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Photocatalysis Using CdSe Quantum Dots

Abstract

In this project, we synthesized water soluble CdSe quantum dots (QDs) that photocatalyzed the reduction of resazurin to resorufin. Absorption spectra of the CdSe QDs in water solution is the same as in the toluene suspended QDs solution. The retention of optoelectric properties implies that the QDs retain their chemical properties upon water solubilization. Absorption spectra also showed photoreduction of resazurin to resorufin after a period of light exposure only in the presence of quantum dots. These preliminary results suggest that CdSe quantum dots could be a viable photocatalyst for production of hydrogen gas through the water splitting reaction.

I. Introduction

A. Background

Prior to the development of coal and oil-dependent processes, all energy used by man was renewable; with the primary sources being man and/or animal power, water, wind, and fire. This period of world history, characterized by the dramatic change from man to machine labor, is known as the Industrial Revolution and it allowed various countries around the world to flourish and achieve better standards of living[1]. However, as the world's population increased, so did the demand for energy. Since the beginning of the 20th century that need has been increasingly filled by non-renewable resources such as coal and oil. Given the limited availability of these , scientists have commenced the search for alternative sources of energy.

Among the alternatives, hydrogen gas (H_2) has shown great potential as an environmentally friendly motor fuel[2]. Hydrogen can be used in internal combustion just like gasoline but it is not as readily available. Because of this, three main problems arise regarding the handling and transportation of gaseous H_2: (1) hydrogen gas requires a large space for storage. "Hydrogen needs about four times the volume for a given amount of energy. A 15 gallon automobile gasoline tank contains 90 pounds of gasoline. The corresponding hydrogen tank would be 60 gallons, but the hydrogen would weigh only 34 pounds." (2)Liquid hydrogen can freeze air, and accidents can occur from built-up pressure at plugged valves; an explosion is risked if the hydrogen is stored in a confined space. (3) Hydrogen cannot easily be insulated from the environment, leading to its rapid evaporation[3]

One possible solution to these problems would be the local production of hydrogen gas through the water splitting reaction ($2H_2O \rightarrow 2H_2 + O_2$), which can be triggered with the aid of a photocatalyst. Plants routinely do a similar process through photosynthesis, in which they

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[1] R.F Clermont; Standards of Living in Britain during the Industrial Revolution (1700-1820).

[2] Bockris, John. *Energy: the solar – hydrogen alternative.* New York: John Wiley and Sons, Inc., **1975**. Print

[3] formal.stanford.edu. **2008**. Hydrogen (7-Dec-2008). Web. 18 November 2012.

convert carbon dioxide and water into a sugar and oxygen gas with the help of an electron donor and sun light. The water splitting reaction can be photocatalyzed using nanocrystals (or quantum dots) made out of semiconductor materials such as cadmium sulfide (CdS), cadmium zinc sulfide (ZnS:CdS) and cadmium selenide (CdSe)[4,5,6]. However, despite the importance of this catalytic process in industry, the photolytic activity of the nanoparticles still remains poorly understood. In order to exploit the maximum potential out the photocatalysts above mentioned, a critical understanding of the morphological, chemical and optical properties of such materials is required[7].

Although the ultimate goal of this research project was the *in situ* characterization of CdSe quantum dots, in its early stages (during which my contributions were made) it focused on the development of a system in which the characterization of the nanoparticles can be performed while their stability was guaranteed for a long period of time. In order to find this system, my specific project initially explored the ability of CdSe quantum dots to photocatalyze the reduction of the resazurin molecule in the presence of light in an aqueous environment.

Resazurin ($C_{12}H_7NO_4$) is a non-fluorescent blue dye that becomes highly fluorescent and pink when reduced to resorufin **(**$C_{12}H_7NO_3$**)**. Because of this, the resazurin-resorufin chemical system (**Figure 1**) serves as a fluorogenic probe of photocatalytic reduction. Demonstrating photocatalytic reduction of resazurin using CdSe quantum dots will in turn set the future stage for a fluorescence microscopy-based method for measuring single particle photocatalysis.

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[4] J.F. Reber and M. Rusek; Photochemical hydrogen production with platinized suspensions of cadmium sulfide and cadmium zinc sulfide modified by silver sulfide; *The Journal of Physical Chemistry* **1986** 90 (5), 824-834

[5] F.A. Frame, E.C. Carroll, D.S. Larsen, M. Sarahan, N.D. Browning and F.E. Osterloh; First demonstration of CdSe as a photocatalyst for hydrogen evolution from water under UV and visible light; *Chem. Commun.* **2008** 44 (19), 2206-2208

[6] M.K. Arora, A.S.K. Sinha, and S.N. Upadhyay; Active Cadmium Sulfide Photocatalysts for Hydrogen Production from Water; *Industrial & Engineering Chemistry Research* **1998** 37 (10), 3950-3955

[7] M.G. Bawendi, M.L. Steigerwald, and L.E. Brus; The Quantum Mechanics of Larger Semiconductor Clusters ("Quantum Dots"); *Annual Review of Physical Chemistry* **1990** 41, 477-496

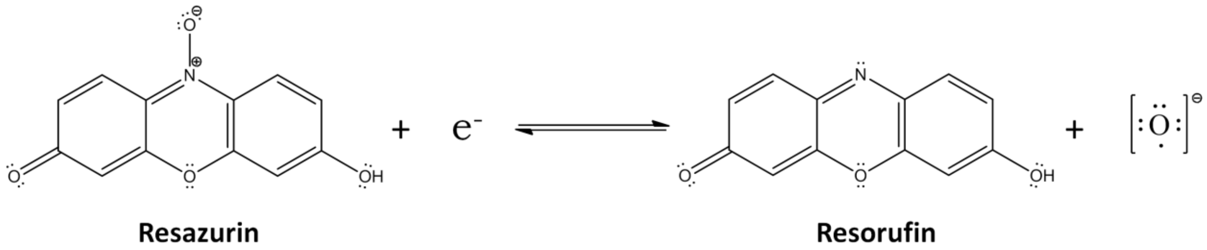

Figure 1. The resazurin-resorufin system. This reaction was expected to be catalyzed (triggered) with the energy released from the CdSe quantum dots after the solution has been exposed to white light.

B. Review of Literature

Nanoparticles made out semiconductor materials have been used for photocatalysis in previous research. Rusek and Reber for example, reported production of hydrogen gas by irradiating suspensions of platinized CdS in solutions of S^{2-} and/or SO_3^{2-} ions, which provided the reducing equivalents. Additionally, this study reported increased efficiency/photocatalytic activity as the surface area of the CdS nanoparticles decreased[4]. A similar result was reported by Osterloh and co workers in 2008, study in which CdSe nanoribbons were used instead[5].

Furthermore, Upadhyay *et al.* conducted a study in which CdS quantum dots were reported to photocatalyze the water splitting reaction with a strong correlation to its semiconducting behavior (n- or p-type). The n-type CdS quantum dots showed superior photocatalytic activity[6].

Moreover, Alivisatos research group studied water soluble CdSe/ZnS quantum dots, which were prepared by embedding the nanoparticles in a siloxane shell and adding thiol and/or amine groups. In their study, silica coating did not affect the optical properties of the nanoparticles and helped with their biocompatibility[8].

Fluorescence imaging has also been performed previously. Webb and co-workers reported usage of water soluble CdSe/ZnS quantum dots for multicolor imaging of biological

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[8] D. Gerion, F. Pinaud, S.C. Williams, W.J. Parak, D. Zanchet, S. Weiss and A.P. Alivisatos; Synthesis and Properties of Biocompatible Water-Soluble Silica-Coated CdSe/ZnS Semiconductor Quantum Dots; The Journal of Physical Chemistry B **2001** 105 (37), 8861-8871

samples[9]. As their article points out, "quantum dots are bright, photostable fluorophores," which make them suitable for fluorescence microscopy single-particle measurements

C. Theoretical

The process of chemical bonding is described by considering the overlapping of individual atomic orbitals and the sharing of the outermost electrons of an atom (**valence electrons**). This overlapping is called a molecular orbital. The process is typically described with a molecular orbital diagram[10] as shown in **Figure 2**.

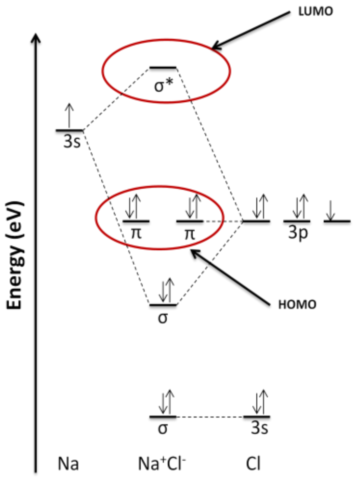

Figure 2. Molecular orbital diagram of sodium chloride (NaCl). This diagram shows the distribution of the valence electrons of each individual atom over the different molecular orbitals formed.

While sodium chloride (molecular formula NaCl) is commonly thought as an ionic compound[11],the NaCl molecule exists in the gas phase and a molecular diagram can be used to illustrate the theoretical model of bonding. Under the assumption that *one and only one atom* of both sodium (Na) and chlorine (Cl) are participating in the formation of a NaCl(g) molecule, the number of valence electrons given by each atom (indicated by ↑ and ↓) must be first counted and then distributed over the different molecular orbitals that their combination generates. See **Figure 2** as an illustration.

The number of valence electrons is determined by the electronic configuration of each atom. In the case of Na and Cl, whose electronic configurations are $3s^1$ and $3s^2 3p^5$ (according to their positions on the periodic table) and are located at the left and right sides of **Figure 2** respectively, there are eight electrons that must be distributed over the different molecular orbitals (middle), which in turn have different **energy levels**. **Figure 2** shows that when

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[9] D.R. Larson, W.R. Zipfel, R.M. Williams, S.W. Clark, M.P. Bruchez, F.W. Wise, and W.W. Webb; Water-Soluble Quantum Dots for Multiphoton Fluorescence Imaging in Vivo; Science **2003** 300 (5624), 1434-1436

[10] Atkins, Peter, and Julio de Paula. *Physical Chemistry Ninth Edition*. New York: W.H. Freeman and Company, **2010**. Print

[11] Kotz, John, Paul Treichel, and John Townsend. Chemistry and Chemical Reactivity. Belmont: Thomson Higher Education, **2009**. Print

chemical bonding occurs and electrons are distributed in the molecular orbitals labeled σ and π (middle), there is a molecular orbital that remains unoccupied (σ^*). This molecular orbital is referred to as the **lowest unoccupied molecular orbital (LUMO)**, while the highest-energy molecular orbital that contains one or more electrons is known as the **highest occupied molecular orbital (HOMO)**. All molecules posses both a HOMO and a LUMO. In the case of NaCl(g) the LUMO is the orbital labelled σ*, while the HOMO is the orbital labelled π

Crystalline structures are more complex than the simple example of NaCl(g) described above. Instead of having a single atom of each element interacting with each other to form a molecule, crystals are a three-dimensional network of several atoms arranged in an ordered pattern. When one considers the more complex crystalline structure in Molecular Orbital Theory, the molecular orbital diagram contains more orbitals, but remains as an extension of the NaCl model. See **Figure 3**.

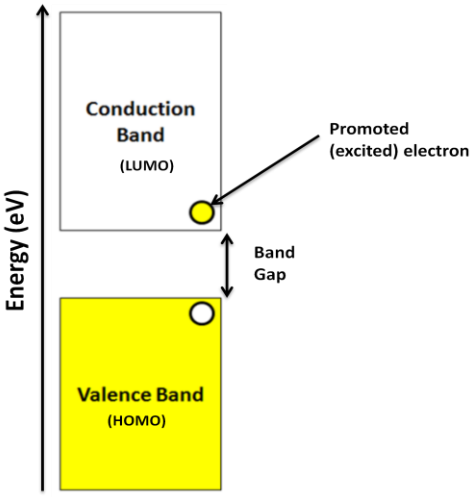

Figure 3. Extension of the NaCl model to a crystal. The HOMO becomes the valence band and is composed by a series of closely spaced molecular orbitals. The LUMO is now known as the conduction band.

Due to the many atomic and electron-sharing interactions taking place in a crystalline structure (which contains billions of NaCl molecules), the number of molecular orbitals and energy levels increases; resulting in a MO diagram with **closely spaced** energy levels. In this case, the HOMO becomes the **valence band** and the LUMO becomes the **conduction band**. *The amount of energy required to promote (move) an electron from the valence band to the conduction band is known as the* ***band gap*** *when dealing with crystalline structures*[12].

For a semiconductor material the energies of the valence band and the conduction band are somewhat similar, resulting in a small band gap of about 2eV (electron-volts) or less. This gap, in many instances, can be overcome through **light exposure** — shining light onto the

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[12] Miessler, Gary, and Donald Tarr. *Inorganic Chemistry Fourth Edition*. Glenview: Pearson Education, Inc., **2011**. Print

crystal can promote (excite) an electron from the valence band to the conduction band. This is how photo diodes (solar cells) work: light energy is converted into energy to move electrons within the crystal. Two electron-volts are equivalent to approximately 620 nm, which means that low energy light (red) is required to excite an electron. This energy can be easily obtained from the sun because it is located within the visible range of light.

Eventually, however, the **excited electron** will *return* to the lower energy valence band. Because energy is conserved in all processes, the energy required to promote this electron will be released in one or many different ways: (a) as light, (b) through charge (electron) transfer or (c) through energy (heat) transfer. When the energy gets released through **non-radiative processes** (b and c), it can be utilized to cause or accelerate (catalyze) a chemical reaction[13].

Such is the case in cadmium selenide (CdSe) quantum dots, which are nanoparticles (2-6 nm in diameter[14]) composed of a semiconductor material (in this case CdSe), and whose capacity to release energy can be used to **photocatalyze** the reduction reaction of resazurin as studied in this research project or ultimately the water splitting reaction . It is important to note that the chemical and optical properties of quantum dots are size-dependent. Smaller quantum dots posses larger band gaps; the larger the band gap, the larger the amount energy released and available for photocatalysis[13,15].

II. Methodology

All chemicals were obtained from Sigma-Aldrich. No purification was required.

A. Synthesis of CdSe quantum dots

While there exists several methods to synthesize and characterize CdSe quantum

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[13] Harris, Daniel. *Quantitative Chemical Analysis Eight Edition*. New York: W.H. Freeman and Company, **2010**. Print

[14] B.O. Dabbousi, J. Rodriguez-Viejo, F.V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober , K. F. Jensen, and M. G. Bawendi; (CdSe)ZnS Core−Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites; *The Journal of Physical Chemistry B* **1997** *101* (46), 9463-9475

[15] D.J. Norris and M.G. Bawendi; Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots; *Physical Review B (Condensed Matter)* **1996** 53 (24), 16338-16346

dots[16,17,18], the CdSe "seeds" utilized in this research project were produced in the following manner:

1. 3.0 g of trioctylphosphine oxide (TOPO), 0.280 g of octadecylphosphonic acid (ODPA) and 60 mg of cadmium oxide (CdO) were mixed in a 25 mL three-neck flask inside a glove box. The flask was then heated to 150ºC outside the glove box and exposed to vacuum for 1 hour (after reaching 100 ºC).
2. In a separate 25mL roundbottom flask, a trioctylphosphine-selenide solution (TOP:Se) was prepared inside a glove box using 0.058 g of selenium powder (Se) and 0.360 g of TOP.
3. Under argon, the solution from step 1 was heated to 320ºC in order to dissolve the CdO (solution turns optically clear and colorless).
4. At this point, 1.5 g of trioctylphosphine (TOP, from glove box) were injected *slowly* into the flask.
5. After 5 minutes, the temperature was raised from 320ºC to 370ºC and the TOP:Se solution (Step 3) was rapidly injected using a 5mL syringe. According to the procedure provided by the Jain lab, the reaction time is modified in order to synthesize CdSe dots of different sizes. 2.3 nm CdSe seeds with green fluorescence can be obtained by removal of the heating mantle immediately after the injection, while 3.1 nm seeds are obtained after heat removal after 3 minutes.
6. After the synthesis, the nanocrystals were precipitated with methanol, and were washed by repeated (~ 2-3 times) redissolution in toluene and precipitation with the addition of

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[16] C.B. Murray, D.J. Norris, and M.G. Bawendi; Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites; *Journal of the American Chemical Society* **1993** 115 (19), 8706-8715

[17] Z.A. Peng and X. Peng; Mechanisms of the Shape Evolution of CdSe Nanocrystals; *Journal of the American Chemical Society* **2001** 123 (7), 1389-1395

[18] Z.A. Peng and X. Peng; Nearly Monodisperse and Shape-Controlled CdSe Nanocrystals via Alternative Routes: Nucleation and Growth; *Journal of the American Chemical Society* **2002** 124 (13), 3343-3353.

methanol. The nanocrystals were finally suspended in toluene and kept inside the glove box to avoid air exposure.

The repeated dissolution and precipitation cycle in the last step of the procedure procures high levels of **monodispersity**[16],which is a measure of the size distribution of the nanoparticles. High levels of monodispersity indicate that more nanoparticles of the same size are present in solution (the distribution in size is smaller). Consistently sized particles are an advantage when the purpose of the project is to find a correlation between morphological, optical and chemical properties.

B. Synthesis of water-soluble CdSe quantum dots

In addition to the steps underlined in the previous section, the following steps were taken to make the CdSe quantum dots soluble in water:

1. Take an aliquot (sample) of the CdSe quantum dots solution stored in toluene and evaporate the toluene with either dry argon or dry nitrogen. Avoid air contact. A solid film should result upon drying.
2. In a separate vial, prepare a 25mL aqueous solution of 50.0 mg of mercaptoundecanoic acid (MUA) and add tetramethylammonium hydroxide (TMAOH) to the solution until its pH is above 12 measured with pH paper.
3. Inject about 5mL of the MUA:TMAOH solution from step 2 to the vial containing the CdSe quantum dots solid film (step 1) and sonicate the solution at room temperature until the solid film dissolves (about 45 minutes).
4. After the solid film has been completely dissolved, the nanocrystals are precipitated with ~1μL of concentrated hydrochloric acid (HCl), and are washed by repeated redissolution in water with TMAOH and precipitation with the addition of HCl. Do not perform this step more than twice. Concentrated HCl can degrade the nanocrystals.
5. The quantum dots are finally stored in water containing a small amount of TMAOH at a pH greater than 12.

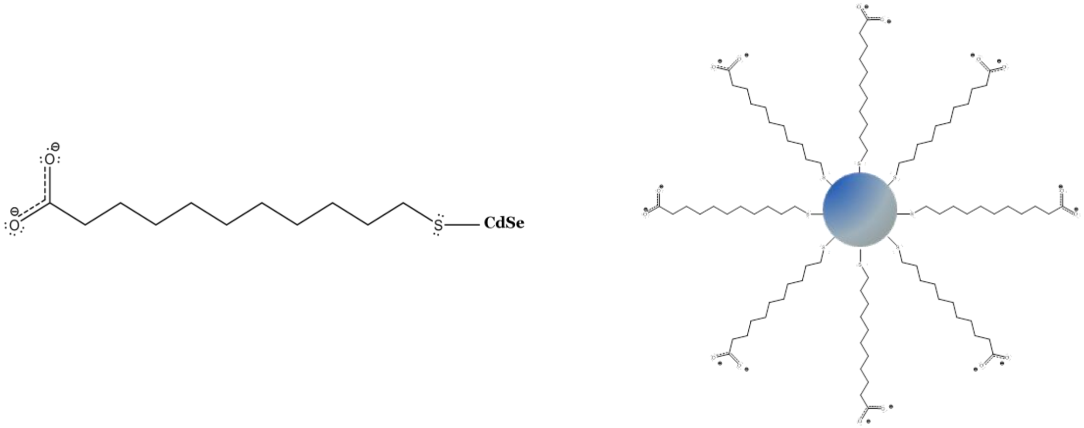

Figure 4. Attachment of mercaptoundecanoic acid chain to surface of CdSe quantum dot. Water solubilization is accomplished through deprotonation of the carboxylic acid with tetramethyl ammonium hydroxide.

C. Fluorescence Measurements

Because the chemical and optical properties of quantum dots are size-dependent[7], CdSe seeds of different sizes have different spectroscopic signatures[5]. Thus, it is possible to determine the level of monodispersity of a solution of quantum dots by analyzing the **fluorescence spectrum** of the solution. Solutions with a high degree of monodispersity should have a narrower fluorescence, while those with lower monodispersity should have a broader fluorescence. For CdSe quantum dots, fluorescence spectra were acquired using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer in (approximately) the visible range of the spectrum of light (450 - 900nm) with an approximate λ_{ex} of 440nm. This measurement were performed while the quantum dots are still suspended in toluene.

D. Absorption Measurements

The absorbance measurements were conducted on a Shimadzu UV 3600 diode array (or scanning) spectrophotometer. While absorption measurements were used to characterize the CdSe quantum dots solution, they also helped in the investigation of photocatalysis due to the presence of the nanocrystals in the resazurin-resorufin system. Absorption spectra of four solutions was collected using the UV-Vis spectrophotometer in the range between 311 - 800 nm in quartz cuvettes with path length of 1.0cm. These solutions were prepared as follows: all four of them contained 20 to 25 drops of a saturated resazurin solution in water (~ 10 mM); solutions 1 and 3 also contain 300μL of the CdSe quantum dots solution. While solutions 1 and 2 are exposed to a xenon arc lamp and monitored with the UV-Vis spectrophotometer at time intervals that vary from 5 to 10 minutes, solutions 3 and 4 are stored in the dark and their absorption spectra is recorded after the reduction of resazurin has reached completion in solution 1. It is important to note that an absorption spectrum of each solution is recorded at a time 0 minutes, which is defined to be the time at which the simultaneous preparation of all solutions has been finished. We did not characterize the number of MUA chains / QD.

III. Results

A. Fluorescence Spectra: Characterization of Nanoparticles

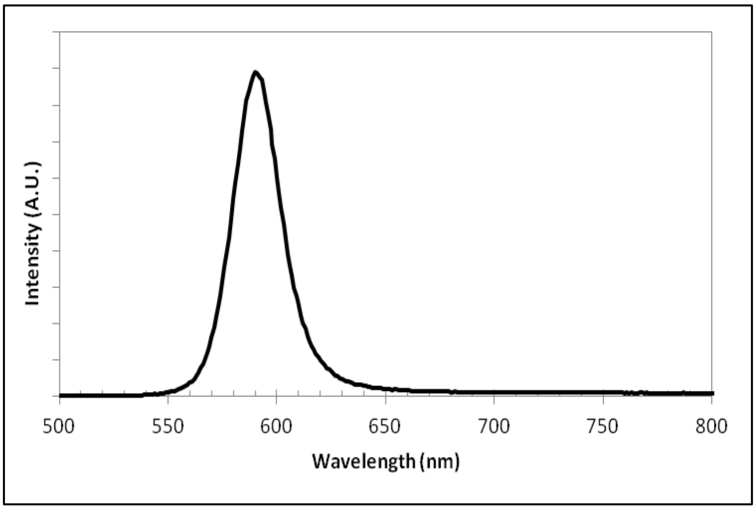

Figure 5. Fluorescence spectrum of CdSe quantum dots. Peak intensity and location provide information about the structure of the nanocrystals.

During this research project, two different “batches” of CdSe quantum dots were prepared. The fluorescence spectrum shown in **Figure 5**, which belongs to the first batch, indicates a high level of monodispersity because the width of the peak at about 590 nm is small. If the size distribution was greater (lower monodispersity), the width of the fluorescence peak would increase. Beyond the width of the peak, the peak's location also gives an idea of the size of the quantum dots and about how much energy is required to overcome the band gap. Energy decreases as the wavelength increases ($E = hc/\lambda$), and so it is possible to conclude that the energy band gap of these particles *is* *"small"*. Because the energy of the exciton band is inversely related to the size of the quantum dot it also means that the CdSe quantum dots present in this solution are *relatively "big"* in size[7,19].

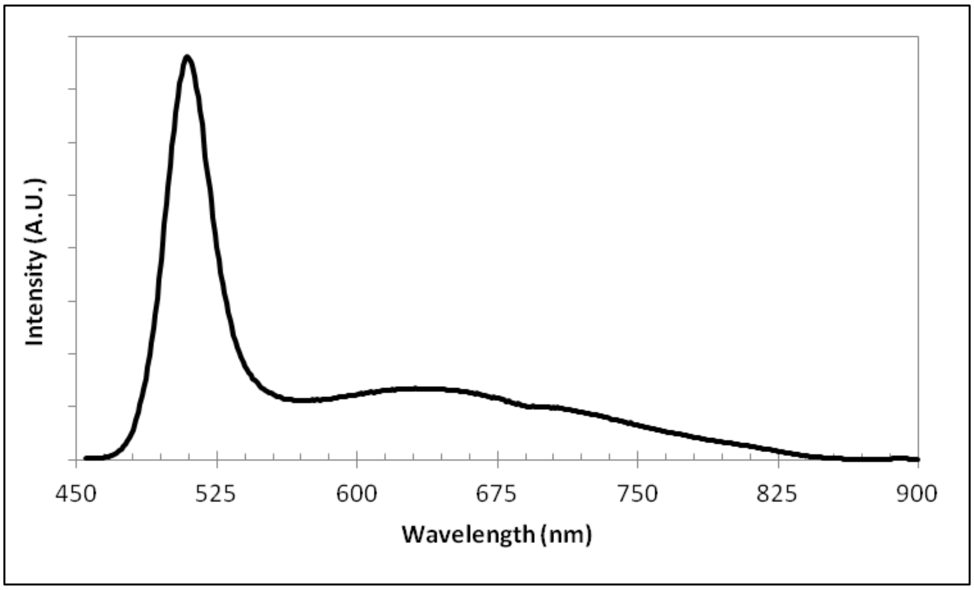

Figure 6. Fluorescence spectrum shows a lower level of monodispersity. Broad peak indicates the presence of quantum dots of various dimensions (broad shoulder between 550-820nm). The peak at 520 nm indicates the presence of smaller QDs compared to those in the first batch.

Figure 6 shows the fluorescence spectrum of the second batch of CdSe quantum dots. Compared to the first batch prepared, this solution possesses a lower level of monodispersity, which is indicated by the presence of a broad peak (shoulder) between 550 – 820 nm. As opposed to the first batch, the second batch contains a significant amount of smaller CdSe quantum dots, as shown by the presence of a sharp peak at about 520 nm.

B. Absorption Spectra

Absorption measurements were collected under three different conditions:

(1) Because direct contact with water leads to the degradation of the CdSe quantum dots and resazurin does not dissolve in nonpolar solvents such as toluene (water is a polar solvent, quantum dots are stored in toluene), methanol was used as the solvent. See Appendix A for results.

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[19] Que, Lawrence, Physical Methods in Bioinorganic Chemistry: Spectroscopy and Magnetism. Sausalito: University Science Books, **2010**. Print

(2) Still using methanol as the solvent, an electron donor (scavenger) such as Na_2S or Na_2SO_3, was used in order to replace the promoted electron in the CdSe seeds and avoid the nanoparticles' decomposition due to charge instability. See Appendix A for results.

(3) Water soluble CdSe quantum dots were synthesized as indicated in the *Synthesis of water-soluble CdSe quantum dots* section of this document. The reduction reaction of resazurin to resorufin is carried out in aqueous environment at pH ~12.

The final condition, which was also the most challenging to produce, guaranteed the interaction of the CdSe quantum dots with the resazurin molecules because there existed the possibility that when carrying the reaction in methanol, the quantum dots would be "trapped" in toluene bubbles.

The absorption spectra in **Figure 7** are from batches 1 and 2 of CdSe quantum dots. The spectra further support the results of the fluorescence measurements. Relative to the absorption spectrum of the second batch, the QD-exciton band of the first batch is red shifted. Because the QD-exciton band of the absorption spectrum of the second batch is located at 492 nm (short wavelength), these quantum dots are smaller compared to the quantum dots in the first batch. To determine the size (diameter) of the QDs, the location of the QD-exciton band is considered along with the absorption intensity at that location. This corresponds to the peak located at 581 nm in the case of the first batch and at 492 nm in the case of the second one,. The absolute size was determined with a calculator provided by group members of the Jain lab[20]. According to the calculator, the average diameter of the CdSe quantum dots were 3.85 nm and 2.27 nm for solutions 1 and 2, respectively. This is consistent with the trends observed from fluorescence spectroscopy of the two batches of QDs.

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[20] Jain, P.K. Personal communication. Summer 2012.

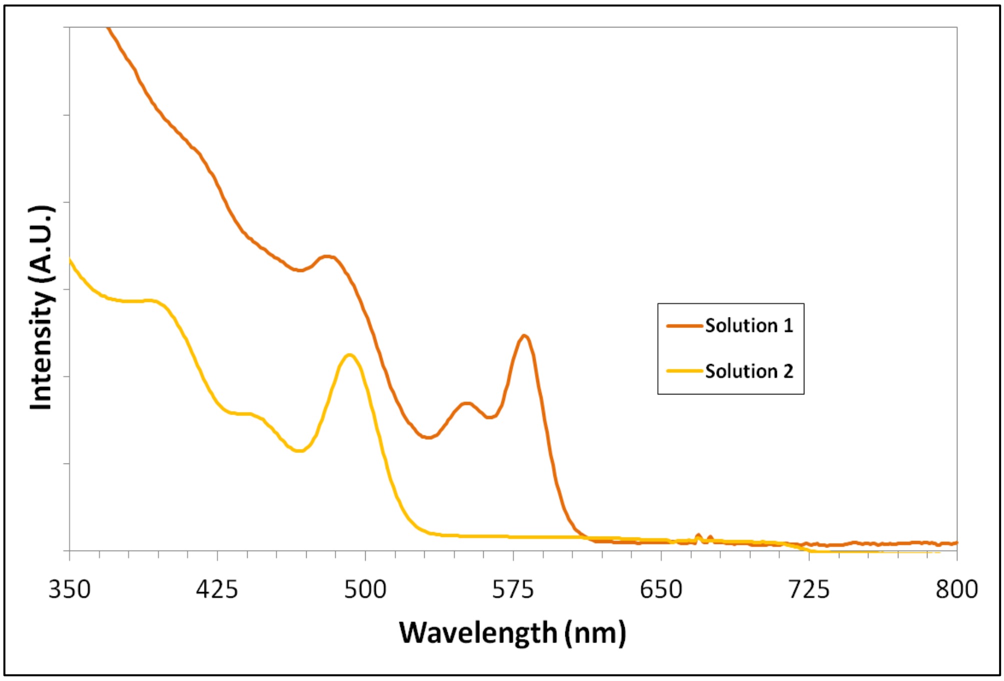

Figure 7. Absorption spectra of two batches of quantum dots. Spectrum of first synthesis is red shifted relative of the spectrum of the second batch, which indicates the presence of bigger CdSe nanoparticles.

Water solubilization of the CdSe quantum dots was corroborated using absorption spectroscopy as well. **Figure 8** shows the absorption spectra of the quantum dots of the second batch before and after water solubilization. The spectra in **Figure 8** suggest that water soluble CdSe quantum dots shared electronic properties with those synthesized according to the procedure outlined above. This is because the absorption spectra of both solutions are similar: the QD-exciton band is located at 492 nm in both spectra and the overall shape of the curve is similar, which suggests that the nanoparticles remained intact.

This is important and indicates that attachment of mercaptoundecanoic acid to the surface of the nanoparticles does not affect their optoelectric properties. The spectra vary in intensity because the water soluble quantum dots were made from an aliquot of the second batch. This means that they were present in lower concentration.

The photocatalytic capacity of the CdSe quantum dots in the resazurin-resorufin system was evaluated through absorption measurements. Because both resazurin and its reduced form (resorufin) possess a unique absorption spectrum (signature), a change from resazurin's spectrum to that of resorufin's was expected to be observed in the presence of CdSe quantum dots only and upon light exposure. Resazurin is highly absorbent at 602 nm, with two other minor peaks between 350 – 400 nm. Resorufin (reduced for of resazurin) absorbs at 572 nm[21].

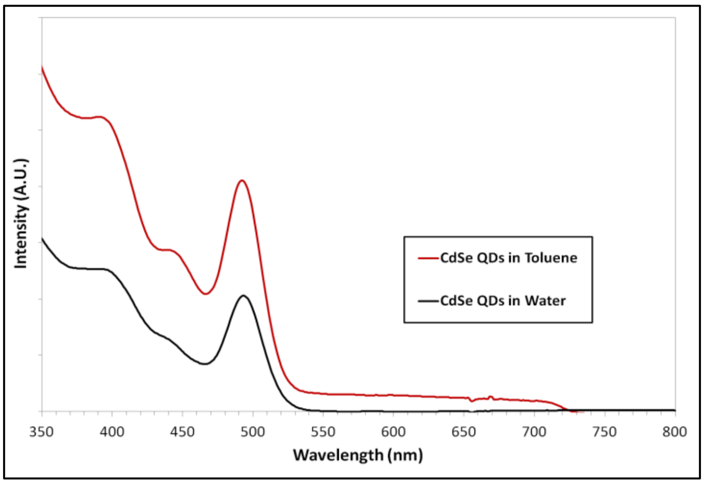

Figure 8. Absorption spectra of CdSe quantum dots before and after water solubilization. The similarity of the spectra indicates that the nanoparticles remain intact after attachment of MUA chain, which was needed for water solubilization.

The results of the study of the photocatalytic properties of the water soluble CdSe quantum dots are summarized in the following table:

Table 1

Resazurin control conditions	Dark	Light
No QD	No photo reduction	No photoreduction
With QD	Limited photo reduction*	PHOTOREDUCTION OBSERVED

*See Appendix B

Spectra of a solution of resazurin shown in **Figure 9** demonstrated photoreduction of resazurin in the presence of water soluble CdSe quantum dots. Before illuminating the sample (time = zero), the spectrum of the aqueous solution of resazurin containing the nanoparticles matches that of pure resazurin (peaks at 602 nm and between 350 - 400nm). This spectrum also shows the QD-exciton band at 492 nm, indicative of their presence in the solution. After 15 min of light exposure however, we observe that the 602nm resazurin peak decreases and another

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[21] C. Bueno, M.L. Villegas, S.G. Bertolotti, C.M. Previtali, M.G. Neumann, and M.V. Encinas; The Excited-State Interaction of Resazurin and Resorufin with Aminesin Aqueous Solutions. Photophysics and Photochemical Reaction; *Photochemistry and Photobiology* **2002** 76: 385–390

peak appears at about 572 nm. This absorption spectrum matches that of resorufin, the reduced form of resazurin. As a reference, an absorption spectrum of resorufin is included[22]. The fact that the exciton peak at 492 nm remains sharp and is of similar (or even more) intensity also demonstrates that the CdSe quantum dots remain intact after complete photoreduction has occurred. A shoulder of unknown origin grows between 600 – 750 nm (partially cut off in the figure). The features of resazurin between 350 – 400 nm also disappear from the spectrum after photoillumination, which is further evidence of photoreduction of resazurin to resorufin, since these peaks are not present in the resorufin absorption spectrum.

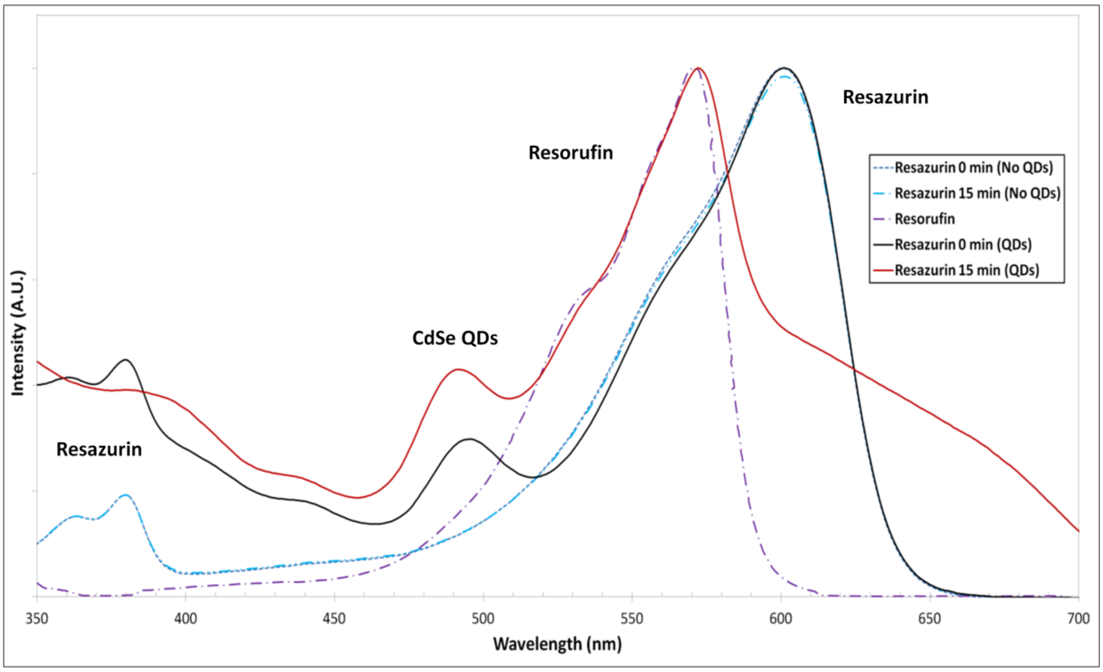

Figure 9. Absorption spectra of resazurin in the presence of quantum dots. After a period of light exposure photoreduction is observed as the peak growing at 592 nm matches that of resorufin. The water soluble CdSe quantum dots are also preserved after reduction. The data are summarized in Table 1.

IV. Discussion

As hoped, the water soluble CdSe quantum dots synthesized in this project were capable of catalyzing the reduction of resazurin. Absorption spectra showed that the water solubilization procedure did not affect the optoelectric properties of the quantum dots. Additionally, the CdSe

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[22] invitrogen.com. **2013**. Product Spectra | Life Technologies. Web. 22 March 2013.

quantum dots appear to have remained intact after complete photoreduction of resazurin. The spectra showed a slight blue shift in the location of the QD-exciton band. Nevertheless, this indicates that these nanoparticles can be reutilized for photocatalysis, which is of special importance in industry and hydrogen gas production. Quantum dot preservation also makes this model system suitable for single particle measurements with fluorescence microscopy because the reduction reaction proceeds without significantly affecting the nanoparticles.

Absorption spectra of the redox reaction of resazurin showed a growing peak between 600 – 750 nm. The origin of this feature is unknown and could belong to by-products caused by the reaction of impurities (some MUA present) with resazurin and possibly quantum dot aggregates. Compared to previous research however, an electron donor (scavenger) was not necessary to trigger photoreduction[5].

V. Conclusions

Synthesis of water soluble CdSe quantum dots was performed by attaching mercaptoundecanoic acid chains to the surface of the nanoparticles and deprotonation of the carboxylic acid with tetramethyl ammonium hydroxide. Absorption and fluorescence spectra of two batches of (non-water solubilized) quantum dots are consistent with the idea that the optoelectrical properties of these nanoparticles depend on their size. After the water solubilization procedure, the spectral signature of the CdSe remains intact, as shown by absorption measurements. Thus, we conclude that the CdSe structures themselves remain intact.

Preliminary results also demonstrate the capacity of these water soluble CdSe quantum dots to catalyze the photoreduction of resazurin. After light exposure (or photoillumination), an absorption spectrum of an aqueous resazurin solution containing quantum dots matches that of resorufin. An unknown shoulder grows between 600 – 750 nm. This could be originated by impurities present in the aqueous solution of the quantum dots.

Finally, after comparison of the QD-based exciton band of the absorption spectrum before and after photoreduction, it is also clear that the quantum dots are preserved (remain intact) after the photoreduction has been completed.

VI. Future Work

Further synthesis of water soluble CdSe quantum dots should be attempted in order to perfect the purification procedure. Additionally, more data to support the photoreduction of resazurin due to the presence of the nanoparticles and determine the origin of the unknown shoulder.

VI. Acknowledgements

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Appendix

Appendix A. Results of other experimental conditions for the study of the resazurin-resorufin redox system.

Argon atmosphere and methanol

In this section, results of other experimental conditions under which the resazurin-resorufin system was studied are shown. **Figure 10** shows photoreduction resazurin in the absence of CdSe quantum dots. According to a member of the Jain Lab, this behavior has been observed when resazurin is present in methanol.

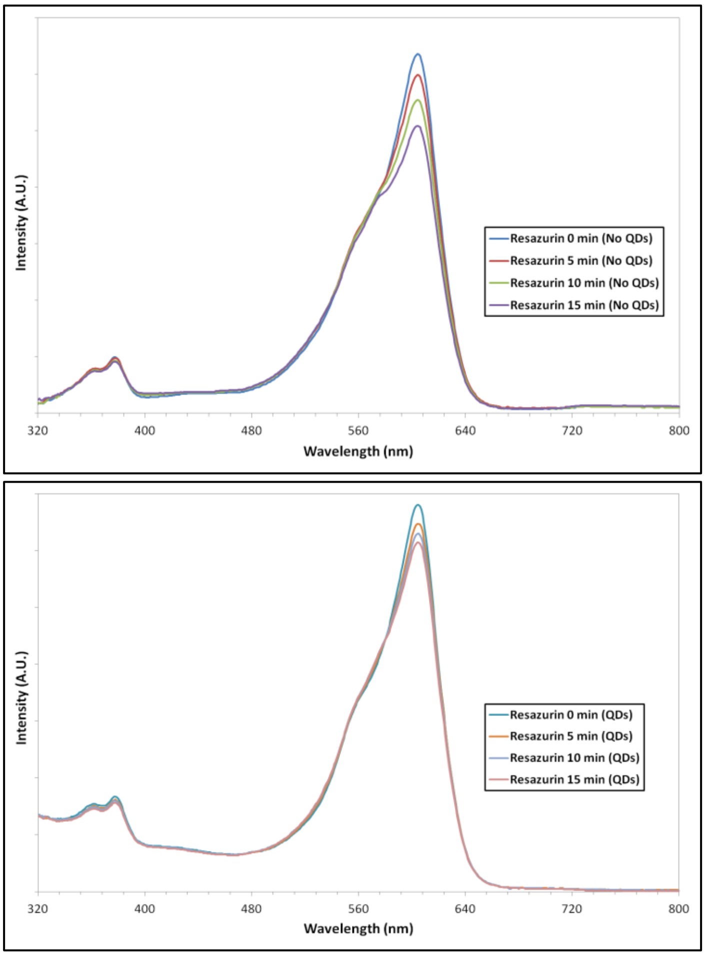

Figure 10. Absorption spectra of resazurin in methanol. Data shows that the quantum dots inhibit photoreduction.

These experiments were performed using the first batch of CdSe quantum dots, which were not subject to the water solubilization procedure. The absorption spectra (both top and bottom) does not show the quantum dots present in solution. This could be for two reasons: (1) because the quantum dots are suspended in toluene, they do not mix with the rest of the solution and are located at the top of it (outside the path of beam of the spectrophotometer), or (2) because the QD-exciton band of the CdSe quantum dots is located at longer wavelength (first batch), the spectrum is masked by resazurin, which is present in much higher concentration.

When the quantum dots are present, however, the reduction of resazurin seems to be inhibited, which might be caused by the decomposition of the quantum dots because of methanol.

Experiments in the presence of an electron donor and methanol

The following data was collected with Na_2S/Na_2SO_3 present in solution in order to replicate the result obtained by Osterloh *et al*[3]. As can be seen, photoreduction is observed regardless of the presence of the CdSe quantum dots in solution.

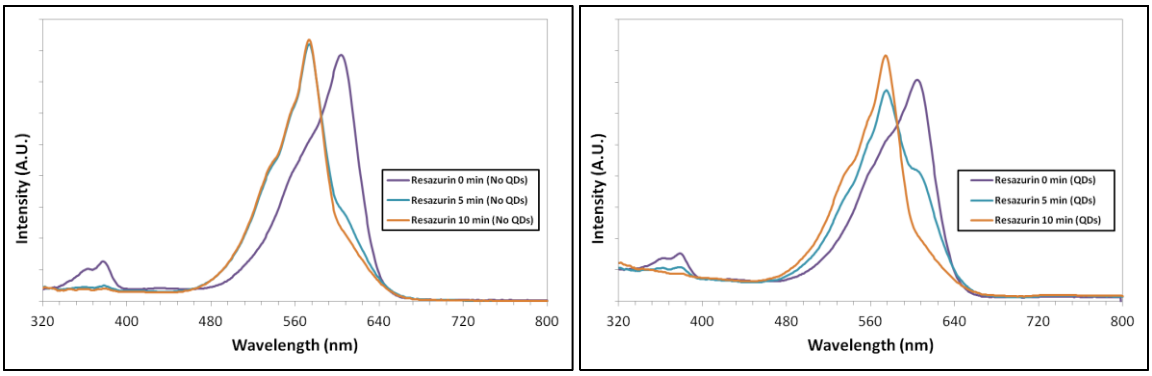

Figure 11. Absorption spectra of resazurin in methanol with Na_2S or Na_2SO_3. Photoreduction is observed regardless of the presence of quantum dots in solution.

Appendix B. Limited photoreduction in the presence of water soluble CdSe quantum dots and the absence of light.

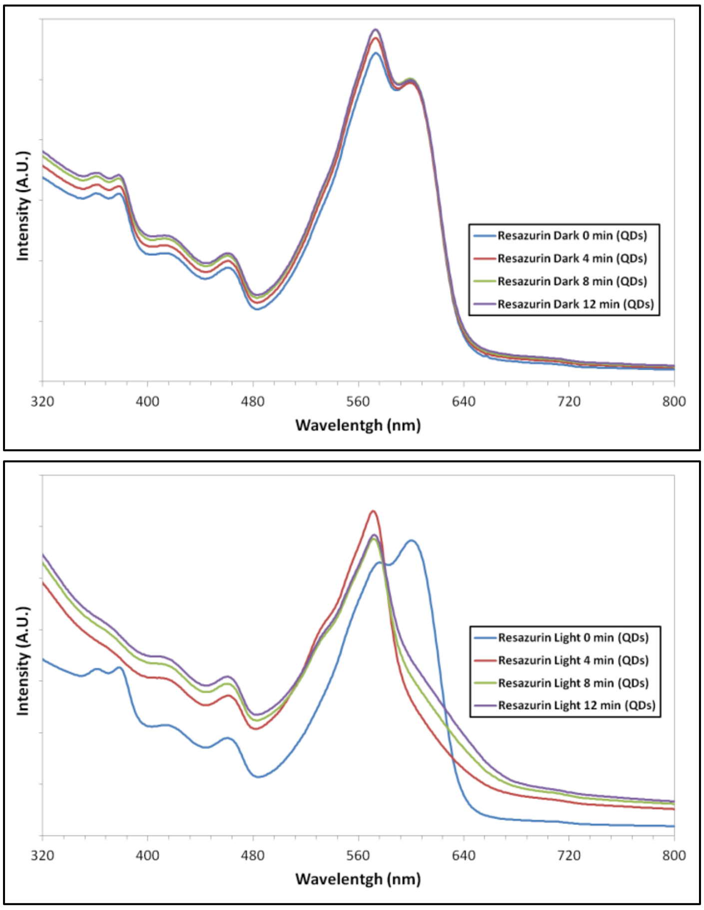

Figure 12. Absorption spectra of aqueous solution of resazurin with CdSe quantum dots. Reduction is observed in the absence of light which might be caused by the presence of impurities.

Figure 12 shows the results of an attempt to replicate the photoreduction of resazurin due to the presence of the water soluble CdSe quantum dots and light exposure. Photoreduction is observed in the absence of light as well (top), which is due to inappropriate purification of the water soluble quantum dots. More data should be collected however, in order to support this conclusion.

It is important to notice that light exposure increases reduction of resazurin which reinforces the conclusion of the main document: it is possible to photocatalyze the reduction of resazurin using CdSe quantum dots and demonstrates that they are a viable photocatalysts to trigger the water splitting reaction.

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