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Photocatalytic activity of enlarged microrods of α-Bi_2O_3 produced using ethylenediamine-solvent

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ABSTRACT

Microrods of α-Bi_2O_3 were prepared by a simple chemical precipitation method, replacing the hydroxyl (OH^-) ions by the ethylenediamine-solvent as both a precipitating and capping agent; it can also function as a morphological template. The influence of the ethylenediamine solvent concentration on the crystalline structure, optical properties, morphology, and photocatalytic activity was investigated. The prepared samples were characterized by X-ray diffraction, diffuse reflectance spectroscopy, scanning electron microscopy, Fourier transformed IR analysis, thermal analysis and photoluminescence spectroscopy. The adsorption capacity in dark conditions and the photocatalytic activity under UV-light were studied as a function of the photocatalyst load by using indigo carmine dye solution. The highest photoactivity was observed for the non-agglomerated Bi_2O_3 microrods obtained with ethylenediamine-solvent at 40 vol%. The photocatalytic mechanism was discussed as a function of surface oxygen vacancies generated along to the microrod surface caused by the ethylenediamine-solvent.

1. Introduction

Semiconductor materials have attracted increasing attention and interest in the past decades, mainly because they can directly convert photon energy into chemical energy upon excitation; they have wide range of applications for degradation of environmental pollutants and energy yield by photocatalytic processes [1,2]. Most of the semiconductor oxides have a narrow band gap capable to absorb visible light, so they are active to promote photocatalytic reactions, which increase their industrial applications [3]. Among various semiconductor oxides, Bi_2O_3 polymorphs are inert towards neutral water, environmental friendly and are considered as one of the most efficient materials for energy conversion due to their physicochemical properties, such as high refractive index, high oxygen-ion conductivity due to the high ratio of oxygen vacancies and a deep valence band [4,5]. Among all phases, α-Bi_2O_3 allows the light absorption in the visible range of the solar spectrum (2.8 eV). This property is useful to decompose organic pollutants by the photocatalytic process, where the separation of photogenerated charge carriers is the key factor for enhancing the photocatalytic activity [5]. Photocatalysis process takes place in the semiconductor surface when the photogenerated charge carriers migrate to the surface to initiate redox reactions; however, it is well known that in the micron-grain sized semiconductors, the surface area is very low and the photogenerated charge carriers cannot be efficiently transferred to the surface, resulting in fast charge-carrier recombination [6]. Therefore, preparing α-Bi_2O_3 semiconductor with reduced grain size would increase its photocatalytic activity making it a promising photocatalyst in future research. Different nanostructures (nanoparticles, nanorods or nanowires) of α-Bi_2O_3 have been prepared by different methods like: femtosecond pulsed laser ablation in liquids [7], simple one pot sol-gel method [4], free sonochemical process [8], via a catalysts-driven vapor transport method [9], by using g-C_3N_4 as a template [10] and so on. Specifically, α-Bi_2O_3 microrods, sometimes mistakenly called as nanorods, have been obtained by a microwave method [11,12] and by a simple chemical precipitation method using inorganic precipitating agents (NaOH, KOH, NH_4OH) [13–19], but in most of these cases, the microrods are thermally treated at temperatures about 450–550 °C. Using this chemical precipitation method, different molar ratios of HNO_3/precipitating-agent lead to variations in the pH solution influencing the crystalline structure, the phase composition, the crystal growth

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and the morphology; needle, plate-like or polyhedral shape of the final Bi_2O_3 can be obtained [12–14]. Pure nanocrystalline α-Bi_2O_3 phase is favorably obtained at pH solutions between 8 and 13 [13]. High concentrations of nitrate (NO_3^-) ions promote the one-dimensional crystal growth of Bi_2O_3 in the [001] direction, resulting in an elongation of the particles; while high concentrations of hydroxyl (OH^-) ions change the preferential crystal growth because the OH^- ions are more favorably linked on the polar faces acting as capping agents [14]. In some cases, the synthesis method is additionally accompanied with the use of a surfactant (PEG-400, PVP, PVA) [20–23] or organic solvent as morphological templates (oleic acid, rambutan extract, glycerin, HMA) [24–27] to obtain different phases and morphologies. Alternatively, ethylenediamine solvent (*EN-solvent*) has also been extensively used as morphological template in the preparation of bismuth-based semiconductor materials (Bi_xMO_y, where M=V, Mo, W, Zn, Nb) by hydrothermal treatment method [28–33]. It has been even used in the preparation of bismuth (III) complexes [34–36], BiOCl [37] and Bi_2S_3 [38,39]. All these bismuth-based materials exhibit nanostructures in flower, rod, wire or fibers morphology, because the *EN-solvent* induces the preferential growth in one-direction. *EN-solvent* can coordinate with Bi^{3+} ions to form complexes [34], decreasing the Bi^{3+} concentration in the aqueous solution [29] and stabilizing the particles due to its low dielectric constant [40]; moreover it facilitates the nucleation and accelerates the reaction [41,42]. In addition, the *EN-solvent* can also act as a strong base in aqueous solution due to the *pKa* value of 9.9 of the ENH_2^{2+} and ENH^+ species in equilibrium, acting as a precipitating agent [40]. In another aspect, the *EN-solvent* can take the role of electron-transfer, acting as moderate reducing agent. So, nanowires of Bi^0 were obtained as a result of the reduction of Bi^{3+} to Bi^0 in a mixture of *EN*-acetone solvent [43]. As a consequence of the properties of *EN-solvent* to act as both precipitating and reducing agents, undesirable products of Bi_2O_3 were formed during the preparation of bismuth-based materials (Bi_xMO_y, Bi_2S_3) using hard synthesis conditions (> 160 °C for 2–6 h) or by microwave (> 140 °C for 10 min) [28,31].

In this work, we propose a simple chemical precipitation method to produce Bi_2O_3 nanostructures without any further thermal treatment using the *EN-solvent* as both precipitating and capping agent, but also taking advantage of its reducing property and using it as a morphological template. The influence of the ethylenediamine aqueous solution on the preparation of Bi_2O_3 oxide was investigated varying the *EN-solvent* concentration in the range of 20–50 vol% and using moderate synthesis conditions (90 °C, 2 h). The adsorption capacity and the photocatalytic activity properties of individual microrods-Bi_2O_3 were also explored for the photodegradation of indigo carmine (*IC*) dye.

2. Materials and methods

2.1. Synthesis of the Bi_2O_3

The bismuth oxide materials were synthesized by a simple chemical precipitation method under mild refluxing conditions (low temperature and short aging time), using ethylenediamine (*EN-solvent*), instead of NaOH, as precipitating agent and as morphological template. In a fixed total volume of EN-H_2O, the Bi^{3+} concentration in water was increased from 25 mM to 49 mM at the same time that the *EN-solvent* content was increased from 20 to 50 vol% (see Table 1). 10 and 60 vol% were also used. Through a typical procedure, appropriate fixed amounts of $Bi(NO_3)_3 \cdot 5H_2O$ (Aldrich) were dissolved in aqueous solution with concentrated HNO_3 (Baker Analyzed), maintaining the $[HNO_3]/[Bi^{3+}]$ molar ratio fixed close to 10, under constant stirring at 40 °C for 15 min and then it was left to cool at room temperature to get a stable transparent solution. Afterwards, the appropriate volume of *EN-solvent* (Aldrich) was added drop wise and the suspension was heated up to the boiling point (90 °C) under vigorous magnetic stirring (800 RPM) for 2 h and subsequently cooled at room temperature at constant stirring. Finally, the resulting precipitated was collected by filtration, washed using an ethanol-water solution and left to dry at room temperature. The products were labeled as BEX, where the X represent the *EN-solvent* vol% (10, 20, 40, 50 and 60). For comparison purposes, bismuth oxide material prepared without ethylenediamine was precipitated with NaOH 10 M and was labeled as BOH^-.

Table 1
Data of the Bi^{3+} and *EN-solvent* concentration, crystal size, bandgap and specific surface area of the prepared Bi_2O_3.

Sample	$[Bi^{3+}]$ mM	*EN-solvent* (vol%)	Crystal size (nm) Halder-Wagner	E_g (eV)	S_g (m^2/g)
*BOH^-	25	00	38	2.82	< 1
BE20	31	20	35	2.84	10
BE40	41	40	33	2.85	< 1
BE50	49	50	29	2.84	< 1

* Bi_2O_3 precipitated with 10 mL of NaOH [10 M], E_g=bandgap energy, S_g=surface area.

2.2. Characterization of the Bi_2O_3

The obtained Bi_2O_3 materials were characterized by powder X-ray diffraction using a SIEMENS D500 diffractometer with Cu Kα radiation of 0.15406 nm (34 kV, 25 mA). The scanning range was between 15 and 60° (2 theta) with a step size of 0.013°/s. For the lattice parameter determination, the Bragg law was used considering a monoclinic structure and for the average crystal size determination, the known Debye-Scherrer equation ($\tau = K\lambda/\beta\cos\theta$) was used. The diffraction patterns were also analyzed using the PDXL2 software to determine the crystallite size (by the Halder-Wagner method). The FTIR absorption spectra of all the samples were recorded on a Thermoscientific Nicolet 6700 spectrometer using an attenuated total reflection (ATR) accessory provided of a diamond crystal. For each measurement, the powder was loaded and the pressure used was of 815 Psi. Typically, 68 scans at a resolution of 4 cm^{-1} in the range between 600 and 4000 cm^{-1} in the transmittance mode were used for the measurements at room temperature. Thermal analysis (DSC/TGA) of the samples were performed up to 600 °C at a heating rate of 10 °C/min in static air atmosphere using a TA Instruments SDT Q600 V8.3 Build 101. The morphology of the Bi_2O_3 was revealed by scanning electron microscopy (SEM) using a JEOL 7600 F operated at 10 kV. The specific surface area of the semiconductors was determined by the BET method from the nitrogen adsorption-desorption isotherms at −196 °C using a Quantachrome Autosorb-1 automatic instrument. Prior to the adsorption procedure, the samples were out-gassed under high vacuum at 150 °C for 6 h. The Brunauer-Emmett-Teller method (BET method) was applied to calculate the specific surface area. The UV–Vis diffuse reflectance spectra (DRS) were recorded on a UV–vis spectrophotometer (Shimadzu 2600) equipped with an integration sphere (ISR 2600) in the range of 190–800 nm and using $BaSO_4$ as a reference blank. The spectra were converted from reflectance to absorbance by the Kubelka–Munk method. The band-gap energy (E_g) was calculated considering an allowed direct transition for α-Bi_2O_3 phase [22], by extrapolating the linear portion of the $(F(R) \times h\nu)^2$ versus $h\nu$ curves to $F(R)=0$ [27]. The photoluminescence was recorded using a He-Cd laser of 325 nm excitation wavelength with a maximum input power of 20 mW and a spectrometer Princeton-Acton SP2500i instrument. The point of