

New Intermediate band sulphide nanoparticles acting in the full visible light range spectra as an active photocatalyst

Raquel Lucena¹, José Carlos Conesa¹, Fernando Fresno¹, Perla Wahnón², Pablo Palacios², Yohanna Seminovski²

¹Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, 28049 Madrid, Spain.

²Instituto de Energía Solar, Universidad Politécnica de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain.

rlucena@icp.csic.es

Nowadays one of the challenges of materials science is to find new technologies that will be able to make the most of renewable energies. An example of new proposals in this field are the intermediate-band (IB) materials, which promise higher efficiencies in photovoltaic applications (through the intermediate band solar cells), or in heterogeneous photocatalysis (using nanoparticles of them, for the light-induced degradation of pollutants or for the efficient photoevolution of hydrogen from water).

An IB material consists in a semiconductor in which gap a new level is introduced [1], the intermediate band (IB), which should be partially filled by electrons and completely separated of the valence band (VB) and of the conduction band (CB). This scheme (figure 1) allows an electron from the VB to be promoted to the IB, and from the latter to the CB, upon absorption of photons with energy below the band gap E_g , so that energy can be absorbed in a wider range of the solar spectrum and a higher current can be obtained without sacrificing the photovoltage (or the chemical driving force) corresponding to the full bandgap E_g , thus increasing the overall efficiency.

This concept, applied to photocatalysis, would allow using photons of a wider visible range while keeping the same redox capacity. It is important to note that this concept differs from the classic photocatalyst doping principle, which essentially tries just to decrease the bandgap. This new type of materials would keep the full bandgap potential but would use also lower energy photons.

In our group several IB materials have been proposed, mainly for the photovoltaic application, based on extensively doping known semiconductors with transition metals [2], examining with DFT calculations their electronic structures. Here we refer to In_2S_3 and SnS_2 , which contain octahedral cations; when doped with Ti or V an IB is formed according to quantum calculations (see e.g. figure 2).

We have used a solvothermal synthesis method to prepare in nanocrystalline form the In_2S_3 thiospinel and the layered compound SnS_2 (which when undoped have bandgaps of 2.0 and 2.2 eV respectively) where the cation is substituted by vanadium at a $\approx 10\%$ level. This substitution has been studied, characterizing the materials by different physical and chemical techniques (TXRF, XRD, HR-TEM/EDS) (see e.g. figure 3) and verifying with UV spectrometry that this substitution introduces in the spectrum the sub-bandgap features predicted by the calculations (figure 4).

For both sulphide type nanoparticles (doped and undoped) the photocatalytic activity was studied by following at room temperature the oxidation of formic acid in aqueous suspension, a simple reaction which is easily monitored by UV-Vis spectroscopy. The spectral response of the process is measured using a collection of band pass filters that allow only some wavelengths into the reaction system. Thanks to this method the spectral range in which the materials are active in the photodecomposition (which coincides with the band gap for the undoped samples) can be checked, proving that for the vanadium substituted samples this range is increased, making possible to cover all the visible light range. Furthermore it is checked that these new materials are more photocorrosion resistant than the toxic CdS which is a well know compound frequently used in tests of visible light photocatalysis.

These materials are thus promising not only for degradation of pollutants (or for photovoltaic cells) but also for efficient photoevolution of hydrogen from water; work in this direction is now being pursued.

References

- [1] A. Luque, A. Martí, Phys. Rev. Lett. **78**, 1977, 5014.
- [2] a) P. Palacios et al. Phys. Rev. B **73** (2006) 085206; *ibid.* J. Chem. Phys. **124** (2006) 014711.
b) P. Palacios et al. Thin Solid Films **515** (2007) 6280; *ibid.* J. Phys. Chem. C **112** (2008) 9525.
c) P. Palacios et al. Phys. Rev. Lett. **101** (2008) 046403.
- [3] a) R. Lucena et al. Chem. Mater. **20** (2008) 5125.
b) P. Wahnón et al. Phys. Chem. Chem. Phys. **13** (2011) 20401.

Figures

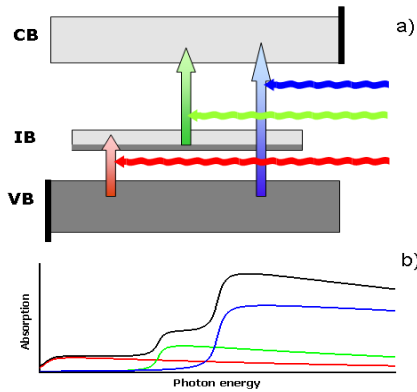


Figure 1- IB working principle: (a) photons of different energies excite electrons from the VB directly to the CB and also from the VB to the IB and from the IB to the CB. (b) A wider photon energy range is thus used

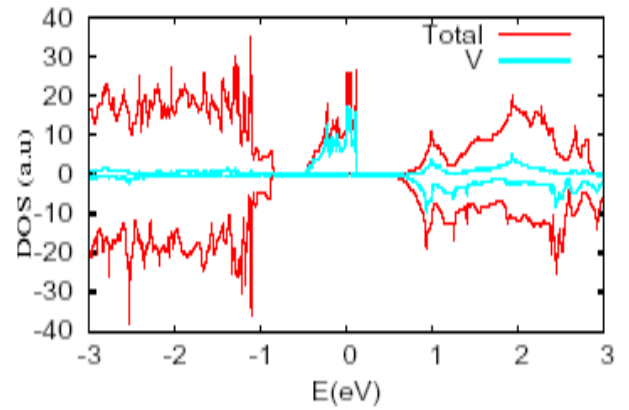


Figure 2 - Density of states (computed with DFT) of In_2S_3 with octahedral In partially substituted by V

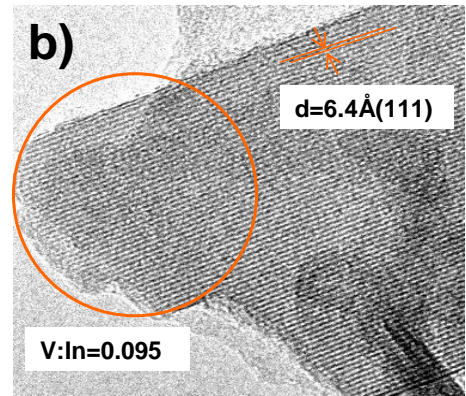
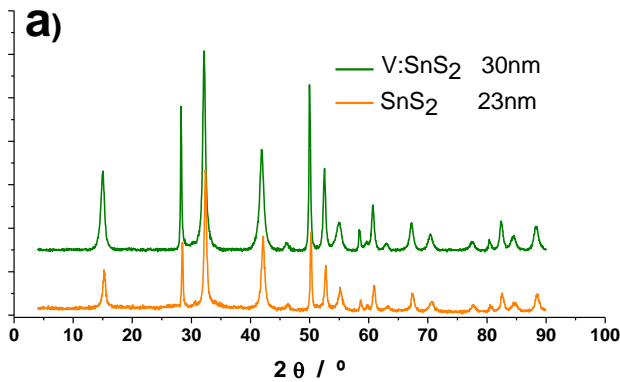


Figure 3 - a) XRD diagram of SnS₂ and V:SnS₂ synthesized materials, indicating the nanocrystal size deduced from linewidths. b) V:In₂S₃ HR-TEM image of In₂S₃ with EDS measurement of the composition at the In₂S₃ nanocrystals

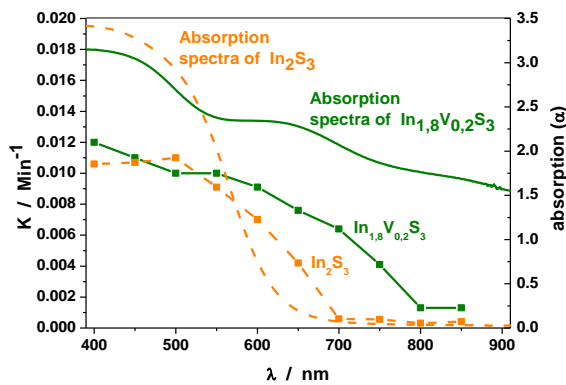


Figure 5 - Rate constant k measured for aqueous HCOOH photooxidation under light of different wavelengths on In_2S_3 with and without $\approx 10\%$ V doping, compared with the respective DR Vis-NIR spectra

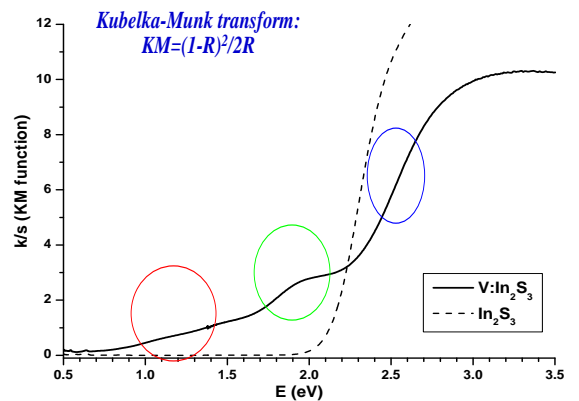


Figure 4 - Experimental diffuse reflectance spectrum of pure and V-doped nanocrystalline In_2S_3