

Optimisation of narrow band gap semiconductors for photocatalytic applications

*Anna P. Finlayson¹, Vassilka N. Tsaneva¹, Bartek A. Glowacki¹
Leslie Lyons², Mike Clark²*

¹ Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK.

² Bentham Instruments Ltd, 2 Boulton Road, Reading, RG2 0NH, UK.

Email: apf23@cam.ac.uk, Tel.: + 44 (0)1223 334375, Fax: + 44 (0)1223 334373

High efficiency photocatalytic water splitting offers a route to carbon-free, high quality hydrogen to power fuel cells. However, achieving high efficiency solar energy conversion has proved extremely challenging. The low absorbance of visible light exhibited by those photocatalysts stable under typical operating conditions hinders attempts to design a highly efficient system.

Decreasing the semiconductor band gap of a metal oxide photocatalyst is one strategy towards increasing the adsorbed fraction of solar radiation. The effect of composition on the semiconductor band gaps of compounds from the Bi- W- oxide system has been investigated to evaluate their potential as water-splitting photocatalysts.

Following from previously presented results [1], samples were prepared by a solid state diffusion route from mixed viscous pastes of Bi_2O_3 and WO_3 with glycerol, suitable for use in a custom-built micro-coextrusion system illustrated in figure 1 and described more fully elsewhere [2]. The system is intended to allow the preparation of samples of systematically varying composition allowing mapping of physical and chemical characteristics.

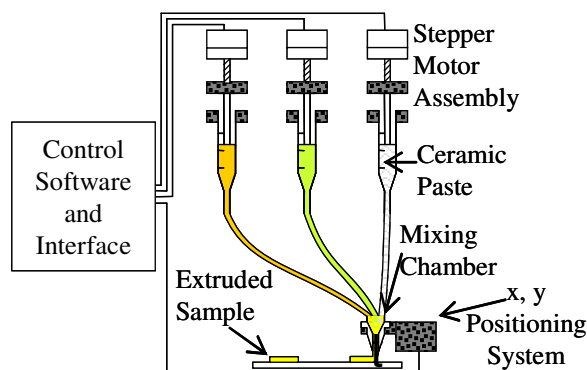


Figure 1: Schematic of the micro-coextruder system for photocatalyst composition optimization.

X-ray diffraction and raman spectroscopy have been used to identify the phases formed in each sample: a) monoclinic $\alpha\text{-Bi}_2\text{O}_3$, b) orthorhombic Bi_2WO_6 with low levels of partially reacted $\text{Bi}_4\text{W}_5\text{O}_{21}$ and $\text{Bi}_7\text{WO}_{13.5}$, c) tetragonal $\text{Bi}_6\text{WO}_{12}$ with

low levels of partially reacted Bi_2WO_6 and $\text{Bi}_{14}\text{WO}_{24}$ and d) monoclinic WO_3 . $\text{Bi}_7\text{WO}_{13.5}$ and $\text{Bi}_6\text{WO}_{12}$ fall within a continuous range of solid solutions and so have not been distinguished by these techniques. These data confirm that the presence of glycerol has had no deleterious effect upon the solid-state diffusion reaction.

The semiconductor band gaps of these samples have been calculated from their diffuse reflectance, measured with an integrating sphere, using the Kubelka-Munk function: $F(R) = (1 - R)^2 / 2R$, to approximate the optical absorbance. These values are in broad agreement with those reported in the literature.

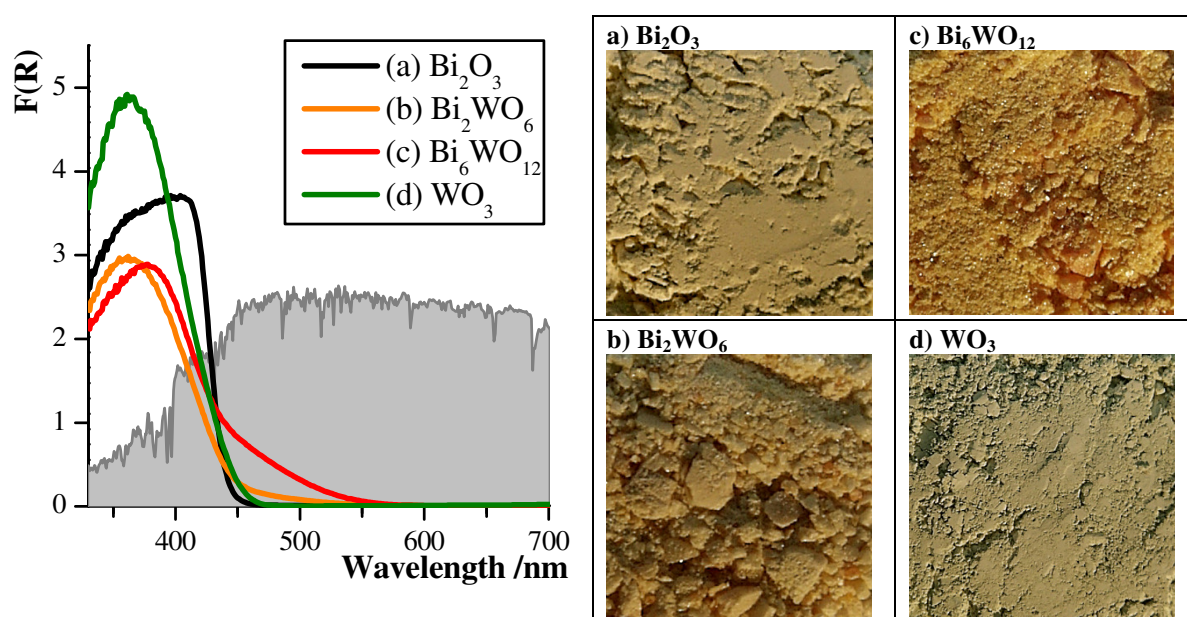


Figure 2: Kubelka-Munk Plot of a) Bi_2O_3 , b) Bi_2WO_6 , c) $\text{Bi}_6\text{WO}_{12}$, d) WO_3 . The shaded area illustrates the solar spectral irradiance at air mass 1.5 (ASTM G-173-03). Sample photographs are presented at a magnification of $\times 3$.

These results [3] demonstrate that the intermediate oxide $\text{Bi}_6\text{WO}_{12}$ exhibits improved optical absorbance in the visible region compared to either parent oxide although the optical band gap is not sufficiently red-shifted to adsorb a significant portion of the energy contained in the solar spectrum. This contribution also considers the chemical stability of Bi- W- oxides with respect to water and discusses other semiconductor photocatalysts to which the micro-coextrusion method of compositional optimisation may be applied.

References:

- [1] Finlayson, A. P., Ward, E., Tsaneva, V. N., Glowacki, B. A., *Study of the photocatalytic properties of WO_3 - Bi_2O_3 compounds deposited by a micro-coextrusion process*, Fuel Cells Science and Technology, Munich, 2004.
- [2] Finlayson, A. P., Ward, E., Tsaneva, V. N., Glowacki, B. A., *Bi_2O_3 - WO_3 compounds for photocatalytic applications by solid state and viscous processing*, Journal of Power Sources, in press.
- [3] Finlayson, A. P., Tsaneva, V. N., Glowacki, B. A., Lyons, L., Clark, M., to be submitted to Physica Status Solidi (A).