Environmental remediation of wastewater containing azo dyes with a heterostructured nanophotocatalyst

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The synthesis, characterization and photocatalytic activity of heterostructured ZnO/TiO$_2$ nanophotocatalyst is reported. The photocatalyst ZnO/TiO$_2$ prepared in molar ratio of 1:9 (ZnO: TiO$_2$) and characterized with X-ray diffraction, SEM-EDX and UV–vis data. The photocatalytic activity has been evaluated using acid orange 7 as a model organic compound. The rate of decolorization has been estimated from residual concentration spectrophotometrically and mineralization rate studied by measuring COD. The results have been compared with TiO$_2$-P25 Degussa. ZnO/TiO$_2$ shows promising photocatalytic activity and 12% higher rate of decolourisation of the dye than that of TiO$_2$ -P25 Degussa. The effect of operational parameters such as pH of reaction medium and concentration of dye on the decolorization rate of AO7 in water has also been investigated. The efficiency of the photocatalyst is maximum at pH 7, an important aspect from the view of its commercial application in waste water treatment technology.

Keywords: Photochemistry, Photocatalyst, Dye degradation, Decolorization, Azo compounds, Wastewater

Human well being is threatened by high concentrations of pesticides, fertilizers, surfactants, dyes, phenols, heavy metals, hydrocarbons, chlorinated hydrocarbons, etc., present in the environment, usually dissolved in water as a result of low-to-medium contaminant concentration (<500 ppm) in industrial effluents. Rising demand for clean and healthy environment calls for novel methods of detoxification of industrial effluents containing organics of different origin. This has led to a flurry of research activities devoted to clean production and abatement technology in the last two decades, leading in some cases to the delivery of very severe regulations. “Advanced oxidation processes” (AOPs) are attractive remediation technologies for degradation and mineralization of organic pollutants in wastewater. Among these, heterogeneous photocatalysis using TiO$_2$ has emerged as an important destructive technology. TiO$_2$ (anatase), particularly P-25 (Degussa), has been reported to show high activity for photocatalytic degradation of organic substrates. However, widespread use of TiO$_2$ is uneconomical for large scale water treatment. Further, it demonstrates high activity only upon irradiation with ultraviolet light with wavelength between 300 and 400 nm, which represents only 5% of the solar spectrum. Thus, development of TiO$_2$-based photocatalysts with high activity has consequently emerged as a research area of considerable importance and urgency.

One approach to modify TiO$_2$ photocatalyst is to dope transition metals into TiO$_2$ while another approach is to form coupled photocatalysts. Various composites formed by TiO$_2$ and other inorganic oxides or sulfides have been reported. Daneshvar et al. reported that zinc oxide is a suitable alternative to TiO$_2$ for the degradation of Acid Red 14, an azo dye, since its photodegradation mechanism is similar to that of TiO$_2$. Lizama et al. reported higher photocatalytic efficiency of ZnO than TiO$_2$ in the color removal of Reactive Blue-19. The biggest advantage of ZnO is that it can absorb over a larger fraction of the UV spectrum; the corresponding threshold of ZnO is 425 nm. While TiO$_2$/ZnO as a film has also been prepared by different methods, no detailed study has been conducted on the relationship between the characteristics and photocatalytic activity of the film. Due to immobilization, the active surface area of the photocatalyst is dramatically reduced, in turn leading to a decrease in the activity. For improving photocatalytic activity and commercial applicability, nanosized photocatalyst can...
be a promising approach. The nanophotocatalyst has the potential for achieving better performance even with immobilized photocatalysts. The oxidation of methyl orange was reported using p-ZnO/TiO₂ prepared by ball milling of TiO₂ in H₂O solution doped with p-ZnO. However, the reported photocatalytic activity is much lower than that of TiO₂.¹⁶

Keeping in view the above, we have focused attention on developing a heterostructured TiO₂/ZnO nanophotocatalyst, having photocatalytic efficiency comparable to that of TiO₂ P-25. This may lead to a cost effective treatment technology for total mineralization of most of the organic pollutants including synthetic dyes. In the present study, a nanosized heterostructured ZnO–TiO₂ was prepared, characterized and its photocatalytic activity was evaluated using acid orange 7 as a model organic compound.

**Materials and Methods**

Titania P-25 (surface area 50 m²/g) was obtained from Degussa. TiO₂, Zn(NO₃)₂·6H₂O, ZnO (5 m²/g) and acid orange 7 were purchased from Merck and used without further purification. Doubly distilled water was used for the preparation of various solutions. The pH of the solution was adjusted with 1 M HCl or 1 M NaOH.

**Preparation and characterization of nanosized photocatalysts**

The nanosized heterostructured ZnO/TiO₂ photocatalyst was prepared using TiO₂ and Zn(NO₃)₂·6H₂O as starting materials, with NaOH as the precipitant without further purification. Zn(NO₃)₂·6H₂O was dissolved in a minimum amount of deionized water with constant stirring until a clear solution was obtained on addition of 1 M NaOH solution, white amorphous precipitates of Zn(OH)₂ were formed. Then the required amount of TiO₂ was added with constant stirring for the preparation of the heterostructured ZnO/TiO₂ photocatalyst with the Zn/Ti molar ratios of 1:9, by maintaining pH at about 7. The precipitate was stirred for 20 h for homogeneous mixing. The precipitate was filtered and washed with deionized water to remove the soluble ions. The wet powder obtained was dried at about 100 °C in air to form the precursor of the heterostructured ZnO/TiO₂ photocatalyst, which was further calcined at 250 °C in air for 3 h. The nanosized photocatalyst was obtained in powder form (labeled as ZT₉). ZnO (Z) was prepared using the same procedure from Zn(NO₃)₂·6H₂O alone.

X-ray powder diffraction (XRD) analysis of the heterostructured ZnO/TiO₂ photocatalyst powder was carried out at room temperature using a Rigaku D/max-III C diffractometer with Cu-Kα radiation (λ = 0.15418 nm), over 20 collection range of 20–100 °. The accelerating voltage of 40 kV, emission current of 30 mA and scanning speed of 4.4 counts/s were used.

UV-vis transmittance spectra were recorded in air at room temperature in the wavelength range of 200–700 nm using Perkin Elmer Lambda 750 UV\vis\NIR spectrophotometer. Microscopic features of catalyst were obtained by scanning electron microscopy (SEM, Hitachi-S-3400N) using fine catalyst powder supported on carbon tape and coated with gold. Elemental analysis was performed with energy dispersive X-ray (EDX) spectroscopy.

**Photocatalytic studies**

Photochemical degradation experiments were carried out in specially designed double walled reaction vessels (vol. 500 mL) in the photoreactor equipped with five UV tubes each of 30 W (Philips) having wavelength 365 nm (see ref. 17 for experimental set up). The intensity of UV light was 2.4 × 10⁶ einstein/ min measured by potassium ferrioxalate actinometry.¹⁸ The temperature was maintained constant throughout the reaction time by circulating water in the jacketed wall reactor. Photocatalytic experiments were performed by irradiating 100 mL of dye solution with required amount of the photocatalyst. The aqueous suspension was magnetically stirred throughout the experiment. At different time intervals, an aliquot was taken out with the help of a syringe and then filtered through Millipore syringe filter of 0.2 µm. Then the absorption spectra were recorded on a UV–vis spectrophotometer (Shimadzu 1600 series). The rate of decolorization was observed in terms of change in intensity at λ_max of the dye. The decolorization efficiency (%) was calculated as:

\[
\text{Decolourization efficiency (\%) = } \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

where C₀ is the initial concentration of dye and C is the concentration of dye after photoirradiation. Similar experiments were carried out by varying the pH of the solution (pH 2–10) and concentration of dye (5–50 ppm). The pH meter (Thermo Orion 920A) was used to adjust the pH of the solution. The mineralization rate was studied by COD analysis using Thermo Orion Aqua Fast II AQ 2040 COD meter.
Results and Discussion

Characterisation of catalyst

The prepared heterostructured TiO$_2$/ZnO photocatalyst (ZT$_9$) was characterized by XRD, SEM, EDX and UV-vis transmittance spectroscopy. The X-ray diffraction pattern of prepared sample (ZT$_9$) is shown in Fig. 1. From the XRD pattern and corresponding characteristics 2$\theta$ values of the diffraction peaks, it can be confirmed that TiO$_2$ is in rutile form having tetragonal structure as the peaks matched with Joint Committee Powder Diffraction Standards (JCPDS) card number 21-1276 while ZnO is in zincite phase (JCPDS card number 36-1451). The low intense peaks of ZnO observed in the XRD pattern of ZT$_9$ are due to small proportion of ZnO. The average crystallite size of ZT$_9$ was calculated to be about 22 nm using the Scherrer equation

$$t = \frac{K \lambda}{B \cos \theta},$$

where $K$ is a coefficient = 0.9, $\lambda = 0.1541$ nm, $B$ is the full width half maximum (FWHM) of the catalyst and $\theta$ is the diffraction angle.

The energy band gap of sample has been calculated according to the equation widely adopted for crystalline semiconductors

$$\alpha h\nu = A (h\nu - E_g)^n/2,$$

where $\alpha$, $\nu$, $A$, $E_g$, and $n$ are the absorption coefficient, incident light frequency, constant, band gap, and an integer (normally equal to 1, 2, 4, or 6), respectively. The $\alpha$ and $\nu$ values at the steep edges of the transmission spectra were used to construct the plots of $(\alpha h\nu)^{1/2}$ against photon energy. The band gap of the sample was determined by the intersection of the extrapolated linear portion of the plot with the energy axis. The calculated band gap value was found to be 3.06 eV.

The structure and morphology of the ZT$_9$ photocatalyst was studied using scanning electron microscopy operated at 15 kV of accelerating voltage. Figure 2 shows the SEM photograph of the ZT$_9$ under 15000X magnification. The coupled photocatalyst, ZT$_9$, consists of nanosized particles and their size seems to be less than 100 nm. The nanorods of ZnO are uniformly distributed between the TiO$_2$ nanoparticles. The nanoparticles aggregate to form flowery clusters. The stoichiometry of the compound formed was confirmed by energy dispersive X-ray spectroscopy, a chemical microanalysis technique used in conjunction with SEM. A typical EDX pattern of the ZT$_9$ is shown in Fig. 3. The elemental composition of the catalyst was found to be 10.18 % Zn and 89.82 % Ti, which confirms that ZT$_9$ consists of ZnO and TiO$_2$ in the molar ratio of 1:9. Also, that the particles are quite homogeneously distributed in the heterostructured nanophotocatalyst formed.

Photocatalytic activity

The photocatalytic activity of the synthesized heterostructured nanophotocatalyst (ZT$_9$) was studied
using AO7, an azo dye, as the model organic compound. AO7 was subjected to photodegradation in presence of ZT9 and UV light. The time-dependent UV-vis spectra of AO7 during the irradiation are illustrated in Fig. 4. The spectrum of AO7 shows peaks at 311 nm, 256 nm and 230 nm in the UV region and a main band with a maximum at 484 nm in the visible region. The absorption peaks corresponding to the dye in the visible as well as in the UV region diminished during photodegradation with the ZT9/UV photocatalytic system, which indicates that the dye has been decolorized and degraded with time. No new absorbance peak appeared in either the visible or ultra-violet regions. The effect of pH on decolorization efficiency of the photocatalyst was studied, by varying pH from 2-10 for constant dye concentration (25 ppm) and catalyst loading (1 g/l) under UV light. The colour removal efficiency of photocatalyst was studied as a function of pH. The photodecolorization efficiency of ZT9 increased with increase in pH and was observed to be maximum at pH 7 (81.09%), and then decreased with further increase in pH. The photocatalytic decolorization of AO7 was carried out by varying the initial concentrations of the dye from 5-50 ppm to study the effect of concentration of dye. Results clearly show that with increase in initial concentration of dye (5-50 ppm), the percentage decolorization of AO7 decreases (21.26 %) with ZT9 indicating that either the catalyst dose should be increased or time span has to be increased for the complete removal. The percentage change in COD was studied for dye samples (initial concentration 25 mg/L) under optimized conditions (ZT9 catalyst dose 1 g/L, pH 7, time 150 min.). The percentage COD reduction was 77.63 % in 2.5 h. The COD reduction is less than the percentage decolorization which may be due to the formation of smaller organic compounds as the reduction of chemical oxygen demand reflects the extent of degradation or mineralization of organic species. Therefore, it appears that to achieve complete mineralization of dye, longer irradiation time is required.

Comparison of photocatalytic activity

In order to compare the photocatalytic efficiency of different catalysts, identical experiments were carried out with TiO2 Degussa, ZT9, ZnO prepared and TiO2 commercial (Merck) on decolorization of acid orange 7. These experimental results show that the coupled oxide ZT9 has higher photocatalytic efficiency (81.09 %) than ZnO prepared (39.98 %) or TiO2 Merck (26.14 %). At the same time, better photocatalytic efficiency of ZT9 has also been observed than Degussa P25 TiO2 (69.09 %). The decolorization rate of AO7 using ZT9 as a photocatalyst is faster than that using TiO2, ZnO, or Degussa P25 TiO2 as a photocatalyst by 54.95, 41.11 and 12 %, respectively. The results clearly indicate that ZT9 is found to be most active in decolorization of acid orange 7. The better decolourization efficiency of ZT9 may be explained on the basis of smaller crystallite size (22 nm). When the catalyst grain size is reduced down to a few nanometers, an elevated density of active sites for substrate adsorption and/or catalysis can be guaranteed, as small crystallite size possess a significantly higher surface-to-volume ratio as compared to the bulk material. Previous work has also confirmed that the concentration of dye in solution decreased more rapidly with a decrease in the crystallite size of photocatalysts. Another possibility of absorption of more light quanta as its determined band gap (3.06 eV) is less than either of TiO2 Degussa (3.14eV) or ZnO (3.2eV)\(^{23}\). The higher photocatalytic activity of TiO2/ZnO nanophotocatalyst is also related to the vectorial transfer of electrons and holes, which takes place in coupled semiconductors possessing different redox energy levels for their corresponding conduction and valence bands. The electron transfer occurs from the conduction band of light-activated ZnO to the conduction band of light-activated TiO2 and, conversely, hole transfer can take place from the valence band of TiO2 to the valence band of ZnO. This efficient charge separation increases the lifetime of the charge carriers and enhances the efficiency of the interfacial charge transfer to adsorbed substrates\(^{24}\). The order of photocatalytic activity of various

![Fig. 4—Time dependent UV absorption spectra of AO7 during photocatalytic reaction. [AO7: 25 ppm; pH: 7; ZT9:1 g/L, 1, 0 min; 2, 30 min; 3, 60 min; 4,90 min; 5, 120 min; 6, 150 min; 7, 180 min; 8, 210 min].](image-url)
photocatalysts for acid orange 7 is: \( \text{ZT}_9 > \text{TiO}_2 \) Degussa > ZnO prepared > TiO\(_2\) ordinary.

**Conclusions**

Nanosized heterostructured ZnO/TiO\(_2\) photocatalyst in a molar ratio of 1:9 (ZT\(_9\)) was prepared using TiO\(_2\) and Zn (NO\(_3\))\(_2\)-6H\(_2\)O as starting materials. The phase structure, morphology and elemental composition of ZT\(_9\) were studied with XRD, SEM and EDX. The band gap as calculated from UV-vis transmittance spectroscopy and XRD studies show that nanocrystals were formed with TiO\(_2\) in rutile form and ZnO in zincite form. The heterostructured ZT\(_9\) has a crystal size of 22 nm and band gap of 3.06 eV. Nanosized ZT\(_9\) heterostructured catalyst has better photocatalytic activity than either of the semiconductor photocatalysts, ZnO or TiO\(_2\). The photocatalytic decolorization rate of AO7 on ZT\(_9\) at pH 7 is faster than commercially available photocatalyst (TiO\(_2\)-P25 Degussa) by 12%. COD analysis reveals that 77.63% COD reduction takes place in 2.5 hours, while for complete mineralization of the dye, longer irradiation time is required. The synthetic heterostructured nanophotocatalyst gave encouraging photocatalytic activity for degradation of AO7, showing a higher rate of decolourisation of dye than commercially available TiO\(_2\)-P25 Degussa). The present study may be extended to other organic pollutants present in wastewater streams, thus applied for wastewater purification.

**References**