SUPPORTING INFORMATION

Photocatalytic Activity of $Ni_{0.5}Zn_{0.5}Fe_2O_4$@Polyaniline decorated BiOCl for Azo dye degradation under visible light - Integrated role and Degradation Kinetics Interpretation

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Chemicals: All chemicals were of analytical grade and used as received. Bismuth oxide (Bi_2O_3), aniline (ANI) monomer, sodium borohydride ($NaBH_4$), methyl orange (MO, Table 1) were purchased from Sigma-Aldrich, USA. Ammonium persulphate (AMPS), sodium hypochlorite (NaOCl), nickel chloride hexahydrated ($NiCl_2.6H_2O$), zinc chloride ($ZnCl_2$), anhydrous ferric chloride ($FeCl_3$) and ethanol (C_2H_5OH) were procured from Merck, Germany. NaOH, HCl, $TiO_{2,}$ methanol, tetrahydrofuran and ammonia solution were provided by SRL Pvt. Ltd., India. Double distilled water was used for preparation of all aqueous solution.

Synthesis of $Ni_{0.5}Zn_{0.5}Fe_2O_4$@Polyaniline nanofibers (N@PAni): The $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanocrystals (NZF) were prepared according to our earlier report.[1] Briefly a stoichiometric quantity of nickel chloride, zinc chloride and ferric chloride was dissolved in deionised water homogeneously. Then this solution was poured into boiling NaOH under stirring. The resultant mixture was kept at 80 °C for 4 h. The obtained precipitates were washed several times with distilled water and methanol followed by vacuum drying at 100 °C for 24 hr.

The $Ni_{0.5}Zn_{0.5}Fe_2O_4$ @ Polyaniline (N@PAni) nanofibers were prepared by an in situ polymerization method.[2] NZF nanocrystals and ammonium peroxydisulate were dispersed in 100 ml of 1mol/l HCl aqueous solution with ultrasonic vibrations for 30 min to obtain a uniform suspension. Aniline was added into this mixture dropwise under shaking, after which, the resulting mixture was allowed to polymerize under shaking for 1 h. Finally the N@PAni nanofibers were filtered out and washed with a large amount of deionized water, and then dried at 60 C until a constant mass reached.

Synthesis of BiOCl: BiOCl powder was prepared by a facile hydrolysis method.[3] About 2 gm of Bi_2O_3 was completely dissolved in concentrated hydrochloric acid solution. The white colloidal solution was obtained by adding aqueous ammonia solution into the above acidic solution to adjust pH value between 2 and 3. The colloidal solution was then heated at 40 ^{0}C for half an hour. White plates like precipitates of BiOCl were obtained. The precipitates were centrifuged and washed several times with ethanol and double distilled water. Finally, product was dried at 80 ^{0}C for 6 h in air oven.

Characterization Techniques: X-ray diffraction patterns were identified on a Rigaku Ultima IV, X-ray diffractometer equipped with Cu Kα radiation. Fourier Transform Infrared (FTIR) spectra (KBr) were recorded on 3000 Hyperion Microscope with Vertex 80, FTIR spectrophotometer in the range 4000-400 cm^{-1} with 1 cm^{-1} resolution. The high resolution transmission electron microscopy (HRTEM) images were recorded on a model JEOL JEM 2100F combined with energy dispersive X-ray (EDS) spectroscopy. Solid UV-Vis diffuse-reflectance spectra were obtained on a Varian Cary 5000 UV-visible spectrophotometer. X-ray photoelectron spectra (XPS) was used to characterize surface elemental compositions and performed on an Escalab 210 X-ray photoelectron spectroscope using Al Kα x-ray source. Photoluminescence (PL) spectra were recorded on an F-4600 fluorescence spectrophotometer with an excitation wavelength of 290 nm. To measure photocatalytic activity and optical absorbance of dye solutions, Hitachi U-2900UV-vis spectrophotometer was used. TOC was measured on TOC analyzer (Shimadzu). Finally, intermediate products resulting from the photocatalytic degradation of dye were identified using GCMS technique. GC/MS analysis was performed at 70 eV on a QP 2010 Ultra-GCMS along with fused capillary column. A temperature gradient was used in the GC separations. The initial temperature was 60°C and it was increased to 360 °C at a rate of 6 °C/min. An electrochemical system (SI 6143 Instrument) was employed to measure the EIS. EIS was performed from 0.1Hz to 100 kHz at an open circuit potential of 0.3 V and an alternating current (AC) voltage amplitude of 5 mV.

Adsorption and Photocatalytic experiments: Experiments were carried out in a constant stirred cylindrical shaped photocatalytic quartz reactor at room temperature. A suspension of 0.20 g of catalyst in 200 ml of an aqueous solution of MO dye (10 mg/l) was magnetically stirred in dark for 1 hour to establish an adsorption-desorption equilibrium. Then solution was exposed to visible light (500 W halogen lamp, Philips India) located 20 cm away from the reaction solution. At specific time intervals, 4 ml aliquots were withdrawn and centrifuged at 12000 rpm for 5 min to separate the photocatalyst powder. The residual dye concentration in supernant was determined from the absorption band at λ_{max} = 464 nm (MO) using Hitachi UV-vis spectrophotometer. For adsorption measurements, the adsorption rate was calculated as

$$\text{Adsorption rate} = (a_0 - a)/a_0 \times 100\ \% \qquad \text{(S1)}$$

where, a_0 and a are the absorbance values of dyes initially and after 1 hr, respectively.

The degradation efficiency was calculated using the following equation:

$$\text{DE } (\eta\ \%) = (A_0 - A) / A_0 \times 100\ \% \qquad \text{(S2)}$$

where, A_0 and A are the absorbance values of dyes initially and after time t (min) of visible light irradiation, respectively.

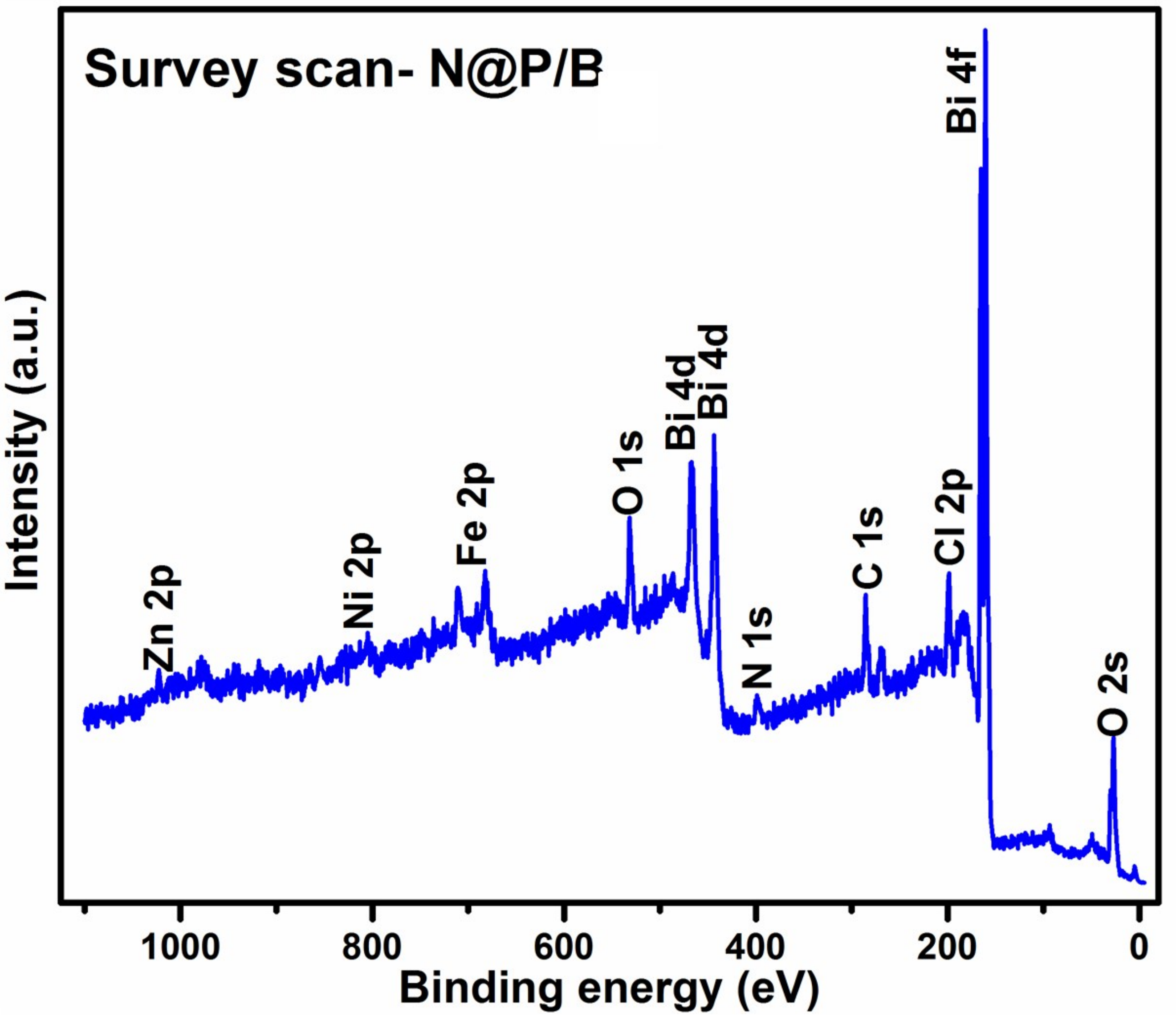
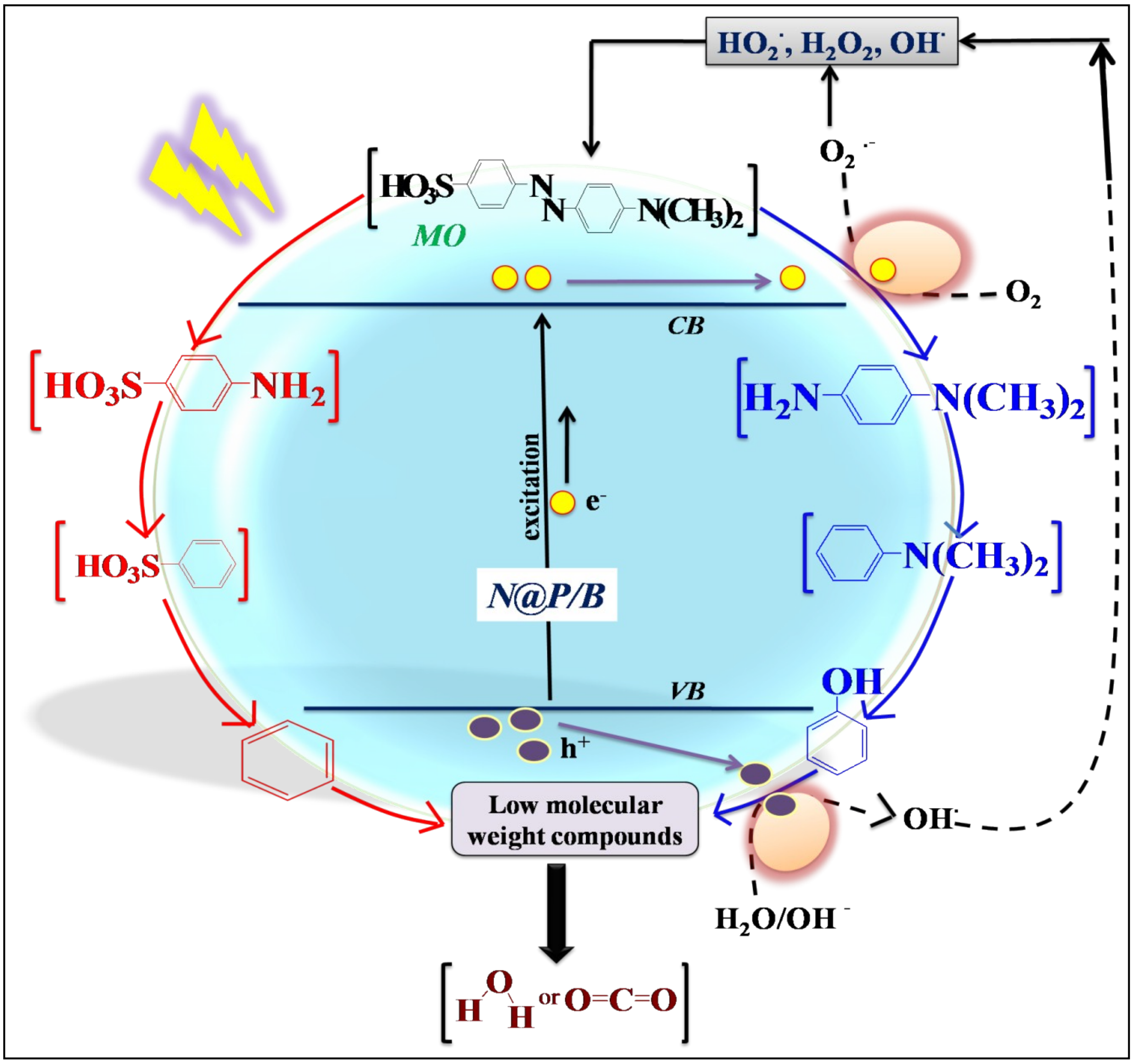


Figure S1. Survey spectrum of N@P/B



Scheme S1. Degradation mechanism of dye/ its intermediates

References

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3) R. Tanwar, S. Kumar and U. K. Mandal, *J. Photochem. Photobio. A: Chem.*, **2017**, 333, 105-116.