Improvement of Catalytic Performance over LaMnO$_3$/Nanographene Platelets Composites

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Abstract. In this work LaMnO$_3$ – NGP composites with various NGP wt. % were prepared using co-precipitation method. The prepared LaMnO$_3$ – NGP composites were characterized by X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, and Fourier Transform Infrared (FT-IR) spectroscopy. The prepared samples were then used to remove methylene blue (MB) as a model of an organic pollutant under visible light and ultrasonic irradiation separately and simultaneously. The obtained results revealed that the catalytic performance of LaMnO$_3$ – NGP composites show better performance than LaMnO$_3$ nanoparticles. The photosonocatalytic activity also shows the highest degradation efficiency. Furthermore, the main influence factors on the catalytic activity were studied and discussed.

1. Introduction

Advanced oxidation processes (AOPs) including photocatalytic and sonocatalytic are known as an alternative method to conventional method for effective complete oxidation of various organic pollutants [1-2]. The generation of reactive radicals such as superoxide (•O$_2^-$) and hydroxyl (•OH) radicals in the each catalytic process could attack a number of organic pollutants in wastewater [3]. Moreover, the combination of photocatalytic and sonocatalytic, i.e. the so-called photosonocatalytic seem to enhance the degradation efficiency because of the increase in the generation of reactive radicals [4]. Although the photocatalytic and the sonocatalytic have been intensively explored individually for the degradation application, very few reports are available on their combination (i.e. photosonocatalytic) [5-6], especially using perovskite materials as a catalyst.

Perovskite especially LaMnO$_3$, has also been used in the catalytic application. As a catalyst, LaMnO$_3$ has been chosen due to its high catalytic activity, low cost, and environmental friendliness [7-8]. We had already reported the catalytic performance of LaMnO$_3$ nanoparticles previously [9]. However, LaMnO$_3$ nanoparticles could not completely degrade the methylene blue organic pollutant because of its high recombination of the photogenerated electron-hole pairs. Therefore, to suppress the recombination of the photogenerated electron-hole pairs in LaMnO$_3$, it can be loaded with nanographene platelets (NGP) since the NGP has superior electrical and mechanical properties, excellent electron mobility, good thermal stability and large specific surface area [10-12]. The aim of this work was to study the effect of NGP incorporation on the catalytic performance of LaMnO$_3$/NGP composites using methylene blue (MB) as a model of organic pollutant. Furthermore, the main factors on the catalytic activity were studied and discussed.
2. Experimental details

2.1. Materials

Lanthanum (III) chloride heptahydrate (LaCl$_3$·7H$_2$O), Manganese (II) chloride tetrahydrate (MnCl$_2$·4H$_2$O), and sodium hydroxide (NaOH) purchased from Merck (Kenilworth, NJ, USA) were used to synthesize LaFeO$_3$ nanoparticles. Nanographene platelets (NGP), purchased from Angstron Materials (Dayton, OH, USA), were then used to synthesize LaMnO$_3$/NGP composites. Distilled water was also used for all of the solutions.

2.2. Synthesis of the LaMnO$_3$/NGP composites

LaMnO$_3$ nanoparticle was synthesized using the co-precipitation method based on our previous work [9]. The obtained LaMnO$_3$ nanoparticle was then used to synthesize LaMnO$_3$/NGP composites. First, NGP was dissolved into distilled water and ethanol through ultrasonic treatment for 2 h. Then, the prepared LaMnO$_3$ nanoparticles were added to the NGP solution, followed by stirring for 2 h. Finally, the suspension was then centrifuged and dried at 70 ºC for 12 h. A series of LaMnO$_3$/NGP composites were prepared by varying the weight ratio of NGP to LaMnO$_3$ at 3, 5, and 10 wt%.

2.3. Characterization

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

2.4. Catalytic Activity

The photo-, sono, and photosono-catalytic activity of LaMnO$_3$/NGP composites were evaluated by using methylene blue (MB) as the model of organic pollutant. The detailed procedures in the catalytic experiments have been described in our previous work [9]. The degradation of MB was measured using a UV-visible spectrophotometer. The results was presented as $C_t/C_0$, where $C_t$ is the MB concentration in each irradiated time interval (15 min) and $C_0$ is the MB initial concentration after dark condition (30 min). In order to obtain the main active species in the catalytic process, diammonium oxalate, sodium sulfate, and tertbutyl alcohol were used as scavengers for a hole, electron, and hydroxyl radical species, respectively.

3. Results and Discussion

The FT-IR measurements were used to confirm the existence of NGP in the LaMnO$_3$/NGP composite. Figure 1a shows the FT-IR spectra of the LaMnO$_3$/NGP composites with various wt% NGP. As a comparison, the FT-IR spectrum of NGP is also shown. The FT-IR spectra of NGP and its composites show a strong absorption at wavenumber 3440 cm$^{-1}$, which corresponds to the O–H stretching vibration [13] and an absorption at 1460–1750 cm$^{-1}$, which is attributed to C=O stretching vibration [13-15]. The incorporation of LaMnO$_3$ in the composites was also confirmed by the presence of metal-oxygen stretching vibration on the absorption peak at wavenumber 539 cm$^{-1}$ [16].

The structural properties of the samples were characterized using XRD measurements. Figure 1b shows the XRD pattern of NGP, LaMnO$_3$ nanoparticle, and LaMnO$_3$/NGP composites with different wt% NGP. The XRD pattern of the composites exhibit characteristic peak assigned to (101), (020), (111), (200), (022), (210) (220), (022), (040), (222), (321), (123), and (004) crystallography planes of the orthorhombic structure of LaMnO$_3$ [17-18] and (200) planes of the graphite structure of NGP [19]. The diffraction peak of NGP in the composites increased with increasing wt% NGP. No other phases or impurities were detected in the XRD pattern of all samples. The crystal size and lattice parameters of all samples are tabulated in Table 1. The lattice parameter obtained by Rietveld refinement method using MAUD program and crystal size <$D>$ of the samples calculated using the Scherrer’s formula [20]. The BET method was also examined to obtain the specific surface area of all samples. The obtained specific surface area values are then summarized in Table 1. The results showed the specific surface area of the composite increase with the incorporation of NGP content.
The photo-, sono-, and photosono- catalytic activity of LaMnO$_3$/NGP composites for degrading MB are illustrated in the Figure 2. For comparison, the photo-, sono-, and photosono- catalytic activity of LaMnO$_3$ nanoparticles are also shown in the figure. It can be seen that MB degradation in the presence of LaMnO$_3$ nanoparticles increases with increasing irradiation time. Moreover, the incorporation of NGP in the composites could further increase the degradation efficiency. The degradation rate of MB was also calculated using the pseudo-first-order kinetic rate equation [21]. As clearly seen in the inset of Figure 2, the obtained result revealed that 5 wt% NGP shows the maximum degradation rate in all of the catalytic processes. In addition, the MB degradation under photosonocatalytic activity exhibits faster degradation rate compared to photocatalytic or sonocatalytic. To detect the main active species responsible in the process of MB degradation, the experiment was repeated using LaMnO$_3$/NGP composite (5 wt%) with the addition of active species like an electron, hole, and hydroxyl radicals. Na$_2$S$_2$O$_8$, diammonium oxalate, and tertbutyl alcohol were used as an electron, hole, and hydroxyl radical scavengers. The addition of scavenger (presented in Figure 3) could decrease the degradation rate of MB: the largest decrease is obtained with the present of hole scavenger. It indicates that the hole plays the most important role in the degradation process of MB.

The higher degradation rate with the NGP incorporation could depend on several factor: the first is electron and hole separation efficiency and the second is the surface area of the catalyst. NGP, with its electron transport layer capacity could inhibit the photo-generated electron and hole of LaMnO$_3$ to recombine by transferring photo-generated electrons in the conduction band of LaMnO$_3$ into NGP layers [7-8]. Therefore, the photo-generated electron and hole could react with oxygen molecules (O$_2$) and hydroxyl groups (OH$^-$) before recombining, to generate superoxide radicals (•O$_2^-$) and hydroxyl...
radicals (•OH) radicals, respectively. These reactive radicals are responsible for degradation of the complex chemical bonds of organic pollutants such as MB. NGP with its large surface area could increase the contact probability between the catalyst and the light, thus increasing the rate of oxidation process [7]. Furthermore, the different mechanism on the photo-, sono-, and photosono- catalytic activity have been explained in our previous work [9]. It was reported that the higher concentrations of

**Figure 2.** The photo-, sono- and photosono- catalytic activity of LaMnO$_3$/NGP composites with different wt% NGP.

**Figure 3.** The effect of scavengers on the photo-, sono- and photosono- catalytic degradation of MB using LaMnO$_3$/5wt% NGP composite.
reactive radicals (especially •OH radicals) were produced during the photosonocatalytic process [3-4], so that it may explain the fastest degradation rate of MB.

4. Conclusion
The influence of NGP incorporation on the photo-, sono-, and photosono- catalytic activity of LaMnO$_3$/NGP composites have been investigated under light or/and ultrasonic irradiation separately and simultaneously. The results showed that NGP could inhibit the electrons and holes recombination and enhance the catalytic performance. The addition of 5 wt% NGP gives maximum degradation rate of MB. In addition, the photosonocataytic showed faster degradation compared to photocatalytic and sonocatalytic alone.

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