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Co-Sensitized Mesoporous TiO_2 Solar Cells: Hybrid Sensitizer of SILAR-Grown CdS Quantum Dot (QD) and Molecular Dye (Z907) with a Metal Oxide Interlayer

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During the past two decades, mesoporous metal oxide film-based solar cells sensitized by molecular dyes or inorganic semiconductors have advanced greatly in terms of power conversion efficiencies and stability.[1,2] As a light harvester, both molecular dyes and nanoscale semiconductors have proved that they can be utilized successfully based on their intrinsic properties and advantages.[3] Therefore, those two chromophores have played an important role in the advancement of dye- or quantum dot-sensitized solar cells. Recently, a kind of hybrid system combining multi-components is attracting great attentions in many research areas because some synergistic effects could be expected by a combination of two or more components doing a similar or complementary role. In mesoscopic solar cells, there have also been a few trials to make a new type of hybrid sensitizers composed of inorganic QDs and organic dyes;[5-8] CdSe or CdS QDs were deposited firstly and then followed by self-assembled adsorption of molecular dyes (Z907, N719, SQ) to prepare inorganic/organic hybrid sensitizer which has finally led to a moderate power conversion efficiency (< ~4%) under somewhat limited conditions. These relatively low or moderate performances in hybrid sensitizers, contrary to high expectations, could be ascribed mainly to difficulties in controlling their relative positions within the cell and unclear interfaces formed by many components. Therefore, more studies under general conditions are strongly needed to understand the basic principle of this new system and then demonstrate a full potential of this promising hybrid sensitizer.

In this study, we have pursued to find a general procedure in making a model hybrid sensitizer onto the surface of mesoporous TiO_2 film with a regenerative redox couple of cobalt-complex in electrolyte which is compatible to both QDs and dyes. To avoid the diffusion problem of cobalt complex through the typical mesopores (pore size: ~20 nm) in TiO_2 film, a more wide-porous film (pore size: ~40 nm)[9] from commercial TiO_2-blend paste was prepared by screen printing onto the FTO glass after the typical $TiCl_4$ treatment. As the first sensitizer, CdS QD was deposited by following the typical SILAR (successive ionic layer adsorption and reaction) process.[10] Then, the yellow-colored TiO_2/CdS film was covered by a very thin film of three different metal oxides (Al_2O_3, ZrO_2, or SiO_2) through hydrolysis of each precursor layer. Finally, ruthenium-dye (Z907) was self-assembled as a second sensitizer. Between the sensitized photoanode and platinized counter electrode, the Co(bipyridine)$_3$ (II/III) redox couple-based electrolyte was injected to make a regenerative cell. The photovoltaic performances of as-prepared cells were checked under standard 1 sun condition and summarized in Table 1.

As can be seen in Table 1 and Figure 1, the overall conversion efficiency of SILAR-deposited CdS QD-sensitized cell has been improved about 100% (from 0.34 to ~0.70%) after over-coated with a very thin metal oxide layer; all three typical metal oxides (Al_2O_3, ZrO_2, SiO_2) having a wide band gap have shown the almost same effect after applied to cover the surface of TiO_2/CdS. This beneficial effect can be ascribed to inhibition of electron back transfer from TiO_2/CdS to the redox electrolyte by the insulating oxide; the surface states of QDs can also be passivated by the applied thin insulating layer for reducing the unwanted recombination processes around QD sensitizers.[3,4]

These positive effects of metal oxide layer upon TiO_2/CdS QDs was observed very reproducibly only after finding an optimum condition of deposition; it was crucial to carry out the hydrolysis of metal oxide precursor layer in H_2O solution for 1 minute before exposed to atmospheric air. Without the H_2O solution-mediated hydrolysis step after dipping the TiO_2/CdS electrode in each precursor solution for 10

Table 1. Photovoltaic data set from CdS/(metal oxide)/(Z907)-sensitized TiO_2 solar cells

Sensitizer	J_{sc} (mA)	E_{oc} (V)	*FF*	CE (η)
CdS8	1.51	0.47	0.48	0.34
CdS8/Al_2O_3	1.94	0.60	0.62	0.72
CdS8/SiO_2	1.88	0.58	0.63	0.69
CdS8/ZrO_2	1.77	0.60	0.64	0.68
CdS8/Al_2O_3/Z907	8.72	0.80	0.69	4.81
CdS8/SiO_2/Z907	8.47	0.78	0.70	4.62
CdS8/ZrO_2/Z907	8.19	0.81	0.69	4.58
CdS8/Z907	7.38	0.79	0.70	4.08

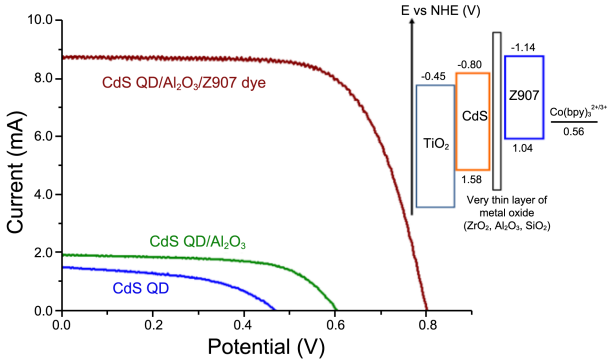

Figure 1. Current density-voltage curves of (1) CdS QD, (2) CdS QD/Al_2O_3, and (3) CdS QD/Al_2O_3/Z907 dye-sensitized solar cells with energy diagram of all active components involved in inset.

minutes, it was very difficult to get a reproducible data set. This observation can be explained by the ineffective and uncontrollable hydrolysis through atmospheric water, of which (%)-content can be changed depending on the time or place for experiment. Judged by a clear increase seen from all main parameters (E_{oc}, J_{sc}, and *FF*), the thin metal oxide layer seems to be working well as a blocking layer to reduce the unwanted back-flow of charges generated by CdS QDs after light-absorption.[3] Since establishing the deposition conditions for CdS QD/thin metal oxide layer, a second sensitizer of molecular dye (Z907) was applied to boost up the efficiencies of light-absorbing and current-generating processes within a finite thicknees of TiO_2 film. As expected, the addition of Z907 dye over TiO_2/CdS QD/metal oxide layer (Al_2O_3, ZrO_2, or SiO_2) could move this model hybrid sensitized cell over ~4.6% power conversion under standard 1 sun condition (Table 1). This huge increase in overall conversion efficiency was observed with a similar reproducibility over all the three oxide layers tested in this study although their conduction bands are lying higher than the LUMO of Z907 dye, which means that electron should be transferred *via tunneling effect* through a very thin insulating layer.[4] The best result was from Al_2O_3 layer by showing a 8.72 mA/cm^2 of J_{sc}, a 0.80 of V_{oc}, and a 0.68 of *FF* for 4.81%. In the case of no metal oxide layer inserted, relatively lower conversion efficiency (4.08%) was observed. This direct contact between the first sensitizer (QDs) and the second sensitizer (dyes) was considered normally not to be beneficial in maximizing the performance of each sensitizer[5] though more studies are still needed in this point. Anyway, by addition of both a thin metal oxide layer and another sensitizer over the first sensitizer of CdS QD, the overall power conversion efficiency was greatly improved thanks to retarding the unwanted recombination processes and enhanced co-sensitization of inorganic and organic chromophores.

In this communication, we have suggested a reproducible way for depositing a thin metal oxide layer between the first sensitizer (QDs) and the second one (dyes), which was considered to be a crucial step towards realizing an efficient inorganic/organic hybrid sensitized solar cell. By utilizing the strategy and result of current study, we will be able to make a variety of useful model hybrid-sensitizer system within mesoscopic metal oxide films to investigate all the basic phenomena occurring at the interfaces and finally to achieve a powerful synergistic hybrid light-harvester in solar cell devices.

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Supporting Information. Experimental details are given.

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