

Vanadium-Doped In and Sn Sulphides:

Photocatalysts Able to Use the Whole Visible Light Spectrum

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Using photocatalysis for energy applications depends, more than for environmental purposes or selective chemical synthesis, on converting as much of the solar spectrum as possible; the best photocatalyst, titania, is far from this. Many efforts are pursued nowadays to use better that spectrum in photocatalysis, by doping titania or using other materials (mainly oxides, nitrides and sulphides) to obtain a lower bandgap, even if this means decreasing the chemical potential of the electron-hole pairs.

Here we introduce an alternative scheme, using an idea recently proposed for photovoltaics: the intermediate band (IB) materials [1]. It consists in introducing in the gap of a semiconductor an intermediate level which, acting like a stepstone, allows an electron jumping from the valence band (VB) to the conduction band (CB) in two steps, each one absorbing one sub-bandgap photon. For this the IB must be partially filled, to allow both sub-bandgap transitions to proceed at comparable rates; must be made of delocalized states to minimize nonradiative recombination; and should not communicate electronically with the outer world. For photovoltaic use the optimum efficiency so achievable, over 1.5 times that given by a normal semiconductor, is obtained with an overall bandgap around 2.0 eV (which would be near-optimal also for water photosplitting). Note that this scheme differs from the doping principle usually considered in photocatalysis, which just tries to decrease the bandgap; its aim is to keep the full bandgap chemical potential but using also lower energy photons.

In the past we have proposed several IB materials based on extensively doping known semiconductors with light transition metals, checking first of all with quantum calculations that the desired IB structure results [2].

Subsequently we have synthesized in powder

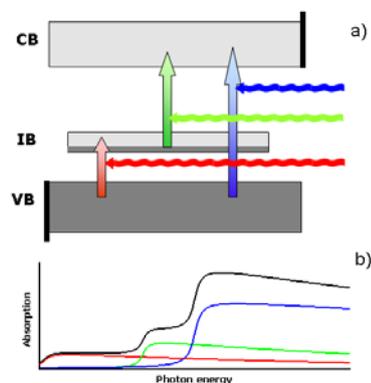


Fig. 1 IB working principle: (a) photons of different energies excite electrons from the VB directly to the CB and also from the VB to the IB and from the IB to the CB. (b) A wider photon energy range is thus used.

form two of them: the thiospinel In_2S_3 and the layered compound SnS_2 (having bandgaps of 2.0 and 2.2 eV respectively) where the octahedral cation is substituted at a $\approx 10\%$ level with vanadium, and we have verified that this substitution introduces in the absorption spectrum the sub-bandgap features predicted by the calculations [3].

With these materials we have verified, using a simple reaction (formic acid oxidation), that the photocatalytic spectral response is indeed extended to longer wavelengths, being able

to use even 700 nm photons, without largely degrading the response for above-bandgap photons (i.e. strong recombination is not induced) [3b, 4]. These materials are thus promising for efficient photoevolution of hydrogen from water; work on this is being pursued, the results of which will be presented.

[1] A. Luque, A. Martí Phys. Rev. Lett. 78, 1977, 5014.

[2] a) P. Palacios et al., Phys. Rev. B 73 (2007) 085206; ibid. Thin Solid Films 515 (2007) 6280; ibid. Phys. Rev. Lett. 101 (2008) 046403.

[3] a) R. Lucena et al.: Chem. Mater. 20 (2008) 5125. b) P. Wahnón et al. PCCP, in press (DOI: 10.1039/c1cp22664a).

[4] R. Lucena et al., submitted.

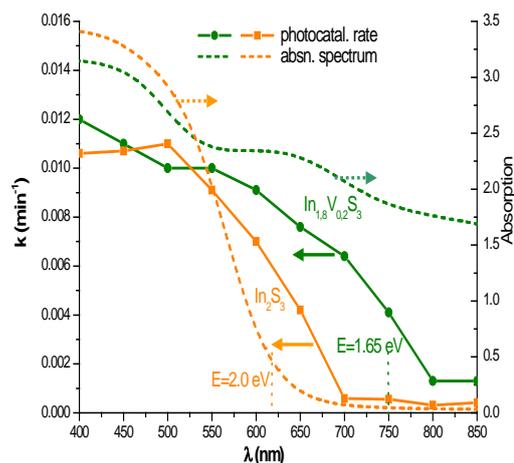


Fig. 2 Rate constant k measured for aqueous HCOOH photooxidation under light of different wavelengths on In_2S_3 with and without 10% V doping, compared with the respective DR Vis-NIR spectra