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TiO$_2$–SnO$_2$ Nanocomposites for Photocatalytic Environmental Remediation under UV-Light

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Abstract: The photocatalytic removal of water contaminants for ecological systems has become essential in the past few decades. Consequently, for commercialization, cost-efficient, earth-abundant and easy to synthesize photocatalysts for dye degradation are of urgent need. We have demonstrated a simple and feasible approach for fabricating TiO$_2$–SnO$_2$ nanocomposite photocatalysts via urea-assisted-thermal-decomposition with different mass ratios. The as-synthesized materials were characterized by different physicochemical techniques. The phase formation and crystallite size were calculated by using XRD. The STEM, UV-Vis, DRS, HR-TEM and EDS revealed the effective formation of the heterojunction between TiO$_2$ and SnO$_2$, and enrichment in the UV-absorption spectrum. All synthesized materials were used for the photocatalytic degradation of methyl orange (MO) under UV light. The optimized results of the TiO$_2$–SnO$_2$ nanocomposite showed excellent photostability and photocatalytic activity over a number of degradation-reaction cycles of methyl-orange (MO) dye under the illumination of ultraviolet light. In addition, the recent method has great potential to be applied as a proficient method for mixed-metal-oxide-nanocomposite synthesis.

Keywords: TiO$_2$–SnO$_2$; urea; nanocomposite; combustion; photocatalysis

1. Introduction

Dyes play a prominent role in modern life, such as in clothes, beauty products, the paper industry, and foods [1]. Dyes are categorized into metal-complex dyes, functional dyes, azo dyes and reactive dyes [2]. They are organic compounds with functional groups R−N = N−R', R and R' substituents [3]. The methyl orange is a dye-containing the azo group, so it is called an azo dye [4,5]. These dye-industry wastes are considered toxic, poisonous and non-biodegradable. Generally, these wastes are discharged into rivers,
hence becoming the cause of serious water pollution [6,7]. In addition, it gives rise to various problems such as lower sunlight penetration into streams, toxic life for mammals, fishes and other sea life. Therefore, the main task in the present era is to reduce water pollution and have safe water for the ecological community. Towards this endeavor, the degradation of dyes is executed by various methods such as precipitation and adsorption, which involve oxidase and hydroxylase enzymes [8]. TiO$_2$ nanoparticles are considered to be the most efficient at reducing organic dyes due to their excellent features such as low cost, high reactivity and chemical stability [9,10]. Additionally, they exhibit high photostability, non-toxicity, and greater oxidation strength with good crystallinity, surface area, and crystallite size, and hence are used as semiconductor photocatalysts for water and air purification [11–15]. TiO$_2$ is present in the form of allotropes that are categorized as rutile, brookite and anatase. Amongst these, the anatase phase has more surface area and a high crystallinity, which increases photoactivity [16,17]. However, the band gap of TiO$_2$ (~3.2 eV) is quite large, which results in the fast recombination of the exciton and the lack of visible-light utilization, which in turn hampers its potential applicability as a photocatalyst at the commercial level. In this case, it is necessary to combine TiO$_2$ with another semiconductor metal oxide in order to reduce the fast recombination of excitons. SnO$_2$ semiconductors with a lower bandgap can trap the photogenerated charge carriers and decrease the recombination rate. SnO$_2$ mixed with TiO$_2$ increases the catalytic activity due to the generation of an intermediate band gap [18–20]. The photocatalytic efficiency depends upon the recombination rate of the electron-hole pair coming from the surface-charge transfer. The semiconductor decreases the recombination rate of the produced charge carriers, demonstrating the enhancement in photocatalytic activity [21–26]. The extensive use of the combination of TiO$_2$/SnO$_2$ as photocatalyst is due to its higher quantum yield. The effective separation of the electron-hole pair of photoionized compound is because of the different CB of TiO$_2$ and SnO$_2$ [27–29]. Most of the synthesis techniques for the preparation of the TiO$_2$/SnO$_2$ composites are complicated due to the addition of SnO$_2$, which in turn aids in decreasing crystallinity. Therefore, we converted the anatase to the rutile phase by using the combustion method with the suitable condition. The complex metal oxides such as TiO$_2$/SnO$_2$ photocatalyst were prepared by using the stearic-acid method [30,31].

Herein, we reported the convenient strategy for the preparation of TiO$_2$/SnO$_2$ nanocomposites through combustion method, which resulted in an anatase structure, high surface area, high crystallinity and excellent photocatalytic activity. In the present study, the TiO$_2$/SnO$_2$ nanocomposite showed enhanced photocatalytic activity towards the MO-dye degradation under ultraviolet-light irradiation.

2. Experimental

2.1. Materials

- Stannous chloride (SnCl$_4$·H$_2$O) (Merck, Mumbai, India), Titanium oxysulphate (TiOSO$_4$·H$_2$O) (Sigma Aldrich, Mumbai, India), Urea (NH$_2$CONH$_2$) purchased from Merck (Mumbai, India), and Methyl Orange (Molychem, Mumbai, India) of analytical grade were used.

2.2. Synthesis of SnO$_2$, TiO$_2$ Nanoparticles (NPs) and TiO$_2$–SnO$_2$ Nanocomposite

The SnO$_2$ and TiO$_2$ NPs were prepared following the urea-assisted combustion method as per our previous report [32]. The as-obtained TiO$_2$ and SnO$_2$ were represented as TU and SU, respectively. For the preparation of TiO$_2$–SnO$_2$ nanocomposites, the SnCl$_4$·H$_2$O, TiOSO$_4$·H$_2$O and NH$_2$CONH$_2$ were grounded into fine powders in mortar and pestle and subjected to heat treatment at high temperature (600 °C) with a heating rate of 15 °C/min for 3 h. The synthesized photocatalyst was washed away by utilizing the distilled water (DW) then dried in an oven at 110 °C. The fine powder was obtained by grinding this final product. Photocatalyst TiO$_2$–SnO$_2$ nanocomposites were obtained with different mass ratios of TiOSO$_4$·H$_2$O:SnCl$_4$·H$_2$O (0.950:0.050, 0.900:0.100, 0.850:0.150, 0.800:0.200,
0.750:0.250, and 0.700:0.300) and denoted as TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70, respectively.

2.3. Structural Characterization

The nanocrystalline structure of as-synthesized SnO$_2$ NPs, TiO$_2$ NPs and TiO$_2$–SnO$_2$ nanocomposites were studied with the help of XRD with CuKα radiation ($\lambda = 1.5406 \text{ Å}$) (Pan analytical diffractometer, Almelo, The Netherlands). The morphological features were analyzed by and scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM) (Titan G2 ChemiSTEM Cs Probe, FEI Company, Hillsboro, OR, USA). The elemental location and chemical composition of a particular selected area were analyzed with the help of scanning–transmission electron microscopy. The elemental mapping and X-ray energy-dispersive spectrometer (Titan G2 ChemiSTEM Cs Probe, FEI Company, Hillsboro, OR, USA) were useful for the analysis of chemical composition and elemental location in the particular area. The absorption of light by the photocatalyst was studied with the help of diffuse reflectance spectra (DRS) and UV-Vis’s spectrophotometer (LABINDIA Analytical UV-3092, Shimadzu, Model-UV-3600, Kyoto, Japan). The spectrofluorometer (JASCO, Model FP.750, Tokyo, Japan) was used for the identification of photoluminescence spectra (PL) of various synthesized materials.

2.4. Photocatalytic Degradation of Methyl Orange (MO) Dye

The photocatalytic activity of as-prepared samples (TU, SU, TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70) were measured under UV-light irradiation. In this experiment, 0.1 gm catalyst was mixed with 100 mL of 20 ppm aqueous MO solution. At room temperature, the reaction mixture was stirred (by using a magnetic stirrer) for half an hour before light irradiation. This was helpful for the formation of adsorption–desorption methyl-orange (MO) molecules for the equilibrium on the surface of the catalyst. At a specified interval of time, 3 mL solution was withdrawn. Quantitative determination of MO was performed by measuring the intensity of absorption peak using a UV-Vis spectrophotometer. For ultraviolet-light irradiation, Philips lamp HPL-N (250 W, Amsterdam, The Netherlands) was used as a light source. The UV-Vis spectrophotometer (Shimadzu, Model-UV-3600) was used for absorbance measurement of MO, and it was measured at 464 nm. In each run, distilled water was used for washing the separated photocatalyst. For monitoring MO recyclability, the washed photocatalyst sample was added to a fresh solution of methyl orange for the next cycle, and the absorbance of the MO was measured.

3. Results and Discussion

3.1. XRD Analysis

Figure 1 shows the XRD pattern of the as-synthesized photocatalyst such as TU, SU, TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70. The TU sample shows peaks at $2\theta = 25.3^\circ$, 37.7$^\circ$, 48.0$^\circ$, 53.9$^\circ$, 55.1$^\circ$, 62.6$^\circ$, 68.8$^\circ$, 70.3$^\circ$, and 75.1$^\circ$ that resemble the (hkl) planes of (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively. The observed peak is related to the anatase phase of TiO$_2$ (JCPDS 21-1272) [32]. Furthermore, the characteristics peaks of SnO$_2$ (SU) appear at 26.4$^\circ$, 33.7$^\circ$, 37.8$^\circ$, 51.6$^\circ$ and 61.7$^\circ$, which are indexed to the (hkl) planes of (110), (101), (200), (220) and (002), respectively. The SU shows the rutile tetragonal structure of SnO$_2$, and it is well matched with the JCPDS card number 77-0452.
Figure 1. XRD patterns of pure TiO\(_2\) (TU), pure SnO\(_2\) (SU) and TiO\(_2\)–SnO\(_2\) nanocomposites (TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70) synthesized by combustion method.

The XRD pattern of TSU95 and TSU90 does not show any typical diffraction peaks of SnO\(_2\) due to its minor weight ratio in the nanocomposites. In contrast, in the TSU85, TSU80 and TSU75 nanocomposites, the slight appearance of characteristic peaks of SnO\(_2\) in the range of 25–38° were observed, which correspond to the \((hkl)\) planes of (110), (101) and (200). No extra peaks were observed in any of the nanocomposites, which showed the successful coupling of the anatase TiO\(_2\) and the tetragonal SnO\(_2\). Hence the formation of the TiO\(_2\)–SnO\(_2\) nanocomposite is confirmed.

The crystallite size \((D)\) of all prepared composites was studied by applying Scherrer’s equation:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

where the wavelength of the X-ray is \(\lambda\), \(\theta\) is the angle of diffraction and \(\beta\) is the full width at half maximum (FWHM). The diffraction peak present at the (101) plane of all the samples was used for calculating the crystallite size. The crystallite size of the TU, SU, TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70 samples was observed to be 14, 25.96, 13.43, 14.05, 13.5,
13.75, 13.78, and 13.77 nm, respectively. The chemical composition, structural and optical parameters of the as-synthesized samples are summarized in Table 1. TiO$_2$ is the major component of the TiO$_2$–SnO$_2$ nanocomposite. When the concentration of Ti is increased in the source precursor, it can effectively prevent the accumulation of Sn, leading to the high dispersion of Ti and Sn, which prevents the agglomeration and particle growth. As a result, relatively small SnO$_2$–TiO$_2$ nanocomposites can be formed and the nanocomposites display a high surface area which is beneficial for catalytic application [33,34].

Table 1. Composition, Structural and Optical parameters of as synthesized samples.

| Sr. No | Sample | Weight Ratio of Precursors (mg) (TiOSO$_4$·H$_2$O:SnCl$_4$·H$_2$O) | Crystallite Size (nm) | Band Gap (eV) |
|--------|--------|---------------------------------------------------------------|----------------------|--------------|
| 1      | Pure TiO$_2$ (TU) | 1000 | 14 | 3.22 |
| 2      | Pure SnO$_2$ (SU) | 1000 | 25.96 | 3.5 |
| 3      | TSU95 | 950:50 | 13.43 | 3.25 |
| 4      | TSU90 | 900:100 | 14.05 | 3.23 |
| 5      | TSU85 | 850:150 | 13.5 | 3.25 |
| 6      | TSU80 | 800:200 | 13.75 | 3.03 |
| 7      | TSU75 | 750:250 | 13.78 | 3 |
| 8      | TSU70 | 700:300 | 13.77 | 3 |

3.2. Morphological and Structure Analysis of TiO$_2$–SnO$_2$ Nanocomposite

The structure and morphology of the as-synthesized TiO$_2$–SnO$_2$ nanocomposites were analyzed by using HRTEM, EDX, SEM and STEM. Figure 2a–f represents the SEM images of the TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70 nanocomposite at different magnifications. Figure 2d (TSU80 sample) shows well-aggregated, composed and porous nanoparticles (NPs) of SnO$_2$ and TiO$_2$ with sizes of 10–30 nm. The interfacial interaction and production of the heterojunction between SnO$_2$ and TiO$_2$ NPs contained spherical-shaped NPs.

Figure 2. SEM images of as-synthesized TiO$_2$–SnO$_2$ nanocomposites (a) TSU95, (b) TSU90, (c) TSU85, (d) TSU80, (e) TSU75 and (f) TSU70.
Figure 3a–d show the TEM images of the TSU80 sample recorded at different magnifications. Figure 3a shows a low-resolution TEM image of the TSU80 sample. From Figure 3b, it can be seen that the material has interconnected, porous, aggregated, and spherical NPs with sizes of 10–30 nm. Figure 3d depicts the high-resolution TEM image of the TSU80 sample. The crystallographic planes of SnO$_2$ show the interplanar distance of 0.26 nm (101) and 0.34 nm (110), respectively. On the other hand, the interplanar distance 0.356 nm was observed for TiO$_2$, which corresponds to the crystallographic plane (101) and is in good agreement with the XRD data. Furthermore, Figure 3e–h shows the elemental mapping that confirms the uniform distribution of Ti, Sn and O elements throughout the nanocomposite. They also show that the SnO$_2$ nanoparticles are uniformly spread over the surface of the TiO$_2$ nanostructure, which reveals the coupling of TiO$_2$–SnO$_2$. The SEM and TEM and images of the TSU80 sample reveal no separate boundary between the SnO$_2$ and TiO$_2$ phase because of the identical morphology and structure of the TiO$_2$ NPs and SnO$_2$ NPs.

3.3. Optical Properties

The photocatalytic activity mainly depends on the absorption of light and its wavelength. Figure 4a shows the UV-Vis diffuse reflectance spectra of the TU, SU, TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70 samples. From the Figure 4a, the remarkable absorption peaks can be observed. The optimized nanocomposites of the TSU80 sample show higher absorption in terms of UV and visible regions, which may easily be due to transferring the electron from the valence band (VB) to the conduction band (CB). Band-gap energies were calculated using the following equation

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

where $\alpha$ is the absorption coefficient, $A$ is a constant related to the effective mass of the electrons and holes, $E_g$ is the energy gap and $n$ is a constant related to the type of optical transition; $n = 2$ for indirect transition and $n = 1/2$ for the direct transition.

The estimated $E_g$ values from Tauc plots (Figure 4b) were found to be 3.22, 3.5, 3.25, 3.23, 3.25, 3.03 and 3 eV for TU, SU, TSU95, TSU90, TSU85, TSU80 and TSU75, respectively. The band-gap energy was reduced upon the combination of SnO$_2$ with TiO$_2$ due to the intimate interfacial interaction [33,35].
3.4. PL Spectra

Photoluminescence (PL) spectra were acquired to gain more insights into charge-carrier separation. The PL spectra of photocatalysts (TU, TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70) were measured at the excitation wavelength of 295 nm for TiO$_2$ and TiO$_2$–SnO$_2$ nanocomposite at room temperature as shown in Figure 5. The PL spectra depicts the two broad emission peaks centered at 410 and 470 nm, which are attributed to band-edge emission and oxygen vacancies, respectively. When the TiO$_2$–SnO$_2$ heterojunction was formed, the PL intensity of the TSU80 nanocomposite was drastically reduced, indicating recombination of the charge carrier is suppressed due to interfacial charge transport from TiO$_2$ and SnO$_2$ was reduced. This is advantageous for the improvement of the photocatalytic performances for the degradation of methyl-orange dyes under light irradiation.
3.5. Photocatalytic Degradation of Methyl Orange Applying UV Light

Photocatalyst performances of TU, SU, TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70 were evaluated for MO-dye degradation under UV-light irradiation. The photocatalytic performance was studied by monitoring the absorbance of MO (\(\lambda_{\text{max}} = 464\) nm) at regular intervals of time using UV-Vis spectroscopy. The degradation efficiency was estimated by using the following equation [36],

\[
D\% = \frac{(C_0 - C)}{C_0}
\]

where \(C_0\) is the initial concentration and \(C\) is the final concentration of methyl orange, respectively. Figure 6a depicts the relationship between irradiation time and MO-dye degradation in the presence of UV light by different photocatalysts. The degradation activity of the as-synthesized photocatalyst for MO degradation was found to be 79.03, 69.5, 84, 88, 92, 98, 95 and 90\% for TU, SU, TSU95, TSU90, TSU85, TSU80, TSU75 and TSU70, for 60 min of light irradiation. The produced TSU80 (~98\%) exhibited excellent photocatalytic activity than the pure-phase TU (79.03\%) and SU (69.5\%) over 60 min of light irradiation. This could be attributed to the intimate interfacial connection and the heterojunction effect between TiO\(_2\) and SnO\(_2\), which could greatly contribute to charge-carrier (electron/hole) separation and utilization. The degradation of MO was found to increase with an increase in the incorporation of SnO\(_2\); however, the excessive inclusion of SnO\(_2\) (>80\%) had a negative effect on the photocatalytic activity, indicating that TSU80 is an optimal catalyst. Figure 6b shows the UV-Vis-absorbance spectra for the degradation of MO dye using TSU80 catalyst.

![Figure 6](image-url)

The photostability and recyclability are vital factors for a photocatalyst to be applied for commercial applications. Therefore, the stability of the as-synthesized composites was evaluated under similar conditions by collecting the photocatalyst after measurement and reuse. As shown in Figure 7, the photocatalytic activity was retained to ~90\% after five successive cycles, demonstrating that these photocatalysts can be used multiple times.

The schematic representation illustrates the charge-transfer pathway on the TiO\(_2\)-SnO\(_2\) nanocomposite for photocatalytic MO-dye degradation (Scheme 1). Based on the above discussion and band-gap energy of SnO\(_2\) (rutile tetrahedral, 3.5 eV) and TiO\(_2\) (anatase, 3.2 eV), the TiO\(_2\)-SnO\(_2\) nanocomposite exhibits type II band alignment [37]. Upon light irradiation, both SnO\(_2\) and TiO\(_2\) excited the electrons from the valence band (VB) to the conduction band (CB) and created photoexcited holes (h\(^+\)) in the VB and electrons (e\(^-\)) in the CB. The TiO\(_2\) has a higher negative CB than that of SnO\(_2\), which is likely form heterojunction between the SnO\(_2\) and TiO\(_2\). The electrostatic field generated at the interfaces of TiO\(_2\)-SnO\(_2\) provides a driving force for the transfer of an electron from the CB of TiO\(_2\)
to the CB of SnO$_2$, as the CBM of TiO$_2$ is more negative than that of SnO$_2$. Meanwhile, the photogenerated holes (h$^+$) in the VB of SnO$_2$ transfer into the VB of TiO$_2$ [37]. This process increases the separation ability and lifespan of the induced electron-hole pairs. The formed charge carriers then migrate to the surface of SnO$_2$, capturing molecular oxygen that forms superoxide radicals (•O$_2^-$). Similarly, holes (h$^+$) in the VB of TiO$_2$ oxidize the H$_2$O, thereby producing hydroxyl radicals (•OH). These •OH and •O$_2^-$ radicals act as strong oxidizing agents towards the degradation of methyl orange in wastewater at an impressive reaction rate.

Figure 7. Reusability of TSU80 catalyst for degradation of MO dye under UV light irradiation.

Scheme 1. Schematic representation illustrating the charge-transfer pathway of TiO$_2$/SnO$_2$ (TSU80) nanocomposite for MO degradation under UV light irradiation.
From these results, it is evident that MO-dye degradation directly depends upon the dosage of Sn (IV). The Sn (IV) incorporation can efficiently increase the rate of photocatalytic reaction in the TiO$_2$/SnO$_2$ nanocomposite. The enhancement of photocatalytic activity depends on several factors. (i) The number of holes and photogenerated electrons are relatively low in pure TiO$_2$ due to a higher recombination rate, therefore the photodegradation of methyl orange requires more time. In the case of TiO$_2$/SnO$_2$, the degradation of MO was high due to due to increasing the separation of photogenerated holes and electrons. (ii) The calcination at high temperature (600 °C) is beneficial for the separation of holes and electrons because it greatly produces the photoactive phases such as anatase and rutile. (iii) The as-synthesized nanocomposite photocatalyst exhibits a higher specific surface area that can greater increase active-site exposure for the catalytic reaction than TiO$_2$.

4. Conclusions

In summary, an inexpensive, easy and simple combustion technique was used for the fabrication of a TiO$_2$–SnO$_2$ nanocomposite. The as-synthesized TiO$_2$–SnO$_2$ composite showed excellent photocatalytic efficiency for methyl-orange degradation under UV light irradiation compared to pure TiO$_2$ and SnO$_2$. The enhanced surface area of the nanocomposite enables higher MO-dye adsorption while type II band alignment at the interface leads to a reduction of unwanted electron hole recombination and likely enhance photoactivity (98.4%/60 min). This significant photoactivity was retained even after repeated use (five cycles), indicating possibility for practical applications in wastewater treatments. Thus, unique synthesis method developed in this study may lead to innovative designs of active photocatalysts for environmental remediation applications.

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