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Communications

SUPPORTING INFORMATION

Quantum Dot-Sensitizers Prepared by SILAR and Cation-Exchange Processes

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Experimental

Materials

All chemicals were used as received; Cadmium nitrate tetrahydrate [$Cd(NO_3)_2 \cdot 4H_2O$, ≥99.0%], cadmium acetate dihydrate [$Cd(CH_3COO)_2 \cdot 2H_2O$, reagent grade, 98.%], sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$), sodium sulfide (Na_2S), antimony(III) chloride ($SbCl_3$, ACS reagent, ≥99.0%), silver nitrate ($AgNO_3$, ACS reagent, ≥99.0%), bismuth nitrate pentahydrate [$Bi(NO_3)_3 \cdot 5H_2O$, ACS reagent, ≥98.0%], copper nitrate hydrate [$Cu(NO_3)_2 \cdot xH_2O$, 99.999%], lead nitrate [$Pb(NO_3)_2$, 99.999%], and triethanolamine (TEA, reagent grade, 98%) were purchased from Sigma-Aldrich. Ethanol and methanol were of HPLC-grade.

Cobalt Electrolyte

0.20 M Co(II) complex of $[Co(bpy)_3](PF_6)_2$, 0.05 M Co(III) complex of $[Co(bpy)_3](PF_6)_3$, and 0.10 M, lithium perchlorate ($LiClO_4$) were dissolved in acetonitrile. Here, bpy stands for bipyridine.

Electrodes

For a thin TiO_2 blocking layer, fluorine-doped tin oxide (FTO)-coated glass electrode (Solaronix, 8 Ω/□) was treated with 40 mM $TiCl_4$ aqueous solution for 30 min at 70 ºC and then washed with pure water. The electrode was gradually heated to 500 ºC. Using screen-printing machine and commercial TiO_2 pastes, about 5 μm thick TiO_2-blend layer (Dyesol, 18NR-AO; TiO_2 particle size 20~450 nm) which is responsible for adsorbing most of sensitizers in the electrode and ~4 μm scattering layer (Dyesol, WER2-O; TiO_2 particle size 150~250 nm) were deposited sequentially and then sintered up to 500 ºC to make a mesoporous TiO_2 film. Finally, the typical $TiCl_4$ post-treatment was applied as the same manner with the pre-treatment of $TiCl_4$. A platinium (Pt)-counter electrode was prepared by following procedure; a 10 nM solution of chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Sigma-Aldrich) in ethanol was dropped onto the FTO electrode and dried in air for 20 min. Then, the electrode was annealed gradually to 450 ºC for 30 min under atmospheric conditions.

Cation-exchanged QDs from SILAR-deposited CdS QD

To grow CdS QD sensitizer, the typical SILAR process was done by alternative dipping of as-prepared FTO/TiO_2 electrodes in 0.05 M $Cd(NO_3)_2$ and 0.05 M $Na_2S \cdot 9H_2O$ aqueous solutions, respectively for 1 minute, which was repeated five times. Between dipping, a washing step was included for 1 minute in pure water. After depositing CdS by following the SILAR process, the cation-exchange process was done by dipping the as-deposited CdS/TiO_2/FTO electrode into 0.10 M $AgNO_3$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, or $Pb(NO_3)_2$ aqueous solution for 30 seconds [0.10 M $Bi(NO_3)_3$, was saturated due to its low solubility in water]. The yellow color of CdS/TiO_2/FTO electrode was changed immediately by a cation-exchange for new target QDs.

Preparation of Cation-exchanged Sb_2S_3 QD

SILAR and cation exchange processes were used to prepare Sb_2S_3 QD sensitizer. For SILAR-growing of CdS, a 0.10 M $Cd(CH_3COO)_2 \cdot 2H_2O$ and 1 M triethanolamine in ethanol/water (1:1, v/v), and a 0.10 M $Na_2S \cdot 9H_2O$ in methanol/water (1:1, v/v) were used for each cationic and anionic source. The mesoporous TiO_2 film-covered FTO electrode was dipped into Cd^{2+} solution, pure ethanol (then dried in air), the S^{2-} solution, and then pure methanol (then dried in air) successively for 1 min each. Such immersion cycle was repeated 9 times. After this SILAR process, the electrode of TiO_2/CdS was immersed into a 0.10 M $SbCl_3$ in ethanol for 10 min to induce cation exchange process at room tempera-

ture. A post-treatment of annealing in N_2 atmosphere was applied by increasing temperature from 100 °C to 300 °C for 20 min. The color change was observed on the TiO_2/Sb_2S_3 electrode during the annealing procedure, which was orange before annealing and gradually turned dark brown as the temperature increased. But, in the case of CdS, there was only a slight change in the intensity of color.

Direct Deposition of Sb_2S_3 QD by SILAR Process

A 0.020 M $SbCl_3$ in ethanol and 0.020 M Na_2S in ethanol were used for each cationic and anionic source for depositing Sb_2S_3 by the SILAR process, which was repeated 5 times with a dipping time of 90 seconds each. Between the dipping in each precursor solution, the electrode was washed in pure ethanol in 3 minutes. The as-prepared Sb_2S_3-deposited electrode was annealed to 300 °C for 20 minutes under nitrogen.

Cell Assembly

To make QD-sensitized solar cells with a counter electrode of the typical platinized FTO glass, the as-prepared QD-sensitized photoanode and Pt-cathode were combined by hot-press machine through the Surlyn film, and the electrolyte solution was injected through a pre-drilled hole through the counter electrode.

Measurements

The current-voltage and open-circuit voltage decay characteristics were analyzed under a standard illuminating condition (1 sun, 100 mW cm^{-2}) using a solar simulator (Peccell, PEC-L01) and a potentiostat (IVIUM, Compactstat). Various irradiance intensities from 0.1 to 1.0 sun could be provided with optical attenuators. The incident photon-to-current efficiency (IPCE) data were collected by a light source (ABET 150W Xenon lamp, 13014) with a monochromator (DONGWOO OPTORN Co., Ltd., MonoRa-500i) and a potentiostat (IVIUM, Compactstat) based on DC method without chopper and light bias. Optical absorbance was measured with a UV-VIS spectrophotometer (PerkinElmer Lambda 25).

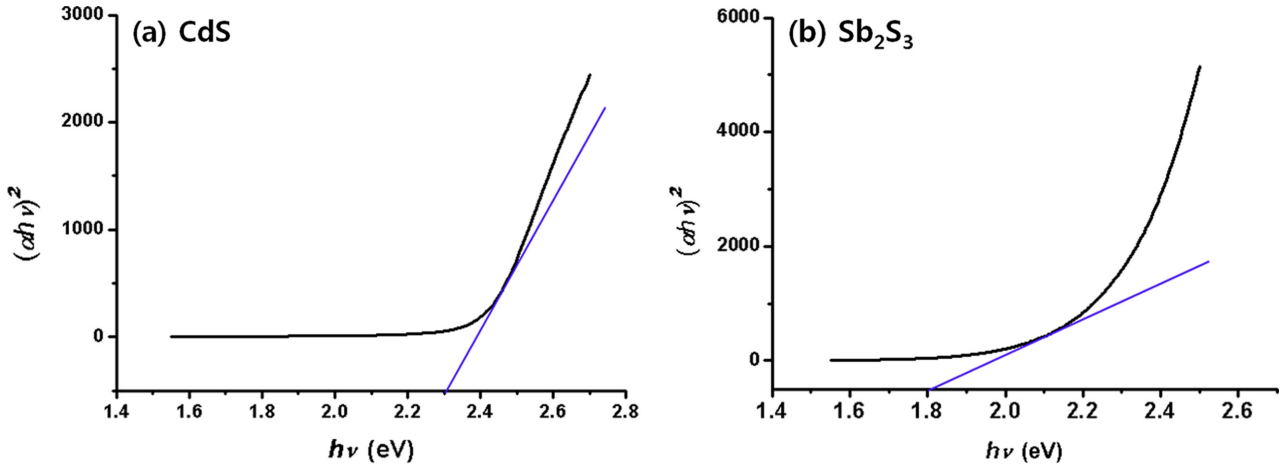

Figure S1. Tauc plots of (a) CdS- and (b) Sb_2S_3-QD sensitized TiO_2 films.

***Table* S1.** Phototovoltaic data from different preparation of QD sensitizers

QD sensitizer	Light intensity	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
SILAR-deposited CdS	0.1 sun	0.35	0.30	0.53	0.57
	0.3 sun	1.05	0.35	0.54	0.65
	0.5 sun	1.72	0.37	0.54	0.68
	1.0 sun	3.05	0.38	0.48	0.55
Cation-exchanged Sb_2S_3 from CdS	0.1 sun	0.60	0.28	0.50	0.82
	0.3 sun	1.89	0.32	0.49	0.99
	0.5 sun	3.06	0.34	0.48	1.01
	1.0 sun	5.22	0.35	0.46	0.84
Direct SILAR-deposited Sb_2S_3	1.0 sun	2.06	0.36	0.54	0.40