Supplementary Information

Experimental

Raman spectroscopy was performed using a Renishaw inVia Raman microscope in backscattering configuration and an excitation line of 514.5 nm provided by an Argon laser.

Transient optical studies were carried out as described previously.[1] The excitation wavelength was generated using pulses from a nitrogen laser pumped dye laser (<1ns pulse duration, 4 Hz) with power intensities around 20 $\mu J \cdot cm^{-2}$ (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 InxGa1-xAs (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 N_2.

TAUC Analysis:

The lowest energy transition in Sb_2S_3, obtained by theoretical calculations, has been reported both as indirect[2] or direct[3]. Experimentally, the optical absorption of Sb_2S_3 thin films and particles using a TAUC analysis, plotting $(h\nu\alpha)^n$ vs $(h\nu)$, using values of n of 2 and 0.5 (corresponding to direct allowed and indirect allowed transitions[4, 5]) shows a better fit using the direct bandgap case. Using such an analysis in our case leads to a direct bandgap of ~2.44 eV for TiO_2/Sb_2S_3 and ~2.07 eV for TiO_2/Bi_2S_3.

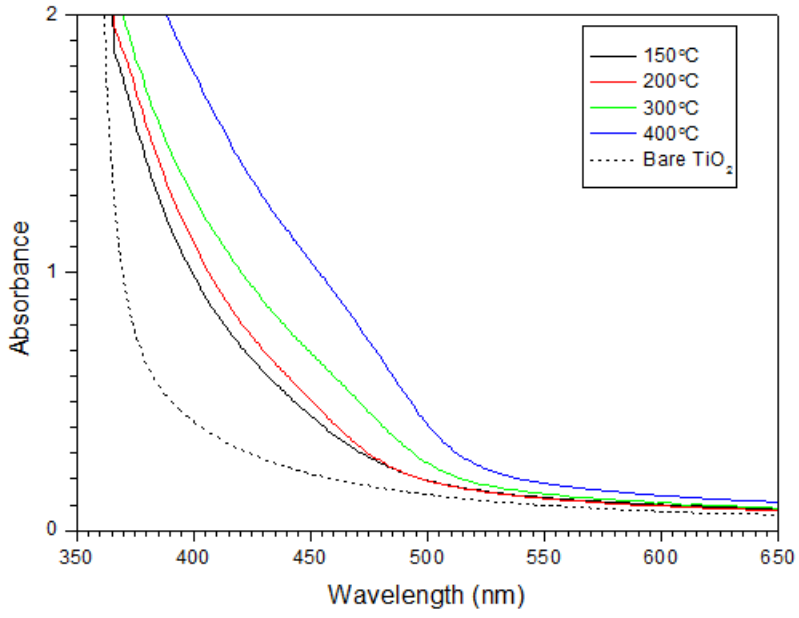

Figure S1: UV-visible absorption spectrum of TiO_2 films sensitised with a solution of xanthate of cadmium annealed at 200°C (black trace), 300°C (red trace) and 400°C (green trace).

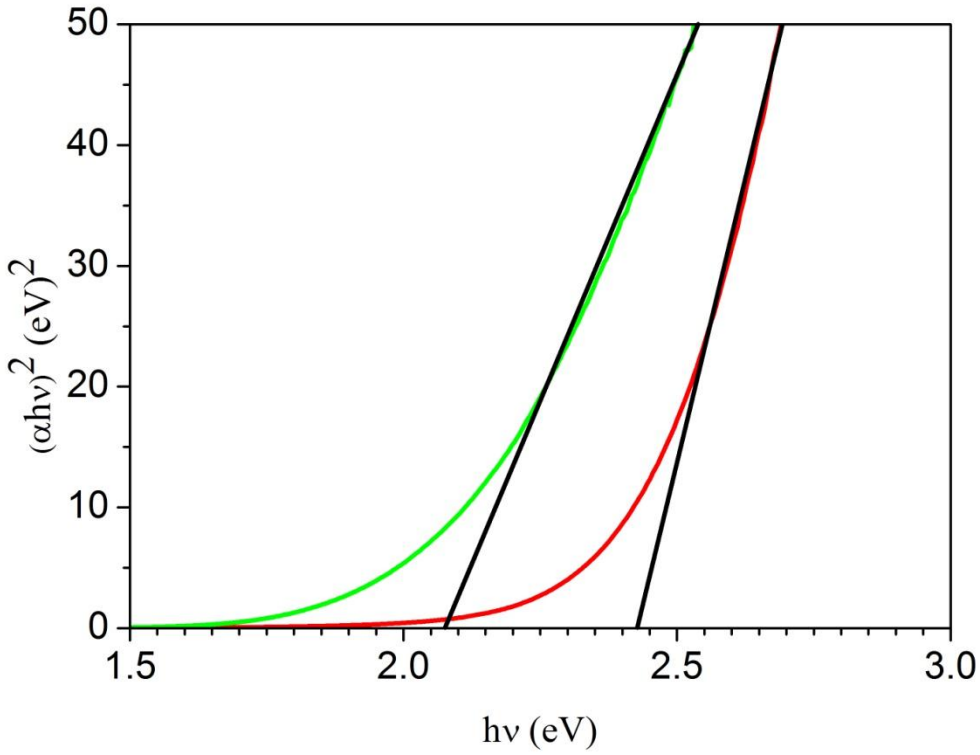

Figure S2: TAUC analysis in the case of a direct bandgap of a TiO_2 film annealed at 200°C after sensitisation with a solution of antimony (red trace) or bismuth (green trace) xanthate.

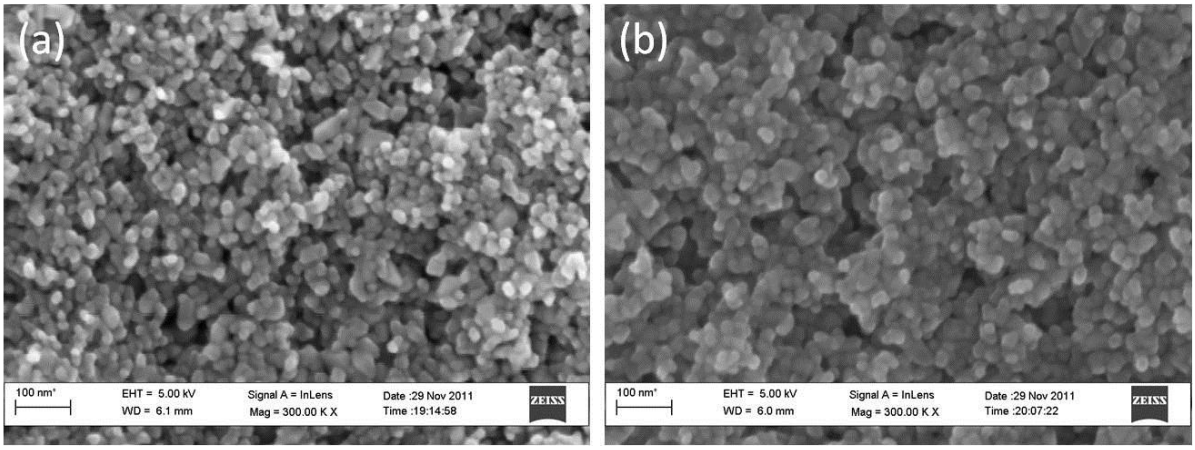

Figure S3: SEM images of a TiO_2 film (a) and a TiO_2 film coated with antimony xanthate precursor and annealed at 400°C (b). The TiO_2 particles can be seen to be coated with a thin layer giving the appearance of a smoothing of the edges of the particles whilst still retaining a porous network. Scanning electron microscopy was performed using a Carl Zeiss Ultra Plus Field Emission SEM.

References

1. E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz and J. R. Durrant, *Journal of the American Chemical Society*, 2002, **125**, 475-482.
2. T. Fujita, K. Kurita, K. Takiyama and T. Oda, *Journal of the Physical Society of Japan*, 1987, **56**, 3734-3739.
3. T. Ben Nasr, H. Maghraoui-Meherzi, H. Ben Abdallah and R. Bennaceur, *Physica B: Condensed Matter*, 2011, **406**, 287-292.
4. S. Shaji, A. Arato, J. J. O'Brien, J. Liu, G. A. Castillo, M. I. M. Palma, T. K. D. Roy and B. Krishnan, *Journal of Physics D: Applied Physics*, 2010, **43**, 075404.
5. B. Krishnan, A. Arato, E. Cardenas, T. K. Das Roy and G. A. Castillo, *Applied Surface Science*, 2008, **254**, 3200-3206.