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Environmentally Benign Organic Dye Conversion under UV Light through TiO₂-ZnO Nanocomposite

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Abstract: In this work, we developed a very simple and novel approach for synthesizing TiO₂-ZnO nanocomposites via the urea-assisted thermal decomposition of titanium oxysulphate and zinc acetate at different weight ratios. The synthesized nanocomposite samples were studied by means of HR-TEM, XRD, STEM, UV-Vis DRS, PL and EDS. The observed results demonstrate that the TiO₂-ZnO nanocomposite consists of an anatase crystal phase of TiO₂ with a crystallite size of 10–15 nm. Combined characterization, including UV-Vis DRS, STEM, EDS and HR-TEM, revealed the successful formation of a heterojunction between TiO₂ and ZnO and an improvement in UV spectrum absorption. The photocatalytic activity was explored using MO degradation under ultraviolet light illumination. The results of the optimized TiO₂-ZnO nanocomposite show excellent photocatalytic activity and photostability over a number of degradation reaction cycles. In addition, the current approach has immense potential to be used as a proficient method for synthesizing mixed metal oxide nanocomposites.

Keywords: TiO₂-ZnO; urea; nanocomposite; combustion; photocatalysis

1. Introduction

The major pollutants released into the ecosystem due to increased population and industrialization have turned out to be an environmental concern. These pollutants have been converted into nontoxic as well as less toxic substances using various physical, chemical and biological techniques. Recently, advanced oxidative methods such as semiconductor metal oxide-based photocatalysis have received enormous attention for their effective degradation of pollutants present in air, water and soil. This technique is low cost, is environmentally friendly, can function at ambient reaction conditions and is useful for a wide range of pollutants [1–3].

Numerous metal oxides such as ZnO, TiO₂, Fe₂O₃, Ta₂O₅ and Bi₂O₃ have been used as photocatalysts for the degradation of various aqueous dye pollutants [4–8]. Among

the various metal oxides, TiO_2 has been used as a photocatalytic material with great potential due to its excellent photocatalytic activity, wide energy band gap (3.2 eV), nontoxic nature, chemical stability and cost effectiveness [9]. However, the main problem with TiO_2 is its wide band gap of 3.2 eV, which requires UV light for performing photocatalytic reactions [10].

To date, different approaches have been tested in order to improve the photocatalytic activity of TiO_2 such as cation and anion doping to alter the band gap, loading of noble metal nanoparticles and coupling with other semiconductor-based metal oxides/sulfides for the effective separation of photogenerated charge carriers [11–13]. The coupling of TiO_2 with different metal oxides such as CuO , NiO , Ta_2O_5 , Nb_2O_5 and ZnO shows a great enhancement in photocatalytic activity due to the increase in the lifetime of photogenerated charge carriers, the effective electron–hole pair separation and the modification of optical properties [14–18].

Among the various studied metal oxides, the coupling of ZnO with TiO_2 creates one of the most efficient photocatalysts because of the development of heterojunction structures. Notably, ZnO possesses a wide band gap of 3.37 eV, high electron mobility, large exciton binding energy (60 meV) and similar band gap energies to TiO_2 [19]. It is suggested that the formation of the type II heterojunction in the TiO_2 - ZnO composite might possibly facilitate the transfer of electrons from the conduction band (CB) of TiO_2 to the CB of ZnO under UV light irradiation. Consequently, the electron–hole recombination rate is suppressed and photocatalytic activity is enhanced [20]. Further, the TiO_2 - ZnO nanocomposite's activity can be enhanced by changing the synthesis method.

More recently, some methods have been developed for the fabrication of TiO_2 - ZnO nanocomposites including sol–gel, hydrothermal, atomic layer deposition and microwave methods [21–24]. Despite these advanced methods, these strategies possess some drawbacks such as the fact that they are time consuming and costly and involve hazardous substrates and complicated reaction procedures. In this regard, we have developed a thermal decomposition approach for the large-scale synthesis of the nanostructured TiO_2 - ZnO heterostructure as a rapid, easy, low-cost and eco-friendly technique. TiO_2 - ZnO nano-heterostructures were prepared by varying the ZnO concentration, and we studied their photocatalytic performance towards the degradation of aqueous methylene blue dye. To the best of our knowledge, this thermal decomposition approach for the one-step synthesis of TiO_2 - ZnO nano-heterostructures is the first attempt of its kind and could be the easiest possible method.

2. Experimental Section

2.1. Materials

Titanium oxysulphate ($\text{TiOSO}_4 \cdot \text{H}_2\text{O}$) zinc acetate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$) and urea (CON_2H_4) were purchased from Sigma-Aldrich (Bangalore, India). Methyl orange purchased from Molychem (Mumbai, India) was of analytical grade and was used as received, without further purification.

2.2. Preparation of TiO_2 , ZnO and TiO_2 - ZnO Composite

TiO_2 and ZnO nanostructures were separately prepared using a urea-assisted thermal decomposition method in a similar manner to our previous report [25]. In the typical synthesis of the TiO_2 - ZnO nanocomposite, grinding of titanium oxysulphate, zinc acetate and urea was carried out for 15 min using a mortar and pestle. The obtained powder was heated at 600 °C in a muffle furnace with a heating rate of 15 °C per minute for 3 h. Then, the final product was washed with distilled water (DW) and dried in the oven at 80 °C. The obtained products were finally ground into a fine powder in a mortar and pestle. TiO_2 and ZnO were also synthesized with the addition of urea and denoted as TU and ZU, respectively. The precursors (titanium oxysulphate and zinc acetate) had weight ratios of 0.95:0.05, 0.90:0.10, 0.85:0.15, 0.80:0.20, 0.75:0.25 and 0.70:0.30 and were denoted as TZU95,

TZU90, TZU85, TZU80, TZU75 and TZU70, respectively. The as-prepared products were used for further characterization.

2.3. Characterization

The crystalline structures of the as-prepared TiO₂ and ZnO nanomaterials and TiO₂-ZnO nanocomposites were identified by the X-ray diffraction technique (Pan analytical diffractometer, Almelo, The Netherlands) using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$), which provides detection limits in the range of 0.1 to 1 wt.% per phase. With the help of field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800 with an accelerating voltage range of 10.0 kV), field-emission transmission electron microscopy (Titan G2 ChemiSTEM Cs Probe, FEI Company, Hillsboro, OR, USA) the morphological features of the samples were investigated. The chemical composition and element allocation in a selected area were analyzed by scanning transmission electron microscopy elemental mapping using an X-ray energy-dispersive spectrometer (Titan G2 ChemiSTEM Cs Probe, FEI Company, Hillsboro, OR, USA). The absorption profile and band gap of the composites were studied using a UV–Vis spectrophotometer (Shimadzu, Model-UV-3600, Kyoto, Japan), and photoluminescence spectra (PL) were analyzed using a spectrofluorophotometer (JASCO, Model FP.750, Tokyo, Japan).

2.4. Evaluation of Photocatalytic Performance

The photocatalytic activities of TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70 were evaluated by observing the degradation of methyl orange (MO), as an organic dye, at room temperature. For this purpose, 0.1 g of the photocatalyst was dispersed in 100 mL of aqueous solution with 20 ppm of MO dye. A Philips HPL-N (Amsterdam, Netherlands, 250 W, wavelength range of 200–600 nm) lamp was utilized as a UV–visible light source, at room temperature. Before the irradiation, the reaction mixture was stirred (on a magnetic stirrer) in the dark for half an hour, in order to achieve adsorption–desorption equilibrium between the methyl orange molecules and catalyst samples.

At definite time intervals, 3 mL of solution was removed, and the catalyst was separated by centrifugation. The concentration of the dye solution was quantitatively calculated by monitoring the absorbance of MO at 464 nm through the UV–Vis spectrophotometer (Shimadzu, Model-UV-3600, Kyoto, Japan). The recyclability study was also carried out using the used catalyst by maintaining the same reaction conditions.

3. Results and Discussion

3.1. XRD Analysis

The crystalline structures of as-prepared materials were studied using XRD analysis. Figure 1 exhibits the XRD pattern of TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70. As shown in Figure 1, the characteristic peaks of TU, observed at $2\theta = 25.3^\circ$, 37.8° , 48.0° , 53.9° , 55.1° , 62.7° , 68.9° , 70.3° and 75.1° , correspond to the reflection planes of (101), (004), (200), (105), (211), (204), (116), (220) and (215), respectively, which indicates the formation of TiO₂ in the anatase phase and clearly matches with the reported pattern (JCPDS 21-1272) [25]. For the ZU sample shown in Figure 1, the characteristic peaks of ZnO appear at 31.63° , 34.29° , 36.32° , 47.54° , 56.72° , 62.83° and 67.93° and can be indexed to the planes of (100), (002), (101), (102), (110), (103) and (112), which indicates the existence of the hexagonal wurtzite structure of ZnO (JCPDS 36-1451) [26]. For the TZU95 and TZU90 nanocomposite samples, no characteristic diffraction peaks of ZnO are found; this may be because the lower weight ratio of the ZnO precursor is below the detection limit of XRD. On the other hand, the TZU85, TZU80 and TZU75 nanocomposite samples show the slight appearance of the characteristic peaks of wurtzite ZnO, ranging from 30° to 38° , which correspond to the reflection planes of (100), (002) and (101). XRD confirmed that the thermal decomposition of titanium oxysulphate, zinc acetate and urea is a very proficient method for the successful formation of the TiO₂-ZnO nanocomposite. In addition, no impurity peaks are observed in the TZU95, TZU90, TZU85, TZU80 and TZU75 samples, indicating

that the coupling of the TiO₂ anatase phase and the ZnO hexagonal wurtzite forms the TiO₂-ZnO nanocomposite. Furthermore, coupling of ZnO with TiO₂ in the TZU95, TZU90, TZU85, TZU80 and TZU75 samples still maintains the anatase phase of TiO₂. However, it should be noted that the TZU70 sample shows weak peaks at 28.8°, suggesting the formation of a new Zn₂TiO₄ phase [27].

Figure 1. XRD patterns of TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70.

The crystallite sizes (D) of the TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70 samples were calculated using Scherrer's equation [28].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where ' λ ' indicates the wavelength of the X-ray employed, ' θ ' stands for the angle of diffraction for a more intense diffraction peak and ' β ' stands for the full width at half maximum of the most intense diffraction peak (FWHM). The diffraction peak (101) was

used to calculate the crystallite sizes of the samples. The crystallite sizes of the TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70 samples are about 14, 13.9, 12.8, 15.2, 14.8, 15.3, 13.3 and 15 nm, respectively.

3.2. Structure and Morphological Analysis

The morphology and structure of the TiO_2 -ZnO nanocomposite were studied using SEM, EDX, HRTEM and STEM. Figure 2a–d portray the SEM images of the TZU75 nanocomposite with various magnifications. It can be clearly seen that the TZU75 nanocomposite is composed of porous and aggregated nanoparticles (NPs) of TiO_2 and ZnO. In addition, spherical-shaped NPs are interconnected which may lead to interfacial interaction and to the formation of a heterojunction between TiO_2 and ZnO NPs.

Figure 2. SEM images of (a–d) TZU75 nanocomposite.

Figures 2a–d and 3a–d show the SEM and TEM images of TZU75, which reveal no distinct boundary between the TiO_2 and ZnO phases; this might be because of the similar structure and morphology of the TiO_2 and ZnO NPs. For further proof of the existence of the nanocomposite, TEM was used to examine the morphology of the samples. Figure 3a–d show that TiO_2 NPs with ZnO are found in the form of interconnected, aggregated, spherical, slightly hierarchical and porous NPs with a higher surface area. The size of the NPs is well within the range of 10 to 30 nm and, notably, matches with the XRD results. HR-TEM, STEM and elemental mapping of the TZU75 nanocomposite were carried out to check the presence of Zn and Ti. Lattice fringes of 0.356 and 0.262 nm, measured in the HRTEM image of the TZU75 sample, correspond to the interplanar distances of the (101) and (002) crystallographic planes of TiO_2 and ZnO, respectively [29]. Furthermore, the elemental mapping (Figure 3e–h) demonstrated the uniform distribution of Ti, O and Zn atoms throughout the nanocomposite. Interestingly, the elemental mapping showed that the ZnO NPs consistently spread over the entire surface of the TiO_2 nanostructure, signifying the formation of the nano-heterostructure.

Figure 3. (a,b) TEM, (c,d) HRTEM and (e) STEM images and the corresponding (f–h) elemental mapping of the TZU75 nanocomposite.

3.3. Optical Properties

The activity of the photocatalyst is highly dependent on the absorption of light together with its quantity and wavelength. To investigate the optical properties, we used UV–Vis diffuse reflectance spectra for the TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70 samples. As shown in Figure 4, TU and ZU exhibit pronounced absorption in the UV region. Remarkably, the addition of ZnO to TiO₂, the TZU75 nanocomposite exhibited increased absorption in both the UV and visible regions, which is ascribed to the transfer of electrons from the valence band (VB) to the conduction band (CB) [30]. The successful formation of TiO₂–ZnO heterojunctions reduces the recombination rate of the photoinduced electron–hole pair and enhances the photocatalytic activity of the TiO₂–ZnO nanocomposite.

3.4. PL Spectra

Photoluminescence (PL) spectra were implemented to study the recombination rate of the photoinduced electron–hole pair and the scope of charge separation. The photoluminescence spectra of the photocatalysts had an excitation wavelength of 295 nm for TiO₂ and the TiO₂–ZnO nanocomposite, at room temperature, as depicted in Figure 5. The PL spectra depict two broad emission peaks centered at 410 and 470 nm, which correspond to the high rate of electron–hole pair recombination or band edge emission, and to oxygen vacancies, respectively. However, in the TiO₂–ZnO nanocomposite, the PL intensity of the TZU75 nanocomposite was considerably reduced with the introduction of ZnO and the formation of the TiO₂–ZnO heterojunction which has interfacial charge transport from TiO₂ to ZnO, or vice versa.

Figure 4. UV-Vis diffuse reflectance spectra of TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70.

Figure 5. Photoluminescence (PL) spectra of TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70.

Due to this, the electron–hole pair recombination rate extensively decreased, and the photocatalytic activity of the TiO₂-ZnO nanocomposite increased.

3.5. Photocatalytic Degradation of Methyl Orange Using UV–Visible Light

The photocatalytic performances of TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70 were independently evaluated for the degradation of aqueous methyl orange as a pollutant in the presence of a UV–visible light source. The quantity of the aqueous MO solution was calculated from the absorbance ($\lambda_{\text{max}} = 464 \text{ nm}$), using UV–Vis spectra. The percent photodegradation ($D\%$) of MO under UV light irradiation over the photocatalyst was estimated using the following equation:

$$D\% = \frac{(C_0 - C)}{C_0} \times 100\% \quad (2)$$

where C and C_0 are the final and initial concentrations of MO, respectively. The photocatalysis by the as-prepared photocatalysts for MO degradation under UV light illumination is exhibited in Figure 6a–b. The photocatalytic activity of MO is 79.0, 70, 8, 87, 90, 94, 99.1 and 88% for TU, ZU, TZU95, TZU90, TZU85, TZU80, TZU75 and TZU70, after being irradiated with UV light for 60 min. It was found that TZU75 showed a much better performance than its counter parts TU (79.03%) and ZU (70%) within 60 min, which is ascribed to the constructive heterojunction and interfacial contact between TiO₂ and ZnO. It should be noted that the TU and ZU photocatalysts exhibit lower photocatalytic efficiency due to the higher recombination rate of the photogenerated electron–hole pair. Moreover, the photodegradation performance increased with the increasing content of ZnO, due to the formation of the effective heterojunction and the inhibition of electron–hole pair recombination [31]. However, when the ZnO content was exceeded in TZU70, there was a saturation value and the overall heterostructure was unstable, leading to a decrease in the effective charge transfer process in the heterostructure and a decrease in photocatalytic efficiency [29].

Figure 6. Photocatalytic activity of MO solution over TZU75 under UV light irradiation: (a) absorbance against wavelength; (b) degradation against irradiation time.

The most noteworthy principles of a perfect photocatalyst in a real-world application are its photostability and recyclability. To verify the photostability of the TZU75 nanocomposite, a number of reaction cycles were performed for the degradation of MO under the same reaction conditions. As shown in Figure 7, after five reaction cycles, the TZU75

nanocomposite did not display any noteworthy loss of activity. It was observed that the MO photocatalytic activity dropped to 6% after five consecutive reaction cycles. This result indicates that the TZU75 nanocomposite shows good photostability and recyclability.

Figure 7. Reusability of TZU75 for MO degradation under UV light irradiation.

On the basis of the above result, the comprehensive plausible mechanism for the photodegradation of MO dye over the $\text{TiO}_2\text{-ZnO}$ nanocomposite is delineated in Scheme 1. As per the process of the photodegradation of the dye, the photocatalytic activity of the $\text{TiO}_2\text{-ZnO}$ nanocomposite correlated to the formation of a suitable type II heterojunction between the interface of ZnO and TiO_2 , with band gaps of 3.37 eV and 3.2 eV, respectively. Under UV–visible light illumination, both ZnO and TiO_2 were excited and produced electrons (e^-) in the CB and holes (h^+) in the VB. More significantly, due to the establishment of the heterojunction between ZnO and TiO_2 , the CB level of ZnO is lower than the CB level of TiO_2 . Photogenerated e^- in the CB of TiO_2 have affinity to transfer into the CB of ZnO through the interface; conversely, photogenerated h^+ in the VB of TiO_2 could travel into the VB of ZnO [32]. This route could efficiently enhance the lifespan and separation ability of the photoinduced electron–hole pair. Consequently, the photoinduced and separated e^- in the VB of TiO_2 capture the surface-adsorbed molecular oxygen to form superoxide radicals ($\bullet\text{O}_2^-$), whereas the h^+ migrate into the VB of ZnO to oxidize H_2O and to generate hydroxyl radicals ($\bullet\text{OH}$). Finally, both $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals act as strong oxidizing agents to oxidize MO into carbon dioxide and water molecules.

Scheme 1. Plausible mechanism for the photocatalytic degradation of MO over TZU75 under UV light irradiation.

4. Conclusions

In summary, we rationally developed a simple, inexpensive and novel technique for the synthesis of TiO₂-ZnO nanocomposites, using a thermal decomposition method. The as-synthesized TiO₂-ZnO nanocomposite was employed for the photodegradation of methyl orange (MO) in the presence of UV–visible light illumination. The degradation study revealed that the TiO₂-ZnO nanocomposite showed superior photocatalytic activity to pure TiO₂ and ZnO. More importantly, the photocatalytic activity of the TiO₂-ZnO nanocomposite did not exhibit any noticeable decrease and remained stable even after five recycles. The remarkable photocatalytic activity can be ascribed to enhanced charge separation at the interface and to the formation of a heterojunction between TiO₂ and ZnO. It is hoped that our unique approach for the synthesis of mixed metal oxide heterostructure nanocomposites may open up a new opportunity for wastewater treatment.

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