Ag modified LaMnO₃ nanoparticles for methylene blue degradation via photosonocatalytic activities

Y D Susanti, N Afifah and R Saleh

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

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

Corresponding author: rosari.saleh@gmail.com

Abstract. Catalyst incorporating Ag nanoparticles with LaMnO₃ nanoparticles have been successfully synthesized using the co-precipitation method. The characteristics of the materials are characterized using x-ray diffraction (XRD), UV-Visible spectrometer and thermogravimetric analysis (TGA). The results show that the Ag/LaMnO₃ composite show orthorhombic structure of the LaMnO₃ nanoparticle and the cubic structure of Ag nanoparticle. The Ag/LaMnO₃ composite show better photosonocatalytic activities of methylene blue (MB) than LaMnO₃ nanoparticle under the combination of ultrasonic irradiation and visible light irradiation. Ag can be used as an electron capture in the photosonocatalytic process, because Ag can capture the electron transport along LaMnO₃ nanoparticles leading to a high recombination rate of electrons and holes.

1. Introduction

Perovskite nanomaterial with a general structure (ABO₃) has attracted attention from many researchers because of its excellent performance as catalyst materials under visible light irradiation. Unfortunately, similar to other catalysts electron and hole recombination still easily occurs in pure perovskite nanomaterial during the catalysis process. Many methods have been explored to determine an effective way to inhibit the recombination of electrons and holes further increasing the degradation of organic pollutants such as methylene blue (MB). Coupling it with semiconductor or modifying it with noble metal are some methods that have been explored by researchers to increase the degradation of organic pollutants [1–2]. Furthermore, noble metal such as silver (Ag) have been widely studied to modify some catalyst nanomaterials to hinder the electron and hole recombination [3–4].

Hu et al. [5] reported that Ag could be used as an agent to capture electrons so holes cannot be recombined with electrons, which can improve the photocatalytic process of LaMnO₃/graphene composite. Furthermore, Ag nanoparticles could be used as emerging visible-light driven photocatalysts that has been attracted many researchers.

This work, we reports the synthesis of Ag modified LaMnO₃ nanoparticles via the co-precipitation method. In particular, the photosonocatalytic of Ag modified LaMnO₃ nanoparticles was evaluated by the photosonodegradation of aqueous methylene blue as an organic pollutant. In addition, the effects of various scavengers were also evaluated in this research.

2. Experimental

2.1. Materials

All the chemical reagents were analytical grades so further purification is not carried out in their use.
Figure 1. XRD pattern of LaMnO₃ and Ag/LaMnO₃ composite.

Lanthanum (III) chloride heptahydrate (LaCl₃.7H₂O, Merck, 99%), manganese (II) chloride tetrahydrate (MnCl₂.4H₂O, Merck, 99%), sodium hydroxide (NaOH, Merck, 99%), silver nitrate (AgNO₃), sodium dodecyl sulfate (SDS), sodium carbonate (Na₂CO₃), and ethylene glycol (EG, Merck).

2.2. Preparation of Ag/LaMnO₃
LaMnO₃ nanoparticle were synthesized using the co-precipitation method as described previously [6] but without vacuum treatment in the calcination process. In contrast, Ag nanoparticles were synthesized using microwave-assisted methods [7]. Then, the Ag/LaMnO₃ composite was synthesized by the same method as the LaMnO₃/Fe₃O₄ nanocomposite [8].

2.3. Characterizations
Instruments used to analyse the samples are X-ray diffraction (XRD), thermogravimetric analysis (TGA) and UV-Visible spectrometer. XRD measurements were done by using Rigaku Miniflex 600 (Cu-Kα (λ = 1.54060) with 20 mA and 40 kV) to get the phase and crystal structure of the sample. Thermal stability of the samples is obtained from the results of TGA measurement carried out from room temperature to temperature of 1000 °C. UV-Visible spectrometry was used to investigate the surface plasmon resonance of the sample and was performed using Hitachi 5300.

2.4. Photosonocatalytic experiment
Methylene blue is an organic pollutant used in this study as a model. The photosonocatalytic of Ag/LaMnO₃ was investigated by observing the degradation of MB for concentrations of 20 mg/L and pH 13 at room temperature with a combination of two irradiations by visible light and ultrasonic waves simultaneously. The catalyst was dissolved in 100 mL of a MB solution and was continuously stirred using a magnetic stirrer in the dark to ensure that the adsorption-desorption process from MB molecule to the catalyst surface reaches its equilibrium. Then, the solution was irradiated under visible and ultrasonic irradiation and several solution samples were collected every 15 minutes through centrifugation. Then, it was measured using Hitachi 5300 UV-vis spectrophotometer. The solution was irradiated using a 40 W Xe lamp light as visible light irradiation and using ultrasonic bath that was operated at a fixed frequency of 40kHz and 150 W as ultrasonic irradiation.

3. Results and discussion
Figure 1 shows the XRD pattern of LaMnO₃ nanoparticle and Ag modified LaMnO₃ nanoparticle with different Ag nanoparticle weight percentages. The XRD pattern of Ag modified LaMnO₃ nanoparticles confirm the orthorhombic structure of LaMnO₃ nanoparticle and cubic phase of silver nanoparticles. Figure 1 shows that when the Ag content is less than 20wt.% the peak of Ag cannot be seen or only
The lattice parameter and grain size <D> of LaMnO₃ nanoparticle and Ag/LaMnO₃ composite.

| Samples          | Lattice Parameter LaMnO₃ | Lattice Parameter Ag | <D> LaMnO₃ | <D> Ag |
|------------------|-------------------------|----------------------|------------|-------|
|                  | a (Å)       | b (Å)     | c (Å)   | a=b=c(Å) | (nm) | (nm) |
| LaMnO₃           | 5.46323    | 5.5341   | 7.7499 | -       | 41   | -    |
| 10wt.% Ag/LaMnO₃ | 5.47462    | 5.5358   | 7.7527 | 1.4877  | 28   | 10   |
| 20wt.% Ag/LaMnO₃ | 5.51255    | 5.4447   | 7.7646 | 4.0827  | 22   | 13   |
| 30wt.% Ag/LaMnO₃ | 5.53014    | 5.4749   | 7.7839 | 4.0996  | 17   | 15   |

The thermogravimetric analyses of the sample Ag/LaMnO₃ composite with different wt. % of Ag are depicted in figure 2a. The overall weight loss of the sample was associated to decomposition of the organic matter. The first stage weight loss of the sample from 30 °C to 300 °C was attributed to the removal of water [9]. The second stage from 300 °C to 550 °C was attributed to the decomposition of organic compounds. Furthermore, the weight loss from 820 °C to 1000 °C was attributed to the oxidation of lanthanum manganite in the perovskite structure. Moreover, the addition of Ag on LaMnO₃ increased the thermal stability of the sample from room temperature to 1000 °C [10]. Figure 2b shows the surface plasmon resonance of the sample LaMnO₃ nanoparticles and Ag/LaMnO₃ composite. The Ag/LaMnO₃ show the characteristic an expected strong broad absorption in visible region around 400–500 nm after the addition of Ag nanoparticle on LaMnO₃ nanoparticle. Furthermore, as the weight percentage of Ag increased, the absorption of Ag/LaMnO₃ composite increased in the region of 400–500 nm.

The photosonocatalytic activities of LaMnO₃ nanoparticles and Ag modified LaMnO₃ nanoparticles with different Ag weight percentages are shown in figure 3a. Figure 3a shows that Ag modified LaMnO₃ nanoparticles have superior photosonocatalytic activity than pure LaMnO₃ nanoparticles. In addition, the degradation of MB was increased by adding Ag modified LaMnO₃ nanoparticles until 20 wt.% of Ag was obtained. This effect can be due to the following reasons. First, Ag can extend the...
utilization of the light adsorption spectrum, and Ag can capture electrons that are transported along LaMnO$_3$ nanoparticles and inhibit the recombination of electron and hole pairs [5]. Moreover, the degradation of MB using Ag modified LaMnO$_3$ nanoparticles decrease by adding more Ag to LaMnO$_3$ nanoparticles. The degradation of MB was decreased at 30 wt.% of Ag, which is caused by the decreased electron generation [11]. Furthermore, the excess of Ag could hinder the incoming of visible light so it does not irradiate the Ag/LaMnO$_3$ composite. Figure 3b shows a constant rate of LaMnO$_3$ nanoparticles and Ag/LaMnO$_3$ composite. The figure also shows that the Ag/LaMnO$_3$ composite with 20 wt.% of Ag has the highest constant rate.

The proposed photosonocatalytic mechanism of MB is shown in Figure 4. The Ag/LaMnO$_3$ composite was irradiated using visible light and ultrasonic irradiation. The visible light irradiation can make the electrons from valence band excite to the conduction band and leave holes in the valence band. Then, the electrons from the valence band of LaMnO$_3$ nanoparticles can react with oxygen (O$_2$) and form a superoxide radical (O$_2^-$). In addition, the holes in the valence band of the LaMnO$_3$ nanoparticles can react with a water molecule and form a hydroxyl radical (OH$^-$). Both O$_2^-$ and OH$^-$ directly oxidize organic pollutants such as MB. Furthermore, ultrasonic irradiation can form microbubbles because of the cavitation effect. However, microbubbles can suddenly collapse and create hotspots and sonoluminescence. Hotspots with high temperature can make water (H$_2$O) split and...
form H+ and OH-. For sonoluminescence, ultrasonic irradiation could act as a light irradiation and have a wide wavelength because of the cavitation effect. Furthermore, the process of sonoluminescence follows the same role as visible light irradiation and could oxidize organic pollutants MB. Moreover, the Schottky barrier that is formed between Ag and LaMnO3 nanoparticles can inhibit the electrons and holes recombination. The Ag could act as an electron capture, leading to the high recombination of electrons and holes and having superior photosonocatalytic than pure LaMnO3 nanoparticles.

Figure 5 shows the photosonocatalytic of MB by adding several scavengers, electrons (e-) holes (h+) and hydroxyl radicals (OH-). Figure 5 shows that the addition of several scavenger can inhibit the degradation of MB. Furthermore, the figure shows that the hole is the most active species in the photosonocatalytic activities of the Ag/LaMnO composite.

4. Conclusions
Ag/LaMnO3 with various weight percentages of Ag has been successfully synthesized using the co-precipitation method. The XRD measurement of Ag/LaMnO3 composite confirms the cubic phase of Ag and the orthorhombic phase of LaMnO3 nanoparticles. The photosonocatalytic activity of MB was investigated under the combination of visible light and ultrasound irradiation. Furthermore, the addition of Ag on LaMnO3 could increase the degradation of MB until 20 wt.%, and it will the degradation of MB decreases on at 30 wt.% of Ag. By adding some scavengers on in the photosonocatalytic process, it can be found that the results show that holes as are the most active species to degrade MB using Ag/LaMnO3.

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