, the nano-porous top of the nanotube array may trap vapor or gas into the porous structure, which blocks the contact between the surface and precipitate [293]. Therefore, the adhesion between the precipitate and the electrode surface is weak and the formed fouling layer can be easily wiped off from the Co/Bi/TiO$_2$ NTA.
While pH plays an important role in the solubility of precipitates, one easy way to remove electrode fouling is to apply a positive potential on the electrode, creating an acidic environment for precipitate dissolution. As mentioned previously, polarity switching could be particularly appealing for TiO$_2$ NTA based electrodes ascribed to the “reactivation effect” of cathodic polarization (self-doping). Therefore, polarity switching was included in the following investigation on the coupled processes to alleviate the electrode fouling as well as to take advantage of unique self-doping capacity of TiO$_2$ NTA.

5.3.4 Meropenem degradation in coupled anodic/cathodic processes

Here, the possibility of coupling cathodic reduction and anodic oxidation for Meropenem degradation was investigated in two treatment schemes, i.e. sequential and simultaneous (Figures 5.4&5). 6 mA/cm$^2$ and 5 mA/cm$^2$ were selected as the applied current density in RO concentrate and SE, respectively, according the results of preliminary tests (Figure S5.10). As illustrated in Figure 5.4, the sequential oxidation/reduction treatment scheme was examined in a two-compartment electrochemical cell where Co/Bi/TiO$_2$ NTA served as both the anode and cathode. Hence the Meropenem degradation
during sequential oxidation-reduction and reduction-oxidation was simultaneously obtained from each compartment by switching the polarity regularly (every 10 min and 20 min). Similar trends in terms of Meropenem removal were observed for the sequential treatment scheme in both SE and RO concentrate (Figure 5.4). In general, the oxidation-reduction pattern outperformed the reduction-oxidation pattern. While similar performance was achieved for oxidation only and sequential oxidation-reduction in RO concentrate, the removal in the sequential oxidation-reduction particularly at 20 min switching intervals was slightly better than that of oxidation. Moreover, compared with reduction only, sequential reduction-oxidation always resulted in a higher efficiency which was even more apparent in RO concentrate with a 10 min switching interval. Given the fact that faster degradation kinetics was achieved through electrochemical reduction than oxidation in synthetic electrolyte, all these results have implied the significant effects of electrode fouling on the elimination of contaminants from environmental matrices. A fast removal at the beginning is important for the overall efficiency. However, mass transfer of the target compound to the electrode can be impeded by the fouling, the effect of which seems particularly appreciable when the concentrate is relatively high. Therefore, although polarity switching can help “refresh” the electrode, only limited performance enhancement was achieved when the sequential treatment started with the reduction process.
The simultaneous treatment scheme (oxidation & reduction) was tested in a single-compartment cell using Co/Bi/TiO₂ NTA as both anode and cathode, where the polarity was switched every 10 or 20 min (Figure 5.5). While no appreciable difference was observed between oxidation only and simultaneous oxidation and reduction for SE, noticeable improvement of Meropenem removal was realized in RO concentrate. This may further underline the effects of electrode fouling which is more pronounced in RO concentrate with high contents of the precipitate precursors. Moreover, the energy consumption (EE/O; Text S5.5) for simultaneous oxidation & reduction was 3.267 kWh/m³ for SE and 2.575 kWh/m³ for RO concentrate, whereas EE/O for oxidation only was 4.054
kWh/m$^3$ and 3.202 kWh/m$^3$ for SE and RO concentrate respectively. Considering the lower energy consumption, the relative simple reactor setup of one-compartment cell and that no post-adjustment of the effluent pH is needed (Figure S5.11) a simultaneous oxidation & reduction with regular polarity switching seems to be a preferred treatment scheme especially for challenging matrices such as RO concentrate.

Figure 5.5 Simultaneous oxidation & reduction treatment scheme for Meropenem degradation in secondary effluent (SE) and RO concentrate [Experimental condition: Hg/HgO (20% KOH) reference electrode].

In addition to the treatment performance, the physical/electrochemical stability of the Co/Bi/TiO$_2$ NTA electrode under the proposed treatment scheme is also an important concern for practical applications. Here, the stability of Co/Bi/TiO$_2$ NTA electrode was
examined in 10 mM NaClO₄ (similar conductivity as that of RO concentrate) at 10 mA/cm² in a single-compartment cell with a polarity switching frequency of 20 min. As shown in Figure S5.12, the anodic potential increased gradually over time and raised ~1V in a ~5 day experiment. Moreover, the nanotube layer was delaminated from the Ti substrate (Figure S5.13). This phenomenon indicates that the stress exerted by the frequently switched anodic and cathodic potential has led to severe distortion of the nanotube structure, which was also confirmed by the SEM images of the Co/Bi/TiO₂ NTA electrode used in the bipolar stability test (Figure S5.13). The destruction of the tubular nanostructure will eventually result in the electrode deactivation. In order to alleviate the “shocking stress”, we also tried to apply a 30 seconds rest phase (0 mA/cm²) between the polarity switching. However, similar results were obtained (data not shown). According to our tests, the Co/Bi/TiO₂ NTA electrode seems to be able to survive ~280 switches of polarity before it gets destroyed, corresponding to ~4 days at a switching frequency of every 20 min, which would make the proposed treatment scheme infeasible for practical applications. On the other hand, no appreciable difference in Meoepenm removal was observed when the polarity was switched every 10 min, 20 min, or no switching during the 40 min run. These results indicate the electrode lifetime for the simultaneous oxidation & reduction treatment scheme could possibly be increased by increasing the switching interval. For example, the electrode may last for ~1 year when the polarity is switched every 1~2 days. However, cathode fouling may lead to gradually deteriorated performance during each cycle. Nonetheless, the adhesion between the nanotube layer and the Ti substrate as well as the mechanical stability of the nanostructure needs to be further improved to fully realize the advantages of coupled oxidation/reduction treatment schemes for practical applications.
5.3.5 Hybrid electrolysis system

As discussed previously, another strategy to utilize the full cell potential during water purification is to couple anodic oxidation of the organic contaminants and cathodic hydrogen evolution. Hydrogen (H\textsubscript{2}) is considered to be a clean energy which can help combat climate change because of the greenhouse gas emission [295,296]. In this study, we tested such a hybrid electrolysis system employing the Co/Bi/TiO\textsubscript{2} NTA electrodes. The high oxidizing capability and anodic stability of Co/Bi/TiO\textsubscript{2} NTA have been demonstrated in our previous study [297]. Moreover, TiO\textsubscript{2} NTAs have been reported to have a good H\textsubscript{2} evolution capacity [295,296,310–312]. Here, the hybrid treatment scheme was evaluated in a continuous flow reactor (Figure S5.14), where RO concentrate containing 30µg/L Meropenem was continuously pumped through the anodic chamber at a flow rate of 1 mL/min (hydraulic detention time 80 min). On the other hand, 0.1 M Na\textsubscript{2}SO\textsubscript{4} was continuously stir-mixed and recirculated through the cathodic chamber a flow rate of 10 mL/min for hydrogen production. Effluent samples from the anodic chamber were collected and measured for Meropenem and the H\textsubscript{2} gas was collected in an air bag. The continuous flow experiment was run for 72 hrs, with the anode and cathode switched every 24 hrs (one cycle). As shown in Figure 5.6, the effluent concentration of Meropenem reached equilibrium (~5 µg/L) after about one hydraulic retention time and maintained relatively constant throughout the experiment. We also observed that while it fluctuated and slightly increased during each cycle, the overall cell potential tended to decrease after the anode and the cathode were switched. This also led to a decrease in EE/O, which was calculated to be 11.038 kWh/m\textsuperscript{3}, 10.259 kWh/m\textsuperscript{3}, and 9.610 kWh/m\textsuperscript{3} in the 1\textsuperscript{st}, 2\textsuperscript{nd}, and 3\textsuperscript{rd}
cycle, respectively. These results validate our assumption that although anodic oxidation may gradually deactivate the TiO$_2$ NTA based electrode due to surface passivation, cathodic polarization can effectively recover the anode activity attributed to the unique nanostructure of TiO$_2$ NTA, thus realizing “in-situ” electrode regeneration. It should also be pointed out that apparent higher energy consumption in the hybrid system than those in simultaneous oxidation & reduction and oxidation only processes was mainly due to the lower initial concentration of Meropenem (30 µg/L vs. 500 µg/L), where mass transfer may limit the reaction kinetics. In addition to Meropenem degradation, a steady TOC mineralization of 57±1% reduction was also achieved (Figure S5.15). Furthermore, approximate 93±10 mL of H$_2$ was generated per cycle (24 hours). As reported in the literature, the cathode faradic current efficiency (CE) for H$_2$ evolution during anodic oxidation of water pollutants is usually >40%. [313–316]. One concern of a divided electrolysis cell is that the effluent from the anode chamber after treatment has a low pH, which may need to be adjusted before discharging into the environment. pH of the treated RO concentrate was ~3 in our experiment. Preliminary tests indicated about 0.136 g of sodium hydroxide (NaOH) or 3.780 g of sodium bicarbonate (NaHCO$_3$) salt is required to raise the pH of 1 L effluent to 7. Therefore, if needed, sodium hydroxide may be the preferred chemical for this purpose and the required dose may be adjusted depending on the disposal option and/or the receiving water characteristics.

It is worth mentioning that the anodic lifetime of Co/Bi/TiO$_2$ NTA electrode was estimated to be ~25,000 hours (~1000 days) without any “regeneration” at 10 mA/cm$^2$ in our previous study [297]. In this study, the 24 hr switching frequency was selected to demonstrate the proof of concept. Given the high anodic stability of Co/Bi/TiO$_2$ NTA,
there should be a great flexibility in this regard. For example, if the electrode is switched every week, the Co/Bi/TiO₂ NTA electrode can be good for ~2000 days, where the limiting factor would be the bipolar stability (assume ~280 switches here). All these preliminary estimation indicates the great potential of utilizing Co/Bi/TiO₂ NTA electrodes to achieve a high overall energy efficiency for electrochemical water treatment, whereas the optimal treatment scheme and operational conditions will depend on the specific application such as water characteristics, treatment goal, energy requirements, and final disposal/discharge options.

Figure 5. 6 Meropenem degradation in flow-through tests [Experimental conditions: 10 mA/cm², Flow rate: 1 mL/min, initial Meropenem concentration: 30 µg/L, matrix: RO concentrate, Ag/AgCl (3M NaCl) reference electrode].

5.4 Conclusion

In this work, several coupled anodic oxidation and cathodic reduction processes were investigated to utilize the full cell potential in water/wastewater treatment applications. A novel Co/Bi/TiO₂ NTA electrode was employed in the coupled processes for the elimination of a widely-used antibiotic, Meropenem. The results obtained from this
study could provide insights into design and development of electrochemical treatment schemes with high energy efficiencies. Specific conclusions include:

- While degradation of Meropenem via electrochemical reduction can proceed in a much more energy-efficient way than electrochemical oxidation in synthetic electrolytes, the cathodic reduction of Meropenem was suppressed significantly in environmental matrices (e.g. SE and RO concentrate) due to the competition and the inhibition effects of co-existing species (e.g. bulk organics and bicarbonate) as well as electrode fouling;
- CaCO$_3$ and MgO were identified as the main cathode foulants;
- Compared to the sequential oxidation/reduction process, simultaneous oxidation & reduction with regular polarity switching appeared to be the preferred treatment scheme for both RO concentrate and SE with simpler setup and higher energy efficiency; however, the bipolar stability of the nanostructured electrode may limit the practical application of such treatment schemes;
- A hybrid electrolysis system coupling anodic oxidation of organic pollutants with cathodic hydrogen generation demonstrated a satisfactory performance in a flow-through setup and the advantageous effects of in-situ electrode regeneration through cathodic polarization; and
- Future research should focus on improvement of the mechanical stability of TiO$_2$ NTA based electrodes; selection and design of coupled electrochemical processes for water purification need take matrix effects into consideration.
5.5 Supporting Information

Text S5.1

Briefly, the cleaned titanium foil (0.1 mm, 99.6%) was anodized in a mixture of ethylene glycol (EG), 2.5 wt% H2O, and 0.2 wt% NH4F under constant potential (45V) for 16 hours. Afterwards, an additional anodization was performed for 5 minutes at 60V in a fluoride-free electrolyte (5% H3PO4 in EG solution) to enhance the physical stability of nanotube layer to the Ti substrate. Subsequently, the TiO2 NTA electrode was dipped into the aqueous solution containing 125 mM cobalt (Co) and 60 mM bismuth (Bi) for 1 min and pulled up at the rate of 1 cm min⁻¹. The dip-coating method was repeated three times. The Co/Bi/TiO2 NTA electrode was annealed for 1 hour at 450 °C with a rate of 2 °C min⁻¹ in 5% H2/Ar environment. Finally, the cooked Co/Bi/TiO2 NTA electrode was cathodized for 90s at constant current density (17 mA cm⁻²) in a buffer solution (100 mM phosphate) for full activation. In this study, carbon paper (0.18 mm, AvCarb P50T) was used as a control electrode.

Text S5.2

The concentration of Meropenem was measured at 290 nm using a high-performance liquid chromatography (HPLC-Agilent 1100 series) with a Hypersil Gold 100 x 2.1 mm C18 column and a diode array detector (DAD). The mobile phase was acetonitrile/KH2PO4 (20:80, vol:vol%, pH:3) with a flow rate of 0.2 mL/min. The concentration of ions (Cl⁻ and SO₄²⁻) were measured by ion chromatography (Thermo Dionex ICS-1600 with an IonPac AS 19 anion-exchange column (4 x 250 mm). The mobile phase was delivered at a flow rate of 1.0 ml/min, with the following stepwise gradient
elution program: 0 → 5 min (10 mM KOH), 5 → 10 min (10 → 18 mM KOH). Total organic carbon (TOC) was measured using TOC-LCPH (Shimadzu). The metal (Co, Bi) loading and leaching were analyzed using ICP-MS (ICP-MS Thermo X-Series II, XO 472, Thermo Fisher Scientific, Waltham, Massachusetts).

Text S5.3

The XRD patterns of TiO₂ NTA and Co/Bi/TiO₂ NTA are shown in Figure S1C. Most diffraction peaks of the samples are in good agreement with anatase-phase TiO₂ standard pattern (JCPDS No. 21-1272) with the preferential {101} exposed facets [92,173]. As mentioned in our previous study, the {101} exposed facets are sensitive to the nanotube surface modification, where the (101) and (004) crystal planes were decreased and increased after metal loading, respectively, without changing the exposed facet [297,317]. The peaks corresponding to the bismuth oxide can be observed at 28.3 and 32.6 degree. The EDX spectrum of Co/Bi/TiO₂ NTA electrode is shown in Figure S1D. The Ti, O, Co, and Bi peaks are observed with a weight percentage of 61.46%, 37.33%, 0.78%, and 0.43%, respectively. According to the full XPS survey scan spectra in Figure S2A, the as-prepared Co/Bi/TiO₂ NTA electrode is mainly composed of Ti, O, Co, and Bi elements. The deconvolution of high-resolution O 1s, Ti 2p, Co 2p, and Bi 4f spectra was presented in Figure S2B-E. The peak at 530.06 eV is attributed to the O 1s, which is fitted with two peaks at 529.78 (Ti-O) and 531.28 eV(surface O-H) [126]. The Ti 2p spectra shows two peaks at 464.48 and 458.54 eV, which correspond to the Ti 2p₁/₂ and Ti 2p₃/₂, respectively. These two peaks can be deconvoluted into two sets of peaks. One refers to the Ti³⁺ at 458.58 and 463.76 eV, and the other applies to the Ti⁴⁺ with binding energy of 464.58 and
The Co 2p pattern shows two peaks at 786.28 and 780.58 eV, which were deconvoluted into three peaks centered at 786.18, 781.88, and 780.48 eV. The peaks located at 781.88 and 780.48 eV are attributed to Co$^{2+}$ and Co$^{3+}$, respectively [205]. The peaks at the binding energy of 163.98 and 158.68 eV are assigned to the Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively [185].

Text S5.4

In order to examine the possible reduction of Meropenem via direct electron transferring with Co/Bi/TiO$_2$ NTA surface, CV tests were performed in the range of -1.6V to 0.0V/SCE in the presence and absence of Meropenem in an undivided cell. As shown in Figure S5A, the peak in the range of -1.0V to -0.8V/SCE, which was detected after the addition of Meropenem into the background electrolyte, represents the direct reduction of Meropenem on the Co/Bi/TiO$_2$ NTA electrode. The contribution of atomic hydrogen (H$^*$) in Meropenem degradation via the indirect reduction mechanism was investigated by employing t-buOH (TBA) as a scavenger [318,319], where the electrochemical stability of TBA was first confirmed (Figure S5B). As shown in Figure S5C, the removal of Meropenem decreased with the addition of TBA, demonstrating the active role of H$^*$ in Meropenem degradation. It has been reported that the surface defects (e.g. Ti$^{3+}$ or O vacancies/OVs) that may be generated on TiO$_2$ NTA during cathodic polarization are the reactive sites for dissociative adsorption of H$_2$O/H$^+$ leading to the formation of surface adsorbed H$^*$ [173,320]. In addition, the possible formation of H$_2$O$_2$ during electrolysis was examined using a colorimetric method reported previously (1–120 × 10$^{-6}$ M) [122,243]. The formation of H$_2$O$_2$ in the presence and absence of Meropenem was shown in Figure
S5D. The higher amount of H₂O₂ detected in the absence of Meropenem may indicate the possible reaction between these two compounds.

Text S5.5

In this study, the EE/O value was calculated using eq. 1 & 2 with data from batch and continuous flow experiments, respectively. [207].

\[
EE/O = \frac{A \times I \times U \times t}{1000 \times V \times \log\left(\frac{C_0}{C}\right)} \quad \text{eq. 1}
\]

\[
EE/O = \frac{A \times I \times U}{1000 \times Q \times \log\left(\frac{C_0}{C}\right)} \quad \text{eq. 2}
\]

where EE/O is the electric energy consumed to degrade the concentration of Meropenem by one order of magnitude in 1 m³ wastewater (kWh/m³), A is the surface area (cm²), I is the applied current density (A/cm²), U is the average overall potential (V), V is the volume of wastewater (m³), t is the time of electrolysis (hr), Q is the flow rate in continuous flow-through runs (m³/hr), and C is the concentration of Meropenem (μg/L).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Simulated Secondary effluent</th>
<th>Simulated RO concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ (mg L⁻¹)</td>
<td>18.07</td>
<td>71.55</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>7.50</td>
<td>31.50</td>
</tr>
<tr>
<td>K⁺ (mg L⁻¹)</td>
<td>1.28</td>
<td>4.16</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>44.50</td>
<td>176.00</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>38.50</td>
<td>141.68</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>0.80</td>
<td>3.50</td>
</tr>
<tr>
<td>HCO₃⁻ (mg/L)</td>
<td>86.00</td>
<td>395.00</td>
</tr>
<tr>
<td>NO₃⁻ (mg/L)</td>
<td>6.00</td>
<td>23.50</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>28.90</td>
<td>114.08</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>385</td>
<td>1710</td>
</tr>
</tbody>
</table>
Figure S5. 1 Co/Bi/TiO$_2$ NTA electrode characterization, A&B) SEM image; C) XRD pattern; D) EDX spectra.
Figure S5. 2 XPS spectra of Co/Bi/TiO$_2$ NTA electrode: A) Full scan, B) O 1s, C) Ti 2p, D) Co 2p, E) Bi 4f.
Figure S5. 3 Meropenem degradation using Co/Bi/TiO$_2$ NTA and carbon cathode [Experimental conditions: pH=7; applied potential: -1.2 V vs SCE; background electrolyte: ~30 mM NaClO$_4$; Hg/HgO (20% KOH) reference electrode].

Figure S5. 4 Effects of co-existing ions on Meropenem removal: A) Chloride, B) Sulfate, C) bicarbonate [Experimental conditions: pH=7; applied potential: -1.2 V/SCE; background electrolyte: ~30 mM NaClO$_4$ except A, A) ~30 mM Na$_2$SO$_4$ (conductivity of the electrolyte was adjusted to be equal to that of 30 mM NaClO$_4$ when other ions were added); Hg/HgO (20% KOH) reference electrode].
Figure S5. 5 Meropenem reduction mechanism: A) Direct reduction of Meropenem on Co/Bi/TiO$_2$ NTA electrode; B) Performance of TBA on Co/Bi/TiO$_2$ NTA electrode; C) Meropenem degradation in the presence and absence of TBA; D) H$_2$O$_2$ formation during the electrolysis [Experimental conditions: A) 5mg/L Meropenem, background electrolyte: A) 5 mM NaClO$_4$, B) 2 mM NaClO$_4$, C&D) 30 mM NaClO$_4$; TBA concentration: B&C) 1mM TBA; Hg/HgO (20% KOH) reference electrode].
Figure S5. 6 Overall potential in electrochemical oxidation and reduction of Meropenem [Experimental conditions: pH=7; background electrolyte: 30 mM NaClO₄; Reference electrode: A) Ag/AgCl (3M NaCl), B) Hg/HgO (20% KOH)].

Figure S5. 7 LC/MS Spectrum of Meropenem transformation products in the positive EIS mode [M+H]⁺: A) Reduction; B) Oxidation.
Figure S5. 8 Meropenem degradation in different water matrices including secondary effluent (SE), RO concentrate (RO), simulated secondary effluent (SSE), simulated RO concentrate (SRO), synthetic electrolyte [30 mM NaClO₄] (Syn), synthetic electrolyte with 200 mg/L HCO₃⁻ (Syn with 200 mg/L HCO₃⁻), and synthetic electrolyte with 800 mg/L HCO₃⁻ (Syn with 800 mg/L HCO₃⁻) [Experimental condition: applied potential: -1.2V/SCE for syn, syn with 200 mg/L HCO₃⁻, and syn with 800 mg/L HCO₃⁻, -1.6V/SCE for SE, RO, SSE, and SRO; Hg/HgO (20% KOH) reference electrode].

Figure S5. 9 Photos of A) Pristine Co/Bi/TiO₂ NTA electrode; B) Co/Bi/TiO₂ NTA electrode used in synthetic electrolyte; and C) Co/Bi/TiO₂ NTA electrode used in RO concentrate; SEM images of D) Co/Bi/TiO₂ NTA electrode used in RO concentrate, and E) Precipitates collected from the surface of the used electrode.
Figure S5. 10 Effects of operational conditions on Meropenem removal in coupled anodic and cathodic processes [Experimental condition: Hg/HgO (20% KOH) reference electrode; treatment scheme: simultaneous].

Figure S5. 11 pH evolution during simultaneous oxidation & reduction processes in different environmental matrices: A) RO concentrate, B) SE [Experimental conditions: A) 6 mA/cm², B) 5 mA/cm²; Hg/HgO (20% KOH) reference electrode].
Figure S5. 12 Bipolar stability test of Co/Bi/TiO$_2$ NTA electrode in simultaneous oxidation & reduction processes [Experimental condition: Ag/AgCl (3M NaCl) reference electrode; polarity switching frequency: every 20 min].

Figure S5. 13 Deactivated Co/Bi/TiO$_2$ NTA electrode in bipolar stability tests.
Figure S5. 14 Schematic diagram of the **Hybrid electrolysis system** [Experimental conditions: Flow rate: anodic chamber (1mL/min), cathodic chamber (10mL/min), reactor volume: anodic chamber (80 mL), cathodic chamber (80 mL), electrode surface area: 6 cm$^2$, current density: 10 mA/cm$^2$, Reference electrode: Ag/AgCl (3M NaCl)].

Figure S5. 15 TOC mineralization during flow-through tests [Experimental conditions: 10 mA/cm$^2$, Flow rate: 1 mL/min, initial Meropenem concentration: 30 µg/L, matrix: RO concentrate; Ag/AgCl (3M NaCl) reference electrode].
CHAPTER VII

CONCLUSION AND FUTURE WORK

6.1 Conclusion

Titanium dioxide (TiO$_2$) can be an ideal material for environmental applications attributed to many advantageous properties such as chemical stability, low-cost, and nontoxicity. This dissertation focused on engineered modifications of the main structure parameters of titanium dioxide including the crystallinity, shape, size, surface structure, and defects to improve the electrochemical functionalities of TiO$_2$, which can then be used as a novel electrode material (both anode and cathode) in different electrochemical water and wastewater treatment applications. TiO$_2$ nanotube array (NTA) can be synthesized by simple electrochemical anodization using metallic Ti as the substrate. The 1-D nanostructure may provide a unique combination of the highly functional features of TiO$_2$ with a regular and controllable nanoscale geometry as well as beneficial features of directional charge transport and high efficiency of charge separation. In this dissertation, novel TiO$_2$ NTA-based electrodes were developed and evaluated in different water and wastewater treatment applications including, electrochemical disinfection of E.coli (served as an anode), electrochemical oxidation of Meropenem (served as an anode), electrocatalytic reduction of nitrobenzene (served as a cathode), and coupled anodic oxidation and cathodic reduction of water pollutants (served as both an anode and a cathode). Results indicate that TiO$_2$ NTA with appropriate modifications is a promising
electrode material for different electrochemical water and wastewater treatment applications. In addition, specific conclusions include:

1- TiO$_2$ NTA based electrodes are able to degrade organic pollutants via both direct and indirect mechanisms, demonstrating the excellent electroactivity of TiO$_2$ NTA based electrodes towards water pollutants. The underlying mechanism for such superior performance is the generation of Ti$^{3+}$ states/oxygen vacancies (O$_V$) on the nanostructured platform during the functionalization process, which can serve as the crucial reactive sites for many reactions such as generation of oxidizing species (e.g., $\cdot$OH, O$_3$, H$_2$O$_2$, $\cdot$O$^-$) and/or reductive species (e.g., H*), both of which are important active species for water purification. In this study, two functionalizing approaches including cathodic polarization, and calcination of anatase TiO$_2$ NTA in H$_2$ environment were successfully employed to enhance the electroreactivity of TiO$_2$ NTA.

2- Co-doping Co/Bi has proved to be a viable approach to enhancing the lifetime and promoting ROS generation of TiO$_2$ NTA electrodes as a cost-effective anode material for environmental applications. Here, Meropenem, a representative recalcitrant antibiotic that is widely present in wastewater but much less studied, was successfully removed from different environmental matrices using Co/Bi/TiO$_2$ NTA as the anode. In addition, this study was the first attempt to identify the transformation products of Meropenem oxidation during water treatment and C$_7$N$_2$O$_2$H$_{12}$ was identified as one of the main intermediates.

3- The control over the nanotube morphology (diameter, length, and exposed facet) may affect the electrocatalytic degradation efficiency of organic pollutants. For example, the {001}-exposed facet, longer nanotube length, and larger nanotube diameter are the structural and morphological features that can lead to enhanced performance of TiO$_2$ NTA.
electrodes. These can be attributed to the increase in the electroactive surface area and better electron transferring, as well as the improved H* storage capacity in the defected nanostructures.

4- Coupled strategies combining both anodic oxidation and cathodic reduction enhanced the removal efficiency of organic contaminants and decreased energy consumption by taking advantages of the synergistic action of each electrode. In a coupled treatment scheme, the anodic oxidation gradually deactivates the self-doped TiO$_2$ NTA electrodes due to surface passivation (at a much slower rate with cobalt doping), while the cathodic reduction process may recover the deactivated electrode through cathodic polarization. Therefore, a regular polarity switching between electrodes can enhance the anodic lifetime of TiO$_2$ NTA electrodes. However, the weak adhesion between the nanotube layer and the Ti substrate as well as the mechanical stability of the nanostructure may limit the practical application of coupled treatment scheme with polarity switching.

5- The treatment efficiency of organic pollutants or pathogens is affected by the working matrix. For example, in environmental matrices like RO concentrate or secondary effluent, competition and/or inhibition effects of co-existing species as well as electrode fouling may result in a decreased removal efficiency of the target compound. In addition, the low conductivity in environmental matrices also increases energy consumption.

### 6.2 Future Work

Increasing interest in TiO$_2$ NTA has been observed in the last decade. At present, the literature can be classified into three main fields:
1- Theoretical modeling of the nanotubes with the trend of obtaining a unified theory of anodic growth of the metal oxide.

2- Formation and growth of TiO₂ NTA and empirical manipulation and control of their properties.

3- Applications and other advanced nanostructures modification of TiO₂ NTA for specific engineering processes.

Studies on the theoretical modeling of TiO₂ NTA have been of great interest among the research groups and the results indicated that the mechanism of TiO₂ NTA growth is very similar to that of Al₂O₃ pore formation. Therefore, many theoretical and experimental ideas were borrowed from the well-studied Al₂O₃ pores and directly applied to the formation and modification of TiO₂ nanotubes. However, more experimental work is needed to prove its versatility and validity for self-doped TiO₂ NTAs. This study belongs to the second and the third category, particularly focusing on water/wastewater treatment applications. Based on the research results obtained in this study, the following future work is suggested:

1- Despite increasing work on the applications of the TiO₂ NTA electrode for water and wastewater treatment, some aspects still need further improvements. For example, the weak adhesion between the nanotube layer and the Ti substrate as well as mechanical stability may limit the practical application of TiO₂ NTA. The mixture of the organic electrolytes like ethylene glycol (EG), glycerol, dimethyl sulfoxide (DMSO), etc. which was used for growing the nanotube may change the structure of nanotube (spaced, single-wall, double-wall, etc.) [241,321,322] as well as the growing rate. For example, the doping approach can be more efficient on spaced or single-wall nanotube structures as metals may
be doped between nanotubes or penetrate into the tubes, which enhance the mechanical stability of the electrode. So far several methods like two-step anodization and tube in tube structure have been taken to improve the mechanical stability [21,323]. However, further investigation is still needed to develop an effective and reliable method to enhance the mechanical stability of the nanotube structure.

2- Since the electrochemical degradation of organic pollutants was investigated using a 2-dimensional (plate) TiO\textsubscript{2} NTA electrode in this study, the mass transfer limitation was the most challenging part. A unique property of grown nanotube via anodization method is that the nanotube can be successfully grown on any regular and irregular Ti substrate. For example, Ti sponge with a much higher specific surface area than the plate can be used as a good substrate to grow the TiO\textsubscript{2} NTA on. These 3-D electrodes are generally granular or fragmental materials filled between working and counter electrodes. At an appropriate voltage, these particles will be polarized to form a large number of charged microelectrodes which can be considered as the anode at one site and cathode on the other site (bipolar particle electrodes). Also, these particles can be placed near the working electrode and serve as an anode or a cathode separately, depending on the working electrode charge.

3- Scale-up from the lab-scale is of significant importance for the application of the TiO\textsubscript{2} NTA as novel electrode materials. Studies on the upscaling potential of the material are needed. For example, Pablos et al. focused on the performance of TiO\textsubscript{2} photoanodes for the oxidation of methanol and the disinfection of E.coli from tertiary wastewater. Since the majority of their results have been carried out by using photoelectrodes at a laboratory scale, an additional study has been done to scale-up their small electrodes for commercial
applications [324]. Also, Garcia-Segura et al. investigated the fundamental parameters for electrocatalytic degradation of nitrate in full-scale water treatment applications [325]. These two studies can be a good start point for further investigation of the scale-up applications of electrochemical technology for water and wastewater treatment.

4- Besides the technical aspects of the TiO$_2$ NTA based electrodes, economic feasibility should also be considered for practical applications. Therefore, techno-economical evaluation and life cycle analysis of the applications of TiO$_2$ NTA based electrodes are highly recommended for future study.
REFERENCES


[121] USEPA. Water by membrane filtration using modified membrane-thermotolerant Escherichia coli agar (Modified mTEC) 2010.


[139] Haaken D, Dittmar T, Schmalz V, Worch E. Influence of operating conditions and wastewater-specific parameters on the electrochemical bulk disinfection of


[184] Yang Y, Hoffmann MR. Synthesis and stabilization of blue-black TiO$_2$ nanotube


[255] Lei C, Markoulidis F, Ashitaka Z, Lekakou C. Reduction of porous carbon/Al


Sheng T, Qi YJ, Lin X, Hu P, Sun SG, Lin WF. Insights into the mechanism of nitrobenzene reduction to aniline over Pt catalyst and the significance of the

195


[300] Currie M, Graham N, Hall T, Lambert S. The effect of bicarbonate on ozone-


