Photocatalytic degradation of methylene blue (MB) by UV-light irradiation using SnO$_2$/CeO$_2$ modified nanographene platelets (NGP)

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Abstract. The main task of this present work is to enhance the photocatalytic degradation of methylene blue (MB) under UV-light irradiation by using SnO$_2$/CeO$_2$ that combined with nanographene platelets (NGP) composite catalysts. A facile approach for the synthesis of SnO$_2$/CeO$_2$/NGP composites was demonstrated via co-precipitation method. The nanographene platelets (NGP) concentrations in composites were altered between 5–15 weight percent (wt.%). The structure and thermal stability obtained composites catalyst were thoroughly studied by various techniques including X-ray diffraction (XRD) and thermogravimetric analysis (TGA), respectively. XRD analysis reveals that the composites have the tetragonal structure of SnO$_2$ nanoparticle, the cubic phase of CeO$_2$ and the graphitic-like structure from NGP. TGA curves prove the presence of NGP materials in the composites by the decrement in mass at the temperature about 600°C. The synthesized SnO$_2$/CeO$_2$/NGP 10 wt.% composite exhibits higher photocatalytic activities than SnO$_2$/CeO$_2$ and pure SnO$_2$ nanoparticles for the degradation of MB dye under UV light irradiation. The photocatalytic activities of the synthesized samples show an increasing degradation in the order of SnO$_2$<SnO$_2$/CeO$_2$<SnO$_2$/CeO$_2$/NGP 5 wt.%<SnO$_2$/CeO$_2$/NGP 15 wt.%<SnO$_2$/CeO$_2$/NGP 10 wt.%. The enhanced photocatalytic performance could be ascribed to the high electron accepting nature of graphene and increase the number of active sites owing to high charge carrier mobility and high specific surface area of graphene material. The other parameter such as catalyst dosage, irradiation time and scavenger were also analyzed to find out the optimum degradation condition. The SnO$_2$/CeO$_2$/NGP 10 wt.% composite reach optimum photodegradation when irradiation time, catalyst dosage and scavenger are 120 min, 0.3 g/L, and hole, respectively. The tests for reusability tests have also been conducted to ensure the stability of the used catalysts.

1. Introduction

Critical issues water pollution arising from the refractory organics discharge have caused great concerns nowadays. This wastewater can influence the balance of aquatic plant and influence our daily human life finally [1]. Photocatalysis using semiconducting materials has attracted significant interest since it provides promising methods to overcome the current major issues pertaining to energy crisis and environmental pollution [2]. Indeed, upon band gap excitation of the semiconductor photocatalyst, the photoinduced electrons and positively charged holes can reduce and oxidize the species adsorbed on the semiconductor particles [3]. SnO$_2$ is the n-type semiconductor with wide band gap (3.6 eV) and has potential applications in various fields such as sensors, photocatalysis, anodes for lithium ion batteries and dye-sensitized solar cells [4]. Moreover, SnO$_2$ has no adverse health effects and is poorly...
absorbed by the human body when injected or inhaled [5]. Thus SnO, is potentially an ideal photocatalyst.

However, there are limitations, which hinder the applications of SnO, as a photocatalyst. Pure SnO, has the rapid recombination rate of electron-hole pairs that could hinder the photocatalytic performance for degradation of dyes on water solution. To solve this problem, mixed oxide composite materials can often be more efficient photocatalyst than pure substance by improving the charge separation. Cerium dioxide (CeO,) is rare earth metal oxide that considered to be a suitable candidate to combine with SnO, because of its narrow band gap and the Ce(IV)/Ce(III) reversible redox couple [6]. The redox couple of Ce-/Ce and the high capacity to store/release oxygen under oxidizing/reducing conditions of CeO, have gained additional importance in the application of heterogeneous catalysis [7]. It has found that well-coupled metal oxide semiconductor and CeO, composites can produce a special electron transfer process that increases the yield of the electron-hole pairs and improves the photocatalytic activity [8]. In addition, graphene is also a good choice as an additive because it is a two-dimensional material with a large specific surface area and perfect electrical properties [9]. By coupling the composite photocatalyst with graphene material, it believed that photocatalytic performance of composite photocatalyst could be enhanced. It is found that this conjugated carbon can inhibit the recombination of photocarriers efficiently, leading to the amazing photocatalytic performance of composite photocatalyst [10].

So, the aim of this study is to clarify the photocatalytic efficiency of this composite semiconductor SnO,/CeO,/NGP prepared by a co-precipitation method. Methylene Blue (MB) has been used as a model organic pollutant. The crystal structural and thermal behaviour of the as-prepared composition is characterized by X-ray diffraction (XRD) and thermogravimetric analysis (TGA), respectively. The other parameters such as the effect of NGP weight percent (wt.%) in composites from 5 until 15 wt.%, catalyst concentration and scavengers of these composite materials is also reported. As a comparison, the photocatalytic performance of pure SnO, nanoparticle also investigated. As expected, the result shows that a combination of SnO,/CeO, and graphene materials showed superior photocatalytic behavior as compared to SnO,/CeO,and pure SnO, for degradation of methylene blue (MB) under UV-light irradiation.

2. Materials and methods

2.1. Chemicals
All reagents used in this study were of analytical grade and were used in the as received condition. Anhydrous tin chloride (SnCl,), sodium hydroxide (NaOH), cerium (IV) sulfate (Ce(SO,).4H,O), methylene blue (MB), and ethanol were procured from Merck (Kenilworth, NJ, USA). Nanographene Platelets (NGP) was purchased from Angstrom Material.

2.2. Synthesis of SnO, nanoparticle
A variant of the process published by Li et al. [11] was adopted to synthesize SnO, nanoparticles. A pre-measured concentration of SnCl, was dissolved in a mixture containing ethyl alcohol and aqueous solution. The mixed solution was subsequently included into sodium hydroxide solution under constant stirring using a magnetic stirrer. Then, the mixed solutions were subjected to a heat treatment at 180 °C for 3 h and were subsequently cooled to room temperature. The cooled solution was precipitate centrifuged multiple times with aqueous and ethanol solutions in order to collect the precipitate. Finally, the precipitate was vacuum dried at 80 °C to obtain SnO, particles upon calcination for 3 h at 700 °C.

2.3. Preparation of CeO,
Wet-chemical sol-gel method was used to synthesize CeO, nanoparticles. Initially, Ce(SO,).4H,O and sodium hydroxide were dissolved in deionized water, separately for a short duration. Subsequently, under severe magnetic stirring, a solution of sodium hydroxide was included into Ce(SO,).4H,O at 80 °C. The suspension thus prepared was subjected to centrifugation, cleaned with deionized water and ethyl alcohol many times to remove impurities. The centrifuged suspension were dried in an oven at 150 °C for 5 h. The dried powder was finally calcined in air atmosphere at a temperature of 600 °C for 1 h to obtain pure CeO, particles.

2.4. Preparation of SnO,/CeO, composite
The composites of SnO and CeO were prepared by the ultrasonic-assisted method. A mixture of SnO nanoparticles and CeO was prepared in a mixture of ethyl alcohol and aqueous solution. The mixture was placed in an ultrasonic bath for 2 h and was centrifuged. When the resultant product was vacuum dried at 80 °C for 12 h, SnO/CeO composites were obtained.

2.5. Preparation of SnO/CeO/NGP composite

The SnO/CeO/NGP composite was prepared by co-precipitation method. NGP powder was subjected to ultrasonic treatment by dissolving in distilled water and ethanol for 2 h. The previously prepared SnO/CeO composite was added to the solution under magnetic stirring. The thoroughly mixed solution heated at 120 °C for 3 h, centrifuged and then dried in vacuum at 70 °C.

2.6. Characterization

The structural and thermal studies of the sample was conducted by XRD (Rigaku Miniflex 600, Tokyo, Japan) using Cu K-α radiation (λ = 1.5406 Å) and thermal gravimetric analysis (TGA) (Rigaku TG8121) between 27 °C until 900 °C.

2.7. Photocatalytic experiments

The photocatalytic studies was conducted by adding the prepared sample into 100 mL methylene blue (MB) solutions that is utilized as pollutant model with concentrations of 20 mg/L. The pH of the solution was adjusted using NaOH. In order to obtain equilibrium in the adsorption and desorption process, the solution was allowed to stand in stirring state. While conduction the photocatalytic test, the solution was irradiated by UV light power of 40 W and wavelength of 320–400 nm for a duration of 2 h. The MB solution’s composition was monitored periodically (every 15 min) using UV-vis spectrometer.

2.8. Scavenger experiments

In order to evaluate the chemical species that influence the sonocatalytic activity the most, it was provided the difference radical-scavenger in methylene blue (MB) solution. Ammonium oxalate, sodium sulfate, and tert-butyl alcohol (TBA) were utilized each for scavenger hole, electron and hydroxyl radical. The measurement was conducted in a similar manner as explained earlier.

3. Results and discussion

The crystal structures of SnO/CeO and SnO/CeO/NGP with different weight percent (wt.%) of NGP samples were characterized by XRD analysis, which shows in figure 1. As can be seen, the XRD patterns of pure SnO nanoparticle in figure 1 shows some sharp narrow peaks at 2θ = 26.5°, 33.8°, 38°, 39°, 51.8°, 54.8°, 58°, 62°, 64.7°, 65.8°, 71.2°, 78.2°, 81.2°, and 83.7° are noticed, which reveal the (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202), (321), (400), and (222) reflections of tetragonal phase SnO. In comparison to the pure SnO nanoparticle, SnO/CeO/NGP composites exhibited new diffraction peaks at 2θ = 28.41°, 37.86°, 47.37°, and 56.22°, marked with “#”, which are indexed to (111), (004), (200) and (211) diffraction planes of the cubic phase CeO. The XRD pattern of SnO/CeO composites exhibits all characteristic peaks of SnO and CeO, indicating that the presence of SnO and CeO in SnO/CeO composite. XRD pattern of NGP shows a sharp peak at 2θ = 25°, which matched with the (002) reflection of NGP, thereby confirming the existence of NGP. However, we fail to notice distinct peaks of the NGP material in all various NGP content on SnO/CeO/NGP composites, possibly due to the relatively low content of NGP, covering up of the peaks by the diffraction signals of SnO nanoparticle at around 2θ = 25° [12]. No additional peak, matching with crystalline impurities or any marked shift in diffraction peaks was noticed.

To analyze thermal stability and confirm the existence of NGP materials in SnO/CeO/NGP composite, thermogravimetric analysis were performed. The TGA results of SnO/CeO and SnO/CeO/NGP with different composition of NGP (5, 10, 15 wt.%) composites are shown in figure 2. The result shows that SnO/CeO have a good thermal stability up to the temperature of 1000 °C. Compared with TGA curve of SnO/CeO, SnO/CeO/NGP shown two distinct composites degradation were observed. The first weight loss of about 2% below 125 °C is attributed to the removal of adsorbed water on SnO/CeO/NGP composites surface. The second weight loss can be found in temperature around 600 °C owing to combustion effect of NGP materials [13]. Based on the TGA curve, the weight loss of NGP content 5, 10, 15 wt.% in SnO/CeO/NGP composites is estimated to be...
approximately 6.8, 10, and 16 %, respectively that is well in agreement with the expected value. Furthermore, the TGA curved can confirm the total amount and the existence of NGP in the composite samples by the loss mass of the composites.

The photocatalytic performance of all prepared samples was evaluated by the degradation of MB under UV light irradiation. Figure 3 shows the photocatalytic performance at pH 13 of pure SnO$_2$, SnO$_2$/CeO$_2$, and SnO$_2$/CeO$_2$/NGP with varying weight percent (wt.%) of NGP content. It is noticed that SnO$_2$/CeO$_2$ show superior photocatalytic behaviour than pure SnO$_2$ nanoparticle. This observation suggests that the coupled effect of SnO$_2$ and CeO$_2$ can significantly improve the photocatalytic activity of pure SnO$_2$. The behavior could be attributed to the formation of SnO$_2$/CeO$_2$ heterojunction and coexistence of Ce$^{4+}$ and Ce$^{3+}$ has the potential to separate the photogenerated electron-hole pairs, thus leading to the enhancement of photocatalytic degradation [14]. For the SnO$_2$/CeO$_2$/NGP, it shows that with the increase of NGP content in composite also exhibit better photocatalytic degradation of MB until 10 wt.% of NGP. The presence of NGP particles aid in preventing the recombination of electron-hole pairs. It is reported that NGP particles behave as acceptors of electron and extend the charge carrier recombination process for a longer duration [15]. However, with the increasing NGP content until 15 wt.%, the photocatalytic activity of composite decrease, which indicates the optimum photocatalytic performance of the SnO$_2$/CeO$_2$/NGP composite reach when the NGP content is 10 wt.%. The photocatalytic activity was also fitted for pseudo-first-order kinetics as shown by the equation: $-\ln (C/C_0) = kt$, where, $C$ is MB concentration when time $t$, $C_0$ is the initial concentration of MB, and $k$ is the apparent rate constant.

In order to find out the effects of catalyst dosage concentration on the photocatalytic degradation of methylene blue (MB), a series of experiments were carried out within range (0.1–0.4 g/L) catalyst concentration at 0.1 g/L intervals for SnO$_2$/CeO$_2$/NGP 10 wt.% composite. As shown in figure 4, the photocatalytic activities of SnO$_2$/CeO$_2$/NGP 10 wt.% composite increase with the increasing of catalyst dosage until 0.3 g/L. The improved process in the photocatalytic activity is mainly attributed to the increase active sites of the composites caused by the increasing of catalyst dosage [16]. However, when the catalyst dosage of composite reaches 0.4 g/L, the photocatalytic activity of the sample decrease. It could be due to when the catalyst dosage further increase than 0.3 g/L, which result the number of active sites on the composite catalyst surface decrease due to aggregation of samples at high concentration [17].

In order to further analyze the key reactive species responsible for methylene blue degradation, a set of trapping experiments by including various scavengers were conducted using SnO$_2$/CeO$_2$/NGP 10 wt.% as the best photocatalyst. Di-ammonium oxalate, sodium sulfate and tertbutyl alcohol were

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**Figure 1.** XRD pattern of SnO$_2$/CeO$_2$ nanocomposite and SnO$_2$/CeO$_2$/NGP with different NGP concentration.

**Figure 2.** TGA plot of SnO$_2$/NGP nanocomposite and SnO$_2$/CeO$_2$/NGP with different NGP concentration.
Figure 3. Photocatalytic behaviour of SnO$_2$/CeO$_2$ nanocomposite and SnO$_2$/CeO$_2$/NGP with different NGP levels.

Figure 4. Influence of catalyst concentration on photocatalytic behaviour of SnO$_2$/CeO$_2$/NGP 10 wt.% composites.

Figure 5. Influence of scavengers on photocatalytic performance of SnO$_2$/CeO$_2$/NGP 10 wt.% composites.

Figure 6. Reusability on sono and sonophoto-catalytic activity of SnO$_2$/CeO$_2$/NGP 10 wt.% composites.

included as hole, electron and hydroxyl radical, respectively. Figure 5 reveals minimum degradation of methylene blue in the presence of di-ammonium oxalate. This observation proves that hole, in the samples considered for photocatalytic reaction; hole is the most significant reactive species.

For practical application in wastewater treatment, it is important to evaluate the extent of reuse of the photocatalyst. This was accomplished by repeating 4 times the recycling process using centrifuge processes. As shown in figure 6, the reused catalyst fails to reveal any noticeable modification in the degradation efficiency of catalytic activity, thus proving the excellent stability of the catalysts.

4. Conclusions
The SnO$_2$/CeO$_2$/NGP with various weight percent (wt.%) of NGP content were successfully prepared via co-precipitation method. It can be concluded from the results that effective degradation of organic dyes especially MB is possible by the photocatalytic processes in the presence of SnO$_2$/CeO$_2$/NGP. The as-prepared SnO$_2$/CeO$_2$/NGP composites exhibited enhanced photocatalytic activity in degrading MB
dye compared with the SnO$_2$/CeO$_2$ composite and pure SnO$_2$, which can be attributed to enhance the electron-hole separation and the increase of the active surface area. From the experiment, we know that the optimum photocatalytic performance of the SnO$_2$/CeO$_2$/NGP composite reach when the NGP concentration is 10 wt.%. The effect of catalyst dosage shows that the optimum catalytic degradation is 0.3 g/L. Hole is the most significant reactive species for the samples. Good stability of the catalyst is confirmed because the repeated used catalyst fails to demonstrate any measurable modification in the degradation efficiency of catalytic activity.

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