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Relationship between the component synthesis order of zinc ferrite–titania nanocomposites and their performances as visible light-driven photocatalysts for relevant organic pollutant degradation

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ABSTRACT

The main objective of this work was to investigate the influence of the order of component synthesis of zinc ferrite–titania nanocomposites on their structural, morphologic, textural, light absorption properties, and performances as photocatalysts. In this respect, nanocomposite materials with 10ZnFe₂O₄–90TiO₂ (wt %) composition were prepared via a two-step synthesis procedure by alternating the order of the component addition during the preparation protocol and characterized by X-ray diffraction, transmission electron microscopy, energy dispersive X-ray, small-angle X-ray scattering, nitrogen sorption, and UV–vis diffuse reflectance spectroscopy. The photocatalytic activity of nanocomposites was evaluated on Rhodamine 6G degradation under visible light illumination. The photocatalytic performances of nanocomposites were clearly superior to the classical TiO₂. Nevertheless, preparing titania in the presence of a presynthesized zinc ferrite led to superior characteristics in terms of band gap value, specific surface area, and grain sizes crucial for the enhancement of the photocatalytic performances.

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1. Introduction

Synthetic organic dyes are widely used in various industries (textile, leather, paper, plastic, cosmetics, photographic, and biomedical) as coloring agents because of their wide spectrum of shades, such as ability for covalent attachment to fibers, ease of application, brilliant colors, and minimal energy consumption [1]. These properties justify the annual production over 7×10^5 tons of dyes [1,2]. Unfortunately, their proved toxic, mutagenic, and carcinogenic characteristics [3,4] represent an

important ecological concern, as a significant part of the total production of dyes (about 15%) is lost and discharged into the environment as effluents during dye production and dying processes [1,5,6]. Improper handling of water pollution with dyes can affect the quality of the drinking water for several generations.

In this regard, numerous chemical, physical, and biological methods have been developed for the efficient removal of organic dye pollutants from wastewaters [7–9]. Among chemical methods, photocatalysis is very often used for the effective removal of organic dyes from industrial effluents. Frequently, the photodegradation of these refractory pollutants is successfully mediated by titanium dioxide (TiO₂) because of strong oxidizing capacity, chemical and biological stability in aggressive reaction

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environment, cost effectiveness, and nontoxicity [10,11]. In spite of these benefits, two major drawbacks are often mentioned in the literature to hinder the practical application of TiO_2 as photocatalysts for these kinds of processes: (1) absorption limited to ultraviolet light, which represents only about 4% of the solar spectrum, because of its relatively wide band gap (around 3.2 eV depending on structural parameters) [12–14] and (2) difficulties in recovering from the reaction environment and recycling of the photocatalyst [10]. The solution to simultaneously solve these problems is to dope the TiO_2 with a narrow band gap magnetic material [10,15]. The most appropriate doping compounds are the spinel ferrites, and particularly the zinc ferrites, because of their good magnetic properties, band gap ranging between 1.0 and 2.0 eV (depending on chemical composition and synthesis method), chemical and physical stability in photodegradation medium, low cost, and relatively easy preparation [12,16–18]. Several strategies were adopted to obtain ferrite– TiO_2 composites. Two main approaches for the synthesis of such composites should be taken into account either by one-pot method [17] or by two-step method [18,19]. The two-step synthesis procedure consists of two possible preparation routes: one refers to preparing the spinel ferrite in the presence of titania [18] and the other to the synthesis of TiO_2 over preprepared dopant nanoparticles [19]. Nevertheless, to the best of our knowledge, no study dealing with the influence of the order of the component synthesis on the properties of the resulted photocatalysts for the two-step procedure was previously reported.

In the present work, nanocomposite materials having $10\text{ZnFe}_2\text{O}_4$ – 90TiO_2 (wt %) composition, prepared via a two-step synthesis procedure by alternating the order of the component addition during the preparation protocol are studied. Furthermore, their performances as visible light–driven photocatalysts for Rhodamine 6G degradation are evaluated.

2. Experimental section

2.1. Materials

Analytical grade nickel nitrate, zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], citric acid monohydrate [$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$], Pluronic F-127, titanium isopropoxide (TIPO) [$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$], isopropanol [$\text{C}_3\text{H}_8\text{O}$], and Rhodamine 6G [$\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$] dye were used without further purification as purchased from Sigma–Aldrich.

2.2. Synthesis of TiO_2 (T)

A mixture of 10% Pluronic F-127 in a 1:1 water/isopropanol solution was ultrasonicated for 1 h at 25% amplitude with a horn–probe sonic tip (750 W; VibraCell) with ON and OFF cycle set for 2 s. Further, the required volume of TIPO was added ($\text{F127}/\text{TIPO} = 1/1.7$). The as-obtained mixture was subjected to the ultrasonication treatment for 1 h at 25% amplitude, with 2 s ON/OFF cycles. The resulted white precipitate was separated by filtration, washed with distilled water, dried, and finally calcinated at 450°C to obtain the pure TiO_2 .

2.3. Synthesis of spinel ferrite (ZF)

ZnFe_2O_4 spinel ferrite (ZF) was prepared by a sol–gel autocombustion method using citric acid as a chelating/combustion agent [7]. In a typical synthesis approach, stoichiometric amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the molar ratio $\text{Zn}^{2+}/\text{Fe}^{3+}$ of 1:2 were dissolved in distilled water. Furthermore, the as-obtained nitrate solution was mixed with an aqueous solution of the fuel agent (citric acid). The molar ratio of total metallic cations to citric acid was 1:1. The resulting mixture was stirred and heated to 80°C in a water bath until a viscous gel was obtained. The gel was heated up to 350°C when the autocombustion was clearly observed. The resulting powder was finally sintered at 450°C for 5 h.

2.4. Nanocomposites' preparation (ZFT and TZF)

Nanocomposite materials with the $10\text{ZnFe}_2\text{O}_4$ – 90TiO_2 (wt %) composition were prepared in two steps, alternating the order of the component addition during the synthesis protocol, as described in the synthesis flowchart shown in Fig. 1. Thus, to obtain the ZFT composite material, zinc ferrite was synthesized in the presence of titania (preprepared TiO_2 was added in the nitrate solution and the mixture was further treated according to the ZF preparation protocol), whereas for the TZF sample the titania was prepared in the presence of the zinc ferrite by adding the ferrite to the Pluronic F-127 solution and following further the T obtaining procedure.

2.5. Material characterization

The structural order of the samples was evaluated by recording the X-ray diffraction (XRD) patterns with a Bruker-AXS D8 Advance powder diffraction system equipped with a transmission-type goniometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The powder samples were scanned from 10 to 80° (2θ) using a scanning step of $0.02^\circ/\text{s}$.

The morphology and composition of the samples were studied by means of transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) on a Hitachi HT7700 microscope equipped with a Bruker XFlash 6 EDS detector operated at 120 kV in high contrast mode. The microscopic samples were prepared by dispersing the powders in ethanol using an ultrasound bath and then placing a small drop on the TEM grid. Finally, the solvent was evaporated at 50°C in vacuum for 24 h before the measurements.

The particle size distribution and average particle sizes were determined by small-angle X-ray scattering (SAXS). SAXS measurements were performed on a Bruker-Nanostar U instrument equipped with a 3-pinhole collimation optics. This system provides a precisely parallel X-ray beam with virtually no background and high intensity, leading to short measuring times and very high resolution. The scattering intensity was measured as a function of scattering vector $q = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle and λ is the X-ray wavelength ($\text{Cu K}\alpha = 1.54 \text{ \AA}$).

The textural properties of the powder were studied by nitrogen sorption on a Quantachrome Nova 2200

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