Synchronously achieving surface Bi⁰ metallisation and incorporation of Bi³⁺/⁵⁺ ions into W⁶⁺, N³⁻ doped TiO₂ lattice by the hydrothermal-reduction method: surface plasmonic resonance effect for efficient photocatalysis

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Supplementary File

S1. Details of analytical techniques and irradiation procedure

Powder X-ray diffraction (PXRD) data of synthesized materials was recorded using Panalytical X’pert Pro MPD diffractometer using Cu Kα radiation (λ=1.5418 Å) with nickel filter. The data were collected with a scan rate of 2° min⁻¹, in the 2θ range of 10° to 80°. The database of the Joint Committee on Powder Diffraction Standards (JCPDS) was used to identify the crystalline phases of the powders. UV-Vis diffuse reflectance measurements were performed on a Schimadzu-UV 3101 PC UV-VIS-NIR UV-Vis spectrophotometer with spectral-grade BaSO₄ as the reference material. Energy dispersive X-ray (EDX) analysis and scanning electron microscopy (SEM) measurements were performed on a ULTRA 55 microscope equipped with EDX attachment operating at 25 kV on the specimen upon which a thin layer of platinum had been evaporated. An electron microprobe is used in the EDX mode. Nitrogen adsorption/desorption isotherms for the materials were collected from Digisorb 2006 surface area, pore volume analyser Nova Quanta Chrome Corporation instrument multipoint BET.
adsorption system. The samples were outgassed for 12 h under vacuum at 450°C prior to adsorption. The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area from the adsorption branch. The pore size distribution was calculated by analyzing the adsorption branch of the nitrogen sorption isotherm using the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectra (XPS) was performed on an AXIS ULTRA from AXIS 165 spectrometer that was equipped with a monochromatic Al-Kα source and a charge neutralizer (hν = 1253.6 eV). The binding energy (BE) values were obtained with reference to the C 1s peak at 285.2 eV of the surface adventitious carbon.

The photocatalytic activity experiments were carried out in a circular borosilicate glass reactor of the exposure area of 176.6 cm² containing 250 mL of a 10 mg/L aqueous solution of glyphosate. The amount of prepared catalyst was 0.1 g/L. Prior to irradiation, the reaction mixture was stirred for 30 min to ensure the establishment of an adsorption-desorption equilibrium. Photocatalysis under solar light was performed between 11 am to 2 pm during the summer season in the months of April-June at Bangalore India. The latitude and longitude are 12.58 N and 77.38 E respectively. The average solar intensity was found to be 0.799 kWm⁻² (using solar radiometer). The intensity of solar light was concentrated by the convex lens and the reaction mixture was exposed to this concentrated solar light. An aliquot of the aqueous suspension was periodically taken from the reactor and centrifuged. In the experiments requiring oxidants, the calculated amount of reagent was introduced into the reaction mixture. The absorbance of the clear solution was measured using a UV-visible spectrophotometer in the wavelength range of 200-800 nm and then glyphosate concentration was deduced from a calibration curve.
Fig. S2. Urbach energy curves of BiWNT and Bi⁰-BiWNT samples.
Fig. S3. FTIR spectra of TiO$_2$, WNT, BiWNT and Bi$^0$-BiWNT samples.
Fig S4. A plot of $C/C_0$ versus time of three cycles for the reuse of Bi$^0$-BiWNT catalyst under solar illumination.