CdS Quantum Dots Sensitized TiO_2 Sandwich Type Photoelectrochemical Solar Cells

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For the first time, we report highly stable CdS quantum dots sensitized TiO_2 sandwich type photoelectrochemical solar cells. A unique combination of a sensitized electrode and a polysulfide electrolyte has provided the most stable solar cell with the highest IPCE of approximately 70%.

Metal chalcogenide semiconductor quantum dots (QDs) have received significant interest in the various fields of optoelectronic devices, e.g., biological sensors,[1] luminescence devices,[2] and solar cells.[3] Their overwhelming advantage is their ability to control the band gaps dependent on the QD size by the quantum size effect. Specifically, this effect can be employed to adjust the QD absorption range[4,5] and the excited state relaxation dynamics.[5,6] By controlling the latter kinetics, introducing hot electron injection,[6] or exciton multiplication induced by the impact ionization,[7] the solar cell efficiency is thought to be improved up to 86%.[8] Despite these properties the fundamental issue is the development of the cell structure, and this remains a major target for improvement of the energy conversion efficiency.

The sensitization of wide band gap semiconductors, for example TiO_2, ZnO, and SnO_2, by the QDs is one of the most advantageous structures for photovoltaic applications.[4,9–12] However, such sensitizations are generally achieved by utilizing a 3-electrode configuration,[4,9] effectively neglecting hole transports and counter electrode reactions. Despite efforts to fabricate sandwich type, 2 electrodes based, photoelectrochemical solar cells, their efficiency needs to be improved;[11,12] owing to chalcogenide QDs being unstable under light irradiation (photocorrosion) or unavailable efficient redox couples for regenerating the QDs.

Photoelectrochemical applications of metal sulfide films, i.e., bulk state semiconductors, were intensively studied.[13,14] Although relatively high cell efficiencies were reported, light absorption, charge separation and charge transport occur in the same metal sulfide phase, thereby increasing the chances of charge recombination. Therefore, the idea concerning the interfacial charge separation, initiated by the QDs excitation, may be advantageous to optimize the cell efficiency and to realize the concept of the third generation solar cells.[8]

In this paper, we have investigated several electrolytes for CdS QD-sensitized photoelectrochemical cells, regarding both QD stability and the functioning redox activity, demonstrating a highly efficient sandwich type regenerative photoelectrochemical solar cell.

Transparent TiO_2 nanocrystalline films, thickness 6–7 µm, were screen-printed on a F-doped SnO_2 glass using a TiO_2 paste (Solaronix SA, Ti-Nanoxide HT/SP). The sensitization was performed by the well-established method, "successive ionic layer adsorption and reaction" (SILAR) technique.[4,15] The TiO_2 film was dipped in 0.1 M $Cd(ClO_4)_2$, and subsequently in 0.1 M aqueous Na_2S solutions at room temperature. The coatings were repeated to obtain appropriate absorbance; the spectral change with the coatings is provided in the supplementary information. The QD diameter after 5 coatings was roughly estimated by observing an absorption spectrum (4–5 nm),[16] XRD (2.4 ± 0.5 nm), and FE-SEM (2–4 nm), implying that the size has a wide range of distribution (2–5 nm). Larramona et al. recently reported the presence of a CdS thin layer and dispersed larger dots on the TiO_2 surface,[17] and thus our observations may suggest a similar QD formation manner. The sandwich cell was fabricated by binding an electrolyte in a PET spacer (thickness 25 µm) with the sensitized TiO_2 electrode and the Pt counter electrode.[18] A Xe lamp light source with a monochromator (Bunko Keiki, SM-25) was used to characterize IPCE spectra, *I–V* curves and transient photocurrent for the cells.

Figure 1a compares IPCE spectra for the CdS QDs sensitized films (5 coatings) using various electrolytes. When the I_3^-/I^- electrolyte[18] (redox potential, E_{red}: +0.45 V vs NHE[19]), typically employed for the Ru dye-sensitized solar cells, is used, the IPCE spectrum indicated no response in the visible wavelength range (>400 nm). A similar result was noted with the Fe^{3+}/Fe^{2+} electrolyte (E_{red}: +0.6 V vs. NHE[20]) consisting of 0.1 M $LiClO_4$, 0.1 M $FeCl_2$, and 0.05 M $FeCl_3$ in H_2O. In contrast, a visible light spectral response was obtained with the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ electrolyte (E_{red}: +0.15 V vs. NHE[20]) consisting of 0.1 M $LiClO_4$, 0.1 M $K_4Fe(CN)_6$, and 0.05 M $K_3Fe(CN)_6$ in H_2O. Remarkable improvement was observed with the Na_2S_x/Na_2S, polysulfide, electrolyte (E_{red}: −0.45 V vs. NHE[21]), consisting of 2 M Na_2S and 3 M S in water. The data clearly suggest that the photocurrent response/amplitude

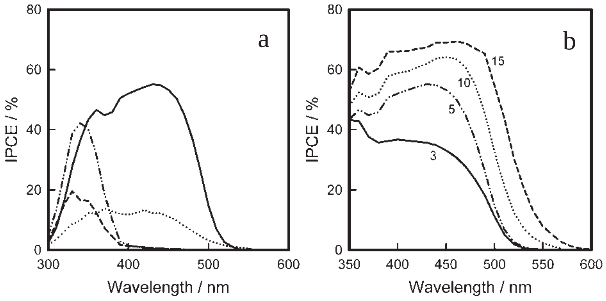

Figure 1. (a) IPCE spectra of CdS QD-sensitized solar cells for various electrolytes. The employed electrolyte is Na_2S_x/Na_2S (—), I_3^-/I^- (– · ·), Fe^{3+}/Fe^{2+} (– –), and $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ (· · ·). (b) Dependence of the QD coating times on IPCE spectra using the Na_2S_x/Na_2S electrolyte. The number in the figure indicates the coating times.

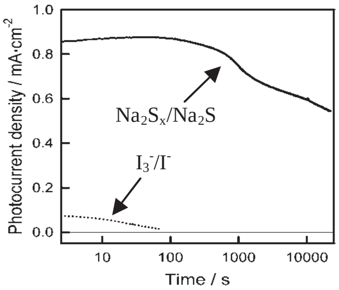

Figure 2. Photocurrent transients observed for the CdS-sensitized (5 coatings) cells with the Na_2S_x/Na_2S and I_3^-/I^- electrolytes at 450 nm.

is not dependent on the electrolyte redox potential since the QD valence band edge potential is located more positively than the bulk band edge (+1.6 V vs. NHE).

Figure 1b shows dependence of the CdS coating times on IPCE spectra using the polysulfide electrolyte. The IPCE increases with the coating times owing to the increase in the light harvesting efficiency (LHE). The highest IPCE of about 70% was achieved with 15 coatings. Noticeably, the IPCE onset shifted to a longer wavelength as the coating times increased. This shift can be attributed to decrease in the band gap resulting from the QD size increase with the coating times.

The CdS photocorrosion is well known, and thus the QD may be unstable in the particular electrolyte under the light irradiation. In order to investigate this instability, the transient photocurrents were measured for the polysulfide and I_3^-/I^- electrolytes under the continuous light irradiation at 450 nm (6.47 mW/cm^2) as shown in Figure 2. The photocurrent amplitude for the polysulfide is about 10 times greater than the I_3^-/I^-, and is maintained over several hours. Considering the electrolyte volume inside the spacer, the photocurrent observed for 10,000 s corresponds to the electrolyte turnover number (the number of collected electrons over the electrolyte moles) of about 5, verifying that the polysulfide is functioning as an electron mediator. The film indicated almost identical absorption spectra prior to and after the measurements, suggesting the QDs are stable under the light irradiation. Note that the cell was not sealed through the stability measurement, suggesting that the photocurrent decrease may originate from the electrolyte leakage. For the I_3^-/I^- electrolyte, reproducibility of the transient data proved difficult. The yellow CdS color occasionally disappeared immediately after the electrolyte was injected to the cell, indicative of the photocorrosion.[11,13,22] The electron injection from the QD into the TiO_2 occurs on the ultrafast time scales,[15,23] and the charge recombination can be slow, similar to the dye-sensitized TiO_2.[24] The photocorrosion reaction of the long-lived hole competes with the QD re-reduction by I^-. Thus, the QD re-reduction occurs slower than the photocorrosion.

Figure 3 shows the *I–V* characteristics under 450-nm light using the same series of electrolytes. As anticipated, both *Jsc* and *Voc* are small for the I_3^-/I^- and Fe^{3+}/Fe^{2+} electrolytes. For the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$, the fast reversible reaction at the F–SnO_2/electrolyte interface was observed (see ohmic *I–V* line), being identical to the data reported by Gregg et al. for ferrocene/ferrocenium couple.[25] *Jsc* and *Voc* were remarkably higher for the Na_2S_x/Na_2S electrolyte. These results, therefore, demonstrate the polysulfide electrolyte can be used as the active redox electrolyte and for stabilizing the QDs.

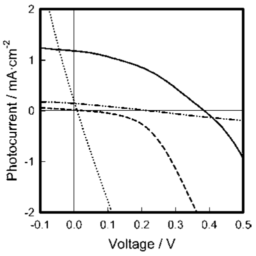

Figure 3. *I–V* characteristics obtained for QD-sensitized solar cells under 450-nm light using various electrolytes: Na_2S_x/Na_2S (—), I_3^-/I^- (–··), $FeCl_3/FeCl_2$ (– –), or $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ (····).

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