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Synthesis, Photostability and Photocatalytic Properties of Water-suspended CdSe and CdSe/CdS Quantum Dots

by

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ABSTRACT

Synthesis, Photostability, and Photocatalytic Properties of Water-suspended CdSe and CdSe/CdS Quantum Dots

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Photocatalysis offers exciting opportunities in the development of a renewable energy source and environmentally-friendly chemical processes. Previous studies focused on titanium dioxide and non-oxide semiconductor nanoparticles (quantum dots), such as CdS, ZnS, MoS₂ for photocatalytic breakdown of organic molecules. Catalytic performance has been limited by materials issues, e.g. low quantum yields and photocorrosion. CdSe quantum dots are a model semiconductor nanoparticle material with great potential in luminescence application, but they have not been studied for photocatalysis. In this study, the synthesis of the water-suspended CdSe and CdSe/CdS quantum dots was thoroughly studied. The CdSe and CdSe/CdS core/shell quantum dots were found to photocatalyze the degradation of 4-nitrophenol in water upon the UV-vis irradiation. Quantum efficiencies were low. The pH of the suspending fluid was found to be important in controlling colloidal stability, chemical stability, and reaction during irradiation.
Acknowledgments

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Chapter 1. Introduction

Achievement in nanoscience and nanotechnology will benefit many aspects of our life once people know how to manipulate atoms and molecules precisely at this scale [1,2]. Consequently, widespread interest has developed in the use of nanomaterials [1,2], which have at least one dimension in the nanometer regime.

Depending on how many dimensions are in the nanometer regime, Nanomaterials can be divided into 2-D (quantum well), 1-D (quantum wire), 0-D (quantum dots) materials, in which the dimensionality of nanosize confinement will strongly affects the material properties [3]. When the characteristic dimensions of a semiconductor particle approach its bulk exciton diameter (For example, the Bohr radius for bulk CdSe material is 5.4 nm), which is in the nanoscale, the wave function of an excited electron occupies the entire crystal and is constrained by the nano-size particle boundaries, which renders molecular-like discrete energy level [3, 4]. This phenomena is known as the quantum confinement effect [3-7, 12].

Of particular interest in this work are the 0-D semiconductor nanocrystals with three dimensions (quantum dots) all in nanoscale. Although the crystal structures of those nanocrystals are the same with their corresponding bulk materials, their electrical and optical properties are size-dependent due to the quantum
confinement effect. For instance, due to the size-dependence of band-gap of the absorption edge in the UV-visible absorbance spectra of a quantum dots (QDs) colloidal suspension, which would correspond to the band gap energy in bulk crystals, blue-shifts with decreased particle size. Furthermore, the fluorescence of a QD colloidal suspension is also size-dependent. It luminesces with very sharp spectral resolution upon UV-vis irradiation, and the emission color of QDs can be tuned with great precision, depending on their composition and particle size. Other properties, such as the electron and hole redox potentials, are also size dependent [5,6]

Due to those exciting properties derived from quantum confinement effects, chemical synthesis methods of producing highly quality semiconductor nanocrystals have attracted a lot of attention in the past decade [3-10]. Previous methods resulted in non-uniformly sized QDs. One of the most important breakthroughs was reported in 1993, when C. B. Murray et al. [7,11,12] reported the synthesis of high-quality CdE (E=S, Se, Te) QDs through the rapid injection of organometallic reagents into a hot coordinating solvent. This method and its later alternatives [13-19] yield the best known nanocrystals samples in terms of high crystal quality and monodispersity. Another important improvement of chemical synthesis is the developing of core/shell QDs [20-24]. It is reported that the shell protects the core surface from contact with oxygen species, substantially improving photostabilities. The shell also eliminates e⁻ and h⁺ traps that reduce photoluminescence, and leads to high fluorescence quantum yields, as was demonstrated in CdS/Cd(OH)₂ [24] CdSe/ZnS [20-22], and CdSe/CdS [23, 25-27]
core/shell quantum dots.

Because of the increasing availability of high quality QDs, numerous applications of QDs have become clear. Although the eventual applications of QDs are in light-emitting diodes, (LEDs), lasers, telecommunication devices, and quantum computing [28], currently, studies are mainly focused in the biotechnology field [10, 28-30], such as biological reagents, biosensor, bio-labeling, and cellular imaging. Some companies (such as Quantum Dots Corp., Evident Technologies Inc.) already start providing commercialized QDs.

Photocatalysis process is another important potential application for QDs. Photocatalysis is the process which can convert the solar energy into chemical energy for environmental remediation and chemical synthesis [31-34]. Semiconductor compositions can catalyze reactions upon the absorption of light, because the electron-hole pairs generated by solar radiation can catalyze redox reactions [31-34]. Currently, the most studied photocatalytic material is TiO$_2$ [31-35]; this material has shown great promise, with many beneficial properties. However, TiO$_2$ powder only absorbs light in the visible part of energy spectrum (TiO$_2$ powder only can harvest 3% of the solar spectrum [36]). Thus, great interest recently have developed particularly in semiconductor materials that absorb light in the visible part of the solar energy spectrum since most part of solar energy is in the visible region.

Studies have shown that QD colloid suspensions, such as CdS [38, 39, 41, 42, 44-46], ZnS [39, 40, 43], MoS$_2$ [36, 37], SnO$_2$ [37], ZnO [45], and TiO$_2$ [35] can serve as photocatalysts for a variety of reactions. Some of those materials, such
as CdS, ZnS, ZnO, TiO$_2$ only can absorb light in the UV region; MoS$_2$, and SnO$_2$ can work as photocatalyst under the visible light [36, 37]. The benefit of using QDs as photocatalyst is that the colloid suspension can eliminate light scattering losses, provide very high surface area, and tune the electron and hole redox potentials of QDs to achieve increased redox power. However, the prospect of QDs as candidates to replace TiO$_2$ is low, mostly due to the greater susceptibility to photocorrosion caused by the higher exposed surface areas [36, 37, 42]. As mentioned above, a good way to enhance the photostability and quantum yield is coating a shell of other semiconductor material on the bare QDs, such as CdSe/CdS, CdS/Cd(OH)$_2$, CdSe/ZnS. Thus, this system of materials holds exciting promise to work as a photocatalyst with high stability and high efficiency. However, this system of materials is still unexplored for the photocatalysis.

Photocatalysis and biological processes are typically situated in the aqueous environment [10]; therefore, hydrophilic QDs surface is desired for those applications. QDs prepared in TOPO or other organic solvents are normally heavily capped with organic molecules that can stabilize the nanocrystals in non-polar solvents like toluene or chloroform and prevents agglomeration, but their surface is hydrophobic and therefore they are not directly soluble in aqueous solution. There are two ways to get water-soluble QDs. One popular way to obtain a hydrophilic surface is by exchanging the hydrophobic surface capping compounds with some other hydrophilic thiol-compounds [29, 30, 47~49]. Unfortunately, the stability of the thiol-stabilized nanocrystals is not acceptable due to the photooxidation of the nanocrystals ligands complex [48], especially in
the case of photocatalysis. The unstable nature of those nanoparticles under light irradiation makes them inapplicable to any photocatalysis procedures. Another way to synthesize water-suspended QDs is to prepare them in aqueous solution directly. Almost all of the published photocatalysis studies of semiconductor nanocrystals are using those kinds of QDs [36-46]. Quality of these kinds of QDs is not as high as QDs prepared in TOPO or other alternative high-temperature ways if we consider in terms of monodispersity and fluorescent quantum yield. However, for the applications in aqueous solution, these kinds of QDs have their own unique advantages. For example, the chemistry for those kinds of synthesis could be very simple and in mild conditions [17, 50], and the stability and solubility in aqueous solution are unapproachable for those QDs prepared in TOPO.

The work described herein is a response to the tremendous potential that the QDs hold for the development of exciting new technologies. The focus of the Chapter Two is the thorough study on a modified route for the synthesis of the citrate-stabilized water-suspended CdSe and CdSe/CdS semiconductor QDs. By selecting appropriate pH value, selenium and cadmium precursor, and stabilizer, we demonstrate the control of the synthesis of water-suspended CdSe and CdSe/CdS core-shell QDs. In Chapter Three, we discussed the prospect of CdSe, CdSe/CdS and CdSe/Cd(OH)$_2$ QDs working as photocatalysts for the photodegradatation of 4-nitrophenol. We expect the shell can substantially improve photostabilities and efficiencies of those core/shell QDs in photocatalysis.
References


1638-1645.


Chapter 2. Synthesis of Water-Suspended CdSe and CdSe/CdS Core/Shell Quantum Dots

2.1 Introduction

Methods of producing highly luminescent and monodisperse QDs have attracted a lot of attention in the past decade [1-5]. Arrested precipitation of CdS QDs growth with polyphosphate was developed in Henglein’s group in 1984 [22] and provided the first routine method for QDs synthesis. Janos Fendler in 1984 [23] showed for the first time that CdS QDs could also be synthesized within inverse micelles. With the work of M. L. Steigerwald and co-workers [24, 25], the inverse micelle method of particle synthesis was thoroughly explored for the synthesis of CdSe QDs and led to much of the early understanding of these materials. One of the most important breakthroughs is in 1993, Murray et al. [2, 6, 26] from Bawendi group at MIT reported the synthesis of high-quality CdE (E=S, Se, Te) nanocrystals through the rapid injection of organometallic reagents (TOPSe, or TOPTe with cadmium source, Me₂Cd, dissolved in trioctylphosphine) into a hot coordinating solvent, TOPO (trioctylphosphine oxide). This method yields the best known QDs samples for the high crystal quality and monodispersity, but suffers with the high temperature and the pyrophoric, moisture sensitive and expensive Me₂Cd precursor. In an important development, Peng’s group at University of Arkansas [13, 14, 27-30] reported similar high-quality CdSe nanocrystals synthesized using safer and lower cost alternative
route. Fatty acids, amines, phosphate oxides, and phosphoric acid are among possible solvent systems, and CdO was found to be a more desirable source of cadmium since it is cheaper and more stable compared to Me₂Cd. Recently, Yu and Peng [14] successfully synthesized II-VI semiconductor nanocrystals in non-coordinating solvents. In details, CdS, CdSe, and ZnSe nanocrystals were synthesized in octadecene with oleic acid, or steric acid as ligands to stabilize the nanocrystals and the cationic precursors.

By carefully controlling the growth conditions, the size, and even the shape of QDs can be accurately controlled [26-30]. The ability to control these parameters has a profound impact in materials science since it means we can control the nanoscale unit with totally novel characteristics. At this point, the prominent focus of former studies has been the optical properties and the size distribution of the semiconductor QDs. By the above classic route developed by Murray and its alternatives, highly monodispersed (<5%) and relative highly quantum yield CdSe QDs can be produced [6, 11, 13, 14].

With capping another wider band-gap energy semiconductor material on a QD core, as 100% high quantum yield core-shell dots can be made [9, 10, 15, 18]. The chemical synthesis of core/shell QDs is another very important improvement in the study of QDs [31-35]. It’s reported that the shell protects the core surface from contact with oxygen species, substantially improving photostabilities, and the shell also eliminates e⁻ and h⁺ traps that reduce photoluminescence, which leading to high fluorescence quantum yields, as was demonstrated in CdS/Cd(OH)₂ [35] CdSe/ZnS [31-33], and CdSe/CdS[34, 36-38] core/shell QDs.
Due to the increasing availability of high quality QDs (in terms of monodispersity and photoluminescence), numerous applications of QDs have become clear, such as their use in biochemical probes and optoelectronic devices [5, 7, 8]. Photocatalysis process is another very important potential application for QDs [16, 17].

Biological processes are typically situated in the aqueous environment [5]; and the most important applications of photocatalysis are in the remediation of wastewater. Therefore, hydrophilic QDs surface is desired for those applications. For the QDs prepared in TOPO or other organic solvents, they are normally heavily capped with stabilizer layers which can stabilize the nanocrystals in non-polar solvents like toluene or chloroform and prevents agglomeration, but their surface is hydrophobic and therefore they are not directly soluble in aqueous solution.

There are two ways to get water-soluble QDs. One way to obtain a hydrophilic surface is by exchanging the hydrophobic surface capping compounds with some other hydrophilic compounds [7, 19-22]. For example, we can remove the TOPO molecules and replace them with some derivatives of silanes. The resulting particles have mercapto (-SH) and phosphate groups (PO₄⁻) or amino (NH₂) groups facing the solution which ensure the solubilization of those particles in aqueous solution. Disadvantages of those kind of methods are the significantly enlargement of particle size and the very slow hydrolysis of the silane layer which eventually leads to precipitation of the nanoparticles. We also can use thiol (-SH) groups to replace the TOPO molecules. Thiols are probably the most utilized
ligands for stabilizing semiconductor [6, 7, 20]. Thiol-stabilized nanocrystals have been used exclusively in the biomedical-related studies. Unfortunately, the photostability of the thiol-stabilized nanocrystals is not satisfactory due to the photooxidation of the nanocrystals ligands complex [20], especially in the case of photocatalysis, the nature of those nanoparticles makes them inapplicable to any photocatalysis procedures.

Another way to synthesize water-soluble QDs is to prepare them in aqueous environment directly [5]. Almost all of the published photocatalysis studies of semiconductor nanocrystals are using those kinds of QDs [5, 25]. Quality of this kind of QDs is not as high as QDs prepared in TOPO or other alternative high-temperature ways in terms of monodispersity and fluorescent quantum yield. However, for the applications in aqueous solution, these kinds of QDs have their own advantages. For example, the chemistry for those kinds of synthesis could be very simple and in mild conditions [15], and the stability and solubility in aqueous solution are unapproachable for those QDs prepared in TOPO or other organics.

In this work, we are particularly interested in the synthesis of water-soluble CdSe and CdSe/CdS QDs. CdSe QDs are the most commonly studied QDs. The emission spectra of CdSe QDs are narrow, symmetric, and the color of their fluorescence is tunable from blue to red [6, 26, 30]. By the coating of CdS shell, CdSe/CdS core/shell QDs can be highly fluorescent [34, 36~38]. Those properties make CdSe QDs in some cases superior to the existing fluorophores and other QDs in the bioapplications. Moreover, CdSe and CdSe/CdS core/shell QDs have absorbance in the visible light region, therefore, CdSe and CdSe/CdS QDs have
the potential be work as novel visible absorbed photocatalysts, but still are unexplored for their photocatalytic properties.

In this work we made a thorough study on a modified route for the synthesis of the citrate-stabilized water-soluble CdSe and CdSe/CdS semiconductor QDs based on the work of Rogach et al. [15]. By selecting appropriate pH value, selenium and cadmium precursor, and stabilizer, we can control our synthesis of water-soluble CdSe and CdSe/CdS core-shell QDs. Quantum yield of our CdSe QDs is normally below 1%. Quantum yield of our CdSe/CdS QDs is normally around 10%.

2.2 Experimental Section

2.2.1. Chemicals and Materials

All chemicals used in our experiments, including cadmium perchlorate (Cd(ClO4)2·6H2O), N,N-dimethylelenselenourea, sodium citrate (Aldrich), thioacetamide (Aldrich), and NaOH, were purchased from Sigma-Aldrich. Rhodmine 6G used in the calibration of quantum yield was also purchased from Sigma-Aldrich.

2.2.2. Synthesis of Water-Suspended CdSe QDs

This procedure is modified from the reported method in the reference [15]. The citrate-stabilized water-soluble CdSe QDs were prepared by the following procedure: 45ml DI water and 0.05 g sodium citrate and 2ml of 0.04M cadmium perchlorate were added into a 50 ml three-neck flask. pH was adjusted to 9 by
adding 0.1M NaOH dropwise. After bubbling with argon for 20 minutes, the flask with the mixture was heated to 100°C by using a 60W Gal-Col 50ml heating mantle. 2 ml 0.01M N,N-dimethylselenourea was injected into the flask immediately after removing the heating mantle. Then, the flask was moved into a silicone oil bath to keep at the desired temperature for a desired time. During the experiment, aliquots were withdrawn to study the temporal evolution of QDs growth. The result QDs can be precipitated by adding acetone into the produced suspension.

2.2.3. Synthesis of Water-Suspended CdSe/CdS Core/Shell QDs

Preparation of core-shell CdSe/CdS nanocrystals was also modified from the procedure of reference [15]. Citrate-stabilized CdSe nanoparticles synthesized in aqueous solution as described above (Cd:Se molar ration 4:1) were used as the initial material with thioacetamide as a sulfur source. To a given volume of CdSe nanoparticle solution as prepared was added a 0.05M solution of thioacetamide in a quantity that molar ratio of S_{added}:Se was 1:1. The mixture was heated in a sealed flask in a silicon oil bath at 70~80°C. Time and S_{added}/Se ration can be varied to control the process.

2.2.4. Characterization

UV-vis absorption spectra were carried out using a Shimadzu UV-2401PC spectrophotometer. Photoluminescence spectra were recorded on a SPEX-3 spectrofluorimeter. Particle size was estimated from the UV-vis absorption spectra. In table 1, X. Peng et al. [12] previously calibrated the variation of the
photoluminescence energy and UV-vis absorbance peak of the QD versus particle size by TEM.

UV-Vis exciton peaks, PL peaks vs. TEM sizes of CdSe nanocrystals.

<table>
<thead>
<tr>
<th>UV-Vis peak (nm)</th>
<th>PL peak (eV)</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>484</td>
<td>2.47</td>
<td>2.1</td>
</tr>
<tr>
<td>488</td>
<td>2.46</td>
<td>2.1</td>
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<tr>
<td>516</td>
<td>2.34</td>
<td>2.4</td>
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<td>526</td>
<td>2.3</td>
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<td>560</td>
<td>2.17</td>
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<td>4.7</td>
</tr>
<tr>
<td>610</td>
<td>2</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Table 2-1. UV-vis exciton peaks, PL peaks vs TEM sizes of CdSe QDs (from Ref. [12])

One more piece of Information that can be extracted from the UV-vis spectra is the concentration of QDs in the suspension. Using the published extinction coefficient of CdSe QDs [39], the particle concentration can be calculated from Beer-Lambert Law:

\[ \text{Absorbance} = \varepsilon L C_{\text{particle}} \]

where \( \varepsilon \) is the extinction coefficient, \( L \) is the path length of the sample, \( C \) is the
concentration of particles.

\[ e \left(10^6 (\text{mol particle}^{-1} \cdot \text{cm}^{-1})\right) \]
\[
\begin{array}{c|c|c|c|c|c|c}
\hline
\text{particle diameter [nm]} & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\
\hline
\text{e} \left(10^6 (\text{mol particle}^{-1} \cdot \text{cm}^{-1})\right) & 0 & 1 & 2 & 3 & R6G & \text{diazaperylene} & \text{diazaperylene} \\
\hline
\end{array}
\]

**Figure 2-1.** Extinction coefficient vs. particle diameter of CdSe QDS [39]

Quantum yields were determined relative to rhodamine 6G. TEM and HRTEM were performed on a JEOL 2010cx transmission electron microscope. Dynamic Light Scattering is studied via a Brookhaven ZetaPlus 90.
2.3 Results and Discussion

Figure 2-2 shows absorption and fluorescence emission spectra of the products. The presence of a steep absorbance edge and relative peak centered at 527 nm, which is attributed to the first exciton transition, are characteristic of QD systems. The estimated bandgap is 527 nm, or 2.35 eV, and is blue-shifted from the band gap value of bulk CdSe, 1.74 eV (712nm), as the consequence of quantum confinement effect. These CdSe QDs exhibited photoluminescence (PL) upon excitation at 380nm, emitting a peak at 565 nm, with a FWHM (full width at half-maximum) of 39 nm. The emission peak did not shift when excited at other, higher wavelengths, indicating that the emission was due to a real electronic transition in the material. It is attributed to radioactive relaxation of the band edge.

\[ \text{Figure 2-2. UV-vis absorption and fluorescence spectra for a typical product.} \]
\[ \text{Experiment was done in a 50ml flask, 45ml nanopure water, 0.05g sodium citrate, 2ml 0.04M Cd(ClO}_4)_2, add NaOH pH\rightarrow9, bubble Ar 20 minutes, heating to 100}^\circ C, \text{ Inject@100}^\circ C 2ml 0.01M DMSU (Cd/Se=4/1), keep cooking 30 minutes} \]
exciton. The FWHM is slightly wider than products by the TOPO route. FWHM is an indicator of particle size distribution, indicating the polydispersity of particle size of our QDs is broader than the QDs by TOPO route. Stokes’ shift is 34 nm, also wider than products by the TOPO route. Quantum yield was 0.3%. Quantum yield of CdSe QDs prepared in TOPO were reported to be higher (~10% [6, 26]). It could be due to the TOPO route using much higher temperature (250~350°C), the presence of oxygen in water during synthesis.

Particle size was estimated from the UV-vis peak positions. Peng et al. [12] previously calibrated (Table 2-1.) the variation of the photoluminescence energy and UV-vis absorbance peak of the QD versus particle size by TEM. So we can either estimate particle size by photoluminescence energy or by UV-vis absorbance peak. In our case, UV-vis peaks were chosen to estimate the particle size since there are other factors, such as the shape and agglomeration, which can influence the photoluminescence performance.

<table>
<thead>
<tr>
<th>Cd/Se</th>
<th>UV-vis peak, nm</th>
<th>Particle diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>571</td>
<td>3.62</td>
</tr>
<tr>
<td>2</td>
<td>566</td>
<td>3.54</td>
</tr>
<tr>
<td>3.2</td>
<td>560</td>
<td>3.38</td>
</tr>
<tr>
<td>4</td>
<td>535</td>
<td>2.85</td>
</tr>
<tr>
<td>6</td>
<td>517</td>
<td>2.52</td>
</tr>
<tr>
<td>8</td>
<td>516</td>
<td>2.51</td>
</tr>
<tr>
<td>16</td>
<td>515</td>
<td>2.49</td>
</tr>
<tr>
<td>32</td>
<td>509</td>
<td>2.39</td>
</tr>
</tbody>
</table>

The particle size can be controlled via Cd/Se ratio (Table 2-2.). Fig 2-3 shows how UV-vis absorption spectra and fluorescence spectra change with Cd/Se ratio. By increasing the Cd concentration it is possible to synthesize smaller CdSe QDs.
Figure 2-3. UV-Vis absorption and fluorescence spectra of CdSe quantum dots vs. Cd/Se ratio, (a) UV-Vis absorption spectra, (b) Fluorescence spectra. Experiments were done in a 50ml flask, 45ml nanopure water, 0.05g sodium citrate, 2ml 0.04M Cd(ClO₂)₂, add NaOH pH 9, bubble Ar 20 minutes, heating to 100°C, Inject some 0.01M DMSU (Cd/Se ratio 1: 1.6, 2: 2, 3: 3.2, 4: 4, 5: 6, 6: 8, 7: 16, 8: 32), keep cooking 30 minutes.

Figure 2-4, TEM (left) and HRTEM (right) of CdSe QDs growth in aqueous solution, QDs were prepared in a 50ml flask, 45ml nanopure water, 0.05g sodium citrate, pH 10, 2ml 0.04M Cd(ClO₂)₂, bubble Ar 20 minutes, heating to 100°C, 1st Inject@100°C 2ml 0.01M DMSU (Cd/Se=4/1), take out 3ml samples each time.
TEM and high-resolution TEM studies found the CdSe QDs to be roughly spherical nanoparticles (Fig. 2-4), and can exist as single particles or clusters in the colloid suspension. DLS data also suggested there are very large clusters in the solution (Fig 2-5). DLS measures temporal variation of intensity of scattered light by particles and is presented through intensity autocorrelation function [40]. Thus, if the particles exist in the solution as loose clusters, DLS can not recognize each particle and will treat the clusters as single particles. According to the theory of DLS [40], the intensity of scattered light single is proportional to the sixth order of particle diameter [40]; therefore, the signal from the clusters is much stronger than from the single particles. Thus, it is possible that DLS results only show one peak for clusters even if there also are single particles in the solution. The combined data indicate that the CdSe QDs are ~200 nm aggregates in suspension.

![Graph showing intensity vs. particle diameter](image)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-Vis</td>
<td>3.0 nm</td>
</tr>
<tr>
<td>TEM</td>
<td>4.5 nm</td>
</tr>
<tr>
<td>DLS</td>
<td>200 nm</td>
</tr>
</tbody>
</table>

*Figure 2-5*, DLS (left) sizing results of CdSe QDs growth in aqueous solution, QDs were prepared in a 50ml flask, 45ml nanopure water, 0.05g sodium citrate, ph→10, 2ml 0.04M Cd(ClO₄)₂, bubble Ar 20 minutes, heating to 100°C, 1st Inject@100°C 2ml 0.01M DMSU (Cd/Se=4/1), take out 3ml samples each time
3 ml aliquots were withdrawn during the reaction. At all times the optical spectra of the resultant QDs retained the general absorbance and PL features as those of the QDs prepared at 30 min except the first spectra (5s) since at 5s nucleation and the subsequent growth happened simultaneously. The optical features red-shifted with time indicate enlargement of QDs with time (Fig. 2-6a, c). The fluorescence quantum yields also increased with time (Fig. 2-6 b, d), suggesting an increase in crystal perfection. Fig 2-6d also shows the FWHM of the fluorescence peaks decreased with time. The FWHM represent the particle size distribution. The decreasing of FWHM suggested particle size distribution narrowed with synthesis time. The particle concentration decreased with time and the average particle size increased with time (Fig. 2-6e). However, as indicated in the Fig 2-6f, the selenium precursor was consumed immediately after the injection. Thus, the observed subsequent growth and size focusing of CdSe QDs was attributed to the Ostwald ripening. In Ostwald ripening, small particles in the system slowly dissolved with time, and large particles grow at the expense of the small particles. The smaller particles act as "nutrients" for the larger particles, resulting in decreased total concentration of particles and increased mean particle size with synthesis time.
Figure 2-6, CdSe quantum dots growth in aqueous solution, (a) UV-vis absorption spectra vs. time, (b) fluorescence spectra vs. time, (c) fluorescence peaks and UV-vis peaks vs. time, (d) FWHM of the fluorescence spectra and quantum yield vs. time, (e) CdSe quantum dots particle size and concentration vs. time, (f) Cd and Se precursor concentrations in the reaction flask vs. time. Experiment was done In a 50ml flask, 45ml nanopure water, 0.05g sodium citrate, pH→10, 2ml 0.04M Cd(ClO₄)₂, bubble Ar 20 minutes, heating to 100°C, 1st Inject@100°C 2ml 0.01M DMSU (Cd/Se=4/1), take out 3ml samples each time.
The reaction process could be divided into three steps roughly (Fig. 2-7). (a): the mixture of water, sodium citrate and cadmium perchloride was bubbled with argon, and then was heated to 100°C. (b): Heating mantle was removed, then selenium precursor was injected into the reaction flask. (c): Immediately after the injection of selenium precursor, move the reaction flask into a silica oil bath. The basic idea of this procedure is trying to temporally separate the nucleation event from the slower controlled growth of the existing nuclei. Rapid addition of reagents to the reaction flask raises the precursor concentration, resulting in a short nucleation burst. Then, due to the consumption of the Se precursor and the drop of the temperature, nucleation is slowed down or stopped.

(a) Water + Cd²⁺ + Sodium Citrate (Stabilizer) @pH=10 Heated up to 100°C
(b) Inject N,N-dimethylselenourea aqueous solution (Se precursor)@100°C After injection, temperature drops 5~10°C
The multiple injection experiment results can be used to test the idea of Ostwald ripening. A second injection of Se precursors refocused the size distribution (Fig 2-8b), and quenched the fluorescence. Fig 2-8c showed the particle size and particle concentration exhibit a significant increase after the second injection, indicating nucleation and growth occurred simultaneously when additional Se precursor was injected into the reaction mixture which contained excess cadmium. The nucleation of new particles occurred even at 80 °C.
After initial injection:
1: 10 sec, 2: 60 sec, 3: 120 sec, 4: 300 sec, 5: 720 sec, 6: 1800 sec, 7: 6000 sec, after second injection
8: 6010 sec, 9: 6420 sec, 10: 17100 sec

Diagram (a) shows absorption spectra over time and wavelength.
Diagram (b) shows normalized intensity over time and wavelength.
Diagram (c) shows particle size and concentration over time.
Figure 2-8, CdSe quantum dot growth in aqueous solution with multiple injection of Se precursor, (a) UV-vis absorption spectra vs. time, (b) fluorescence spectra vs. time, (c) CdSe quantum dots particle size and concentration vs. time, (d) Cd and Se precursor concentrations in the reaction flask vs. time. Experiment was done in a 50 ml flask, 45 ml nanopure water, 0.05g sodium citrate, pH=10, 2ml 0.04M Cd(ClO₄)₂, bubble Ar 20 minutes, heating to 100 °C, 1st Inject@100°C 4ml 0.005M DMSU (Cd/Se=4/1), 2nd injection@6000 seconds, inject 2ml 0.005M DMSU (Cd/Se=2/1).

CdSe/CdS core-shell QDs were made in two steps. Bare CdSe QDs were prepared according to the above synthesis in the first step. In the second step: thioacetamide was added in the CdSe QDs solution and kept into a 70 ~ 80 °C silica oil bath up to 24 hours. Fig. 2-9 shows the UV-vis absorption and fluorescent spectra of the original bare CdSe QDs and CdSe/CdS core/shell QDs. After the coating of CdS shell, both absorption and fluorescent spectrum underwent apparent changes as compared to just heating without adding the thioacetamide. The UV-vis absorption spectrum got an obvious red-shift (Fig. 2-9a); meanwhile,
the fluorescence had a great enhancement. Fluorescence quantum yield increased about 50 times from 0.3% to 12.

Fig 2-9. UV-vis absorption spectra (a) and fluorescence spectra (b) of CdSe/CdS and CdSe QDs. Experiment was done in a 50ml flask, 40ml bare CdSe QDs (Cd/Se =4/1), add thiocacetic acid 0.005m 4.5ml (Se/S=1), reaction time: 13 hours.

The red-shift of UV-vis absorption spectrum indicated the QDs particle size estimated via UV-vis spectra had an obvious increase after the coating, while is contrary to what Alivisatos and co-workers observed with their synthesis of CdSe/CdS core/shell QDs. Since the amount of the thioacetamide was calculated to just coat a single layer of CdS shell on the CdSe core, this particle size increase is not due to the coating shell. One possible explanation is show in Fig. 2-10. As indicated by the DLS and TEM results, CdSe QDs can exist as clusters in the colloidal suspension. When the thioacetamide was added in the system, the CdS shell may be coated on the whole cluster instead of single particles. After the coating, the QDs clusters were combined more tightly due to the CdS shell.
Therefore, the UV-vis may treat the shell coated QDs cluster as a larger non-spherical particle, thus, the measured UV-vis absorbance red-shifted after the coating.

Fig 2-10. Schematic diagram of Proposed formation mechanism of water-suspended CdSe/CdS QDs

The fluorescence enhancement indicates the formation of CdS shells on CdSe cores, which can passivate CdSe core surface defects. In Fig 2-11, instead of the multiple injections of Se precursors, a second and a third injection of the S precursor were applied to the reaction. For the second injection, an increase of the particle size and a dramatic decrease of the particle concentration were observed immediately after the injection (Fig 2-11d), suggesting that smaller particles were aggregating into larger particles. For the third injection, the increase of the particle size and decrease of the particle concentration also were observed, but those changes occurred slowly, indicating the existed aggregates grew slowing with synthesis time and no new aggregations occurred
Figure 2-11. CdSe/CdS QDs growth in aqueous solution with multiple injection of thioacetamide. (a) UV-vis absorption spectra vs. time, (b) Fluorescence spectra vs. time, (c) UV-vis absorption peaks and fluorescence peaks vs. time, (d) QDs particle size and concentration vs. time. Experiment was done in a 50ml flask, 45ml nano-pure water, 0.05g sodium citrate, pH=10, 2ml 0.04M Cd(ClO₄)₂, bubble Ar 20 minutes, heating to 100°C, 1st inject@100°C 4ml 0.005M DMSU (Cd/Se=4/1), 2nd inject@100 minutes, inject 1ml 0.005M thioacetamide (S/Se=1/1), 3rd inject@200minutes, inject 0.5ml 0.005M thioacetamide (S/Se=2/1)
We varied the reaction time for the coating the CdS shell. Fig 2-12 shows absorption and emission spectra for CdSe/CdS core-shell QDs prepared in different reaction time. The results suggest we can expect the increased quantum yields and red-shifting of UV-vis absorption peaks when we increased the reaction time. Thioacetamide amount also can be varied during the reaction. Fig 2-13 shows absorption and emission spectra for CdSe/CdS core-shell QDs prepared with different S/Se ratio. The UV-vis red-shifted if the S/Se increased. Moreover, there was an optimum in quantum yields.

![Absorbance vs Wavelength](image1)

![Normalized Intensity vs Wavelength](image2)

**Fig 2-12**, UV-vis absorption spectra (a) and fluorescence spectra (b) of CdSe/CdS in different reaction time. Experiment was done in a 50ml flask, 40ml bare CdSe QDs (Cd/Se =4/1), add thiocetamide 0.005m 4.5ml (Se/S=1), keep cooking up to 13 hours, take out 4ml samples each time.
Fig 2-13, UV-vis absorption spectra (a) and fluorescence spectra (b) of CdSe/CdS in S/Se ratio. Experiment was done in 4 50ml flasks, put 40ml bare CdSe QDs (Cd/Se =4/1), in each flask, add thiocacetamide 0.005m 0ml (S/Se=0), 2ml (S/Se=0.5), 4.5ml (S/Se=1), 9ml (S/Se=2), keep cooking up to 15 hours.

2.4 Conclusions

In this Chapter, a modified method of the synthesis of water-soluble CdSe and CdSe/CS core/shell was developed. By selecting appropriate pH value, selenium and cadmium precursor, and stabilizer, we can controlled our synthesis of water-soluble CdSe and CdSe/CdS core-shell QDs. Although our particle size distribution and photoluminescence quantum yield was lower than that of QDs grown in TOPO, we synthesize the product very easily and under mild conditions. The size range of the QDs was about from 2 to 5 nm. The quantum yield of the CdSe QDs was typically below 1%, and the quantum yield of the CdSe/CdS QDs is normally about 10%. The higher quantum yield resulted from the formation of CdS shell, and not to the extended heating time.
2.5 References


9463-9475.


Chapter 3. 4-Nitrophenol Photodegradation by CdSe and CdSe/CdS Quantum Dots

3.1 Introduction

Photocatalysis is the process which can convert the sunlight energy into chemical energy for environmental remediation and chemical synthesis [1-4]. As an important method of water purification, photocatalysis has substantial advantages, which destroys toxins rather than merely transferring them to another phase, and does so without the use of potentially hazardous oxidants [1-5].

Semiconducting materials absorb light with energies at or above their characteristic band gap energy ($E_g$). Upon absorption of a photon by the semiconducting materials, an electron, $e^-$, is excited from the valence band to the conduction band, leaving a hole, $h^+$, behind in the valence band, as illustrated in Fig 3-1. At the material surface, electrons and holes can participate in redox half-reactions [15]. Semiconductors that can absorb light in the ultraviolet (UV, 200-400 nm) and visible (vis, 400-700 nm) regions of the electromagnetic spectrum, such as TiO$_2$, MoS$_2$, CdS, ZnS, CdSe [1-5], are particularly useful.
TiO$_2$ is the most commonly studied photocatalyst for the photocatalytic oxidation of aqueous and gaseous pollutants, because it is inexpensive, readily available, non-toxic, and photo-chemically stable [1-5]. However, with a band gap of 3.0-3.2 eV, TiO$_2$ only absorbs in the UV region but cannot absorb the light with wavelength longer than $\sim$410 nm. Considering that 6% of the solar energy lies in the UV region (only 3% can be absorbed by TiO$_2$ powder [18]) and 42% is in the visible region [16], a photocatalyst that harvests a wider range of sunlight than TiO$_2$ is highly desirable. Lots of studies have been made to improve the photocatalytic performance of TiO$_2$ through the use of organic dyes. However, it is not clear that those approaches will ultimately be commercially viable, since dye molecules themselves can be photo-oxidized [17].

Metal chalcogenides, such as CdS, ZnS and MoS$_2$, are also active semiconductor compositions for photocatalytic reactions [6-13,18,19]. Many of them have band gap energies appropriate for absorption in the visible light region.
(Eg > 1.8 eV). However, metal chalcogenides are severely limited as photocatalysts by their low activities and high propensity for photo-induced corrosion [1-4].

One approach to increasing photocatalytic (as well as catalytic) activity may be through the use of semiconductor QDs, for which the band gap is size-dependent [15-23]. When the semiconductor nanocrystals diameter is comparable to or less than the bulk exciton diameter, size-dependedependent optoelectronic properties result. [20-23]. Therefore, through particle size control, electron and hole redox potentials of semiconductor nanocrystals can be tuned to achieve increased redox power for use in wastewater decontamination, or other photocatalysis processes [6-14, 18, 19, 24]. Using QDs colloidal suspensions as photocatalyst, some other benefits can also be expected for the improvement of efficiencies of the photocatalytic processes, for example, light scattering losses can be nearly eliminated, and very high surface area to volume ratios can be easily gained.

Mostly due to the greater susceptibility to photocorrosion caused by the higher exposed surface areas, the prospect of visible-light-absorbing QDs as candidates to replace TiO₂ is low [6-14, 18, 19, 24]. CdS and MoS₂ QDs photocorrode due to the oxidative attack of the surface, in which a photogenerated hole diffuses to a surface chalcogenide anion, and the anion reacts with adsorbed oxygen species to create a volatile oxide species (e.g. SO₄²⁻ and SeO₂) [18,19, 25,26].
The QD surfaces usually are covered by capping ligands for colloidal stability [27]. The surface of QDs impacts greatly the properties vital to photocatalytic applications, such as fluorescence lifetimes and quantum yields, surface charge and ionicity, particle solubility, and flat-band redox potentials [15]. In fact, it has been reported that electron transfer from the semiconductor to the reactant can compete with e\(^{-}\)h\(^{+}\) recombination only if the reactants are adsorbed on the particle surface [15], and a number of studies show that the electron transfer efficiency are greatly effected by the reactant and product binding on the semiconductor surface [15].

4-nitrophenol (also known as p-nitrophenol, p-NP) is a very common pollutant [28, 29] in the wastewater from the textile, leather and petrochemical industries, and dyes, explosives, pesticides, herbicides, insecticides, and drugs production. Reported by the United States Environmental Protection Agency [28], 4-nitrophenol poses significant health and environmental risk due to its mutagenic and carcinogen activity, and is also listed among the top 114 organic pollutants. Therefore, the 4-nitrophenol concentration is stipulated below 20 ppd by the law [28]. In order to address this significant problem, lots of researchers are trying to develop advanced methods to eliminate this chemical compound from the environment [11,12,28,29]. The most intensively studied semiconductor compound for 4-nitrophenol degradation is TiO\(_2\) [5, 29]. There are also some reports on using CdS and ZnS QDs for photo-oxidation [11, 12].

There are several reports on the mechanism of 4-nitrophenol degradation via photocatalysis using TiO\(_2\) as photocatalysis [29, 32, 33, 34]. When TiO\(_2\) is
illuminated with photons with $\lambda < 380$ nm, upon absorption of a photon by the TiO$_2$ particle, the electron, e', and hole, h', pair can be formed. Due to the position of the valence band edge of TiO$_2$ (+3.1 V vs. NHE at pH 0 for anatase), the hole is a potent oxidant and can oxidize organic molecules at the surface, eventually mineralizing them to CO$_2$. Similarly, the hole can oxidize water or hydroxide ions to form hydroxyl radicals, -OH, which are also efficient oxidants of organic

\[ \text{4-Nitrophenol} + \text{OH}^- \rightarrow \text{NO}_3^- + \text{CO}_2 + \text{H}_2\text{O} \]

**Fig 3-2.** Schematic diagram of the photocatalytic process of photodegradation of 4-nitrophenol by oxygen molecules. In order for the oxidation process to proceed effectively, the photo-generated electrons must also be removed from the TiO$_2$ particle. Typically, oxygen is used as the electron acceptor. Oxygen can be reduced to hydrogen peroxide or water.

As mentioned earlier, the advantage of using TiO$_2$ is inexpensive, readily available, non-toxic, and photo-chemically stable, but the disadvantage is TiO$_2$ only have absorbs in the UV region. CdS ($E_g=2.40$eV), ZnS ($E_g=3.60$eV) also only
have absorbs in the UV region as well. It is obvious that there is a strong need of developing a new material that can absorb in the visible region.

An unexplored system of materials for photocatalysis is core/shell QDs. If QDs are encased by a shell of another semiconductor, it is reported that the shell protects the core surface from contact with oxygen species, substantially improving photostability. The shell also eliminates e- and h+ traps that reduce PL, leading to high quantum yields. CdS QDs were made photochemically stable by reacting surface S\textsuperscript{2−} with excess Cd\textsuperscript{2+} at high pH, which was surmised to form a protective layer of Cd(OH)\textsubscript{2} [30]. This idea was taken a step further by growing an epitaxial layer of ZnS or CdS around CdSe QDs [31]. Theoretical modeling results suggest e\textsuperscript{−} is more delocalized than h\textsuperscript{+} in the core/shell QDs because it can tunnel more easily into the shell. Thus, charge separation of the e\textsuperscript{−}h\textsuperscript{+} pair is enhanced in

---

**Fig 3-3.** Schematic diagrams of energy levels of a semiconductor in several forms. (a)bulk, (b)quantum dot nanoparticle,(c)core/shell quantum dot nanoparticle  
(M.S.Wong, 2001)
the shell, and should be highly beneficial to photocatalysis (Fig. 3-3). We expect there to be a shell thickness that is optimum for stable photocatalysis. If the shell is too thin, then the QD would be photo unstable, and if the shell is too thick, the photoreaction would not proceed due to the relative inaccessibility of the hole. Further, the stabilizing agent could interfere within the surface reactions.

In this study, 4-nitrophenol photodegradation using CdSe and CdSe/CdS QDs as photocatalysts is described. The photostability of CdSe and CdSe/CdS is also examined. The aim of our research is to examine these nanocomposites for photoactivity and photostability in oxidation reactions; and to correlate their nanostructural features to photocatalytic behavior and photocorrosion resistance.

3.2 Experimental Section

3.2.1 Nanocrystals Preparation

Citrate stabilized CdSe and CdSe/CdS core/shell QDs are prepared, according to the method discussed in Chapter 2. 5ml DI water and 0.05 g sodium citrate and 2ml of 0.04M cadmium perchlorate were added into a 50 ml three-neck flask. Then pH was adjusted to 9 by adding 0.1M NaOH drop wise. The solutions were purged with argon for 20 minutes. After that, the flask with the mixture was heated to 100°C by using a 60W 50ml heating mantle. The heating mantleeaas removed and 2 ml 0.01M solution of N, N-dimethylselenourea was injected into the flask immediately. After that, the flask was moved into a 70°C silica oil bath to keep reaction for a desired time. For CdSe/CdS core/shell QDs, citrate-stabilized CdSe nanoparticles synthesized in aqueous solution as described above (Cd:Se molar
ratio 4:1) were used as the initial material with thioacetamide as a sulfur source. To a given volume of CdSe nanoparticle solution as prepared was added a 0.05M solution of thioacetamide in a quantity that molar ratio of $S_{\text{added}}$:Se was 1:1. The mixture was heated in a sealed flask in a silicone oil bath at 70~80°C. Time and $S_{\text{added}}$/Se ration was varied to control the shell thickness and coverage. To celan the QDs, QDs used in these experiments are redispersed in water after precipitated by acetone from the original synthesis suspension.

3.2.2. Experiment Setup

All photostability and photodegradation experiments were performed in a quartz cell. The quartz cell with the samples was placed before an Oriel Model#66901 light source which was housing an Oriel 300W ozone free Xenon lamp (Fig 3-4.). The lamp can give out continuous light in UV and visible range. We can use optical filters to control the wavelength range of the output light.

![Schematic diagram of quartz cell reactor for 4-NPI photodegradation and photostability studies](image)

**Fig 3-4.** Schematic diagram of quartz cell reactor for 4-NPI photodegradation and photostability studies
3.2.3 UV-vis Absorbance Spectra and Fluorescence Spectra

The absorbance spectra of the products mixture were recorded on a Shimadzu UV2401 spectrophotometer to monitor the reaction. For the photodegradation of 4-nitrophenol, it is difficult to get the exact concentration of 4-nitrophenol in the reaction suspension only via absorbance spectra, since there are many factors affecting the absorbance spectra of the reaction mixture. One of the factors is the photocorrosion of QDs. Details of this phenomenon will be discussed below in Section 3.3.1. The pH changes during the photo-reaction also can influence the absorbance spectra, especially the absorbance spectra of 4-nitrophenol (Fig 3-5). Although it is hard to get the actual concentrations, the absorbance spectra are still very useful information for the qualitative analysis of the photoreaction.

![Spectra diagram](image)

1: pH=7.82, 2: pH=7.48, 3: pH=7.39, 4: pH=7.17, 5: pH=6.96, 6: pH=5.64

**Fig 3-5.** Absorbance Spectra of 4-nitrophenol vs. pH
Concentration of 4-nitrophenol is 0.000125M, pH was adjusted by adding 0.1M NaOH dropwise
The fluorescence spectra were recorded on a Spex-3 spectrofluorimeter, and the excitation wavelength is always 380 nm. Emission and excitation slit both are set as 1 nm.

### 3.2.4 Ferrioxalate Actinometry

Quantum yield of photoreactions were calibrated via ferrioxalate actinometry [39]. Quantum yield for photoreactions based on the ratio of the moles of product formed relative to the number of moles of photons absorbed:

\[
\Phi = \frac{\#\text{product}}{\#\text{photons}}
\]  

(3-1)

There are two pieces of information required before a quantum yield can be determined. First, the number of photons absorbed must be known. Second the number of moles of product must be measured. The number of moles of product can be estimate via UV-vis absorption spectra. In order to determine the number of photons absorbed, we need to measure the photon flux (F) of light source. If we know the photon flux and the duration of the exposure, we can determine the number of photons passing into the sample. In this study, we use a standard ferrioxalate actinometer to calibrate the photons flux [39]. The brilliant green solutions of ferrioxalate (Fe$^{3+}$) are irradiated with light. A photochemical reaction takes place that produces Fe$^{2+}$. The yield of Fe$^{2+}$ is measured by observing the intense red complex between Fe$^{2+}$ and 1,10-phenanthroline.

\[
2\text{Fe}^{3+} + C_2\text{O}_4^{2-} \xrightarrow{hv} 2\text{Fe}^{2+} + 2\text{CO}_2
\]

This photochemical reaction has been well studied and the quantum yield of product formation is well known [39]. By measuring the conversion of products of
the actinometer as a function of time the photon flux can be determined:

$$F = \frac{n_B}{\Phi_B t}$$

(3-2)

In this equation, $\Phi_B$ is the quantum yield for the actinometer, in this case $\Phi_B = 1.21 \, @ \, 360 \, \text{nm}$ [39]. $n_B$ is the number of moles of Fe$^{2+}$ produced and $t$ is the irradiation time in seconds.

Exact experimental procedure is as following: First step is the preparation of potassium ferrioxalate [38]. Add ferric chloride (3.3 ml of a 0.4 g/mL solution) to a hot solution containing potassium oxalate monohydrate (5 g in 8.5 ml DI water). Cool the solution with ice water bath and keep until crystallization is complete. Recrystallise by decanting off mother liquor and dissolving in 8 ml warm water. Wash with cold water and dry in air.

Second step is the preparation of ferrioxalate solution [39]. Prepare a solution of potassium ferrioxalate (0.006 M, 0.262 g) in water (90 ml) and 1.0 M sulphuric acid (10 ml) in darkroom. Prepare a solution of 1,10-phenanthroline (1.0909 g/l) in DI water and a buffer solution made up of 60 ml of 1 M sodium acetate, 36 ml of 1 M sulphuric acid and 4 ml of DI water. Store both solutions in darkness.

Third step is the light intensity measurements [39]. Pipette into cell 3 ml of potassium ferrioxalate (Fig. 3-6(a)). Irradiate for an appropriate amount of time (~2 mins). Mix irradiated solution thoroughly and pipette into a 25 ml volumetric flask. Add 3 ml of phenanathroline solution and then add 3 ml of buffer solution. Make up the mix to 25 ml. Prepare a blank solution of unexposed ferrioxalate
solution, phenanthroline and buffer solution. Store both solutions in the darkness for 4 hours to allow complexation to occur. The quantity of Fe$^{2+}$ formed was determined by measuring the absorbance of each of the solutions at 510 nm via Beer-Lambert's law (Fig. 3-6). Extinction coefficient of ferrous phenanthroline complex at 510 nm is 1.11x10$^4$ l*mol*cm$^{-1}$ [39].

Fig. 3-6 (a) Absorbance spectra of potassium ferroxalate which was used as actinometer. (b) Absorbance spectra of ferrous phenanthroline complex which was made from phenanthroline and potassium ferroxalate w/o irradiation of light (1) without irradiation, (2) with irradiation, using the sample in (1) as background.

After the photon flux is got, quantum yield of a photoreaction can be calculated by:

$$\Phi = \frac{n}{Ft} \quad (3-3)$$

Where n is the number of consumed reactant molecules, t is the irradiation time.
3.3 Results and Discussion

3.3.1 Photostability of CdSe and CdSe/CdS QDs

The photostability of our QDs can be monitored by recording the UV-vis spectra of the samples in water solution at different times. Fig 3-7~3-10 show the size-dependent absorption of the citrate stabilized CdSe and CdSe/CdS QDs can be a sensitive and convenient way to monitor their own photostability. Both of the experiments in Fig 3-7 (a) & (b) were done in the pH~8 aqueous environments and were stopped after exposed to light for 30 and 60 minutes. In Fig. 3-7 (b), citrate was added in the system to test the effect of additional stabilizer. The absorbance of QDs colloidal system decreased with time when exposed to light around pH=8. No precipitation of QDs was found. No change in the QD

![Graph](image1)

**Fig 3-7.** Effect of UV-vis absorption spectra versus time on the photostability of 3.0 nm CdSe quantum dots solution at initial pH=7.85. (a) Without additional citrate, [cit] =3.4x10^{-3}M, (b) With additional citrate, [cit] =6.8x10^{-3}M [CdSe]=1.5x10^{-6} mole particle/l, light Source: 200nm~800nm light.
suspension was detected without UV-vis irradiation, indicating that the QDs photo-corroded upon the UV-vis irradiation. Additional citrate accelerated the photo-corrosion process (Fig. 3-7(b)).

In Fig. 3-8, both of the two experiments were done in the around pH=12 aqueous environments and were stopped after the observation of the precipitation of QDs. Fig. 3-8(b) shows that the suspension system was very stable after adding additional citrate and at pH=12 environments. The system can kept stable for over 24 hours when expose to light (Fig 3-8b). Fig. 3-8(a) suggests QDs photo-corroded. However, a precipitate was detected, indicating that the suspension destabilized. This data suggest that the higher pH leads to more photo-corrosion-resistant QDs, and also that the citrate is needed for keeping colloidal stability. The overall mechanism of the photostability of citrate stabilized CdSe QDs are complicated. These experimental results indicate that the system

![Graph](image)

**Fig 3-8.** Effect of UV-vis absorption spectra versus time on the photostability of 3.0nm CdSe quantum dots solution at initial pH=12.20, (a) without additional citrate, (b) with additional, [cit] = 5x10^{-3}M citrate. [CdSe] =1.5x10^{-6}mole_{particle}/l. Light: 200nm~800nm
behaves differently at different pH's.

There are two types of stability involved. One is the colloidal stability of the suspension, and the other is the chemical stability of the QDs. At lower pH (weak basic, pH ~ 8), experimental results (Fig. 3-7) indicated the absorbance of the samples decreased with the reaction time and all QDs were dissolved eventually. This is due to the oxidation of QDs themselves. When light is exposed on the QDs suspension, it influences is the chemical stability of the nanocrystals. Citrate is not a very strong stabilizer. Citrate capped on the nanocrystals surface is lost easily. Therefore, the oxygen in water can act on the nanocrystals surface directly, the nanocrystals themselves are oxidized. At high pH, based on a similar CdS system [30], we believe the high pH leads to the formation of a Cd(OH)$_2$ shell (Fig. 3-9(a)), thus yielding a Cd(OH)$_2$/CdSe core/shell QD. The shell protects the nanocrystals surface from contacting with oxygen in the water, reducing the photooxidation of the nanocrystals. However, the surface capped citrate can be photocatalytically oxidized under radiation of light with CdSe nanocrystals acting as the photocatalysts. Thus, QDs precipitated out of the solution by losing their surface stabilizer (Fig. 3-8(a)). However, if additional free citrate existed in the solution, they replaced the oxidized citrate and kept the nanocrystals stable in solution for a longer period of time.
\[ \text{Cd}^{2+} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2 \]

**Fig. 3-9(a)**, Schematic diagram of formation mechanism of CdSe/Cd(OH)$_2$ QDs

The layer of Cd(OH)$_2$ also can enhance the fluorescence of the QDs (Fig. 3-9(b)). Fig. 3-9(b) shows that the fluorescence of quantum dots increased when pH of the solutions increases. Fig. 3-9(c) shows how the pH effect impacted on the absorption spectra of CdSe QDs. The absorption edges of CdSe QDs blue-shifted with the pH of the QDs colloid solution decreased. This phenomenon suggests that the mean size of the QDs decreased when pH of the system decreased.

**Fig. 3-9(b)**, Fluorescence spectra of 3.0 nm CdSe quantum dots versus pH.
Fig 3-9(c). Absorbance spectra of 3.0 nm CdSe quantum dots versus pH

Comparing with the results of CdSe QDs experiment, Fig 3-10 (a) and (b) indicate the core/shell type QDs follow the same tendency. At lower pH (Fig. 3-10 (a)), the core/shell QDs suspension system was unstable even with additional citrate when the system was exposed to light. The reason maybe is the CdS shell of the core/shell QDs itself also can be oxidized. But at higher pH (Fig. 3-10(b)), additional citrate and the possible Cd(OH)$_2$ layer can help the stability of the colloid system.
**Fig 3-10(a).** Effect of UV-vis absorption spectra versus time on the photostability of 2.9 nm CdSe/CdS core-shell quantum dots solution at initial pH=7.11 with additional citrate. Concentration of citrate: 0.005M. Concentration of quantum dots: 1.2*E-6 mole\(_{\text{particle}}/\text{l}\). Exposure to 200nm~800nm light.

**Fig 3-10(b).** Effect of UV-vis absorption spectra versus time on the photostability of 2.9 nm CdSe/CdS core-shell quantum dots solution at initial pH=12.1 with additional citrate. Concentration of citrate: 0.005M. Concentration of quantum dots: 1.2*E-6 mole\(_{\text{particle}}/\text{l}\). Exposure to 200nm~800nm light.
3.3.2 Absolute Energy Positions of Conduction and Valence Bands of CdSe, CdSe/CdS Core/Shell QDs at the Semiconductor/Electrolyte Interface.

In photocatalysis, the key step is the transfer of electrons between the semiconductor and absorbed reactants [15, 35]. The energy level of energetic states of reactants undergoing an electron transfer can be approximated by the standard redox potential ($E^0$), whereas relevant energy levels for a semiconductor are the energies of the valence band ($E_v$) and the bottom of the conduction band ($E_c$).

A photocatalytic reaction normally happens in the aqueous solution containing redox species, thus electrons have to be transferred across the semiconductor/electrolyte interface until the chemical potentials of the semiconductor and solutions are equal [15, 35]. Thus, a comparison between the energy position of band edges of semiconductor interface in an electrolyte environment and the redox potential of the reactant is needed [35].

Although band gap energies ($E_g$) are well known for most semiconductors in handbook, unfortunately, $E_v$ and $E_c$ have not been determined accurately for most of semiconducting materials [35]. Furthermore, the standard redox potentials for aqueous redox couples are normally reported with respect to the normal hydrogen electrode (NHE). In contrast, the energy position of band edges of semiconducting materials is normally reported respect to Fermi level of the material, rather than on the absolute vacuum scale (AVS). Thus, it is necessary to express the energies in one standard way.
For a $M_a X_b$ compound, it is reported that the absolute energy positions of conduction and valence band edges at the semiconductor/electrolyte interface with respect to Absolute Vacuum Scale (AVS) can be estimated by [35]:

$$E_C = -(\chi_M^a \chi_X^b)^{(a+b)} + \frac{E_g}{2} + 0.059(PZC - pH)$$

$$E_V = -(\chi_M^a \chi_X^b)^{(a+b)} - \frac{E_g}{2} + 0.059(PZC - pH)$$  \hspace{1cm} (3-4)

Where $\chi_M$ and $\chi_X$ are the absolute electronegative of atoms M and X

$E_g$ is the band gap energy,

PZC is the pH at the zero point of charge

The results from equation (3-1) are with respect Absolute Vacuum Scale (AVS). The energy positions of band edges in the NHE scale can be converted from the values in AVS scale using [35]:

$$E(\text{NHE}) = -E(\text{AVS}) - 4.50$$  \hspace{1cm} (3-5)

Fig. 3-11 shows the absolute energy positions of conduction and valence band edges of selected semiconducting materials at the semiconductor/electrolyte interface in AVS and NHE scales. In this figure, all the energy positions of the band edges are calculated from Equation (3-1) and (3-2). For the calculation, $\chi_M$ and $\chi_X$ are obtained from reference [35] and [36]. For the bulk semiconductor, $E_g$ are obtained from reference [35] and [37]. For the QDs, $E_g$ are obtained from reference [37] and our experiment data. PZC can be found in reference [35].

Fig. 3-11 also shows how the quantum confinement effect influences the absolute positions of band edges of QDs. In comparison with the relevant bulk material, the $E_v$ of QDs is more positive and the $E_c$ is more negative with respect to NHE scale. This phenomenon shows that QDs will have stronger ability
working as either an electron accepter or electron donor (i.e., more active photocatalyst), compared to corresponding bulk materials.

Fig 3-11. Absolute energy positions of conduction and valence bands of selected semiconductor material at the semiconductor/electrolyte interface

As indicated in the Equation 3-1, pH of the aqueous solution plays a crucial role in the calculation since pH can influence the surface charge and the thickness of the Helmholtz layer and the thickness of the space charge layer. [35]. pH also plays a very important role in the deciding of the redox potential of a redox couple. From Nernst equation [38]:

\[ E = E^\circ - (0.0592/n)\log Q \]  

(3-6)

where \( Q \) = equilibrium constant of the redox reaction

\( n \) = number of moles of electrons in the reaction
\[ E^0 = \text{the standard redox potential of the aqueous redox couple with respect to the NHE scale.} \]

As indicated in the mechanism of 4-nitrophenol photodegradation (Fig 3-2), the redox couples \( \cdot \text{OH}/\text{H}_2\text{O} \) and \( \text{O}_2/\text{H}_2\text{O} \) are very important in the reaction cycle. For TiO\(_2\), the oxidation process appears to be dependent on the formation of hydroxyl radicals \( \cdot \text{OH} \) which probably are absorbed on the surface of the TiO\(_2\) particles by valence band holes, with a corresponding reduction of dissolved molecular oxygen by conduction band electron if there no other possible electron acceptor [19]. At pH=7, the redox potential of \( \cdot \text{OH}/\text{H}_2\text{O} \) is +2.27 V, and the redox potential of \( \text{O}_2/\text{H}_2\text{O} \) =+0.83 V [5]. Thus, the production of \( \cdot \text{OH} \) will occur if the semiconductor valence band potential is more positive than 2.27 V, and reduction of dissolved molecular oxygen will occur if the conduction band potential is less positive than 0.83 V or negative.

If we assume the mechanisms for 4-nitrophenol photodegradation of using CdSe and CdSe/CdS QDs are similar to using TiO\(_2\), the photodegradation reaction will happen when the QD valence band potential is larger than the redox potential of \( \cdot \text{OH}/\text{H}_2\text{O} \) and the QD conduction band potential is smaller than the redox potential of \( \text{O}_2/\text{H}_2\text{O} \). As indicated in Fig 3-12, the conduction band potential, \( E_c \), of 3.1 nm CdSe QDs is always smaller than the redox potential of \( \text{O}_2/\text{H}_2\text{O} \), but the valence band potential, \( E_v \), is larger than the redox potential of \( \cdot \text{OH}/\text{H}_2\text{O} \) only if pH>10. However, the reaction may also occur when pH<10 since it is said that the nitrophenoxide anions (nitrophenol has a pK\(_a\) value of 7.15) can be absorbed directly on the surface of the semiconductor and be an electron donor (Fig. 3-2)
[5,19, 29,32,33,34]. No matter which way the photo-reaction follows, all the above discussion suggests choosing a higher pH will help the oxidation reaction. The photostability experiment results also shows this since higher pH can help the photo-stability due to the formation of the Cd(OH)$_2$ layer.

![Graph showing energy vs. pH for different redox couples and CdSe quantum dots](image)

**Fig 3-12** Redox potential of O$_2$/H$_2$O and *OH/H$_2$O redox pair, and absolute energy positions of conduction and valence bands of CdSe quantum dots vs. pH

### 3.3.3 Photodegradation of 4-Nitrophenol

#### 3.3.3.1 Using CdSe QDs

With the initial pH=11.9, CdSe QDs can serve as photocatalyst to drive 4-nitrophenol degradation. Fig 3-13 shows the temporal evolution of the absorbance spectrum of the 4-nitrophenol and 3.1 nm CdSe QDs mixture when
the mixture was exposed to light (200nm~800nm). The experiment was stopped shortly after the precipitation of the QDs. 4-nitrophenol and CdSe QDs mixture absorbed strongly at $\lambda_{\text{max}}=400\text{nm}$. This peak probably was due to the 4-nitrophenol absorption since the 3.1nm CdSe QDs don't have absorbance peaks at 400nm (Fig 2-1, and Fig 3-5). The absorbance changes shown in Fig 3-13 are not due to the pH dropping during the reaction (Fig 3-5, which would influence the absorbance of 4-nitrophenol since the absorbance at $\lambda=300\text{nm}$ also decrease, and the absorbance at $\lambda=400\text{nm}$ decrease too significantly.

**Fig 3-13.** Absorbance spectra temporal evolution of 4-nitrophenol photodegradation, using CdSe quantum dots, and exposure to 200nm~800nm light. Experiment conditions: Initial pH=11.9, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe particle (QD): 2E-6 mole\text{particle}/L, molecule ratio (4-NP/QD): 125 , Time Scale: 0~30 hour
Fig 3-14 shows the absorbance spectra of the 4-nitrophenol and 3.1 nm CdSe QDs mixture did not change too much with time without the exposure to light. Comparing Fig 3-13 and 3-14, it is very reasonable to claim that the photoreaction goes significantly faster than the reaction in the dark. Control experiments indicated, in the absence of CdSe QDs, the 4-nitrophenol concentration did not change with time, with or without irradiation. All the results suggest that the photoreaction actually occurred under this condition. The photoreaction also caused the drop of the pH of the system (Fig. 3-15).

![Absorbance spectra](image)

**Fig 3-14.** Absorbance spectra temporal evolution of 4-Nitrophenol photodegradation, using CdSe quantum dots, and without exposure to light. Experiment Conditions: Initial pH=11.9, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe quantum dots: 2E-6 mole_{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 0~30 hour

From the Fig 3-13, it is clear that the reaction went very slow under that condition since the whole processes took almost 30 hours. In comparison, control experiments were done using TiO_{2} (anatase) as photocatalyst to degrade 4-nitrophenol. If using same surface area of TiO_{2}, it would only need less than one
hour to decompose the nitrophenol and make the suspension showed white color (at basic condition, 4-nitrophenol solution is yellow-green).

Fig 3-15 pH temporal evolution of 4-Nitrophenol photodegradation, using CdSe quantum dots, and exposure to 200nm~800nm light. Experiment Conditions: Initial pH=11.9, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe quantum dots: 2E-6 mole\textsubscript{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 0~30 hour

Fig 3-5 shows 4-nitrophenol doesn't have absorbance if $\lambda > 500$. Therefore, in Fig 3-13 and 3-14, the $\lambda > 500$ part of the spectra are only due to the absorbance from QDs. As indicated in Fig 3-13, the absorbance from QDs decreased with time. This phenomenon might be attributing to the photocorrosion of QDs.

From the photostability study, we concur that adding additional citrate can significantly increase the photostability of the QDs solution. Fig 3-16 shows the temporal evolution of the absorbance spectra of 4-nitrophenol and CdSe QDs mixture exposed to 200nm~800nm light with additional citrate and initial pH=12. The experiment was stopped shortly after the precipitation of the QDs. As seen
from Figure 3-16, there were photocatalysis occurred. The whole process took 19 hours.

Fig 3-16. Absorbance spectra temporal evolution of 4-Nitrophenol photodegradation, using CdSe quantum dots, and exposure to 200nm~800nm light, with additional citrate. Experiment Conditions: Initial pH=12, concentration of 4-nitrophenol (4-NP): 0.00005M, concentration of 3.1 nm CdSe quantum dots: 0.8E-6 mole\_particle/L, molecule ratio (4-NP/QD): 125, time Scale: 0~19 hour, 1:0 hour, 2:19 hour

Fig 3-17 shows the temporal evolution of the absorbance spectra of 4-nitrophenol and CdSe QDs mixture exposed to 380nm~800nm light with additional citrate and initial pH=12. As seen from Fig 3.17, there was no apparent change after exposed the reaction mixture to light for over 22 hours. This may suggest the reaction won’t occur if only use visible light under this condition. Furthermore, being consistent with the photostability experiment results, high pH and additional citrate can increase the photostability of the CdSe QDs.
Fig 3-17. Absorbance spectra temporal evolution of 4-Nitrophenol photodegradation, using CdSe quantum dots, and exposure to 380nm~800nm light, with additional citrate. Experiment Conditions: Initial pH=12, concentration of 4-nitrophenol (4-NP): 0.00005M, concentration of 3.1 nm CdSe quantum dots: 0.8E-6 mole\textsubscript{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 0~22 hour, 1:0hour, 2:22hour

Fig 3-18 shows the temporal evolution of the absorbance spectra of 4-nitrophenol and CdSe QDs mixture exposed to 380nm~800nm light with additional citrate and initial pH=7.37. As seen from Fig 3-18, the evolution of the absorbance spectra is very apparent, however, this evolution can not attribute to the photodegradation of 4-nitrophenol. If we compare Fig 3-18 and Fig 3-19 with Fig 3-5, we can find the tendencies of their evolution with pH are quite similar except when $\lambda >500$. Furthermore, if we observe the temporal evolution of optical density when $\lambda >500$ in Fig 3.18, we may find the QDs decayed with time. Apparently, the photocorrosion of the QDs caused the pH changes of the system. And, the pH changes of the system caused the significant changes of the absorbance of the 4-nitrophenol. Under this condition, there was no photodegradation of 4-nitrophenol.
Fig 3-18. Absorbance spectra temporal evolution of 4-Nitrophenol photodegradation, using CdSe quantum dots, and exposure to 380nm~800nm light, with additional citrate. Experiment Conditions: Initial pH=7.37, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe quantum dots: 2E-6 mole_{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 1 hour

Fig 3-19. pH temporal evolution of 4-Nitrophenol photodegradation, using CdSe quantum dots, and exposure to 380nm~800nm light, with additional citrate. Experiment Conditions: Initial pH=7.37, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe quantum dots: 2E-6 mole_{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 1 hour
3.3.3.2 Using CdSe/CdS QDs

With the initial pH=11.86, CdSe/CdS core/shell QDs also can serve as photocatalyst to drive 4-nitrophenol degradation. Fig 3-20 shows the temporal evolution of the absorbance spectra of the 4-nitrophenol and 3.3 nm CdSe/CdS QDs mixture when exposed to 200nm~800nm light. The experiment lasted for 12 hours. The results (Fig 3-20 and 3-21) are quite similar with the CdSe result shown in Fig 3-13, therefore, based on the same discussion, it is reasonable to say that there were photocatalysis occurred. Additionally, the control experiment (Fig 3-22) showed there are no apparent change happened on the absorbance spectra without irradiation.

![Absorbance Spectra](image)

**Fig 3-20.** Absorbance spectra temporal evolution of 4-NP photodegradation, using CdSe/CdS quantum dots, and exposure to 200nm~800nm light, with additional citrate. Experiment Conditions: Initial pH=11.86, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.3 nm CdSe/CdS quantum dots: 2E-6 mole\textsubscript{particle}/L, molecule ratio (4-NP/QD): 125, time scale: 12hour
Fig 3.21. pH temporal evolution of 4-Nitrophenol photodegradation, using CdSe/CdS quantum dots, and exposure to 200nm−800nm light, with additional citrate. Experiment Conditions: Initial pH=11.86, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.3 nm CdSe/CdS quantum dots: 2E-6 mole\textsubscript{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 12hour

Fig 3.22. Absorbance at 400nm, using CdSe/CdS quantum dots, and exposure to 200nm−800nm light, with additional citrate. Experiment Conditions: Initial pH=11.86, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.3 nm CdSe/CdS quantum dots: 2E-6 mole\textsubscript{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 12hour
Fig 3-23 shows the temporal evolution of the absorbance spectra of 4-nitrophenol and CdSe/CdS QDs mixture, which was exposed to 380nm~800nm light, with additional citrate and initial pH=11.8. As indicated in the Fig 3-23, the spectrum curve had apparent shift during the reaction. If we observe the >500nm part of the spectrum curves, we can find the QDs had no apparent photocorrosion during the reaction. Thus, the spectrum curve shift can only be contribute to the photodegradation of 4-nitrophenol. However, comparing with Fig 3-13 and Fig 3-20, the reaction went very slow.

Fig 3-23. Absorbance spectra temporal evolution of 4-nitrophenol photodegradation, using CdSe/CdS quantum dots, exposure to 380nm~800nm light, with additional citrate. Experiment Conditions: Initial pH=11.8, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.3 nm CdSe/CdS quantum dots: 2E-6 mole_{particle}/L, molecule ratio (4-NP/QD): 125, time Scale: 12hour
Fig 3-24 shows the temporal evolution of the absorbance spectra of 4-nitrophenol and CdSe/CdS QDs mixture, which was exposed to 380nm~800nm light, without additional citrate. The initial pH was 7.56. The experiment was stopped shortly after the precipitation of the QDs. As indicated in the Fig 3-24, the spectrum curve had apparent shift during the reaction. However, If we observe the >500nm part of the spectrum curves, we can find the QDs had apparent photocorrosion during the reaction. Furthermore, curve 3 equal to curve 2 plus curve 0. If we compare curve 3 with curve 1, only slightly difference can be found around $\lambda = 300$nm. All of those suggest that there are no photodegradation of 4-nitrophenol under this condition.

![Absorbance spectra](image)

**Fig 3-24.** Absorbance spectra temporal evolution of 4-Nitrophenol photodegradation, using CdSe/CdS quantum dots, exposure to 380nm~800nm light, with additional citrate. Experiment Conditions: Initial pH=7.56, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe quantum dots: 2E-6 mole\text{particle/L}, molecule ratio (4-NP/QD): 125, time Scale: 36 hour
Although the pH changes during the reaction will influence the absorbance, the spectra can be used to get the estimated quantum yield of the photoreaction. From Fig. 3-15 and Fig. 3-31, the pH of the reaction system decreased if there was photoreaction going on. From Fig. 3-5, the absorbance of 4-NP at 400 nm decreases with pH, thus the concentrations calculated from absorbance at 400 nm neglecting the pH increase are smaller than the actual values. Thus, the quantum yields calculated from the concentration changes and actinometry are larger than the actual values. In another word, the actual quantum yield can not large than those number. Neglecting the influence of pH and QD photocorrosion, Fig. 3-25 and Fig. 3-26 shows the concentration of 4-NP changes with time. The concentrations in Fig. 3-25 are derived from the spectra in Fig. 3-13 and Fig. 3-14. From the actinometry, the quantum yield of this reaction is 0.05% using CdSe QDs as photocatalyst. The concentrations in Fig. 3-26 are derived from the spectra in Fig. 3-20 and Fig. 3-22. From actinometry, quantum yield of this reaction is 0.07%. The result suggests quantum yield of CdSe/CdS core/shell QDs is faster than CdSe QDs. However, those numbers are smaller than the published quantum yield of TiO$_2$ powder (~1%~20% [5]) and CdS QDs (1% ~ 20% [10]),
Fig 3-25. 4-NP concentration vs. time, using CdSe quantum dots, exposure to 200 nm~800 nm light. Experiment Conditions: Initial pH=11.9, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe quantum dots: 2E-6 mole\textsubscript{particle}/L, molecule ratio (4-NP/QD): 125, reaction time: 30 hour

Fig 3-26. 4-NP concentration vs. time, using CdSe/CdS quantum dots, exposure to 200 nm~800 nm light. Experiment Conditions: Initial pH=11.86, concentration of 4-nitrophenol (4-NP): 0.000125M, concentration of 3.1 nm CdSe quantum dots: 2E-6 mole\textsubscript{particle}/L, molecule ratio (4-NP/QD): 125, reaction time: 12 hour
3.4 Conclusions

The photostability of citrated-stabilized water soluble CdSe and CdSe/CdS QDs was studied in this chapter. Two types of photostability are encountered: colloid stability of the QD suspension and chemical stability of QDs. At neutral pH, based on our experimental results, the QDs photo-corroded. At high pH, a Cd(OH)$_2$ layer was formed on the surface of the QD, which protected the surface from photocorrosion. This increase in chemical stability allowed photo-oxidation of citrate ions to be observed upon UV-vis irradiation, with CdSe or CdSe/CdS QDs acting as the photocatalysts. The QDs subsequently precipitated out of the solution with the loss of the surface citrate stabilizer. The colloidal stability was enhanced with additional citrate ions. The layer of Cd(OH)$_2$ enhanced the fluorescence of the QDs.

Another important topic in this chapter is the photodegradation of 4-nitrophenol. The photostability study results, and the absolute energy positions of conduction and valence bands of CdSe and CdSe/CdS core/shell QDs surface, indicated CdSe and CdSe/CdS QDs functioned as photocatalysts for the photodegradation of 4-nitrophenol at very high pH condition (pH >11), though, the quantum yield were relatively low. Furthermore, additional citrate did not show too much influence on the reaction efficiency, but additional citrate can help the stability of reaction suspension. Visible light (380nm~800nm) did not promote photocatalysis using CdSe QDs, but did so when using CdSe/CdS QDs. The reason may be the shell of Cd(OH)$_2$. Cd(OH)$_2$ is not a semiconducting material. Thus, the outside Cd(OH)$_2$ shell on the QDs blocked the electron transportation.
This resulted the very low quantum yield. When only visible light was used, the reaction went even more slow due to the reduced light intensity. From the actinometry, the quantum yield of CdSe/CdS core/shell QDs was higher than CdSe QDs. Thus, pH is very important in the reaction. One reason is that it can influence the redox potential of the involved materials and reactants, Also the photostability of the QDs and the thickness of Cd(OH)₂ shell depends on the pH of the system greatly.

3.5 References


Chapter 4. Summary and Recommendation for Future Work

4.1 Summary

This work described herein is a response to the great potential that the QDs hold for the development of visible light absorbing photocatalyst. In this work, CdSe and CdSe/CdS QDs were used as model materials agents. We made a thorough study on a modified route for the synthesis of the citrate-stabilized water-suspended CdSe and CdSe/CdS semiconductor QDs. We studied the CdSe and CdSe/CdS QDs as photocatalysts for the photodegradation of 4-nitrophenol.

The photostability study results, and the absolute energy positions of conduction and valence bands of CdSe, CdSe/CdS core/shell QDs at the semiconductor/electrolyte interface, suggest CdSe and CdSe/CdS QDs may work as photocatalyst for the photodegradation of 4-nitrophenol at very high pH condition (pH >11). Our experimental results also show, with the initial pH around 12 and under UV-vis light, CdSe and CdSe/CdS core/shell QDs can serve as photocatalyst to drive 4-nitrophenol degradation, though, the reactions are relatively slow compare to TiO₂. If we only use visible light (380nm~800nm), there was no reaction when using CdSe QDs, and there was
very slow reaction went on when using CdSe/CdS QDs.

4.2 Recommendation of Future Work

In this thesis, we applied CdSe and CdSe/CdS core/shell QDs on the photodegradation of 4-nitrophenol. The oxidation potential of QDs should be sufficiently positive to produce ·OH radicals. However, if we compare the oxidation potential of CdSe QDs with TiO₂, the oxidation potential of TiO₂ is much more positive than CdSe QDs (Fig 3-11). Moreover, the surface of CdSe QDs is easy to be oxidized. Thus, the CdSe QDs are not appropriate for oxidation reactions, and the experiment results also show low efficiencies. However, for photoreduction applications, such as CO₂ reduction, CdSe QDs may be useful. In Fig 3-11, we may find the reduction potential of CdSe QDs can be very negative, at least much more negative than TiO₂. And in a reduction application, the oxidative pathway becomes less important and a reducing agent, such as methanol, can be used to interact with the photo-generated hole. Thus, we may expect better efficiencies of CdSe and CdSe/CdS QDs as visible light absorbing photocatalyst.

In our studies, photostability of those QDs is always a great difficulty. It is possible to void this problem but still benefits from the advantages of those QDs, e.g. visible-absorbing and size-depending properties. One good way to try this is to deposit QDs onto support materials, such as SiO₂. Catalytic materials are often times deposited onto support materials. This is done not
only to prevent the catalyst from agglomerating, but often because reaction rates can be synergistically increased through interactions between the catalyst and support material. This strategy also can be applied to semiconductor photocatalysts and, for CdSe or CdSe/CdS core/shell QDs. Deposition on a support material not only increase photostability, but also can increase the possibility of electron or hole transfer between the two combined different semiconductor materials if we deposit QDs on another semiconductor material.