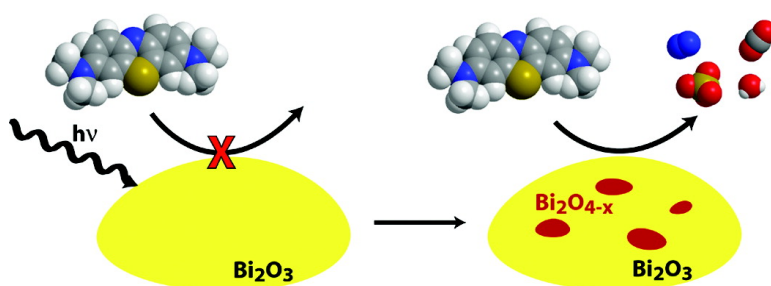


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Surface Phases and Photocatalytic Activity Correlation of Bi₂O₃/Bi₂O_{4-x} Nanocomposite

Abdul Hameed,^{†,‡} Tiziano Montini,[†] Valentina Gombac,[†] and Paolo Fornasiero^{*†}

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: pforasiero@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”. TiO₂-based systems have found useful applications despite their large band gap (3.0–3.2 eV). In fact, TiO₂ doped with C, N, or B¹ 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 (Bi₂O₃) 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.^{2,3} As a photocatalyst,⁴ Bi₂O₃ 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 O₂^{•-} and OH[•] 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 Bi₂O₃ leading to the formation of Bi₂O₃/Bi₂O_{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 Bi₂O₃/Bi₂O_{4-x} nanocomposite was evaluated in comparison with that of Bi₂O₃ and Bi₂O_{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.

Bi₂O₃/Bi₂O_{4-x} nanocomposite was synthesized by irradiating a water dispersion of Bi₂O₃ (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 Bi₂O₃ was prepared from Bi(NO₃)₃·5H₂O by hydrolysis under basic conditions (Supporting Information) while the pure Bi₂O_{4-x} (brown) was synthesized accordingly to Prakash et al.⁵

The X-ray diffraction (XRD) profile of the pure Bi₂O₃ (Figure 1a) is clearly attributable to monoclinic Bi₂O₃ (α-Bi₂O₃). No other

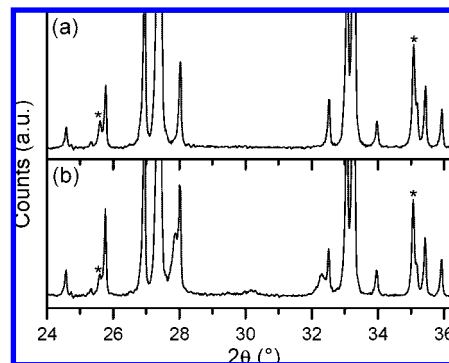


Figure 1. XRD of (a) pure Bi₂O₃ and (b) after UV irradiation Bi₂O₃. (* indicates α-Al₂O₃ added as internal reference material).

phases are present as is to be expected on the basis of the calcination temperature adopted in the synthesis.⁵ The XRD profile of the irradiated Bi₂O₃ shows the presence of a main phase, α-Bi₂O₃, with a minor phase exhibiting two characteristic reflections at $2\theta = 27.9^\circ$ and 32.3° (Figure 1b). Despite the high number of polymorphs of Bi₂O₃, these reflections can clearly be indexed with the presence of the oxidized Bi₂O_{4-x} species.⁵ A reasonable fit of the XRD profile, using a mixture of α-Bi₂O₃ and Bi₂O_{4-x}, reveals that the sample contains about 8% of Bi₂O_{4-x}. The XRD results demonstrated that after irradiation the crystallite size of bulk α-Bi₂O₃, as estimated by the Scherrer’s equation, remains almost unchanged (~300 nm) whereas the new phase, Bi₂O_{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 m²/g), using Kr as a probe molecule, was observed after irradiation. This increase can be associated with the formation of smaller crystallites of Bi₂O_{4-x} and the opening of pores on the surface of the large particles of α-Bi₂O₃. Notably, in line with the metastable nature of the Bi₂O_{4-x} phase,⁵ 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 Bi₂O_{4-x}. Furthermore, TGA indicates that the amount of Bi₂O_{3.56} formed upon irradiation for 3 h is 14 wt% (Supporting Information). The band gap value of 2.2 eV found for the Bi₂O₃/Bi₂O_{4-x} nanocomposite by UV–visible spectroscopy (Supporting Information) is much higher than the reported value of 1.4 eV for pure Bi₂O_{4-x},⁵ while the value of 2.8 eV for pure α-Bi₂O₃ is in accordance with the literature.⁴ The high band gap value of the mixed material can be explained as originating from bulk O(2p)–Bi³⁺(6p^o) excitations and surface O(2p)–Bi⁵⁺(6s^o) transitions made available by irradiation treatment.

[†] University of Trieste.

[‡] PINSTECH.

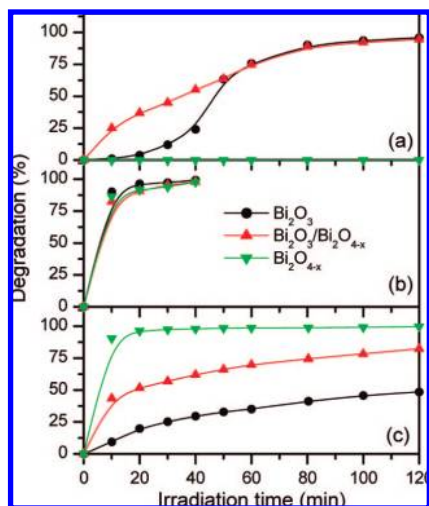


Figure 2. Comparison of photocatalytic degradation of (a) MB, (b) MO, and (c) phenol over Bi_2O_3 , $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$, and $\text{Bi}_2\text{O}_{4-x}$.

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.⁶ These photogenerated superoxide radicals, instead of causing the oxidation of the contaminants present in solution, can oxidize Bi^{3+} to Bi^{5+} with formation of additional $\text{Bi}^{5+}-\text{O}$ bonds at the surface, thus leading to $\text{Bi}_2\text{O}_{4-x}$. The calculated band gap, XRD and BET measurements, are consistent with the presence of $\text{Bi}_2\text{O}_{4-x}$ mainly at the surface of $\alpha\text{-Bi}_2\text{O}_3$ particles. In fact, only in this scenario, the modest amount of $\text{Bi}_2\text{O}_{4-x}$ would be able to affect the global band gap by partial surface coverage.

Figure 2a shows the photocatalytic degradation of MB on Bi_2O_3 , $\text{Bi}_2\text{O}_{4-x}$ and $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$. Within the first 40 min of irradiation of MB on Bi_2O_3 , most of oxidizing species produced are consumed in the formation of $\text{Bi}_2\text{O}_{4-x}$ 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 $\text{Bi}_2\text{O}_{4-x}$ become available for the production of hydroxyl radicals, which cause a significant increase of the degradation rate. Notably, for pure $\text{Bi}_2\text{O}_{4-x}$, 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 $\text{Bi}_2\text{O}_{4-x}$ surface states (2–3 wt% from XRD), although unable to degrade MB, can enhance the activity of the bulk Bi_2O_3 , through alternative mechanisms such as charge transfer (as the surface $\text{Bi}_2\text{O}_{4-x}$ 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, $\sim 90\%$ for Bi_2O_3 , $\sim 86\%$ for $\text{Bi}_2\text{O}_{4-x}$, and $\sim 82\%$ for $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$. These degradation values are similar ($\sim 90\%$) to that of one of the best commercially available TiO_2 -based catalysts (Degussa P-25). However, an enormous difference in surface area between our systems and Degussa P-25 must be emphasized: $55 \text{ m}^2/\text{g}$ for TiO_2 versus $< 1 \text{ m}^2/\text{g}$ 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 $\text{Bi}_2\text{O}_{4-x}$ 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 $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$ nanocomposite and pure $\text{Bi}_2\text{O}_{4-x}$ with respect to Bi_2O_3 . 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 $\text{Bi}_2\text{O}_{4-x}$. Furthermore, it must be emphasized that after 6 h of irradiation (70% phenol degrade) no traces of $\text{Bi}_2\text{O}_{4-x}$ were revealed by XRD in the Bi_2O_3 sample. On the contrary, after the degradation of phenol was complete, traces of $\text{Bi}_2\text{O}_{4-x}$ 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_2O_3 , $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$, and $\text{Bi}_2\text{O}_{4-x}$ (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 $\sim 100\%$ was observed for Bi_2O_3 , $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$, and $\text{Bi}_2\text{O}_{4-x}$, respectively, in 2 hours. Notably, due to resonance stability, phenol is very hard to mineralize, although some reports indicate that TiO_2 -based photocatalysts can do it efficiently.⁷ 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 $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$ -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_2O_3 together with energetic considerations suggests that similar photoinduced structural modifications, albeit present, should be of minor importance for TiO_2 -based materials. So far, only careful designed thermal treatments were able to produce interesting anatase/rutile nanocomposites with superior photocatalytic activity.

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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>.

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