Supplementary Information

Sunlight Highly Active TiO_2-Bi_2WO_6 Heterostructures for Rhodamine B degradation

G. Colón, S. Murcia López, M.C. Hidalgo and J.A. Navío

Synthesis of Photocatalysts

The preparation of Bi_2WO_6 was carried out by mixing the corresponding amounts of $Bi(NO_3)_3$ and Na_2WO_4 . Thus, 0,01 mol of the Bi precursor were dissolved in 10 ml of glacial acetic acid while the stoichiometric amount of Na_2WO_4 (0,005 mol) was dissolved in 90 ml of bidistilled water. These two solutions were finally mixed to form a white suspension (pH=2 aprox) which was kept under stirring for 1 hour. Similar series were prepared but in this case after the precipitation the pH was settled at 9 by adding triethylamine (TEA) as precipitating agent. Then, the resulting suspension was transferred into a Teflon recipient inside of stainless steel autoclave. The hydrothermal treatment was performed at 140ºC for 20 hours. The precipitate was then filtered, repeatedly washed and dried overnight at 120ºC. Afterwards, thus obtained samples were submitted to a further calcination treatment at 300ºC for 4 hours.

On the other hand the TiO_2 sample was obtained by means of a hydrothermal method elsewhere described. In brief, a TiO_2 colloidal solution was obtained by adding certain amount of Ti^{4+}-isopropanol solution (38,4 ml of TTiP + 38,2 ml of isopropanol) to 400 ml of distilled water at pH=2 achieved by means of acetic acid. After TTiP addition a white precipitate is obtained that upon stirring at room temperature for one week evolve to a milky homogeneous solution. A certain amount of triethylamine (TEA) was then added drop wise to the Ti-solution aliquot till the pH value was 9. Afterwards, the obtained white precipitate suspension was then placed in a Teflon recipient inside of stainless steel autoclave reactor. The hydrothermal treatment was performed at 140ºC, 20 hours. The as obtained precipitate was then filtered, repeatedly washed and dried overnight at 120ºC. Then TiO_2 powder was submitted to a further calcination treatment at 300ºC for 4 hours.

TiO_2-Bi_2WO_6 heterostructures were obtained based on the above described methods for the preparation of single pristine photocatalysts. Thus, to the Bi-W white solution the corresponding volume of the TiO_2 sol was added in order to accomplish the desired TiO_2/Bi_2WO_6 molar relationship (5, 10 and 50 molar%). Then, similar procedure is followed to achieve to the final composite photocatalyst.

Materials characterization

BET surface area and porosity measurements were carried out by N_2 adsorption at 77 K using a Micromeritics 2010 instrument.

X-ray diffraction (XRD) patterns were obtained using a Siemens D-501 diffractometer with Ni filter and graphite monochromator. The X-ray source was Cu Kα radiation (0.15406 nm).

The chemical composition of the samples was determined by X-ray fluorescence spectrometry (XRF) in a Panalytical Axios sequential spectrophotometer equipped with a rhodium tube as the source of radiation. XRF measurements were performed on pressed pellets (sample included in 10 wt % of wax).

Micro-Raman measurements were performed using a LabRAM Jobin Yvon spectrometer equipped with a microscope. Laser radiation (λ = 532 nm) was used as excitation source at 5 mW. All measurements were recorded under the same conditions (1 s of integration time and 30 accumulations) using a 100x magnification objective and a 125 mm pinhole.

The morphology of samples was followed by means of field emission-SEM (Hitachi S 4800). The samples were dispersed in ethanol using an ultrasonicator and dropped on a copper grid.

UV−vis spectra (Cary 100, Varian) were recorded in the diffuse reflectance mode (*R*) and transformed to a magnitude proportional to the extinction coefficient (*K*) through the Kubelka−Munk function, $F(R_\infty)$. Samples were mixed with $BaSO_4$ that does not absorb in the UV−vis radiation range (white standard). Scans range was 240−800 nm.

Photocatalytic Experimental Details

The rhodamine B (*RhB*) oxidation reactions were performed using a batch reactor (250 ml) using a Osram Ultra-Vitalux lamp (300 W) with sunlike radiation spectrum. The intensity of the incident UVA light on the solution was measured with a PMA 2200 UVA photometer (Solar Light Co.) being ca. 130 W/m^2 (UVA PMA2110 sensor; spectral response 320-400 nm). On the other hand, the intensity of light in the visible range measured in this case is 156 W/m^2 (Photopic PMA21300 sensor; spectral response 400-700 nm). In the oxidation tests, an oxygen flow was employed what produces a homogenous suspension of the catalyst in the solution. Before each experiment, the catalysts were settled in suspension with the reagent mixture for 15 min. The evolution of the initial Rhodamine concentration (ca. 5 ppm) was followed through the evolution of the characteristic 553 nm band using a filtered aliquot ca. 2 ml of the suspension (Millipore Millex25 0,45 mm membrane filter). The visible photocatalytic experiments were performed by using a polyester UV filter sheet (Edmund Optics) showing 90% of absorbance below 400 nm (0.15 W/m^2 for $\lambda<400$ nm and 150 W/m^2 for $\lambda>400$ nm). Total organic carbon was followed by means of a TOC analyser (Shimadzu TOC VCPH).

Table 1. Specific surface areas (m^2/g) for TiO_2-Bi_2WO_6 series.

Sample	S_{BET} (m^2/g)		Crystallite size (nm)		Band gap (eV)		Ti/W % molar	
	pH=2	pH=9	pH=2	pH=9	pH=2	pH=9	pH=2	pH=9
Bi_2WO_6	25	18	9,8	22,6	2,80	2,82	---	---
Ti5BW	52	25	9,1	17,6	2,78	2,79	5,8	7,6
Ti10BW	43	20	8,4	20,8	2,82	2,82	12,1	8,5
Ti50BW	70	37	7,1	16,5	2,79	2,78	48,3	48,0
TiO_2	117	110	12,4	20,4	3,07	3,14	---	---

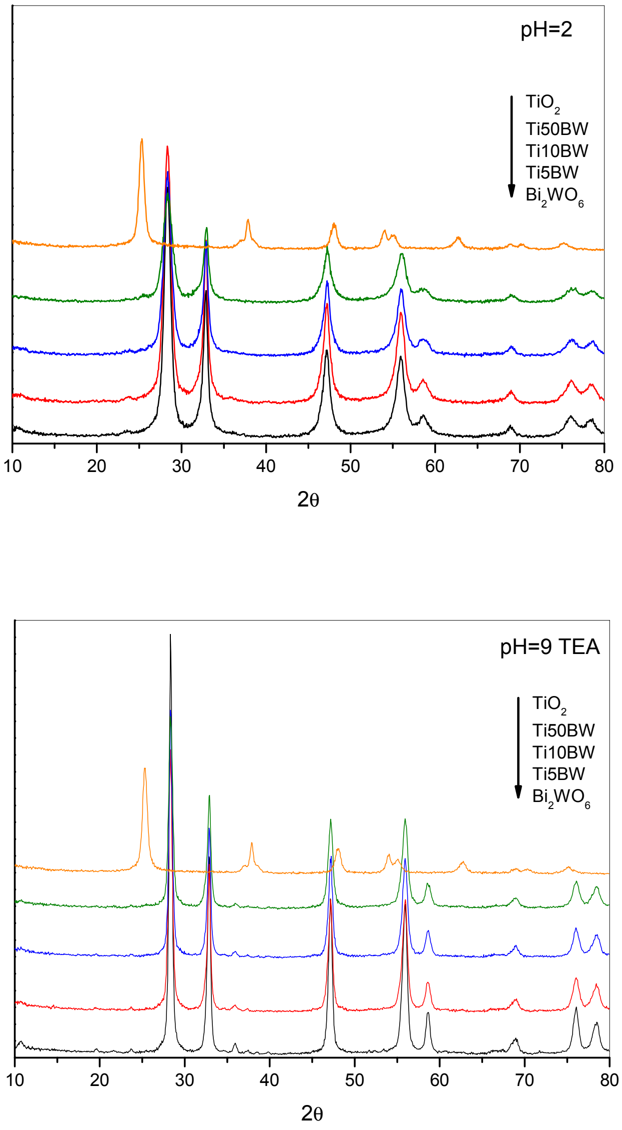

Figure S1. X-ray diffraction patterns for different TiO_2-Bi_2WO_6 series.

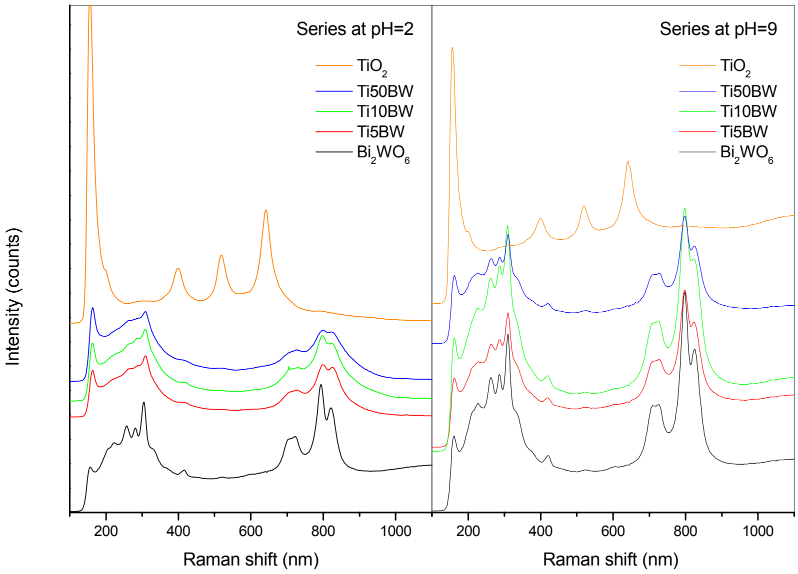

Figure S2. Raman spectra for TiO_2-Bi_2WO_6 series prepared at pH=2 and pH=9.

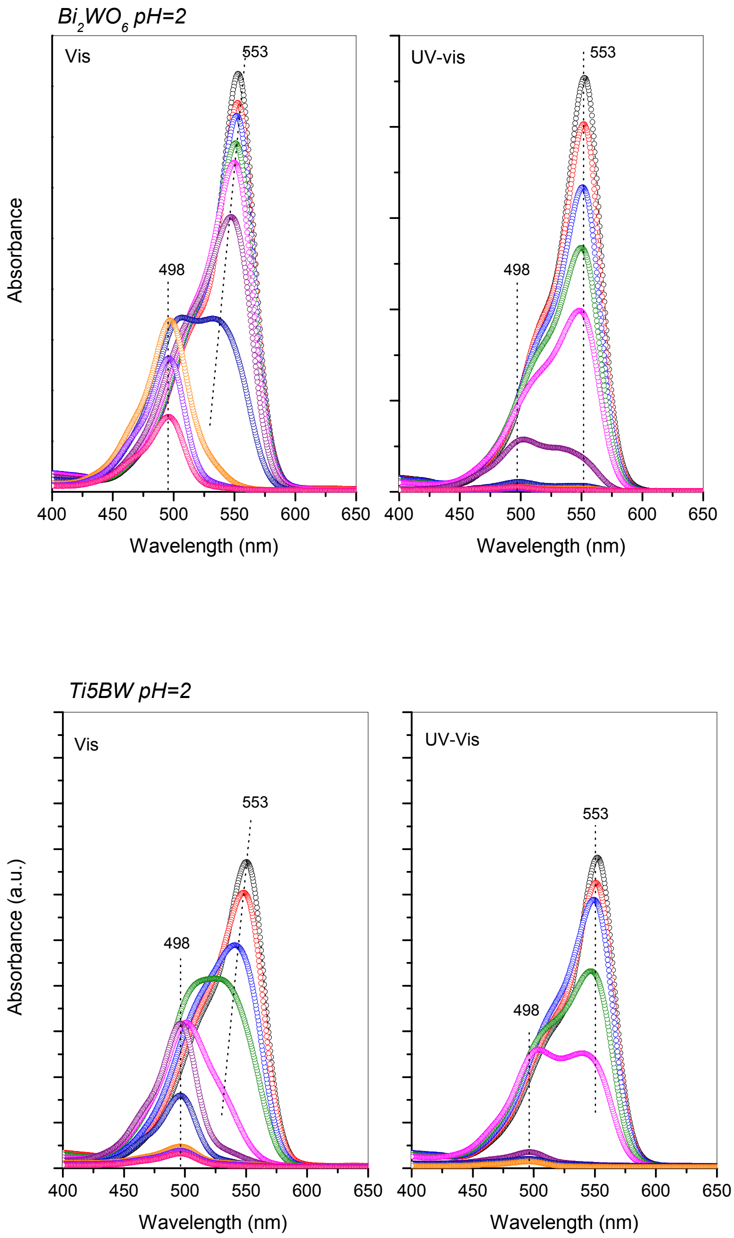

Figure S3. Evolution of *RhB* during the photocatalytic degradation reaction for selected catalysts prepared at pH=2.

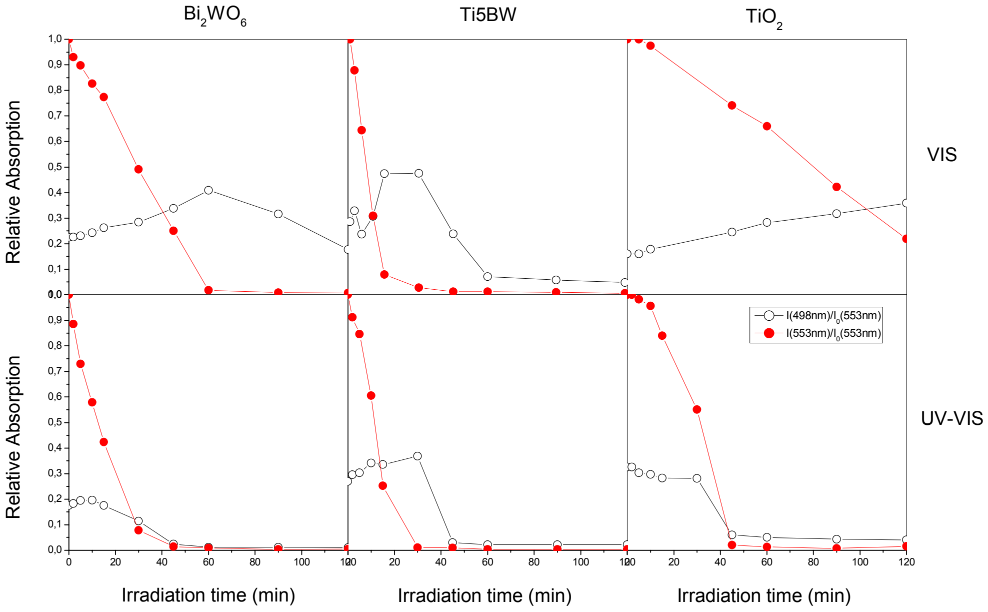

Figure S4.a. Evolution of *RhB* absorption bands during reaction run for different TiO_2-Bi_2WO_6 series prepared at pH=2.

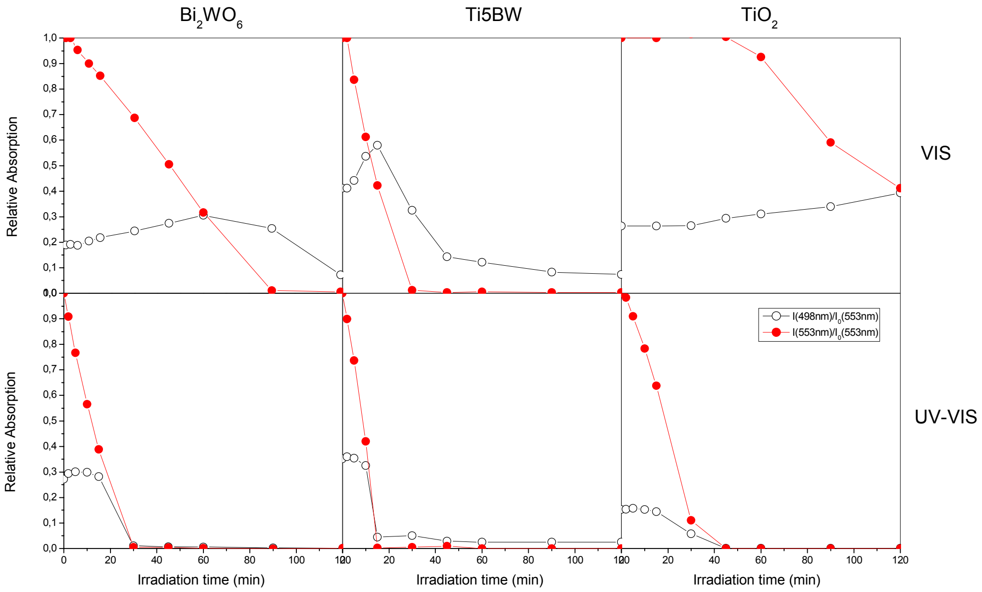

Figure S4.b. Evolution of *RhB* absorption bands during reaction run for different TiO_2-Bi_2WO_6 series prepared at pH=9.