# Good practices for reporting photocatalytic evaluation of visible-light active semiconductors

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**Abstract**

Photocatalysis is an important research subject these days due to its strong impact towards sustainable development, however, we consider that relevant data and discussion about processes that occur during photocatalysis are usually disregarded in many of the published papers. Identification of processes such as (i) photodiscoloration due to adsorption or photolysis, (ii) dye self-sensitization, (iii) actual photodegradation with the unavoidable formation of intermediate products and (iv) mineralization of the intermediates products, is significant for the correct interpretation of the photocatalytic activity of a semiconductor. In this paper, we remark the importance of distinguishing the contribution of each of these processes on the reported data in order to accomplish an adequate interpretation of the photocatalytic activity, proposing a follow-up work plan to obtain the information and achieve a proper interpretation. To do so, we compared theoretical and experimental absorbance spectra of the dyes during the photodegradation process, since theoretically it is possible to determine the changes in the spectrum and predict degradation pathways. As examples, three different dyes were used: Rhodamine-B (RhB), Acid Blue 113 (AB) and Indigo Carmine (IC). Theoretically, the absorbance spectra of the dye molecules and their intermediates were calculated considering the structure of the molecule at the experimental

pH conditions. Photocatalytic degradation of the dyes using the same semiconductor material ($Bi_2O_3$) was done using standard spectrocolorimetric method but taking care to appropriately consider the processes mentioned above. Furthermore, to evaluate the mineralization of these dyes as the product of the photocatalytic degradation, total organic carbon (TOC) analysis was performed. The commonly used evaluation of the results suggests that certain degree of photodegradation and mineralization was achieved. However, a careful analysis indicates that it was mainly due to a decrease in the relative concentration of the dye molecules because of their adsorption on the semiconductor's surface, and not due to a complete degradation. Moreover, for the AB dye, the photodegradation kinetics could not be estimated due to a clear indication of dye sensitization. Conversely, for the other dyes no sensitization was observed, but for RhB the photodegradation was dubious. These conclusions could not have been reached without following the steps proposed in our methodology.

## Supporting Information

1. *Synthesis of α/β-$Bi_2O_3$ composite photocatalyst*

Synthesis of α/β-$Bi_2O_3$ composite was reported previously [1]. Briefly, powder form α/β-$Bi_2O_3$ material was synthesized through solid state reaction by direct heating of $Bi(NO_3)_3 \cdot 5H_2O$ salt (Sigma-Aldrich) at 150 °C for 30 min in order to evaporate the water content. The temperature was then raised to 250 °C and kept constant for 2 hours. The obtained powder was then annealed at 550°C for 2 hours and allowed for slow furnace cooling.

2. *Characterization of α/β-$Bi_2O_3$*

The phase composition of the calcined sample was characterized by X-ray diffraction (XRD) using a SIEMENS D500 X-ray diffractometer (Cu-Kα X-ray source). The diffraction patterns were analyzed using the PDXL2 software to identify each phase,

determining the grain size (Halder-Wagner method) and the relative amount of each phase in the phase-mixtures (Relative Intensity Ratio, RIR method) [2], as shown in Fig. S1.

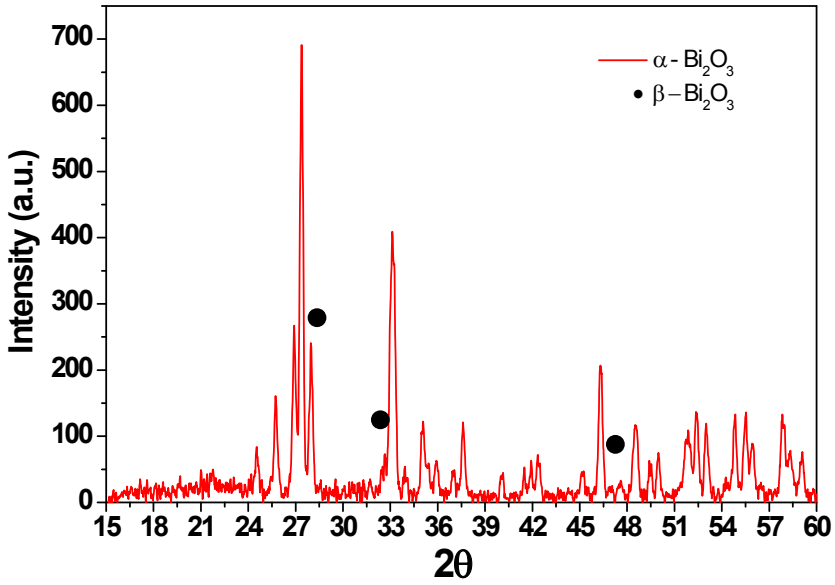


Figure S1. XRD of α/β-$Bi_2O_3$ material.

The UV–vis diffuse reflectance spectra (DRS) were recorded on a UV-vis spectrophotometer equipped with an integration sphere (Shimadzu 2600) and using $BaSO_4$ as a reference. The spectra were converted from reflectance to absorbance by the Kubelka–Munk method. The band-gap energy (Eg) was calculated considering an allowed direct transition for α-$Bi_2O_3$ phase, by extrapolating the linear portion of the $(FR \times hv)^2$ *vs* hv plot to FR=0 [3]. The observed energy band gap was 2.79 eV, a value in between those of the separated α and β phases, as shown in the inset of Fig. S2. As reported previously [1], the sample is formed by an α/β-$Bi_2O_3$ mixture with a low proportion of β-phase (20%).

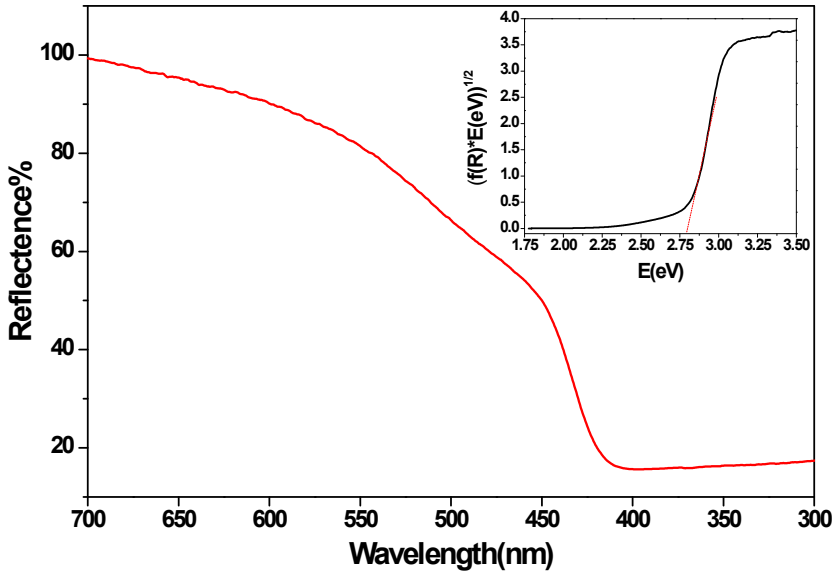


Figure S2. Reflectance spectrum of α/β-$Bi_2O_3$ sample. The inset shows the K-M analysis indicating the band gap.

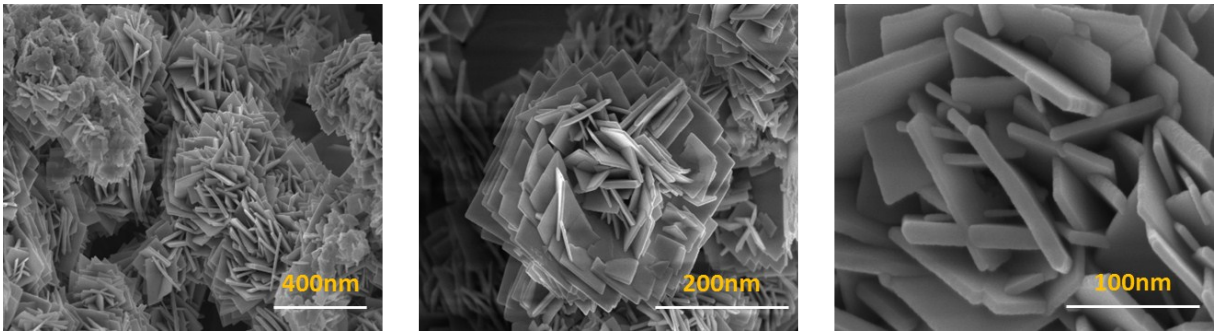


Figure S3. FESEM images α/β- $Bi_2O_3$ at different magnification scales.

FESEM images were acquired with a Zeiz Merlin 4248 field emission scanning electron microscope. Morphology of the α/β-$Bi_2O_3$ powder is shown in Fig. S3. The sample shows a porous bouquet-like nano-layered structure where the thickness of the layers is in the range 40 to 120 nm.

**Additional references**

[1] T.A. Gadhi, A. Hernández-Gordillo, M. Bizarro, P. Jagdale, A. Tagliaferro, S.E. Rodil, Efficient α/β-Bi2O3 composite for the sequential photodegradation of two-dyes mixture, Ceramics International, 42 (2016) 13065-13073.
[2] J. Medina, M. Bizarro, C. Gomez, O. Depablos-Rivera, R. Mirabal-Rojas, B. Monroy, A. Fonseca-Garcia, J. Perez-Alvarez, S. Rodil, Sputtered bismuth oxide thin films as a potential photocatalytic material, Catalysis Today, 266 (2016) 144-152.
[3] L. Shan, G. Wang, D. Li, X. San, L. Liu, L. Dong, Z. Wu, Band alignment and enhanced photocatalytic activation of α/β-Bi 2 O 3 heterojunctions via in situ phase transformation, Dalton Transactions, 44 (2015) 7835-7843.