Applied Catalysis B: Environmental 162 (2015) 352–363

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Charge carriers injection in tandem semiconductors for dyes mineralization

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ARTICLE INFO

Article history:
Received 5 April 2014
Received in revised form 5 June 2014
Accepted 14 June 2014
Available online 8 July 2014

Keywords:
Tandem structures
Interface control
Optoelectric properties
Cu_xS/MO_x
Photocatalysis

ABSTRACT

Four mono-component and three tandem structures were prepared by robotic spray pyrolysis deposition using different precursor compositions and deposition temperatures. The structures of the electronic bands and the light generation/injection of the charge carriers trough the tandem layers (Cu_xS, CuO, SnO_2, ZnO, TiO_2) were studied using electrical (*J–V*, photocurrent) and optical (UV–vis transmittance) measurements. The crystalline structures and crystallite sizes were evaluated by X-ray diffraction and the morphologies were studied via atomic force microscopy. The wettability properties and the surface energy were calculated based on contact angle measurements using two liquids with different polarities (glycerol and ethylene glycol). The photocatalytic investigations show that the sample containing TiO_2–CuO–Cu_xS–SnO_2 has the highest photo-mineralization efficiency (78% removal of total organic carbon). It was found that copper sulfide compounds increase the photosensitivity properties of the tandem structure especially in vis region of the spectra. The efficiency and kinetics data of the photocatalytic processes were in agreement with the electronic bands alignment, which shows that tandem structures with suitable band energy values and at least one active interface allow high charge carrier mobility and the generation of oxidative species during photocatalysis.

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1. Introduction

The advanced treatment of wastewaters with complex organic pollutants load resulted in industrial processes (especially textile industry) becomes a major issue for all scientific and technological research groups. Even if the traditional techniques for wastewaters treatment are still in use, the advanced oxidations processes (AOPs), based on the generation of reactive species (•OH radicals), are more and more recommended for the oxidative degradation of pollutants, targeting water reuse [1,2]. Wastewater treatment via AOPs, using semiconductor nanomaterials as photocatalysts, seems to be the most promising AOP technology, because photoactivated semiconductors can completely mineralize different types of toxic and non-biodegradable pollutants to CO_2, H_2O and mineral acids under mild conditions: room temperature and atmospheric pressure [3,4].

The photocatalytic performances of metal oxide semiconductors such as TiO_2 [5,6], ZnO [7,8] and SnO_2 [9,10] were intensively investigated, while only few studies [11,12] are reported for Cu_xS ($x = 1–2$). Except copper sulfides, all above mentioned semiconductor photocatalysts have band gaps in the UV region, ($E_g > 3.2$ eV, $\lambda = 387$ nm), limiting the use of sunlight in industrial applications [13,14] and significantly increasing the process costs. Therefore, to develop market acceptable AOP, many studies are focusing on the synthesis of different coupled tandem semiconductors, such as ZnO/TiO_2 [15], WO_3/TiO_2 [16], SnO_2/TiO_2 [17], Cu_xS/TiO_2 [18] and ZnO/Cu_2O [19], aiming at extending the photocatalytic response in the vis spectral region. A common problem of these systems is finding suitable candidates with band energy values that allow high charge carriers mobility, able to generate oxidative species during photocatalysis. One way to increase the photocatalytic activity of a tandem system is to introduce a compound with photosensitive properties in both UV and vis regions.

Therefore, the main purpose of this study is to present an alternative to increase the UV–vis efficiency of a photocatalyst by coupling different semiconductor materials according to their electronic band structures; the aim is to outline the optimal conditions that support the injection of light generated charge carriers (electrons and holes) and suppress their recombination in the photocatalytic material.

The paper presents a detailed investigation on two—(Cu_xS/SnO_2) and multi-component (ZnO/Cu_xS–CuO/SnO_2 and TiO_2/Cu_xS–CuO/SnO_2) thin films tandem structures, obtained by the successive deposition of individual semiconductor layers,

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http://dx.doi.org/10.1016/j.apcatb.2014.06.059
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using robotic spray pyrolysis deposition (RSPD). These types of composites/tandem systems are promising materials for pollutants degradation under UV–vis light irradiation inducing a synergistic effect on charge separation [20]. The use of binary and ternary systems is expected to increase the solar radiation (UV + vis) absorption, by facilitating the charge carrier mobility with positive consequences in photocatalytic reactions. The combinations between the cooper compounds and the metal oxides were selected based on the compatibility between the crystalline structures and the suitable position of the energy bands. Further on, this study demonstrates the influence of composition, crystalline structure and morphology of the individual layers on the interfaces and, consequently on the opto-electrical and photocatalytic properties of the tandem systems.

2. Experimental procedure

2.1. Precursor preparation and deposition parameters

Seven samples were prepared by RSPD using microscopic glass (Heinz Herenz) as substrate for thin films deposition [21]; a set of samples were simultaneously deposited on FTO (fluorine doped tin oxide, F:SnO_2, coated glass—Libbey Owens Ford TEC 20/2.5 nm) for the opto-electric analyses. Samples of $2 \times 2\,cm^2$ substrate were cleaned by successive immersion in ethanol and acetone using an ultrasonic bath.

The precursor solutions for individual metal oxide layers were prepared by mixing tin chloride ($SnCl_4$, 99.99%, Alfa Aesar), titanium chloride ($TiCl_4$, 99.99%, Alfa Aesar) or zinc chloride ($ZnCl_2$, 99.99%, Alfa Aesar) with ethanol (C_2H_5OH, 99.99%, Alfa Aesar) to form 0.1 M solutions. The precursors solution for Cu_xS layers was prepared from 0.3 M copper chloride ($CuCl_2$, 99%, Scharlau) and thioureea ($SC(NH_2)_2$, 99%, Scharlau) in 1:3 molar ratio, using as solvent a mixture of water, ethanol and glycerol ($C_3H_8O_3$, 99.5%, Scharlau) in 7:2:1 volume ratio.

The mechanism of film formation includes: nucleation, formation of the incipient layer and formation of the bulk structure based on aggregates sintering. Previous work [9] showed that the use of inorganic precursors leads to fast nucleation and increases the film uniformity. The number of spraying sequences was 20 for all components but the breaks between two pulses was optimized at: 45 s for tin oxide, 60 s for titanium oxide, 30 s for zinc oxides and 30 s for copper compounds. The carrier gas was air at 1.4 bar and the distance between the spraying nozzle and the substrate was fixed at 15 cm. The abbreviations of the tandem structures consider the metal oxide obtained during the deposition, the layers sequences, the precursors and the deposition temperatures and are presented in Table 1. A schematic representation of the tandem structures is presented in Fig. 1.

After deposition, the samples were annealed at 500 °C for 6 h. The samples containing Cu_xS were annealed after the deposition of TiO_2 or ZnO as top layer to prevent thermal degradation (oxidation) and sublimation. Due to the thermal instability of Cu_xS, the sample Sn_Cu was not annealed.

The deposition and annealing temperatures were optimized in preliminary experiments, based on the stability and polymorphism variation with temperature, and considering the main output property, the efficiency in the dyes photo-mineralization.

2.2. Photocatalysis experiments

The photodegradation reactor consists of a static cylindrical flask, open to air. Combined UV and vis radiation was employed during the photocatalytic experiments by using one F18 W/T8 (black light tubes, UVA, typically 340–400 nm, with λ_{max} = 365 nm, flux intensity 3 lx, Philips) and two TL-D Super 80 18 W/865 lamps (white cold light tubes, vis, typically 400–700 nm, with λ_{max} = 565 nm, flux intensity 28 lx, Philips), placed annular to the photoreactor. This combination was chosen as well resembling the solar spectrum (excluding the IR part). In order to prevent light scattering the light sources are circularly positioned around the photocatalytic system. Consequently the radiation is uniformly distributed all over the samples.

The pollutant dye tested in this work was 0.0125 mM methylene blue (99.8%, Merck) prepared by dissolving the powder in ultra-pure water (Direct-Q3 Water Purification System). The photocatalytic degradation of methylene blue was evaluated using a total organic carbon and total nitrogen analyzer (TOC-L + TNM-L, Shimadzu model TOC-LCPH). Experiments used the auto-sample mode at 1 h interval during 6 h.

Before irradiation, each sample ($2 \times 2\,cm^2$) was inserted in the dye solution into a 25 mL quartz beaker and kept in dark for 1 h to reach the adsorption equilibrium. The changes in concentration were evaluated based on the UV–vis calibration curve, at 665 nm (Perkin Elmer Lambda 950), hourly measured up to 6 h of photocatalysis.

2.3. Thin films characterization

The crystalline structure and the layers composition were evaluated by X-ray diffraction (XRD, Bruker D8 Discover Diffractometer) using the locked-couple technique with 0.002 degree scan step and 0.01 s/step. The surface morphology of the individual and tandem layers was investigated using an atomic force microscope (AFM, NT-MDT model BL222RNTE). The images were taken in semicontact mode with Si-tips (NSG10, force constant 0.15 N/m, tip radius

Table 1
Individual and tandem Cu_xS/MO_x layers structures obtained by RSPD.

Sample abbreviation	Sample structure	Precursors and deposition temperature for each layer		
		1st layer	2nd layer	3rd layer
Sn	SnO_2	**SnO_2** $SnCl_4$, C_2H_5OH; 450 °C	–	–
Zn	ZnO	**ZnO** $ZnCl_2$, C_2H_5OH; 350 °C	–	–
Ti	TiO_2	**TiO_2** $TiCl_4$, C_2H_5OH; 400 °C	–	–
Cu	Cu_xS	**Cu_xS** $CuCl_2$, $SC(NH_2)_2$, C_2H_5OH, $C_3H_8O_3$; 300 °C	–	–
Cu_Sn	Cu_xS/SnO_2	SnO_2	Cu_xS	–
Ti_Cu_Sn	$TiO_2/Cu_xS/SnO_2$	SnO_2	Cu_xS	TiO_2
Zn_Cu_Sn	$ZnO/Cu_xS/SnO_2$	SnO_2	Cu_xS	ZnO

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