Influence of Dithiocarbamate Cross-Linking Ligands on CdSe Quantum Dot Film Conductivity

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Abstract

Cadmium selenide (CdSe) quantum dots have low conductivity upon synthesis with the original capping ligands. The conductivity can be altered by the addition of other ligands. Thiols, amines, and carboxylic acids, as well as other functional groups, have been shown to improve conductivity in quantum dot films. This investigation describes the synthesis of alternate dithiocarbamate cross-linking ligands and determines their ability to either improve or inhibit the conductivity of CdSe quantum dot films.

Introduction

Semiconducting nanocrystals (NCs), referred to as quantum dots (QDs), are especially interesting because their fundamental properties of photoluminescence and conductivity can be altered by controlling their sizes, shapes, and interactions with other molecules or surfaces, fine-tuning them for uses across various fields.[1–5] These uses include medical imaging, environmental energy efforts, and engineering and scientific research, with the potential for economic development accompanying them all.[6]

Though many researchers have explored the properties of nanocrystalline structures, there is still only a fundamental level of understanding of the modification and optimization of charge transport through these structures. Modern-day solar cells use doped semiconducting solid materials to absorb light energy that eventually can be converted to electricity. The materials require extensive and expensive doping processes in order to generate the charge separation needed to move charge through the materials, resulting in the low efficiency of bulk semiconductor solar cells.[7] It has been hypothesized that QDs have the potential to increase the efficiency of solar cells.[8] QDs can be synthesized in colloidal solutions and can be attached to electrodes in solar cells to provide for a more flexible and inexpensive solar cell. The development of efficient charge transport in QD films can provide the basis for a more productive alternative to present-day solar cells.[2,9]

The purpose of this experiment was to use the inherent semiconducting abilities of cadmium selenide (CdSe) QDs and find a cross-linking molecule that interacts with CdSe QDs in order to produce a material with conductivity that is greater than that of CdSe QDs with original capping ligands.

Background

The properties of CdSe QDs have been extensively researched and are particularly attractive to study because the absorption spectra can easily predict the size of the QDs.[2,10] Also, when CdSe NCs are synthesized, they are spherical and monodisperse.[11] Monodispersity allows for the entire sample to be readily used for characterization and manipulation, eliminating the need to separate QDs by size after synthesis.

The inherent semiconducting abilities of QDs can be explained using two fundamental theories from quantum mechanics. The first, quantum confinement, explains how the electronic properties of QDs can be modeled using the wave-like features of electrons.[3] Quantum confinement limits the mobility of a particle to a scale on the order of the de Broglie wavelength. Every particle has wave characteristics, including electrons, and can be described by the de Broglie wave function: Since each particle has a distinct wavelength, if that wave is confined to a smaller volume, the energy of that particle increases. As a result, smaller QDs have higher band-gap energy absorptions.[12]

In addition to quantum confinement, electron tunneling can be used to explain the semiconducting abilities of CdSe QDs. Electron density can be modeled using a wave function. In a system of QDs, the spacing between each dot allows for the overlap of these electron wave

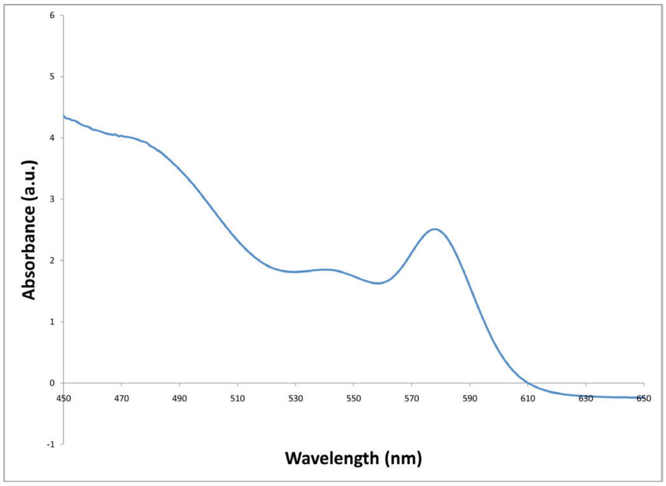

Figure 1. The ground-state absorption spectra of the CdSe QDs in chloroform with λ_{max} = 578 nm.

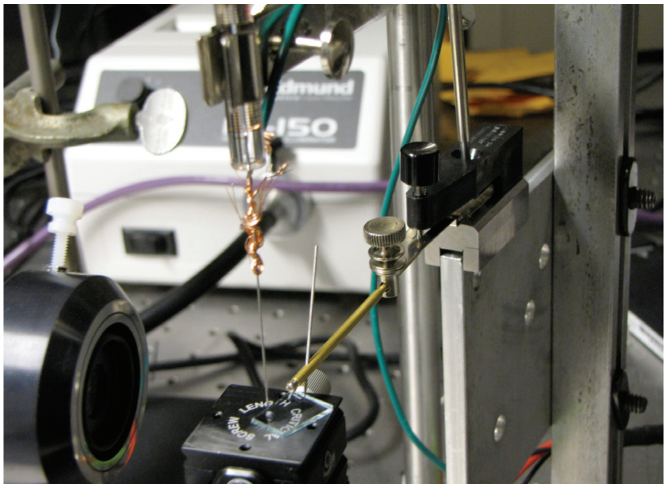

Figure 2. Digital photograph of the completed conductivity setup. Pictured are the ground electrode in contact with ITO (right), EGaIn electrode (left), and the camera used to measure the junction diameter between the EGaIn electrode and the sample.

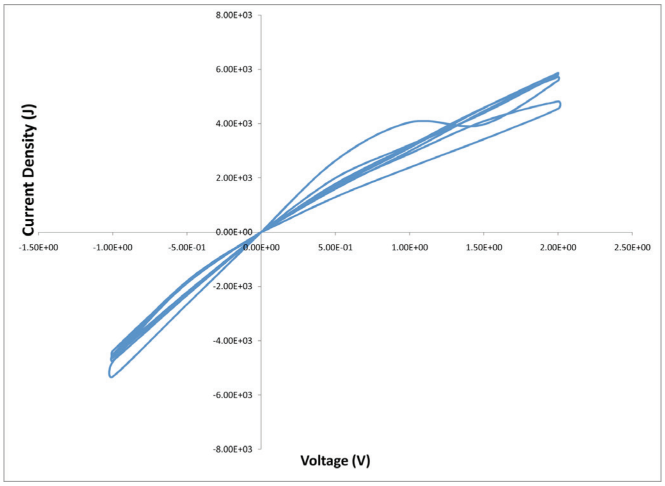

Figure 3. Voltage versus current density for a bare ITO slide.

functions. This distance either promotes or inhibits the ability of the electron to transfer to the adjacent dot. If electrons can tunnel between QDs, the system's overall conductivity improves.[3]

The addition of other cross-linking molecules can affect the conducting ability of an assembly of QDs. Ligands remain associated with the QDs upon synthesis,[11] and they can control the inter-QD spacing.[3] Cross-linking molecules can serve as electron tunneling bridges, which can drastically improve the conductivity of the QDs.[13] This investigation was undertaken to study the ability of linker molecules to facilitate electron tunneling through quantum dot assemblies.

Approach

Synthesis of CdSe QDs

The cadmium selenide QDs used were synthesized according to the methods performed by Qu and coworkers.[11] All CdSe QDs were synthesized with a trioctylphosphine oxide (TOPO) capping ligand. The quantum dot samples were precipitated in methanol and redispersed in chloroform. Figure 1 shows the ultraviolet and visible spectrum of the QDs used to make films.

Spin Coating Films

Films of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and CdSe QDs were used in the conductivity experiments. A 3:1 water-PEDOT:PSS solution was made for film conductivity measurements. A film of the PEDOT:PSS was first spin coated[14] at 5,000 RPM for 1 min on a glass slide coated with tin-doped indium oxide (ITO). ITO is commonly used as a conducting oxide for electrodes.[2] After the addition of PEDOT:PSS, the slide was annealed for 3.5 hr at 125° C to ensure a dried sample. The QDs were then added to the PEDOT layer using the same spin-coating technique. A small corner was left bare to expose pure ITO to use as a blank during the experiments. The ligands were added by dipping the slides into a 10 mM solution of the molecules dissolved in methanol. After treatment, they were annealed at 125° C for 1 hr.

Synthesis of Dithiocarbamate Ligands

Two dithiocarbamates were synthesized in this experiment. Sodium benzyldithiocarbamate (BDT) was prepared according to a modified procedure of Hodgkins et al.[15] Disodium p-phenylenebisdithiocarbamate (PBDT) was synthesized according to a modified procedure outlined by Wessels et al.[1] Collection and extensive analysis of ^{13}C and ^{1}H NMR spectra verified that the compounds synthesized were the desired ligands.

Conductivity Measurement Setup

A setup using eutectic gallium indium (EGa-In) as an electrode was constructed. EGa-In is used to study charge transport across self-assembled monolayers.[2,16] The EGa-In electrode was formed by suspending a drop of EGa-In from a 10 μL syringe, bringing the drop into contact with a sacrificial film of Ag, and retracting the needle slowly. The EGa-In adhered to both the needle and the Ag.[16] The EGa-In tip protruded from the needle and was then placed on the sample. The ground electrode attached to the subfemptoamp remote sourcemeter was brought into contact with the bare ITO portion of the slide. The completed setup is pictured in Figure 2.

Results

Data were gathered using a Keithley subfemptoamp remote sourcemeter. The thickness of the cross-linking molecule films was not calculated, but the slides were suspended in the solution for a consistent time period. The voltage (V) and current density (J) relationships were compared graphically. The slides compared included a bare ITO slide, a slide with one layer of PEDOT, a slide with a monolayer of QDs, and multiple slides with the various ligands. No particular attention was paid to the consistency of the distance between the EGaIn electrode and the detecting electrode. The voltage applied to all films remained consistent at +1 V to -2V. Current density was recorded for all samples.

Figure 3 shows the graphical representation of the current density of a bare ITO slide. The linearity of the graph indicates that charge moves in both the positive and negative directions — in other words, the

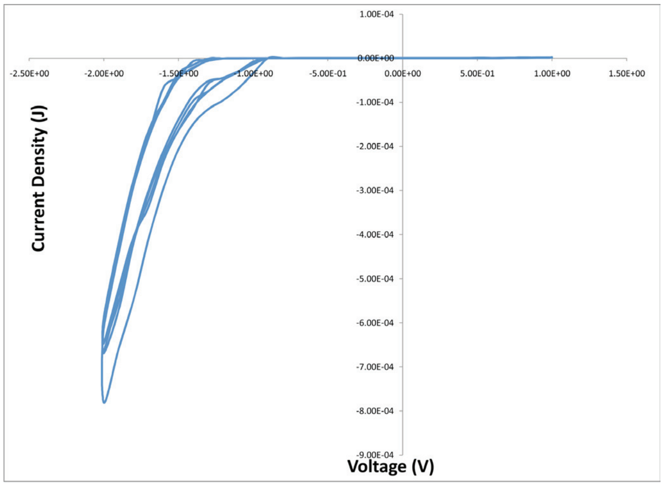

Figure 4. Voltage versus current density for a slide with a PEDOT:PSS layer.

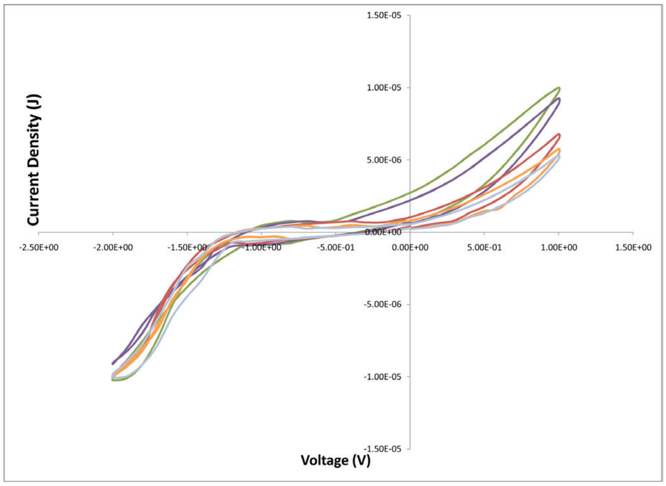

Figure 5. Voltage versus current density for a slide with a PEDOT:PSS layer and a QD layer.

material is highly conductive. The multiple traces on the graph indicate multiple scans that were taken on the same film sample. This graph was formulated for comparison with the other slides used in the experiments.

Figure 4 shows the current density as a function of voltage for a slide with a layer of PEDOT:PSS. This layer is a hole-transporting conductive polymer, meaning it can only carry a positive charge. As a result, there is a rectifying current through the film. A rectifying current is ideal because the charge will only be flowing in one direction, resulting in diode formation in the film — the basis of the solar cell photodiode.

The scans taken with TOPO ligands on the QDs were all ohmic, and hysteresis is prominent. This suggests that the quantum dot films with original capping ligands have some holes or defects that prevent a rectifying current and an even scan. The TOPO ligands have long alkyl chains that can prevent the current from flowing uniformly, resulting in a defect current, which is shown in Figure 5. In addition, after approximately six scans on the film, the consistency between scans began to diminish. The overall consistency of the films with TOPO ligands on the QDs is low and is not reproducible because of defects in the film.

When the BDT ligand is added to the QD films, the current density observed was only slightly ohmic; current flows in both forward and reverse directions. Ohmic behavior is not as evident as it was with the QD film with TOPO ligands, suggesting that the ligands allow for a more rectifying current. This may be due to the ligands' ability to correct any defects that may have been in the QD film with original ligands. Additionally, the ligand exchange removes the long alkyl chains of the original capping ligands that previously resulted in defective current. In addition, the current density increased by a factor of 10^2 between the quantum dot film with the BDT ligand and the QD film with original capping ligands. This shows that the ligand has an impact on the conductivity of the film. Additionally, there is less hysteresis in the graph, showing a more uniform and reproducible scan.

After the addition of PBDT, there was also an increase in current density. However, compared with the system that had BDT, the scan was not as uniform and exhibited more hysteresis. Generally, the scans were not as consistent as with BDT. Since PBDT is a bulkier molecule than BDT, it may either be unable to adhere to the surface of the quantum dot as well as BDT does or be too big to make a difference in the evenness of the film. BDT-exchanged QDs produce a better current density graph than do the QDs with TOPO.

Discussion

The proposed mechanism of the charge transport through the film is thoroughly outlined by Weiss et al.[12] The EGa-In electrode pumps electrons through the film, and CdSe, an n-type semiconductor, can move those electrons through the film. The PEDOT:PSS layer serves as a hole-transporting polymer that can move the positive charge from the ITO into the film. The PEDOT:PSS-QD intersection is the point where neither electrons nor holes are moving; charge recombination occurs at this junction. This setup creates a diode, which is necessary to form the photodiodes used in solar cell technology. The purpose of the ligand is to help facilitate this movement of electrons through the film, and the results indicate that the ligands studied exhibit this effect. With the addition of BDT, the movement occurs relatively uniformly through the film and generally in one direction. The ligand allows for the correction of the defects in the QD film, resulting in a more efficient movement of charge from the EGa-In through the QD film. The current density observed through the BDT ligand-exchanged films is of higher magnitude than that of QD films having original capping ligands. This effect should be expected due to the molecules' predicted ability to delocalize charge and provide a better electron hopping junction. As for PBDT, the expected higher current density was achieved but not at the magnitude expected. PBDT is expected to delocalize the charge better than BDT does, but the observed current density does not reflect this. Another factor is the spacing of the molecules between the QDs, which can influence the behavior of the QDs.[3] If there is a small enough space between QDs for the electrons to hop through the sample to the charge recombination junction, the system's conductivity will improve. The decreased current density from the PBDT-exchanged QDs may be explained by this phenomenon.

Conclusions

Quantum dot film conductivity is of great importance to the field of nanotechnology due to its direct applications in solar cells. This investigation attempted to modify the CdSe QD film conductivity

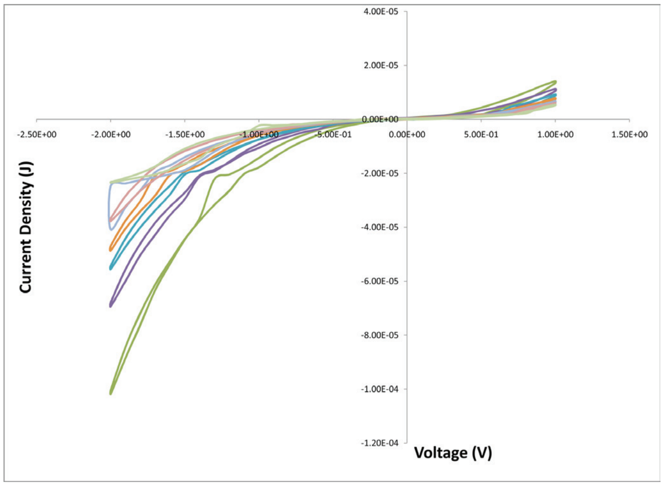

Figure 6. Voltage versus current density for a slide with a PEDOT:PSS layer and QDs after ligand exchange with BDT.

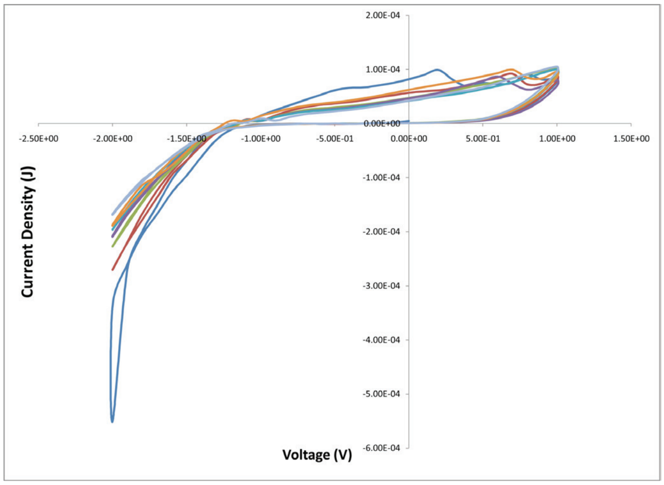

Figure 7. Voltage versus current density for a slide with a PEDOT:PSS layer and QDs after ligand exchange with PBDT.

by the addition of dithiocarbamate cross-linking molecules. The reported results contribute to a larger research project that addresses the overall charge transport through quantum dot films. The results indicate a promising future for the use of quantum dot films in solar cells. The ligand exchanges and additions affect the conductivity of the films, but without extensive statistical analysis of the films, the degree of improvement is undetermined. These preliminary results show an increase in the current density and a substantial rectifying current through the film. It would be useful in future work to establish the magnitude of improvement, as well as ways to maximize the effects of the ligand on the conductivity of the film.

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