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Bismuth–titanium oxide nanopowders prepared by sol–gel method for photocatalytic applications

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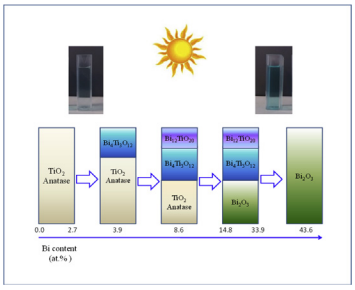
HIGHLIGHTS

- Bismuth–Titanium oxide nanopowders were synthesized by the sol–gel technique.
- The evolution of the different crystalline phases was determined.
- Materials with band gap as low as 1.4 eV were obtained.
- Good photocatalytic activity using visible light was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO_2 has been widely studied for photocatalytic applications; however, its band gap is so large (Eg = 3.2 eV for anatase) that it can only be excited by ultraviolet light which accounts for only 5% of the incoming solar energy. Thus, it is important to develop a visible light driven photocatalyst with a lower band gap value. For this purpose, different TiO_2–Bi_2O_3 binary compounds were prepared by the sol–gel technique. The obtained materials were characterized by Energy Dispersed Spectroscopy, X Ray Diffraction, Transmission Electron Microscopy, Raman Spectroscopy and Diffuse Reflectance Spectroscopy, in order to obtain information on their chemical composition, crystalline structure, vibrational features and optical properties. Compositional characterization reveal that the Bi content can be varied from 0.3 to 43.6 at.% in an easy way in the binary compounds. Structural characterization shows that the starting material corresponds to the crystalline anatase phase of TiO_2 and upon Bi addition a phase transition to bismuth titanates and finally to bismuth oxide occurs. Raman results suggest the formation of titanates for compounds with a low content of Bi whilst for higher metal contents a mixture of oxides is obtained. HRTEM results demonstrated that the prepared nanopowders are quite crystalline. Optical measurements reveal that the band gap narrows from 3.2 eV to values as low as 1.4 eV. The photocatalytic activity was tested in the degradation of Malachite Green dye under illumination using a solar simulator with good results.

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1. Introduction

In the last few years, the development of photocatalytic materials has been the focus of intense research owing to their potential

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applications to solve some environmental problems [1–3]. However, the rapid recombination of photogenerated charge carriers and the limited spectral response range restrict seriously their performance. Designing semiconductor photocatalysts, by combining or modifying semiconductors with other materials, can not only effectively expand the visible-light absorption, but also improve the photogenerated charge carriers' separation, which would effectively solve the above problems improving the photocatalytic activity.

Titanium dioxide (TiO_2) has been widely investigated as photocatalyst owing to its high photoactivity, low cost, low toxicity and good chemical and thermal stability in aqueous solution, being able to completely oxidize a variety of organic compounds, including persistent pollutants [4]. However, it must be pointed out that photocatalytic applications of TiO_2 have been limited by its low photoactivity when irradiated with visible light due to its relatively high band gap (3.2 eV for the anatase phase). In order to overcome these disadvantages, several strategies to extend the TiO_2 light absorption into the visible region have been investigated. The modification of the TiO_2 with metals as Fe, Ni, Co, Au, Ag, Cr, Sn, La, Ce, has been widely studied using a variety of methods, such as sol–gel [5], chemical vapor deposition [6], solvothermal process [7], reverse micelle method [8], liquid phase deposition [9], and hydrothermal treatment [10]. Among them, the sol–gel technique has been the most widely used method because it is an easier and inexpensive technique to prepare materials since it provides a good control on the chemical composition, crystalline structure and morphology. This method has been widely used to prepare metal oxides with different properties taking advantage of the easiness to vary precursors, solvents, as well as different additions sequences of compounds and thermal treatments. The photocatalyst based on $Bi_{12}TiO_{20}$ [11] and $Bi_4Ti_3O_{12}$ [12] crystals for photo-decolorization of methyl orange have been examined under UV irradiation with high photocatalystic activity, very similar in both cases. It was reported that $Bi_{12}TiO_{20}$ shows weak photo-absorption in the visible light region ($\lambda > 420$ nm), which means that the photocatalysts have the ability to respond to wavelengths in the visible light region. However, these photocatalysts show a very low photocatalytic activity under visible light irradiation. On the other hand Bi_2O_3 has been proven to be a valuable photocatalyst and it can efficiently oxidize various organic pollutants in water under UV light, and visible light [13]. In this work, we report on the synthesis of bismuth-titanium oxide nanopowders, that span from TiO_2 to Bi_2O_3 varying the Bi content, forming composites of TiO_2 + bismuth titanates + Bi_2O_3 at intermediate stages, through the sol gel method as well as their photocatalytic performances in the degradation of malachite green (MG) dye under visible light irradiation.

2. Experimental

2.1. Powder synthesis

Bismuth–Titanium Oxide nanopowders with different Bi content were synthesized by the sol–gel method. As first step solutions were prepared using 4 ml of titanium isopropoxide (i-PrO, 97% Aldrich) and 0.1183, 0.5628, 0.9634, 2.2480, 3.3649, 5.2432, 8.9879 and 4.164 g of bismuth nitrate ($Bi(NO_3)_3$ $5H_2O$, Aldrich) to obtain powders with 0.05, 0.2, 0.3, 0.5, 0.6, 0.7, 0.8, and 1.0, of Bi_2O_3 weight fraction respectively. This was done in order to have different contents of bismuth and, as consequence, diverse mixtures of compounded oxides. The starting materials were mixed in the indicated proportions and dissolved in 25 ml of 2-propanol (Fermont) under vigorous stirring for 4 h to obtain a sol; then, stirring was stopped in a closed system and the samples were aged for 12 h, afterward an excess of water was added to hydrolyze completely the system. The resulting gel was dried overnight followed by annealing at 400 °C for 4 h. The annealing temperature was chosen to dehydroxilate and to produce a crystalline material.

2.2. Powder characterization

Determination of the atomic bismuth content incorporated in the powders was done by Energy Dispersive X-ray Spectroscopy (EDS) using a microprobe attached to a JEOL JSM 6510LV electron microscope; additionally, surface morphology was observed from Scanning Electron Microscopy (SEM) micrographs using the same microscope. The crystalline structure of the deposited films was determined by X-ray Diffraction (XRD) using a Siemens D-5000 diffractometer with a Cu–Kα radiation source ($\lambda_k = 1.5406$ Å). The crystalline structure was analyzed with the Rietveld method, the refinement was performed using the FULLPROF98 code, peak profiles were modeled with pseudo-Voigt functions containing average crystallite size and microstrains as two of the characteristics parameters. The refinement was made according to the reported elsewhere [14]. Raman Spectroscopy (RS) was used to study the structural features of the powders; the Raman spectra were acquired using an HR LabRam 800 system equipped with an Olympus BX40 confocal microscope. A Nd:YAG laser beam (532 nm) was focused with a 50 × objective onto the sample surface. A cooled CCD camera was used to record the spectra, typically an average of 50 accumulations of 10 s was done in order to improve the signal to noise ratio. All spectra were calibrated using the 521 cm^{-1} line of monocrystalline silicon. Diffuse Reflectance Spectroscopy (DRS) measurements were carried out on a Perkin Elmer lambda 35 spectrophotometer; from the DRS spectra the band gap was determined using the Kubelka-Munk method. The structural analysis was performed in a Jeol JEM 2100F Transmission Electron Microscope, with a resolution of 1.9 Å. Samples were prepared by dispersing the powders in ethanol and depositing a drop on a carbon-coated Cu grid. The photocatalytic performance of the prepared nanopowders was evaluated studying the degradation of a malachite green (MG) dye solution with an initial concentration of 10 μmol/l. Each reaction solution was prepared by adding 50 mg of the prepared nanopowders into a 25 ml aqueous MG solution contained in a 100 ml glass vessel; afterwards, were subjected to ultrasound for 10 min under constant magnetic stirring in dark condition in order to establish adsorption/degradation equilibrium. The powders were activated by illuminating them with a solar simulator using an average intensity of about 60 mW/cm^2, keeping the distance between the liquid surface and the light source at 5 cm. The MG degradation was followed by the decrease of its characteristic absorption band peaking at 619 nm. This was done by taking an aliquot each 30 min of reaction time.

3. Results

3.1. Composition (EDS)

The chemical composition of the Bi:TiO_2 powders with different Bi content is summarized in Table 1. The deviations from stoichiometry of both oxides, TiO_2 and Bi_2O_3, observed in the data of Table 1, correspond to experimental measurements of elemental composition of the synthesized powders, therefore these values are affected by the uncertainties associated to the quantification technique as well as deviations attributed to the preparation method. It is worth noting that the observed deviations are in the range from 1% to 9%, this is within our experimental uncertainties.

Fig. 1 shows that upon increasing the Bi content from 0.3 to 43.6 at.%, the Ti content decreases almost linearly from 33.1 to 0.0 at.% whilst the O content remains around 60 at.%. These results indicate that synthesis procedure by sol–gel makes possible the

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