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## Photocatalytic detoxification of Acid Red 18 by modified ZnO catalyst under sunlight irradiation



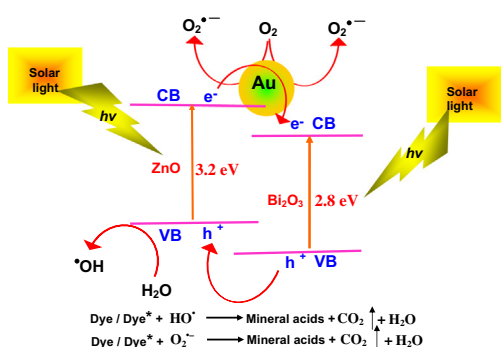
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### HIGHLIGHTS

- Hybrid structured Bi–Au–ZnO composite was prepared.
- Bi–Au–ZnO heterojunction photocatalyst was more stable and reusable.
- Heterostructured Bi–Au–ZnO showed higher photocatalytic activity than other catalysts.
- A possible mechanism is proposed for the degradation of AR 18 dye under sun light.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this work, hybrid structured Bi–Au–ZnO composite was prepared by precipitation–decomposition method. This method is mild, economical and efficient. Bi–Au–ZnO was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectrum (EDS), diffuse reflectance spectra (DRS), photoluminescence spectra (PL) and BET surface area measurements. Photocatalytic activity of Bi–Au–ZnO was evaluated by irradiating the Acid Red 18 (AR 18) dye solution under sun light. Heterostructured Bi–Au–ZnO photocatalyst showed higher photocatalytic activity than those of individual Bi–ZnO, Au–ZnO, bare ZnO, and TiO<sub>2</sub>-P25 at pH 11. The effects of operational parameters such as the amount of catalyst dosage, dye concentration, initial pH on photo mineralization of AR 18 dye have been analyzed. The mineralization of AR 18 has been confirmed by chemical oxygen demand (COD) measurements. A possible mechanism is proposed for the degradation of AR 18 under sun light. Finally, Bi–Au–ZnO heterojunction photocatalyst was more stable and could be easily recycled several times opening a new avenue for potential industrial applications.

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### Introduction

Environmental pollution and the energy crisis have become two biggest problems for human society and seriously intimidate the quality of life. Photocatalysts have consistently drawn much more

attention for many of the environmental challenges facing the modern world since they can provide an easy way to use light for environmental remediation and organic transformations. Semiconductor oxides TiO<sub>2</sub>, ZnO, Bi<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> have been engaged as photocatalysts in pollutant degradation and water splitting reactions [1–5]. Among them TiO<sub>2</sub> and ZnO are significant candidates for use in multiple applications because of wide band gap (3.37 eV) and the large exciton binding energy of 60 meV [6,7]. But, TiO<sub>2</sub> and ZnO can be stimulated only by ultraviolet

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(UV) light which occupies only 4% in the solar spectra, which greatly impeded the photocatalytic activity of these catalysts in the direct use of solar light.

Further the photocatalytic efficiency of ZnO is still insufficient for the practical applications due to the fast recombination of electron and holes in nanoseconds [8]. Doping or loading of transition metal (or) inner transition metals on to the surface of the ZnO semiconductor traps the electron and it could enhance the light absorption of ZnO in UV region to entire visible region [9–16]. Coupling of two semiconductors with different band gap materials could progress the stability necessary for practical applications.  $\text{Bi}_2\text{O}_3$  is a semiconductor with several properties of interest, such as high oxygen ion conductivity, very high refraction index or good photoconductive response, which enable the application of this material in optoelectronics, gas sensing, catalysis and other fields [17–19].  $\text{Bi}_2\text{O}_3$  has four main polymorphs [20,21], but only the monoclinic  $\alpha$ -phase and the face centred cubic  $\delta$ -phase are stable.  $\text{Bi}_2\text{O}_3$  is a promising candidate because of its small band gap (2.85 eV), high oxidation power of valence hole ( $\sim +3.13$  V versus NHE), and non-toxic property as  $\text{TiO}_2$  [22].

But  $\text{Bi}_2\text{O}_3$  shows poor photocatalytic efficiency for the destruction of organic waste due to a hasty recombination of the photo-induced electron and hole pairs [23]. Hameed et al. synthesised of  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$  nanocomposites and studied their superior photocatalytic activity under visible light irradiation [24]. They also synthesised  $\text{NiO}-\text{Bi}_2\text{O}_3$  and  $\text{ZnO}-\text{Bi}_2\text{O}_3$  composites for photocatalytic applications [25,26]. Nowadays, several research works were reported on the efficient visible-light-driven photocatalysis using noble metal-deposited on  $\text{Bi}_2\text{O}_3$  [27,28]. The influences of the loaded Au and the electron transport paths, decide the photocatalytic activity of  $\text{Au}/\text{Bi}_2\text{O}_3$ . This promoted our interest in the development of a noble metal doped semiconductor oxide. In the present study we reported the synthesis and characterization of a heterostructured of Bi loaded Au-ZnO and its photocatalytic activity on Acid Red 18 dye degradation under sun light illumination.

## Experimental

### Materials

The commercial AR 18 dye, (molecular formula =  $\text{C}_{20}\text{H}_{11}\text{N}_2\text{Na}_3\text{O}_{10}\text{S}_3$ ; molecular weight 604.47 and dye content 80%) obtained from s.d. fine chemicals was used as such. The chemical structure of the dye and its UV-vis spectrum are given in Fig. 1. Oxalic acid dihydrate (99%) and zinc nitrate hexahydrate (99%) were obtained from Himedia chemicals.  $\text{Bi}(\text{NO}_3)_3$  (Merck), ZnO (Himedia) and  $\text{AuCl}_3$  (Sigma Aldrich) were used as received. A gift sample of Degussa  $\text{TiO}_2$ -P25 was obtained from Evonik (Germany). It is a 80:20 mixture of anatase and rutile phase. It has a particle size of 30 nm and surface area of  $50 \text{ m}^2 \text{ g}^{-1}$ . The double distilled water was used to prepare experimental solutions. The pH of the solutions prior to irradiation was adjusted using  $\text{H}_2\text{SO}_4$  or NaOH.

### Preparation of Bi loaded Au-ZnO

Bi loaded Au-ZnO was prepared by precipitation-decomposition method. Aqueous solutions of 100 mL of 0.4 M zinc nitrate hexahydrate and 100 mL of 0.6 M oxalic acid in deionized water were brought to their boiling points separately. About 0.041 g of  $\text{AuCl}_3$  in 5 ml of water was added to zinc nitrate solution. Solutions of zinc nitrate and  $\text{AuCl}_3$  were mixed with oxalic acid solution. Precipitation of zinc oxalate with Au occurred (1 wt% Au related to ZnO). To this 0.251 g of  $\text{Bi}(\text{NO}_3)_3$  in 5 ml of water was added (few drops of concentrated nitric acid was also added to get a clear solution of bismuth nitrate) and stirred for 3 h. Precipitate of Bi with Au-zinc

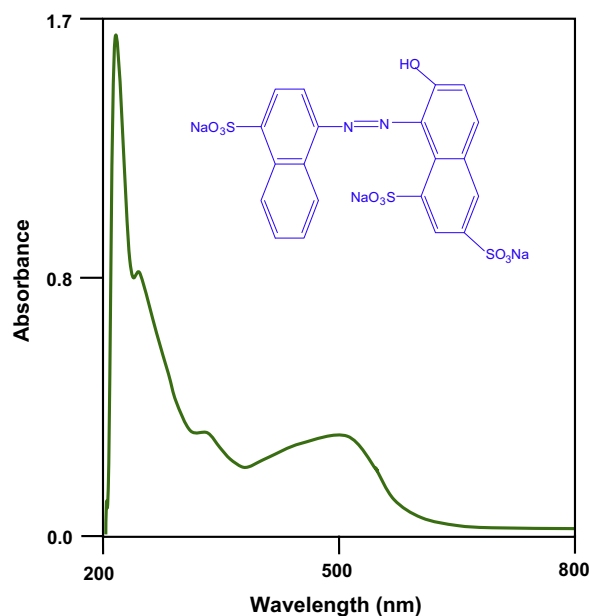


Fig. 1. The structure and UV-visible spectrum of AR 18.

oxalate was homogeneous in dimension. Bi-Au-zinc oxalate precipitate was washed several times with distilled water, air-dried overnight and dried at  $100^\circ\text{C}$  for 5 h. It was calcined in the muffle furnace at the rate of  $20^\circ\text{C min}^{-1}$  to reach the decomposition temperature of zinc oxalate ( $450^\circ\text{C}$ ). After 12 h, the furnace was allowed to cool down to room temperature. The Bi loaded Au-ZnO catalyst was collected and used for further analysis. This catalyst contained 4 wt% of Bi (related to ZnO). Catalysts with 1, 2, 3 and 5 wt% of Bi were prepared with the same procedure. The bare ZnO was prepared without addition of  $\text{Bi}(\text{NO}_3)_3$  and  $\text{AuCl}_3$ . Bi-ZnO and Au-ZnO were prepared by the same procedure with respective precursors.

### Analytical methods

Powder X-ray diffraction patterns were obtained using X'Per PRO diffractometer equipped with a  $\text{Cu K}\alpha$  radiation (wavelength  $1.5406 \text{ \AA}$ ) at 2.2 kW Max. Peak positions were compared with the standard files to identify the crystalline phase. The transmission electron microscopic (TEM) observation was carried out on a Hitachi H-7000, Japan, with an acceleration voltage of 100 kV. The specimens were prepared by depositing a drop of the suspension of sample powder, which was ultrasonically dispersed in acetone for 10 min, on a carbon-coated copper grid, followed by drying at room temperature. On an observation with a JEOL JSM-6500F cold field emission scanning electron microscope (FE-SEM), the samples were mounted on a gold platform placed in chamber. Energy dispersive X-ray spectrum (EDS) was examined using a JEOL-JSM 5610 LV. Diffuse reflectance spectra (DRS) were recorded using Shimadzu UV-2450. Photoluminescence (PL) spectra at room temperature were recorded using a Perkin Elmer LS 55 fluorescence spectrometer. The nanoparticles were dispersed in carbon tetrachloride and excited using light of wavelength 300 nm. The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of BET equation using a Micromeritics ASAP 2020 V3.00 H. UV spectral measurements were done using Hitachi-U-2001 spectrometer.

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