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# Characterization and Optimization of the Synthesis of Bioconjugated Core-Shell Silica Coated CdTe Quantum Dots

by

**Veera Venkata Naga Manohar Devarasetty**

An Honors Capstone

submitted in partial fulfillment of the requirements

for the Honors Diploma

to

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of

The University of Alabama in Huntsville

April 21, 2020

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April 21<sup>st</sup> 2020

Date

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**Abstract**

Bioconjugated Core-Shell Silica Coated CdTe Quantum Dots (QDs) were synthesized in five steps. Core-Shell CdTe QDs were originally synthesized in a large scale in the aqueous phase. The thioglycolic acid on the surface of QDs was exchanged with dodecanethiol to transfer the QDs to the organic phase. These organic phase CdTe QDs were then silica coated to increase surface reactivity and colloidal stability. Then, silane-PEG-NHS was added to the silica coated CdTe QDs to serve as a linker to the ConA protein. These silica coated CdTe QDs conjugated with ConA can play critical roles in future studies targeting specific pathogens.

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## 1. INTRODUCTION

The use of nanoparticles (NPs) and the field of nanotechnology have grown considerably over the last half century since Richard P. Feynman presented his "*There's Plenty of Room at the Bottom*" at the annual American Physical Society meeting in 1959 [1]. NPs can be synthesized from various materials and generally defined to have at least one dimension in the range of 1-100 nm [2]. Due to small size of NPs, visualizing them requires the use of an electron microscopes which have a significantly higher resolving power due to their use of electrons in vacuum as the source of illumination. While bulk materials have constant properties, slight variations in the size of nanoparticles allows those same properties to be tunable [3]. Some examples of tunable properties include their optical, thermal, catalytic and solvent affinity [3].

While size and shape are critical are crucial in determining the properties of the NPs, the chemical composition still plays a key role [4]. Carbon-based NPs is one category which includes carbon nanotubes, fullerenes and other NPs made using various allotropic forms of carbon. The biocompatibility of these NPs have made them useful for in-vivo therapies and imaging [5]. Metal NPs are another big category that include Au, and other transition and alkali metals. Their broad absorption band and localized surface plasma resonance (LSPR) attributes makes them excellent candidates for various applications such as obtaining superior quality Scanning Electron Microscopy (SEM) images of biological samples [6]. Lipid-based NPs such as nanoemulsions, dendrimers and liposomes is another emerging category due to the roles they can play in targeted drug delivery with minimum toxicity to the carrier [7].



The last crucial category of NPs are semiconducting NPs, known as Quantum Dots (QDs), which have interesting characteristics due to quantum confinement, zero dimensional topology and the particle in the box principle [8]. This results in non-linear optical properties, luminescence and tunable bandgaps that are highly specific to the size of the QDs [8]. Although QDs can be synthesized as part of ternary compounds such as CdSeS and AgInSe<sub>2</sub>, more commonly, QDs are made of binary compounds consisting of one metal and one nonmetal element [9]. Two of the most prominently studied QDs are made from the binary compounds CdSe and CdTe.

CdTe QDs with their very narrow band gap exhibit very high fluorescent properties, a desirable characteristic property for applications [10]. Additionally, there are numerous synthesis protocols that can be used to synthesize them in an easy, cost effective manner [11-15]. Compared to organic phase synthesis, an aqueous synthesis offers significant benefits. An aqueous synthesis does not require high temperature injections, offers more control over the growth of QDs, and is more cost effective and environmentally friendly [16]. Most importantly, it also offers biocompatibility benefits as these QDs have surface chemistries that can readily be modified for biological applications rather than requiring extensive processing [17].

One of the most useful ways of modifying the surface chemistry of QDs is to silica coat them. Silica coating has been a procedure that has been studied for several decades now because they have a very rich surface chemistry, tunable thickness of the coating and transparency to avoid fluorescence quenching [18]. 3-aminopropyltrimethoxysilane (APTMS) and tetraethyl orthosilicate (TEOS) play crucial roles in functionalizing the surface of QDs with alkoxysilane molecules. Then, triethoxysilane-polyethylene-glycol-N-

hydroxysuccinimide (Silane-PEG-NHS) can be used as a linker for uniformly distributing the desired protein on to the QDs [19]. An advantage with Silane-PEG-NHS is that it allows for single-molecule experiments which are specific to certain spatial and temporal moieties rather than interacting nonspecifically with a variety of molecules [20]. Additionally, the cytotoxicity of QDs has been documented to be reduced when this process is followed [21]. Due to these reasons, QDs coated with silica and attached to biomolecules through a linker molecule have been emerging for a wide variety of clinical applications of bioconjugation [22, 23].

One of the most promising diagnostic applications for highly functionalized QDs are for detection of infectious diseases [24]. While treatments exist for most infectious diseases, limited access to healthcare means that not everyone is able to get treated for their condition. For instance, CdTe QDs conjugated with the antibody anti-F protein are used to detect respiratory syncytial virus (RSV), a life-threatening pathogen that is the leading cause of hospitalizations for 70-80% of young children [25]. Similar types of diagnostics have been developed to detect diseases such as malaria, cholera, anthrax and tuberculosis [26-28].

Tuberculosis is a disease that is responsible for the deaths of 1.5 millions individuals each year and it is estimated to have infected nearly one third of the world's population [29]. The lectin Concanavalin A (ConA) has been found to bind to an glycoprotein from the cell wall *Mycobacterium tuberculosis* [30]. ConA has been shown to be mediated through a cluster of threonine residues that have been mannosylated [31]. Therefore, silica coated QDs bioconjugated with ConA through Silane-PEG-NHS can have a meaningful impact against the world's fight another tuberculosis.

## 2. EXPERIMENTAL PROCEDURE

**2.1 Materials and Instruments.** Cadmium acetate dihydrate (CAD, 98%), thioglycolic acid (TGLA, 99%), potassium tellurite (KT, 95%), Cyclohexane (CL), sec-butanol (BT), 3-Aminopropyltrimethoxy silane (APTMS, 97%), IGEPAL CO-520 (IGEPAL, Mn 441), ammonium hydroxide (NH<sub>4</sub>OH, 30%), tetraethyl orthosilicate (TEOS, 99%) and Concanavalin A (ConA) were purchased from Sigma Aldrich. Sodium hydroxide (NaOH, 98.5%) was purchased from Lab Chem. Sodium borohydride (NaBH<sub>4</sub>, 98%) and 1-Dodecanethiol (DDT, 98%) was purchased from ACROS Organics. Silane-PEG-NHS (1k) was purchased from Nanocs. Acetone (ACT), toluene (TL), methanol (MeOH) and absolute ethanol (EtOH) was purchased from Thermo Fisher scientific. Deionized (DI) Water used was from a Milli-Q water ultrapure water purification system.

The particle size was determined by using a Dynamic Light Scattering (DLS) Malvern Zetasizer (Malvern Panalytical Specs Company, USA). Absorbance and fluorescence spectra of particles were obtained with a Spectramax M2 plate reader (Molecular Devices Limited, Silicon Valley, USA). Fourier- Transform Infrared (FTIR) spectroscopic analysis was done using Nicolet is50 ATR FTIR (ThermoFisher Scientific, USA). Thermogravimetric analysis (TGA) was done on a Discovery Q500 TGA (TA Instruments, MA, USA).

**2.2 Synthesis of Aqueous CdTe QDs.** 0.001 mol of CAD (0.2665 g) was dissolved in 50 mL of DI water in a 250 mL 3-neck flask. Then, 0.00129 mol of TGLA (90  $\mu$ L) was added to the 3-neck-flask along with a magnetic stir bar. The pH of the solution was then adjusted to approximately 11.5 with a 1 M NaOH solution and stirred for 5 minutes. Afterwards, a 50 mL solution containing 0.0002mol of KT (0.0508 g) dissolved in DI water was transferred

to the 3-neck-flask and stirred for 5 minutes. 0.01057 mol of NaBH<sub>4</sub> (0.4 g) was also added to the 3-neck-flask and stirred for 5 minutes. The 3-neck-flask was then attached to a reflux condenser and refluxed at 100 °C under open-air conditions. The solution was sampled at hourly intervals to ensure the QDs had the desired absorbance and emission spectra before the refluxing was stopped. The concentration of the CdTe QDs in cyclohexane can be determined by weighing the mass of the precipitate after centrifuging 0.75 mL of this solution with 0.75 mL BT.

**2.3 Ligand Exchange of CdTe QDs from Aqueous to Organic Phase.** 5 mL of aqueous CdTe QDs, 5 mL DDT and 10 mL ACT were all added to a 20 mL borosilicate glass scintillation vial along with a magnetic stir bar. The scintillation vial was placed in an oil bath at the boiling point of ACT (56 °C) while stirring for 10 minutes. The scintillation vial was removed from the oil bath and allowed to cool to room temperature for 5 minutes. The darker, organic layer on top was then transferred to a 50 mL falcon tube with the use of a disposable glass Pasteur pipette. To this, 5 mL TL and 10 mL MeOH were added and centrifuged at 7830 rpm for 10 minutes. The supernatant was discarded and the precipitate was dissolved in 5 mL CL. The concentration of the CdTe QDs in CL can be determined by weighing the mass of the precipitate after centrifuging 0.75 mL of this solution with 0.75 mL BT.

**2.4 Silica Coating of CdTe QDs.** A solution with 5 mg of CdTe QDs in CL was transferred to a 20 mL borosilicate glass scintillation vial along with a magnetic stir bar. A 1 mL APTMS-CL solution was prepared by adding 17.5 µL of APTMS and 983 µL of CL. 28 µL of this APTMS-CL solution was then transferred to the 20 mL borosilicate glass scintillation vial and the mixture was stirred for 30 minutes. A IGEPAL-CL solution was prepared by

adding 0.126 g of IGEPAL and 5 mL of CL, and transferred to the 20 mL borosilicate glass scintillation vial. 56  $\mu\text{L}$  of  $\text{NH}_4\text{OH}$  was also added to the 20 mL borosilicate glass scintillation vial and stirred for 60 minutes. 2  $\mu\text{L}$  of TEOS was then added to the 20 mL borosilicate glass scintillation vial and stirred for 30 minutes. 0.75 mL of the final product mixture and 0.75 mL of EtOH were added to the microcentrifuge tubes and centrifuged at 15,000 rpm for 10 minutes. The supernatant was discarded and the precipitate was dissolved by sonication in 100  $\mu\text{L}$  of EtOH. The concentration of the silica coated CdTe QDs in EtOH can be determined by weighing the mass of the precipitate after centrifuging 0.75 mL of this solution with 0.75 mL BT.

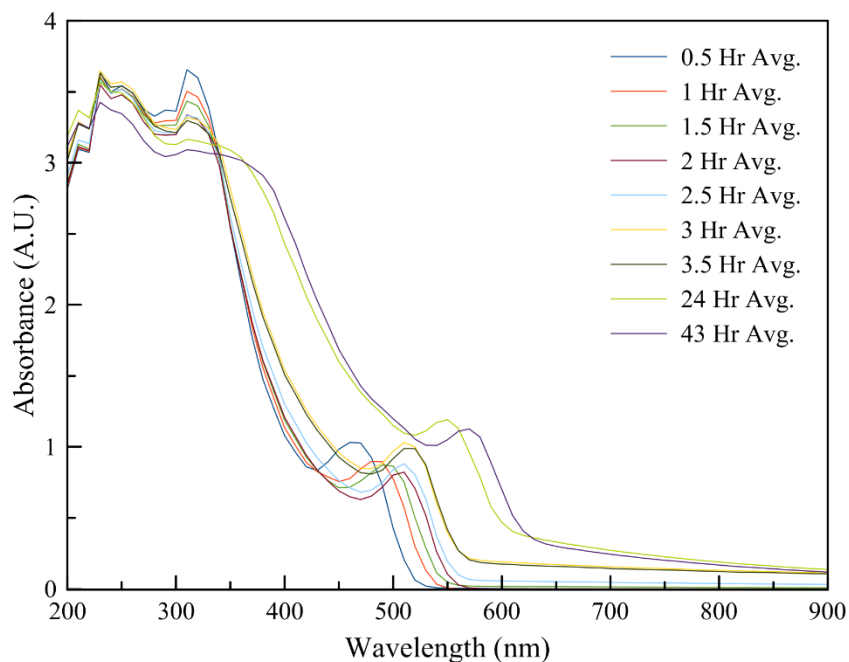
**2.5 Silane PEG-NHS and ConA Conjugation of CdTe QDs.** The mass of Silane-PEG-NHS and ConA to be added for bioconjugation was calculated using Equation 1 below.

$$\frac{4\pi(\text{Radius of QDs})^2}{\text{Footprint of Molecule}} * \frac{10^{-3}}{\text{Mass of QDs}} * \frac{1}{6.023 * 10^{23}} * \text{Molar Mass of Molecule} = \text{Mass of Molecule}$$

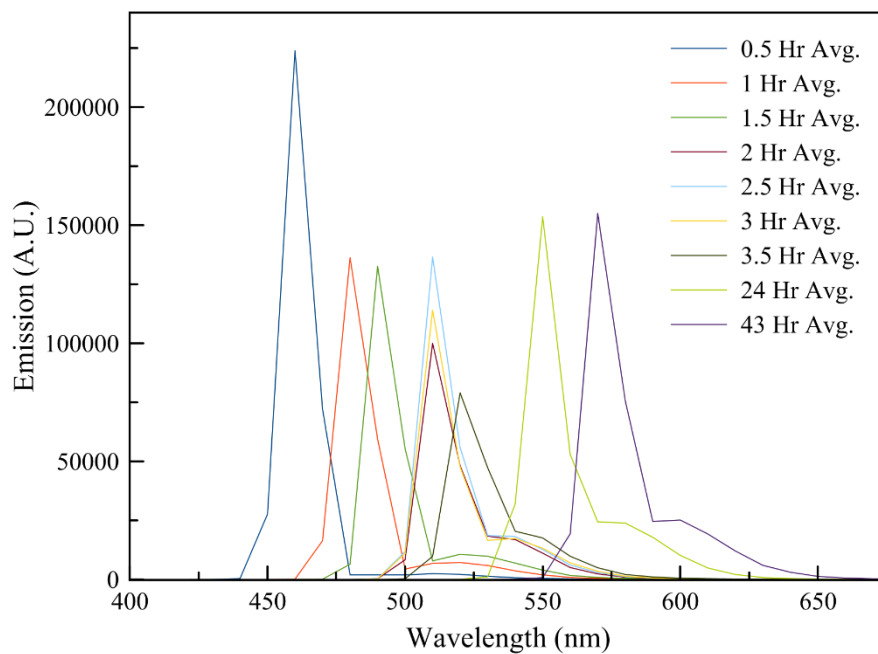
**Equation 1: Determining Mass of Silane-PEG-NHS and ConA for Conjugation**

The radius of QDs was determined from measuring the hydrodynamic diameter of the silica coated QDs using a DLS Malvern Zetasizer. The required mass of Silane-PEG-NHS was added to the 20 mL borosilicate glass scintillation vial with silica coated QDs and stirred for 24 hours. Afterwards, the required mass of ConA was added to the same solution and stirred for another 24 hours.

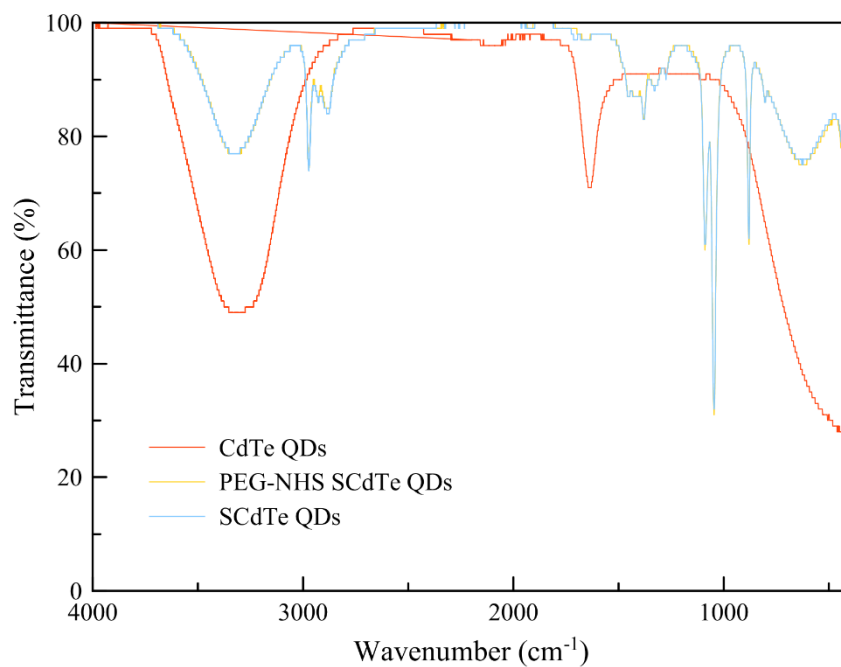
### 3. Results



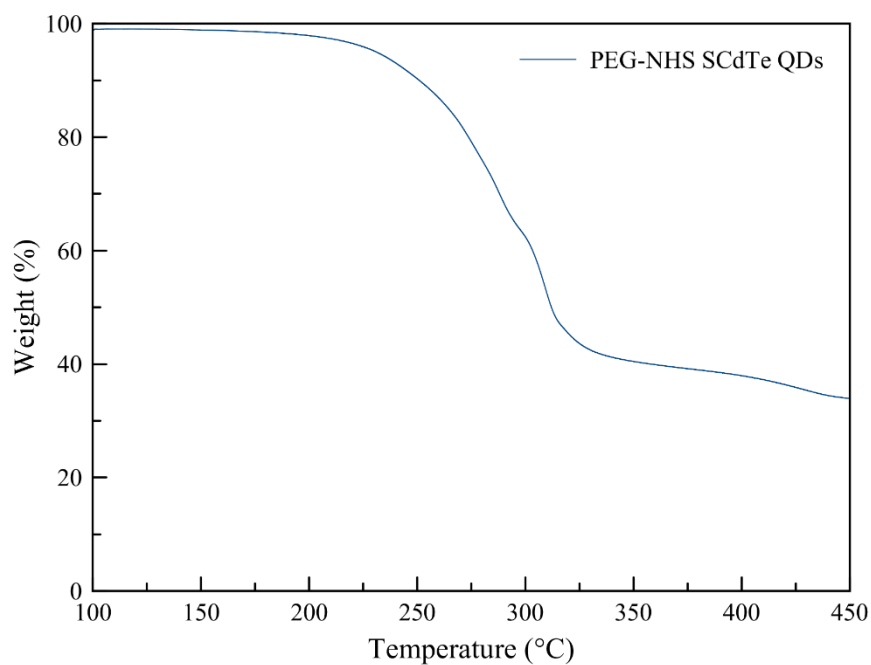
**Figure 1: Absorbance of CdTe QDs.** Absorbance spectra of CdTe QDs refluxed for varying periods of time.



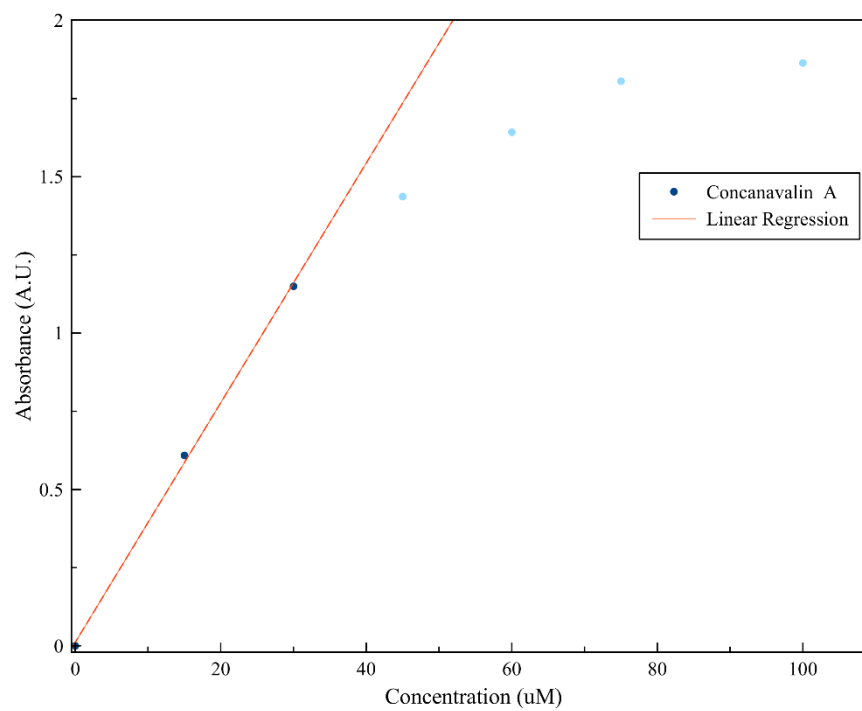
**Figure 2: Emission of CdTe QDs.** Emission spectra of CdTe QDs refluxed for varying periods of time.



**Figure 3: FTIR Spectra of Modified CdTe QDs.** FTIR spectra of CdTe QD, silica coated CdTe QDs, and silica coated CdTe QDs conjugated with PEG-NHS.



**Figure 4: Thermogravimetric Analysis of CdTe QDs.** A TGA Spectrum was obtained for the silica coated CdTe QDs conjugated with PEG-NHS.



**Figure 5: Linear Regression for Concanavalin A Detection.** The absorbance over a range of concentrations of Concanavalin A was measured and a linear model was prepared.



## Chapter IV: Discussion

As the CdTe QDs were being refluxed using the synthesis procedure outlined above, samples were outlined to ensure the desired absorbance and emission spectra were obtained. As expected, the first excitonic peak of the QDs shifted to higher wavelengths for the absorbance spectra as the QDs were refluxed for a greater period of time. A corresponding shift was also observed in the fluorescence spectra.

IR spectra was also obtained for characterizing all the modified QD solutions to confirm whether the intended surface chemistry had been properly altered. The silica coated CdTe QDs had the peaks characteristic to the CdTe QDs along with the Si-O due to the silication of the surface of the QDs. The silica coated CdTe QDs conjugated with PEG-NHS had a nearly identical IR Spectrum to the silica coated CdTe QDs with very minimal changes. This is reflective of the small amount of PEG-NHS that is present on the surface relative to the chemical composition of the QDs themselves.

A thermogravimetric analysis was performed only for the silica coated CdTe QDs conjugated with PEG-NHS. Although no other data was obtained for the other modified CdTe QDs complexes, the obtained thermogravimetric curve was very similar to data reported by other groups investigating polymer-functionalized CdTe QDs [32-33].

To determine the concentration of ConA that must be bioconjugated with the silica coated CdTe QDs already conjugated with PEG-NHS for it to be detected through absorbance spectrometry. The linear range was determined to be between a 0 and 30 micromolar concentration.

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