Controllable synthesis of SnO₂ photocatalyst with superior photocatalytic activity for the degradation of methylene blue dye solution

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ABSTRACT
SnO₂ photocatalyst was successfully synthesised by novel chemical route in hydrothermal environment and annealed at two different temperatures viz 550 and 600 °C, respectively. The crystal structure, optical properties, surface and bulk morphology have been characterised using various tools like X-ray diffraction (XRD), UV visible spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscope (TEM) and scanning electron microscope (SEM). Cubic, spheres and porous like morphology of SnO₂ photocatalyst was successfully confirmed using SEM micrographs and TEM. In addition to this the photocatalytic activity was evaluated towards the degradation of methylene blue dye solution. SnO₂ photocatalyst annealed at 600 °C exhibits excellent photocatalytic efficiency which may be attributed to the unique morphology, high crystalline nature and charge separation. The photocatalyst efficiency was further tested towards the concentration of dye, catalyst dosage and pH of the dye. The involvement of •OH in the photocatalytic reaction was evidenced using trapping experiment by employing different scavengers. The photocatalyst was moderately active, stable upto its fifth usage and stability of the photocatalyst before and after the photocatalytic reaction was also been studied using XRD and SEM.

1. Introduction

Environmental pollution by industrial waste water is a serious concern and the purification of the waste water is also being a growing threat of the current energy crisis.[1] Utilisation of solar energy to complete degradation of organic pollutants released from industry using highly effective photocatalyst has long been considered the ultimate solution. Since the semiconductor-based photocatalysis is an ambient temperature and green process which efficiently degrades the pollutants.[2] In the past few decades, metal oxides, [3–5] metal sulphides,[6] and bismuth-based [7] and Ag-based compounds [8] were
extensively developed for photocatalytic applications. Among different kinds of semiconductors, metal oxides were one of the attractive and promising materials owing to their abundance, low cost, non-toxicity and relatively high chemical stability.

SnO₂ is a typical n-type semiconductor material which possesses excellent optical, gas-sensing properties and chemical stability, which was widely used in sensors,[9] solar cells [10,11] and lithium ion batteries.[12] However, SnO₂ has been an excellent photocatalyst for the degradation of organic pollutants, water splitting and hydrogen production.[13,14] The quick recombination rate of the SnO₂ under UV light illumination is considered to be major drawback. Nevertheless, there are several efforts that have been made for the prevention of electron—hole pair recombination viz metal/metal oxide doping,[15] modified synthesis protocols,[16] unique morphology,[17] bandgap tailoring [18] and incorporation of chalcogens,[19] non-metal [20] and halogens.[21]

Morphology-based materials have attracted researchers and recently, many efforts have been devoted to synthesise three-dimensional SnO₂ nanostructures with unique morphology.[22–24] There are no reports available for the porous hollow spheres of SnO₂ photocatalyst by simple chemical method. Hence we made an attempt to develop a novel simple wet chemical route for the synthesis of porous hollow spheres of SnO₂ photocatalyst at different annealing temperatures for the photodegradation of methylene blue (MB) dye solution for the first time from the best of our authors. The prepared SnO₂ was characterised by X-ray diffraction (XRD), transmission electron microscope (TEM), scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectroscopy and UV visible spectroscopy (UV) and discussed in detail. The prepared SnO₂ photocatalyst exhibited improved photocatalytic performance towards the degradation of MB. The photocatalyst efficiency was further tested towards the dye concentration, catalyst dosage, light intensity and pH of the dye. The mechanism of the photocatalytic degradation of MB dye solution was evidenced using trapping experiment by employing different scavengers. The stability of the photocatalyst before and after the photocatalytic reaction was also being investigated extensively.

2. Experimental section

2.1. Preparation of photocatalyst

SnO₂ photocatalyst was synthesised by wet chemically induced self-assembly in the hydrothermal environment. Typically, certain amount of stannous chloride dihydrate (SnCl₂·2H₂O) was dissolved in 35 mL of deionised water containing 2.6 g of resorcinol to form a mixture. Afterwards, 3.4 mL of 35 wt% formaldehyde was added under vigorous stirring. The resulting mixture was then transferred to a 50 mL Teflon-lined stainless steel autoclave and heated in a drying oven at 85 °C for about 3 h. Once the autoclave was cooled to room temperature, the intermediate products were washed with distilled water and ethanol and dried at 55 °C for about 12 h in a hot air oven. Then, the intermediate products were annealed at 550 and 600 °C for 2 h respectively. Further, it was cooled to room temperature to obtain the final products. The SnO₂ photocatalyst prepared with different annealing temperatures was used as a photocatalyst.
2.2. Characterisation of photocatalyst

XRD was performed to examine the crystal structure of the SnO₂. Crystallinity of microspheres and effect of annealing temperature on crystallisation of microspheres were recorded with a Philips PW 1710 X-ray diffractometer (Eindhoven, The Netherlands) with crystal monochromated CuKα radiation (λ = 1.540598 Å) in the angular range of 10°–80° (2θ) with an accelerating voltage of 40 kV and a current of 20 mA. SEM was carried out with an (Model SUPRA 40 Scanning Electron Microscope) acceleration voltage at 3–5 kV with a working distance of 5–9 mm. Shimadzu diffuse reflectance UV Vis-2600 spectrometer was used to analyse the nanomaterials. FTIR spectrum was recorded in Shimadzu FTIR 8400.

2.3. Photocatalytic activity of the photocatalyst

The photocatalytic activity of SnO₂ was evaluated using Heber multi-lamp photo reactor, India. 50 mg of SnO₂ photocatalyst was added to 75 mL of the MB dye solution in 150 mL reaction vessel. At given time intervals, 5 mL of aliquots was collected. The degraded solutions were analysed using the absorption peaks at 664 nm. Prior to irradiation, the suspensions were magnetically stirred in the dark condition for 1 h to ensure the equilibrium of the working solution.

3. Results and discussion

3.1. Structural analysis

SnO₂ photocatalyst with different annealing temperatures was prepared by hydrothermal method. The phase and crystallographic structure of the prepared SnO₂ photocatalyst at different annealing temperatures (550 and 600 °C) were determined by XRD which is shown in Figure 1. The diffraction peaks of SnO₂ were indexed to the tetragonal structure and well matched with the standard JCPDS Card No. 88-0287. The diffraction peaks at the diffraction angles of 26.7, 33.9, 38.0, 39.05, 51.8, 54.8, 57.85, 61.9, 64.8, 65.9, 71.2 and 78.72 were ascribed to (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (311).

Figure 1. XRD patterns of as prepared SnO₂ photocatalyst annealed at 550 and 600 °C.
(202) and (321) planes indicating the crystalline nature of SnO$_2$ formation and it has been further cross checked with the literature.[25,26] Notably, the XRD pattern preferred (110) orientation which has the higher intensity suggested that the SnO$_2$ photocatalyst grown along the (110) plane. The intensity of the (110) orientation of SnO$_2$ at 600 °C is higher compared to that of SnO$_2$ at 550 °C which may due to the higher crystallinity.

The average crystallite size of the SnO$_2$ photocatalyst was determined by the full width at half maximum (FWHM) of the X-ray diffraction peak using Scherer’s equation as follows:

$$X_s = \frac{k\lambda}{\beta \cos \theta}$$  

where $X_s$ is the crystallite, $\lambda$ is the X-ray wavelength, $\beta$ is the FWHM of the diffraction peak, $\theta$ is the diffraction angle and $k$ is the Scherer’s constant of the order of unity. The average crystallite size was estimated by using the reflections of characteristic planes such as to (110), and the average crystallite size is 65.8 and 41.36 nm for samples prepared at 550 and 600 °C, respectively.

### 3.2. Morphological analysis

The surface morphology of the as synthesised SnO$_2$ photocatalyst at different annealing temperatures has been investigated by SEM which is shown in Figure 2. Figure 2(a) showed SnO$_2$ photocatalyst contains a porous surface with the average particle size of 500 nm and the interior of the porous structure contains small grains. Figure 2(b) is the SEM micrographs of SnO$_2$ photocatalyst annealed at 600 °C. It shows the smooth surface with the smaller porous area which indicates the SnO$_2$ photocatalyst was well grown at higher annealing temperature than in the low reaction temperature.

The surface morphology and particle size were further evidenced by TEM analysis which is shown in Figure 3. The TEM images of SnO$_2$ photocatalyst annealed at 500 °C
showed the aggregated particle which attached each other with a particle size of 200 nm (Figure 3(a)). Interestingly, SnO₂ photocatalyst annealed at 600 °C showed unique morphology with cube and sphere like structures which is shown in Figure 3(b) and 3(c) with an average diameter of about 22 nm. The surfaces were clean and clear which may be attributed to the high crystallinity of the sample.

3.3. Compositional analysis

The composition of the as synthesised SnO₂ photocatalyst was analysed by energy dispersive X-ray (EDX) analysis which is shown in Figure 4. The results clearly indicated that the SnO₂ photocatalyst contains Sn and O only with the weight percentage of 24.72% and 75.28%, respectively. No elements were present in the SnO₂ photocatalyst which suggested the purity of the photocatalyst. Furthermore, the elemental mapping of SnO₂ photocatalyst has also been carried out as shown in Figure 5, which showed the presence of Sn and O.
3.4. UV-visible diffuse reflectance spectra analysis

The determination of the band gap of the photocatalyst is a vital parameter for the selection of the right kind of light needed for the degradation of dye. The UV-visible (DRS mode) absorption spectra of SnO2 photocatalyst are shown in Figure 6 and there is a sharp absorption steep for SnO2 photocatalyst at 380 nm. Tauc’s relationship for optical band gap calculations for the photocatalyst is described by using the following equation:

\[
\alpha = \frac{A}{h v (h v - E_g)^{1/2}}
\]

where \(\alpha\) is the absorption coefficient of the semiconductor at a certain value of wavelength \(\lambda\), \(h\) is Planck’s constant, \(v\) is the frequency of light, \(A\) is a constant which is related to the effective masses associated with valence band (VB) and conduction band (CB), \(E_g\) is the gap between bottom of CB and top of VB. From the Tauc’s plot the band gap energy is calculated.

Tauc’s plot for the SnO2 photocatalyst is given in Figure 7, where \((\alpha h v)^2\) is plotted against the photon energy \((h v)\). The band gap energies are estimated from the extrapolated lines and the values are 3.37 eV for SnO2 at 550 °C and 3.41 eV for SnO2 at 600 °C.

3.5. Fourier transform infrared analysis

The structural information was further evidenced by FTIR spectra for the prepared SnO2 photocatalyst (600 °C) which are given in Figure 8. In general, the stretching vibration of metal–oxygen appeared in the range of 400–600 cm\(^{-1}\).[27] The stretching vibration mode of photocatalyst appeared at 470 cm\(^{-1}\).[28,29] The peaks observed at 534 and...
545 cm$^{-1}$ correspond to Sn–O bonds. The peak at 1040 cm$^{-1}$ is assigned to the stretching mode of O–O bond. No other bands are observed in the spectra which confirmed that only metal and oxygen functional groups are present.

3.6. BET analysis

The N$_2$ adsorption–desorption isotherms were studied for the SnO$_2$ synthesised at 600 °C which is shown in Figure 9. SnO$_2$ exhibited the type IV isotherm with an H3 type hysteresis loop in the range of 0.6—0.9 $P/P_0$, suggesting the mesoporous structures. These
mesopores should be formed by the agglomeration of SnO$_2$ nanocrystals. The increased surface area may be attributed to the small assembled hierarchical building blocks. Such type of hierarchical structure with a high surface area may be beneficial for applications as the catalysts for water treatments.

3.7. Adsorption of the dye solution on the photocatalyst surface

The adsorption experiment was carried out for the SnO$_2@550$ °C and SnO$_2@600$ °C to find out the adsorption efficiency of the photocatalyst. The adsorption of the dye solution on the photocatalyst is a paramount important fact which results in the dye sensitised effects.[30–33] Both SnO$_2@550$ °C and SnO$_2@600$ °C have some adsorption of the dye.
solution, but that was insignificant which is shown Figure 10. However, the SnO$_2$@550 °C showed a relatively higher adsorption capacity due to its amorphous nature.

### 3.8. Photocatalytic activity of SnO$_2$ photocatalyst

The photocatalytic activity of the SnO$_2$ photocatalyst was carried out by degradation of MB dye solution under UV light irradiation which is given in Figure 11. The complete degradation of the dye solution occurred within 50 min and the main absorption peak of MB at ($\lambda$) 664 nm nearly disappeared completely. After 50 min of irradiation, the value of $C/C_0$ reaches almost zero which also evidences the complete degradation of the dye solution. There was almost no degradation in the solution with and without catalyst in the dark. Interestingly, the dye does not adsorb on the surface of the catalyst.
Effect of annealing temperature causes significant enhancement in the efficiency of the photocatalytic degradation of MB solution which is shown in Figure 12. In the case of SnO$_2$ photocatalyst prepared at 550 °C, the rate of MB dye degradation is relatively low when compared to SnO$_2$ photocatalyst prepared at 600 °C. It is noted that the fast recombination rate of the photo generated electron—hole pairs will hinder the degradation of dyes.[34] The enhanced photocatalytic activity may be due to the small crystallite size and prevention of electron—hole recombination. However, SnO$_2$ hollow spheres increased the photocatalytic efficiency by increasing the charge separation and extended photo responding range. Moreover, the uniform morphology of SnO$_2$ photocatalyst also favours the transfer of both electrons and holes generated inside the crystal lattice and facilitates the degradation of dye solutions.[35]
3.9. Physicochemical factors that influence the dye degradation

This section examines the effects of various physicochemical parameters including light intensity, initial dye concentration and amount of photocatalyst on the degradation of the dye solution under UV light illumination for different lengths of time. To minimise the energy and chemical wastages, SnO$_2$ photocatalyst prepared at 600 °C which showed enhanced activity was used for further process.

The effect of initial MB concentrations on the photocatalytic degradation was investigated by varying MB concentrations from 1 to 20 ppm in the presence of 50 mg SnO$_2$ photocatalyst under UV light irradiation. As shown in Figure 13(a), the rate of MB photodegradation was increased while the MB concentration increased from 1 to 10 ppm. However, the MB photodegradation rate was not further increased and maintained at nearly a constant rate upon increasing the concentration of MB dye solution from 1 to 10 ppm concentrations. At a fixed light intensity, the decreased photodegradation rate of RhB was observed with an increased dye concentration which might be attributed to the greater amount of dye competing for the degradation and the reduction in the light intensity that reaches the SnO$_2$ photocatalyst surface. At very high concentrations (10–20 ppm), much of the light is screened by the solution and fewer photons are able to reach the SnO$_2$ surface. Thus, the generation of electron–hole pairs is greatly reduced and in turn the dye degradation is reduced due to absence of oxidising species.

The effect of photocatalyst dosage on photocatalytic degradation of MB dye solution in the presence of SnO$_2$ photocatalyst was assessed by varying catalyst dosage from 10 to 75 mg and the results are presented in Figure 13(b). The increment of photocatalyst dosage from 10 to 50 mg results in the increased photodegradation efficiency sharply from 50.50% to 99.45% after 50 min irradiation, whereas the photodegradation efficiency declines with further increase of photocatalyst dosage. The enhanced degradation rate with catalyst dosage is due to the increase of accessible active sites for MB degradation. However, further increasing photocatalyst amount may suppress the light transmission in the suspension system, leading to the lowered photo-irradiation on the photocatalyst surface and the obvious agglomeration of photocatalysts, thus to the reduction of utilisation rate of UV light. Therefore, 50 mg was optimised as the efficient photocatalyst dosage for photocatalytic reaction under our experiment conditions.

Figure 12. Percentage degradation of MB solution with the catalyst prepared annealed at 550 and 600 °C.
Before and after the photocatalytic reaction the pH of the dye solution is 5.0 and 7.3 respectively. The pH of the solution has been increased upon the photocatalytic reaction which suggested that the complete mineralisation of the dye solution has been achieved. Solution pH is one of the dominant parameters controlling photocatalytic degradation of dye-containing waste water by photocatalyst. Figure 13(c) showed the photocatalytic degradation of MB dye solution by SnO$_2$ photocatalyst at five pH values from 2 to 12. Obviously, increasing pH of the dye solution could decrease the degradation efficiency of MB dye solution by SnO$_2$ photocatalyst. The complete degradation (99.7%) of MB solution was obtained under UV light irradiation within 50 min at pH 2.0. However, 91.6% and 60.9% of MB dye solution was degraded within 50 min while pH of solution increased to 6.0 and 12.0, respectively. However, the rate of photocatalytic degradation of MB dye solution by SnO$_2$ photocatalyst at pH 2.0 is about 4.75 times higher than that at pH 12.0. The pH changes may influence the adsorption of dye molecules onto the photocatalyst surfaces, an important step for the photocatalytic oxidation to take place.[36]
3.10. **Detection of reactive oxidative species**

The effect of different scavengers on the photocatalytic degradation of MB dye solution was investigated to find out the reactive oxidative species involved in the mechanism as shown in Figure 14. The hydroxyl radical (•OH) scavenger, benzoic acid (BA) was used for the detection of involvement of •OH in the photocatalytic reaction.[37] It was found that the degradation rate of MB was suppressed upon addition of BA which suggested the involvement of •OH. Triphenylphosphene (TPP), azide ion (AZ) and acrylamide (AA) are the singlet oxygen generator and superoxide radical anion (O2−) quencher, respectively, which enhanced the rate of photocatalytic reaction preceded by the O2−.[38] In the present study, the rate of photodegradation was normal and there is no enhancement which confirmed the absence of O2− in the photocatalytic degradation of MB. Hence, the photocatalytic degradation was preceded by the involvement of •OH alone.

3.11. **Photocatalytic degradation mechanism**

On the basis of the experimental results and from the literature, the photocatalytic degradation mechanism of MB dye solution by the SnO2 photocatalyst under UV light irradiation was proposed by Equations (3) — (8).

\[
\begin{align*}
\text{SnO}_2 + h\nu & \rightarrow \text{SnO}_2(\hat{h}_{vb}^+) + \hat{e}_{cb}
\tag{3} \\
\text{SnO}_2(\hat{e}_{cb}) + \text{O}_2 & \rightarrow \text{SnO}_2 + \cdot \text{O}_2^-
\tag{4} \\
\cdot \text{O}_2^- + \text{H}^+ & \rightarrow \cdot \text{HO}_2
\tag{5} \\
\text{SnO}_2(\hat{e}_{cb}) + \cdot \text{HO}_2 + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2
\tag{6} \\
\text{H}_2\text{O}_2 + \text{SnO}_2(\hat{e}_{cb}) & \rightarrow \cdot \text{OH} + \text{OH}^-
\tag{7} \\
\text{OH}, \cdot \text{HO}_2, \cdot \text{O}_2^- \text{ Or } \hat{h}_{vb}^+ + \text{dyes} & \rightarrow \text{X, Y } \rightarrow \text{Z}
\tag{8}
\end{align*}
\]

X = peroxy derivatives  
Y = hydroxylated derivatives  
Z = degraded products

![Figure 14. Effect of different scavengers on the photocatalytic degradation of MB dye solution.](image-url)
Upon irradiation of photocatalyst by UV light an electron (e\text{cb}^-) in the VB was excited to the CB, and a hole (h\text{vb}^+) was generated in the VB simultaneously (Equation (3)). The electrons at the photocatalyst surface were inhibited by the ubiquitously present molecular oxygen to yield first the superoxide radical anion, \( \cdot \text{O}_2^- \) (Equation (4)). The superoxide radical anion \( \cdot \text{O}_2^- \) further combined with H to generate \( \cdot \text{HO} \) (Equation (5)). The \( \cdot \text{OH} \) radical can be formed from the trapped electron after formation of the \( \cdot \text{HO}_2 \) radical (Equations (7) and (8)). Lastly, the photocatalytic degradation of the dyes can take place through Equation (8). The active oxygen species (\( \cdot \text{OH}, \cdot \text{HO}_2 \) or \( \cdot \text{O}_2^- \) radicals) or the \( h\text{vb}^+ \) attacked the dyes, and the dyes were degraded gradually.[39] For example the basic dye adsorbs the proton and protonates and this protonation continues and the degraded products are obtained after the certain period of time.

The reaction kinetics follows pseudo first-order kinetics as indicated by the formation of straight line when a plot is made between logarithm of concentration ratio (\( \ln\frac{C}{C_0} \)) and irradiation time (\( t \)).

\[
k = \frac{\ln(C/C_0)}{t}
\]

\( k \) – rate constant  
\( C \) – absorption peak intensity of MB samples at each irradiated time interval  
\( C_0 \) – the absorption intensity of initial concentration  
\( t \) – time  

The rate of the reaction is highest for the SnO\(_2\) prepared at 600 °C, the rate constant values are \( k = 1.67, 2.26, 2.32, 3.35 \) and 4.26 for the photodegradation of MB dye solution. The degradation rate of MB dye solution increased linearly with increasing irradiation time (Figure 15). For the SnO\(_2\) hollow sphere prepared at 550 °C the rate constant values are \( k = 1.32, 1.44, 1.86, 2.31, \) and 3.16 for the photodegradation of MB.

\[\text{Figure 15.} \text{ Comparison of rate constants of photocatalyst prepared at different annealing temperatures.}\]
3.12. Stability of the photocatalyst

The cyclic stability of the as synthesised SnO₂ photocatalyst has been studied and presented in the revised manuscript as shown in Figure 16. The as synthesised SnO₂ photocatalyst showed moderately stable upto its fifth cycle. Moreover, the stability of the as synthesised SnO₂ photocatalyst before and after the photocatalytic reaction has also been investigated using XRD analysis which is shown in Figure 17. The results suggested that the crystallinity of the SnO₂ becomes relatively low after its fifth usage which may be due to the photo corrosion and photo dissolution of the catalysts. In addition, the morphology of the SnO₂ photocatalyst before and after the photocatalytic reaction has also been

![Figure 16. Recycle efficiency of the SnO₂ photocatalyst.](image)

![Figure 17. XRD pattern of the photocatalyst before and after the photocatalytic degradation of MB dye solution.](image)
investigated using SEM analysis which is shown in Figure 18. After the fifth run the photocatalyst loses its porous structure and looks like clusters which aggregate with each other particles. These results suggest that the catalyst was relatively stable.

4. Conclusions

SnO$_2$ hollow spheres were successfully prepared via simple wet chemical route in hydrothermal environment, and calcined at two different temperatures such as 550 and 600 °C respectively. Unique hollow sphere morphology and smaller crystalline size were observed by SEM, TEM and XRD. SnO$_2$ photocatalyst prepared at 600 °C shows more number of spheres on the surface. Moreover, hollow sphere with higher annealing temperature shows excellent photocatalytic activity towards the degradation of methylene blue. The optimised conditions for the effective degradation of the MB dye solution were also studied. The mechanism of the photocatalytic degradation of MB dye solution was observed and involvement of $\cdot$OH was evidenced using trapping experiment by employing different scavengers. The photocatalyst was moderately active, stable upto its fifth usage and stability of the photocatalyst before and after the photocatalytic reaction was also studied using XRD and SEM.

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Disclosure statement

No potential conflict of interest was reported by the authors.
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