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Photocatalytic discoloration of methyl orange dye by δ-Bi_2O_3 thin films

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ABSTRACT

Cubic delta bismuth oxide (δ-Bi_2O_3) thin films were deposited on glass substrates using magnetron sputtering onto Corning glass slides with different roughness. The efficiency of the Bi_2O_3 films as a photocatalytic semiconductor for the discoloration of dyes was tested by using methyl orange (MO) solutions as the probe under UV, sunlight and white light. Moreover, the effect of the substrate roughness, as a parameter to enhance the active surface area, was also evaluated. The results indicated that similar discoloration percentages (98% in 180 min) were obtained for the three illumination ranges for surfaces with average roughness below 1.5 μm. The discoloration reaction rate was significantly higher when the UV light was used in comparison to visible and sunlight. In order to appreciate the significance of these results, the photodiscoloration efficiency of the optimized δ-Bi_2O_3 films was compared to TiO_2 films deposited by magnetron sputtering and TiO_2-P25 Degussa particles. The outcomes showed better color removal of the dye when using the rough Bi_2O_3 thin films in comparison to both TiO_2 materials, suggesting that δ-Bi_2O_3 films are a rather promising photocatalytic material. Moreover, the photoinduced wettability change of the films was measured showing that δ-Bi_2O_3 films present a photoinduced hydrophilicity, similarly to TiO_2.

1. Introduction

Synthetic dyes are extensively used in the textile industry and their disposal into effluents is a serious environmental problem. Due to the nature of the synthetic dyes, conventional biological treatments are ineffective for achieving both discoloration and degradation of the wastewater. During the last decades, there has been a lot of interest on the use of advanced oxidation processes as a more effective method for the elimination of aqueous and gaseous pollutants. Such works reported about the photocatalytic activity of oxide semiconductors for either the oxidation of organic compounds in residual water [1–3], or reduction of pollutants or toxic gases (air purification) [4–6] as well as oxidation–reduction of heavy metals in soils or water effluents [7–10].

In the case of water purification, the semiconductor photocatalytic materials are usually used as slurry mixing the nano/micropowders with the contaminated water. Thus, a secondary process of filtration or separation has to be implemented, making the process costly and slow. An alternative approach is to deposit the semiconductor photocatalytic material as a coating on a substrate or directly in the water container [11,12] with the disadvantage that flat surfaces have lower active areas compared to the powders and therefore the photocatalytic efficiency is reduced. Therefore, for such alternative procedure the use of more efficient photocatalytic materials is a critical issue.

Among the photocatalytic semiconductor materials, the titanium dioxide (TiO_2) has been the most studied due to its large efficiency, chemical stability and low cost. However, TiO_2 only works using ultraviolet (UV) light, unless it is doped or modified by other elements to increase the light absorption in the visible range [12–16]. In parallel, there is also a constant activity focused on the development of other photocatalytic materials that present larger absorption in the visible range, as well as appropriate chemical stability, efficiency and cost. In the review of 2012 published by Di Paola et al. a long list of alternative materials are presented including binary oxides (ZnO, Cu_2O, V_2O_5, ZrO_2, Bi_2O_3, …) and sulfides (CdS, ZnS, Bi_2S_3), as well as ternary and quaternary oxides or oxyhalides [17]. Among the different materials studied, bismuth (Bi) appears as a common element in the various lists of binary, ternary and quaternary oxides or oxyhalides. On the other hand, other groups have reported doping of TiO_2 or ZnO using bismuth [18,19] or the use of ternary bismuth oxides [20,21] for photocatalytic applications.

Table 1 shows a review of different works where the photocatalytic activity and/or photodiscoloration efficiency of Bi_2O_3 compounds has been evaluated. In those papers, the efficiency is associated to the larger optical absorption of Bi_2O_3 in the visible range compared to TiO_2;

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Table 1
Review of recent works concerning the photocatalytic activity of Bi_2O_3.

Ref.	Phase and structure	Gap (eV)	Organic molecule	Light	Degradation
[60]	Alpha nanoneedles	Direct: 2.57	Toluene gas	Vis	80% (230 min)
[61]	Alpha and beta mixed nanowires	Direct: 2.6	Rhodamine 6G	UV	90% (4 h)
[62]	Alpha nanorods	Direct: 3.8	Rhodamine B	UV	86% (75 min)
[63]	Alpha powders	Direct 2.7	Methyl orange	Vis	86% (100 min)
[64]	Alpha nanoneedles	Direct 2.7–2.8	Methylene blue	UV	38% (3 h)
[30]	Alpha–beta thin films	–	Rhodamine B	UV	92%(2 h)
[65]	Alpha beta delta powders	Direct α: 2.8 β: 2.48 δ: 3.01	Methyl orange 4-Chlorophenol	Vis	β > α > δ MO: b 87% (90 min) 4-Ph: b 80% (90 min)
[22]	Alpha and beta nanosperes	Direct α: 2.82 β: 2.36	Rhodamine B	Vis	b: 83.3%(4 h)
[66]	bi_2o_3		Methylene blue	Vis	76%(240 min)
[24]	Beta nanoparticles	Direct 2.13	Rhodamine B Other organic pollutants	Vis	100% (150 min)
[64]	Beta nanostructures	Direct 2.69–2.82	Methylene blue	UV	Morphology dependent
[67]	Beta powders	Indirect 2.8	Malachite green	VIS	24% (180 min) improves with Ni doping 88% (180 min)
[68]	Beta nanospheres	Direct 2.78	Acetaminophen	Vis	93.6% (180 min)

however, as each of these works used different conditions to test the photocatalytic activity, a direct comparison is not possible and the information provided must be handled with care. Summarizing the information in Table 1, we can see that the most reported crystalline phases are the monoclinic-α phase and the tetragonal-β. However, Bi_2O_3 is a polymorphic oxide presenting 6 different crystalline phases, each one with different optical band gap (values between 2.2 and 3.9 have been reported [22–26]). The alpha (α) is the stable phase at atmospheric conditions, while the delta (δ) phase is only stable in the range of 725–825 °C. During cooling from the high temperature phase, other metastable phases have been found: beta (β), gamma (γ), omega (ω) [27,28] and the recently synthesized epsilon (ε) [28]. Since α is the stable phase in atmospheric conditions, most of the reported papers refer and compare to commercially α-Bi_2O_3 micro-sized particles, showing that the photocatalytic activity is substantially enhanced at the nanoscale [29]. Similarly, as can be observed in Table 1, different methods to synthesize nanoparticles (NPs) end up with the production of the metastable β-Bi_2O_3 phase, hence it was possible to investigate its photocatalytic activity. However, concerning the photocatalytic activity of bismuth oxide thin films, not many reports can be found [30–33]. Moreover, as mentioned above, modern environmental laws consider the use of sludge as hazardous wastes that require further treatment, so the use of thin films or supported photocatalytic materials is desirable. Therefore in this paper, we propose the evaluation of the photodiscoloration efficiency of methyl orange solutions (a common probe molecule for the discoloration of azo dyes) by bismuth oxide films deposited by magnetron sputtering.

It has been shown that different Bi_2O_3 phases can be obtained in thin film form, including the cubic δ-Bi_2O_3 phase [34–36]. In previous works, we tested 12 different deposition conditions leading to films with δ, β + α and probably a least known Bi_4O_7 phase [37]. The results indicated that optical absorption in the low energy range was larger for the films with the δ-cubic phase, which also enhanced its photocatalytic activity [38]. Hence in the light of a better use of the non-UV part of the solar spectrum we have selected δ-Bi_2O_3 thin films. Discoloration of methyl orange solutions was used as a screening test to evaluate their photocatalytic activity. The effect of the pH, dye concentration, surface roughness and the wavelength-range of the illumination on the photocatalytic discoloration of MO was also investigated. Finally, the δ-Bi_2O_3 performances in terms of the photodiscoloration activity and the photoinduced changes in the wettability were compared to those of TiO_2 powders and films deposited by magnetron sputtering.

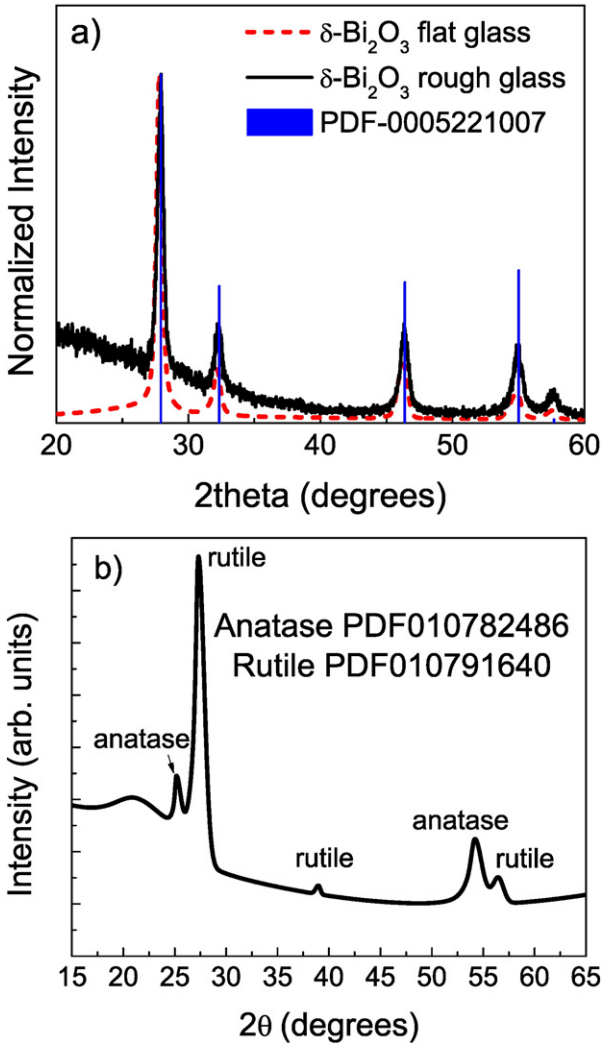

Fig. 1. (a) XRD patterns of the δ-Bi_2O_3 films. (b) XRD pattern of the TiO_2 film, the presence of both anatase (7%) and rutile (93%) can be observed.