Highly active carbon supported Sn/SnO₂ photocatalysts for degrading organic dyes

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Abstract. In this work, the heterostructure carbon supported tin/tin oxide (Sn/SnO₂) photocatalysts has been developed. The target heterostructure was prepared by precipitation method followed by carbothermal reduction using tin tetrachloride (SnCl₄) as precursor for SnO₂, activated carbon as reducing agent, and ammonia solution as precipitating agent. The photocatalytic activity of the as-prepared photocatalysts was investigated by degrading methylene blue (MB) dye. The photocatalytic decomposition of methylene blue in solution under UV light irradiation revealed that the heterostructure Sn/SnO₂ photocatalysts catalyst led to higher activities than pure SnO₂. The suppression of charge separation in the heterostructure carbon supported Sn/SnO₂ due to space charge region between SnO₂ and Sn led to higher catalytic activity for the degradation of MB. The results also showed that the pH of solution had a direct influence on the photocatalysis process and neutral pH was favorable for the degradation of MB. In addition, the photocatalysts could be easily recycled without significant change in the catalytic activity which indicated the stability and reproducibility of the catalysts. The results suggested that the as-prepared carbon supported Sn/SnO₂ can be applied as a promising photocatalyst for the treatment of wastewater containing organic pollutants.

1. Introduction
Rapid growth in the industrial sector is playing a vital role in the economy of Bangladesh. Mainly the growth has been concentrated in garments which are export oriented industries. To support garments, a large number of other textile production processes including the washing, dyeing and finishing (WDF) of textiles and the number of wet processing units have been established and more are growing to be set up shortly [1]. A large quantity of water is used for dyeing and washing purposes. It is reported that 2 million m³ effluents are discharged to water bodies every day from Textile sector in Bangladesh [2] which causes serious water pollution. This polluted water is causing serious health hazard in the neighbourhood, damaging fertility of the land, killing fishes and aquatic lives. Moreover, most industrial dyes are toxic, carcinogenic, and mutagenic, and have low biodegradability. Thus, finding a sustainable solution to treat the wastewater discharged from fast growing industry is of high priority. Currently available conventional water treatment methods such as adsorption, coagulation, sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary pollutants into the ecosystem [3]. In this regard, 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 drinking water and industrial effluents. Among these AOPs, heterogeneous photocatalysis employing semiconductor catalysts (TiO$_2$, ZnO, SnO$_2$, Fe$_2$O$_3$, CdS) has demonstrated its efficiency in degrading a wide range of ambiguous refractory organics into readily biodegradable compounds, and eventually mineralized them to innocuous carbon dioxide and water [4-8]. However, the photoinduced charge carrier in single bare semiconductor particles has a very short lifetime because of the high-recombination rate of the photogenerated electron/hole pairs, which reduces photocatalytic efficiency and hinders its further application in industry [9, 10]. Therefore, suppression of the recombination of photogenerated charge carriers in a semiconductor and effective utilization of solar energy still remain challenge in photocatalytic application. Among various techniques, deposition of metal on the semiconductor to reduce the charge recombination has received the most attention recently owing to their excellent catalytic activity.

Tin oxide (SnO$_2$), cassiterite structure, is a typical wide band gap n-type semiconductor (3.8 eV) [11] and one of the most widely used semiconductor oxides due to its chemical and mechanical stabilities. It is well known that Sn and SnO$_2$ nanomaterials can be used in energy production/storage devices. Herein, we report the synthesis of tin/tin oxide (Sn/SnO$_2$) nanocrystallites by novel carbothermal reduction method, while the activated carbon acts as both reducing agent and support in formation of Sn-SnO$_2$/C catalyst. Photocatalytic properties of Sn/SnO$_2$ nanoparticles were studied through the degradation and mineralization of methylene blue in water upon illumination with UV light. This simple technique to synthesize Sn/SnO$_2$ nanoparticles could allow its wide-scale use for the degradation of methylene blue and other toxic organic compounds.

2. Materials and Methods

2.1. Preparation of photocatalyst
The heterostructured Sn/SnO$_2$ nano-photocatalyst was prepared by precipitation method followed by carbothermal reduction method using tin tetrachloride (SnCl$_4$) as precursor and 12.5% Ammonia solution (NH$_4$OH) as precipitating agent and activated carbon as reducing agent. In a typical procedure, 5 mL of SnCl$_4$ was dissolved in 100 mL distilled water in an ice bath. Then 1g activated carbon prepared from peanut shell was added to the SnCl$_4$ solution followed by drop wise addition of ammonia solution under continuous stirring. A white precipitate of tin hydroxide [Sn(OH)$_4$] was appeared with the addition of ammonia solution. The addition of ammonia solution was continued until the pH of the solution was neutral. Subsequently, the resulting was kept stirring overnight. The mixture was then separated by centrifuging at 4000 rpm and washed several times with distilled water. The wet powder was then dried at 100°C for 10 hour followed by calcination at 800°C for 2 hour. Similar procedure was followed for the preparation of pure SnO$_2$ except that no carbon was added to SnCl$_4$ solution before adding ammonia solution. The synthesis of photocatalyst was optimized by changing the calcination temperature and time.

2.2. Evaluation of photocatalytic activity
Photocatalytic activities of the as-synthesized samples were evaluated by the degradation of methylene blue (MB) dye. All the experiments were conducted at room temperature open to air. In most of the experiment, 0.1 g photocatalyst was dispersed in 200 mL of MB (10 mg/L) to obtain the concentration of the catalyst at 0.50 g/L. The experiments were carried out in a pyrex beaker illuminated with a 125 W high pressure mercury lamp. The UV lamp was positioned above the solution beaker. Prior to irradiation, the suspension was stirred in the dark for 30 min to reach adsorption/desorption equilibrium. The solutions were continuously stirred during the experiments. At given irradiation time intervals, 5 mL of the suspensions were collected, and then centrifuged (4000 rpm, 10 min) to separate the photocatalyst particles. The concentrations of MB were measured by UV-Visible
Spectrophotometer (Shimadzu, UV-2600 pc) at \( \lambda_{\text{max}} = 664 \) nm. In each case, blank experiments were also conducted with the catalysts in the absence of light and without the catalysts when the solution containing the dissolved dye was illuminated. Repetitive photodegradation of MB during three consecutive cycles was performed with 1.0 g/L of catalyst at 10 mg/L dye concentration in order to investigate the stability of the photocatalysts. After each cycle, the catalyst was washed with distilled water and a fresh solution of MB was added before each photocatalytic run.

3. Results and discussion

3.1. Preparation mechanism of Sn/SnO\textsubscript{2}

The possible formation mechanism of Sn/SnO\textsubscript{2} photocatalysts may include the following steps as: (1) conversion of A.C/SnCl\textsubscript{4} into A.C/Sn(OH)\textsubscript{4} by precipitation; (2) conversion of Sn(OH)\textsubscript{4} to SnO\textsubscript{2} by calcination at high temperature under open atmospheric conditions; (3) then, reduction of SnO\textsubscript{2} by activated carbon and CO to form SnO. As it is known that SnO is metastable, it will continue its reaction and passes into a stable state via reduction by activated carbon or CO to form metallic Sn and decompose into Sn and SnO\textsubscript{2} at high temperature; (4) oxidation of as-formed SnO and metallic Sn by \( O_2 \) in atmosphere. The simplified reaction processes may be summarized as below:

\[
\begin{align*}
A.C/SnCl_4 + 4NH_4OH & \underset{\Delta}{\rightarrow} A.C/Sn(OH)_4 + 4NH_4Cl \\
A.C/Sn(OH)_4 & \underset{\Delta}{\rightarrow} A.C/SnO_2 + 2H_2O \\
SnO_2 + C & \underset{\Delta}{\rightarrow} SnO + CO \\
SnO_2 + CO & \underset{\Delta}{\rightarrow} SnO + CO_2 \\
SnO + CO & \underset{\Delta}{\rightarrow} Sn + CO_2 \\
2SnO & \underset{\Delta}{\rightarrow} Sn + SnO_2 \\
SnO + \frac{1}{2}O_2 & \underset{\Delta}{\rightarrow} SnO_2
\end{align*}
\]

These results verified that activated carbon simultaneously play support and reducing agent role in formation of Sn/SnO\textsubscript{2} photocatalysts.

3.2. Evaluation of photocatalytic activity

To evidence the photocatalytic efficiency of the as-synthesized Sn/SnO\textsubscript{2} nanoparticles, experiments of the photocatalytic decomposition of methylene blue (MB) was performed as a test reaction according to the literature. Furthermore, blank experiments in the presence of irradiation without the photocatalyst were carried out to rationalize the photocatalytic activity of the as-synthesized Sn/SnO\textsubscript{2} photocatalyst. The degradation efficiency of the as-synthesized samples was defined as \( C/C_0 \), where \( C_0 \) and \( C \) are the initial concentration and the concentration of MB during the reaction time, respectively. Blank experiment results showed that MB could not be decomposed without the photocatalyst under UV irradiation (Figure 1(a)). With only catalyst, adsorption equilibrium study also showed that there was no appreciable adsorption of dyes on the catalyst.

In order to investigate the photocatalytic activity of Sn/SnO\textsubscript{2} photocatalyst, a set of parallel experiments were conducted with Sn/SnO\textsubscript{2} and SnO\textsubscript{2} photocatalysts. Figure 1(a) shows the photocatalytic activity of Sn/SnO\textsubscript{2} and SnO\textsubscript{2} photocatalysts for the degradation of MB under UV irradiation. It was found that the efficiency of SnO\textsubscript{2} was 41% after 210 min irradiation whereas for Sn-SnO\textsubscript{2} it was 96%. The composite nanoparticles showed higher photocatalytic activity than that of pure SnO\textsubscript{2}.

For a better understanding of the photocatalytic efficiency of the as-synthesized samples, 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 rate equation of Langmuir–Hinshelwood which is
\[
\ln \left( \frac{C}{C_0} \right) = -kt
\]
where \( C_0 \) is the initial concentration of dyes and \( C \) is the concentration at reaction time. \( k \) represents the kinetic rate constant.

**Figure 1.** (a) Photocatalytic degradation of MB with as-prepared photocatalysts (b) kinetic study of methylene blue photodegradation

Degradation rate is quantitatively measured from the value of kinetic rate constant \( k \). It can be understood how fast or slow a reaction is through the value of \( k \). The rate constant, \( k \) was calculated by the linear regression of the slope of \( \ln \left( \frac{C}{C_0} \right) \) vs. \( t \) plot. Fig. 2 shows the plots of \( \ln(C/C_0) \) against \( t \) for different as-synthesized photocatalysts for the degradation of MB. The different values of \( k \) (0.0132 for Sn/SnO\(_2\), and 0.0028 for SnO\(_2\)) shown in Figure 1(b) indicate the different degradability of the photocatalyst. The higher \( k \) value of Sn/SnO\(_2\) photocatalyst indicates its higher photocatalytic degradation efficiency compared to bare SnO\(_2\).

**3.3. Photocatalytic Mechanism of heterostructure Sn/SnO\(_2\) photocatalyst**

Figure 2 shows the mechanism of photogenerated charge separation at the interface of heterojunction Sn-SnO\(_2\) nanoparticles and its photocatalytic process. The higher photocatalytic activity of heterostructure Sn/SnO\(_2\) nanoparticles is related to the role of Sn on the surface of SnO\(_2\) nanoparticles. It is known that the work function of Sn (4.42 eV) is smaller than that of SnO\(_2\) (4.84 eV). The Fermi energy level of Sn is higher than that of SnO\(_2\) due its smaller work function. Accordingly, when the metallic Sn is attached to SnO\(_2\) nanoparticles, the electrons will migrate from Sn to SnO\(_2\) in order to achieve the Fermi level equilibration. As a consequence, the Fermi level of the semiconductor and metal in the interface is same that results in the formation of an electron depletion region and surface inward-bent band in the semiconductor. This electron depletion region formed at these Schottky barrier leads to an internal electric field at the interface of the heterojunction Sn/SnO\(_2\) nanoparticles at thermal equilibrium. Under UV light irradiation, the electron in the VB of SnO\(_2\) is excited to the CB by leaving a hole in the VB. The photogenerated electron hole pair can be separated effectively by the internal electric field developed at Sn/SnO\(_2\) interface. The generated electrons tend to move to the positive side of the internal electric field; the electrons are transferred to the metal side take part in the reduction of dissolved oxygen forming superoxide radical anions, \( O_2^- \), yielding hydroperoxy radicals \( HO_2^- \) on protonation and finally \( OH^- \) radicals., while the photogenerated holes are transferred to SnO\(_2\) particles and oxidize the surface hydroxyl group or physisorbed water molecules forming hydroxyl radical, \( OH^- \). \( OH^- \) radicals are a strong oxidizing agent well-known to decompose organic substrates as MB dye. Thus, an internal electric field caused the vectorial charge transport and transfer of electrons and holes into different directions and then retarded the photogenerated electron hole pair recombination, resulting in a better photocatalytic activity.
H₂O, OH⁻, dye
OH*, intermediates
ECB
O₂
H⁺ + O₂⁻
•−
HO•
hν
SnO₂
EVB
hν
Degradation products
Sn

**Figure 2.** Schematic diagram of photogenerated charge separation by internal electric field at Sn/SnO₂ heterojunction and its photocatalytic process.

### 3.4. Effect of pH

The pH is an important parameter in the heterogeneous photocatalysis process. It influences the surface charge properties of the photocatalyst and therefore, the adsorption behavior of the pollutant. The pH of the dye solution was adjusted by adding NaOH or HCl. The role of pH on the photocatalytic degradation of MB was studied in three pH values (2.65, 6.50 and 10.50) at constant dye concentration (10 mg/L) and photocatalyst amount 0.5 g/L.

**Figure 3.** (a) Effect of pH of dye solution on the photocatalytic degradation of MB and (b) Cyclic runs in the photodegradation of MB using the Sn/SnO₂ photocatalyst under UV-light irradiation.

Figure 3(a) demonstrates the effect of pH on the photocatalytic degradation of methylene blue with different pH values. Figure 3(a) shows that MB photodegradation increased with increasing pH value from 2.65 to 6.50. Further increase in pH decreases the degradation efficiency. The degradation efficiency increases from 32% to 96% with increasing pH from 2.65 to 6.50 and subsequently the efficiency decreases to 49% with increasing pH to 10.50. The variation of solution pH changes the surface charge of the photocatalysts and shifts the potentials of catalytic reactions. As a result, the adsorption of dye on the surface is altered thereby causing a change in the reaction rate. Considering the positive charge of cationic MB dye in solution, the effect of pH on the photocatalytic degradation of MB can be rationalized on the basis of electrostatic adsorption model where cations are more readily accumulated at the negative sites on the heterostructure Sn/SnO₂. This can be explained on the basis of the point of zero charge (pHpzc) of Sn/SnO₂ particle. At lower pH, the surface of the catalyst
is positively charged, but at higher pH it becomes negatively charged. Since MB is a cationic dye, high pH favors adsorption on the catalyst surface which results in the formation of thin film on the surface of the photocatalyst. This film acts as shield that inhibits the irradiated UV light to reach the catalyst surface resulting lower degradation of the dye at higher pH. On the other hand, at lower pH the electrostatic repulsion between the MB cations and positively charged oxide surface greatly reduces the adsorption of the MB dye resulting in a drastic decrease in degradation rate. The above discussion suggests that the neutral pH is favorable for the degradation of MB with the as synthesized Sn/SnO$_2$ photocatalyst.

3.5. Recyclability of synthesized Sn/SnO$_2$ for the degradation of methylene Blue

The reuse of catalyst is a critical criterion for commercialization of this technology, as this is a major factor contributing to the operating cost of the system. A photocatalyst should be resistive to photocorrosion, stable under different reaction conditions, and able to promote reactions efficiently upon repetitive use of Sn/SnO$_2$. The Sn/SnO$_2$-nanocatalyst can be recycled and reused without significant loss of efficiency, which is a key requirement for a possible industrial application. Thus, the photocatalytic efficiency of the Sn/SnO$_2$ heterojunction photocatalyst for the 3-cycling reuse was 99.4, 73.2 and 58% after 360 min of reaction time, respectively (Figure 3 (b)). The degradation efficiency decreased because of the loss of catalyst during recovery for several runs.

4. Conclusions

Nanostructured Sn/SnO$_2$ photocatalysts have been successfully prepared by precipitation method followed by carbothermal reduction using activated carbon as reducing agent. The synthesized Sn/SnO$_2$ photocatalysts represented excellent photocatalytic activity for the degradation of MB under UV light irradiation. The pH of solution had a direct influence on the photocatalysis process and neutral pH that was favorable for the degradation of MB. Furthermore, the photocatalysts could be easily recycled without significant change in the catalytic activity which indicated the stability and reproducibility of the catalysts. This concept of semiconducting nanocatalysts with high photocatalytic activity should find industrial application in the future to remove undesirable organics from the environment.

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References

[1] The Bangladesh Responsible Sourcing Initiative: a new model for green growth 2014 The World Bank
[2] Dey S and Islam A 2015 Resourc. Environ. 5 15-44
[3] Gaya U I and Abdullah A H 2008 J. Photochem. Photobiol. C: Photochem. Rev. 9 1-12
[4] Fujishima A and Honda K 1972 Nature 238 37-38
[5] Chen X, Wu Z, Liu D and Gao Z 2017 Nanoscale Res. Lett. 12 143
[6] Uddin, M T, Sultana Y and Islam M A 2016 J. Sci. Res. 8 (3) 399-411
[7] Liu Y, Yu L, Hu Y, Guo CF, Zhang FM and Lou XW 2012 Nanoscale 4(1)183-187
[8] Jing Z, Tan L, Li F, Wang F, Fu Y and Li Q 2013 Indian J. Chem. 52A 57-62
[9] Linsebigler A L, Lu G and Yates J T 1995 Chem. Rev. 95 735-758
[10] Zhang M, Sheng G, Fu J, An T, Wang X and Hu X 2005 Mater. Lett. 59 3641-3644
[11] Rockenberger J, Felde U, Tischer M, Troger L, Haase M and Weller H 2000 J. Chem. Phys. 112 4296-4304