Supporting Information

Metal Cluster Sensitized Solar Cells. A New Class of Thiolated Gold Sensitizers Delivering Efficiency Greater Than 2%

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Experimental Method

Materials. All reactions were carried out under an air atmosphere. Solvents were distilled from appropriate reagents. $Co(bpy)_3(PF_6)_2$, $Co(bpy)_3(PF_6)_3$ were synthesized using the procedure described in the literature.[1]

Au_x-SH Cluster Synthesis. Au_x-SH cluster was synthesized using a reported method with modification.[2] Briefly, 0.24 g of gold (III) chloride trihydrate (99.9%, Sigma-Aldrich) and 0.276 g of L - glutathione (reduced, 98%, Sigma-Aldrich) were mixed in 300 mL deionized water (DI water) at room temperature. The mixture was kept stirring until a colorless solution was obtained and subsequently heated to 70^{o}C for 24 hr. The as-synthesized Au_x-SH cluster was purified by adding acetonitrile to recrystallize the cluster and then thoroughly washed with DI water and acetonitrile mixture (1:3 in volume) and finally re-dispersed in DI water.

TiO_2 Colloid Solution Synthesis. TiO_2 colloid solution was prepared by adding titanium isopropoxide (98%, Sigma-Aldrich) into pure ethanol slowly under stirring. (25 mM)

Optical and Electrochemical Measurements. All experiments were carried out at room temperature. Absorption spectra were measured with a Varian Cary 50-Bio UV-vis spectrophotometer. Emission spectra were recorded using an SLM-S 8000 spectrofluorometer. A Princeton Applied Research model PARSTAT 2263 was used for recording I-V characteristics. Newport Oriel® QE Kit (QE-PV-SI) was used for measuring IPCE values. TEM image was taken using FEI Titan 80 – 300 microscope under 300 kV with Gatan Image Filter.

Nanocrystalline TiO_2 Electrode Preparation. FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min,

rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM $TiCl_4$ (aqueous) at 70 ℃ for 30 min and washed with water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by doctor blade printing TiO_2 paste (Solaronix, Ti-Nanoxide T/SP) and then dried at 25℃ for 2 h. The TiO_2 electrodes were gradually heated under an air flow at 325 ℃ for 5 min, at 375 ℃ for 5 min, at 450 ℃ for 15 min, and at 500 ℃ for 15 min. A paste for the scattering layer containing 400 nm sized anatase TiO_2 particles (CCIC, PST-400C) was deposited by doctor blade printing and then dried for 2 h at 25 ℃. The TiO_2 electrodes were again gradually heated under an air flow at 325 ℃ for 5 min, at 375 ℃ for 5 min, at 450 ℃ for 15 min, and at 500 ℃ for 15 min. The TiO_2 electrodes were treated again by $TiCl_4$ at 70 ℃ for 30 min and sintered at 500 ℃ for 30 min.

Sensitization of Au_x-SH Clusters onto TiO_2 film. The TiO_2 were immersed into the Au_x-SH cluster solution (4.6 wt. %, pH ~4, adjusted by NaOH) and kept at room temperature for 48 h followed by through washing with pure water and ethanol.

Sensitization of CdS/ZnS onto TiO_2 film. Sensitizaion with CdS and ZnS using (Successive Ionic Layer Adsorption and Reaction) SILAR techniques followed. The CdS SILAR consisted of five cycles of one 1 min dip into 0.1 M $Cd(NO_3)_2$ in methanol, followed by one 1 min dip into 0.1 M Na_2S in H_2O/methanol (1:1, v/v) with 30 s of methanol rinses between dips. ZnS was deposited using 0.1 M $ZnAc_2$ in methanol and 0.1 M Na_2S in H_2O/methanol (1:1, v/v) with 1 min dips, followed by rinsing for a total of two cycles.

Solar Cell Fabrication. The Au_x-SH clusters sensitized TiO_2 film is used as a working electrode. The FTO plate (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) used for the counter electrodes was cleaned with ultrasonic bath in H_2O, acetone and 0.1 M HCl aq., subsequently. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on the cleaned FTO plate and sintered at 400 ℃ for 15 min. The Au_x-SH clusters adsorbed TiO_2 electrode and Pt-counter electrode were assembled into a

sealed sandwich-type cell by heating at 80 °C with a hot-melt ionomer film (Surlyn SX 1170-25, Solaronix) as a spacer between the electrodes. A drop of electrolyte solution (electrolyte of 0.22 M $Co(bpy)_3(PF_6)_2$, 0.033 M $Co(bpy)_3(PF_6)_3$, 0.1 M $LiClO_4$, and 0.5 M 4-*tert*-butylpyridine in acetonitrile.) was placed over a hole drilled in the counter electrode of the assembled cell and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness).

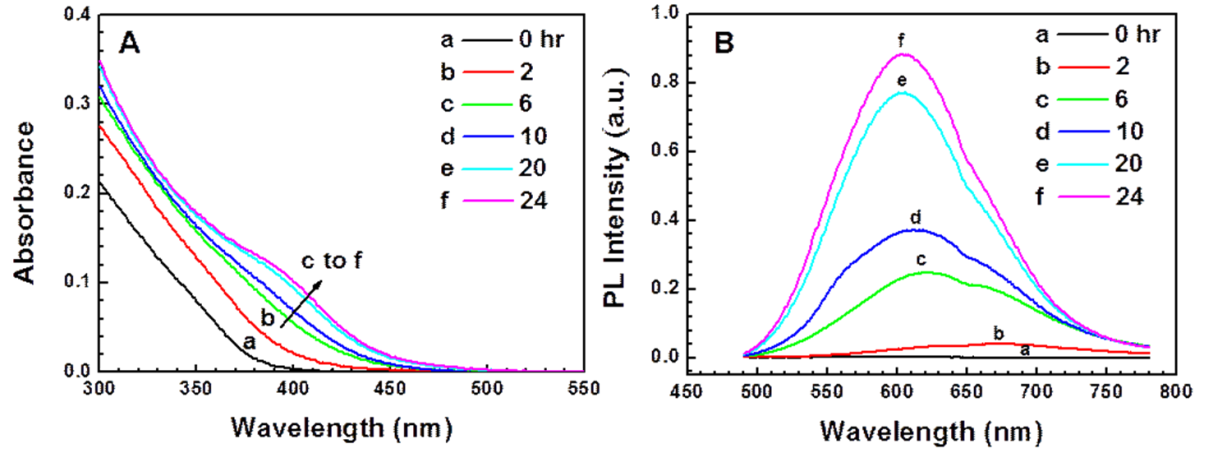

Figure S1. (A) Absorption and (B) Emission spectra recorded during the growth of Au_x-SH: (a) 0 hr, (b) 2 hr, (c) 6 hr, (d) 10 hr, (e) 20 hr, and (f) 24 hr.

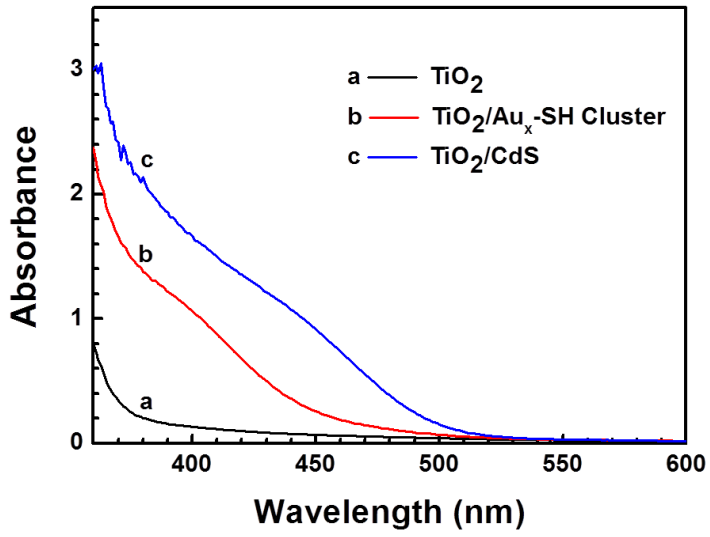

Figure S2. Absorption spectra of (a) TiO_2, (b) TiO_2 modified with Au_x-SH cluster, and (c) TiO_2 modified with CdS photoanodes.

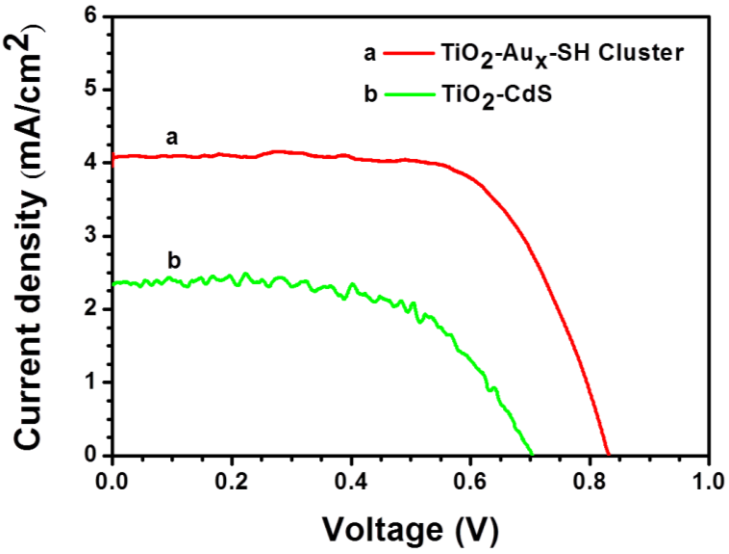

Figure S3. *J-V* characteristics of MCSC and QDSC employing photoanodes: (a) TiO_2 modified with Au_x-SH cluster and (b) TiO_2 modified with CdS. (From reference 3)

References

(1) Feldt, S. M.; Gibson, E. A.; Gabrielsson, E.; Sun, L.; Boschloo, G.; Hagfeldt, A. *J. Am. Chem. Soc.* **2010**, *132*, 16714-16724.

(2) Luo, Z. T.; Yuan, X.; Yu, Y.; Zhang, Q. B.; Leong, D. T.; Lee, J. Y.; Xie, J. P. *J. Am. Chem. Soc.* **2012**, *134*, 16662-16670.

(3) Choi, H.; Santra, P. K.; Kamat, P. V. *ACS Nano.* **2012**, *6 (6)*, 5718-5726