Alternative Bi precursor effects on the structural, optical, morphological and photocatalytic properties of BiOI nanostructures

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Abstract

BiOI nanostructures were synthetized through a hydrothermal process using either bismuth acetate or subsalicylate as Bi precursor. Regardless of the used Bi source, the same crystalline structure of BiOI was obtained; nevertheless, the nature of the Bi precursor had an evident impact in the color appearance of the obtained sample. Another notable difference was observed in the resulting morphology, where ∼1.6 μm flower- and dandelion-like shapes were obtained for acetate and subsalicylate, respectively; both structures assembled by around 30 nm thick nanoflakes with rounded and straight edge, respectively. UV–vis diffuse reflectance shows an energy gap around 1.8 eV. Raman spectroscopy confirms also the tetragonal phase of BiOI. The photocatalytic activity was evaluated through degradation of methyl orange dye using visible and UV light sources, comparing results with P25 TiO2. Both BiOI nanostructures presented an improvement of photocatalytic activity when irradiated with visible light, having the best photoactivity the sample synthetized with bismuth acetate.

Introduction

The study of photocatalytic processes in semiconductors is of great interest due to their potential applications in water cleaning [1], water splitting [2], air cleaning [3] and antibacterial applications [4]. In particular, they could help to decompose certain contaminants, such as dyes and medicines, into simpler and harmless compounds from an environmental point of view [5, 6]. A family of them is the bismuth oxyhalides, that is, compounds with the form BiOX, where X corresponds to a halogen element, usually Cl, Br or I. These compounds have been reported to have a band gap energy around 3.2, 2.6 and 1.8 eV at room temperature, respectively [7–9]. Their crystal lattice is tetragonal, where the atoms are arranged such that they form (X–Bi–O–Bi–X) layers. One of the main goals in the photocatalysis field is to obtain efficient photocatalysts with band gap energy as small as possible, since less than 10% of the solar radiation is in the ultraviolet range, with photons having energies larger than 3.1 eV; with a lower band gap energy, more sunlight can be used to activate the photocatalytic process [10].

In this regard, bismuth oxyiodide (BiOI) is a potential candidate as a visible light photocatalyst, in addition to its others features such as physical and chemical stability and non-toxicity [9, 11, 12]. Its synthesis has been reported using different techniques, such as hydrothermal [5, 13–17], hydrolysis [18], annealing [19], chemical vapor transport [20], among others. In almost all reports, independent of the synthesis method, BiOI compound is obtained using bismuth nitrate, Bi(NO3)3, as bismuth precursor, with quite few exceptions [20, 21]. On the other hand, from a chemical point of view, using a different Bi precursor could lead to dissimilar reactions, since they might have distinct melting points, solubilities and / stabilities. Others aspects to consider should be not only the costs, but the use of environmental friendly methods for the production of the starting material; even more, the residuals emitted during the synthesis of the final compound. Nevertheless, one of the most important
goals of using another chemical precursor is the possibility of changing the size, shape and stoichiometry of the obtained material [22, 23]; in this direction, as known in material science, the properties shall be modified or even new ones could appear [9]. Therefore, it would be valuable to explore possible advantages of using alternative Bi precursors and their effect on growth mechanism and photocatalytic activity. In this work, we present a study of the effects of the Bi precursor (bismuth acetate and subsalicylate) on the structural, optical, morphological and photocatalytic properties of BiOI nanostructures synthesized through a hydrothermal chemical route.

Materials and methods

Sample preparations

Bismuth acetate (BiAc; Bi(CH₃COO)₃ > 99.99% purity), bismuth subsalicylate (BiSs; C₂H₃O₄Bi 99.9% purity) and sodium iodide (NaI > 99.5% purity) were purchased from Sigma Aldrich and used without further purification. In a typical procedure, a 0.1 M bismuth solution was prepared by dissolving an appropriate amount of Bi precursor in glacial acetic acid under vigorous stirring. Separately, an equimolar NaI solution was prepared. After, the bismuth solution was added dropwise to the transparent NaI solution under continuous stirring. Then, the resulting opaque red suspension was transferred to a Teflon-lined stainless-steel autoclave for a treatment at 160 °C during 12 h with a heating up rate of 1 °C min⁻¹ (Temperature controller; Parr, 4848 Reactor controller), after that, the reactor was let cooling freely. The obtained reddish precipitate was washed three times with bi-distilled water and finally with ethanol and let drying at room temperature. Thus synthesized samples, using bismuth acetate and subsalicylate are labeled hereafter as BiOI(Ac) and BiOI(Ss), respectively.

Characterization techniques

The synthesized powders were studied by powder x-ray diffraction (XRD; Pananalytical, Empyrean diffractometer); with the CuKₐ (λ = 1.5406 Å). Morphology and microstructure of the samples were studied by field emission scanning electron microscopy (FE-SEM; TESCAN MIRA 3 LMU); samples were dispersed on a conductive carbon tape, no surface metallization was applied. Morphology was also characterized by transmission electron microscopy (TEM; JEOL JEM-1010, with tungsten filament running at 80 keV); for sample preparation, the powders were suspended on water, sonicated during 5 min, and dropped on a 300-mesh Cu grid with formvar film.

Optical properties were studied by UV–vis diffuse reflectance spectroscopy (DRS; Agilent Cary 5000 UV–vis-NIR spectrophotometer equipped with a DRA-CA-301 accessory). Raman spectra were excited using a 473 nm DPSS laser, and then analyzed with an Acton SpectraPro 2755i coupled with a Hamamatsu photomultiplier tube R925; for these measurements, the powder was gently compacted to make a pellet without applying temperature.

Photocatalytic activity test

The decoloration of an azo-dye was measured under UV (black light, Lights of America F17T8/BLB, 17 W, 30000 K temperature color) and visible light (white LED, Phillips 3PM5, 14 W, 5000 K temperature color); methyl orange (MO) was used as model molecule, in order to evaluate the photocatalytic activity of the samples. For this purpose, 0.5 mg of catalyst samples were dispersed into 5 ml aliquots of a 10 mg l⁻¹ MO dye solution. Prior to irradiation, the suspension was left in dark for 24 h to ensure adsorption-desorption equilibrium [13, 24]. After, the light source was turned on, the actual concentration of the MO was determined at regular time intervals by spectrophotometry (λ = 465 nm). Before every aliquot measurement, the solid phase was separated by centrifugation at 5000 rpm during 5 min. The photocatalytic performance of the synthesized BiOI samples was compared against P25 TiO₂ standard photocatalyst.

Results and discussion

XRD patterns of the studied samples are shown in figure 1; the red pattern (upper) and the blue one (lower) correspond to samples BiOI(Ss) and BiOI(Ac), respectively. The XRD patterns confirm the achievement of the desired BiOI stoichiometry, with tetragonal phase (PDF# 10-0445). This phase has been already reported by several groups but using mainly Bi(NO₃)₃ as bismuth source [5, 14–17], [25–32], most of them by hydrothermal methods. Therefore, the same crystalline phase can be obtained regardless of the used precursor; in our case, bismuth acetate (BiAc) and subsalicylate (BiSs) by a simpler hydrothermal route. Pictures of dried samples at petri dishes are shown as insets in figure 1, having a variation in tonality; similar photographic records have been reported by other authors [24, 31]. Nevertheless, after grinding for storage, powders from both samples got similar color. In this case, the color of BiOI does not depend on the crystalline phase.
The average crystallite sizes were calculated through Scherrer equation [33]:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where $\tau$ is the crystallite size in nm, $K = 0.9$ is a dimensionless shape factor, $\beta$ is the full width at half maximum (FWHM) of the diffraction peak and $\theta$ is the Bragg angle. We found an average crystallite size of 25 nm for the BiOI(Ac) and 20 nm for the BiOI(Ss) sample.

FE-SEM images of the studied samples are shown on figure 2; on the left side, two magnifications of sample BiOI(Ac), and on the right side, sample BiOI(Ss) with the same magnifications. At figures 2(a) and (b), both samples appear with similar quasi-spherical morphology of few microns, being the particles of BiOI(Ss) sample slightly bigger and rounder. Nevertheless, at a higher magnification, figures 2(c) and (d), we can observe the BiOI (Ac) sample has a flower-like appearance; meanwhile, the BiOI(Ss) sample has more of a dandelion-like shape. Both, assembled by nanoflakes with thicknesses around 35 nm and 25 nm, respectively. In spite of both structures already reported, for BiOI grown by hydrothermal processes, with the same crystalline phase, the flower shape has been rarely obtained [17, 28]; it is worth mentioning that most reports used Bi(NO$_3$)$_3$ as precursor. Therefore, we show that the use of bismuth acetate as precursor also might lead to nanostructured flower-like particles. Considering the whole structure as spheres, the size distribution can be observed at the bottom of the figure 2. Dandelion-like structure presented more symmetric size distribution around 1.67 microns, perhaps it is a result of the quasi-spherical shape; on the other hand, flower-like structure presented a mean size of 1.50 microns; however, this size would be affect depending of the projection of the flower.

TEM images can be observed in the figure 3, for the BiOI(Ac) (left-hand column) and BiOI(Ss) (right-hand column) samples. The projection of (a) the flower- and (b) dandelion-like shapes are quasi-spherical as expected, with diameters of few microns. As observed in SEM images, both structures are assembled with nanoflakes; however, TEM images show that the flakes for BiOI(Ac) have rounded edges, while for BiOI(Ss) they have straight edges. Since both samples were synthesized at the same hydrothermal route conditions, it suggests that the nanoflake geometry is induced by the Bi precursor. In addition, TEM images reveal that the flakes in the dandelion-like have a larger area than in the flower-like structures. Finally, a larger amount of standing alone flakes were observed during the analysis for the sample BiOI(Ss), suggesting that dandelion-like structures were disassembled more easily with the 5 min of sonification for sample preparation.

The above results, SEM and TEM, suggest a possible mechanism for the formation of the microstructure. To have more information on the growth mechanism for each Bi precursor, 3 additional samples were grown with the same heating up rate under the following conditions: (0 h, 100 °C), (0 h, 160 °C) and (4 h, 160 °C). Where 0 h means that reactor heating is shut down right after reaching the set temperature. Figure 4 shows representative SEM images of these samples (micrographs are 2 microns by side), along with a schematic description of the growth mechanisms.

A common factor for both precursors is the initial formation of small laminar particles (schematically shown on the center-left side of figure 4). For Bi acetate precursor, upper side of figure 4, the formation of these particles is followed by their agglomeration (piling up); later, at 160 °C (0 h), although the agglomerates show no significant increase, the border particles seem to start spreading out; continuing with the inner particles, at 160 °C (4 h), leading to a blossoming effect at 160 °C (12 h), into a flower-like microsphere formed with rounded-edge flakes. Meanwhile, for Bi subsalicylate precursor, lower side of figure 4, at 100 °C (0 h) the laminar particles seem to embed into each other chaotically; at 160 °C (0 h), an increasing number of flakes is observed,
which could be due to lateral growth of the smaller particles; then, at 160 °C (4 h), the density of flakes is enough to obtain quasi-spherical shapes; finally, at 160 °C (12 h), the embedded nanoflakes continue to extend and multiply, with straight-edges, into a dandelion-like microsphere. Therefore, under this synthesis conditions, the formation of flower- and dandelion-like structures using bismuth acetate and subsalicylate, is differentiated within the first stages in the growth process.

An important parameter in a semiconductor is the energy band gap, it can strongly affect the photocatalytic activity, determined by the energy range for excitation photons. The left-hand side of figure 5 shows the absorbance spectra of the BiOI(Ac) (blue line) and BiOI(Ss) (red line) samples, as calculated from UV-vis diffuse reflectance measurements. It can be seen an absorption edge starting around 650 nm. In the righthand side of the figure 5, Tauc plots with the linear fit for energy band gap estimation, giving 1.81 eV for BiOI(Ac) and 1.80 eV for BiOI(Ss) as indirect band gap [17]. As both gaps are so close to each other, the tone of as-dried samples cannot be solely associated with it; nor the band gap is clearly affected by the morphology or the crystallite size of the samples. Experimental BiOI energy gap has been reported in a wide range of values for the same crystalline phase, as low as 1.71 eV [25] and as high as 2.17 eV [14], depending strongly on several synthesis parameters; nevertheless, the estimated energy gap in our samples agrees with the most reported value. This value of the energy gap makes it possible for visible light stimulate the BiOI for photocatalytic processes.

Figure 6 shows the Raman spectra of both BiOI samples over the range 100–500 cm⁻¹, BiOI(Ss) and BiOI (Ac) corresponding to read and blue lines, respectively. The vibrational modes of this material are: $\Gamma = 2A_{1g}$ (Raman) + $2A_{2u}$ (IR) + $B_{1g}$ (Raman) + $3E_{g}$ (Raman) + $2E_{u}$ (IR), having only three Raman active modes, that
Figure 3. TEM images for BiOI nanostructures. Images (a) and (c) correspond to the BiOI(Ac); images (b) and (d) correspond to the BiOI(Ss). Both structures are assembled with nanoflakes, but the edges are rounded for BiOI(Ac) and straight for BiOI(Ss).

Figure 4. Schematic representation of the formation of BiOI(Ac) and BiOI(Ss) microspheres.
have been reported at 85, 151 and 340 cm$^{-1}$ for $A_{1g}$, $E_g$ and $B_{1g}$, respectively [34]. Although, in general, only the mode $E_g$, corresponding to an internal Bi–I stretching mode, is observed and it is used to confirm the presence of BiOI [35]. This mode has been reported from 148 [36] up to 159 cm$^{-1}$ [32]; in our spectra, it is associated with a peak observed around 155 cm$^{-1}$. Regarding the peaks obtained around 130 and 310 cm$^{-1}$, they could be related with peaks reported around 118 and 310 cm$^{-1}$ for samples of BiOI [27, 37]. However, a more likely explanation for these peaks is that they appear due to the energy supplied locally by the laser irradiation during the Raman measurement, providing enough energy to induce changes in the crystalline phase [38]. There is a report showing that BiOI is sensible to thermal processes, losing I-atoms while gaining O-atoms simultaneously, as temperature increases until it is transformed to $\beta$-Bi$_2$O$_3$ [30]; even at lower temperatures [39]. This increase of temperature could be explained by a poor thermal conductivity of the BiOI powders.

One of the most important applications of BiOI is its photocatalytic activity, especially because its band gap energy lies at the visible spectrum. Figure 7 shows the decoloration curves of MO solutions under UV (upper-side) and visible light irradiation (lower-side), of both BiOI samples, as well as the reference measurements with TiO$_2$. The irradiation profiles of both sources are shown as insets in each case. As mentioned above, the measurements were carried out after 24 h in darkness, in order to get an absorption-desorption equilibrium; furthermore, the decrease of decoloration percent from 24 to 48 h in dark conditions was 0.0, 0.2 and 0.1% for P25, BiOI(Ss) and BiOI(Ac), respectively. Therefore, the decoloration results shown in figure 7, can be attributed to the photocatalytic process, activated by light irradiation. Under UV irradiation, a strong degradation of the dye is observed when using P25 TiO$_2$, with decoloration completed after only 2 h. Conversely, the obtained BiOI powders degraded only about 5% in the same period. This can be explained by the emission range of the
excitation source (330–380 nm), closer to the energy gap of TiO₂ (∼3.2 eV) and far enough for BiOI (1.8 eV). However, changing the irradiation source (430–660 nm) in the visible region, the degradation by P25 TiO₂ reduces to less than 2% in 12 h, whereas the photoactivity of BiOI powders improves significantly. This can be explained also by the energy gap, since now the energy of the photons is closer to the BiOI gap, and is not enough for TiO₂. If we analyze only the BiOI samples, we found that the BiOI\(^{\text{Ac}}\) presents higher degradation power than BiOI\(^{\text{Ss}}\) under both irradiation sources. It could be due to the structure of the microspheres, where the flower-like form of the BiOI\(^{\text{Ac}}\) sample allows the dye molecules to have more contact with the nanoflakes surface, increasing the photoactivity.

**Conclusions**

BiOI powders were successfully synthetized through a hydrothermal route using alternatively bismuth acetate and subsalicylate as bismuth precursors. This change had an effect on the microstructure of the final product; using Bi acetate and Bi subsalicylate precursors induced flower-like and dandelion-like microspheres, respectively. The proposed growth mechanism indicates that the route into the formation of each structure diverge within the first stages. In both cases, microstructures were assembled with nanoflakes a few tens of nanometers thick and energy band gap around 1.8 eV. BiOI samples presented high sensitivity to the thermal effect by the laser irradiation. BiOI had a much better photocatalytic activity under visible light than UV light. In any case, flower-like BiOI has better photocatalytic activity than dandelion-like BiOI; therefore, related to the morphology of the microsphere.
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