Comparison of Photocatalytic Performance of Different Types of Graphene in Fe_3O_4/SnO_2 Composites

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Abstract. We have reported the role of annealing temperature Fe_3O_4/SnO_2 nanocomposites as a photocatalyst for remove methylene blue (MB) dye from aqueous solution. However, how to enhanced the degradation performance of Fe_3O_4/SnO_2 nanocomposites is important to its photocatalytic application. Therefore, in this work Fe_3O_4/SnO_2 nanocomposites was combined with two different types of graphene materials (NGP and grahene) to improve the photocatalytic performance for remove methylene blue (MB) dye. Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene have been successfully synthesized by co-precipitation method. The influence of two types graphene on Fe_3O_4/SnO_2 nanocomposites properties were systematically investigated by means of X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Thermal gravimetric analysis (TGA). Degradation of methylene Blue (MB) in aqueous solution was studied in detail under photocatalytic process. Effect of catalyst dosage (0.1-0.4 g/L) and scavengers on dye degradation were carried out to check the efficiency of photocatalyst. The results indicated Fe_3O_4/SnO_2/graphene displayed higher photocatalytic activity than other catalyst. The reusability tests have also been done to ensure the stability of the used photocatalyst.

1. Introduction

In recent years heterogeneous photocatalysis has attracted much attention to developed sustainable technologies for energy production and storage, green chemical synthesis, and water treatments [1-2]. Semiconductor nanoparticles are useful as an effective technique to eliminate pollutants from air and wastewater due to their unique optical and electronic properties [3]. Among various semiconductor nanoparticles, such as SiC, TiO_2, ZnO, Fe_2O_3, WO_3, SnO_2 nanoparticles have attracted considerable attention because of their high physicochemical stability, low cost, lack of toxicity, easy production, and good photoactivity [4-6]. Because of their several advantages, SnO_2 potentially to be ideal catalyst. However, as a photocatalyst, SnO_2 has several fundamental issue for photocatalytic application such as: (1) the difficulty process of splitting the catalyst material from dye waste after photocatalytic process [7]; (2) The recombination rate of electron and hole pairs are too rapid [8].

To overcome the problem, one strategy is to make magnetically separable photocatalyst for recovery and reuse of SnO_2 nanoparticle [9]. Combining SnO_2 nanoparticle with magnetic material such as Fe_3O_4 was used to enhance separation properties of the photocatalyst from the treated water [10]. Furthermore, hybridizing SnO_2 nanoparticle with graphene materials is a good method to enhance the photocatalytic activity of SnO_2 for degrade organic dyes by enhancing the electron mobility and also inhibit the recombination of photogenerated electron and hole pairs. Due to

graphene properties such as excellent electronic conductivity, mechanical properties and high surface area [11]. Therefore, it is believed that, combining SnO_2, Fe_3O_4 and graphene materials would exhibit excellent photocatalytic performance with highly effectively recovery by magnetic separation technique.

In this study, Fe_3O_4/SnO_2 nanoparticle will be combined with two different types of graphene materials: 1) nanographene platelets (NGP); 2) graphene that are applied as photocatalyst to degrade methylene blue (MB) dye. To hybridize with graphene materials, Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene nanocomposites were prepared using co-precipitation method. Photocatalyst powders are characterized by using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Thermal gravimetric analysis (TGA). In the present study, the photocatalytic activity of the Fe_3O_4/SnO_2 nanocomposites with two different types of graphene materials were analyzed using methylene blue as organic pollutant model in aqueous solution under UV light irradiation. As expected, the result shows Fe_3O_4/SnO_2 combined with graphene materials exhibit better photocatalytic performance than Fe_3O_4/SnO_2 for degradation of methylene blue (MB).

2. Experimental

2.1. Chemicals

All reagents used were analytical grade and were used without further purification. Anhydrous tin chloride ($SnCl_2$), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium hydroxide (NaOH), methylene blue (MB), ethanol, ethylene glycol (EG) were purchased from Merck (Kenilworth, NJ, USA). Graphene and nanographene platelets (NGP) were bought from Angstron Material.

2.2. Preparation of SnO_2 nanoparticle and Fe_3O_4/SnO_2 nanocomposites

The Fe_3O_4 nanoparticles were synthesized using the same method used in our previous study [12]. The SnO_2 nanoparticles were synthesized using a modification of the method reported by Yue Li and co-workers [13]. First, $SnCl_2$ was dissolved in a mixture of ethanol and aqueous solution, which was then added into the NaOH solutions using magnetic stirring. Then, the mixed solutions were heated at 180 °C for 3 h, then chilled to room temperature. The precipitate was obtained by centrifugation and washed using aqueous solutions and ethanol several times. The precipitated particles were dried under vacuum at 80°C, and SnO_2 particles were obtained by calcination for 3 h at 700 °C.

The Fe_3O_4/SnO_2 nanocomposites were synthesized using the sol-gel method. First, SnO_2 nanoparticles were mixed with Fe_3O_4 in a mixture of ethanol and aqueous solution. Each mixture was ultrasonicated for 2 h and then centrifuged to obtain the precipitate. The resulting product was then dried under vacuum at 80 °C for 12 h to obtain Fe_3O_4/SnO_2 nanocomposites with the molar ratio 1:2.

2.3. Preparation of Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites

Fe_3O_4/SnO_2/graphene is synthesized using the hydrothermal method. First, graphene is dissolved into DI water and ethanol through ultrasonic treatment for 2 hours, then Fe_3O_4/SnO_2 nanocomposites is poured into the solution and stirred magnetically. The mixed solution is then heated at 120 °C for 3 hours. The result of solution is then centrifuged and dried at 70 °C under vacuum condition. The same method is also applied to synthesize Fe_3O_4/SnO_2/NGP.

2.4. Characterization

The sample was characterized by XRD using a Rigaku Miniflex 600 (Rigaku, Tokyo, Japan) with a Cu K-α radiation source (λ =1.5406 Å), the spectrum of infrared absorption from the samples is obtained using Shimadzu FTIR spectrophotometer in the range of 400-4000 cm^{-1} and thermal gravimetric analysis (TGA) of the sample is obtain using Rigaku TG8121 with the temperature from 27^{o}C until 900^{o}C.

2.5. Photocatalytic experiments

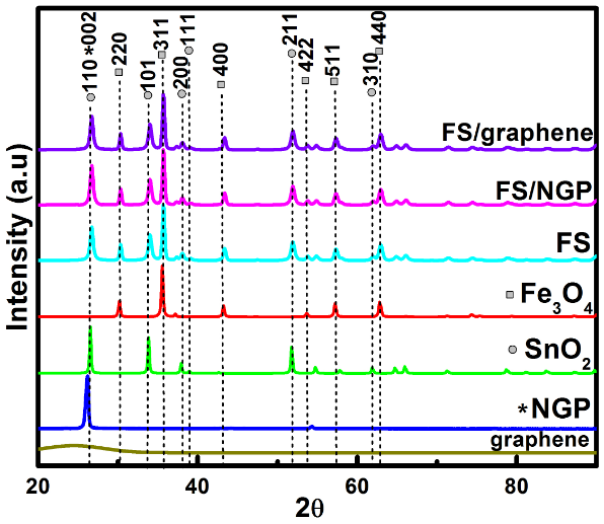

FIGURE 1. XRD pattern of Fe_3O_4/SnO_2 nanocomposite, Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites.

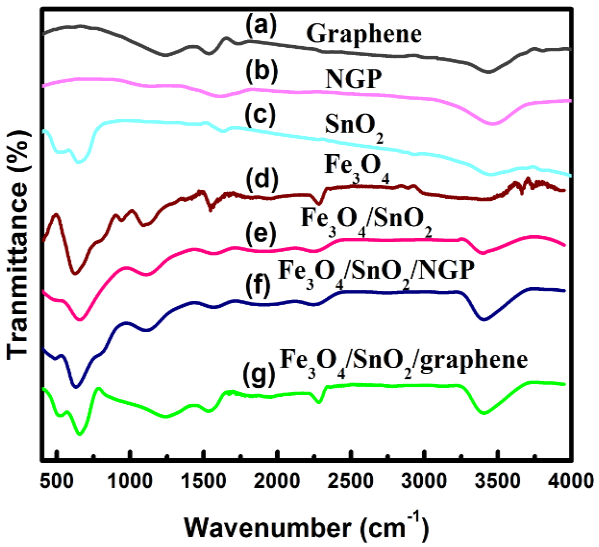

FIGURE 2. FTIR spectra of (e) Fe_3O_4/SnO_2 nanocomposite, (f) Fe_3O_4/SnO_2/NGP and (g) Fe_3O_4/SnO_2/graphene composites.

The photocatalytic experiment was done by mixing the sample into 100mL methylene blue (MB) solutions used as pollutant model with concentrations 20mg/L respectively, and pH solutions adjusted NaOH. The solution was allowed to stand in stirring state for adsorption and desorption balance. The photocatalytic test, the solution was given UV light irradiation with power 40W and wavelength of 320-400 nm. The solution was given UV light irradiation for 2 hours. Every 15 minutes span the concentration of MB solution was analyzed using UV-vis spectrometer. The maximum degradation were calculated using the following equation:

$$\text{Maximum degradation (\%)} = \frac{(C_t - C_0)}{C_0} \text{x } 100\% \quad (1)$$

where C_0 is the initial concentration of MB dye solution (mg/L), C_t is the concentration of dye at certain irradiation time (mg/L).

2.6. Scavenger experiments

To determine the most influential species in sonocatalytic activity, it was given the difference radical-scavanger in methylene blue (MB) solution. Ammonium oxalate, sodium sulfate, and tert-butyl alcohol (TBA) were used each for scavenger hole, electron and hydroxyl radical. The measurement done in the same way as described above.

3. Result

The X-ray diffraction (XRD) patterns of the Fe_3O_4/SnO_2 nanocomposite, Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites which labeled as FS, FS/NGP and FS/graphene are shown in Fig. 1, respectively. The diffraction pattern of Fe_3O_4 sample observed at the value 2θ = 30.14°, 35.49°, 43.28°, 57.20°, 62.83° and 74.8° which shows each area (220), (311), (400), (511), (440) and (533) of the cubic spinel structure. Diffraction pattern of SnO_2 nanoparticle sample observed at value 2θ = 26,5°, 33.8°, 38°, 39°, 51.8°, 54.8°, 58°, 62°, 64.7°, 65.8°, 71.2°, 78.2°, 81.2°, 83.7° which shows the existence of areas (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202), (321), (400), (222) of tetragonal structure of SnO_2 nanoparticle. The XRD pattern of Fe_3O_4/SnO_2 nanocomposites shows the existence of cubic spinel phase of Fe_3O_4, followed by the addition of tetragonal SnO_2 nanocomposites. The peak at 2θ of 26.0° indicates (002) plane of the NGP structure. For graphene, there is only a broad peak at around 2θ of 25°, which indicates the structure of

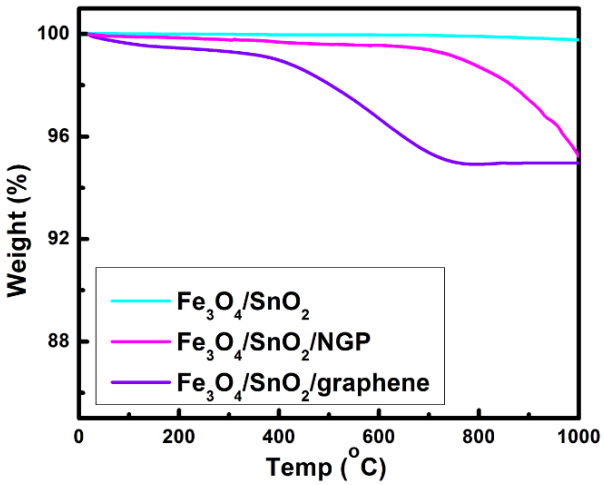

FIGURE 3. TGA curve of Fe_3O_4/SnO_2 nanocomposite, Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites.

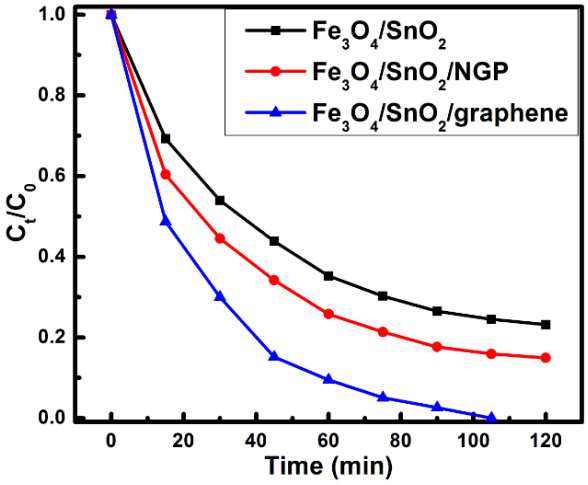

FIGURE 4. Photocatalytic degradation of Fe_3O_4/SnO_2 nanocomposite, Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites.

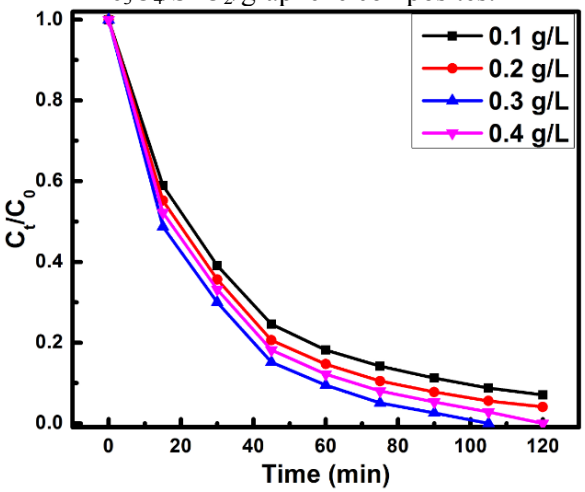

FIGURE 5. Effect of dosage on photocatalytic activity of Fe_3O_4/SnO_2/graphene composites.

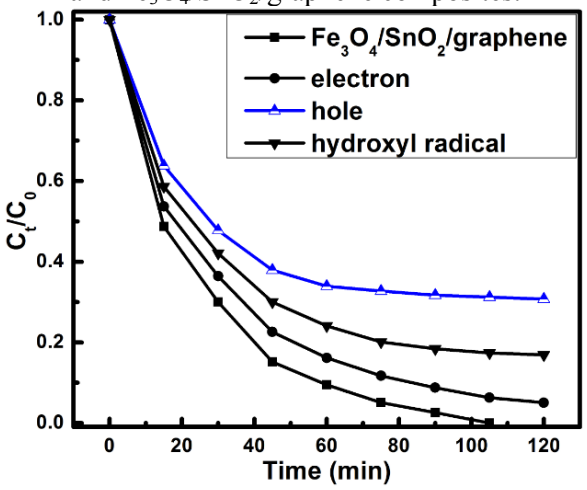

FIGURE 6. Effect of scavengers on photocatalytic activity of Fe_3O_4/SnO_2/graphene composites.

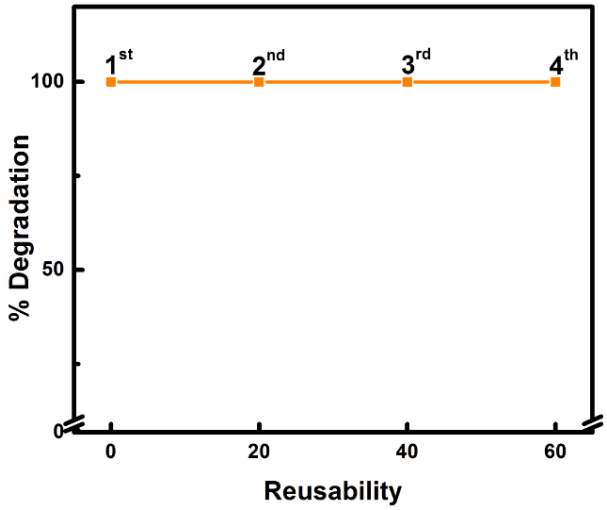

FIGURE 7. Reusability of Fe_3O_4/SnO_2/graphene composites.

graphene. The diffraction peaks of SnO_2, NGP and graphene at Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites are overlapped at 2θ of around 26°. As it is clear from this figure, there is no any impurity in the nanoparticle sample.

The FTIR spectrum of Fe_3O_4/SnO_2 nanocomposite, Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites are presented in Fig. 2. Fig. 2f shows the FTIR spectra for Fe_3O_4/SnO_2/NGP composites, while the FTIR spectra for Fe_3O_4/SnO_2/graphene composites is shown in Fig. 2g. The absorption of SnO_2 nanoparticle appears in the range of 540-660 cm^{-1} which indicates O-Sn-O and Sn-O stretching vibration modes. The Fe_3O_4 show the characteristic band of Fe-O stretching vibration at 594 cm^{-1} [7]. The absorptions in range of 3400 cm^{-1} and 1634 cm^{-1} indicate the O-H group stretching and bending vibration modes originating from water molecule [14] while absorption in the range of 1220 cm^{-1} and 1527 cm^{-1} indicates the C-OH and C-O stretching vibration modes [15,16].

Figure 3 shows the weight loss curve for Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composites obtained from TGA measurement. As can be seen, Fe_3O_4/SnO_2 nanoparticle do not exhibit the significant percentage loss in the result of TGA measurement. Which indicate that Fe_3O_4/SnO_2 nanoparticle without any addition of graphene is stable until 1000°C. The weight loss started around 100°C due to the volatilization of adsorbed water [17]. The weight loss stage from 400°C to 600°C which indicates the combustion effect from NGP and graphene material and thereafter no further decomposition takes place thereafter [18]. Furthermore, the weight loss of graphene at TGA measurement can confirm the existence of the NGP and graphene in Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene composite samples.

The photocatalytic activities of prepared Fe_3O_4/SnO_2, Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene catalysts were investigated under UV light irradiation in aqueous solution of methylene blue (MB) dye (Fig 4). It can be seen that photocatalytic activities of Fe_3O_4/SnO_2/graphene composite are obviously better than the Fe_3O_4/SnO_2/NGP composite, especially better than Fe_3O_4/SnO_2 nanocomposite. More than 95% of MB has been degraded over them within 90 min. However, only 76.83% and 85.1% of MB could be decomposed over Fe_3O_4/SnO_2 and Fe_3O_4/SnO_2/NGP after 120 min, respectively.

Fig. 5 shows the effect of Fe_3O_4/SnO_2/graphene dosage, from 0.1 g/L to 0.4 g/L, on the decolorization efficiency of methylene blue at pH 13. As shown in Fig. 5, maximum degradation at Fe_3O_4/SnO_2/graphene dosages of 0.1 g/L, 0.2 g/L, 0.3 g/L and 0.4 g/L were 92.97%, 95.93% after 120 min, 97.4% after 90 min and 97% after 105 min, respectively. The decreasing maximum degradation at dosage 0.4 g/L it could be due to as the amount of Fe_3O_4/SnO_2/graphene increasing, the scattering of UV by Fe_3O_4/SnO_2/graphene also increased, because of shielding effect [19]. The above observation indicates the optimal Fe_3O_4/SnO_2/graphene dosage was 0.3 g/L.

To know the most involved reactive species MB degradation to the all samples, the addition scavenger was done. In Fig. 6 shows the result of MB degradation in the photocatalytic process with scavenger addition influence. The scavenger addition serves to bind the reactive species to not take role in the photocatalytic process. The result obtained shows that the addition of hole scavenger shows the lowest degradation capacity. This indicates that the most influential reactive species for the samples is hole.

The stability of Fe_3O_4/SnO_2/graphene composite was investigated by a 4-run cycling test under the same condition. For each run, the photocatalyst was recycled, cleaned, and dried from its solutions using magnetic external. The photodegradation efficiency of Fe_3O_4/SnO_2/graphene composite shows no apparent decrease after the 4 reuse cycles, indicating Fe_3O_4/SnO_2/graphene composite is stable (Fig. 7).

4. Conclusion

The hybridizing Fe_3O_4/SnO_2 with two different types of graphene material (Fe_3O_4/SnO_2/NGP and Fe_3O_4/SnO_2/graphene) have been successfully synthesized via co-precipitation method. Fe_3O_4/SnO_2/graphene compsite show the best photocatalytic activity under UV light irradiation. More than 95% of MB has been degraded over them within 90 min. The optimum catalyst dosage for Fe_3O_4/SnO_2/graphene composite sample is 0.3 g/L. Scavengers experiment shows that the most

influential reactive species for the samples is hole. Sample showed good cycling capacity result after reuse three times.

5. Reference

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