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Plasmon-Exciton Interactions in All-inorganic Nanocrystal Thin Films

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HONORS PROJECT

Submitted to the University Honors Program at Bowling Green State University in partial fulfillment of the requirements for graduation with UNIVERSITY HONORS

29 April 2013

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Abstract
Weak coupling regimes between metallic nanoparticles and semiconductor quantum dots have been shown to increase efficiency in quantum dot solar cells by 80%. This phenomenon is also known to scale up non-linearly. Increasing the efficiency of solar cells with the use of plasmon-exciton coupling will help solar cells to become competitive with other energy sources.

Another weakness of current quantum dot solar cells is the thermal, chemical, and electrical instability that ligand-terminated nanocrystals are subject to. Our new SMENA encapsulation matrix increases thermal stability of the nanocrystal array by using large band-gap semiconductor shells to cap the exciton generating core. These semiconductor shells lead to much greater thermal stability and refractive index of the film.

For this Honors Project, a study of fluorescent thin films has been conducted. This study intended to utilize the SMENA methodology, as well as localized surface plasmon resonance to show that metallic nanoparticles might be used to increase NC solar cell efficiency.

Introduction
It has become clear that solar power is an important alternative to harmful fossil fuels. However, in many respects solar power is still not a practical solution. Traditional silicon solar cells are expensive. The monocrystalline silicon wafers necessary for silicon solar cells require high vacuum and high temperatures to fabricate (1). Semiconductor nanocrystals (NCs), however, present a possible alternative to expensive silicon solar cells. In contrast to silicon solar cells, semiconductor NCs can be synthesized at low temperatures, making them inexpensive and simple to produce.

At the moment, NC solar cells are much less efficient than silicon solar cells (2). Current efficiencies of NC solar cells do not permit them to be competitive with traditional solar cells. Inefficiencies in NC solar cells come from several sources. First of all, semiconductor NCs have poor stability in heated or oxygenated environments (3). This is a result of surface-passivating organic ligands that can be oxidized in air. When these ligands are oxidized, they leave unpassivated surfaces, known as trap states, which can cause energy to be lost. NC solar cells also suffer from a low mobility of electrical charges. Our previous research (3) aimed to address these concerns by creating a new method for creating solar cells.
We presented a method for creating an all-inorganic NC film. In this method, displayed in figure 1, we began by synthesizing semiconductor NCs and growing an insulating shell of another semiconductor NC around it. These colloidal NCs were then spin coated onto an FTO glass substrate and, using layer-by-layer methodology, we removed the ligands and fused the NC shells by heating. This produced an all-inorganic film. Pores between individual NCs were then filled through chemical bath deposition. This resulted in a Semiconductor Matrix Encapsulated Nanocrystal Array (SMENA). NC thin films fabricated in this way are more thermally and chemically stable than their organic/inorganic hybrid counterparts. The semiconductor shell, which stands in for organic ligands, in the role of surface passivation is much more resilient in the high temperature conditions that solar cells must endure.

We now aim to further enhance the efficiency of solar cells by taking advantage of localized surface plasmon resonance. Localized surface plasmon resonance is a phenomenon exhibited by metal nanocrystals. It occurs when a photon is incident on the NC, inducing an electric field, which moves conduction band electrons, inducing a current. This begins a back and forth movement of electrons within the NC which serves to focus light (4). Localized surface plasmon resonance has been shown to increase fluorescence in weak coupling regimes (5).

Our research takes advantage of this plasmon resonance by combing metal nanocrystals with semiconductor nanocrystals to create mixed thin films. Weak coupling regimes between metallic nanocrystals and semiconductor quantum dots have been shown to increase efficiency in quantum dot solar cells by 80% (5). This phenomenon is also known to scale up non-linearly. Increasing the efficiency of solar cells with the use of plasmon/exciton coupling will help solar cells to become competitive with other energy sources.

The phenomenon of plasmon resonance can be utilized in thin films by combining both metal NCs and semiconductor NCs. Au was selected as the metal NC and CdSe/CdS as the semiconductor NCs, as the absorbance peak of CdSe/CdS matches the resonance peak of Au, as shown in figure 2.
However, before we could create the thin films, we had several problems which needed to be solved. First, Au NCs are not lattice matched with CdSe/CdS. A film of the two NCs alone is not possible. Furthermore, we needed to electrically insulate the Au NC, and ensure that it remains thermally stable. To solve this problem, we grew non-epitaxially semiconductor shell around the Au NC. A ZnS shell was grown around the Au NC through ion exchange (6).

We first synthesized Au NCs. Ag shells were then grown on to the Au NCs. In the next step, the shell was polluted with sulfur anions. In the final step, the remaining Ag cations were replaced with Zn or Cd cations using ion exchange techniques. This resulted in Au/ZnS or Au/CdS core/shell heteronanostructures.

Once the NCs were synthesized, we tested them by the method shown below, in figure 3. The Au/ZnS and CdSe/CdS NCs were used to create fluorescent thin films. Our SMENA methodology was used for these films. Initially, 2 films were tested. One film of CdSe/CdS was made as a standard. A second film was made in proportions of 1 unit Au/ZnS : 50 units CdSe/CdS. Fluorescence lifetime (τ) was measured. Fluorescence lifetime tells us how quickly an excited electron recombines with its hole. When we test the lifetime of colloidal NCs we see a very long fluorescence lifetime. This is due to the lack of trap states in solution. This is in contrast to a rapid decrease in lifetime when NCs are placed in a film. When we create a film of NCs, trap states are created. Both through trap states and through tunneling, many of the electron-hole pairs never recombine and the efficiency of the film suffers. It is our hope to increase the lifetime of our NCs in a film, so that they will comparable to colloidal NCs. The measurements of fluorescence lifetime will test how the NCs fluorescence is affected by the Au nanoparticles. While this is a measure of fluorescence, it will be useful in helping us make a better solar cell.
Experimental Section

Materials

Selenium powder (Se, 99.5%; Acros), Tributylphosphine (TBP, 97%; Aldrich), 1-Octadecene (ODE, 90%; Aldrich), Cadmium Oxide (CdO, 99%; Strem Chemical), Stearic Acid (97%; Acros), ODA, Triocylphosphine (TOPO, 99%; Aldrich), n-Octadecylyphosphonic Acid (ODPA; PCI Synthesis), n-Hexylphosphonic Acid (HPA; PCI Synthesis), Tri-n-Octylphosphine (TOP, 97%; Strem Chemicals), Sulfur (S, 99.999%; Acros), Chloroform (anhydrous, 99%; Aldrich), Ethanol (anhydrous, 95%; Aldrich), Gold (III) Chloride (Au(III)Cl₃, 99%; Aldrich), Silver Nitrate (Ag(NO₃)₂, 99%; Aldrich), Zinc Nitrate Hexahydrate (Zn(NO₃)₂, 98%; Strem Chemical), Methanol (anhydrous, 99.8%; Aldrich), Acetone (Amresco), 2-Propanol (anhydrous, 99.8%; Acros), Octane (anhydrous, 99%; Aldrich), 3-Mercaptopropionic acid (3-MPA, 99%; Alfa Aesar) were used as received without any further purification. All reactions were performed under argon atmosphere by the standard Schlenk technique. Fluorine-doped tin oxide (FTO) glass (TEC 15, 12 14 Ω/sq) was obtained from Pilkington Glass. All Spectra were taken under UV/VIS Spectroscopy.

Methods

Synthesis of CdSe – To grow the CdSe NCs 0.158g Se was placed in a flask and put under Ar. 0.583 mL TBP was injected and the flask was sonicated to dissolve the Se. 1.73 mL ODE was then added. In another flask, .0256g CdO was combined with .0227g Stearic Acid and
2.53 mL ODE. This flask was heated to 200°C until almost clear and then cooled to room temperature. At room temperature, still under Ar flow, 1.5g ODA and 0.5g TOPO were added and the flask was heated to 280°C. The flask containing Se was added the second flask and cooked for 12 minutes. The NCs cleaned in chloroform and acetone, then stored in chloroform.

Synthesis of CdSe/CdS core/shells – The CdS shells was grown around the CdSe NC by the following process. A cadmium precursor was prepared of 3.00g TOPO, 0.29g ODPA, 0.08g HPA, and 0.60g CdO. This was heated to 150°C, and degassed and stirred for one hour. It was then cooled to room temperature. A second flask of 3ML TOP was degassed for one hour at 120°C. 2mL of the pumped TOPO was then injected into 0.12g S under Ar. This was heated to 200°C to dissolve the sulfur, then cooled to 120°C. At this point, the CdSe cores from the last step were injected and the solvent was allowed to evaporate. This was injected to the first flask and allowed to cook 7 minutes. The NCs were cleaned in chloroform and ethanol and stored in chloroform.

Synthesis of Au NCs – The Au NCs were synthesized by combining 0.011g Au(III)Cl₃ with oleylamine under Argon. It was heated to 100 degrees C for 30 minutes. The newly formed Au NCs were then precipitated out of oleylamine by adding ethanol and centrifuging the solution. The nanocrystals were then redissolved in toluene. Finally, they were size-selectively precipitated in toluene and ethanol.

Synthesis of Au/Ag NCs – To grow the silver shell around the gold nanocrystals, 0.062g Ag(NO₃)₂, 4.5 mL oleylamine, and 30 units of Au NCs were places under Ar and heated to 120°C. The absorbance spectrum of the solution was then measured regularly until the desired blueshift of the Au NCs' plasmon resonance peak occurred. UV/VIS absorbance was used to monitor the blue shifting by dissolving. A 40nm shift signaled a shell of appropriate thickness (2-3 monolayers) had been grown. Again, the nanocrystals were precipitated out of oleylamine using a similar technique as above. The Au/Ag NCs were then cleaned in 4:5 ratio of ethanol and toluene using size-selective precipitation.

Synthesis of Au/Ag₂S – For the Ag₂S shell, 2.0mL oleylamine was first degassed for an hour. 0.005g S was placed under Ar and the oleylamine was injected. This mixture was moved to another flask and diluted four times with more oleylamine. The Ag/Au NCs were then injected with the sulfur mixture drop-wise, while stirring, at room temperature. The spectrum of this mixture was checked regularly until the plasmon absorbance peak has disappeared. NCs were cleaned in toluene and ethanol under Ar.

Synthesis of Au/ZnS – In one flask, the zinc precursor was prepared. 0.080g Zn(NO₃)₂ and 1mL Methanol were placed under Ar and dissolved. The precursor was then added to a flask of the Au/Ag₂S. These were cooked and stirred for twenty hours. NCs were cleaned in toluene and ethanol under Ar.

Fabrication of Au/ZnS CdSe/CdS Thin Films – FTO-coated glass was cut into 1 inch x 1 inch squares and rinsed clean in deionized water. It was then sonicated in methanol, acetone, and 2-propanol for 5 minutes in each solvent. The substrates were then dried with Ar flow. To fabricate the film layer-by-layer methodology was used. All steps were performed inside the
glovebox. Typically, 8-12 drops of a combined solution of Au/ZnS and CdSe/CdS in octane were placed onto the FTO glass slide and allowed to spread until the substrate was covered. The NC solution was left to soak until the center dried and then spun at 2500 rpm for 40 seconds. Next, 10 drops of a 1:3 MPA/methanol solution was placed on the film, fully covering the surface, which was then spun at 2500 rpm for 10 seconds. The film was washed with 10 drops of methanol and subsequently spun at 2500 rpm for 10 seconds, then washed once again with 10 drops of octane in the same manner. The film was annealed at 150°C for 15 min after every two layers. Overall, 8-14 layers were used to make each of our films.

**Results and Discussion**

Once the films were created, following the methods above, their fluorescence lifetimes were tested. The data, shown below in figures 3 and 4, was not as expected. The fluorescence lifetime of the Au films had the same lifetime as a standard film, showing no enhancement. This result is puzzling; however, only one test has been run.

This may have been caused by poor quality of the test films. Unfortunately, despite following our standard procedure for creating the films, they were very transparent and rough. This could have something to do with the air sensitive nature of Au/ZnS NCs, as well as their tendency to fall out of solution. In the near future, we will work to refine these films to see if any fluorescence lifetime enhancement can be achieved. We will also be working to optimize the ratio of Au NCs to CdSe/CdS NCs if we do begin to see fluorescence enhancement.

Other project using plasmon resonance are also planned. We will be studying how plasmon-exciton interactions are affected by placing a potential barrier between them. We will also be working on creating solar cells that utilize localized surface plasmon resonance to enhance efficiency.

![Figure 3](image-url)
References


(1.5) Schneider and Decher, Nano Letters, 2006, Vol. 6, No. 3, 530-536.