

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5255410>

# Surface phases and photocatalytic activity correlation of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$ nanocomposite

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · AUGUST 2008

Impact Factor: 12.11 · DOI: 10.1021/ja803603y · Source: PubMed

CITATIONS

157

READS

188

## 4 AUTHORS:



**Abdul Hameed**

King Abdulaziz University

53 PUBLICATIONS 988 CITATIONS

SEE PROFILE



**Tiziano Montini**

Università degli Studi di Trieste

105 PUBLICATIONS 3,131 CITATIONS

SEE PROFILE



**Valentina Gombac**

Università degli Studi di Trieste

48 PUBLICATIONS 1,602 CITATIONS

SEE PROFILE



**Paolo Fornasiero**

Università degli Studi di Trieste

238 PUBLICATIONS 8,909 CITATIONS

SEE PROFILE

Surface Phases and Photocatalytic Activity Correlation of  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$  NanocompositeAbdul Hameed,<sup>†,‡</sup> Tiziano Montini,<sup>†</sup> Valentina Gombac,<sup>†</sup> and Paolo Fornasiero<sup>\*,†</sup>

Chemistry Department, ICCOM-CNR Trieste Research Unit, INSTM Trieste Research Unit, Center of Excellence for Nanostructured Materials, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy, and Fuel Cell Division, PINSTECH, 44000, Islamabad, Pakistan

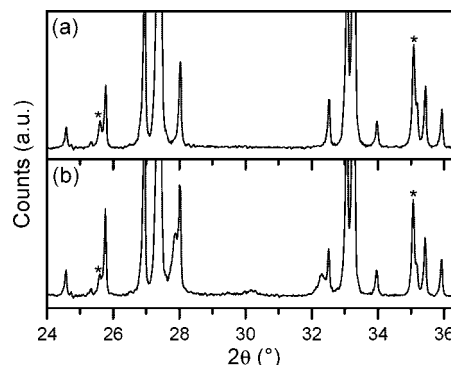
Received May 14, 2008; E-mail: pfornasiero@units.it

The study of water decontamination is a major area of scientific activity. As a result, numerous methods have been developed to facilitate degradation of xenobiotic compounds in water body. Photocatalysis, which uses sunlight, particularly UV light, is one of them, and it has recently grown as a “technology provider”.  $\text{TiO}_2$ -based systems have found useful applications despite their large band gap (3.0–3.2 eV). In fact,  $\text{TiO}_2$  doped with C, N, or B<sup>1</sup> has opened new perspectives because it could be used under visible light irradiation. Rarer are the investigations on alternative materials. In this respect, bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) is an attractive material because of its good electrical conductivity and thermal properties. It is widely used in various applications such as microelectronics, sensor technology, and optical coatings.<sup>2,3</sup> As a photocatalyst,<sup>4</sup>  $\text{Bi}_2\text{O}_3$  is a p-type semiconductor with conduction and valence band edges +0.33 and +3.13 V relative to NHE, respectively. These values account for its ability to oxidize water and possibly generate highly reactive species, such as  $\text{O}_2^{\cdot-}$  and  $\text{OH}^{\cdot}$  radicals, which may act as initiators of oxidation reactions.

The aim of this study is that it is possible to introduce active species on the surface of a photocatalyst by using a nonconventional approach. To this purpose, we employed UV–visible radiations to induce surface modifications in  $\text{Bi}_2\text{O}_3$  leading to the formation of  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$  nanocomposite. The novel features of the process are the mild operating conditions and the possibility to control the amount of surface active species by an appropriate selection of the exposure time. This simple and low cost approach is a step forward toward tailoring photocatalysts for various purposes, and it can valuably contribute to photocatalyst design. After characterization, the photocatalytic performance of  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$  nanocomposite was evaluated in comparison with that of  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_{4-x}$  in the degradation of methylene blue (MB), methyl orange (MO) and phenol. The first two compounds are representative of dyes, while phenol is a highly persistent pollutant. We studied their photocatalytic degradation processes on exposure to simulated sunlight using pyrex glass as a cutoff filter for wavelengths below 320 nm; the radiation intensity within the 300–380 nm range was approximately 10% of the total spectrum of a mercury lamp as measured by radiometer.

$\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$  nanocomposite was synthesized by irradiating a water dispersion of  $\text{Bi}_2\text{O}_3$  (yellow) with a 450 W medium pressure mercury lamp for 3 hours. After irradiation the color of the powder changed from yellow to brown. Pure  $\text{Bi}_2\text{O}_3$  was prepared from  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  by hydrolysis under basic conditions (Supporting Information) while the pure  $\text{Bi}_2\text{O}_{4-x}$  (brown) was synthesized accordingly to Prakash et al.<sup>5</sup>

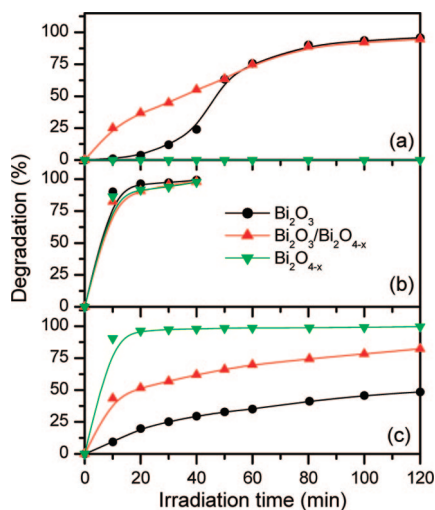
The X-ray diffraction (XRD) profile of the pure  $\text{Bi}_2\text{O}_3$  (Figure 1a) is clearly attributable to monoclinic  $\text{Bi}_2\text{O}_3$  ( $\alpha\text{-Bi}_2\text{O}_3$ ). No other



**Figure 1.** XRD of (a) pure  $\text{Bi}_2\text{O}_3$  and (b) after UV irradiation  $\text{Bi}_2\text{O}_3$ . (\* indicates  $\alpha\text{-Al}_2\text{O}_3$  added as internal reference material).

phases are present as is to be expected on the basis of the calcination temperature adopted in the synthesis.<sup>5</sup> The XRD profile of the irradiated  $\text{Bi}_2\text{O}_3$  shows the presence of a main phase,  $\alpha\text{-Bi}_2\text{O}_3$ , with a minor phase exhibiting two characteristic reflections at  $2\theta = 27.9^\circ$  and  $32.3^\circ$  (Figure 1b). Despite the high number of polymorphs of  $\text{Bi}_2\text{O}_3$ , these reflections can clearly be indexed with the presence of the oxidized  $\text{Bi}_2\text{O}_{4-x}$  species.<sup>5</sup> A reasonable fit of the XRD profile, using a mixture of  $\alpha\text{-Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_{4-x}$ , reveals that the sample contains about 8% of  $\text{Bi}_2\text{O}_{4-x}$ . The XRD results demonstrated that after irradiation the crystallite size of bulk  $\alpha\text{-Bi}_2\text{O}_3$ , as estimated by the Scherrer's equation, remains almost unchanged ( $\sim 300$  nm) whereas the new phase,  $\text{Bi}_2\text{O}_{4-x}$  appears with a lower crystallite size (40 nm). As a result of their large crystallite size, these samples have very low surface area. A significant increase in the surface area (0.49 versus  $0.62 \text{ m}^2/\text{g}$ ), using Kr as a probe molecule, was observed after irradiation. This increase can be associated with the formation of smaller crystallites of  $\text{Bi}_2\text{O}_{4-x}$  and the opening of pores on the surface of the large particles of  $\alpha\text{-Bi}_2\text{O}_3$ . Notably, in line with the metastable nature of the  $\text{Bi}_2\text{O}_{4-x}$  phase,<sup>5</sup> after degassing under vacuum (a necessary pretreatment for the Brunner–Emmet–Teller (BET) measurements) the powder turned to its original yellow color while it showed good and prolonged thermal stability in air in the range 20–120 °C. From thermogravimetric analysis (TGA) it is possible to estimate a value of 0.44 for  $x$  in  $\text{Bi}_2\text{O}_{4-x}$ . Furthermore, TGA indicates that the amount of  $\text{Bi}_2\text{O}_{3.56}$  formed upon irradiation for 3 h is 14 wt% (Supporting Information). The band gap value of 2.2 eV found for the  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$  nanocomposite by UV–visible spectroscopy (Supporting Information) is much higher than the reported value of 1.4 eV for pure  $\text{Bi}_2\text{O}_{4-x}$ ,<sup>5</sup> while the value of 2.8 eV for pure  $\alpha\text{-Bi}_2\text{O}_3$  is in accordance with the literature.<sup>4</sup> The high band gap value of the mixed material can be explained as originating from bulk  $\text{O}(2p)\text{--Bi}^{3+}(6p)$  excitations and surface  $\text{O}(2p)\text{--Bi}^{5+}(6s)$  transitions made available by irradiation treatment.

<sup>†</sup> University of Trieste.<sup>‡</sup> PINSTECH.



**Figure 2.** Comparison of photocatalytic degradation of (a) MB, (b) MO, and (c) phenol over Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>4-x</sub>, and Bi<sub>2</sub>O<sub>4-x</sub>.

In the aqueous semiconductor suspension under band gap illumination, a cascade of highly oxidizing species can be generated as a result of the capture of conduction band electrons by oxygen either adsorbed or present in solution. Among all the oxidizing species, superoxide radical has the highest oxidation power and the sufficiently long lifetime.<sup>6</sup> These photogenerated superoxide radicals, instead of causing the oxidation of the contaminants present in solution, can oxidize Bi<sup>3+</sup> to Bi<sup>5+</sup> with formation of additional Bi<sup>5+</sup>–O bonds at the surface, thus leading to Bi<sub>2</sub>O<sub>4-x</sub>. The calculated band gap, XRD and BET measurements, are consistent with the presence of Bi<sub>2</sub>O<sub>4-x</sub> mainly at the surface of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> particles. In fact, only in this scenario, the modest amount of Bi<sub>2</sub>O<sub>4-x</sub> would be able to affect the global band gap by partial surface coverage.

Figure 2a shows the photocatalytic degradation of MB on Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>4-x</sub> and Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>4-x</sub>. Within the first 40 min of irradiation of MB on Bi<sub>2</sub>O<sub>3</sub>, most of oxidizing species produced are consumed in the formation of Bi<sub>2</sub>O<sub>4-x</sub> at the surface, thus preventing the dye molecules from being degraded. After that, an increase in the rate of degradation is observed. This can be interpreted by assuming that, with the formation of a significant number of surface states, the oxygen and electrons consumed in the formation of Bi<sub>2</sub>O<sub>4-x</sub> become available for the production of hydroxyl radicals, which cause a significant increase of the degradation rate. Notably, for pure Bi<sub>2</sub>O<sub>4-x</sub>, no degradation of MB was observed, but rather its adsorption and desorption under irradiation. The comparable activity of both catalysts observed after 50 min suggests that Bi<sub>2</sub>O<sub>4-x</sub> surface states (2–3 wt% from XRD), although unable to degrade MB, can enhance the activity of the bulk Bi<sub>2</sub>O<sub>3</sub>, through alternative mechanisms such as charge transfer (as the surface Bi<sub>2</sub>O<sub>4-x</sub> has the band gap of ~1.4 eV).

Figure 2b shows the photocatalytic degradation of MO over the same systems as a function of irradiation time. In all cases, within the first 10 min of irradiation, a very high rate of dye removal was observed, namely, ~90% for Bi<sub>2</sub>O<sub>3</sub>, ~86% for Bi<sub>2</sub>O<sub>4-x</sub>, and ~82% for Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>4-x</sub>. These degradation values are similar (~90%) to that of one of the best commercially available TiO<sub>2</sub>-based catalysts (Degussa P-25). However, an enormous difference in surface area between our systems and Degussa P-25 must be emphasized: 55 m<sup>2</sup>/g for TiO<sub>2</sub> versus <1 m<sup>2</sup>/g for the Bi-based materials. The high rates of MO degradation observed can be associated with a charge transfer process through dye sensitization. In fact, MO absorbs in

the 380–530 nm range with  $\lambda_{\text{max}} = 446$  nm. Consistently, in the presence of the dye a large amount of light becomes inaccessible to catalyst particles thus preventing significant *in situ* formation of Bi<sub>2</sub>O<sub>4-x</sub> until MO is present in solution. After 90% conversion, the decrease in the dye removal rate is largely due to a low dye concentration.

The degradation of phenol on the three catalysts is compared in Figure 2c. A significantly higher degradation rate can be observed for Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>4-x</sub> nanocomposite and pure Bi<sub>2</sub>O<sub>4-x</sub> with respect to Bi<sub>2</sub>O<sub>3</sub>. This can be attributed to the presence of surface active species on the former catalysts, owing to their nonstoichiometric nature. Notably, a very remarkable increase of activity is observed in the presence of small amounts of Bi<sub>2</sub>O<sub>4-x</sub>. Furthermore, it must be emphasized that after 6 h of irradiation (70% phenol degrade) no traces of Bi<sub>2</sub>O<sub>4-x</sub> were revealed by XRD in the Bi<sub>2</sub>O<sub>3</sub> sample. On the contrary, after the degradation of phenol was complete, traces of Bi<sub>2</sub>O<sub>4-x</sub> appeared at XRD. Phenol degradation increases with the increase in response of the catalyst in the visible region as inferred from the band gaps of the three catalysts Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>4-x</sub>, and Bi<sub>2</sub>O<sub>4-x</sub> (2.8, 2.2, and 1.4 eV, respectively) again emphasizing that phenol is mainly degraded by visible light. An overall phenol degradation of ~48, ~80, and ~100% was observed for Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>4-x</sub>, and Bi<sub>2</sub>O<sub>4-x</sub>, respectively, in 2 hours. Notably, due to resonance stability, phenol is very hard to mineralize, although some reports indicate that TiO<sub>2</sub>-based photocatalysts can do it efficiently.<sup>7</sup> Under our experimental conditions (Supporting Information), Degussa P25 was not able to degrade phenol.

In conclusion, despite the complexity of the degradation mechanisms, which depend on the nature of the pollutants, our results indicate that Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>4-x</sub>-based materials are very promising as photocatalysts. In the case of MB, surface modification of the material induced by irradiation can lead to a significant increase in the photocatalytic activity of the bulk material. The higher band gap with respect to Bi<sub>2</sub>O<sub>3</sub> together with energetic considerations suggests that similar photoinduced structural modifications, albeit present, should be of minor importance for TiO<sub>2</sub>-based materials. So far, only careful designed thermal treatments were able to produce interesting anatase/rutile nanocomposites with superior photocatalytic activity.

**Acknowledgment.** The authors thank Prof. M. Graziani and G. Pitacco (University of Trieste) for helpful discussions and the University of Trieste, ICTP TRIL Program, CNR (ICCOM), INSTM and FISIR2002 for financial support. A.H. thanks Higher Education Commission (Pakistan) for support.

**Supporting Information Available:** Catalysts preparation, characterization methods, photocatalytic activity, degradation profiles (absorption spectra) of MB, MO, and phenol. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- In, S.; Orlov, A.; Berg, R.; García, F.; Pedrosa-Jimenez, S.; Tikhov, M. S.; Wright, D. S.; Lambert, R. M. *J. Am. Chem. Soc.* **2007**, *129*, 13790–13791.
- Hyodo, T.; Kanazawa, E.; Takao, Y.; Shimizu, Y.; Egashira, M. *Electrochemistry* **2000**, *68*, 24–31.
- Bandoli, G.; Barreca, D.; Bresciani, E.; Rizzi, G. A.; Tondello, E. *Chem. Vap. Deposition* **1996**, *2*, 238–242.
- Xu, Y.; Schoonen, M. A. A. *Am. Mineral.* **2000**, *85*, 543–556.
- Prakash, A. S.; Shivakumara, C.; Hegde, M. S.; Dupont, L.; Tarascon, J.-M. *Mater. Res. Bull.* **2007**, *42*, 707–712.
- Hirakawa, T.; Yawata, K.; Nosaka, Y. *App. Catal., A* **2007**, *325*, 105–111.
- MacHado, N. R. C. F.; Santana, V. S. *Catal. Today* **2005**, *107–108*, 595–601.

JA803603Y