Supporting Information

Towards Antimony Selenide Sensitized Solar Cells: Efficient Charge Photogeneration at *Spiro*-OMeTAD/Sb₂Se₃/Metal Oxide Heterojunctions

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1.- Experimental Section

1.1.-SILAR procedure for the Sb₂Se₃ deposition

The method relies on successive immersions of the substrate in the following solutions:

- a) Antimony source: the substrate is immersed for 30 s in a 10 mM SbCl₃ (Sigma Aldrich) acetone solution.
- b) Washing (I): the electrode is dipped in acetone (99.9 %, VWR) for 1 min and subsequently in EtOH (>99.7 %, VWR) for 30 s. The first solution is intended to remove the excess of non-adsorbed precursor, while the second to replace the acetone by EtOH.
- c) Selenium source: The substrate is immersed for 30 s in a 30 mM Se²⁻ ethanolic solution. This selenium source was prepared by following the method described by Klayman et al.¹ In this case 0.24 g of selenium powder (100 mesh, 99.99 %, Alfa Aesar) are stirred with 100 ml of EtOH in a round bottom flask under N₂ atmosphere. Subsequently, 0.113 g of NaBH₄ is added to the suspension. As observed the solution turns from black to colourless in 15-20 min. This solution must be kept under N₂ atmosphere during all the preparation and the SILAR process, using a continuous N₂ flow.
- d) Washing (II): The substrate is soaked in EtOH for 1 min and subsequently in acetone.

This SILAR cycle was repeated several times to prepare the sensitized samples as mentioned in the main text.

1.2. - Preparation of mesoporous metal oxide substrates and electrodes

Mesoporous TiO₂ films were prepared by doctor blading the commercial paste Solaronix (Ti-Nanoxide T37) over glass substrates, and subsequently annealing at 450 °C for 30 min. The thickness of the films was measured to be 2.5 μ m with a profilometer AlphaStep D-100 (KLA Tencor). Mesoporous ZrO₂ films were prepared using a homemade paste (20-30 nm) following the same procedure described for TiO₂. In this case the thickness was 5 μ m.

Mesoporous TiO_2 electrodes for electrochemical measurements were prepared as described above but using F-doped SnO₂ conductive glass as a substrate. Furthermore, SILAR was carried out directly on FTO in order to measure the location of the conduction band, as described below.

1.3.-Addition of the spiro-OMeTAD

The *spiro*-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-*p*-methoxyphenyl-amine)-9,9'-*spiro*bifluorene, Merck) was employed as hole transporting material (HTM). It was introduced in the mesoporous structure by spin-coating 40 μ l·cm⁻² of a 0.17 M *spiro*-OMeTAD, 10 mM Li(CF₃SO₂)₂N (bis(trifluoromethane)-sulfonamide 99.5 %, Aldrich) and 19 mM tertbutylpyridine solution in chlorobenzene as described elsewhere.² The HTM solution was allowed to penetrate for 60 s before spin coating at 1000 r.p.m. The samples were dried in air for 1 week.

1.4.- Annealing

The annealing of the samples was carried out both in air and N_2 atmosphere. The annealing in air was performed in a hot plate at the desired temperature for 30 min in the dark. In order to

perform the annealing under N_2 , the same procedure was followed but, in this case, placing the sample inside a flat bottom flask and maintaining a constant N_2 flow during the process.

1.5.- Deposition of $In_x(OH)_yS_z$

The $In_x(OH)_yS_z$ layer was prepared by the chemical bath deposition reported by Bayón et al.³ Briefly, a 25 mM InCl₃, 0.1 M thioacetamide and 0.1 M acetic acid solution was prepared with ultrapure water. The electrodes were immersed in this solution for 1 h at 70 °C. Finally the electrodes are removed from the bath and rinsed thoroughly with ultrapure water.

1.6.- Characterization of sensitized metal oxide samples

The steady-state absorption spectra of Sb₂Se₃-sensitized metal oxide films were obtained by means of a Perkin-Elmer Lambda 750 UV-vis-nIR spectrometer. Raman spectra were recorded with a Renishaw inVia Raman microscope in a backscattering configuration. The excitation line was provided by an Ar laser at 514.5 nm. Atomic Force Microscopy (AFM) was carried out using a Nanoscope III (Digital Instruments) operated at room temperature in air. Images were recorded in tapping mode using silicon tips (Veeco) at a driving frequency of \Box 270 kHz.

1.7. – Preparation of the rutile single crystal and deposition of Sb₂Se₃ QDs.

 TiO_2 rutile (110) single crystals were purchased from Commercial Crystal Laboratories, Inc. In order to define an atomically smooth surface, the single crystal was submitted to a treatment as previously described.⁴ The SILAR method was performed on the rutile single crystal following the aforementioned procedure.

1.8.- Electrochemical measurements

Electrochemical measurements were carried out at room temperature in a three-electrode cell equipped with a fused silica window using a computer-controlled Autolab PGSTAT30 potentiostat. All the potentials were measured against and referred to an Ag/AgCl/KCl (saturated) reference electrode while a Pt wire was used as a counter electrode. The working electrolyte was a N₂-purged solution of 0.5 M Na₂SO₃ (98%, Alfa Aesar) prepared in ultrapure water. In photoelectrochemical measurements a 150 W Xe arc lamp (Osram) was used for electrode illumination from the substrate side. The light intensity was measured with an optical power meter (Oriel Model 70310) equipped with a photodetector (thermo Oriel 71600). The photocurrent measurements were performed using the full output of the lamp equipped with a UV filter (cutoff λ <380 nm, 75 mW·cm⁻²). Cyclic voltammetry was carried out at 20 mV·s⁻¹ in the dark.

1.9.- Transient Absorption Spectroscopy measurements

Transient optical studies were carried out as described previously.⁵ The excitation wavelength was 450 nm using pulses from a nitrogen laser pumped dye laser (<1ns pulse duration, 4 Hz) with power intensities around 40 μ J·cm⁻² (exact values stated in the corresponding figures). Photoinduced changes in the optical density were probed using a 100 W tungsten lamp coupled to monocromators to select the wavelength (before and after the sample). The detection systems used were homemade photodiodes based on Si and In_xGa_{1-x}As (for detection below and above 1000 nm, respectively). Changes were monitored and recorded with a Tektronix TDS 1012 oscilloscope coupled with computer acquisition software. The measurements were carried out under N₂.

2.- Detailed morphological and compositional analysis

Figure S1 presents the TEM images of mesoporous TiO_2 films before and after modification with Sb₂Se₃. After 3 cycles the roughness of the TiO₂ particle surface changes noticeably due to the deposition of nanoparticles grown by the SILAR method. After 5 cycles, big aggregates can be seen together with small particles evenly distributed. Finally, modification with 8 SILAR cycles gives rise to a complete coverage of the TiO₂ nanoparticle surface. In this case, even the structure of the TiO₂ nanoparticles is hidden by the as-generated nanoparticles whose crystallographic planes are easily distinguished.

The EDX analysis performed simultaneously reveals an excess of Sb, much larger for the 8 cycles SILAR sample. As discussed in the main text, given that Raman Spectroscopy does not reveal presence of Sb₂O₃; this could be ascribed to amorphous Sb generated by the reduction of Sb (III) by NaBH₄ during the immersion in the selenide solution.



Figure S1. TEM images of bare mesoporous TiO_2 (A), and after sensitization with 3 cycles (B), 5 cycles (C) and 8 cycles of SILAR (D). Atomic ratio Sb:Se obtained by EDX is shown in the images.

Figure S2 shows the AFM images obtained for a TiO_2 rutile (110) single crystal before and after Sb_2Se_3 deposition. Before sensitization, only TiO_2 with the characteristics monoatomic steps can be seen. After 5 SILAR cycles, the surface is spotted by small nanoparticles, in contrast to the high coverage observed in TEM images. Cross-section analysis reveals flat nanoparticles with an apparent diameter of 60 nm and height of 2.5 nm) (figure S3). No corrections were applied to take into account eventual tip-induced distortions in the AFM images. When the number of cycles increases to 8, the size of the nanoparticles are larger and big aggregates of NCs are detected.



Figure S2. AFM images of bare rutile (110) single crystal prior (A) and after modification with 5 cycles (B) and 8 cycles (C,D) of SILAR.



Figure S3. Cross section analysis of the sample for 5 cycles.

3. - Determination of the Sb₂Se₃ energy levels

SILAR was carried out on a FTO substrate and the resulting film annealed at 80 °C. Figure S4A shows the Tauc plot fitting of the absorption spectra of the sample, measuring an average band gap of 2 eV. In order to determine the position of the conduction band edge, photocurrent transients at different potentials were performed (figure S4B). Upon light absorption, electrons are injected into the electron collector (FTO) while the holes are swiftly scavenged by Na₂SO₃.4 As shown, the photocurrent decreases as the Fermi level shifts upward (decrease of the applied potential), until complete quenching from -0.77 V onward. We consider complete quenching of the photocurrent when both the current recorded in dark and under illumination match,without taking into account the spikes appearing at the beginning and the end of the transient. In this situation, we consider that the Fermi level of the substrate coincides with the donor energy level of Sb₂Se₃, i.e. the conduction band (CB) edge. Therefore, the CB of the Sb₂Se₃ is located at - 0.77 V (vs Ag/AgCl/KCl (sat.)) or -3.87 eV vs vacuum. We assume that the potential of the standard hydrogen electrode corresponds to a value of -4.44 eV in the vacuum scale.⁶ It must be underlined that this is just an approximation of the location of the conduction band, which may change depending on the contacting medium.

The location of acceptor states (CB or surface states) in the TiO_2 was also measured, but in this case using cyclic voltammetry. As shown in figure S5, at -0.77 V there is indeed a significant capacitive current indicating available density of empty states which are able to accept charge. This exponential distribution of states below the conduction band is usually ascribed to surface states in the metal oxide.^{7,8} According to that we locate at -0.5 V (vs Ag/AgCl/KCl (sat.)) or -4.2 eV the beginning of the exponential distribution of surface states.



Figure S4. Tauc plot fitting of the absorption of Sb_2Se_3/FTO electrode (A) and photocurrent transients performed at different (labeled) potentials (B). The electrolyte employed in electrochemical measurement was N₂-purged 0.5 M Na₂SO₃. Irradiance: 75 mW·cm⁻².



Figure S5. Cyclic voltammetry of TiO_2/FTO at 20 mV·s⁻¹ in the dark. Measurements were done in N₂-purged 0.5 M Na₂SO₃.

4.- Transient Optical studies

4.1.- Optimization of the number of cycles

Figure S6A shows the transient absorption spectra for Sb_2Se_3/TiO_2 films recorded 10 µs after the excitation pulse (450 nm). In all the cases a negative signal is followed by a positive plateau. As explained in the main text, the first one is ascribed to the ground state bleaching whereas the positive featurless band can be ascribed to either electrons in TiO_2^{9} or localized holes into the Sb_2Se_3 nanocrystal.¹⁰ As observed, in agreement with the shift in the absorption spectra of the samples, the transient spectra is red shifted when increasing the number of cycles.



Figure S6. Transient absorption spectra of Sb_2Se_3/TiO_2 films, measured 10 µs after excitation (A). Transient kinetics monitored at 1200 nm (B). Samples were excited at 450 nm (fluency 38 µJ·cm⁻²), all the measurements were carried out under N₂ atmosphere.

Transient decay dynamics were measured for the Sb₂Se₃/TiO₂ films as a function of the number of cycles at 1200 nm (figure S6B). As shown, the charge separation is improved by repeating the SILAR cycles until saturation.

4.2- Annealing effect

Figure S7 shows the transient optical decays of Sb₂Se₃/TiO₂ (3 cycles) annealed at different temperatures in air and N₂. Thermal treatments at 80 °C (in air) and 100 °C (in N₂) give rise to a threefold enhancement of the transient signal (recorded at 1 μ s), i.e. an increase in the yield of long-lived charge-separated states. Higher temperatures yield poorer performance in both cases, accounted for the QD surface oxidation and/or aggregation, as inferred from the apparent blue and red shifts in the absorption spectra. Annealing at 80 °C in air was also applied to the rest of the samples (Figure S8). As expected, in all the cases the charge separation is improved, but the 3 cycles SILAR sample gives rise to the most efficient charge separation, likely due to a high coverage and large driving force for injection.



Figure S7. Transient decays and absorption spectra of Sb₂Se₃/TiO₂ (3 cycles) films after annealing at different temperatures and atmospheres: in air (A,C) and under N₂ atmosphere (B,D). Transient dynamics were obtained exciting the sample at 450 nm (fluency: $38 \mu J \cdot cm^{-2}$) and probing at 1200 nm. The measurements were carried out under N₂.



Figure S8. Transient dynamics for Sb_2Se_3/TiO_2 films annealed at 80 °C in air as a function of the number of SILAR cycles. The samples were excited at 450 nm (fluency: 38 μ J·cm⁻²), and probed at 1200 nm. The measurements were carried out under N₂.

5.- The role of the $In_x(OH)_vS_z$ layer in the charge recombination

The deposition of a intermediate layer of $In_x(OH)_yS_z$ on the TiO₂ prior to the QD deposition seems to be beneficial to the performance of solid state QDSCs.¹¹ Figure S9 shows transient optical studies to unravel its effects on recombination. As can be seen, after $In_x(OH)_yS_z$ deposition the back electron transfer (i.e. recombination between electrons in TiO₂ and holes in QD) is slowed down. This is not unexpected since this layer acts as a barrier increasing the resistance for the back electron transfer. However, no difference is observed in the recombination with the HMT. This result suggest that the high QD coverage, revealed by TEM, plays the role of a physical and energetical barrier for the electron transfer from the TiO₂ to the HMT, introducing a charge resistance higher than that of the $In_x(OH)_yS_z$, and thus controlling the process.



Figure S9. Transient decays of Sb₂Se₃/TiO₂ films prior and after introducing the intermediate $In_x(OH)_yS_z$ layer (either annealed and non-annealed samples are tested).Excitation was carried out at 450 nm (fluency: 38 μ J·cm⁻²). The measurements were carried out under N₂.

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