Supplementary Information

Sixfold Enhancement of Photocurrent by Surface Charge Controlled High Density Quantum Dot Coating

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Methods

1. Preparation of photoelectrode

Fluorine-doped tin oxide (FTO) glass (Pilkington, TEC-8,8 Ω/sq) was cleaned using ultrasonic cleaner in ethanol bath and UV/Ozone cleaner for 15 min. A dense TiO_2 blocking layer was formed on the cleaned FTO glass by spinning 0.1 M Ti(IV) bis (ethyl acetoacetato) diisopropoxide (Aldrich, 98%) in 1-butanol (Aldrich, 99.8%) solution, which was annealed at 500 ^oC for 15 min. TiO_2 paste was prepared by mixing hydrothermally synthesized TiO_2 nanoparticles (ca. 20 nm), terpineol (Aldrich, 99.5%), ethyl cellulose (Aldrich, 46 cp) and lauric acid (Fluka, 96%) with nominal composition of 1.25:6:0.3:0.1.[1] The TiO_2 paste was coated on the blocking layer coated FTO substrate using screen printer and annealed at 550 ^oC for 1 h in air. Thicknesses of the annealed mesoporous TiO_2 layers were measured by an alpha-step IQ surface profiler (KLA Tencor). PbS:Hg QDs were formed on surface of TiO_2 by using SILAR method as described elesewhere.[2] Mesoporous TiO_2 coated electrode was first dipped in aqueous solution consisted of 0.1 M $Pb(NO_3)_2$ (Aldrich, 99.99%) and 6 mM $HgCl_2$ (Sigma-Aldrich, 99.5%) for 1 min, followed by dipped in 0.1 M Na_2S (Aldrich) for 1 min. The electrode was thoroughly washed with deionized (DI) water after each dipping. For the control of TiO_2 surface charge, 1 M of triethanolamine (TEA, 99%, sigma) was added to cationic precursor solution. Dipping in anion solution following dipping in cation solution denoted one coating cycle. Effects of the concentration of the cationic solution and the duration time for coating on the photovoltaic performance were also investigated for the case of the absence of TEA. The duration time (dipping time) for the reference condition (bare) was 1 min in 0.1 M $Pb(NO_3)_2$ and 6 mM $HgCl_2$ solution and 1 min in 0.1 M Na_2S solution. Dipping time×2 represents 2 min dipping in the same cationic and anionic solutions. Concentration×2represents 1 min coating in 2-fold increased concentration of 0.2 M $Pb(NO_3)_2$ and 12 mM $HgCl_2$. ZnS passivation layer was deposited after PbS:Hg QD formation using aqueous solution of 0.1 M $Zn(CH_3COO)_2$ (Aldrich, 99.99%) and 0.1 M Na_2S.[3]

2. Solar cell fabrication

Brass foil (Alfa Aesar, 0.25 mm thick) was used as a substrate and a precursor to form a Cu_2S as well for counter electrode material. The brass foil was etched by dipping in hydrochloric acid (Samchun, 35.0 ~ 37.0%) at 80 ^oC for 15 min, which was washed with DI water and dried using air gun. Aqueous polysulfide solution composed of 1 M Na_2S (Aldrich) and 1 M S (Sigma-Aldrich, 99.5%) was dropped on etched brass and black colored Cu_2S immediately formed on the brass foil. The electrode was thoroughly washed with DI water after 10 min and used as a counter electrode. Double-side silicon-binder-coated polyimide tape (ca. 80 μm) was used as a sealant to assemble the PbS:Hg QD-sensitized working electrode and the Cu_2S-brass counter electrode. Polysulfide redox electrolyte composed of 1 M Na_2S (Aldrich), 1 M S (Sigma-Aldrich, 99.5%), and 0.3 M CsOH[4] (Aldrich, 99.9%, 50 wt% solution in water, *Caution: Since CsOH is highly corrosive, protection gears are essential for handling of CsOH*) in DI water was injected through the 0.75 mm-diameter hole on the working electrode and the holes were sealed using polyimide tape.

3. Characterization

The active area was measured by a digital microscope camera (DCMe 500) equipped with an image analysis program (Leopard 2009). Current density and voltage curves were measured using solar simulator (Oriel Sol 3A class AAA) equipped with 450 W Xenon lamp (Newport 6279NS) and a Keithley 2400 source meter. The light intensity was adjusted to AM 1.5G one sun illumination (100 mW/cm^2) using NREL-calibrated Si solar cell having BK7 window (without optical KG filters). The aperture mask was applied during the measurement. External quantum efficiency (EQE) was measured by a specially designed EQE system (PV measurement Inc.). A 75 W Xenon lamp (USHIO, Japan) was used as a white light source to generate monochromatic beam. Absorption spectra were measured by UV-Vis spectrometer (PerkinElmer, Lambda 35). Morphology and size of PbS:Hg QDs adsorbed on the TiO_2 surface were investigated using a high-resolution transmission electron microscope (HR-TEM, Jeol, JEM-2100F) at an acceleration voltage of 200 kV. Average diameter of QDs was determined from TEM micrograph using image J program (version 1.45s).

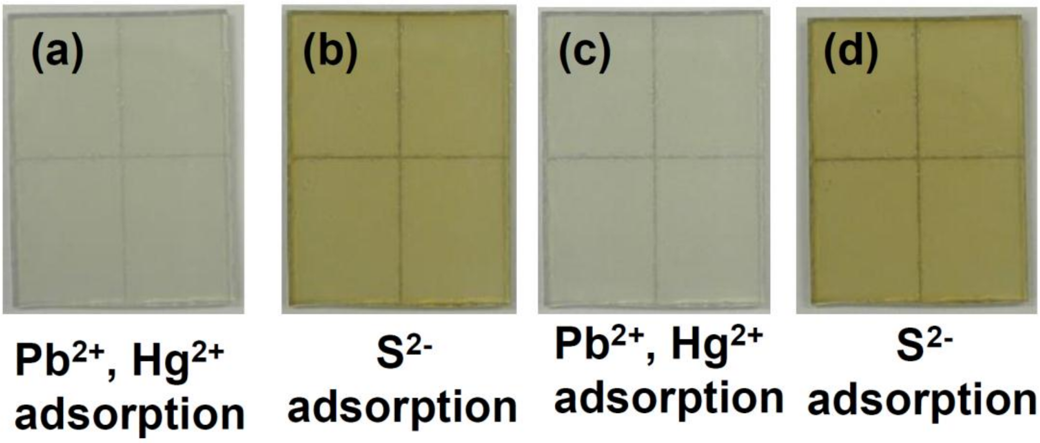

Figure S1. TiO_2 coated FTO glass during the 2 cycles coating of PbS:Hg quantum dot in the absence of TEA. The first coating cycle (a) → (b) and the second coating cycle (c) → (d).

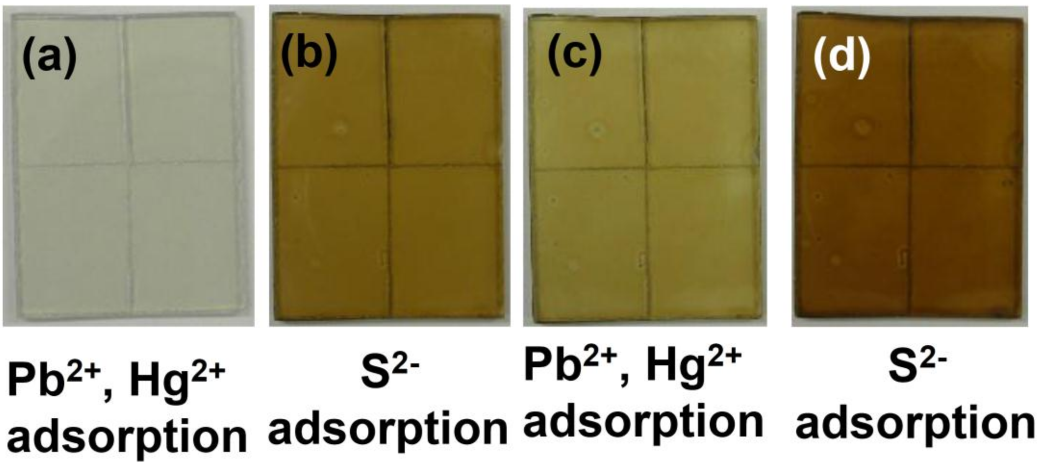

Figure S2. TiO_2 coated FTO glass during the 2 cycles coating of PbS:Hg quantum dot in the presence of TEA. The first coating cycle (a) → (b) and the second coating cycle (c) → (d).

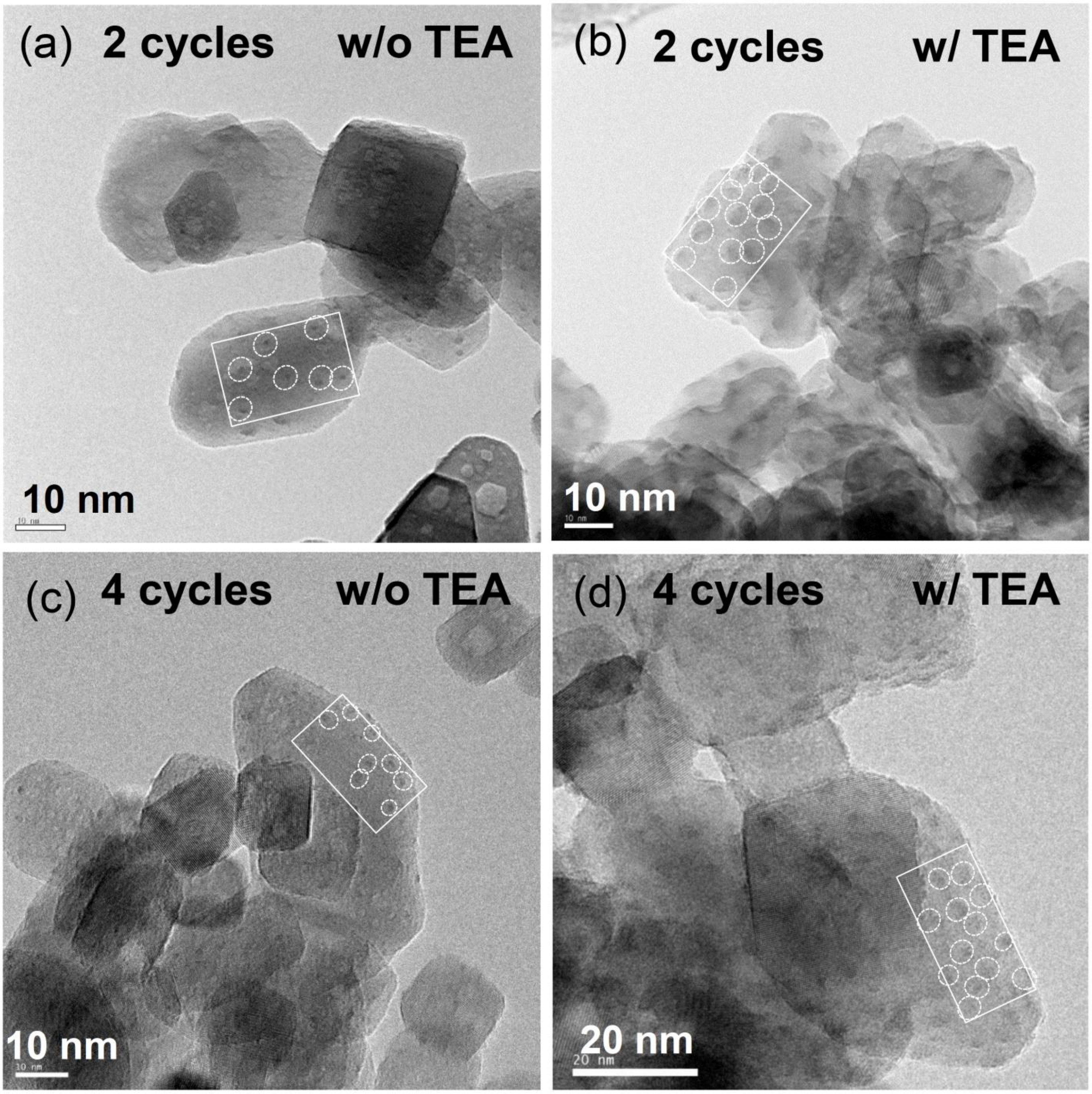

Figure S3. TEM micrographs of PbS:Hg QDs adsorbed TiO2 using cationic precursor solution (a), (c) without TEA and (b), (d) with TEA. SILAR coating cycle was 2 for (a), (b) and 3 for (c), (d). White rectangle boxes in (a), (b), (c) and (d) are Gaussian box and the dotted circles indicate the QDs adsorbed on TiO2 surface.

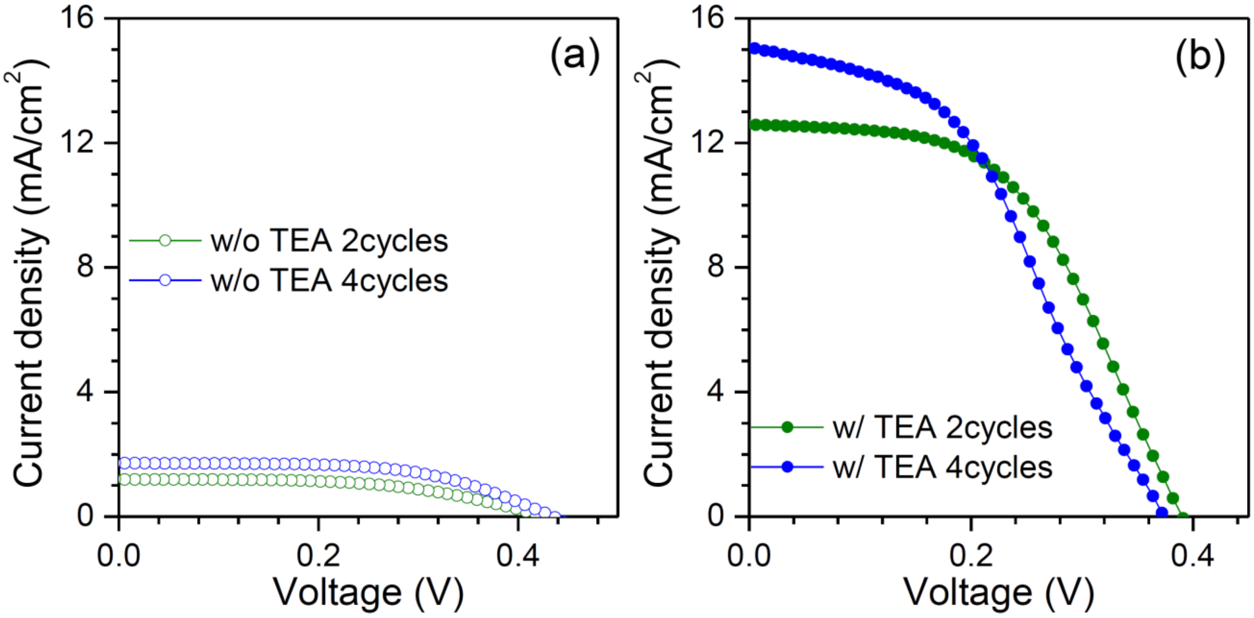

Figure S4. J-V curves of PbS:Hg QD-sensitized solar cell using cationic precursor solution (a) without TEA and (b) with TEA as a function of coating cycle. Thickness of TiO_2 was 2.37 ± 0.07 µm and active area was 0.44 ± 0.04 cm^2. Polysulfide solution composed of 1 M Na_2S, 1 M S and 0.3 M CsOH in DI water was used as a redox electrolyte. Cu_2S on brass sheet was used for counter electrode.

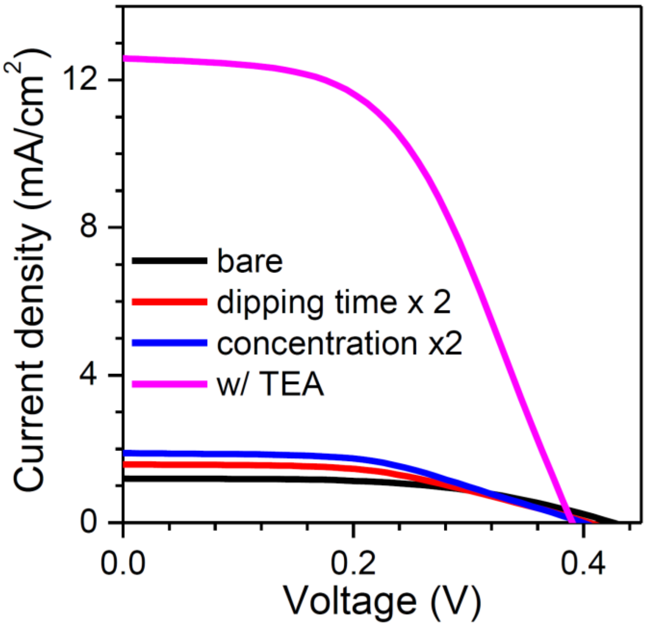

Figure S5. Effects of 2-fold longer dipping time and 2-fold higher concentration of the cationic solution on J-V curves of PbS:Hg QD-sensitized solar cell for the case of absence of TEA. Number of coating cycle was fixed to be 2. Polysulfide solution composed of 1 M Na_2S, 1 M S and 0.3 M CsOH in DI water was used as a redox electrolyte. Cu_2S on brass sheet was used for counter electrode. Measurement was carried out under simulated one sun (100 mW/cm^2).

Table S1. Photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and PCE (η) of PbS:Hg QD-sensitized solar cells depending on the dipping time and the concentration of cationic solution for the case of absence of TEA. Polysulfide solution composed of 1 M Na_2S, 1 M S and 0.3 M CsOH in DI water was used as a redox electrolyte. Cu_2S on brass sheet was used for counter electrode. Measurement was carried out under simulated one sun (100 mW/cm^2).

Device ID	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)	Area (cm^2)	Thickness (μm)
bare	1.21	0.426	0.53	0.27	0.431	2.31
dipping time × 2	1.58	0.405	0.49	0.31	0.455	2.36
concentration × 2	1.89	0.400	0.49	0.37	0.437	2.30
w/ TEA	12.59	0.390	0.51	2.52	0.421	2.46

References

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