Supporting Information

Dynamics of Photogenerated Charge Carriers in WO_3/$BiVO_4$ Heterojunction Photoanodes

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XRPD analysis

In Figure SI1A the XRPD patterns are reported for the three here investigated films; the diffraction pattern recorded with FTO alone is also shown for comparison. The patterns of both individual materials fit well with monoclinic structures (JCPDS 05-0363 for WO_3 and JCPDS 75-1867 for $BiVO_4$). WO_3 patterns didn't match completely in the 23-25 degrees 2 θ region, where the three closely spaced peaks typical of the monoclinic structures overlap. Peak broadening could be probably attributed to non-constructive scattering due to the small crystallite size of the WO_3 film.[1,2] The combined $WO_3/BiVO_4$ electrode shows peaks of both monoclinic materials. The $BiVO_4$ peak at 18.6 degrees was much lower in magnitude with respect to those of single material films (a magnification of the four XRPD patterns in the 17-37 degrees 2 θ region is reported in Figure SI1B). A possible explanation is that the $BiVO_4$ layer grows with a preferential orientation on the underlying WO_3.

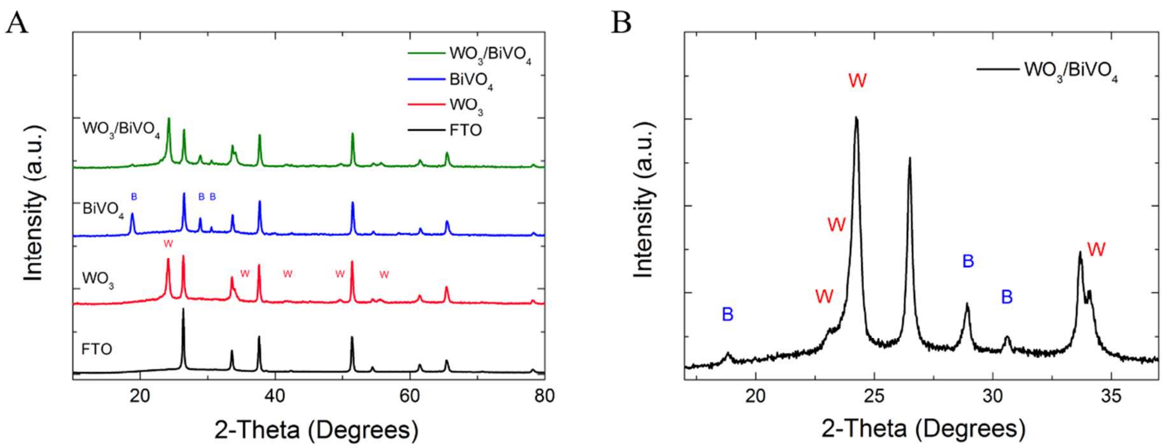


Figure SI1. (A) XRPD patterns of the materials. From the bottom: FTO glass and WO_3, $BiVO_4$ and $WO_3/BiVO_4$ electrodes on FTO after 8 h annealing at 500°C. (B) Magnification of the XRPD patterns of the composite $WO_3/BiVO_4$ material, exhibiting patterns of both WO_3 and $BiVO_4$, labelled as W and B, respectively.

Estimation of the band gap position of WO_3, $BiVO_4$ and $WO_3/BiVO_4$ electrodes

In order to confirm the band gap position of the materials, PEC experiments were carried out with the films in contact with a Na_2SO_3 solution. This electron donor quickly fills surface holes, thus minimizing electron-hole recombination. By this way the photocurrent onset is shifted to negative potentials providing a good approximation of the flat band potential. PEC measurements are reported in Figure SI2, with the insets showing magnified views of the photocurrent profiles near the onset potential.

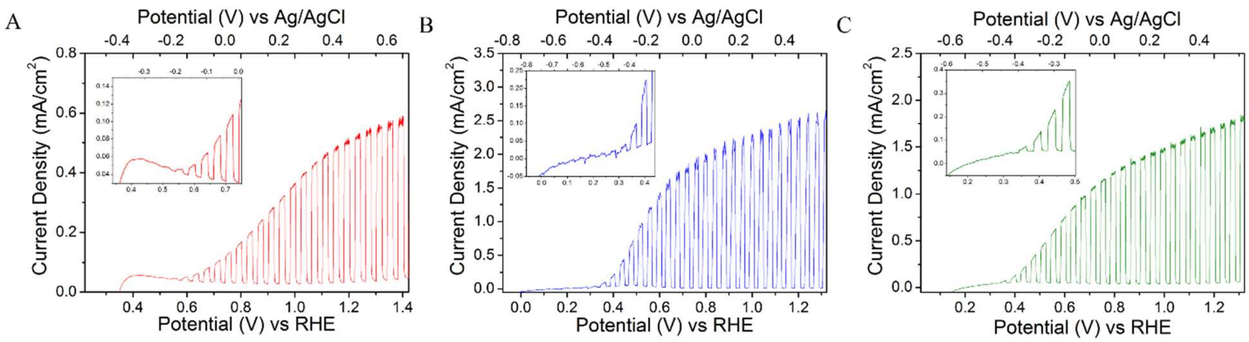
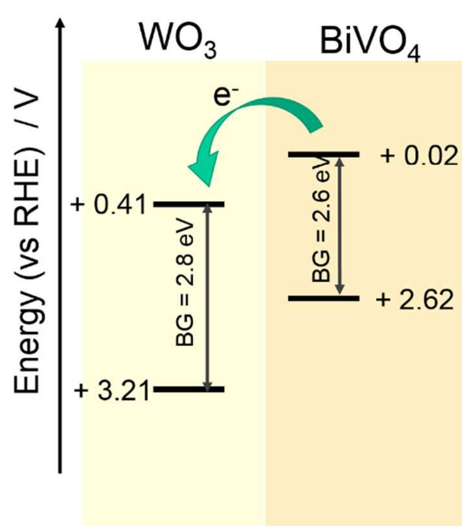


Figure SI2. Current density *vs* applied potential experiments in the presence of Na_2SO_3 (electron donor) measured with A) the WO_3, B) the $BiVO_4$ and C) the $WO_3/BiVO_4$ electrode. The insets show magnifications close to the onset potential.

The conduction band edge positions of WO_3 and $BiVO_4$ are +0.41 V and +0.02 V, respectively (Scheme SI1), in agreement with those reported in the literature.[3] When compared to the flat band potential of $BiVO_4$, that of the composite material results shifted by 170 mV to positive potentials. The positive shift is consistent with a shift of the Fermi level due to electron equilibration at the interface between the two materials. The conduction bands of all investigated materials are more negative in energy than the TH reduction potential (+0.48 eV).[4]



Scheme SI1. Diagram of the band edge positions of the single materials.

References

(1) Pokhrel, S.; Birkenstock, J.; Schowalter, M.; Rosenauer, A.; Mädler, L. Growth of Ultrafine Single Crystalline WO_3 Nanoparticles Using Flame Spray Pyrolysis. *Cryst. Growth Des.* **2010**, *10*, 632–639.

(2) Pokhrel, S.; Simion, C. E.; Teodorescu, V. S.; Barsan, N.; Weimar, U. Synthesis, Mechanism, and Gas-Sensing Application of Surfactant Tailored Tungsten Oxide Nanostructures. *Adv. Funct. Mater.* **2009**, *19*, 1767–1774.

(3) Hong, S. J.; Lee, S.; Jang, J. S.; Lee, J. S. Heterojunction $BiVO_4/WO_3$ Electrodes for Enhanced Photoactivity of Water Oxidation. *Energy Environ. Sci.* **2011**, *4*, 1781–1787.

(4) Kamat, P. V. Photoelectrochemistry in Colloidal Systems. *J. Chem. Soc. Faraday Trans. 1* **1985**, *81*, 509–518.