

Cadmium Selenium Quantum Dot Photodiodes

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Abstract

A simple cadmium selenium (CdSe) quantum dot photodiode was assembled. The device is composed of two electrodes, indium tin oxide (ITO) and ITO/titanium dioxide (TiO₂) plates, two layers of 3-mercaptopropionic acid, and a thin layer of CdSe quantum dots. With this simple configuration, photocurrents up to 0.5 μ A were detected under room light excitation. In addition, the diode photocurrent action spectra closely resembled the absorption spectrum of the parent colloidal CdSe quantum dots, indicating CdSe-TiO₂ coupling. Most interestingly, cyclic voltammetry scans revealed the photodiode properties of the device.

Introduction

The emission and absorption spectra of CdSe quantum dots are highly tunable making this one of the most studied nanocrystalline semiconductors. TiO₂ is widely used as an anode material in photovoltaic cells due to its superb performance as a charge carrier. Therefore, a CdSe/TiO₂ coupled system is expected to be an efficient and tunable photoanode.

In the past, CdSe and CdSe/TiO₂ systems have been grown from their precursors on a substrate [1,2]. Such methods yield a densely packed, well-connected nanocrystalline structure, in which the CdSe absorbs visible photons, while the TiO₂ network acts as a charge transfer system. In previous reports, however, the size and shape of the CdSe quantum dots could not be precisely controlled. In contrast, direct deposition of as-prepared quantum dots on TiO₂ coated substrates fails due to poor CdSe-TiO₂ coupling.

Here, we demonstrate an alternative method to assembling an effective photoanode using colloidal CdSe quantum dots and an intermolecular linker, 3-mercaptopropionic acid. The acid linker is a bifunctional molecule in which the thiol group on the linker binds to the CdSe quantum dots, while the carboxylic acid group attaches to the TiO₂ network.

Experimental Procedure

Chemical Preparation. Colloidal CdSe quantum dots were synthesized using the hot injection method as described in Qu, et al., 2001 [3]. By washing extensively with butanol and toluene, excess ligand in solution and on the surface of the CdSe quantum dots were removed. The bare nanocrystals were then suspended in tetrahydrofuran (THF) (Solution 1). In addition, 3-mercaptopropionic acid was diluted in ethanol (Solution 2). Lastly, 0.66 mmol of TiO₂ nanoparticles and 5 drops of polystyrene spheres were suspended in 10 ml of ethanol (Solution 3).

Electrode Preparation. Indium tin oxide (ITO) was chosen due to its transparency and low cost. ITO plates were cut into

rectangular pieces, approximately 0.5 \times 1.0 in. in dimension. After cleaning with ethanol and toluene, half of the cut ITO plates were spin-coated with Solution 3. These plates were then annealed at 450°C for 30 minutes. Before being stored under dry condition, the plates were rinsed thoroughly with ethanol.

Device Assembly. Solution 2 was drop-coated onto the TiO₂ coated ITO plate. When most of the ethanol had evaporated, Solution 1 was deposited. It took a few hours for the THF to evaporate. After that, an uncoated ITO plate was offset on top, and the whole device was secured using binder clips. Finally, copper tapes were pasted on the edges of the electrodes to enhance electrical connections. The cross sectional view of the device is shown in Figure 1.

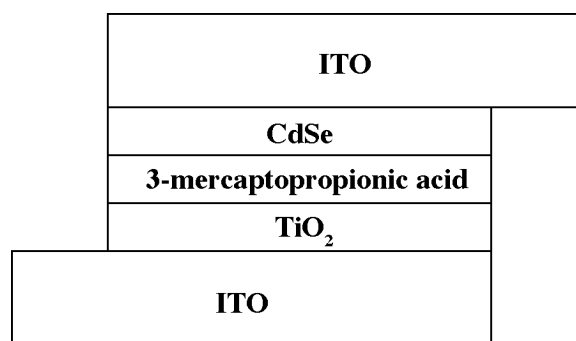


Figure 1: Device configuration (drawing not to scale).

Characterization. All measurements were done using MicroAutoLab-TypeII apparatus.

Result and Conclusions

In Figure 2, the incident photo-to-current conversion efficiency, IPCE4, spectra resembled the absorption spectrum of CdSe colloidal quantum dots at wavelengths longer than 520 nm. In

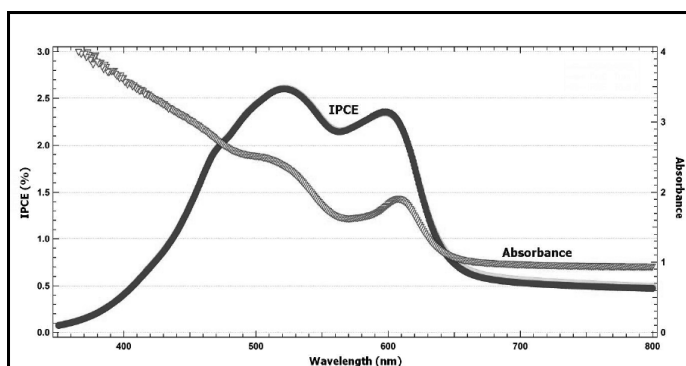


Figure 2: Photocurrent action and absorbance spectra (monochromator rate at 1.44 nm/s; applied potential at 1.0 V).

other words, CdSe quantum dots were producing current under photo-excitation.

The most cyclic voltammetry characteristics of the device are presented in Figure 3. The observed current at 1.0 V is 13 times greater than that at -1.0 V. In addition, the cell shows ohmic behavior from 0.0 V-1.0 V. This cyclic voltammetry scan provides strong evidence that the cell possesses photodiode characteristics.

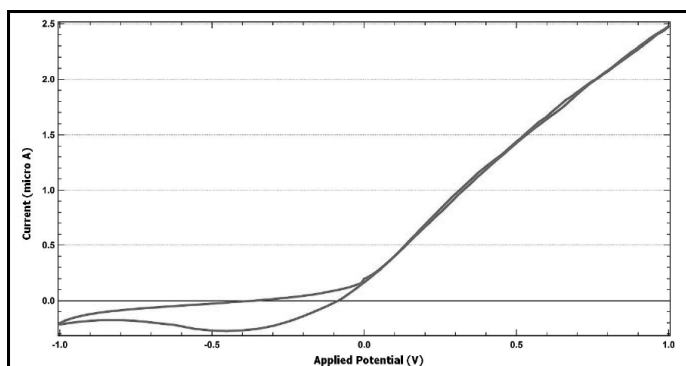


Figure 3: Cyclic voltammety scans (scan rate at 0.001 V/s; 25 cm below a 20 halogen lamp).

The proposed photoelectrical mechanism of the CdSe-TiO₂ coupled system involves electron tunneling. Upon irradiation, CdSe quantum dots absorb energy and promote electrons from the valence band to the conduction band (exciton generation). The applied voltage then helps inject the excited electrons into the TiO₂ network, and subsequently into the ITO and the closed circuit. Since the valence band offsets between CdSe and either TiO₂ or ITO are large, the holes are confined to the CdSe. In contrast, the conduction band offsets between CdSe and TiO₂ and ITO are relatively small. With sufficient applied potential, electrons could “hop” from the plain ITO plate to re-fill electron deficiencies (see Figure 4).

The probability of successful electron tunneling decreases exponentially with distance. Thus, the ideal position of the holes

is in the middle of the film. If the film were too thick, electron tunneling would be greatly inhibited. If the film were too thin, there would not be enough CdSe quantum dots to absorb the photons.

The film used in this project was fairly thick (~ 50 μm). Since the absorption spectrum of the CdSe-TiO₂ system increased dramatically at shorter wavelength (< 500 nm), most photons were absorbed well before they reached the middle region. As a result, charge separation was less efficient and less photocurrent was detected. The decrease in IPCE at wavelengths shorter than 520 nm in Figure 2 is therefore due to the large film thickness.

In conclusion, CdSe-TiO₂ coupled photoelectrodes were successfully prepared using 3-mercaptopropionic acid as a linker. A simple device assembled from these photoelectrodes showed high sensitivity to various wavelengths and possessed photodiode properties.

Acknowledgements

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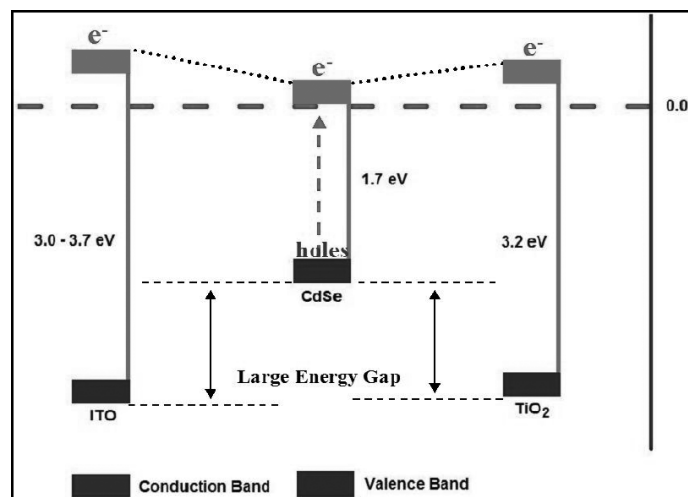


Figure 4: Electron tunneling.