



Mesoporous metal oxide/silica composites with photocatalytic activity and magnetic response



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ABSTRACT

In this work, a novel class of mesoporous metal oxide/silica composites was prepared. Both ZnO and magnetite (Fe_3O_4) nanoparticles were embedded within the mesoporous silica architecture. The solids display a high surface area, narrow pore size distribution and a regular array of mesoporous hexagonal channels with long range ordering. All the materials were tested for the photodegradation of Rhodamine B and the catalytic performance compared with analogous mesoporous solids exclusively bearing ZnO nanoparticles in the silica framework. All the materials present good photocatalytic performance and magnetic response. The best catalyst containing 15 wt% ZnO and 5 wt% Fe_3O_4 particle loading, displays a higher turnover number than unstructured ZnO nanoparticles and commercial ZnO nanopowder and can be easily separated from the reaction mixture by simply applying a magnetic field as weak as the one generated by a common magnetic stirring bar.

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1. Introduction

Over the past decades, water pollution caused by organic compounds has dramatically increased generating a growing interest in the scientific community toward highly efficient and environmentally sustainable waste water treatments. Photocatalytic degradation of organic pollutants provides a good alternative to reduce the amount of water contaminants in a sustainable way [1,2]. In order to achieve this objective, various semiconducting metal oxide nanoparticles have been used. Titanium dioxide and zinc oxide are two of the most studied and promising candidates for photocatalytic applications due to their ability to produce electron–hole pairs upon light irradiation thereby creating highly reactive radical species, such as hydroxyl radicals (HO^\bullet) and superoxy radical anions ($^{\bullet}\text{O}_2^-$), that can degrade organic molecules into mainly carbon dioxide and water [3–8]. An additional advantage of these semiconductors is represented by their high durability and resistance to corrosion.

It is known that the particle size distribution of the selected semiconducting metal oxide plays a crucial role as it strongly influences the photocatalytic performance [9,10]. Smaller particles display a high surface to volume ratio hence an increased amount

of accessible active species [11–13]. A drawback of the reduced particle size is represented by the tendency to sinter or aggregate during the reaction and the chemical or thermal treatment required for their reuse. A solution is given by the possibility to stabilize the nanoparticles by supporting them on suitable inorganic materials [14–16]. Among all the possible supports, mesoporous materials have been largely employed owing to their high specific surface area, reduced diffusion limitations of reactant and products compared to microporous solids as well as for their chemical and thermal stability [17–21]. Independent from the synthesis procedure selected for materials preparation, heterogeneous catalysts have the advantage of an easier separation from the reaction medium compared to homogeneous analogues making them more attractive from an industrial point of view [20,22–24]. A straightforward approach to further improve the separation procedure is represented by the introduction of a magnetic response in the heterogeneous solid [25–27]. Extensively used approaches adopted to reach this goal include the incorporation of iron oxide nanoparticles as well as the synthesis of core–shell structures [28–30]. Different synthesis approaches can be selected in order to achieve a successful incorporation of metal oxide nanoparticles within a mesoporous silica framework [31–33]. The “co-synthesis” procedure, in which preformed metal oxide nanoparticles are co-condensed with the inorganic silica precursor (usually tetraethyl orthosilicate), offers the advantage of a homogeneous distribution of catalysts particles whose dimensions are known in advance and are preserved during the reaction [18,34].

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Recently we proposed the synthesis of mesoporous materials embedding ZnO nanoparticles with increased photocatalytic performance with respect to the unstructured ZnO particles as well as to commercial ZnO nano-powder [35]. In this article, a new class of mesoporous silica composites, embedding both zinc oxide and magnetite (Fe₃O₄) nanoparticles is presented. Three catalysts have been prepared using a co-synthetic procedure, by varying the relative proportion of the two different oxides. The photocatalytic performances were studied for the degradation of Rhodamine B. The materials display good photocatalytic performances and clear magnetic response. To the best of our knowledge this is the first time that a ZnO containing photocatalyst displaying magnetic response is synthesized by using the “co-synthesis” approach.

2. Experimental

2.1. Materials

The reagents employed to prepare the ZnO nanoparticles and Fe₃O₄ nanoparticles were zinc acetate dihydrate (Zn(Ac)₂·2H₂O, purity ≥98%, Aldrich), iron(II) chloride tetrahydrate (FeCl₂·4H₂O, purity ≥99.0%, Aldrich), iron(III) chloride hexahydrate (FeCl₃·6H₂O, purity ≥99%, Aldrich), absolute ethanol (EtOH purity ≥99.5%, Aldrich), hexane (C₆H₁₄ purity ≥95%, Aldrich), ammonium hydroxide solution (NH₄OH 28.0%, Aldrich), lithium hydroxide monohydrate (LiOH·H₂O, purity 56% in LiOH, Acros) and Milli-Q water (18.2 MΩ cm⁻¹). For the preparation of mesoporous composite materials cetyltrimethylammonium bromide (CTAB purity ≥99%, Aldrich), ammonium hydroxide solution (NH₄OH 28.0%, Aldrich), tetraorthosilicate (TEOS 99.999%, Aldrich), absolute ethanol (EtOH purity ≥99.5%, Aldrich) and Milli-Q water (18.2 MΩ cm⁻¹) were used. All chemicals were employed as received without further purification.

2.2. Preparation of ZnO nanoparticles

The preparation of ZnO follows a procedure described in the literature [36,37]. 2.20 g Zn(Ac)₂·2H₂O were dissolved in 150 mL absolute ethanol (80 °C, inert atmosphere) and heated for 3 h under reflux. At the end of this procedure, part of the solvent (90 mL) was removed under reduced pressure and the remaining suspension was cooled at 0 °C. In parallel, a solution of LiOH·H₂O (0.58 g) dissolved in 90 mL of ethanol was prepared and vigorously stirred for 2 h. The basic solution was slowly added to the Zn(Ac)₂ solution and the mixture was stirred for 2 h. The ZnO nanoparticles were obtained by precipitation induced by the addition of 250 mL of hexane to the previous solution.

2.3. Preparation of Fe₃O₄ nanoparticles

The Fe₃O₄ nanoparticles were prepared based on a chemical co-precipitation method with slight modifications compared with literature [38–40]. 0.0125 mol of FeCl₂·4H₂O and 0.0250 mol of FeCl₃·6H₂O were dissolved in 200 mL of Milli-Q water under a nitrogen flow at room temperature. A solution of NH₄OH (6.0 mL) was added drop wise under vigorous stirring. The black precipitate of Fe₃O₄ nanoparticles immediately formed. The particles were collected by centrifugation, washed three times with Milli-Q water and ethanol and dried for 12 h at 40 °C.

2.4. General synthesis of mpZnO–Fe₃O₄ x/y

A homogeneous suspension of x mg of ZnO nanoparticles and y mg of Fe₃O₄ nanoparticles in absolute ethanol (16.0 mL) was prepared and sonicated for 30 min. In parallel, the cetyltrimethylammonium bromide (CTAB), was added to a basic solution

(NH₄OH) in a polyethylene bottle. The mixture was stirred at 500 rpm for 30 min at a temperature of 50 °C. TEOS and, the previously prepared, nanoparticle suspension were added drop wise and simultaneously to the solution. The weight ratio of the synthesis mixture was 1.00Z:0.12CTAB:32.4NH₄OH:77H₂O where Z corresponds to the sum of precursors of Zn, Fe and Si present. After stirring for 2 h at 50 °C, the polyethylene bottle was transferred to an oven and heated at 100 °C for 96 h. The resulting solid was filtered, washed three times with Milli-Q water and ethanol to remove the excess NH₄OH solution. Finally the powder was calcined at 550 °C under a nitrogen flow for 5 h with a heating rate of 2 °C min⁻¹ then under oxygen for 5 h to remove any organic template. The final samples were denoted as mpZnO–Fe₃O₄ x/y where x indicates the ZnO weight% (5, 10, 15, and 20%) and y corresponds to the Fe₃O₄ weight% (0, 5, 10 and 15%) (see Table 1).

2.5. Photocatalysis tests

The photocatalytic activity of the materials was investigated by following the photodegradation of an aqueous solution of Rhodamine B (RhB). The different catalysts (25 mg) were added to an aqueous solution of RhB (25 mL) with an initial concentration of 2×10^{-5} M (C₀) and sonicated for 30 min. The reaction mixture was stirred in the dark for 30 min in order to establish the adsorption–desorption equilibrium between the catalyst surface and the dye. The suspension was irradiated in a thermostated photoreactor equipped with 6 UV–vis lamps (Philips, TL-D 18 W, with emission wavelength between 330 and 400 nm and λ_{max,em} = 360 nm) positioned around the wall of the tubular reactor. The suspensions were irradiated for either 1 h, 2 h or 3 h. During the photocatalytic reaction, the catalysts were well dispersed by continuously stirring the suspension. The catalyst could easily be separated from the RhB solution via the use of an external magnetic field owing to the presence of magnetic Fe₃O₄. For the samples prepared without magnetite nanoparticles, the catalyst was separated by centrifugation at 8000 rpm for 15 min. The adsorption spectrum of the dye was recorded using a UV–vis spectrophotometer.

The amount of dye degradation was estimated by the following equation:

$$\% \text{ degradation} = \frac{(C_0 - C)}{C_0 \times 100} = \frac{(A_0 - A)}{A_0 \times 100}$$

where C₀ and C correspond to the initial and final concentration of RhB while A₀ and A represent the initial and the final concentration absorbance (after irradiation) of RhB. To ensure a good comparison of the catalysts, the amount of RhB pre-adsorbed onto each catalyst was deduced.

2.6. Characterization

The phase and the size of both nanoparticles were estimated by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). ZnO nanoparticles were also characterized by UV–visible (UV–vis) spectroscopy. All mpZnO–Fe₃O₄ x/y materials were characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), nitrogen adsorption/desorption, energy dispersive X-ray spectroscopy (EDX). Only the samples where y=0 were characterized by diffuse reflectance UV–vis spectroscopy and ²⁹Si magic angle spinning nuclear magnetic resonance (MAS-NMR). The photocatalytic efficiency was evaluated by the decrease of dye coloration by UV–visible spectroscopy. The absorption spectra were collected with a SPECORD PC 205 UV–vis spectrometer using quartz cells. X-ray diffraction (XRD) patterns were obtained with a PANalytical X'pert diffractometer with Cu Kα radiation (λ = 1.54178 Å). Phase identification of the nanoparticles were performed in the 2θ range 4–80° while mesoporosity was

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