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. The excitation wavelength was generated using pulses from a nitrogen laser pumped dye laser (<1ns pulse duration, 4 Hz) with power intensities around 20 μJ·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 monochromators 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 N₂.

TAUC Analysis:

The lowest energy transition in Sb₂S₃, obtained by theoretical calculations, has been reported both as indirect or direct. Experimentally, the optical absorption of Sb₂S₃ thin films and particles using a TAUC analysis, plotting (hvα)ⁿ vs (hv), using values of n of 2 and 0.5 (corresponding to direct allowed and indirect allowed transitions) 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 TiO₂/Sb₂S₃ and ~2.07 eV for TiO₂/Bi₂S₃.

![Absorption Spectrum](image)

Figure S1: UV-visible absorption spectrum of TiO₂ 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


