DESIGN, SYNTHESIS AND CHARACTERIZATION OF DOPED TIN SULFIDE (SnS) PHOTOCATALYSTS FOR HYDROGEN PRODUCTION FROM ORGANIC WASTE WATER

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Introduction

Cost effective production of energy resources, such as hydrogen, water sunlight and a semiconductor photocatalyst has long been a goal for scientists and engineers. Despite tremendous effort in the area of solar "water splitting" over the last 4 decades there has been little real progress primarily due to several fundamental factors including the kinetic limits of the oxygen evolution reaction. New photocatalysts and, more importantly, new hydrogen generating processes may help to ensure sustainable future energy supplies. It is known that aqueous organic compounds, inexpensive carbon and hydrogen source, can be photoxidized at relatively low voltage co-producing hydrogen cathodically. Organic containing wastewater is a low value (or negative value) reactant that allows use of much greater portions of the solar spectrum with materials that have a bandgap of approximately 1 eV. Design of new photocatalysts with a 1 eV bandgap may be aided by theory to predict their electronic structure *a priori* and hasten the new catalyst discovery process. Inexpensive and environmentally benign sulfur or phosphorus based photocatalysts are under investigation by our groups. Many of these compounds are present in nature as minerals, such as SnS - herzenbergerite. Here we described results on investigations of Sb doped tin sulfide (SnS) powders synthesized as model photocatalysts using data obtained from computational density functional theory (DFT).

Experimental

Synthesis. SnS (purity 99.39%) was supplied by American Elements. Sample Sba-SnS (5% Sb) was synthesized by impregnation in excess of volume of antimony (III) acetate and heated up to 800 °C in argon. Sample Sbs-SnS (10% Sb) was synthesized by a physical mixing of Sb_2S_3 and SnS and heating up to 800 °C in argon. In order to make the results more comparable, SnS was also heated up 800 °C in argon.

Theoretical methods. Periodic ab initio solid state program suite CRYSTAL'09 was used in all calculations.[1] It uses the functions localized at atoms as the basis for expansion of the crystalline orbitals via linear combination of atomic orbitals (LCAO) technique. Basis sets have been obtained from the University of Torino CRYSTAL basis set library[2] (accessed Spring 2011). Sn Durand pseudopotential[3] with 21d1G valence configuration and S all electron[4] 86-311d1G basis sets were used; basis set outer exponents were optimized for a bulk SnS structure and set to 0.2 and 0.2533, 0.0935, 0.263, for Sn d-shell and S two outer sp, and one d shells, respectively. Durand pseudopotential with 21(d1) valence basis set was used for Sb.[3] Spin unrestricted Hartree-Fock formalism and hybrid PBE0[5] Hamiltonian was used in all calculations. Density of states (DOS) calculations were performed on a 24 Sn atom containing SnS supercell (S24), optimized in atomic positions.

Results and Discussion

Computational design of doped SnS photocatalyst. Primitive orthorhombic unit cell of SnS with lattice parameters of 11.200, 3.987 and 4.334 Å and *Pnma* space group was used. Sn atoms occupy fourfold *4c* positions with fractional coordinates 0.1194, 0.25 and 0.1198 and S atoms - fourfold *4c* positions with 0.8508, 0.25 and 0.4793. α-SnS structure is comprised of interlayer structure with S atoms having threefold coordination. Experimental structural parameters of experimentally determined α-SnS unit cell and those optimized using PBE0 functional are summarized in Table 1. It can be seen that PBE0 functional represents structural and bandgap parameters of SnS accurately.

Table 1. Structural and electronic parameters of SnS experimental structure and optimized with PBE0 functional.

Parameters	Experimental[a]	UPBE0
a, Å	11.200	10.874
b, Å	3.987	3.939
c, Å	4.334	4.243
Cell volume, Å^3	193.544	181.757
Bandgap, eV	1 – 1.5[b]	1.55

a. Experimental data taken from Wiedemeier *et al*.[6]
b. Experimental data taken from Tanusevski *et al*.[7]

Sb was used as a model dopant to modify electronic SnS properties. Density of states plots of SnS and Sb doped SnS are shown in Figure 1. It can be seen that top of the valence bands is modified in Sb doped SnS due to the addition of filled Sb valence bands. Here, the nature of the charge transfer origin changes from predominantly S3p to Sb5p orbitals. This, in turn, changes the conductivity type of SnS from intrinsic p-type semiconductor to extrinsic n-type semiconductor.
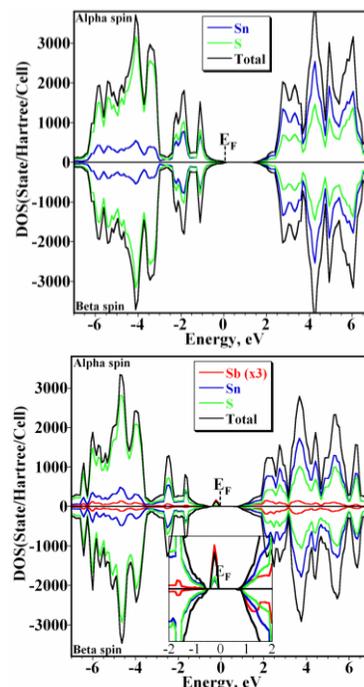

Figure 1. Atom and total DOS of SnS (top) and Sb doped SnS S24 supercell (bottom). Sb doped SnS inset: -2 to 2 eV DOS region.

Synthesis and characterization of the designed photocatalyst. Structural characterization of the powderous samples was performed using X-ray diffraction (XRD) and results are shown in Figure 2. XRD patterns show that after doping SnS with Sb the crystalline structure is preserved and it is difficult to distinguish other compounds. However, small amounts of $Sn_{17}Sb_6S_{29}$ and $Sn_3Sb_2S_6$ in samples Sba-SnS and Sbs-SnS, respectively, cannot be disregarded. It must be pointed out that the presence of Sb increases the crystallinity of the SnS, especially in the case of doping with Sb_2S_3. Presence of Sb in synthesized samples was confirmed using X-ray photoelectron spectroscopy (XPS).
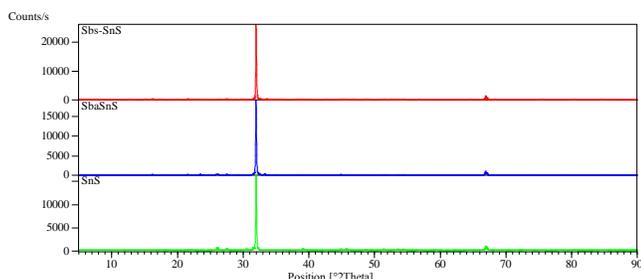

Figure 2. XRD patterns of the samples SnS, Sba-SnS and Sbs-SnS.

UV-VIS-NIR spectra of SnS and Sb doped SnS are shown in Figure 3. These spectra are very similar for the three samples. SnS has a little stronger absorption at wavelengths less than 1150 nm than the doped ones. This difference can be explained by the fact that SnS (1.0 eV) is a narrower band gap than Sb_2S_3 (1.7 eV).
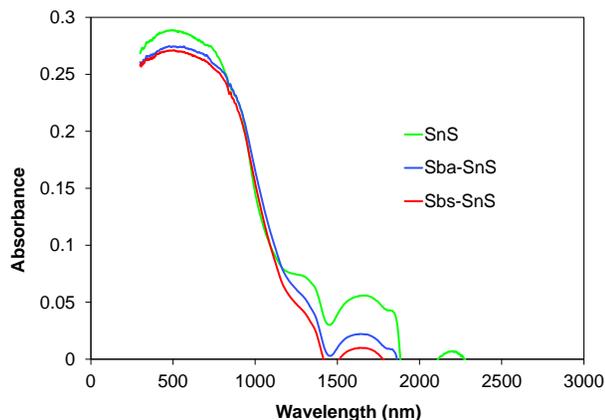

Figure 3. UV-Vis-NIR spectra of the samples SnS, Sba-SnS and Sbs-SnS.

Conclusions

Computational design of the model Sb doped SnS photocatalyst was performed followed by its synthesis and characterization. The experimentally observed bandgap of undoped SnS (~1.5 eV) was reproduced theoretically using a PBE0 hybrid functional. Sb doping resulted in an additional electron filled state at the valence band. Synthesis of powder photocatalyst was performed using two methods, e.g. by impregnation in excess of volume of antimony (III) acetate and by a physical mixing of Sb_2S_3 and SnS and heating up to 800 ºC in argon Structural and optical properties were characterized using XRD, XPS and UV-VIS. XRD showed SnS phase with retained crystallinity after the Sb doping and XPS analysis confirmed the presence of Sb dopant. UV-VIS spectra obtained of doped catalysts showed light absorption properties similar to those of undoped SnS.

This intelligent design of the photocatalysts in the future will be extended to other dopants.

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