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Invited feature article

Fabrication of ZnO-Zn₂TiO₄ nanocomposite from zinc hydroxide nitrate and its photocatalytic efficiency



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ABSTRACT

A nanocomposite containing zinc oxide and zinc titanate spinel was synthesized from a mixture of layered zinc hydroxide nitrate and titanium (IV) oxysulfate (theoretical Zn₂TiO₄:ZnO mass ratio of 10%) by calcination at 700 °C. The resulting material was characterized by XRD, TGA-DSC, FTIR, TEM, SAED, SEM, EDS mapping and Raman spectroscopy, techniques that allowed verifying a heterogeneous material constituted of tubular Zn₂TiO₄ and granular ZnO particles. The resulting ZnO/Zn₂TiO₄ nanocomposite was used as a photocatalyst in the advanced oxidative process (AOP) for degradation of Reactive Black 5 dye in aqueous solution. The results indicate excellent photocatalytic performance with significant removal of the integrated spectral area, which suggests significant dye degradation after 60 min.

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1. Introduction

In the last years, the availability of sensitive analytical tools highlighted a new group of relevant environmental pollutants, which, even in low concentrations, can cause adverse effects on ecosystems and human health. Within this group of organic micropollutants highlight those conveyed by the sewer, including compounds with pharmacological activity (PhACs), hygiene and personal care products (PCPs) and illicit drugs [1,2] which, not being efficiently removed in conventional treatment routines [3], contaminate surface water, groundwater and consumption water [4]. According to recent reports [5], more than 700 emerging pollutants, metabolites, and processing products have been identified in the aquatic environment of Europe.

Because of this reality, new treatment technologies have been evaluated for degradation of emerging pollutants in treated and natural sewage, including physical processes substantiated on the use of advanced materials (e.g. graphene and carbon nanotubes), biological processes substantiated on the use of pure bacterial cultures and photochemical processes based on the use of ultraviolet radiation [6]. Within the context of photo-assisted processes highlights the heterogeneous photocatalysis, mainly with the use of titanium dioxide [7]; and zinc oxide [8], which has

demonstrated high degradation efficiency in relation to many emerging pollutants of relevance [9–11].

In this last year (2016), more than a thousand articles about photocatalytic degradation were published, most of which involves the synthesis of new materials and the assessment of its degradation capacity in relation to model substrates. Within this context, highlights the association of consecrated photocatalysts, such as TiO₂ and ZnO, with carbonaceous materials [12], transition metals [13], metallic nanoparticles [14], among other advanced materials.

Due to the high photocatalytic efficiency of TiO₂ and ZnO, much effort have been devoted to the synthesis of systems containing both photocatalysts, in search of associated synergistic effects, for example, to the improvement in the process of separation of loads [15]. In general, in all these syntheses it is observed the creation of zinc titanates (e.g., ZnTiO₃ and Zn₂TiO₄) especially when high synthesis temperature are used [16]. The zinc titanates present a wide variety of technological applications, mainly due to their dielectric properties [17]. However, few papers report photocatalytic applications of these materials, primarily due to the high bandgap value. Therefore, it is usually the modifications of these semiconductor oxides to doping with transition metals, aiming to increase its radiation absorption capacity of the visible region [18]; [19].

On this paper, a ZnO/Zn₂TiO₄ nanocomposite was synthesized “in-situ” from zinc hydroxide nitrate (ZnHN – Zn₅(OH)₈(NO₃)₂·2H₂O) and titanium oxysulfate (IV) (TiOSO₄), evaluating

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its photocatalytic activity against aqueous solutions of a model dye (reactive black 5 (RB5)).

2. Materials and methods

2.1. Synthesis of ZnO and ZnO/Zn₂TiO₄

The zinc hydroxide nitrate (Zn₅(OH)₈(NO₃)₂·2H₂O, ZnHN) was previously synthesized by the slow addition of 0.5 mol L⁻¹ NaOH aqueous solution (Vetec 99%) into 300 mL of 0.1 mol L⁻¹ Zn(NO₃)₂·6H₂O (VETEC, 99%), until the mixture reaches pH 6.82. This mixture was stirred for 48 h generating the ZnHN in 97% yield after washing and drying (60 °C). Subsequently, a part of the solid, sufficient mass to obtain a ratio of 10% wt of Zn₂TiO₄ in relation to ZnO, was dispersed in distilled water and to this mixture added 6.25 mmol of TiOSO₄ (71%, Aldrich Chemical Co. USA) with stirring for a further 24 h. The resulting solid from this reaction was separated by centrifugation, repeatedly washed with distilled water, dried for 24 h and subjected to calcination for 6 h at a temperature of 700 °C, with a heating rate of 10 °C min⁻¹.

2.2. Characterization of materials

The morphological analysis of the synthesized compounds was performed by scanning electron microscopy (SEM) and its chemical composition by energy dispersive spectroscopy (EDS). SEM images were acquired by anFEI Quanta 450 FEG electronic microscope with AZ Tech software equipped with an x-ray energy dispersive spectroscopic analyzer using an SDD detector. The samples were deposited in copper (Cu) double-face tape and metalized with gold for SEM and carbon for EDS.

The images of transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were obtained with the aid of a JEOL JEM 1200EX-II electronic transmission microscope, with 120 kV beam power with magnifications between 8000 and 60000 times, with the spot rays of the SAED images being calculated with the aid of the ImageJ software. The sample was dispersed in methanol with the assistance of an ultrasonic bath and deposited on a copper grid with 200 mesh aperture coated with a formvar film.

X-ray diffraction analyzes of the powdered materials deposited on aluminum sample port were obtained on a Shimadzu XRD-7000 diffractometer with a scan of 2° per minute and step of 0.02° in a range of 3–70° (2θ). The radiation came from a copper cathode (Kα = 1.5418 Å), being applied to it a current of 20 mA and a voltage of 40 kV.

Measurements of Fourier Transform Infrared Vibrational Spectroscopy (FTIR) were performed in the transmission mode using a Bomem Michelson MB100 model spectroscopy. The samples were prepared with KBr pressed in the form of pellets with the pressure of 6.5 t and the spectra were obtained by accumulation of 32 scans in the range of 4000–400 cm⁻¹ and 4 cm⁻¹ resolution.

The diffuse reflectance spectrum in the visible ultraviolet region was obtained using a spectrophotometer (Shimadzu UV-2401PC) with a ball integration accessory (240–52454-01), being analyzed by reflectance in the region between 240 and 800 nm, after being carefully compressed into the spectrophotometer cell. The obtained reflectance was converted to its derivative using the Kubelka-Munk function ($F(R) = (1 - R)^2/2R$) [20], the bandgap energy (E_g) was calculated according to the formula: $E_g = 1239.7/\lambda$ considering the wavelengths (λ) of the spectrum scan. The bandgap energy of the material was determined by the extrapolation of a linear region of the abscissa axis of the graph (F(R))^{0.5} versus E_g, where F(R) is the Kubelka-Munk function.

The Raman spectrum was obtained using a Raman Witec Alpha 300R confocal microscope, with an integration time of 5.10 s, 20 accumulations, resolution of 3 cm⁻¹ in a range between 50 and 1200 cm⁻¹ and 532 nm radiation using a high power diode laser as the source of excitation. The sample was ground in a grail of agate and deposited on a glass plate where the monochromatic beam would be an incident.

Simultaneous thermal analysis measurements (thermogravimetric analysis – TGA and differential scanning calorimetry – DSC) were performed on a Netzsch STA 449 F3 Jupiter analyzer, using alumina crucibles, synthetic air flow (50 mL min⁻¹), scanning speed of 10 °C min⁻¹ in a temperature range between 25 and 1000 °C.

2.3. Photocatalysis assays

The photocatalytic degradation studies were performed in a 300 mL capacity photochemical bench reactor equipped with magnetic stirring and water jacket cooling (25 ± 2 °C). The radiation was provided by a 125 W mercury vapor lamp, without the original protective glass, inserted into the solution with the aid of a Pyrex glass bulb.

The assays were performed with 200 mL of aqueous solution of a model dye (reactive black 5, C₂₆H₂₁N₅O₁₉S₆Na₄, CI 20505, Aldrich Chemical Co. USA, with a dye content of 55%) in a concentration of 20 mg L⁻¹ and pH value 7.0, this dye being chosen due to its complexity and stability over conventional oxidation methods.

The dye degradation was evaluated by aliquots collected during the reaction time interval where a dark phase step (adsorption step) and a step with radiation (photodegradation step) were carried out, the aliquots removed during the photodegradation step were measured by UV–vis spectrophotometry, using a Varian Cary 50 Bio spectrophotometer and 1 cm optical path quartz buckets.

3. Results and discussion

3.1. Characterization of materials

Initially, the ZnHN prepared by the precipitation method was characterized by XRD (Fig. 1a), being indexed according to the card (JCPDS file number 24–1460). After addition of TiOSO₄ (Fig. 1b), it

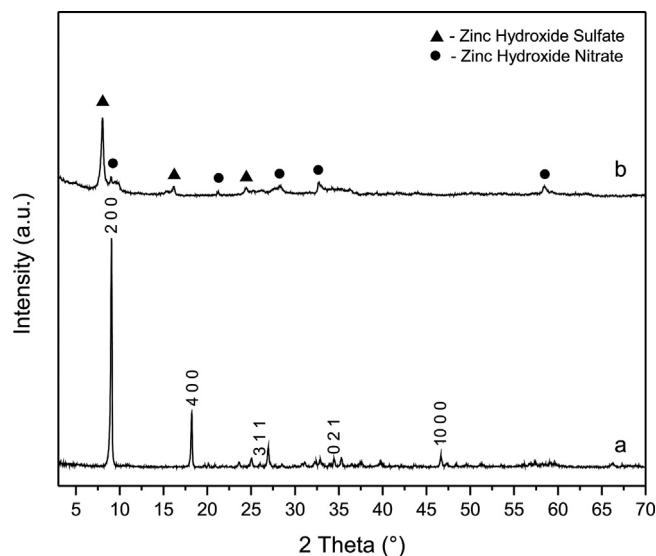


Fig. 1. XRD pattern of (a) Zinc Hydroxide Nitrate (without calcination) and (b) Zinc Hydroxide Nitrate + 1.00 g of TiOSO₄ (without calcination).

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