The photo-, sono-, and sonophoto-catalytic activity of an LaMnO₃/TiO₂/graphene composite for degrading methylene blue in wastewater

Y D Susanti, D Triyono and R Saleh

1. Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

2. Integrated Laboratory of Energy and Environment, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author’s e-mail: rosari.saleh@ui.ac.id

Abstract. Here we describe the successful synthesis of an LaMnO₃/TiO₂/graphene composite using a co-precipitation method and three different weight percentages (wt%) of graphene. The structure of the sample was characterized using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy, and the thermal stability of the sample was characterized using thermogravimetric analysis (TGA) and differential thermal analysis. The XRD pattern of the sample confirmed the orthorhombic phase of the LaMnO₃ nanoparticle and anatase phase of the TiO₂ nanoparticle; however, the graphene peak unidentifiable by XRD was confirmed using TGA and FTIR spectroscopy. Moreover, we found that the photo-, sono-, and photosono-catalytic activities of LaMnO₃/TiO₂ were elevated by the presence of graphene material as an electron trapper, resulting in optimal rates of methylene blue degradation in the presence of 5 wt.% graphene.

1. Introduction

Semiconductor catalysts have attracted increasing attention during the previous decade [1-3], with their subsequent applications in degrading organic pollutants, such as methylene blue (MB), via photo-, sono-, and sonophoto-catalysis [4]. Among catalysts, mixed metal oxides, such as the perovskite oxide LaMnO₃, have been used to degrade organic pollutants based on their narrow band gaps, chemical stability, lack of toxicity, and environment safety [5]. However, there remain limitations with LaMnO₃ in catalytic processes due to high levels of electron–hole recombination and the presence of low surface areas that can inhibit MB degradation [6,7].

MB degradation can be increased by coupling LaMnO₃ and TiO₂ nanoparticles due to the formation of junction levels on the nanocomposite [8]. Moreover, it might be possible to further increase the catalytic activity of the LaMnO₃/TiO₂ composite by adding graphene, which is a two-dimensional material comprising a carbon atom with a large surface area, high electron mobility, and good electrical conductivity [9]. Graphene has attracted increased interest due to its ability as an electron trapper capable of promoting MB degradation [10]. The present study reports the photo-, sono-, and sonophoto-catalytic activity of LaMnO₃/TiO₂/graphene under visible, ultrasonic, and combined visible and ultrasonic conditions.

2. Experimental detail

2.1. Chemicals

All reagents were of analytical grade and commercially available from Merck Darmstadt, Germany.
Figure 1. (a) XRD pattern and (b) FTIR spectra of the LaMnO/TiO/graphene composite at different wt% of graphene.

The reagents used to synthesize the LaMnO/TiO/graphene composite included lanthanum (III) chloride heptahydrate (LaCl$_3$•7H$_2$O; 99% purity; Merck), manganese (II) chloride tetrahydrate (MnCl$_2$•4H$_2$O; 99% purity; Merck), anatase TiO$_2$ (98% purity; Merck), sodium hydroxide (NaOH; 99% purity; Merck), and ethanol.

2.2. Catalyst preparation
The LaMnO nanoparticle was synthesized using a co-precipitation method at 800 °C, as described previously [11]. The LaMnO/TiO$_2$ nanocomposite was synthesized using a sol-gel method [12], and the LaMnO/TiO$_2$/graphene composite was synthesized using different weight percentages of graphene (3, 5, and 10) wt.% using the co-precipitation method [11].

2.3. Characterization
All prepared samples were characterized using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, Brunauer–Emmett–Teller (BET) analysis, thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The crystallite structure of the sample was investigated using XRD on a Rigaku Miniflex 600 system (Rigaku, Tokyo, Japan), with the molecular vibration of the sample evaluated using FTIR spectroscopy on a Shimadzu IR Prestige 21 system (Shimadzu, Kyoto, Japan). The thermal stability of the sample was characterized using TGA and DTA using a Rigaku TG8121 system (Rigaku) during sample heating from room temperature to 1000 °C at a rate of 2 °C/min in the presence of a constant flow of argon.

2.4. Catalytic activity
Photo-, sono-, and sonophoto-catalytic activities were analyzed by observing MB degradation in the presence of the LaMnO/TiO$_2$/graphene composite under visible light, ultrasonic, and a combination of the two conditions. MB degradation determined under alkaline conditions (pH 13) and within a 2-h window using a Hitachi UH5300 UV-visible spectrophotometer (Hitachi, Tokyo, Japan). Active species present during catalysis were determined using electron (sodium sulfate), hole (diammonium oxalate), and hydroxyl radical (tert-butyl alcohol) scavengers.

3. Results and discussion
Figure 1a shows the XRD results of the samples prepared at different wt.% of graphene. All samples displayed the orthorhombic structure of the LaMnO nanoparticle at a 2θ angle of 22.12°, 22.96°, 25.06°, 31.08°, 32.21°, 33.2°, 38.94°, 40.05°, 45.4°, 47.07°, 56.19°, 57.6°, 58.56°, 67.68°, and 75.68° corresponding to reflections of (110), (020), (111), (200), (022), (210), (220), (022), (202), (040), (222), (321), (123), (004), and (412) and anatase phases of the TiO$_2$ nanoparticle at 2θ of 25.24°, 37.82°, 47.9°, 53.59°, and 62.36° corresponding to reflections of (101), (004), (200), (106), and (215).
Figure 2. (a) TGA and (b) DTA of the LaMnO$_3$/TiO$_2$/graphene composite at different wt.% of graphene.

Figure 3. BET analysis of the LaMnO$_3$/TiO$_2$/graphene composite at different wt.% of graphene.

We were unable to identify a graphene peak using XRD; therefore, its presence was confirmed using FTIR analysis. Figure 1b shows the FTIR spectra of the LaMnO$_3$/TiO$_2$/graphene composite, indicating strong absorption at 3440 cm$^{-1}$ and corresponding to an O–H-stretching vibration. The presence of graphene was also identified according to the presence of a strong vibration mode at a range of 1460 cm$^{-1}$ to 1750 cm$^{-1}$ corresponding to C=O- and C–OH-stretching vibrations. Furthermore, FTIR analysis indicated that the LaMnO$_3$/TiO$_2$/graphene composite showed a strong vibration at 555 cm$^{-1}$ corresponding to the Mn–O- and Ti–O-stretching vibrations.

Figure 2a show the TGA results for the LaMnO$_3$/TiO$_2$/graphene composite. We used TGA analysis to investigate sample stability upon heating and total graphene present. We observed a loss of weight in the sample at 150 °C and associated with removal of adsorbed water, as well as at 400 °C in association with the combustion effect of graphene in the LaMnO$_3$/TiO$_2$/graphene composite, with weight loss at 150 °C suggesting the addition of graphene and indicating the amount of graphene used during synthesis.

Figure 2b shows DTA results for the sample at different wt% of graphene. The composite displayed exothermic properties ~380 °C, and increasing amounts of graphene also increased the rate of combustion, with total heat flow in the exothermic process increasing in proportion to the wt% of graphene.

We then used BET analysis to characterize the specific surface area of the sample, as shown in Figure 3. The results showed that the addition of graphene (specific surface area: 400 m$^2$/g) increased
Figure 4. (a) Catalytic activities and (b) rate constants of the LaMnO$_3$/TiO$_2$/graphene composite.

Figure 5. Catalytic activities of the LaMnO$_3$/TiO$_2$/graphene composite following addition of several scavengers.

the specific surface area of the sample. This parameter represents among the most important aspects of the catalysis process, as a high specific surface area can enhance the contact between the sample surface and an organic pollutant, such as MB.

Figure 4 shows the photo-, sono-, and sonophoto-catalytic activities of the LaMnO$_3$/TiO$_2$/graphene composite, which exhibited higher activity than the LaMnO$_3$/TiO$_2$ nanoparticle. Previous studies report that the presence of graphene acts as an electron trap during catalysis and promotes higher catalytic rates [13,14]. We found that 5 wt% graphene allowed for optimal catalytic activity; however, higher wt% of graphene (e.g., 10 wt%) resulted in decreased MB degradation rates. This suggested that excess graphene might promote sample aggregation, thereby hindering access to light in the form of irradiation. Furthermore, we found that sonophoto-catalytic activity displayed better MB degradation based on the synergistic effect of visible light and ultrasonic irradiation through the photo- and sono-catalytic processes.

We then evaluated the effects of different scavengers (electron, hole, and hydroxyl radical) on the catalytic activities of the LaMnO$_3$/TiO$_2$/graphene composite, with the results showing that inclusion of the hydroxyl radical scavenger had the greatest attenuating effect on MB degradation (figure 5).

4. Conclusions

Here, we successfully synthesized an LaMnO$_3$/TiO$_2$/graphene composite using a co-precipitation method with the addition of graphene enhancing the specific surface area of the sample. Our results showed that 5 wt% of graphene was the optimal, resulting in the highest MB degradation activity by
the composite, and that sonophoto-catalysis showed the best results based on the synergistic effects of photo- and sono-catalysis.

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