

Supporting Information

Efficient charge-carrier extraction from Ag₂S quantum dots prepared by SILAR method for utilization of multiple exciton generation

Xiaoliang Zhang ¹, Jianhua Liu ², Erik M. J. Johansson ^{1,*}

¹ Department of Chemistry-Ångström Laboratory, Uppsala University, 75120 Uppsala, Sweden

² School of Materials Science and Engineering, Beihang University, 100191 Beijing, China.

*Corresponding Author: erik.johansson@kemi.uu.se

Experimental Details.

Preparation of TiO₂ film substrate : FTO layer in the center area of FTO glass (TEC15, Pilkington) was etched with Zn powder and HCl solution (2 M). The etched samples were washed in an ultrasonic bath for 30 min in detergent, deionizer water, ethanol and acetone, and then dried in air. The TiO₂-paste (Dyesol DSL 18 NR-T) was covered on the FTO glass using doctor blading technique, obtaining TiO₂ film with a thickness of ~6 μm. The samples were sintered gradually at 180 °C (10 min), 320 °C (10 min), 390 °C (10 min) and 500 °C (60 min) in an oven (Nabertherm Controller P320) in air atmosphere. During sintering treatment, the organic additives in the TiO₂-paste were removed and a mesoporous TiO₂ film was obtained. After sintered, the samples were treated in TiCl₄ (40 mM) solution at 70 °C for 30 min, and sintered again at 500 °C for 60 min.

Preparation of Ag₂S QD and contact electrodes: SILAR method was applied to synthesize Ag₂S QD on the TiO₂ substrate at room temperature according to the reference.¹ Briefly, the TiO₂ film was immersed into 0.1 M AgNO₃ ethanol solution for 3 min, and then rinsed with ethanol to remove the excess precursor solution. Then, the TiO₂ film was immersed into 0.1 M Na₂S methanol solution for 3 min and rinsed with methanol. The above procedures formed one SILAR cycle. Such SILAR cycles were repeated from 6 to 12 times. Finally, a top Au electrode with a thickness of ~80 nm was deposited on the QD layer using a thermal evaporator (LEICA EM MED020) in a vacuum of 4×10⁻⁵ Torr, forming the complete device.

Characterization: The light absorption spectra were measured at room temperature with a UV-Vis-NIR spectrophotometer (Cary 5000). The samples for TEM and EDS measurements were prepared by scraping the Ag₂S/TiO₂ nanostructure film from FTO glass and dispersed in ethanol under ultrasonic desparation. The corresponding solution was dropped onto a carbon film supported by a copper grid, followed by slow evaporation of solvent under ambient condition. TEM and HRTEM images were obtained by using a transmission electron microscope (JSM, 2100) at an accelerating voltage of 200 kV. SEM images were

collected using a scanning electron microscopy (SEM, Zeiss LEO1550) at an accelerating voltage of 5 kV. The crystal structure was characterized using X-ray diffraction (XRD) with Cu K α radiation.

Current-voltage curves measurement: The current-voltage (J - V) characteristic curves were measured in both dark and under illumination. The light of illumination was provided by a 300 W Xenon lamp (Newport), which provided simulated AM 1.5 solar irradiance with an intensity of 100 mW/cm², adjusted using a silicon reference solar cell. The J - V curves were recorded using a Keithley (model 2400) measurement unit. The fitting curves in Figure 4 were prepared with Origin software and smoothed using “Savitzky-Golay” method at “Points of Window” of 30. The differential resistance and static resistance of the Ag₂S/TiO₂ nanostructure film were calculated from the J - V curves.

Photo-induced absorption spectra measurement: Photo-induced absorption (PIA) spectra were recorded using a white probe light generated by a 20 W tungsten-halogen lamp, which was superimposed with a square-wave modulated (on-off) blue LED (Luxeon Star 1 W, Royal Blue, 460 nm) used for excitation, as previous reported.^{2,3} The transmitted probe light was focused onto a monochromator (Action Research Corporation SP-150) and detected by a UV enhanced silicon photodiode connected to a current amplifier and lock-in amplifier (Stanford Research System models RS570 and RS830, respectively). The frequency of 9.3 Hz was used for the excitation LED.

Photon energy dependent carrier extraction measurement: The carrier extraction was measured similar to ref.4, but here using continuous light. Briefly, a Xenon lamp (Spectral Products ASB-XE-175) together with a monochromator (Spectral Products CM110) provided light with different wavelength with light intensity of approximately 10 mW/cm². A Keithley (model 2700) measurement unit recorded the current. A silicon photodetector was used to measure the light intensity at different wavelengths. The wavelength tuned beam was focused to the device area without FTO. A fixed voltage bias (1~4 V) from a voltage source was applied to the device, providing electric field for carrier extraction and collection. Incident photon with energy of 1.5-3.5 eV was used to excite the sample. As to obtain stable carrier extraction, the voltage bias was applied to the device for ~10 min before photoexcitation. The photoexcited current was calculated by subtracting dark current from the photo enhanced current. The TiO₂ film without QDs showed very low photocurrent and it was also subtracted from the results although it had negligible effect on the results. The data was normalized to 1 at photo energy of 1.8 eV (~690 nm wavelength).

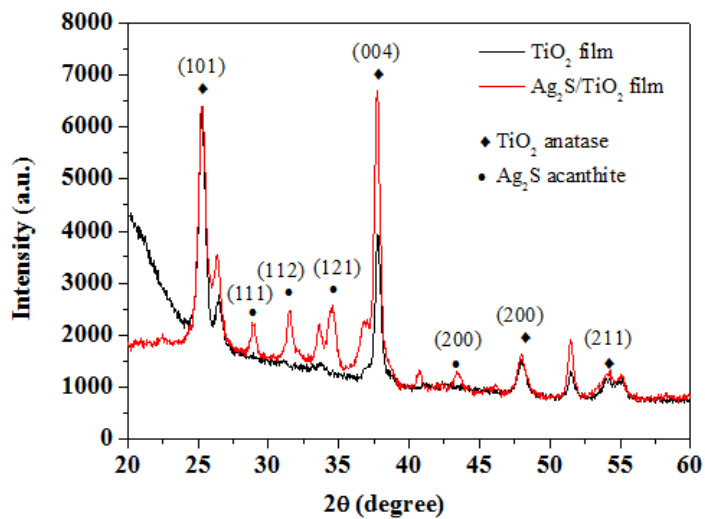


Figure S1. XRD pattern of $\text{Ag}_2\text{S}/\text{TiO}_2$ nanostructure film.

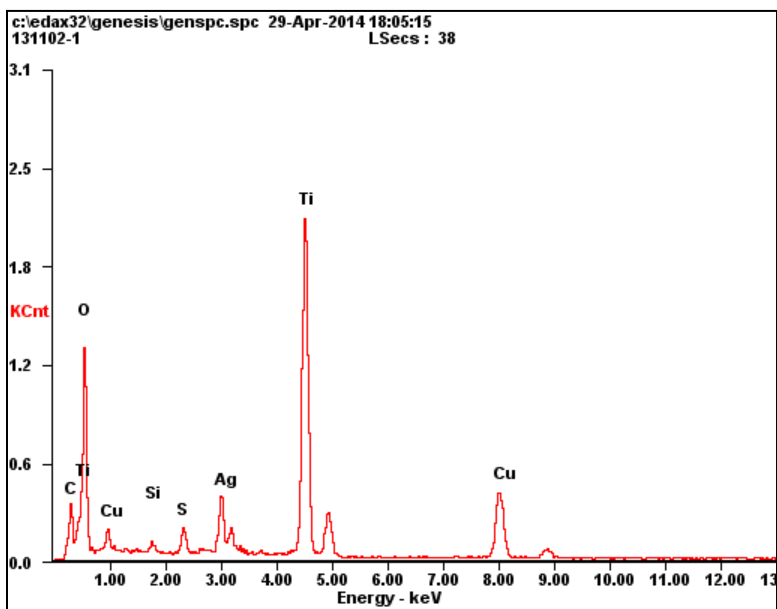


Figure S2. EDS spectrum of $\text{Ag}_2\text{S}/\text{TiO}_2$ nanostructure film. The presence of C and Cu peaks came from the carbon-coated Cu grid used for the TEM and EDS analysis. Ag, S, Ti, and O element came from the Ag_2S QD and TiO_2 nanoparticles.

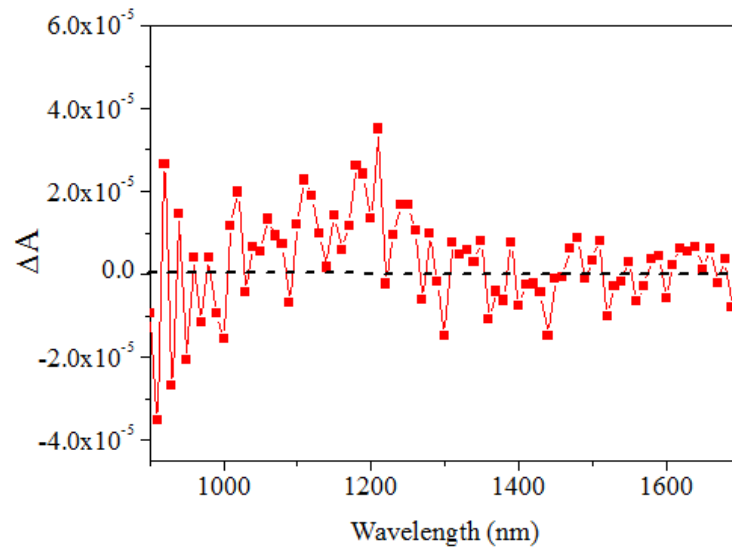


Figure S3. PIA spectra of the $\text{Ag}_2\text{S}/\text{TiO}_2$ nanostructure film. The excitation wavelength is 460 nm, and every point is an average value of 500 measured points.

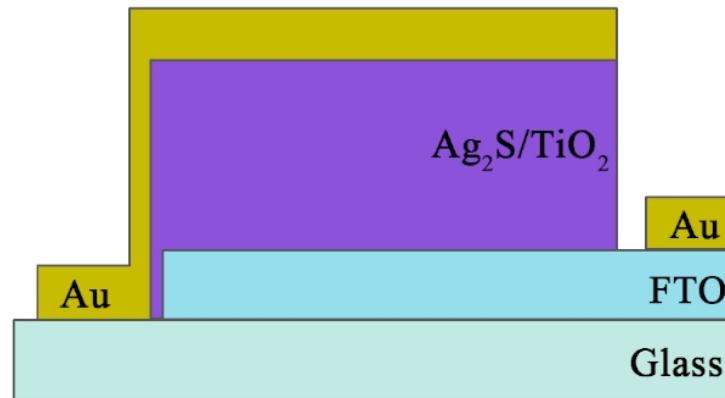


Figure S4. Schematic illustration of J - V measurement. The thickness of $\text{Ag}_2\text{S}/\text{TiO}_2$ nanostructure film is $\sim 6 \mu\text{m}$.

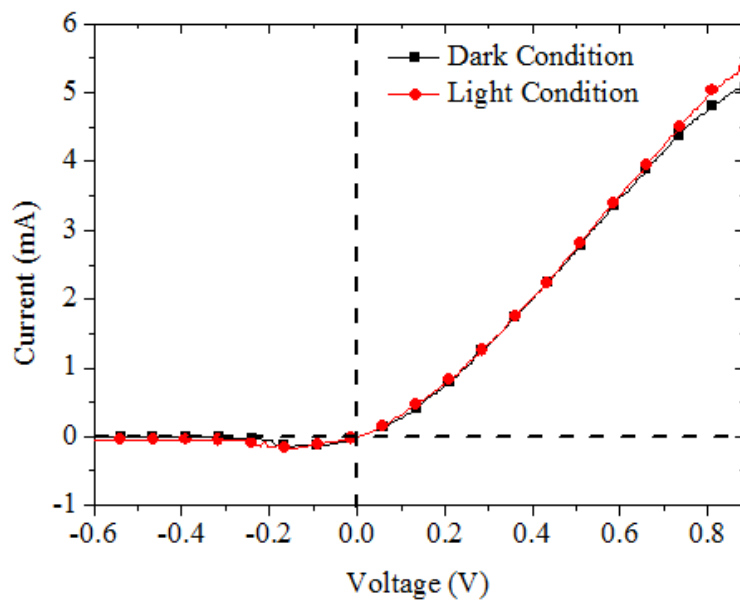


Figure S5. J - V curves under dark and illumination conditions measuring by connecting to the TiO_2 (FTO) layer and the Au contact. The SILAR cycles for QD formation is 12 cycles.

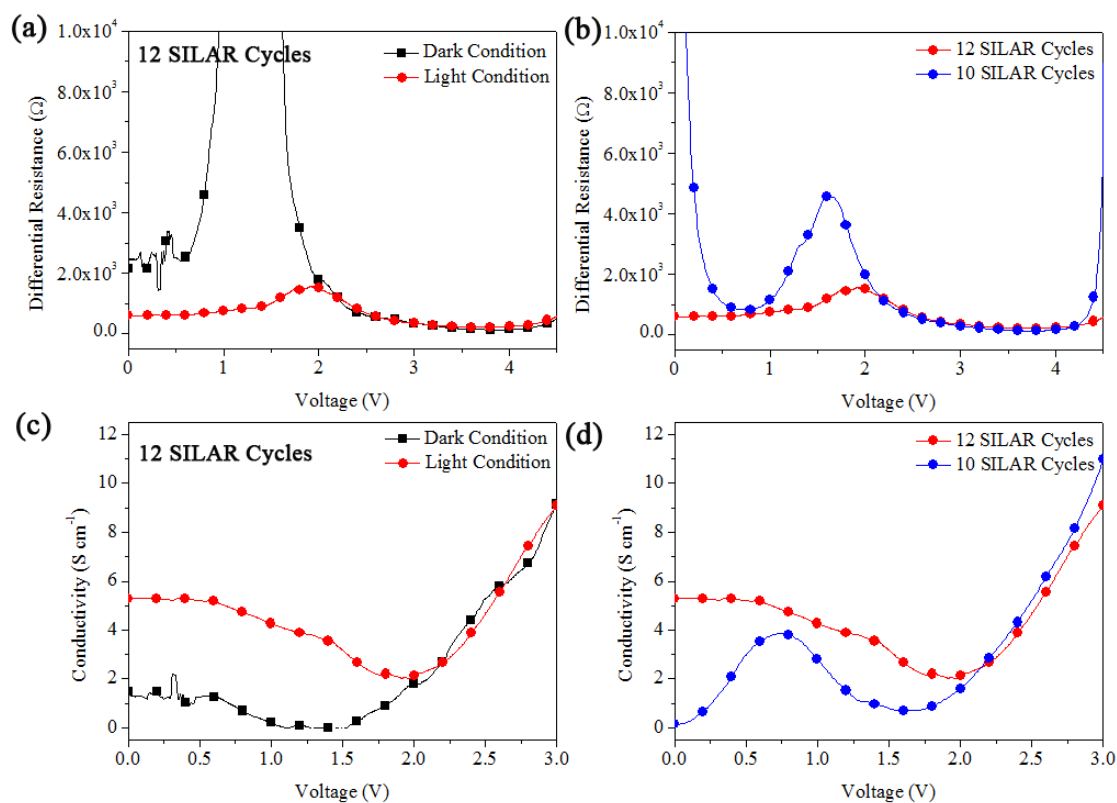


Figure S6. (a) The differential resistance, $R(V_0)_{Diff}$ of the $\text{Ag}_2\text{S}/\text{TiO}_2$ nanostructure film as a function of applied voltage V_0 . The distance between the electrodes is 8 mm, and the SILAR cycles for QD formation

is 12 cycles. The differential resistance $R(V_0)_{Diff}$ was obtained by calculating the derivative of the J - V curves at different applied voltage. In the light condition, the device was under 100 mW/cm² of AM 1.5. (b) The differential resistance of the Ag₂S/TiO₂ nanostructure films with 12 and 10 SILAR cycles for QD formation. (c) The conductivity, σ , through the films as a function of applied voltage bias. Conductivity was calculated as $\sigma = L/(R(V_0)_{Diff} wt)$, where L is the channel length, w is the channel width and t is the film thickness and $R(V_0)_{Diff}$ is the film differential resistance in (a). (d) The conductivity of the Ag₂S/TiO₂ nanostructure films with 12 and 10 SILAR cycles for QD formation.

Figure S6 presents the differential resistance and conductivity of the films under dark and illumination condition. Figure 6a shows the relationship between differential resistance, $R(V_0)_{Diff}$, and applied voltage V_0 . The $R(V_0)_{Diff}$ is film differential resistance at applied voltage V_0 , that is calculate using following equation:^{5,6}

$$R(V_0)_{Diff} = \left. \frac{dV}{dJ} \right|_{V=V_0} \quad (1)$$

Where the $R(V_0)_{Diff}$ is equal to the slop of the J - V curve at the voltage V_0 . As shown in the Figure S6a, the resistance, $R(V_0)_{Diff}$, depends on the applied voltage. In the dark condition, the film exhibits relatively high resistance, however, when the voltage is high enough, the resistance decreases. The current came from the contact electrode. In contrast, when the device was under the illumination, the film possesses lower resistance as the applied voltage $V < 2$ V. As the voltage increases more than 2 V, film shows the similar resistance for both dark and illumination. These results are good agreement with the observation in J - V measurement, which indicate that the photoexcited carriers contribute to the conductivity. However, when applied higher voltage to the device, the device in both dark and illumination conditions have similar differential resistance. We estimated the conductivity, σ , through the film by taking the differential resistance as the gradients of the curves using equation (2):⁷

$$\sigma = \frac{L}{R(V_0)_{Diff} wt} \quad (2)$$

Where L is the channel length, w is the channel width and t is the film thickness and $R(V_0)_{Diff}$ is the film resistance at applied voltage V_0 . In above equation, we neglected the contact resistance between Au electrode and QDs, which was verified without any impact in our device. Figure S6c shows the conductivity through the film as a function of applied voltage. The conductivity of a materials is equal to the product $ne\mu$, where n is the charge density, e is the charge of an electron and μ is the charge mobility. The enhancement in conductivity under illumination may be due to either increasing charge density or enhanced mobility under electric field or a combination of the two. Therefore, it is difficult to estimate which part is contributing more to the conductivity. Snaitth et al also observed similar phenomenon when studied the conductivity of Spiro-MeOTAD film under different illumination intensity.⁷

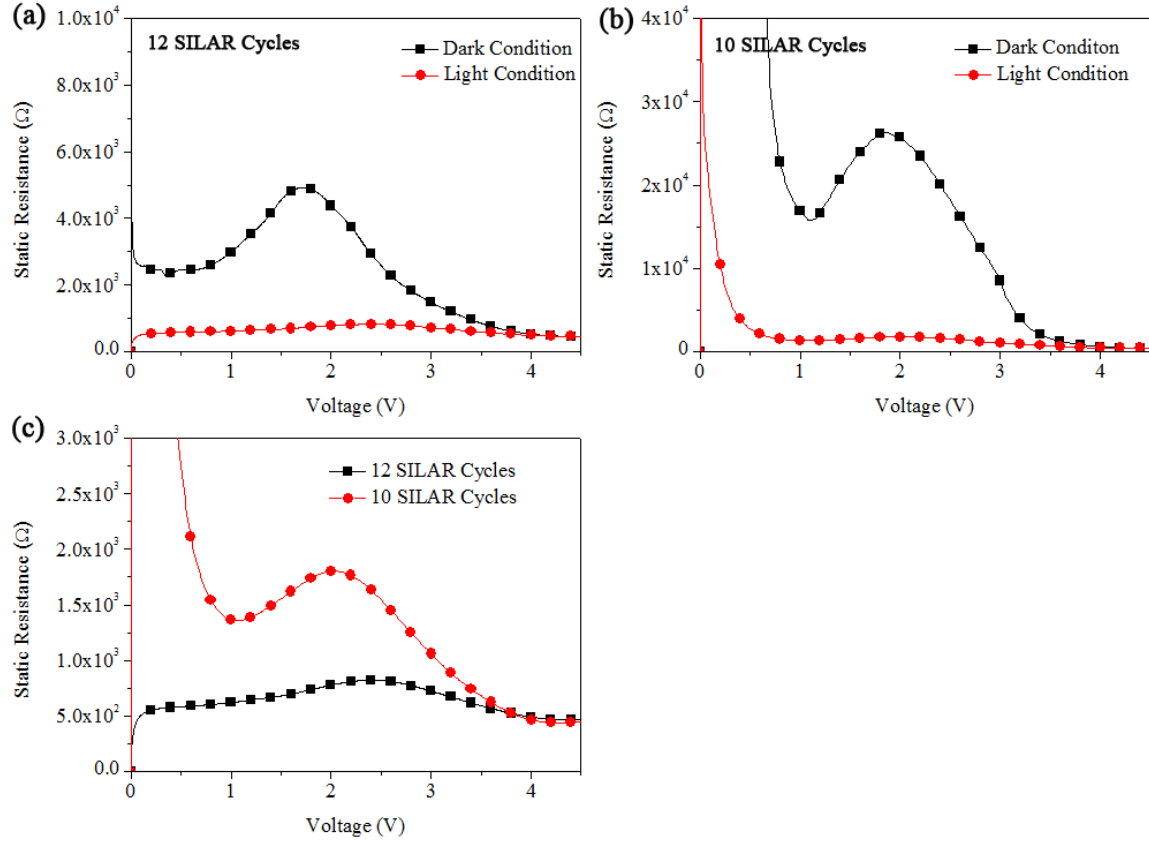


Figure S7. The static resistance, $R(V_0)_{Static}$, of $\text{Ag}_2\text{S}/\text{TiO}_2$ nanostructure films is as a function of applied voltage V_0 for (a) 12 SILAR cycles (b) 10 SILAR cycles for QD formation; (c) The static resistance of the $\text{Ag}_2\text{S}/\text{TiO}_2$ nanostructure films with different SILAR cycles for QD formation. In the light condition, the device was under $100 \text{ mW}/\text{cm}^2$ of AM 1.5.

The static resistance, $R(V_0)_{Static}$, was calculated using following equation:^{5,6}

$$R(V_0)_{Static} = \frac{V}{J} \Big|_{V=V_0} \quad (3)$$

where the $R(V_0)_{Static}$ is the resistance at the applied voltage V_0 from the J - V curves. When under the illumination, the device has relatively lower static resistance. Increase SILAR cycles for QD formation, the static resistance decreases that is similar with differential resistance in Figure S6.

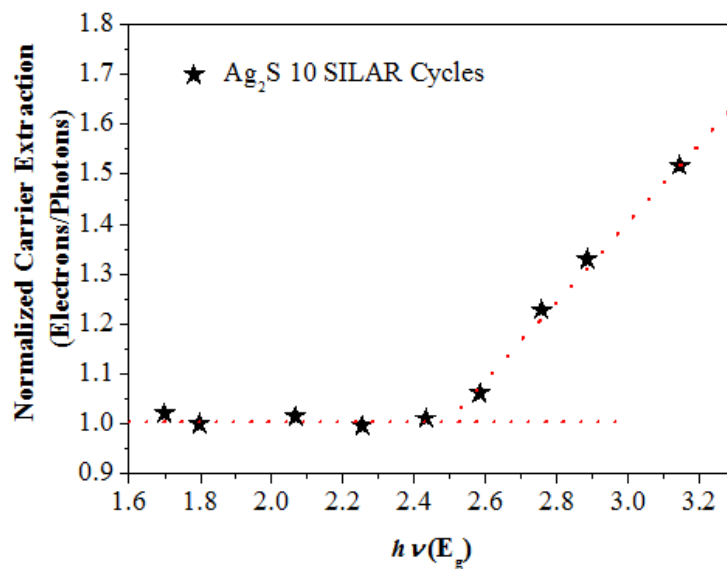


Figure S8. Photo energy dependent carrier extraction measurement. The SILAR cycles for QDs formation is 10 SILAR cycles, and the applied voltage is 3.6 V.

References.

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