Electronic Supplementary Information

Sea urchin TiO₂-nanoparticle hybrid composite photoelectrode for CdS/CdSe/ZnS quantum dot-sensitized solar cells

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Figure S1. The SEM image of the as-synthesized SU TiO₂ without use of ethanol as a dispersing agent.



Figure S2. SEM images of the two films deposited on the FTO glass. Cross-section images of the NP (a) and SU-NP composite films (NP: 14.5 μm, SU-NP: 14.6 μm).

Cubic CdS (200)0.293 nm **Cubic ZnS** (111)0.307 nm Cubic CdSe (220) 0.215 nm Anatase TiO₂ (101)5 nm 0.354 nm

Figure S3. STEM image of the sensitized TiO_2 particles containing the CdS QDs formed on the ZnS layer due to residual Cd^{2+} ions.



Figure S4. SEM images of as-prepared SU TiO_2 at different reaction time: 30 min (a), 1 h (b), 4 h (c), and schematic illustration of the formation mechanism of SU TiO_2 (d). The inset of (c) shows the top view image of nanoneedles grown on a single SU TiO_2 particle.



Figure S5. Diffuse reflectance spectra of the SU film. The inset is the top-view image of the photoanode.



Figure S6. Incident light intensity dependent electron diffusion coefficient and effective diffusion length for the QDSSCs based on the SU-NP composite and the NP films under 625 nm LED illumination (AM 1.5, 100 mW cm^{-2}).



Figure S7. (a) Nyquist plots of the EIS spectra (applied voltage : 0.5 V) and (b) charge recombination resistance for the CdS/CdSe/ZnS QDSSCs with the SU-NP composite and the NP films under dark. The corresponding equivalent circuit and values of fitting parameters are present.

Typical Nyquist plots of both cells were obtained under dark using the equivalent circuit shown in the inset of Fig. S7a. It is known that the second semi-arc at a lower frequency region is related to the recombination resistance (R_r) between the oxide and the polysulphide electrolyte¹. The electron life time (τ_r) is given by I/ω_{max} , where ω_{max} refers to the peak frequency of the second semi-arc². ω_{max} of the ODSSC cell composed of the SU-NP cell is 1.6 Hz which is about 2.54 times smaller than that of the QDSSC cell with the NP cell (4.06 Hz) under a dark condition at applied voltage of 0.5 V. Accordingly, τ_r is estimated to be 625 and 246 ms for the SU-NP and the NP cells, respectively. Fig. S7b shows R_r for both cells which decreases with an increasing applied voltage¹. It is observed that the SU-NP cell has higher R_r than the NP cell at various applied voltages. This result implies that the recombination is greatly suppressed at the SU TiO₂/polysulphide electrolyte interface, which offers a higher V_{oc} , J_{sc} and improved conversion efficiency.

Reference

2. R. Kern, R. Sastrawan, J. Ferber, R. Stangl and J. Luther, *Electrochim Acta*, 2002, 47, 4213.

^{1.} I. Mora-Sero, S. Gimenez, F. Fabregat-Santiago, R. Gomez, Q. Shen, T. Toyoda and J. Bisquert, *Accounts Chem Res*, 2009, **42**, 1848.