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Short Communication

Spectral response and stability of In_2S_3 as visible light-active photocatalyst

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ABSTRACT

Nanocrystalline In_2S_3 is shown to degrade photocatalytically aqueous formic acid using visible light. Its spectral response for this process is verified for the first time, showing that even photons with ≈650 nm are active. In_2S_3 is also shown to be more active and photocorrosion resistant in this process than similarly prepared CdS.

1. Introduction

Photocatalysis with visible light is nowadays actively researched. Several semiconductors have been reported as photocatalysts able to use visible light: doped TiO_2 [1], binary oxides like WO_3, Bi_2O_3, Fe_2O_3 [2] or Cu_2O [3], mixed oxides like $BiVO_4$ [4] or $InTaO_4$ [5], (oxy)nitrides like Ta_3N_5 [6], $LaTiO_2N$ [7] or ZnO:GaN [8] and sulphides like CdS [9], Bi_2S_3 [10] or In_2S_3 [11,12]. Usually the activity with visible light is verified using a cut-off filter to block UV components from some wide spectrum source or testing a single wavelength (e.g. from a LED diode), without checking whether the spectral profile of the photocatalytic activity matches the absorption spectrum of the material.

This is verified here for In_2S_3, a semiconductor for which photocatalysis with visible light (i.e. excluding UV components) has been studied scarcely [11–13]. In its more common forms In_2S_3 has a spinel-type structure with cation vacancies. If these are disordered the structure appears cubic to XRD, being indexable in space group *Fd*-3*m*, and is called α-In_2S_3 [14]; in its most stable form the vacancies are located at tetrahedral sites and ordered so as to produce a superstructure with tripled c axis and tetragonal symmetry (space group *I*4$_1$/*amd*), this is called β-In_2S_3 [15]. A less stable hexagonal form, ε-In_2S_3, is known [16]; besides, another hexagonal form γ-In_2S_3 can be stabilized by doping with As or Sb [17] and can also appear occasionally in the absence of such dopants [18]. In well crystallized form In_2S_3 has a direct bandgap of width $E_g = 2.0$ eV [19] and displays an orange or orange-brown colour; it may be noted that In_2S_3 prepared in aqueous environment, in particular when ill-crystallized or disordered (appearing thus as α phase), frequently contains oxygen in part of the anionic sites, which widens the gap and leads to a yellow colour.

As will be shown here, In_2S_3 is active in the whole wavelength range of its bandgap absorption, i.e. already the lowest energy photons that can excite electrons across its bandgap are able to drive a photocatalytic reaction. Its behaviour is compared also with that of CdS, a widely studied semiconductor having $E_g \approx 2.4$ eV [20].

2. Experimental

In_2S_3 was synthesized hydrothermally from $InCl_3$ and thiourea at 463 K as reported in a previous work [18]; CdS was synthesized similarly from $Cd(CH_3COO)_2.2H_2O$ (Aldrich 99.99+%) and thiourea in 1:4 molar ratio (which favours obtaining only the most stable phase having hexagonal wurtzite structure [21]) at 453 K during 48 h. Elemental compositions were checked with total reflection X-ray fluorescence. Specific surfaces were measured with N_2 at 77 K over samples pre-outgassed at 140 °C. X-ray diffractograms were collected using Cu K_α radiation ($\lambda = 1.542$ Å); from them lattice parameters were obtained by fitting to computed patterns using Powdercell program [22]. Diffuse reflectance UV–vis-NIR spectra were obtained using Spectralon® as reference.

Photocatalytic activity was measured in a thermostated, magnetically stirred suspension containing 40 mg of sulphide in 80 mL of aqueous HCOOH (1.5 mM), which unless stated otherwise was buffered to pH = 2.5 (to avoid any complications in kinetic data interpretation which might arise due to pH changes along the reaction) using a mixture of H_3PO_4 and NaH_2PO_4 in 1:1 molar proportion, and irradiated through a pyrex window using an ozone-free 450 W Xenon lamp

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provided with a water filter and, when so desired, a band-pass optical filter transmitting a wavelength interval of FWHM ≈ 50 nm. The light intensity incident on the liquid was measured with a radiometer. 1.5 mL of suspension was sampled periodically, filtered with a hydrophilic PTFE 0.45 μm filter and analysed for HCOOH in the liquid through its absorbance at λ = 205 nm. The eventual photocatalyst corrosion during reaction was checked by subsequently filtering the solid, washing it with doubly deionised water and analyzing with ICP-OES both metal and sulphur in the liquids obtained.

3. Results and discussion

3.1. Characterization of materials

The synthesized In_2S_3 (an orange powder) has a S:In ratio identical within 1% to the nominal 3:2 stoichiometry and specific surface $S_{BET} \approx 40\ m^2/g$. Its diffractogram shows (Fig. 1a) the pattern of the In_2S_3 defect spinel (JCPDS 32–0456 card), all of its peaks being indexed accordingly; its measured fcc lattice constant is 10.734 Å, close to the reported value (10.774 Å [14]). It may be noted that, if the material contained the cation vacancies ordered as in the β phase, with consequent decrease of the symmetry to tetragonal, a diffraction peak corresponding to the (112) reflection should appear according to the simulations at 2θ ≈ 17.4º, with intensity similar to that at 2θ ≈ 23.4º; no such feature was observed. Indexing of the observed XRD peaks according to the tetragonal phase, which obviously is also possible, has been omitted in Fig. 1. For the synthesized CdS, which showed a S:Cd atomic ratio close to the theoretical one and a specific surface $S_{BET} = 8\ m^2/g$, the XRD pattern (Fig. 2a), revealing a well crystallized material, can be explained on the basis of the sole presence of the hexagonal (wurtzite) phase, with lattice constants $a = 4.134$ Å and $c = 6.751$ Å (reported values: $a = 4.132$ Å, $c = 6.734$ Å [23]); the corresponding indexing is shown in Fig. 2a. The presence of the cubic CdS phase can be excluded since its characteristic (200) reflection at 2θ ≈ 30.7º is absent.

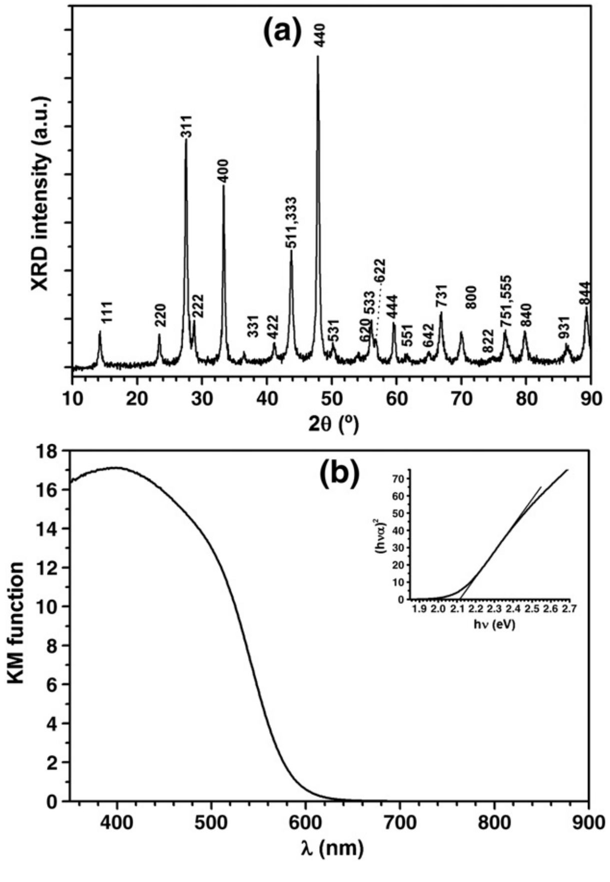

Fig. 1. Data for the hydrothermally synthesized In_2S_3: (a) Powder XRD diagram (with peak indexing corresponding to cubic In_2S_3) and (b) UV–VIS-NIR absorption spectrum (given as Kubelka–Munk transform of the diffuse reflectance); the inset displays the bandgap determination.

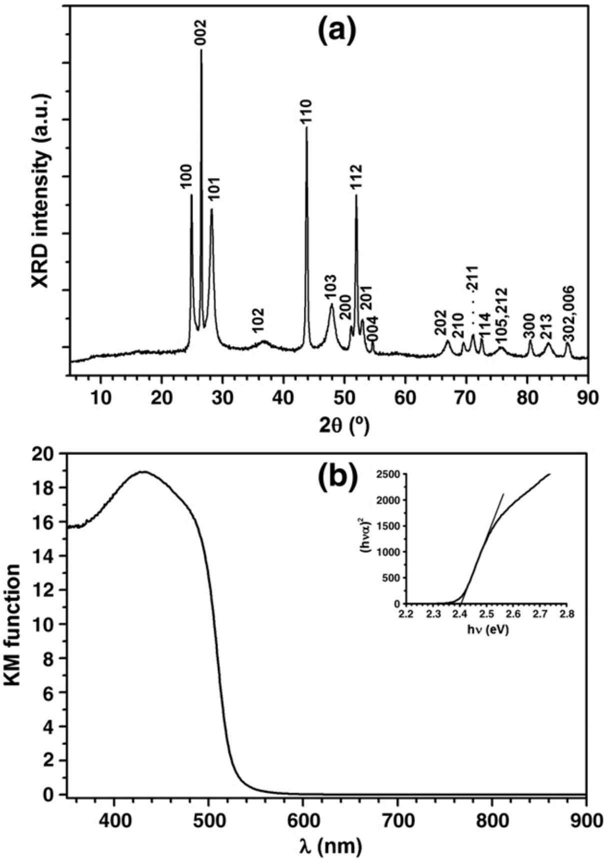

Fig. 2. Data for the hydrothermally synthesized CdS: (a) Powder XRD diagram (with peak indexing corresponding to hexagonal CdS) and (b) UV–VIS-NIR absorption spectrum (given as Kubelka–Munk transform of the diffuse reflectance); the inset displays the bandgap determination.

Fig. 1b displays the diffuse reflectance UV–vis-NIR spectrum of the In_2S_3 sample as Kubelka–Munk transform of the reflectance R ($KM = (1 - R)^2/2R$ [24]). Absorption starts at λ ≈ 600 nm; a Tauc plot of $(h\nu\alpha)^2$ vs. $h\nu$ (see inset in Fig. 1b), as corresponds to the direct nature of its bandgap, yields $E_g = 2.1$ eV, close to the literature value. For CdS (Fig. 2b) the absorption edge starts at λ ≈ 525 nm; the Tauc plot (see inset in Fig. 2b) yields $E_g = 2.4$ eV, also in good agreement with the literature value.

3.2. Photocatalytic activity tests

An In_2S_3 suspension in buffered aqueous HCOOH was first kept in the dark for 30 min to ensure a well equilibrated situation and in particular a stable HCOOH concentration (adsorption was anyway small: it was subsequently verified that only 1.2% of the dissolved amount was adsorbed) and was then irradiated with the unfiltered light of the Xenon lamp. In this setup the total light flux incident on the surface of the suspension was ≈ 115 mW/cm². HCOOH was quickly degraded as shown by the UV spectra of the extracted aliquots (Fig. 3a). Fig. 3b plots the concentration decay during irradiation; a quite similar decay profile was obtained in a test in which synthetic air was bubbled through the suspension during the experiment, showing that the magnetic stirring is quite enough to provide from ambient air the amount of oxygen needed for the reaction. The