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Highly Efficient CdS Quantum Dot-Sensitized Solar Cells Based on a Modified Polysulfide Electrolyte

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S *Supporting Information*

ABSTRACT: A modified polysulfide redox couple, $[(CH_3)_4N]_2S/[(CH_3)_4N]_2S_n$, in an organic solvent (3-methoxypropionitrile) was employed in CdS quantum dot (QD)-sensitized solar cells (QDSSCs), and an unprecedented energy conversion efficiency of up to 3.2% was obtained under AM 1.5 G illumination. The QDs were linked to nanoporous TiO_2 via covalent bonds by using thioglycolic acid, and chemical bath deposition in an organic solvent was then used to prepare the QDSSCs, facilitating high wettability and superior penetration capability of the TiO_2 films. A very high fill factor of 0.89 was observed with the optimized QDSSCs.

Dye-sensitized solar cells (DSSCs) have been investigated extensively during the past two decades, since O'Regan and Grätzel first reported them in 1991.[1] As an alternative, quantum dot (QD)-sensitized solar cells (QDSSCs) have attracted much attention recently because of their efficient charge separation and transport.[2−4] QDs that absorb light in the visible region, such as CdS, CdSe, and PbS QDs, have been used as sensitizers for QDSSCs.[5−9] The advantages of the QD sensitizers over conventional dyes are their quantum-confinement effect (including impact ionization), Auger recombination, and the miniband effect.[10−13] These effects are known to increase the exciton concentration, quantum yield, hot-electron lifetime, and consequently the performance of QDSSCs. Another advantage of the QD sensitizers is their high extinction coefficient, which is known to reduce the dark current and increase the overall efficiency of a solar cell.[14]

Although much effort has been devoted to the development of QDSSCs, their photovoltaic efficiency is still relatively low. One major challenge in this field is how to assemble QDs into the mesoporous TiO_2 matrix to obtain a well-covered monolayer. Bifunctional linker molecules such as thioglycolic acid (TGA) are commonly used to bridge the TiO_2 surface and the QDs, which are prepared by chemical bath deposition (CBD).[15] In this work, we used these two methods to synthesize a CdS-sensitized TiO_2 electrode. The highest efficiency reported to date for a CdS QDSSC using an I^-/I_3^--based electrolyte and a Pt counter electrode is 1.84%.[16] However, the I^-/I_3^- redox couple is corrosive to most metals and quantum dot materials, causing a rapid decrease in the photocurrent.[17] The selection of an appropriate iodine-free electrolyte in which the QDs can work stably without any significant degradation is critical for QDSSCs. The sulfide/polysulfide (S^{2-}/S_n^{2-}) redox couple in aqueous or aqueous/organic solution has been reported to stabilize the QDs.[18−20] Peng and co-workers reported an efficiency of 4.15% with a short-circuit current density (J_{SC}) of 7.82 mA cm^{-2}, an open-circuit photovoltage (V_{OC}) of 1.27 V, and a fill factor (FF) of 0.578 for a QDSSC using a CdS-sensitized TiO_2 nanotube array as the photoanode and a 1.0 M aqueous solution of Na_2S as the electrolyte.[21] However, integration of their incident photon to electron conversion efficiency (IPCE) spectrum showed that the J_{SC} should be less than 4 mA cm^{-2}, which is much less than their observed value (J_{SC} = 7.82 mA cm^{-2}), indicating that their reported 4.15% efficiency is in doubt.

In this paper, we report a new CdS-functionalized QDSSC in which tetramethylammonium sulfide/polysulfide, $[(CH_3)_4N]_2S/[(CH_3)_4N]_2S_n$, was used as the redox couple in the organic solvent 3-methoxypropionitrile (MPN). The configuration of the cells is illustrated in Scheme 1. TiO_2 films were surface-modified by immersion in 0.1 M TGA followed by dipping first into a 0.5 M $Cd(NO_3)_2$ solution in ethanol and then into a 0.5 M Na_2S solution in methanol. The process was repeated up to N times (N = 1−5), and the corresponding electrodes are represented herein as "TiO_2/TGA/CdS-N". Details of the preparation of the TiO_2 photoelectrodes and the organic polysulfide electrolyte together with their optical properties and photovoltaic performances are presented in the Supporting Information.

The cell based on the TiO_2/TGA/CdS-3 photoelectrode was found to give the best performance in this series. Under one-sun illumination (AM 1.5 G, 100 mW cm^{-2}), this cell showed an unprecedented energy conversion efficiency of 3.2%, a large V_{OC} of 1.2 V, and an extremely high FF of up to 0.89 (Figure 1a). As shown in Figure 1b, the IPCE of the TiO_2/TGA/CdS-3-based cell was >60% at 400 nm. The active range in the visible-light region was consistent with the corresponding UV−vis spectrum (see Figure S1 in the Supporting Information). The relatively high IPCE value is probably due to efficient sensitization of the TiO_2 film by the CdS QDs as well as fast regeneration of the QDs

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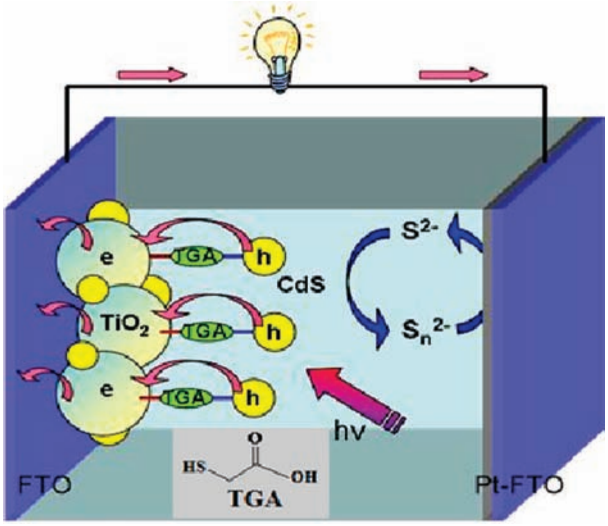
Scheme 1. Schematic Presentation of the CdS-Based QDSSC



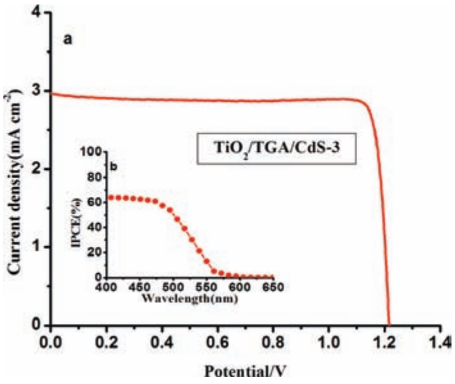


Figure 1. (a) *J*—*V* characteristics of the TiO_2/TGA/CdS-3-based cell measured under one-sun illumination (AM 1.5 G, 100 mW cm^{-2}). (b, inset) IPCE spectrum of the cell based on the TiO_2/TGA/CdS-3 electrode.

by the redox couple, since in organic solution the wettability of the electrolyte is increased.

To understand the high photovoltage of the cell ($V_{OC} = 1.2$ V), an electrochemical study was performed in an acetonitrile solution containing 10 mM $[(CH_3)_4N]_2S$ and 10 mM S. From its cyclic voltammogram (see Figure S2 for the CV curve), an oxidation potential of 1.045 V vs NHE was obtained for the redox couple S^{2-}/S_n^{2-}. This potential is much higher than that for the I^-/I_3^- system. In addition, it was recently reported that the conduction band (CB) energy (V_{CB}) of TiO_2 was significantly shifted toward negative potentials in the presence of the S^{2-}/S_n^{2-} electrolyte.[22] Therefore, the significantly high V_{OC} of 1.2 V for our cell can be explained by the more positive oxidation potential of the redox couple and the more negative potential of the TiO_2 conduction band ($V_{OC} \approx |V_{CB} - V_{redox}|$).

The reason for the unusually high FF of 0.89 is still not totally understood. The low surface tension of the electrolyte solution in the organic solvent and the preparation of the QDs in organic solutions may result in higher wettability and superior penetration capability on the mesoscopic TiO_2 films than in the case of aqueous systems, leading to high coverage of CdS QDs on the surface of the TiO_2 mesopores. Fast reduction of the redox couple on the counter electrode may become the main reason for the high FF value.

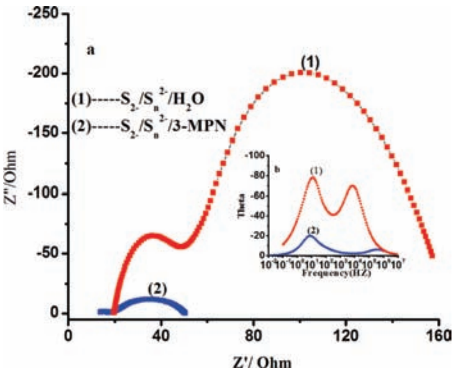


Figure 2. Electrochemical impedance spectra of (1) 0.5 M Na_2S + 2.0 M S in H_2O and (2) $[(CH_3)_4N]_2S/[(CH_3)_4N]_2S_n$ in MPN: (a) Nyquist plots; (b, inset) Bode phase plots. The cells were measured at −1.2 V bias voltage in the dark at frequencies from 10^{-2} to 10^7 Hz at room temperature.

The electrochemical impedance spectra (EIS) of the TiO_2/TGA/CdS-3 electrode with different electrolytes, 0.5 M Na_2S/2.0 M S in H_2O and $[(CH_3)_4N]_2S/[(CH_3)_4N]_2S_n$ in MPN, were measured in the dark (Figure 2). The larger semicircle in the Nyquist plots is attributed to the charge-transfer resistance (R_{CT}) at the counter electrode—electrolyte interface. RCT values of 153 and 2 Ω were found for the aqueous electrolyte system and the electrolyte in the organic solution, respectively. This result suggests that the modified polysulfide redox couple $[(CH_3)_4N]_2S/[(CH_3)_4N]_2S_n$ in organic solution affords a very effective reduction process on the Pt/FTO counter electrode surface, as reflected by the unusually high FF value.

In summary, we have successfully developed an efficient and noncorrosive polysulfide electrolyte for CdS QD-sensitized solar cells. With the use of this polysulfide electrolyte in organic solution, the performance of the TiO_2/TGA/CdS-3-based cell showed an energy conversion efficiency of 3.2% with $V_{OC} = 1.2$ V, $J_{SC} = 3.0$ mA cm^{-2}, and FF = 0.89. This has set a new record for CdS QDSSCs. The low reduction resistance of the electrolyte on the Pt/FTO counter electrode opens the possibility of using nonaqueous polysulfide electrolytes for QDSSCs.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed experimental procedures and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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