Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 3575–3583

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Environmentally friendly photoactive heterojunction zinc tin oxide nanoparticles

T.B. Ivetić[a,*], N.L. Finčur[b], B.F. Abramović[b], M. Dimitrievska[c], G.R. Štrbac[a], K.O. Čajko[a], B.B. Miljević[a], Lj.R. Đačanin[a], S.R. Lukić-Petrović[a]

[a]Department of Physics, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia
[b]Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia
[c]Catalonia Institute for Energy Research–IREC, C. Jardis des les Dones de Negre 1, 08930 Sant Adrià del Besos, Barcelona, Spain

Received 14 September 2015; received in revised form 29 October 2015; accepted 31 October 2015
Available online 10 November 2015

Abstract

Heterojunction zinc tin oxide (ZnO/SnO_2) nanoparticles were prepared using a top–down traditional solid-state method; mechanical grinding followed by annealing, and characterized by X-ray diffraction, multi-wavelength excitation Raman scattering, scanning electron microscopy, diffuse reflectance and photoluminescence spectroscopy. The photocatalytic degradation kinetics of amitriptyline in the presence of the obtained ZnO/SnO_2 nanoparticles under simulated solar and UVA irradiation was determined and used as a model reaction for understanding the photocatalytic mechanism when such mixed oxide semiconductors are used in removing the pharmaceutically active compounds from wastewaters.

Keywords: A. Powders: solid state reaction; B. Spectroscopy; Photodegradation; Amitriptyline

1. Introduction

Both zinc oxide (ZnO) and tin oxide (SnO_2) semiconductors have numerous applications and are widely seen as very desirable and environmentally friendly compounds due to their availability, affordable price, and a non-toxic nature (chemical inertness) [1]. Their photostability accompanied by a good photoactivity when mixed together, are the reasons why they are being considered as the most promising photocatalysts for the environmental applications. Hence, the environmental friendliness of these compounds refers mostly to their ability of being, at the same time, chemically stable and acting as a driving force i.e. catalyst in complex reactions of photodegradation of organic pollutants in wastewaters.

The electron/hole pairs (e^-/h^+) formed in a semiconductor when it is irradiate with light of an energy equal or higher than its band gap [2] play the key role in the photodegradation mechanism. If present in wastewaters they initiate a chain of reactions where the powerful oxidizing agents are formed on the surface of the metal oxide ready to degrade the organic contaminants into harmless products. The only limiting factor in this simple, alternative method compared to conventional methods of water remediation, such as chlorination, ozonation, adsorption or biological degradation [3] is the fast recombination of these charge carries (e^-/h^+) which reduces their efficiency in the photodegradation processes. A way to overpass this problem is generally heading towards coupling of two semiconductors with different conduction band (CB) and valence band (VB) positions in order to keep these photogenerated e^-/h^+ pairs separated for longer, thus prolonging the time before their recombination and thereby making the photocatalytic reaction more efficient.

Mixed zinc oxide–tin oxide (ZnO/SnO_2) is recently studied coupled semiconductor system for applications in heterogeneous photocatalysis. There are reports of its more efficient

*Corresponding author. Tel.: +38 121 4852826; fax: +38 121 459367.
E-mail address: tamara.ivetic@df.uns.ac.rs (T.B. Ivetić).

http://dx.doi.org/10.1016/j.ceramint.2015.10.169
0272-8842/

e^-/h^+ pair separation under UV, artificial visible and solar irradiation, and success in the photocatalytic degradation of some dyes, the most common organic pollutants [1–15]. Usually, mixed ZnO/SnO_2 catalysts are prepared by multistep solvent-based routes, like coprecipitation [8–11], hydrothermal [12,13], sol–gel [14,15] etc. However, solid state mechanochemistry has not been used so much in ZnO/SnO_2 catalyst preparation even though it is a more simple, sustainable and eco-friendly method, since it is based on the toxic organic solvent-free reactions [16,17]. As well as this, there are almost no reports on ZnO/SnO_2 efficiency in photodegradation of psychiatric pharmaceuticals, the most prescribed active substances throughout the world and emerging environment contaminants [18].

As mentioned above, the enhanced photocatalytic activity of heterojunction ZnO/SnO_2 catalyst is mainly attributed to its increased charge separation mechanism [19] that arises from ZnO–SnO_2 coupling. Fig. 1 shows the illustrative scheme of how exactly the charge separation mechanism works in contact type ZnO/SnO_2 heterojunction photocatalyst [3] (band gap values, valence and conduction band positions for starting semiconductor oxides were extracted from Ref. [20]).

Upon light illumination, electrons in the VB are excited to the CB of both oxides, accompanied by the formation of appropriate amount of holes in the VB (h^+). However, more positive SnO_2 CB edge makes it a better electron acceptor than ZnO. This is how a charge carrier separation mechanism occurs i.e. electrons are preferentially collected on the SnO_2 particle, while holes are accumulated on the ZnO particle. As presented on the left-hand side in Fig. 1, holes react with surface hydroxyl groups or physisorbed water molecules on the zinc oxide surface and form hydroxyl radicals ($^\bullet$OH). Whereas electrons on the tin oxide surface react with dissolved oxygen molecules and create superoxide radical anions ($O_2^{\bullet -}$), which then by protonation yield hydroperoxyl radicals ($HO_2^\bullet$), that in the further course of this chain reaction, react with water creating more $^\bullet$OH [3] (as shown on the right-hand side in Fig. 1). The $^\bullet$OH radicals are well known as strong oxidizing agents, powerful enough to decompose organic compounds, like pharmaceuticals, into less harmful products.

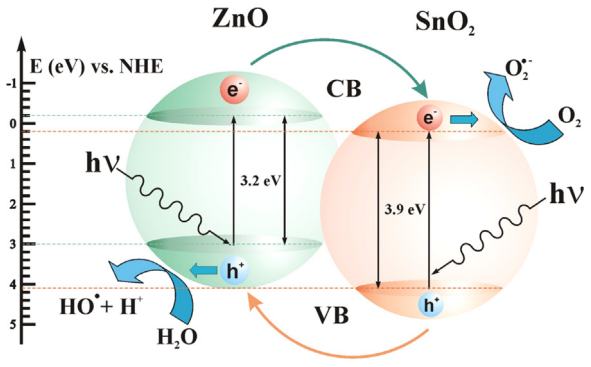

Fig. 1. Illustrative scheme of the charge separation mechanism in contact type ZnO/SnO_2 nanoparticles (VB–valence band; CB–conduction band; NHE–normal hydrogen electrode) when used for photocatalytic degradation processes.

Antidepressants are frequently prescribed pharmaceuticals. Significant antidepressant usage among both humans (due to depression, anxiety and chronic pain) and animals (in treatment of obsessive, compulsive and fearful behavior or separation anxiety) results in the prevalence of pharmaceuticals in the environment [21]. Amitriptyline hydrochloride (3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)-*N*,*N*-dimethylpropan-1-amine hydrochloride, CAS no. 549-18-8, $C_{20}H_{24}ClN$, M_r=313.9) is among the most widely used tricyclic antidepressants and it acts mainly by inhibiting the neurotransmitters norepinephrine and serotonin reuptake in the central nervous system. The drug has been widely used in treating depression, controlling anxiety, and treating a variety of chronic pain syndromes [22]. Amitriptyline was found in drinking water in concentration of 1.4 ng/L [23] as well as in surface waters in the concentration range 0.5–21 ng/L [24]. Since amitriptyline is widely used antidepressant and its continuous input into the environment may result in a potential risk for aquatic and terrestrial organisms, special attention has been paid in finding efficient method for the amitriptyline degradation.

In this work, heterojunction ZnO/SnO_2 nanoparticles, with a Zn to Sn molar ratio of 2:1 were prepared by a simple three-step mechanochemical solid-state method. The phase composition, crystalline structure, morphology and band gap of the obtained coupled catalyst were studied in detail. To the best of our knowledge, its photodegradation performance in degradation of amitriptyline solution was investigated for the first time, under both simulated solar and UVA irradiation.

Also, the role of $^\bullet$OH radicals (adsorbed or free) and h^+ as oxidants in the photocatalytic degradation of amitriptyline was investigated.

2. Experimental procedures

2.1. Materials and characterization

ZnO/SnO_2 nanoparticles powder mixture was prepared by a solid-state method, where starting precursors (ZnO and SnO_2, Sigma-Aldrich, purity 99.9% and particle size ≤ 1 μm) were ground in an agate mortar, annealed at 700 °C in air for 2 h and ground again. X-ray diffraction (XRD) was carried out using Philips PW 1050 instrument, with Cu $K_{\alpha 1,2}$ radiation, and a step scan mode of 0.02°/3s in angular range 2θ=10–90°. Scanning electron microscope (SEM-JEOL JSM 6460LV) was used to investigate the morphology and microstructure of the sample. The diffuse reflectance spectrum (DRS) was obtained using a system based on monochromator SPM2 (Carl Zeiss Jena) with quartz optics and reflection cell $_{45}R_0$. Source of light was tungsten lamp while light detector was photomultiplier EMI 9684B and operating voltage of 1 kV. The multi-wavelength excitation room temperature Raman scattering measurements were obtained using LabRam HR800-UV and iHR320 Horiba Jobin Yvon spectrometers coupled with gas HeCd laser with 325 nm, solid state laser with 532 nm and gas HeNe laser with 633 nm excitation wavelengths [25,26]. The photoluminescence (PL) spectra were measured using 325 nm excitation. In the case of LabRam HR800-UV system,