

# Formation of a junction between TiO<sub>2</sub> and β-Bi<sub>2</sub>O<sub>3</sub> to enable efficient visible-light harvesting in advanced oxidation processes for waste water treatment

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Heterogeneous photocatalysis is a type of advanced oxidation processes (AOPs) where external radiation (either UV or visible light) is used to trigger the catalytic activity of a catalyst, which produces reactive oxygen species (ROS). ROS are able to destroy a wide range of organic compounds dissolved in water. Although TiO<sub>2</sub> [1] is one of the most promising photocatalytic materials for waste water treatment, it has two major drawbacks: (i) the band gap of TiO<sub>2</sub> is 3-3.2 eV, and (ii) a fast electron (e<sup>-</sup>) - hole (h<sup>+</sup>) recombination. The drawbacks could be, for instance, overcome by combining TiO<sub>2</sub> with another low band gap semiconductor [2].

In our work a combustion synthesis procedure was used to form a junction between TiO<sub>2</sub> and a narrow band gap semiconductor β-Bi<sub>2</sub>O<sub>3</sub> (2.4 eV). The role of β-Bi<sub>2</sub>O<sub>3</sub> in the composite is to act as a visible light photosensitizer for TiO<sub>2</sub>. The junction between TiO<sub>2</sub> and β-Bi<sub>2</sub>O<sub>3</sub> enables the transfer of photo-generated charge carriers. Structural, surface and electronic properties of the obtained catalysts were analyzed and correlated to their performance in the photocatalytic oxidation of aqueous bisphenol A (BPA) solution conducted in a batch reactor under visible light illumination. Bisphenol A (BPA) is an endocrine disrupting compound, which is in widespread use in the production of most packaging materials used every day [3]. Results of XRD, TEM and XPS measurements performed on composites reveal that TiO<sub>2</sub> is present as anatase and Bi<sub>2</sub>O<sub>3</sub> as β-Bi<sub>2</sub>O<sub>3</sub>. UV-Vis DR spectra of the composites show that the light adsorption of the composites was shifted into the visible range. This indicates that Bi<sub>2</sub>O<sub>3</sub> acts as a visible light photosensitizer for TiO<sub>2</sub>. Based on the XPS spectra we conclude that if the Ti:Bi ratio is over 1:0.4 a separate Bi phase is formed, which results in a decreasing association of Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Results of EIS and EPR measurements illustrate that there is a junction between TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> resulting in efficient charge carrier separation, which decreases when the Ti:Bi ratio is higher than 1:0.4. The results of BPA degradation runs are in good agreement with these findings: the catalytic activity of the composite drops if the Ti:Bi ratio exceeds the value of 1:0.4. A heterojunction between TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> in the composites supports the transfer of visible-light generated h<sup>+</sup> from the valence band (VB) of Bi<sub>2</sub>O<sub>3</sub> to the upper lying VB of TiO<sub>2</sub>. In addition, a p-n junction between TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> can be formed, which enables the transfer of visible light photo-generated e<sup>-</sup> in the conduction band (CB) of Bi<sub>2</sub>O<sub>3</sub> to the CB of TiO<sub>2</sub>. Under visible light illumination the role of TiO<sub>2</sub> is to act as a sink for visible-light photo-generated charge carriers in Bi<sub>2</sub>O<sub>3</sub> and doing so, prolonging the lifetime of visible-light generated e<sup>-</sup> and h<sup>+</sup> [4].

## References

- [1] M. Ge, C. Cao, J. Huang, S. Li, Z. Chen, K.-Q. Zhang, S.S. Al-Deyab, Y. Lai, J. Mater. Chem. A 4 (2016) 6772-6801.
- [2] S. Malato, P. Fernandez-Ibanez, M.I. Maldonado, M. Blanco, W. Gernjak, Catal. Today 147 (2009) 1-59.
- [3] P. Chen, K.G. Linden, D.E. Hinton, S. Kashiwada, E.J. Rosenfeld, S.W. Kullman, Chemosphere 65 (2006) 1094-1102.
- [4] G. Žerjav, P. Djinović, A. Pintar, Catal. Today 315 (2018) 237-246.