Journal of Water Process Engineering 12 (2016) 32–40

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Facile synthesis of Y_2S_3/ZnO nanocomposite and its catalytic performance in the degradation of Methylene Blue using UV-A/solar illumination

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ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form 1 June 2016
Accepted 5 June 2016

Keywords:
Y_2S_3/ZnO
UV-A light
Solar light
Degradation

ABSTRACT

Y_2S_3/ZnO nanocomposite synthesized by a facile precipitation method combined with a mild ultrasonic technique. Y_2S_3/ZnO was characterized using X-ray diffraction (XRD), Scanning electron microscopy (FE-SEM), Elemental colour mapping, Transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), Photoluminescence spectroscopy (PLS), X-ray photoelectron spectroscopy (XPS) and BET surface area measurements. Photocatalytic activity of Y_2S_3/ZnO was evaluated by the degradation of Methylene Blue (MB, an organic dye) as a model pollutant using UV-A/solar light. The 10.1 wt% Y_2S_3/ZnO degraded dye completely within 60 min at neutral pH 7. It is more efficient than bare ZnO, commercial ZnO, TiO_2-P25 and TiO_2 (Aldrich). The superior photocatalytic performance of 10.1 wt% Y_2S_3/ZnO is attributed to high UV-A/solar light absorption as well as effective charge carrier separation. A possible mechanism of photocatalysis is proposed. This novel composite material has potential applications in the industrial effluent treatment at the neutral pH 7.

1. Introduction

AOPs have been extensively studied as a viable wastewater treatment method [1,2]. Significant attention has been paid to photocatalysts, which accelerate light-driven chemical reactions, due to their interesting properties such as quantum confinement and enhanced reactivity [3–12]. Among the photocatalysts, ZnO is unique because of its superb optical and electrical properties and it becomes a potential candidate for a variety of practical applications including semiconductors, field-effect transistors, luminescence, solar cells, gas sensors, photodetectors, UV-blocking and other aspects [13–16].

Some research groups demonstrated that rare earth metal yttrium (Y^{3+}), is useful in various applications [17–19] and its doping with TiO_2 was found to be successful for improving the photocatalytic response of TiO_2, and photodegradation results revealed that Y^{3+} doping could greatly improve the photocatalytic activity of TiO_2. Photocatalytic degradation of methyl orange by polyoxometalates supported on yttrium-doped TiO_2 was reported by Wang et al., [20]. Methyl orange was totally degraded in 21 min under optimum conditions and the catalyst was stable and easily separable from reaction system for recovery. Ga^{3+} and Y^{3+} cationic substitution in mesoporous TiO_2 photoanodes were prepared for photovoltaic applications [21], and after optimizing their relative concentration level, there was a noticeable manner the power conversion efficiency from 7.4% to 8.1% for gallium and even to 9.0% in the case of yttrium where all three photovoltaic (PV) performance parameters were improved simultaneously.

Studies on Y ions included into wide band gap semiconductor like ZnO [22] and revealed a significant increase in the optical properties, photocatalyst efficiency with enhanced stability of ZnO nanoparticles [22–24]. Y doping also tunes the emission wavelength of ZnO and makes a supersensitive UV detector [24]. It is well known that semiconductor coupling, dye sensitization and metal, non-metal or co-doping have been applied to develop visible light sensitive ZnO [25–30]. Many researchers have coupled metal

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http://dx.doi.org/10.1016/j.jwpe.2016.06.002
2214-7144/

sulfides with ZnO and used them as photocatalysts for effective environmental remediation [31–34].

The rare-earth sulphide materials constitute a special category of the chalcogenides. The excellent thermal stability, strength and possession of good optical properties because of their ability to transmit into the infrared (IR) region, the rare-earth sulphides also made them good candidates for photocatalysis. Y_2S_3 is a narrow gap semiconductor with band gap of 2.58 eV [35,36]. In this work, for the first time a novel yttrium sulphide loaded ZnO (Y_2S_3/ZnO) was fabricated via sonochemically assisted precipitation method with various Y_2S_3 doping concentrations. To the best of our knowledge, the preparation and characterization of the Y_2S_3/ZnO composite for the improved photocatalysis have not been reported yet. The present paper will introduce a new route to improve the photocatalytic activity of ZnO and also provide a clue for semiconductor modification.

2. Experimental

2.1. Chemicals and materials

The commercial Methylene Blue is a heterocyclic aromatic chemical compound (molecular formula = $C_{16}H_{18}N_3SCl$; molecular weight 319.86 and dye content 80%) from Aldrich was used as such. The structure of the dye and its absorption maxima are given in Fig. S1 (see Supplementary data). Oxalic acid dihydrate (99%), and zinc nitrate hexahydrate (99%) were obtained from Himedia chemicals. $Y(NO_3)_3 \cdot 6H_2O$ (Himedia), Na_2S (Qualigens), ZnO (Himedia), TiO_2 (Aldrich) were used as received. A gift sample of Degussa TiO_2-P25 was obtained from Evonik (Germany). It is a 80:20 mixture of anatase and rutile with the particle size of 30 nm and BET surface area 50 $m^2\,g^{-1}$. $K_2Cr_2O_7$ (s.d.fine), Ag_2SO_4 (s.d.fine), $HgSO_4$ and $FeSO_4 \cdot 7H_2O$ (Qualigens) were used as received. The double distilled water was used to prepare experimental solutions. The pH of the solutions before irradiation was adjusted using H_2SO_4 or NaOH.

2.2. Fabrication of Y_2S_3/ZnO

A novel Y_2S_3 loaded ZnO was prepared by sonochemically assisted precipitation-thermal decomposition method (Scheme S1). Aqueous solution of equal volume of 0.4 M zinc nitrate hexahydrate and of 0.6 M oxalic acid dihydrate in deionized water were brought to their boiling points and zinc nitrate solution was added rapidly to the oxalic acid solution to precipitate zinc oxalate. 0.001 M of $Y(NO_3)_3 \cdot 6H_2O$ (0.383 g) in 5 mL of water was mixed with 0.0015 M of Na_2S (0.117 g) in 5 mL solution, and the formed Y_2S_3 was added to the zinc oxalate. The suspension with Y_2S_3 and zinc oxalate was stirred for 3 h in warm condition, and then sonicated for 3 h (Amplitude = 100 KHz, power = 120 W). The zinc oxalate dihydrate crystals with Y_2S_3 were filtered, washed several times with distilled water, air-dried overnight and dried in hot air oven at 100 °C for 3 h. Y_2S_3-zinc oxalate dihydrate mixture was taken in a porcelain dish and heated in the muffle furnace at the rate of 20 °C min^{-1} to reach the decomposition temperature of zinc oxalate (450 °C). After 12 h, the furnace was allowed to cool down to room temperature. The decomposition of zinc oxalate around 450 °C and the stability of Y_2S_3 was confirmed by TGA (Fig. S2, see Supporting information). The Y_2S_3/ZnO catalyst was collected and used for further analysis. This catalyst contained 10.1 wt% of Y_2S_3. Catalysts with 3.4, 5.0, 15.2 and 20.3 wt% of Y_2S_3 were prepared with this procedure using appropriate amounts of $Y(NO_3)_3 \cdot 6H_2O$ and Na_2S. The bare ZnO was prepared using the same procedure without addition of Y_2S_3.

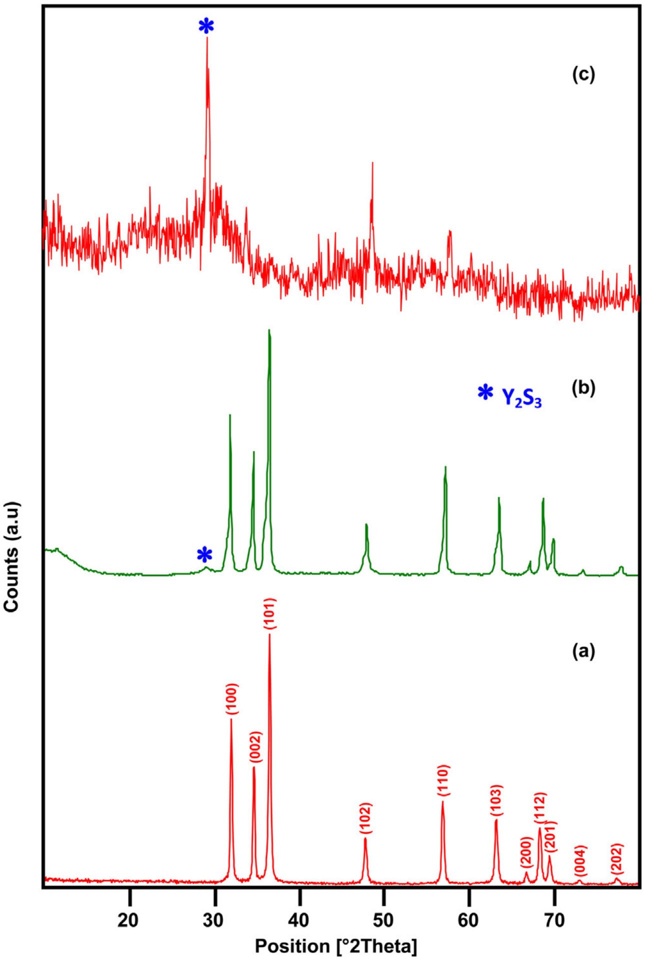

Fig. 1. XRD patterns of (a) bare ZnO, (b) Y_2S_3/ZnO and (c) Y_2S_3.

2.3. Characterization

X'Per PRO diffractometer equipped with a CuKα radiation (wavelength 1.5406 Å) at 2.2 kW Max was used for powder X-ray diffraction measurement's. Peak positions were compared with the standard files to identity the crystalline phase. The transmission electron microscopic (TEM) observation was carried out on a Hitachi H-7000, Japan, with an acceleration voltage of 100 kV. The specimens were prepared by depositing a drop of the suspension of sample powder, which was ultrasonically dispersed in acetone for 10 min, on a carbon-coated copper grid, followed by drying at room temperature. On observation with a JEOL JSM-6500F cold field emission scanning electron microscope (FE-SEM), the samples were mounted on a gold platform placed in chamber. Energy dispersive X-ray spectrum (EDS) was examined using a JEOL-JSM 5610 LV. Shimadzu UV-2450 spectrometer was used for UV-DRS measurements. Photoluminescence (PL) spectra at room temperature were recorded using a Perkin Elmer LS 55 fluorescence spectrometer. The nanoparticles were dispersed in carbon tetrachloride and excited using light of wavelength 300 nm. X-ray photoelectron spectroscopic (XPS) analysis was done in a Kratos Analytical, Ultra Axis (Shimadzu, UK) using Al Kα (1486.6 eV) radiation as the source. The spectra were referenced to the binding energy of C1 s (285 eV). The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of BET equation using a Micromeritics ASAP 2020 V3.00H. UV spectral measurements were done using Hitachi-U-2001 spectrometer. For the degradation by UV-A light (365 nm), a Heber Multilamp photoreactor HML MP 88