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Ternary and coupled binary zinc tin oxide nanopowders: Synthesis, characterization, and potential application in photocatalytic processes

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ABSTRACT

In this paper, ternary and coupled binary zinc tin oxide nanocrystalline powders were prepared via simple solid-state mechanochemical method. X-ray diffraction, scanning electron microscopy, Raman and reflectance spectroscopy were used to study the structure and optical properties of the obtained powder samples. The thermal behavior of zinc tin oxide system was examined through simultaneous thermogravimetric-differential scanning calorimetric analysis. The efficiencies of ternary (Zn_2SnO_4 and $ZnSnO_3$) and coupled binary (ZnO/SnO_2) zinc tin oxide water suspensions in the photocatalytic degradation of alprazolam, short-acting anxiolytic of the benzodiazepine class of psychoactive drugs, under UV irradiation were determined and compared with the efficiency of pure ZnO and SnO_2.

1. Introduction

Very recently published review article [1] marked the mechanochemical synthesis as a promising method for the preparation of catalysts especially those for environmental, energy and chemical synthesis applications. Several examples were emphasized where this method was found to be advantageous compared to the nowadays usual multistep solvent-based synthesis routes. Due to the simplicity and cheapness, and the fact that it provides significantly more active/selective catalysts the mechanochemisty deserves greater attention as a method for the synthesis of heterogeneous photocatalysts. In the mechanochemistry, chemical reactions are initiated through the input of mechanical energy [1] using just simple grinding of two solids in a pestle and mortar, or by its technically improved version, i.e., high-energy ball milling.

Binary semiconducting oxides, like zinc oxide (ZnO) and tin oxide (SnO_2), have a potential to be used in diverse applications such as photocatalysis, solar cells, and gas sensors due to their unique properties [2–5]. Illumination of semiconductors as photocatalysts in wastewaters is a promising alternative method for removing organic pollutants [6]. Recent research [6–8] reports that coupled oxide semiconductors, like ZnO/SnO_2, could be even more efficient than just the individual binary photocatalysts [9], while ternary forms of these oxides were taken into account as well because there is a general perception that they allow even more flexibility in materials designing for desired application [3], as their physical and chemical properties are more easily tailored compared to the binary oxides. The ZnO/SnO_2 (zinc tin oxide, i.e., ZTO) ternary oxide system is known as zinc stannate and it is mostly used as an *n*-type semiconducting oxide, transparent in the visible light region, with a wide band gap [3] in lead-free ferroelectrics, gas sensors, transparent conductors, lithium ion batteries, dye-sensitized solar cells, and as photocatalysts [10]. Depending on Zn/Sn/O ratio, this ternary metal oxide material exists as two types of oxides, spinel-type (Zn_2SnO_4) and perovskite-type ($ZnSnO_3$) [2,3].

Alprazolam (8-chloro-1-methyl-6-phenyl-4*H*-[1,2,4]triazole [4,3,-α-1,4]-benzodiazepine, CAS No. 28981-97-7, $C_{17}H_{13}ClN_4$, $M_r = 308.765$) is benzodiazepine derived from 1,4-benzodiazepines, which is mainly used to treat anxiety disorders [11]. Besides, alprazolam is extensively prescribed for its sedative, hypnotic, skeletal muscle relaxant, anticonvulsant, and amnestic properties [12]. In recent years, drugs and their metabolites have been recognized as environmental contaminants. Considering the fact that alprazolam is the most prescribed benzodiazepine drug [12], its continuous input can cause environmental pollution.

In this paper we report the structural, optical, and thermal properties of ternary and coupled binary zinc tin oxide powders

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prepared by traditional solid-state reaction method and their photocatalytic efficiency in degradation of alprazolam.

2. Experimental

2.1. Synthesis

In order to synthesize the ternary Zn_2SnO_4 form of the zinc tin oxide, the two steps mechanochemical method was conducted. First, the starting powders of commercially available ZnO (Sigma–Aldrich, purity 99.9%, particle size $\leq 1\,\mu m$) and SnO_2 (Sigma–Aldrich, purity 99.99%) were stoichiometrically mixed and mechanically activated in high energy ball mill (Retsch GmbH PM100) using zirconia vial and zirconia balls of 10 mm diameter and standard balls to powder mass ratio of 10:1 for 160 min. The second-step followed which was the additional annealing at 1200 °C for 2 h. Preparation procedure for the synthesis of the perovskite-type $ZnSnO_3$ included only the first-step of mechanochemical processing, i.e., milling of the starting precursors with balls to powder mass ratio of 20:1, in air atmosphere, for 360 min. Choice of synthesis conditions was made based on experimental results available in the literature [13–16]. The binary coupled ZTO were prepared also by two-step mechanochemical processing, where starting powders were mixed in both 2:1 and 1:1 molar ratios, ball milled in air for 120 min (balls to powder mass ratio was 10:1) and annealed at 400 °C for 2 h.

2.2. Materials characterization

X-ray diffraction was carried out using Philips PW 1050 instrument, with Cu $K\alpha_{1,2}$ radiation, and a step scan mode of 0.02°/s in angular range $2\theta = 15 - 70°$. Scanning electron microscope (SEM–JEOL JSM-6460LV) was used to investigate the morphology and microstructure of the samples. The Raman spectra of the samples were measured using the Centice MMS Raman spectrometer equipped with CCD detector. A diode laser operating at 785 nm (1.58 eV) was used as the excitation source. The reflectance spectrum was obtained for all samples using Ocean Optics QE65000 High-sensitivity Fiber Optic Spectrometer, and in accordance with it the Kubelka–Munk function was estimated using SpectraSuite Ocean Optics operating software. All measurements were carried out at room temperature. The thermal characterization (simultaneous thermal gravimetric–differential scanning calorimetry analysis, TGA–DSC) was carried out by using the instrument SDT Q600 V20.9 Build 20 (TA Instruments), in air atmosphere, ranging from 20 °C to 1200–1300 °C at a heating rate of 10 °C/min. The luminescence spectra were acquired at room temperature, on a Fluorolog-3 Model FL3-221 spectrofluorometer system (Horiba Jobin–Yvon), using a 450 W Xenon lamp and R928P photomultiplier tube.

2.3. Measurements of photocatalytic activity

The photocatalytic activity of the zinc tin oxide nanocrystalline powders was evaluated by the degradation of the solution of alprazolam (Sigma–Aldrich). Initial alprazolam concentration was 0.03 mmol/L and the catalysts loading was 1.0 mg/mL. Other chemicals were obtained from Sigma–Aldrich (ethanol) and from Carlo Erba (NaI). The kinetics of the alprazolam photodegradation was monitored with UFLC-DAD at 222 nm (wavelength of alprazolam maximum absorption) [17]. The photocatalytic degradation measurement was in detail described in our recent work [17]. In the investigation of the influence of $^{\bullet}OH$ radical scavengers, ethanol (3.0 mmol/L) was added to the alprazolam solution. Besides ethanol, NaI (3.0 mmol/L) was added in order to estimate the contribution of adsorbed $^{\bullet}OH$ radicals and valence band holes during the heterogeneous photocatalytic degradation of alprazolam. For total organic carbon (TOC) analysis, samples were irradiated at different time intervals and analyzed after filtration on an Elementar Liqui TOC II analyzer.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the X-ray diffraction (XRD) patterns of the obtained ternary zinc tin oxide powder samples. Majority of the sharp peaks in Fig. 1(a) are indexed as face-centered spinel Zn_2SnO_4 (JCPDS card No. 74-2184) with one residual peak (marked with asterisk) that can be assigned to zincite (JCPDS card No. 36-1451). The weakness of this ZnO peak compared to those of Zn_2SnO_4 gives us the right to claim that the amount of ZnO in the sample is negligible. The indicating peaks in Fig. 1 (b) agree well with JCPDS card No. 28-1486 for rhombohedral perovskite $ZnSnO_3$ with $LiNbO_3$ (LN)-type like structure. Lattice constant a of cubic Zn_2SnO_4 structure was calculated ($a = 8.6513(1)$ Å) according to Bragg's law equation for cubic systems: $a = \lambda/(2 \times \sin\theta) \times \sqrt{h^2 + k^2 + l^2}$, for the (311) peak, and it was almost the same as reference value (JCPDS card No. 74-2184: $a = 8.65(1)$ Å). As seen in the $ZnSnO_3$ XRD pattern (Fig. 1(b)), the relative intensity of the (110) peak (84%) was higher than that of the (110) peak in the standard JCPDS card (50%), which suggests non-random $ZnSnO_3$ crystallite orientation (preferred orientation). The crystallite sizes (~40 nm for Zn_2SnO_4 and ~26 nm for $ZnSnO_3$) were estimated using Debye Scherrer's equation by determining the line broadening of the main intensity peaks: (311) for Zn_2SnO_4 and (012) for $ZnSnO_3$. Much higher crystallinity observed for the obtained Zn_2SnO_4 vs. $ZnSnO_3$ (Fig. 1) is the result of additional annealing at high temperature which led to the increased crystallite size as well. The XRDs of the coupled ZnO/SnO_2 powder samples are almost the same, examples shown in Fig. 2. As expected, they confirm a mixture of ZnO (JCPDS card No. 36-1451) and SnO_2 (JCPDS card No. 41-1445) phases. The crystallite sizes, estimated by Debye Scherrer's equation for (101) ZnO and (110) SnO_2 main intensity peaks, were in the range 20–40 nm.

The SEM images (Figs. 3 and 4) gave us more insight to the microstructure and morphology of the obtained two types of ternary ZTO powder samples. The SEM images of both Zn_2SnO_4 and $ZnSnO_3$ display aggregation of particles to some extent which is uppermost the outcome of the preparation process. The Zn_2SnO_4

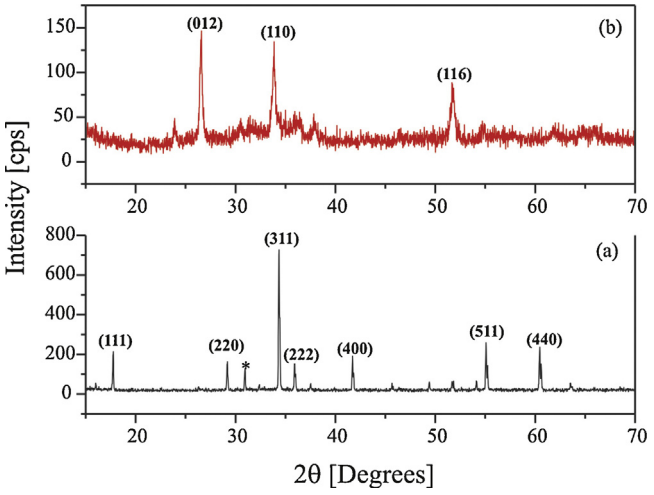

Fig. 1. XRD patterns of the synthesized ternary ZTO powder samples: (a) Zn_2SnO_4 and (b) $ZnSnO_3$.