Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information:

Electron and hole transfer at metal oxide/Sb_2S_3/*spiro*-OMeTAD heterojunctions

*Flannan T.F. O'Mahony,[1] Thierry Lutz,[1] Néstor Guijarro,[1,2] Roberto Gómez,[2] Saif A. Haque [1,]**

[1]Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, U.K.

[2]Institut Universitari d'Electroquímica i Departament de Química Física, Universitat d'Alacant, Ap. 99, E-03080, Alicante, Spain

** Author to whom correspondence should be addressed*

Experimental:

Mesoporous TiO_2 films were deposited on glass slides from Ti-nanoxide T37 paste (37 nm particles, Solaronix) by doctor blading and sintering at 450 °C. Resultant films were measured to ~ 6 μm in thickness by profilometry. ZrO_2 films of 20-30 nm particles were also ~6 μm thick. Sb_2S_3 nanocrystals were grown on the surface of the resulting TiO_2 and ZrO_2 mesoporous films by successive ionic layer absorption and reaction (SILAR) from 0.02 M $SbCl_3$ and 0.02 M Na_2S ethanolic solutions. Reactant solutions were filtered prior to sensitisation. Films were washed in EtOH between immersions in reactant solutions. All immersion times were 1 minute. A single immersion in each reactant solution constitutes one deposition 'cycle'. Annealing was conducted on a hot plate under nitrogen in a glove box. *Spiro*-OMeTAD (2,2′,7,7′-tetrakis-(N,N-di-p- methoxyphenyl-amine)-9,9′-spirobifluorene, Merck) was deposited by spin coating from a 0.17 M chlorobenzene solution at 2000 rpm for 1 minute. The solution was allowed to rest on the surface of the film for 1 minute prior to spin coating.

Steady state absorption spectroscopy was performed using a Perkin-Elmer Lambda 25 UV-vis-IR spectrometer. Raman spectroscopy was performed using a Renishaw inVia Raman microscope in a backscattering configuration with a 514 nm Ar laser excitation. Scanning electron microscopy was performed using a Carl Zeiss Ultra Plus Field Emission SEM**.** Transient absorption studies were carried out as described previously.[1] Sample excitation was induced by a nitrogen laser pumped dye laser (<1 ns pulse duration, 4 Hz). For Figure 4a and Figure 4b, the following laser pulse wavelengths were used: 2 cycles - 450 nm, 3 cycles - 510 nm, 4 cycles - 570 nm, 5 cycles - 650 nm. Photoinduced changes in optical density were probed using a 100 W tungsten lamp with monochromators to select the wavelength before and after the sample, detected with home built Si and $In_xGa_{1-x}As$ photodiode detectors (below and above 1000 nm respectively) and recorded with the use of a Tektronix TDS 0112 oscilloscope.

Characterisation

Raman spectroscopy (see main text) of the as-deposited SILAR deposit of mesoporous TiO_2 shows little to distinguish it from the pristine metal oxide film, although annealing at 300 °C in nitrogen causes the characteristic bending and stretching modes of crystalline stibnite to appear. This leads us to believe that the as-deposited film is amorphous in nature, but crystallises when annealed, which is in agreement with observations reported in the literature for chemical bath deposited Sb_2S_3 on metal oxides.[2,3] Energy dispersive x-ray (EDX) spectroscopy was performed and indicated the presence of both antimony and sulphur on the TiO_2 surface prior to and post annealing. A typical 5 cycle SILAR Sb_2S_3/TiO_2 film gave a ratio of ~ $Sb_{2.45}S_3$. Scanning electron micrographs are shown in Figure S1, and reveal that the Sb_2S_3 coating is not conformal but agglomerates to cover a number of TiO_2 particles.

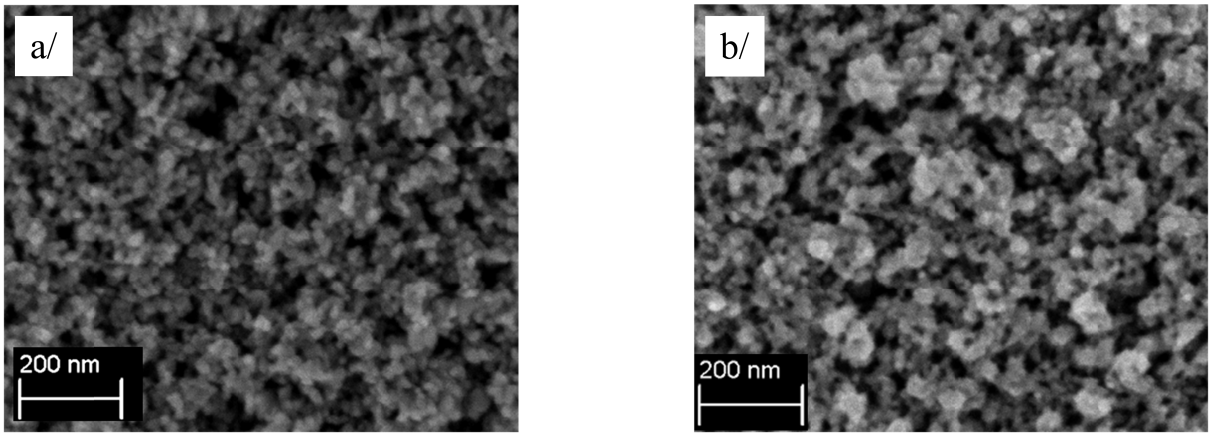

Figure S1 - SEM images of mesoporous TiO_2 before (a) and after (a) 5 SILAR cycles and annealing at 300 °C.

Charge transfer at the TiO_2/Sb_2S_3 interface

Figure S2 illustrates the effect of annealing temperature on the interfacial charge recombination in TiO_2/Sb_2S_3 systems. The data presented therein follows the reaction between the photogenerated electrons and holes in the TiO_2 and Sb_2S_3 respectively and were obtained by monitoring the decay of the transient absorption feature at 800nm. Given that ΔOD is directly proportional to the concentration of absorbing species (photo-oxidised Sb_2S_3 in this case), the amplitude of the transient signal can be used to probe the relative yield of interfacial charge separation at a given time. On this basis, it is apparent from the data presented in Figure S2 that low temperature annealing (up to and including 100 °C – red trace) makes no discernable difference to the yield of long-lived charges generated, whilst annealing at 200 °C (blue trace) and 300 °C (pink trace) leads to increasingly large degrees of charge separation (mΔOD increases from 0.10 to 0.15 to 0.30 at 1 μs respectively). This improved charge separation may result from an enhanced efficiency of electron transfer from Sb_2S_3 to TiO_2 as the Sb_2S_3 becomes crystalline. Indeed, Itzhaik *et al.* have reported that extensive electron trapping occurs in amorphous Sb_2S_3, but that it does not take place following annealing induced crystallisation.[4] Such trapping might be expected to compete with electron injection into the TiO_2 and thus limit the yield of interfacial separation. Moreover, our observations are consistent with the work of Liu *et al.*, who show an increase in Sb_2S_3 crystallinity as annealing temperature is raised to 300 °C and a concurrent improvement in efficiency for ZnO/Sb_2S_3/P3HT devices.[3]

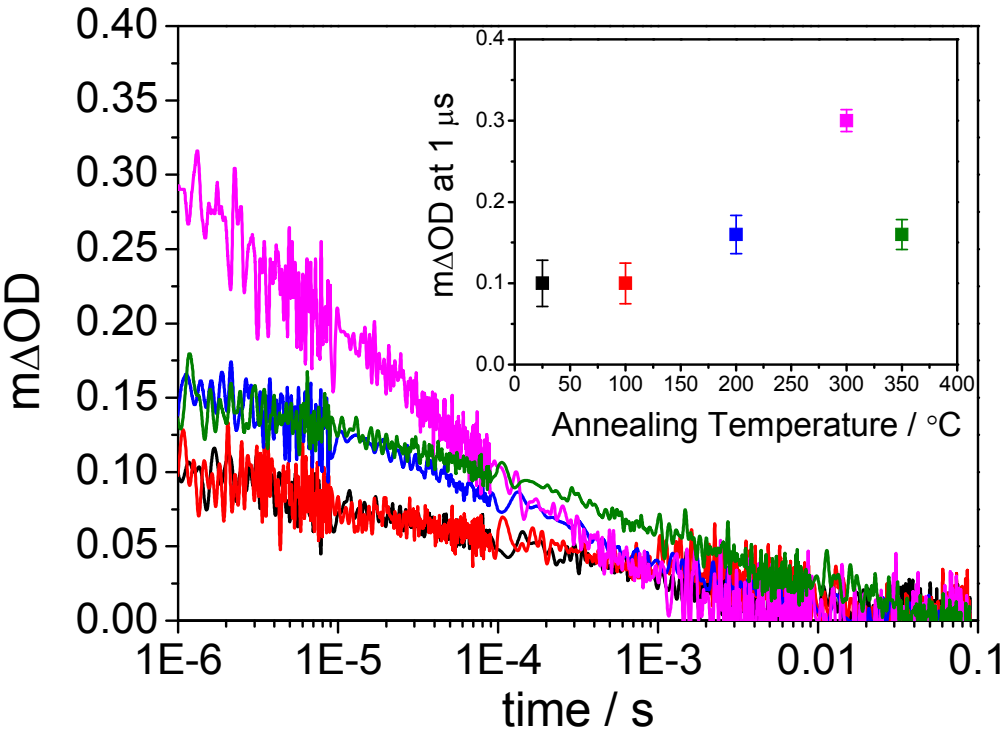

Figure S2 - (b) Transient absorption decay kinetics, probed at 800 nm, of Sb_2S_3-localised holes in TiO_2/Sb_2S_3 films as a function of annealing temperature. Laser pump excitation energy density = 26 μJ cm^{-2}. In both (a) and (b), values of ΔOD are scaled to the number of photons absorbed at λ_{pump}.

Figure S3 shows the decay in transient absorption of a 6-cycle Sb_2S_3/TiO_2 film, highlighting the reduction in the yield of long-lived charge separation at the TiO_2 / Sb_2S_3 interface as the excitation wavelength is red-shifted (red, green and pink traces). For comparison, a 2 cycle Sb_2S_3/TiO_2 film is also shown following excitation at 450 nm. It is important to note that this method (relative to that used for Figure 4a, main text) does not afford the possibility of selectively probing only the most blue-absorbing Sb_2S_3 nanocrystals, which could explain the difference in yield of photogenerated holes for a 2 cycle and a 6 cycle film excited at 450 nm.

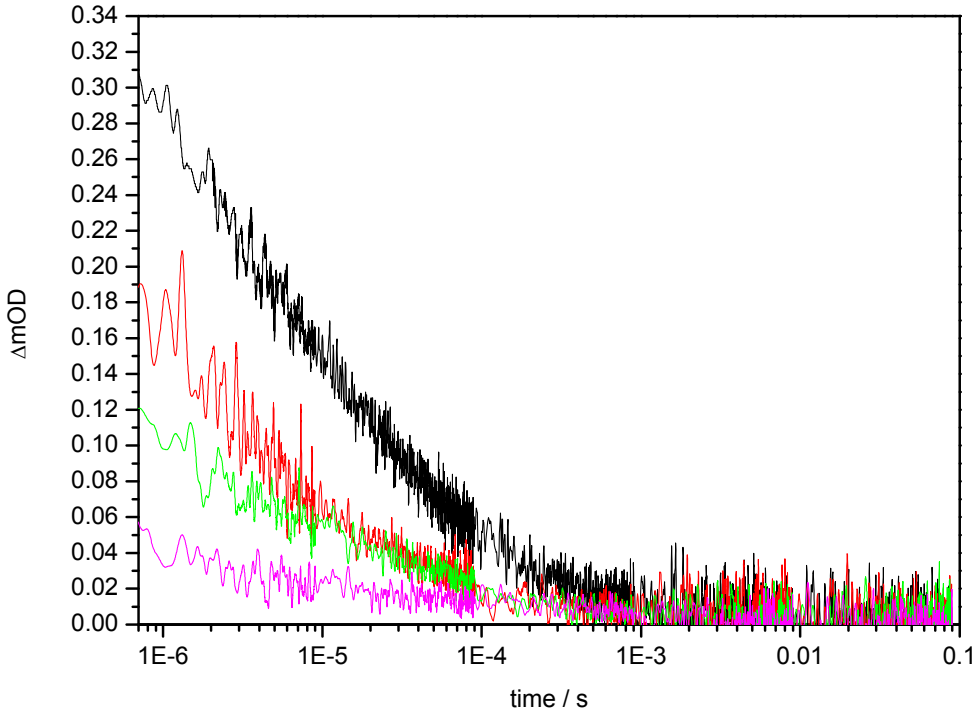

Figure S3 - Transient decay kinetics of Sb_2S_3-localised holes in Sb_2S_3/metal oxide films probed at 800 nm. Values of ΔOD are scaled to the number of photons absorbed at λ_{pump}. Laser excitation energy density = 26 μJ cm^{-2} at 450 nm. Sb_2S_3 layers are grown by SILAR on TiO_2 (2 cycles, λ_{pump} = 450 nm (black), 6 cycles λ_{pump} = 450 nm (red), 510 nm (green), 650 nm (pink)).

References

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