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Facile one-pot synthesis of heterostructure SnO₂/ZnO photocatalyst for enhanced photocatalytic degradation of organic dye†

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In this work, heterostructure SnO₂/ZnO nanocomposite photocatalyst was prepared by a straightforward one step polyol method. The resulting photocatalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption–desorption analyses, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and UV-vis diffuse reflectance spectroscopy (UV-vis DRS). The results showed that the synthesized SnO₂/ZnO nanocomposites possessed mesoporous wurtzite ZnO and cassiterite SnO₂ nanocrystallites. The photocatalytic activity of the prepared SnO₂/ZnO photocatalyst was investigated by the degradation of methylene blue dye under UV light irradiation. The heterostructure SnO₂/ZnO photocatalyst showed much higher photocatalytic activities for the degradation of methylene blue dye than individual SnO₂, ZnO nanomaterials and reference commercial TiO₂ P25. This higher photocatalytic degradation activity was due to enhanced charge separation and subsequently the suppression of charge recombination in the SnO₂/ZnO photocatalyst resulting from band offsets between SnO₂ and ZnO. Finally, these heterostructure SnO₂/ZnO nanocatalysts were stable and could be recycled several times without any appreciable change in degradation rate constant which opens new avenues toward potential industrial applications.

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Introduction

The continuing propagation of industrialization and urbanization produces large amounts of wastewater containing organic substances such as pesticides, insecticides, dyes, phenolic compounds, toxic organics, and heavy metals (lead, cadmium, arsenic, mercury, *etc.*), as well as microbial pathogens. Among these, synthetic dyes are valuable in numerous industries such as textiles, paper printing, food, pharmaceuticals, leather and cosmetics.^{1,2} A substantial amount of water is consumed in the textile industry for manufacturing processes.³ The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition.^{4,5} Discharge of dyeing industry wastewater into natural water bodies is not desirable as the color prevents re-oxygenation in receiving water by cutting off penetration of sunlight.⁶ Most of the dyes, even in very low concentration, are toxic to some microorganisms, aquatic life and human beings as they are carcinogenic and mutagenic.^{7–10} Thus, finding a sustainable solution to treat the dye containing

wastewater is of high priority in terms of environmental pollution remediation.

Various approaches on handling and decontamination of effluents have been reported in the literature.^{11–13} Currently available water treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, but still remain and not being completely eliminated or destroyed. Other conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary pollutants into the ecosystem.¹⁴ These concentrated toxic contaminants are highly redundant and have been concerned worldwide due to the increasing environmental awareness and legislations. Therefore, it is a challenge today to develop sustainable and economically viable technology to treat, recycle and reuse of dye containing wastewater. In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional purification processes. Therefore, the development of eco-friendly methods of destroying these pollutants became an imperative task.

Over the past decade, many research efforts have been devoted around the world to develop a newer, more powerful, and very promising technique called Advanced Oxidation Processes (AOPs) to treat the contaminants of industrial effluents.^{15–18} Among these AOPs, heterogeneous photocatalysis using semiconductor photocatalysts such as titanium dioxide

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(TiO₂),^{19,20} zinc oxide,^{21–23} tin oxide (SnO₂),^{24,25} can be suitably pertained for the photocatalytic degradation of organic pollutants because it can mineralize dye molecules into CO₂, H₂O and mineral acids without producing secondary pollution. Furthermore, the photocatalysts are cheap, non-hazardous, stable, biologically and chemically inert, insoluble under most conditions and reusable. Typically, when a semiconductor photocatalyst is irradiated with photon of energy equal to or greater than the band gap energy of the semiconductor, then the electron from the filled valence band is excited to the conduction band leaving photogenerated holes in the valence band. After excitation the photogenerated holes and electrons migrate to the surface and take part in the redox reaction and mineralize the organic compounds to degradation products, generally to H₂O and CO₂. Among different semiconductor metal oxides, zinc oxide (ZnO) has been considered as a suitable alternative to titania owing to its non-toxicity, close band-gap energy (3.37 eV), high electron mobility (205–1000 cm² V⁻¹ s⁻¹), large excitation binding energy (60 meV), straightforward tailoring of the nanostructures and easy modification of the surface structure.^{26,27} Thus, ZnO showed better efficiency than TiO₂ in the photocatalytic decomposition of organic dyes either in organic or in aqueous media.²⁸ However, the fast recombination rate of photogenerated electron–hole pairs has hampered the industrial applications of ZnO. One interesting way to overcome such limitations and to achieve efficient charge separation is to couple ZnO with other semiconductor metal oxides having suitable band positions. In this context, various semiconductor based heterostructure photocatalysts have been designed and investigated such as Fe₃O₄/ZnO,²⁹ CeO₂/ZnO,³⁰ ZnO–WO_{3–x},³¹ SnO₂/TiO₂,^{32,33} TiO₂/ZnO,^{34,35} CuO/ZnO.³⁶ Recently, Ahmad *et al.* develop ZnO-decorated polypyrrole/chitosan bio-nanocomposites by *in situ* polymerization of pyrrole in order to enhance the photocatalytic activity for the degradation of organic dyes.³⁷ The resulting composite showed higher photocatalytic performance for the degradation of methylene blue, reactive orange-16 and Coomassie brilliant blue R-250 under UV light irradiation. The enhanced photocatalytic degradation of the composite resulted from the low recombination rate of the electron–hole pairs evidenced by decreased PL intensity. In order to obtain visible light active photocatalyst, Di *et al.* synthesized ZnO–GO coupled chitin graphene hydrogel (ZnO–GO/CGH) for degrading methylene blue.³⁸ The as-synthesized nanocomposite exhibited higher photocatalytic activity for the degradation of methylene blue under visible light irradiation. The higher activity was due to the improved charge separation resulting from the movement of the photogenerated holes and electrons to different locations on the surface of ZnO–GO/CGH. In another study, Wang *et al.* fabricated ZnO p–n homojunctions by depositing n-type ZnO nanoparticles on the surface of p-type ZnO nanoparticles.³⁹ The ZnO with oxygen vacancy and metal vacancy resulted n-type ZnO and p-type ZnO, respectively. The built-in potential at p–n homojunction decreased the recombination of photogenerated hole–electron by transfer the charge carriers in opposite direction leading to the higher photocatalytic performance of ZnO p–

n homojunction than the p-type ZnO and n-type ZnO for the degradation of phenol and methyl orange.

It is reported that tin dioxide (SnO₂) is an n-type semiconductor that has a wide range of potential applications in gas sensors, catalysts, batteries, transistors, and transparent electrodes.^{40–43} SnO₂ has a wide band gap of 3.6 eV at room temperature with excellent optical and electrical properties.⁴⁴ Moreover, SnO₂ possesses a high electron mobility (~100–200 cm² V⁻¹ s⁻¹), indicating a faster transport of photoexcited electrons. In addition, the conduction band of SnO₂ is more positive (0.5 V) than that of ZnO and could act as a sink for the photogenerated electrons.^{45,46} Thus, tin oxide (SnO₂) can be combined with ZnO to reduce the recombination of photogenerated electrons and holes owing to its outstanding physical and chemical properties. Using SnO₂ coupled to ZnO, the photogenerated electrons can accumulate on the SnO₂ and the photogenerated holes can accumulate on the ZnO owing to the formation of heterojunction at the SnO₂/ZnO. As a consequence, coupling of SnO₂ with ZnO has been the subject of many research groups for achieving an efficient charge separation and improving the photocatalytic properties of ZnO and SnO₂.^{47–52} In this context, the heterostructure SnO₂/ZnO nanoparticles have been prepared by different methods like coprecipitation,^{53,54} hydrothermal synthesis,^{49,50} precipitation followed by hydrothermal,⁵⁵ sol–gel.^{56,57} The SnO₂/ZnO nanocomposites with a molar ratio Zn : Sn of 2 : 1 synthesised by coprecipitation method showed higher photocatalytic degradation of methyl orange (MO) than the individual ZnO and SnO₂.⁵³ Yu *et al.*⁴⁹ synthesized SnO₂/ZnO nanocomposites *via* hydrothermal technique followed by calcination in air that exhibited considerably higher degradation efficiency for the photodegradation of methylene blue and quinolone antibiotics under mercury lamp irradiation than pure ZnO and SnO₂ analogues. A similar trend has also been observed by Zhang *et al.*⁵⁸ for one-dimensional ZnO–SnO₂ nanofibers synthesized by a simple combination method of sol–gel process and electrospinning technique. However, the nanoparticles synthesized by these approaches tend to agglomerate because of large specific surface area along with high surface energy. Recently, polyol-mediated synthesis has turned out to be well-suited for the preparation of metal oxide nanoparticles.^{59–61} The polyol method is a versatile liquid-phase method utilizing high boiling polyols such as ethylene glycol, diethylene glycol, tetraethylene glycol or glycerol to produce nanoparticles. Here, the polyol serves as a solvent and stabilizing agent that limits the growth of particles resulting suppression of particles agglomeration. Moreover, the synthesis is straightforward to carry out and requires neither multisequential steps nor advanced experimental condition or equipment. However, to the best of our knowledge, the synthesis of SnO₂/ZnO nanoparticles by polyol method is yet to be reported. Therefore, in the present study we would like to present a detailed investigation on the preparation, characterization, and photocatalysis evaluation of heterostructure SnO₂/ZnO synthesized by polyol method.

In this research, heterostructure ZnO/SnO₂ nanocomposites have been prepared by polyol method using zinc acetate and tin tetrachloride as the precursor of ZnO and SnO₂, respectively.



The prepared heterostructure ZnO/SnO₂ nanocomposites were characterized by X-ray diffraction (XRD), nitrogen adsorption-desorption analyses, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and UV-vis diffuse reflectance spectroscopy (UV-vis DRS). Their photocatalytic activity under UV-vis light irradiation was evaluated by the degradation of methylene blue (MB) dye.

Materials and methods

Preparation of heterostructure ZnO/SnO₂ photocatalysts

All chemical reagents were purchased from Sigma Aldrich or Alfa Aesar. All reagents were used as received without further purification. The heterostructure ZnO/SnO₂ nanoparticles were synthesized by polyol method using zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) and anhydrous tin tetrachloride (SnCl₄) as precursor for ZnO and SnO₂, respectively. In a typical experiment procedure, first 6.71 g Zn(CH₃COO)₂·2H₂O and 7.35 g urea were dissolved in 25 mL ethylene glycol and 20 mL water, respectively, to obtain a clear solution. On the other hand, 7.99 g SnCl₄ was dissolved in 50 mL ethylene glycol. The solution of Zn(CH₃COO)₂·2H₂O and SnCl₄ were mixed and the resulting solution was heated under continuous stirring for 4 h. Finally, when the solution temperature reached 130 °C, the solution of urea was added to the mixture of Zn(CH₃COO)₂·2H₂O and SnCl₄. The mixture was further refluxed at 180 °C for 4 h yielding a white precipitate. The resulting suspension was then cooled to room temperature and the obtained precipitate was subsequently collected by centrifugation, washed several times with ethanol, and finally dried at 110 °C overnight. The dried particles were then crushed by mortar and pestle. Annealing of the dried sample in air at 500 °C for about 2 h led to white powder of heterostructure SnO₂/ZnO nanoparticles with molar ratio of SnO₂ : ZnO 1 : 1. Pure SnO₂ and ZnO were synthesized by adopting similar procedure.

Characterization of photocatalysts

To determine the phase structures and crystallite size of the heterostructure SnO₂/ZnO nanocatalyst powder, XRD measurement was carried out by X-ray diffractometer (model 3040XPert PRO, Philips) using Cu K α radiation. A continuous scan mode was used to collect 2θ data from 10° to 80°. The average crystallite size of the powder was determined from the diffraction peak widths using Scherrer's formula. Transmission electron microscopy was performed using a Jeol JEM 2100Plus (Jeol, Tokyo, Japan) operating at an acceleration voltage of 200 kV (wavelength $\lambda = 2.51$ pm). For the TEM sample preparation, the photocatalyst powders were dispersed in ethanol using ultrasonic bath and a small droplet of the suspension was placed on holey carbon (Cu) grid. Upon drying, the samples were lightly coated with carbon to avoid charging under the electron beam. Nitrogen adsorption-desorption measurements were carried out with an ASAP2020PLUS micromeritics equipment on samples degassed at 120 °C under vacuum. The specific surface areas (S_{BET}) were calculated by applying the Brunauer-Emmett-Teller (BET) equation between 0.1 and 0.3 relative pressures.³⁰

The nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature (77 K) taken P/P_0 from 0 to 0.99. Pore size distributions were evaluated by the Barrett-Joyner-Halenda (BJH) model applied to the adsorption branch of the isotherms. X-ray Photoelectron spectra were recorded using Thermo Scientific K-Alpha⁺ XPS (Thermo Fisher Scientific, UK). Monochromatized X-ray ($K\alpha$: 1486.61 eV) from an Al anode used for excitation. The charge effect was evaluated using the main component of the C 1s peak, associated with adventitious hydrocarbons with a binding energy of 285.0 eV as reference for calibration. The base pressure in the sample during the measurements was less than 5×10^{-8} mbar. UV-vis diffuse reflectance spectra (UV-vis DRS) of the samples were measured at room temperature in the wavelength range of 200-800 nm using an UV-vis-NIR spectrometer LAMDA 750 (PerkinElmer, Inc., USA). Sintered PTFE was used as standard reference.

Photocatalytic experiment

The photocatalytic activities of the as-synthesized SnO₂/ZnO nanocomposites, SnO₂, ZnO nanoparticles as well as commercial TiO₂ (Degussa, P25) were evaluated by the photo-degradation of MB in aqueous solution under UV irradiation using 125 W high pressure mercury lamp (Model: MBFU 125 W E27, OSRAM). Photocatalytic experiments were conducted in a reactor system consisting of UV lamp placed horizontally over a 250 mL Pyrex glass beaker. Cooling water circulation was maintained outside the glass beaker to keep the temperature inside the beaker at 25 °C. In each experimental run, 0.1 g of photocatalyst was added to 100 mL of MB dye solution and the resulting suspension was stirred under dark for 30 min to establish adsorption-desorption equilibrium prior to irradiation. The degradation process of MB was assessed by sampling 4 mL solution at appropriate irradiation time intervals. The concentrations of MB of upper clear liquid after centrifugation were obtained using a UV-vis spectrophotometer (UV-1650, SHIMADZU, Japan) by monitoring the absorbance at 664 nm. A blank experiment without photocatalysts but with UV irradiation was also performed. The degradation efficiency was defined by the ratio C/C_0 , where C_0 is the initial concentration of MB at $t = 0$ and C is the concentration at degradation time t . We used the same conditions to recycle and reuse the catalysts for three batches.

COD analysis

Complete mineralization of MB dye was tested by determining chemical oxygen demand (COD) of the MB solution after photocatalytic degradation using photometer (Photometer MD 600, Lovibond, Germany). In a typical procedure, 0.2 mL of sample solution was added to Lovibond COD tube test for the COD in the range 3-150 mg L⁻¹. After adding the sample to Lovibond COD tube test, it was sealed and heated in the reactor (Lovibond RD 125) for two hours at 150 °C. After digestion, the tube was allowed to cool to room temperature and subsequently the COD of the sample was analysed in the photometer. Photometer was calibrated by a blank sample before measuring the COD of the



sample. Blank sample was prepared by adding distilled water to the reagent tube test instead of sample.

Results and discussions

Characterization of nanoparticles

XRD analysis. The crystal structure and phase composition of pure ZnO, SnO₂ and SnO₂/ZnO nanocomposite was investigated by XRD analysis (Fig. 1). XRD pattern of pure ZnO and as-synthesized SnO₂/ZnO nanocatalyst exhibited the diffraction peaks at $2\theta = 31.74^\circ, 34.49^\circ, 36.22^\circ, 47.52^\circ, 56.57^\circ,$ and 62.85° which could be indexed to the planes (100), (002), (101), (102), (110), (103) and (112), respectively, of the ZnO crystal as in the standard data file (JCPDS, card no. 36-1451).²¹ The observed diffraction pattern was a characteristic of crystalline ZnO having hexagonal wurtzite structure. Obvious diffraction peaks for SnO₂ and SnO₂/ZnO samples at $2\theta = 26.6^\circ, 33.9^\circ, 38^\circ, 51.8^\circ$ and 57.9° , corresponded to (110), (101), (200), (211) and (002) planes, respectively, of tetragonal rutile (cassiterite) structure of SnO₂ which was in good agreement with the JCPDS file of SnO₂ (JCPDS card no. 41-1445).²² No extra peak was detected in the

XRD of ZnO, SnO₂ and ZnO/SnO₂ which indicated the complete decomposition of precursors to ZnO, SnO₂ and SnO₂/ZnO.

The average crystallite size of the as-synthesized samples was calculated from the XRD line broadening measurement using the Debye-Scherrer's formula as follows:⁶²

$$D = (0.9\lambda)/(\beta \cos \theta_B) \quad (1)$$

where D is the average grain size, λ is the wavelength of Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$), β is the full width at half maximum (FWHM) for the diffraction peak under the consideration (radian) and θ is the diffraction angle ($^\circ$). The width of the diffraction peaks of pure SnO₂ (Fig. 1c) was considerably broadened, indicating a small crystalline domain size. The crystallite size of SnO₂ powders determined from (110) crystalline plane using Debye-Scherrer's equation was about 4.40 nm. On the other hand, the diffraction peaks of ZnO (Fig. 1a) were sharper indicating highly crystalline nature of ZnO nanoparticles. The mean size of the crystallite of ZnO corresponding to (101) diffraction peak was 14 nm which indicates that the ZnO is more easily crystallized on calcination and consequently tends to have large grain size than that of SnO₂. The average size of the crystallite of ZnO (18.75 nm) in SnO₂/ZnO was larger than that of pure ZnO. These results were agreed with the literature results that the addition of SnO₂ causes an increase in crystallite size of ZnO and that ZnO restrains the growth of SnO₂ crystal.^{48,63}

TEM analysis. The crystallite/particle size, the crystallinity and the morphology of the as-synthesized samples prepared by polyol method were further examined by TEM. Fig. 2 shows the TEM and HRTEM images of the SnO₂/ZnO nanocomposite (with SnO₂ : ZnO molar ratio 1 : 1). As observed in TEM image (Fig. 2A), the shapes of SnO₂ and ZnO in SnO₂/ZnO nanocomposite are spherical and SnO₂/ZnO nanocomposite is composed of aggregated ZnO and SnO₂ nanoparticles, the size of ZnO being larger than that of SnO₂. These results were in good agreement with results obtained from XRD analysis. A large number of small pores were also observed between the nanoparticles implying mesoporous SnO₂/ZnO heterostructures. The lattice plane fringes of the SnO₂ and ZnO

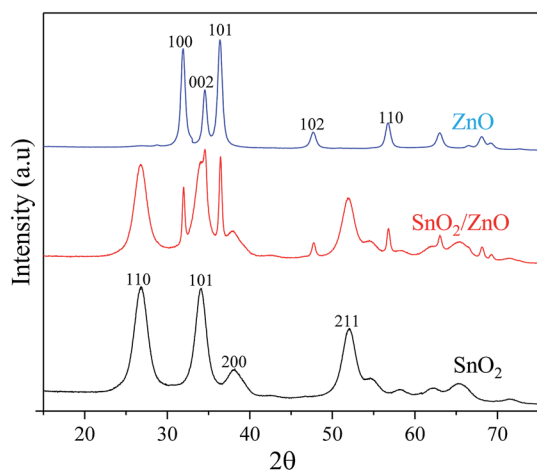


Fig. 1 XRD patterns of as-synthesized samples calcined at 500 °C.

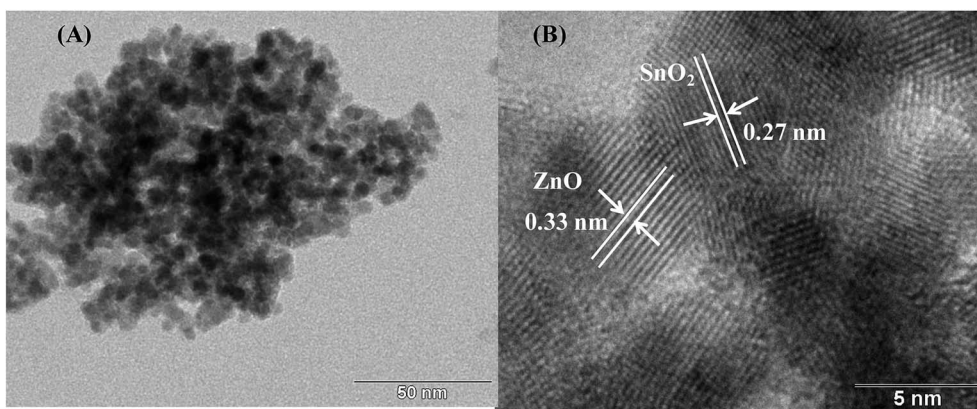


Fig. 2 (A) TEM image and (B) HRTEM image of SnO₂/ZnO nanocomposite.



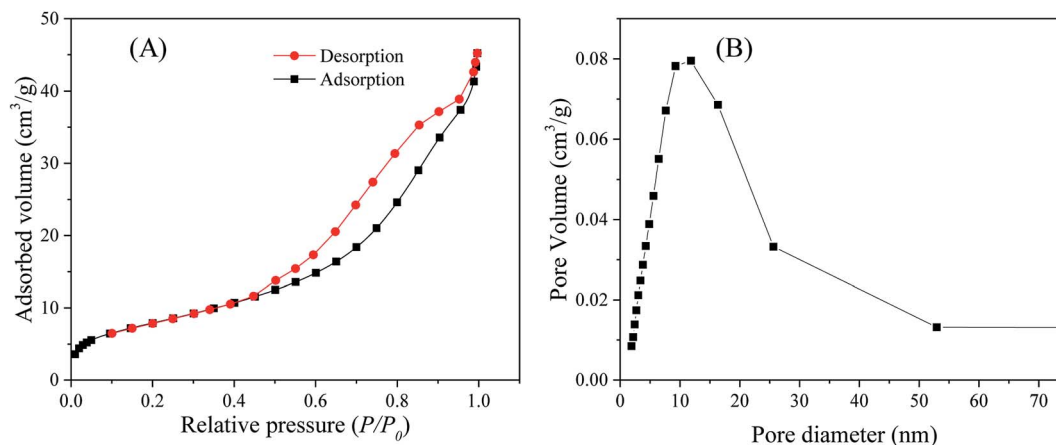


Fig. 3 (A) Nitrogen adsorption–desorption isotherms and (B) pore-size distribution of the SnO₂/ZnO photocatalyst.

nanoparticles were used to calculate the *d*-spacing values, and they were compared with those of bulk SnO₂ and ZnO, indicating the formation of SnO₂ and ZnO nanocrystals. As observed in Fig. 2B, the distances between the two lattice planes for SnO₂/ZnO nanoparticles were around 0.33 and 0.27 nm, which correspond to the *d*-spacing of the (110) plane of tetragonal SnO₂ and the (100) plane expected for the hexagonal wurtzite ZnO, respectively.

N₂ adsorption–desorption analysis. N₂ adsorption–desorption measurements at liquid N₂ temperature (77 K) were conducted to determine the specific surface area and the pore size distribution of the as-synthesized ZnO, SnO₂ and SnO₂/ZnO nanoparticles. The N₂ adsorption–desorption isotherms of the SnO₂/ZnO nanocomposite shown in Fig. 3A exhibited a type IV curve accompanied by a type H2 hysteresis loop, indicating typical mesoporous materials according to the IUPAC classification. The H2-hysteresis loop also designated the presence of pores of nonuniform sizes and shapes, characteristic of solids consisting of particles crossed by nearly cylindrical channels or made by aggregates (consolidated) or agglomerates (unconsolidated) of spheroidal particles.⁶⁴ Similar isotherms were observed for ZnO and SnO₂ shown in Fig. S1.†

The textural properties, namely BET surface area, mean pore diameter and total pore volume of as-synthesized ZnO, SnO₂ and SnO₂/ZnO nanoparticles are given for comparison in Table 1. The ZnO photocatalyst possessed BET surface area of 22.5 m² g⁻¹ with mean pore diameter and total pore volume of 14 nm (within mesopore region) and 0.14 cm³ g⁻¹, respectively. On the other hand, the BET surface area and mean pore

diameter of SnO₂ were found to be 52.1 m² g⁻¹ and 6.9 nm, respectively.

The mesoporous SnO₂/ZnO nanocomposites exhibited lower BET surface area than that of SnO₂ nanoparticles. The SnO₂/ZnO nanocomposites possessed BET surface area of 30 m² g⁻¹ and total volume of pores less than 193 nm diameter at *P/P*₀ = 0.99 of 0.068 cm³ g⁻¹. The pore size distribution of SnO₂/ZnO nanocomposites (BJH model applied to the adsorption branch of the sorption isotherm) was rather large, *i.e.* from 2 to 50 nm, with an adsorption average pore diameter of 8.8 nm (Fig. 3B).

XPS analysis. To investigate the chemical composition and the chemical state of the elements of SnO₂/ZnO nanocomposites, XPS study was conducted and the results are shown in Fig. 4. The survey spectra of SnO₂/ZnO in Fig. 4A only shows the emissions of Sn, Zn and O with very weak emission line of C and no peaks of other elements were observed. The C signal can be attributed to the adventitious carbon-based contaminant which commonly exists for XPS. The survey spectra exhibited the emission lines of Sn 3d, Sn 3p, Sn 4d, Zn 2p, Zn 3s, and Zn 3p core levels and the auger peaks of Sn MNN, Zn LMM and O KLL. The high-resolution spectra of Zn, Sn, and O species are shown in Fig. 4B–D, respectively. For pure ZnO, the emission lines appearing in Fig. 4B were symmetric and centered at 1021.49 and 1044.59 eV, which were attributed to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively. Thus, it could be confirmed that Zn element existed mainly as the form of Zn²⁺ chemical states in the as-prepared samples.⁶⁵ The Zn 2p spectra of SnO₂/ZnO shown in Fig. 4B demonstrated two emission lines, Zn 2p_{3/2} emission line centred at 1021.4 eV and Zn 2p_{1/2} line centred at 1044.5 eV.

Both the emission lines were symmetric and the binding energy difference (23.1 eV) between the two peaks was in good agreement with the standard reference value of ZnO.⁶⁶ The estimated values of binding energies and the binding energy difference of the Zn 2p spectra confirmed the +2 oxidation state of Zn ions in SnO₂/ZnO nanocomposites.^{66,67} The Zn 2p peaks of SnO₂/ZnO were shifted towards lower binding energy. It was found that Zn 2p peaks were shifted to lower binding energies by 0.1 eV from their original values which were likely due to the

Table 1 Nitrogen sorption porosimetry studies of the as-synthesized SnO₂, ZnO and SnO₂/ZnO nanomaterials

Samples	BET surface area, m ² g ⁻¹	Mean pore diameter, nm	Total pore volume, cm ³ g ⁻¹
ZnO	22.5	14.0	0.14
SnO ₂ /ZnO	30.0	8.8	0.06
SnO ₂	52.1	6.9	0.10



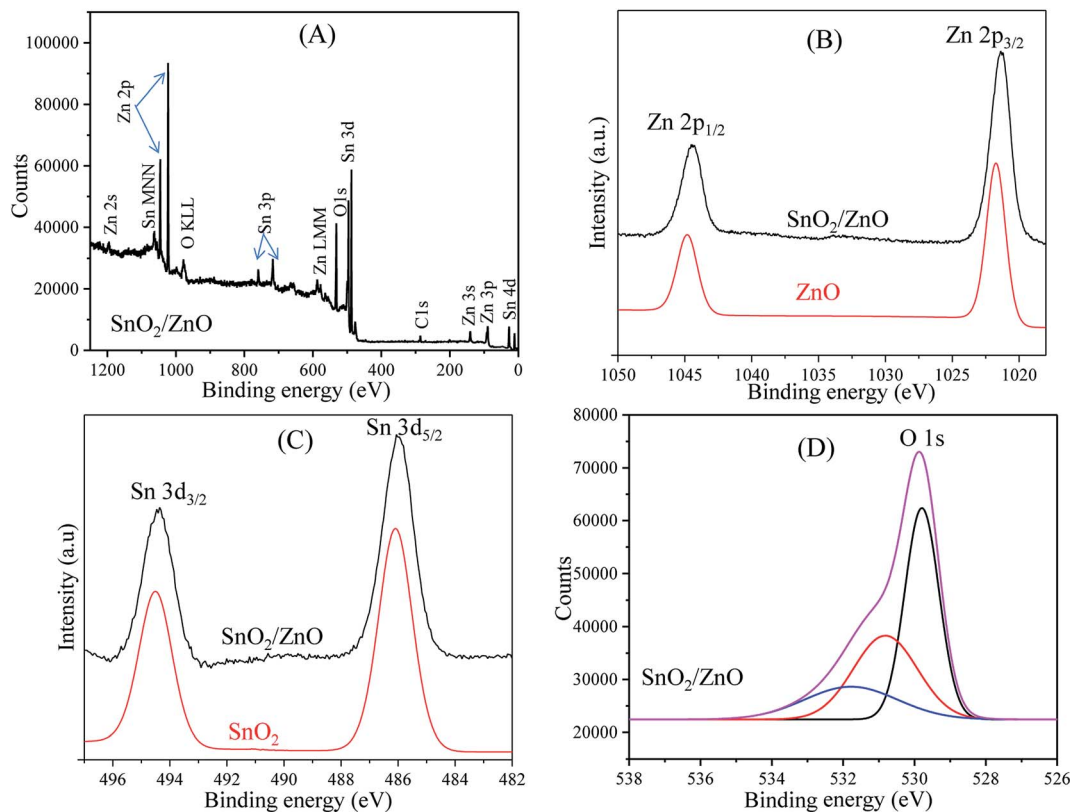


Fig. 4 XPS spectra of as-synthesized nanoparticles; (A) XPS survey spectra of SnO_2/ZnO sample, (B) Zn 2p region, (C) Sn 3d region and (D) O 1s region.

charge transfer at the interface of SnO_2/ZnO at thermal equilibrium. Fig. 4C shows the pronounced splitting of the Sn 3d emission into two symmetric peaks. The high resolution XPS spectra for Sn 3d of SnO_2 demonstrated the spin orbital splitting of the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ core level states of tin centred at 486.3 and 494.7 eV, respectively, which were symmetric and were assigned to the lattice tin oxide. The Sn 3d peaks of SnO_2/ZnO centred at 486.1 eV was attributed to Sn $3d_{5/2}$ and the other one at 494.4 eV to Sn $3d_{3/2}$, indicating a normal oxidation state

of Sn^{4+} in SnO_2 .⁶⁸ The shape of high resolution XPS spectrum of O 1s was asymmetric and broad exhibiting multi-component oxygen species in the as prepared sample (Fig. 4D). The O 1s peak could be de-convoluted into three symmetrical peaks centred at 529.79, 530.80, and 531.77 eV. The first peak at 529.79 eV was attributed to the lattice oxygen in Sn–O–Sn.^{69,70} The second peak at 530.80 eV was assigned to the lattice oxygen of ZnO.⁷¹ The higher binding energy at 531.8 eV was attributed to the chemisorbed oxygen on the surface of SnO_2/ZnO .⁷²

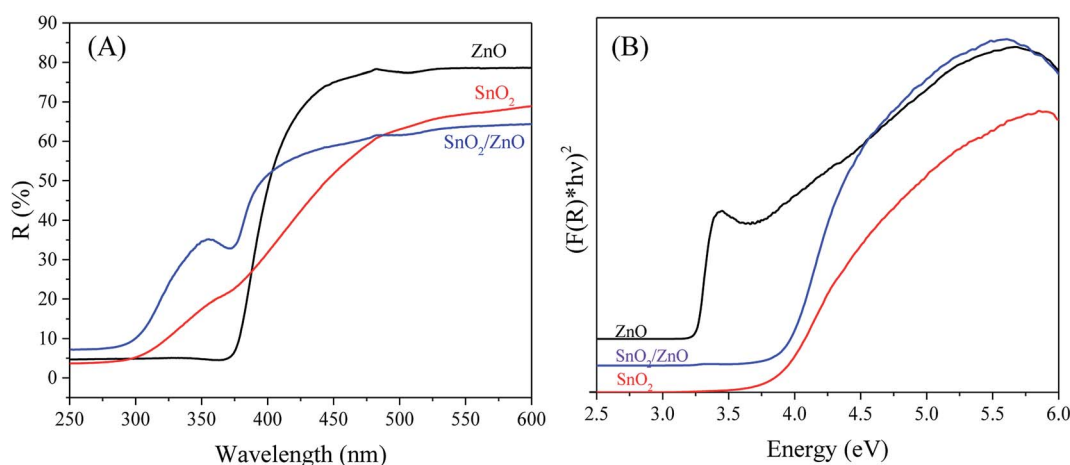


Fig. 5 UV-vis diffuse reflectance spectra (A) and plots of $(F(R)h\nu)^2$ versus photon energy ($h\nu$) (B) of SnO_2/ZnO sample calcined at 500 °C.

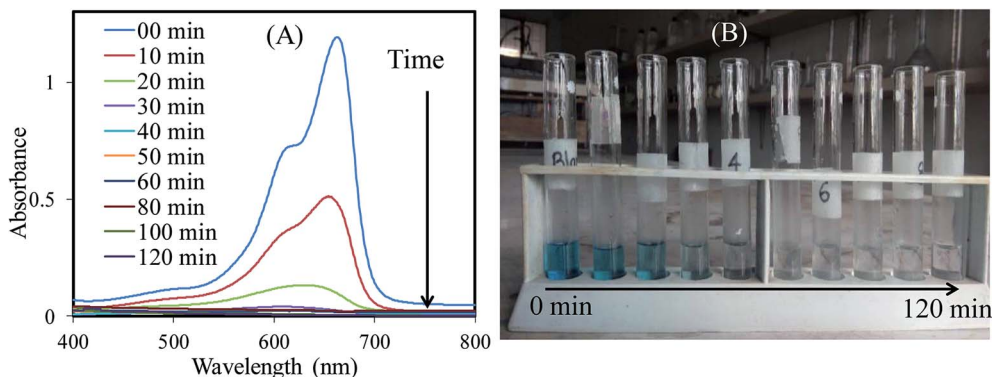


Fig. 6 Change in (A) absorbance and (B) color of MB solution with time under UV light irradiation in the presence of SnO_2/ZnO nanocomposite.

UV-vis DRS analysis. The optical absorption property of as-synthesized nanoparticles was examined by UV-vis DRS. When a semiconductor absorbs photons of energy larger than the band gap of the semiconductor, an electron is transferred from the valence band to the conduction band where there occurs an abrupt increase in the absorbency of the material to the wavelength corresponding to the band gap energy. The UV-vis DRS spectra of the as-synthesized samples are shown in Fig. 5A.

The pure SnO_2 and ZnO exhibited the characteristic spectra of SnO_2 and ZnO with their fundamental sharp absorption edges around 340 nm and 381 nm, respectively. The SnO_2/ZnO nanocomposite showed two absorption edges, at 385 nm ascribed to ZnO and at 345 nm attributed to SnO_2 . Considering direct band gap semiconductor, the band gap energies (E_g) of as-synthesized nanoparticles were calculated from the following equation: $\alpha(h\nu) = A(h\nu - E_g)^{1/2}$ where α , ν , E_g , and A are the absorption coefficient, light frequency, band gap energy, and a constant, respectively.⁷³ The energy band gap was estimated by extrapolating a straight line to the abscissa axis, where α is zero, for $E_g = h\nu$.⁷⁴ It is generally admitted that the absorption coefficient (α) can be replaced by the remission function $F(R)$. The later can be written in terms of diffused reflectance (R) according to the Kubelka–Munk theory: $\alpha/s = F(R) = (1R)^2/(2R)$ where s is scattering coefficient.⁷⁵ The band gap energies (E_g

values) of the as-synthesized samples can thus be estimated from a plot of $(F(R)h\nu)^2$ versus $(h\nu)$ (Fig. 5B), the intercepts of the tangents yielding the band gap energies of the as-synthesized samples. The calculated band gap energies of ZnO , SnO_2 and SnO_2/ZnO were found to be 3.25, 3.7 and 3.65 eV from the extrapolation of the corresponding plot.

Photocatalytic performance evaluation. To evidence the photocatalytic performance of SnO_2/ZnO nanomaterials, photocatalytic degradations of methylene blue (MB) were carried out as a test reaction under UV light irradiation. The time-dependent UV-vis spectra of MB during the UV light irradiation are illustrated in Fig. 6A. As depicted in Fig. 6A the maximum absorption peaks of MB at 664 nm diminished gradually and disappeared completely under UV light irradiation for 50 min in the presence of the SnO_2/ZnO nanomaterials. Meanwhile, the color of the solution changed gradually with time as well, suggesting that the chromophoric structure of MB was decomposed (Fig. 6B). Furthermore, blank experiments in the presence of UV light irradiation without photocatalysts were carried out to rationalize the photocatalytic activity of the as-synthesized SnO_2/ZnO photocatalysts.

In addition, the photocatalytic performance of pure SnO_2 , ZnO and commercial TiO_2 (P25) were investigated as reference in order to compare the photocatalytic activity of SnO_2/ZnO

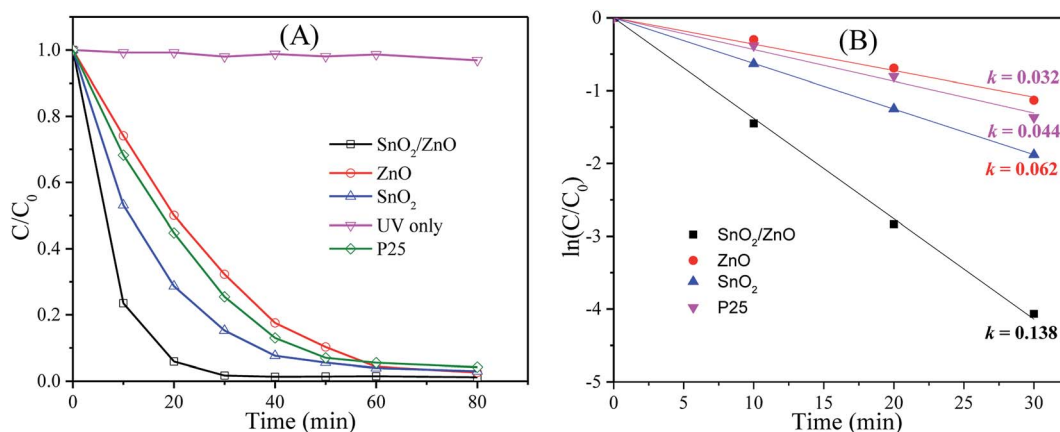


Fig. 7 (A) Photocatalytic degradation efficiencies of MB in presence of different photocatalysts under UV light irradiation, (B) kinetics of MB photocatalytic degradation ($\ln(C_0/C_t)$ versus irradiation time).



nanocomposite. All the photocatalytic experiments were carried out under identical condition. The degradation efficiency was defined as C/C_0 , where C_0 and C are the initial concentration after equilibrium adsorption and the concentration of MB at any time, respectively. The photocatalytic performances of different photocatalysts are presented in Fig. 7. It is obvious from Fig. 7A that MB was not decomposed under only UV light irradiation in the absence of photocatalysts. In contrast, SnO₂/ZnO nanocomposite (with molar ratio 1 : 1) exhibited higher photocatalytic degradation efficiency than that of the pure SnO₂, ZnO and P25. The efficiencies of SnO₂, ZnO and P25 for the photocatalytic degradation of MB were about 85, 68 and 75%, respectively, after 30 min UV light irradiation whereas the value of about 98% was achieved for SnO₂/ZnO nanocomposite indicating faster photodegradation rate of MB with SnO₂/ZnO photocatalysts. To get into insight of the photocatalytic efficiency of the as-synthesized SnO₂/ZnO nanocomposite, the kinetic analysis of MB degradation was discussed. It is well accepted that the photocatalytic decomposition of organic pollutants accords with a pseudo first-order kinetic rate law: $\ln(C/C_0) = -kt$, where k is degradation rate constant. A plot of $\ln C/C_0$ against reaction time t yields a straight line whose slope gives reaction rate constant, k . Fig. 7B shows the plots of $\ln(C/C_0)$ against t for different as-synthesized photocatalysts for the degradation of MB. As revealed in the Fig. 7B, the photocatalytic decomposition of MB followed pseudo-first order rate law and the SnO₂/ZnO nanocomposite had a higher photocatalytic activity than the pure SnO₂, ZnO and P25 nanoparticles, as evidenced by the larger value of k . The SnO₂/ZnO nanocomposite showed the highest photocatalytic activity with a degradation rate constant reaching 0.138 min⁻¹ for the degradation of MB, values 2.23, 4.31 and 3.14 times higher than those measured with SnO₂, ZnO and commercial TiO₂ P25, respectively.

The stability and reusability of the catalysts were evaluated by using the catalyst for three successive times. Fig. 8 shows the repetitive photodegradation of MB during three consecutive cycles. After each cycle, the SnO₂/ZnO nanocomposites was separated by centrifugation and washed with double distilled water and subsequently a fresh solution of MB was added before to prepare solution for the following runs. Thus, the photocatalytic efficiencies for the 3 cycling reuse were 98%, 97% and 93% after 30 min of reaction time, respectively. No significant change in the catalytic efficiency for the degradation of MB evidenced the stability and reusability of the catalysts. The structure stability of the SnO₂/ZnO photocatalyst after repeating photocatalytic tests was further confirmed by XRD analysis (Fig. S2†). According to Fig. S2,† all the diffraction peak lines of the used SnO₂/ZnO photocatalyst was in good agreement with that of fresh SnO₂/ZnO photocatalyst (Fig. 1) which demonstrated that the SnO₂/ZnO photocatalyst was stable after successive use.

It is well known that the activity of photocatalyst depends on many factors such as textural properties as BET specific areas, average pore size and the recombination of the photogenerated electron-hole.⁷⁶ The BET specific areas of SnO₂, ZnO and SnO₂/ZnO were found to be 45.1, 31 and 22.5 m² g⁻¹, respectively. It is reported that BET specific area of P25 is around 45 m² g⁻¹.^{77,78}

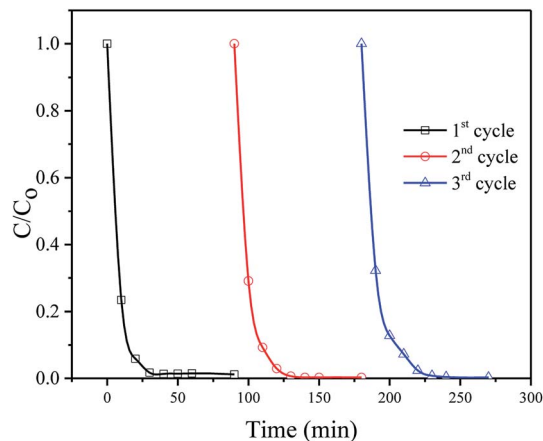


Fig. 8 Cyclic runs in the photodegradation of MB using the SnO₂/ZnO photocatalyst under UV-light irradiation.

Thus, the higher photocatalytic activity of SnO₂ than that of commercial P25 could be rationalized on the basis of the increased BET specific area. The improved photocatalytic activity might also arise from the coupling of semiconductors with different band gap favoring the electron-hole charge separation resulting from band offsets. As a consequence, the enhanced photocatalytic activity found for the SnO₂/ZnO heterostructure can be rationalized on the basis of the band alignment. In this context, the band-edge potential levels of the constituent semiconductors played a crucial role in determining direction of the flow of photoexcited charge carriers in the coupled semiconductors. It is reported that the conduction band (CB) edges of ZnO and SnO₂ are situated -0.2 eV and 0.00 eV, respectively, while the valence band (VB) edges of ZnO and SnO₂ are situated at 3.00 eV and 3.67 eV, respectively.^{79,80} Therefore, the conduction band and valence position of ZnO is higher (more negative) than the corresponding conduction and valence band position of SnO₂.^{45,46} Consequently, there exist conduction and valence band offsets by 0.2 eV and 0.67 eV, respectively, at the interface of heterostructured ZnO/SnO₂ nanocomposite. Recently, band alignment of ZnO/SnO₂ nanocomposite has been studied and conduction and valence band offsets were found to be 0.20 eV and 0.70 eV, respectively.⁴⁸ The conduction band (CB) edge and valence band (VB) edge of ZnO and SnO₂ can be calculated by Mulliken electronegativity equation as below:⁸¹

$$E_{CB} = \chi - E_e - 0.5E_g$$

$$E_{VB} = \chi - E_e + 0.5E_g$$

where χ is the electronegativity of the semiconductor, E_{VB} is the valence band edge potential, E_{CB} is the conduction band edge potential and E_g is the band gap energy of the semiconductor. The estimated band gap energy of ZnO and SnO₂ were found to be 3.25 and 3.7 eV, respectively. E_e is the energy of free electrons on the hydrogen scale (4.5 eV). The χ is 5.79 and 6.25 eV for of ZnO and SnO₂, respectively.^{81,82} The estimated CB and VB edges of ZnO were found to be -0.3 eV and 2.92 eV, and of SnO₂ were -0.10 eV and 3.6 eV, respectively. Based on this calculation and



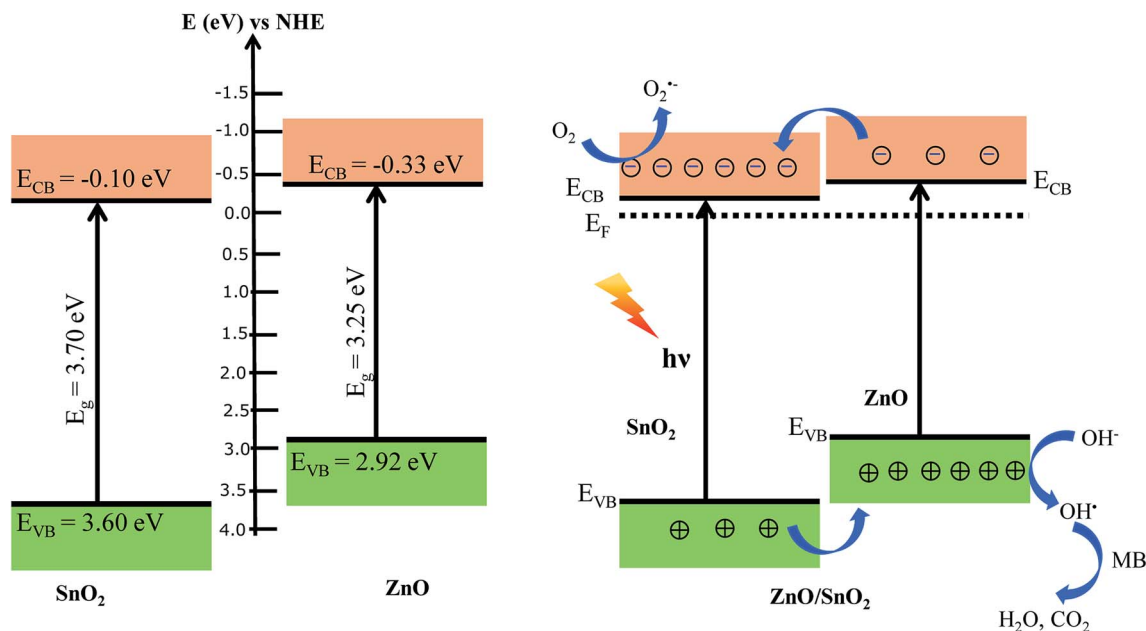
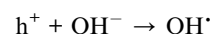
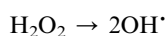
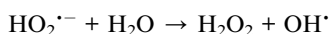
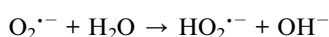
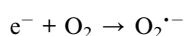
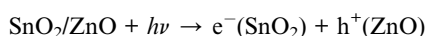


Fig. 9 Proposed schematic representation of band positions and the charge transfer process for the heterostructure SnO₂/ZnO photocatalyst.

considering the flat band potentials, the band alignment of ZnO/SnO₂ nanocomposite was proposed as in Fig. 9. As seen in Fig. 9, there exist energy gradient at the interface that tends to spatially separate electrons and holes on the different sides of the heterojunctions, where electrons may be confined to SnO₂ and holes to ZnO. The charge separation mechanism of heterostructure SnO₂/ZnO photocatalysts is also schematically described in Fig. 9. When heterostructure ZnO/SnO₂ photocatalyst was irradiated with UV light, electrons in the valence band (VB) were excited to the conduction band (CB) of both oxides with the concomitant generation of the same number of holes in the valence band. Photogenerated electrons were then injected from the energetically higher CB edge ZnO to the lower CB edge SnO₂. Simultaneously, holes were injected in the opposite direction due to appropriate valence band offsets. Thus, photogenerated electrons and holes were vectorially transferred to SnO₂ and ZnO, respectively, suggesting efficient charge separation and reduction of charge recombination. The efficient charge separation also increased the lifetime of the charge carriers and enhanced the efficiency of the interfacial charge transfer to adsorbed organic pollutants accounting for the higher photocatalytic activity of the SnO₂/ZnO nanocomposites.

The photocatalytic reaction process can be proposed as follows



The electrons in the conduction band of SnO₂ react with molecular oxygen adsorbed on the surface of SnO₂ to generate superoxide radicals anion (O₂^{•-}). The O₂^{•-} radicals further react with H₂O to produce OH[•] radicals. On the other hand, holes migrated to ZnO react with surface-bound hydroxyl groups (or H₂O) to produce the hydroxyl radical species (OH[•]) which is an extremely strong oxidant for the mineralization of organic chemicals as MB to degradation products like H₂O and CO₂.

COD analysis. The photocatalytic degradation of MB under UV light irradiation changes the solution to a colorless solution. The ultimate products of photocatalytic degradation of organic compound are CO₂ and H₂O. But visualization of color change does not indicate the formation of CO₂ and H₂O. Breaking of chromophore group of organic compounds by photodegradation

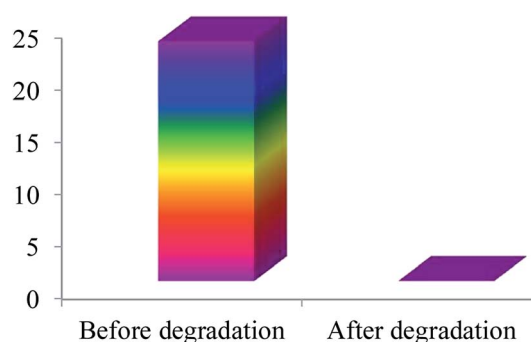


Fig. 10 COD values of MB before and after photocatalytic degradation with SnO₂/ZnO nanocomposite.



can generate low molecular weight colorless organic compounds. The presence of low molecular weight compounds resulting from the photocatalytic degradation of MB can be evidenced by COD analysis. According to the Fig. 10, the COD value of MB solution before UV irradiation was about 24 mg L⁻¹. In contrast, no COD value of the same sample was observed after photocatalytic degradation which indicated that the MB was completely mineralized to CO₂ and H₂O by the photocatalytic degradation with the as-prepared photocatalyst.

Conclusion

The heterostructure ZnO/SnO₂ nanocomposites have been successfully prepared by polyol method. The structural, morphological, optical, electrical, and photocatalytic performances of as-synthesized samples were evaluated. This heterojunction photocatalyst showed higher photocatalytic activity than the pure SnO₂, ZnO and reference commercial TiO₂ (P25) for the degradation of MB dye under UV light irradiation. The higher photocatalytic activity of SnO₂/ZnO nanocomposites was mainly attributed to improved separation of photogenerated electrons and holes resulting from band offsets developed at the interface of SnO₂/ZnO nanocomposites. Furthermore, the heterostructure SnO₂/ZnO photocatalysts could be easily recycled without scarifying catalytic activity which evidenced the stability of the catalysts and the reproducibility of the approach. This concept of semiconducting heterojunction nanocatalysts with improved photocatalytic activity should find industrial application in the future to wastewater treatment technologies as well as to remove undesirable organics from the environment.

Conflicts of interest

On behalf of all authors, the corresponding author declares that there is no conflict of interest.

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