

Supporting Information

Fast and robust infiltration of functional material inside titania nanotube layers: case example for a chalcogenide glass sensitizer

Jan M. Macak^{*a}, Tomas Kohoutek^a, Lidong Wang^b, Radim Beranek^{*b}

^a Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Nam. Cs. Legii 565, 530 02 Pardubice, Czech Republic.

Tel: +420 466037401, E-mail: jan.macak@upce.cz

^b Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitätsstr. 150, D-44780 Bochum, Germany. Fax: +49-234-3214174; Tel: +49-234-3229431; E-mail: radim.beranek@rub.de

Synthesis of As₃S₇

Synthesis of As₃S₇ was performed according to the previously published literature, see e.g. Refs. 34, 36. In brief, the chalcogenide glass was prepared in two steps: 1) by mixing 5N elements of appropriate weights in evacuated quartz ampoules placed in rocking furnace, and 2) following quenching the melt to room temperature.

Photoelectrochemical experiments

The photoelectrochemical setup consisted of a SP-300 BioLogic potentiostat and a three-electrode cell using a platinum counter electrode and a Ag/AgCl reference electrode. The photoelectrodes were pressed against an O-ring of the cell leaving an irradiated area of 0.5 cm². The electrodes were irradiated from the frontside, i.e. through a quartz window and a Na₂SO₄ (0.1 M) + KI (0.1 m) electrolyte. Monochromatic wavelength-resolved measurements of incident photon-to-current efficiencies (*IPCE*) were performed using a tunable monochromatic light source (Instytut Fotonowy, www.fotonowy.pl) provided with a 150 W Xenon lamp and a grating monochromator with a bandwidth of ~10 nm. The monochromatic intensities between 330 nm and 800 nm were in the range of 0.6 – 4.3 mW/cm². Appropriate cut-off filters were used in order to eliminate second-order diffraction radiation. The value of photocurrent density was taken as a difference between current density under irradiation and in the dark. The *IPCE* value for each wavelength was calculated according to equation $IPCE (\%) = (i_{ph}/hc)/(\lambda Pq) \times 100$, where i_{ph} is the photocurrent density, h is Planck's constant, c velocity of light, P the light power density, λ is the irradiation wavelength, and q is the elementary charge. The spectral dependence of lamp power density was measured by the NOVA II optical power meter equipped with a PD300-UV silicon photodiode (Ophir Optronics).

UV-Vis absorption spectra

The UV-Vis electronic absorption spectrum of a spin-coated layer of As_3S_7 on an ITO glass was measured using a Perkin Elmer Lambda 650 UV-Vis spectrophotometer in transmission mode.

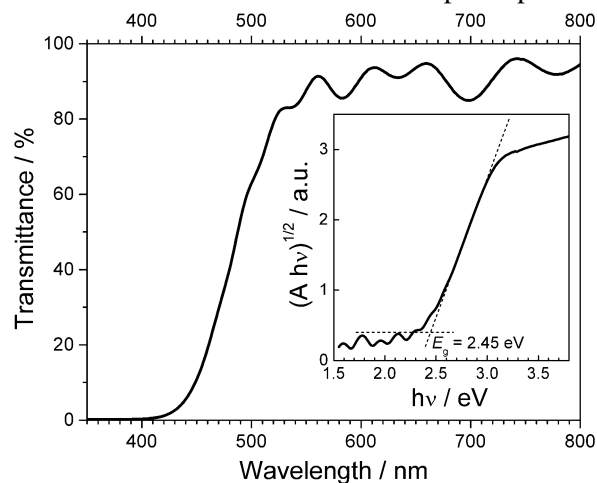


Figure S1: Electronic absorption spectrum of As_3S_7 thin film (thickness approx. 100 nm) on ITO-glass. The inset shows bandgap determination using the Tauc formalism and assuming a non-direct optical transition. The weak sub-bandgap absorption (so called Urbach tail) is probably due to surface and bulk defects in amorphous As_3S_7 .

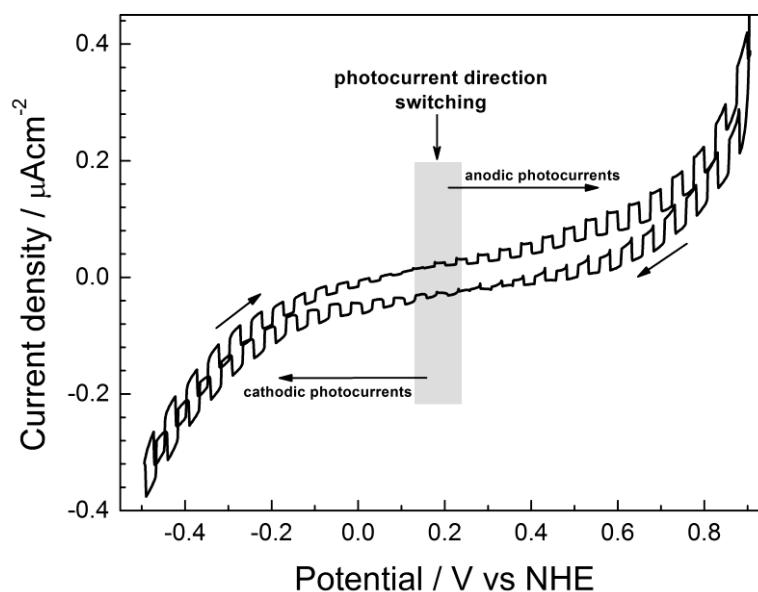


Figure S2: Photocurrent response of As_3S_7 thin film on ITO-glass recorded under intermittent monochromatic irradiation ($\lambda = 430$ nm) in Na_2SO_4 (0.1 M) electrolyte (scan rate = 5 mV/s).

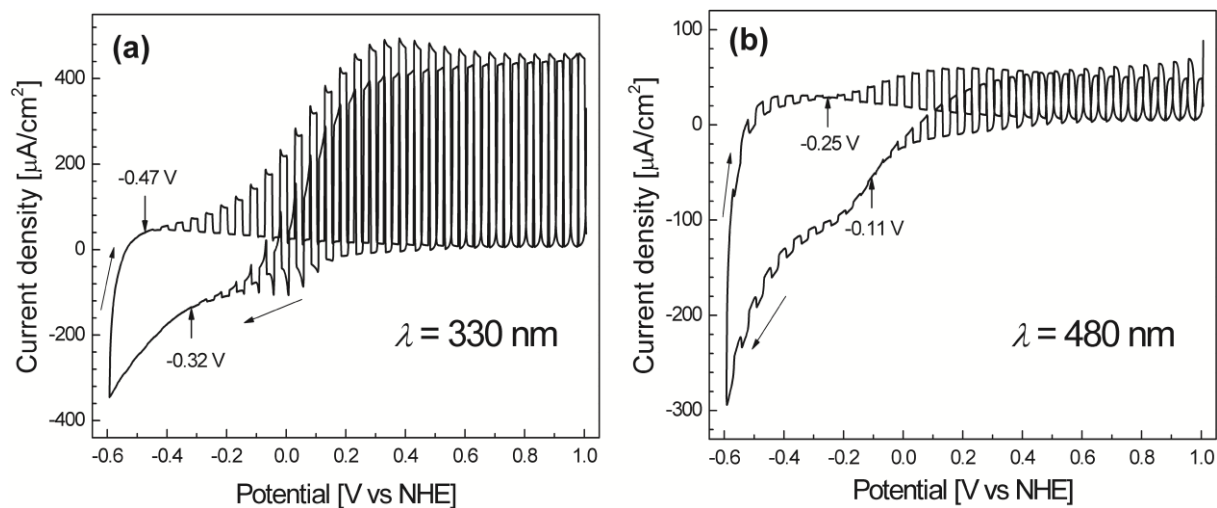


Figure S3: Photocurrent response of TiO₂ nanotubes infiltrated by As₃S₇ (0.1 g/ml) recorded in a Na₂SO₄ (0.1 M) + KI (0.1 M) electrolyte under intermittent monochromatic irradiation at 330 nm (a) and 480 nm (b); scan rate = 5 mV/s.

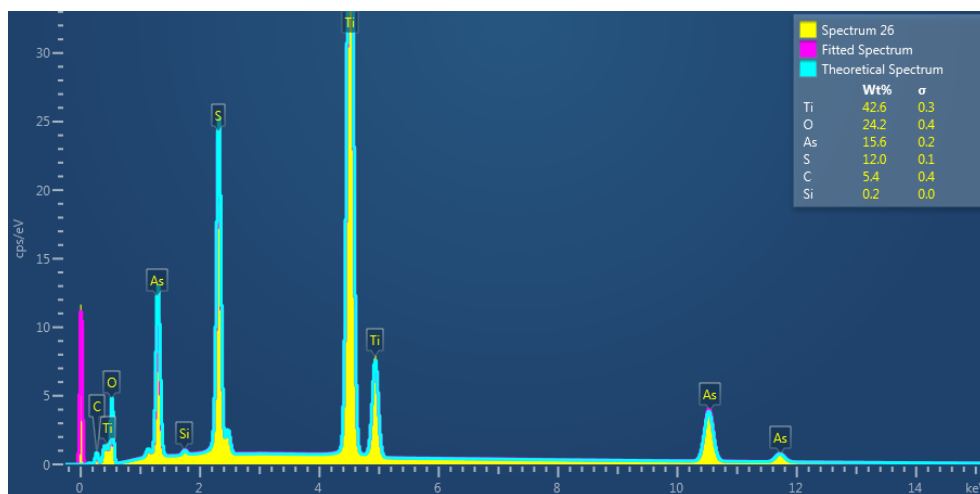


Figure S4 Example of EDX spectra of the As₃S₇ infilled nanotubes confirming clearly the presence of As, S species next to Ti and O species.