Sonocatalytic Degradation of Methylene Blue with LaMnO$_3$ Supported by Different Surface Area of Graphene

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Abstract. The present study compared the sonocatalytic degradation ability of LaMnO$_3$ supported by different surface area of graphene on methylene blue (MB) as a model of the organic pollutant under ultrasonic irradiation. Both sonocatalysts were synthesized by using co-precipitation method and characterized by using X-Ray Diffraction (XRD), Fourier Transform Infrared, and Brunauer-Emmet-Teller (BET) surface area analysis. The orthorhombic structure of LaMnO$_3$ was detected on the composites, while the existence of graphene was also confirmed. The present of graphene in the samples could improve the magnetic properties and surface area of composites as well as the sonocatalytic performance. LaMnO$_3$ supported by different surface area of graphene (SA-1 and SA-2) showed the significant improvement of sonocatalytic activity compared to LaMnO$_3$. LaMnO$_3$/SA-2 composites with the largest surface area showed the highest degradation efficiency. To detect the possible reactive species involved in the degradation of MB, control experiments with introducing scavenger into the solution of MB were carried out. The results indicated that photo-generated hole played an important role in the degradation of MB.

1. Introduction

Photocatalytic degradation of organic pollutant using LaMnO$_3$/graphene composite as a catalyst is promising for water purification. LaMnO$_3$ has been chosen due to its unique physical and chemical properties, its low cost, its high catalytic activity and environmental friendliness. In addition, LaMnO$_3$ also shows good respond as a visible light catalyst which makes it a promising candidate to maximize the utilization of solar energy in the catalytic field [1]. The graphene with a large specific surface area, excellent adsorption capacity, and high chemical stability also can be compounded with LaMnO$_3$ to enhance the catalytic performance[2-3]. It was reported that the catalyst with the large surface area could increase the catalytic activity by increasing the number of active sites which could further degrade the organic pollutant. In order hand, graphene also exhibits the electron transport layer capacity which can inhibit the electron-hole recombination and enhance the catalytic performance [1, 4].

The photocatalytic activity can degrade organic pollutant in wastewater as well as the sonocatalytic activity. Recently, the ultrasonic irradiation is also used for degrading of organic contaminants based on the hot spot and sonoluminescence mechanism [5]. The sonoluminescence involves a broad range of wavelength such as UV light, which makes the catalyst behaves like photocatalyst during sonication

[6-7]. The photocatalytic activity of $LaMnO_3$/graphene composite has been reported by several studies [1, 4]. However, very few reports are available on the sonocatalytic activity using $LaMnO_3$/graphene composite as a catalyst. Therefore, in this work $LaMnO_3$ composite with a different surface area of graphene ($LaMnO_3$/SA) has been synthesized and its sonocatalytic activity has been evaluated by using methylene blue (MB) as a model organic pollutant under ultrasonic irradiation.

2. Experimental details

2.1 Catalyst preparation

$LaMnO_3$ nanoparticles were prepared by using the co-precipitation method based on our previous study [8]. Lanthanum (III) chloride heptahydrate ($LaCl_3.7H_2O$), manganese (II) chloride tetrahydrate ($MnCl_2.4H_2O$), and sodium hydroxide (NaOH), purchased from Merck, were used as the reagents. Nanographene platelets and graphene with different surface areas of 30 m^2/g (SA-1) and 400 m^2/g (SA-2), purchased from Angstron Materials, were used to synthesize the $LaMnO_3$/SA composites, respectively. The $LaMnO_3$/SA composites were prepared by following these steps: Briefly, graphene with different surface areas were dissolved into a solution of water and ethanol through ultrasonic treatment for 2 hours, respectively. After that, $LaMnO_3$ was added to each solution then stirred for 2 hours. The mixture was then heated at 120 °C for 3 h to influence the deposition of $LaMnO_3$ on the graphene sheets. Then, centrifugation was used to separate the precipitate and the solution. At last, the $LaMnO_3$/SA composite powders were obtained by drying the precipitate at 70 °C for 12 hours. The content of graphene in $LaMnO_3$ was constantly held and estimated to be 5 wt.%.

2.2 Characterization

The samples were characterized by using X-Ray Diffraction (XRD), Fourier Transform Infrared, and Brunauer-Emmet-Teller (BET) surface area analysis spectroscopy.

2.3 Sonocatalytic test

The sonocatalytic activities of prepared samples were observed by measuring the degradation of MB under ultrasonic irradiation. The detailed procedure has been described in our previous work [8]. As an irradiation sources, the commercial ultrasonic bath which operated at fixed frequency and power of 40 kHz and 150 W, respectively, was used. The degradation of MB was monitored by using a Hitachi UH5300 UV-visible spectrophotometer. The degradation of MB was recorded as C_t/C_0, where C_t is the concentration of MB at each measurement interval during irradiation and C_0 is the initial concentration of MB after reaching adsorption–desorption equilibrium. The maximum dosage concentration on the sonocatalytic process was checked by varying the amount of catalyst from 0.05/L to 0.40 g/L. The main active species involved in the sonocatalytic degradation of MB were studied by adding several substances such as sodium sulfate, di-ammonium oxalate, and tert-butyl alcohol, which are recognized as scavengers for electron, hole, and hydroxyl radical species, respectively.

3. Results and Discussion

The XRD patterns of $LaMnO_3$ composites with the different surface area of graphene ($LaMnO_3$/SA) are presented in Figure 1a. The XRD patterns of $LaMnO_3$ nanoparticles, nanographene platelets (SA-1), and graphene (SA-2) are also shown in this figure. The orthorhombic structure is detected on both the $LaMnO_3$ nanoparticle and its composites. For $LaMnO_3$/SA-1 composite, the diffraction peaks revealed the presence of graphite structure which confirmed from the observed 2θ values at 26.4° (002) for nano graphene platelets (NGP). However, the present of graphene on $LaMnO_3$/SA-2 composite did not change the main diffraction peaks of $LaMnO_3$. This may be due to the low content of graphene in the composite and the broad XRD peak of graphene. The absence of other phases of $LaMnO_3$ nanoparticles, NGP and graphene diffraction peaks in the spectra confirmed that the synthesized samples were the desired materials, $LaMnO_3$/SA composites. The lattice parameter and

crystallite size <D> values were obtained by using the Rietveld refinement method using MAUD program and were calculated by using Scherrer's formula [9] and also summarized in Table 1.
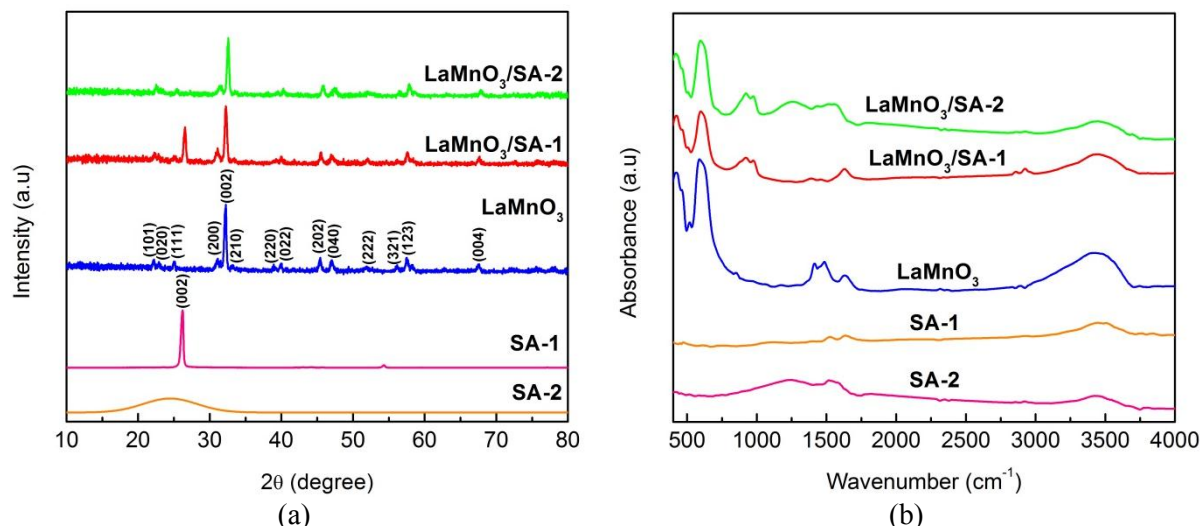

Figure 1. (a) XRD pattern; and (b) FT-IR spectra of $LaMnO_3$ composites with different surface area of graphene.

Table 1. The lattice parameter, grain size <D>, surface area and rate constant of $LaMnO_3$ composites with different surface area of graphene.

Sample	Lattice Parameter			<D> (nm)	Surface Area (m^2/g)	Rate Constant (min^{-1})
	a (Å)	b (Å)	c (Å)			
$LaMnO_3$	5.7419	7.7215	5.5403	44	17	0.0156
$LaMnO_3$/SA-1	5.7586	7.7090	5.5464	23	34	0.0232
$LaMnO_3$/SA-2	5.6859	7.7207	5.4925	21	87	0.0689

Figure 1b displays the FT-IR spectra of the $LaMnO_3$/SA composites with a different surface area of graphene. As a comparison, the FT-IR spectra of NGP (SA-1) and graphene (SA-2) are also shown. As seen in the figure, the spectra of both composites shows a strong absorption peak at 593 cm^{-1}, which could be ascribed to the stretching vibration of metal-oxygen bond in $LaMnO_3$ [10]. The incorporation of NGP and graphene could also be confirmed by the presence of absorption peaks at a wavenumber of 1460–1750 cm^{-1} and 3440 cm^{-1}, which are attributed to the C=O and O-H stretching vibration, respectively [11-13]. The C-OH stretching vibration at a wavenumber of 1236 cm^{-1} was also found; it indicated the formation of graphene in the $LaMnO_3$/SA-2 composite [13].

Figure 2a shows the sonocatalytic degradation rate of MB in the presence of $LaMnO_3$ nanoparticles and $LaMnO_3$/SA composites with a different surface of graphene. As clearly seen in the figure, the incorporation of NGP and graphene in the composites could increase the sonocatalytic performance of $LaMnO_3$ nanoparticles. The rate constant (k_{app}) of the samples was calculated by using the pseudo-first-order kinetic rate equation [4]. The result (Table 1) shows that the incorporation of graphene with a larger surface area in the composites exhibits the best sonocatalytic performance. It has been suggested that the surface area of the catalyst is one of the important factors that plays the roles in degradation efficiency. The catalyst with the large surface area could improve the degradation efficiency by increasing the contact probability between light and its active site. Therefore, the rate at which the oxidation process happens may further increase [1, 4]. The surface area of $LaMnO_3$/SA composites obtained by using BET method is also presented in Figure 2b. The composite BET surface

area increases with the increase of graphene surface area. This result indicates that LaMnO$_3$/SA composite with the largest surface area also shows the highest sonocatalytic performance.

To obtain the maximum dosage concentration for degrading MB under ultrasonic irradiation, the amount of LaMnO$_3$/SA-2 composite with the largest surface area was varied from 0.05 g/L to 0.40 g/L. The results that are shown in Figure 3a suggested that 0.1 g/L of LaMnO$_3$/SA-2 composite shows maximum dosage concentration for degrading MB in the sonocatalytic experiment.
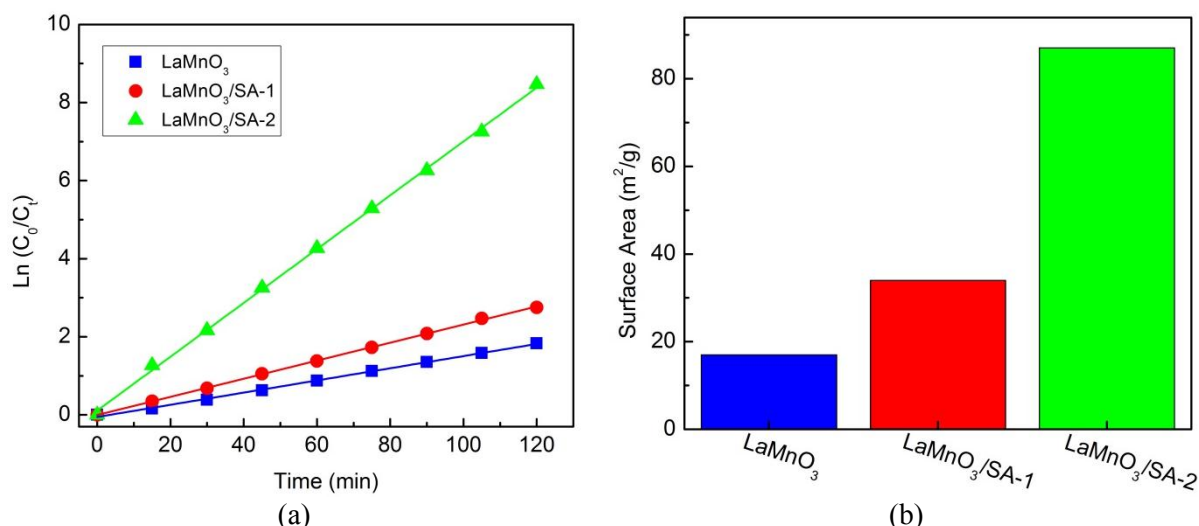

(a) (b)

Figure 2. (a) The sonocatalytic degradation rate of LaMnO$_3$ composites with different surface area of graphene; (b) The BET surface area of the samples
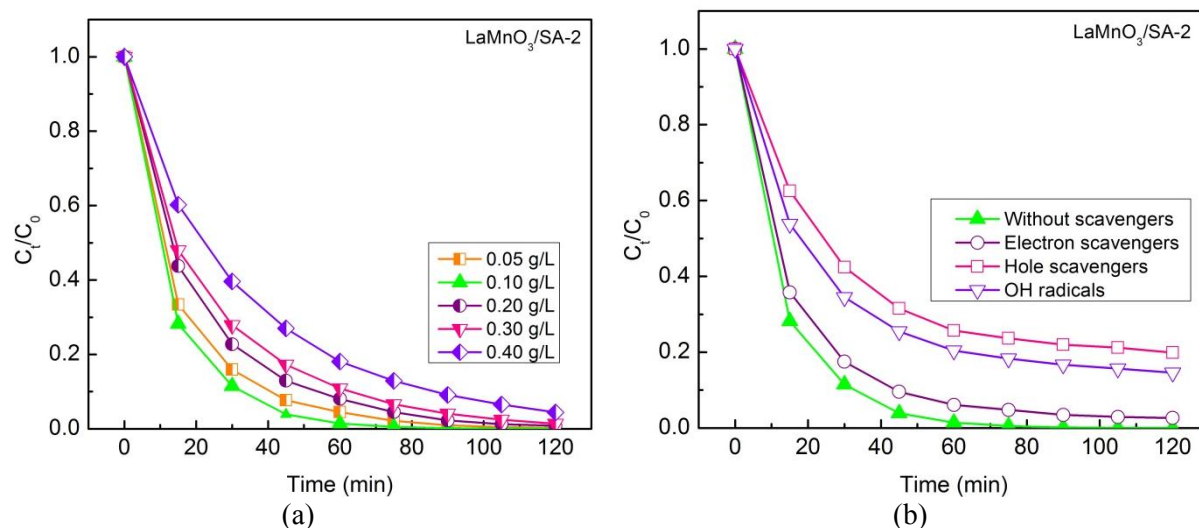

(a) (b)

Figure 3. (a) The effect of catalyst dosage; and (b) scavengers on photocatalytic degradation of MB by using LaMnO$_3$/SA-2 composite;

After getting the maximum dosage concentration of the catalyst, several active species such as an electron, hole, and hydroxyl radical scavengers were added into MB solutions to study the main active species in the sonocatalytic experiment. Na$_2$S$_2$O$_8$, diammonium oxalate, and tertbutyl alcohol were used as an electron, hole, and hydroxyl radical scavengers. The results (shown in Figure 3b) revealed that the presence of scavenger could decrease the degradation rate of MB. The largest decrease was obtained with the present of di-ammonium oxalate as a hole scavenger. It indicates that hole plays an important role in the sonocatalytic experiment. The large surface area of graphene could increase the

sonocatalytic performance as well as its electrons transport layer capacity. During the irradiation time, graphene collected the photo-generated electron in the conduction band of $LaMnO_3$ into its layers to interact with oxygen (O_2) and form superoxide radicals ($\bullet O_2^-$), thus inhibiting the recombination of photogenerated electron-hole pairs [1, 4]. At the same time, the hole left in the valence band of $LaMnO_3$ could move freely to be able to react with water molecules, resulting in the total hydroxyl radicals ($\bullet OH$) obtained in the sonocatalytic process increase [15-16]. Hence, this result confirmed that hole plays important role in the sonocatalytic experiment.

4. Conclusion

The sonocatalytic activity of $LaMnO_3$/SA composites with a different surface area of graphene has been evaluated for degrading MB under ultrasonic irradiation. The presence of graphene in $LaMnO_3$/SA composites could increase the sonocatalytic performance of $LaMnO_3$ nanoparticles. $LaMnO_3$/SA-2 with the largest surface area exhibited the best sonocatalytic performance. The maximum dosage concentration of the catalyst was 0.1 g/L and the hole played a major role in the degradation of MB.

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