Supplementary Information

Cauliflower like SnO_2 hollow microspheres as photoanode with carbon fiber counter electrode for high performance quantum dot and dye-sensitized solar cells

Veerappan Ganapathy,‡[a] Eui-Hyun Kong,‡[b] Yoon-Cheol Park,[c] Hyun Myung Jang,*[b] Shi-Woo Rhee*[a]

[a] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea, Email: srhee@postech.ac.kr

[b] Department of Materials Science and Engineering, and Division of Advanced Materials Science, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea, Email: hmjang@postech.ac.kr

[c] Research Institute of Industrial Science and Technology (RIST), Pohang 790-784, Korea,

* Corresponding authors

‡ V. Ganapathy and E.-H. Kong contributed equally to this work.

1.1 Synthesis of cauliflower-like SnO_2 hollow microspheres and preparation of photoelectrodes

The cauliflower-like SnO_2 hollow microspheres (SnO_2-HMS) were prepared by using a hydrothermal method. All chemicals for the preparation of SnO_2 were of reagent grade and were used without further purification. In a typical synthesis of SnO_2-HMS, 8.5 g of sucrose and 8.7 g of $SnCl_4$-$5H_2O$ were dissolved in distilled water to obtain 50 ml of mixture [1]. The resulting mixture was then transferred to the Teflon-lined stainless steel autoclave. Then, the autoclave was sealed and kept in muffle furnace for 24 h at 190 ºC. After the reaction completion, the autoclave was kept in the furnace to cool naturally till it reaches the room temperature. The resultant black precipitate was filtered and washed several times using water and ethanol to remove the impurities and dried at vacuum oven for 12 h at 80 ºC. The resulting dried powder was a mixture of carbon-SnO_2 composite. And the dried powder was sintered at 600 ºC for 3 h to remove the carbon and highly crystalline cauliflower-like SnO_2 hollow microspheres were obtained. FTO glass was cleaned with soap water, deionized water, acetone, and ethanol for 15 min each, and then dried with nitrogen gas. To prepare a SnO_2 paste, 0.3 g of SnO_2-HMS and 0.1 g of ethyl cellulose were grounded with 1 ml of ethanol for 10 min and α-terpineol was added to the above mixture. Then the resultant paste was screen-printed onto the previously cleaned and $TiCl_4$ treated FTO glass and sintered at 500 ºC for 30 min. An aqueous $TiCl_4$ (40 mM) treatment for 30 min at 70 ºC was performed on the screen-printed SnO_2 photoanode. The substrate was subsequently rinsed with ethanol and dried using nitrogen blow and sintered at 500 ºC for 30 min. The photoelectrode consisting of ~17 μm thick nanocrystalline TiO_2 layer (Ti-Nanoxide HT/SP

from Solaronix) was prepared on the FTO glass by screen-printing. All the other experimental conditions are similar to the SnO_2 photoelectrode preparations.

1.2 Preparation of carbon-nanofiber counter electrode

Carbon-nanofiber counter electrodes (CNF CE) were prepared as follows. 0.5 g of CNF powder (Carbon nano-material tech. co., Republic of Korea, average diameter of 200 nm) was finely ground with mortar and pestle and with the addition of 2 ml carboxy-methyl cellulose (CMC) sodium. The resultant homogeneous, viscous paste was deposited on the cleaned FTO glass using doctor blade technique to obtain films of ~11 μm thickness. The resulting film was kept outside for 7 min to have good leveling and to reduce the surface irregularity. Subsequently, the dried electrodes were baked at 100 ºC for 5 h in a vacuum oven. Traditional Pt-CE was prepared for comparison by depositing Pt precursor (Plastisol, Solaronix) on the FTO glass followed by sintering at 400 ºC for 5 min [2].

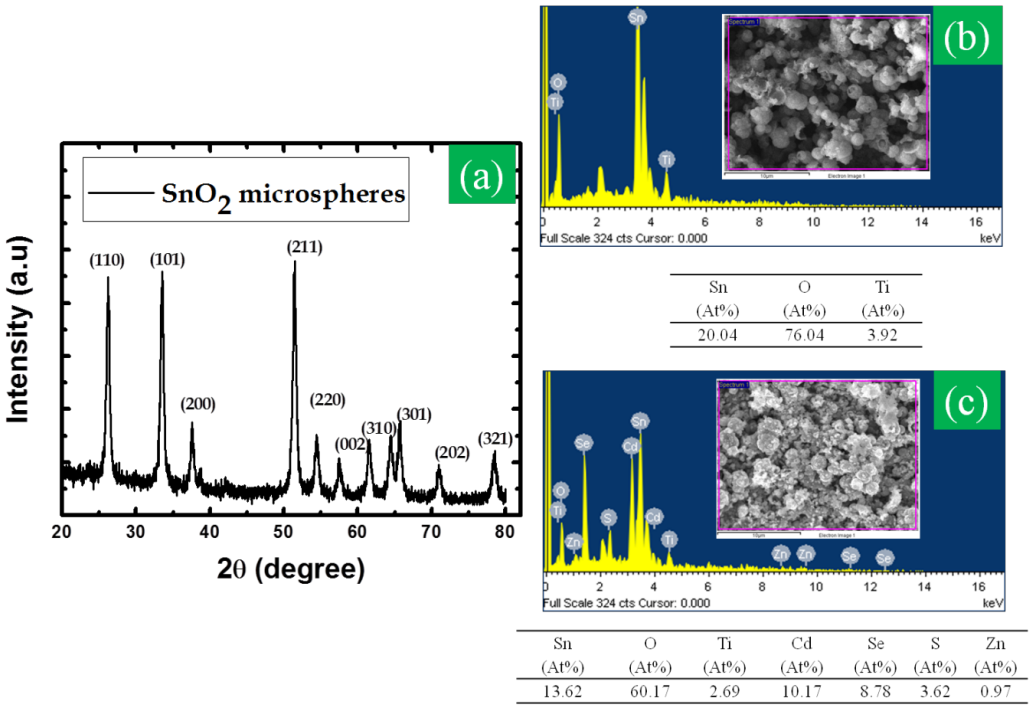
1.3 Characterization

Current-voltage (*I-V*) measurements of the solar cells were performed under AM 1.5 simulated solar light irradiation; a 300 W xenon lamp (Newport, USA) was used as a light source and a standard Si solar cell was employed for calibration. Electrochemical impedance spectroscopy (EIS) was carried out under dark at room temperature in the frequency range from 100 mHz to 100 kHz. The EIS measurements were performed on the symmetric cells to investigate the Sn^{2-} reduction activity by calculating the charge transfer resistance (R_{CT}) at the CE/electrolyte interface. A field-emission scanning electron microscope (FE-SEM, JEOL JSM 7401F) was used to investigate the morphology of the SnO_2-HMS and CNF. Cyclic

voltammogram and Tafel polarization were measured using the CHI instruments. CV experiments were performed at a scan rate of 50 mVs^{-1} with the potentiostat (CHI instruments) with a three electrode configuration, a working electrode with thermally deposited Pt or doctor bladed CNFs, Pt coil as a counter electrode and Ag/AgCl as a reference electrode in the aqueous solution containing 10 mM Na_2S, 10 mM S, and 0.1 M $LiClO_4$. For the Tafel-polarization analysis, symmetric cells were used and measured at a scan rate of 10mV S^{-1}. UV-Vis spectra were recorded within a Perkin Elmer UV-Vis spectrometer (LAMBDA 750S).

References

1. H. X. yang, J. F. Qian, Z. X. Chen, X. P. Ai, Y. L. Cao, *J. Phys. Chem. C,* 2007, **111**, 14067-14071.
2. V. Ganapathy, W. Kwon, S.W. Rhee, *J. Power Sources,* 2011, **196,** 10798-10805.



Sn (At%)	O (At%)	Ti (At%)
20.04	76.04	3.92

Sn (At%)	O (At%)	Ti (At%)	Cd (At%)	Se (At%)	S (At%)	Zn (At%)
13.62	60.17	2.69	10.17	8.78	3.62	0.97

Figure S1 (a) XRD spectra of SnO_2-HMS, SEM image and EDS elemental mapping of (b) as deposited SnO_2 photoanode, and (c) QD-sensitized SnO_2 photoanode.

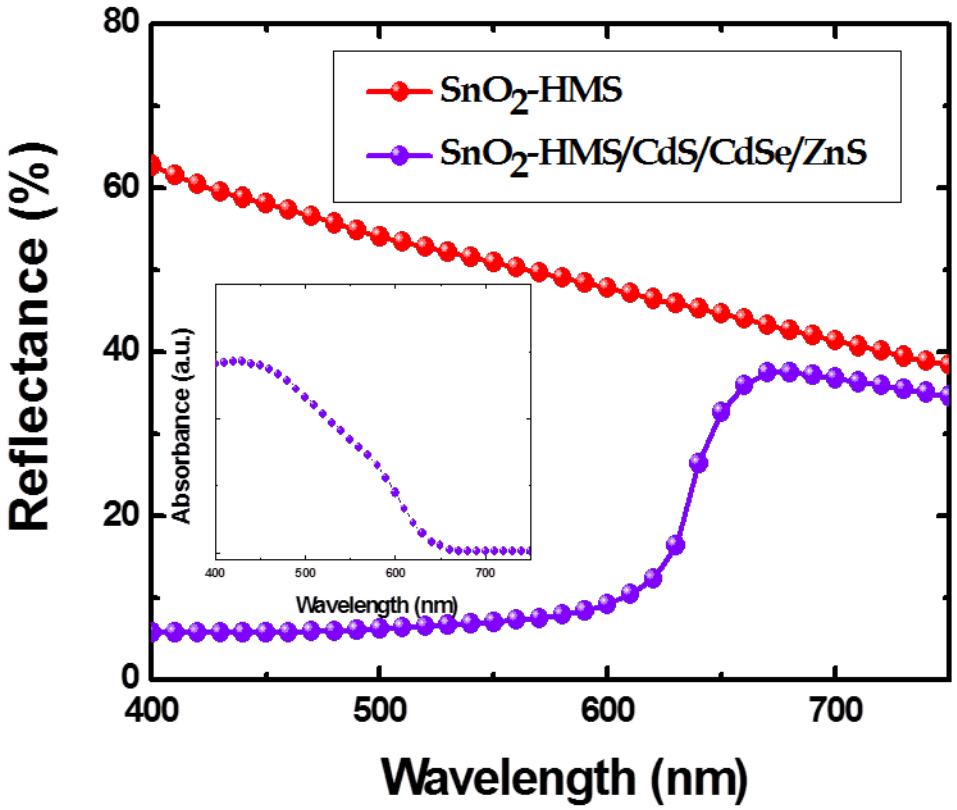


Figure S2 (a) UV-Visible reflectance spectra of bare SnO_2-HMS and QD-sensitized SnO_2-HMS. Inset showing UV-Vis absorbance for QD-sensitized SnO_2-HMS.

Table S1 Photovoltaic performance of TiO_2 photoanodes for QDSCs and DSCs made with various counter electrodes. Measurements under 1 sun illumination

Counter electrode	Sensitizer	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	η (%)
CNF	CdS/CdSe/ZnS	9.2	0.515	44.1	2.1
Pt	CdS/CdSe/ZnS	8.9	0.495	44.9	2.0
CNF	N719	12.5	0.830	66.3	6.9
Pt	N719	12.8	0.818	70.7	7.4