

Enhancement of photoresponse to ultraviolet region by coupling perovskite LaMnO_3 with TiO_2 nanoparticles

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Abstract. Mixed oxides of rare-earth elements and 3d transition metal perovskite materials were studied for their catalytic application. We have previously reported the catalytic performance of perovskite LaMnO_3 nanoparticles under visible light and ultrasonic irradiation separately and simultaneously. However, LaMnO_3 perovskite's narrow optical gap can absorb only a small portion of the solar spectrum in the ultraviolet region, resulting in low catalytic performance. Coupling LaMnO_3 with other metal oxides with an optical gap in the ultraviolet light range offers an effective solution to this problem by improving catalytic performance. To this end, sol-gel was used to prepare $\text{LaMnO}_3/\text{TiO}_2$ nanocomposites with varying LaMnO_3 to TiO_2 molar ratios. The $\text{LaMnO}_3/\text{TiO}_2$ nanocomposites were characterized using X-ray diffraction (XRD), a vibrating samples magnetometer (VSM), and UV-visible diffuse reflectance spectroscopy (DRS). The anatase phase of TiO_2 and the orthorhombic structure of LaMnO_3 facilitate the coupling of LaMnO_3 with TiO_2 , and the incorporation of TiO_2 nanoparticles tends to increase the optical gap of the nanocomposite. The samples were used to remove organic dyes by means of simultaneous light and ultrasonic irradiation. The results confirm that the photosonocatalytic performance of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposites successfully extends to the ultraviolet light region, and the main factors influencing photosonocatalytic activity are studied and discussed.

1. Introduction

ABO_3 -type perovskite (A: rare earth; B: transition metal) has been widely used as a catalyst to degrade organic pollutants contained in wastewater because of its high chemical stability, high electron mobility, non-toxicity, and environmental friendliness [1-2]. LaMnO_3 is one ABO_3 -type perovskite that can be used in this way; its special physical and chemical characteristics and an optical band gap value corresponding to the range of visible light irradiation make it a strong candidate for use as a catalyst. The use of LaMnO_3 as catalyst is of interest because solar energy contains about 46% visible light [1, 3-5].

Catalytic performance could also be improved by combining TiO_2 and LaMnO_3 in nanocomposite form. Catalysts in nanocomposite form are known to inhibit electron-hole recombination, so improving catalytic performance [6-7]. Additionally, the optical gap of TiO_2 (~3.2 eV) would be expected to extend the response of nanocomposite light in the ultraviolet (UV) light range, which accounts for about 5% of solar energy. TiO_2 itself is used as a catalyst because it is high catalytic activity, non-toxicity, and low cost [8].

The catalytic activity of LaMnO_3 nanoparticles has been reported in our previous work [9]. The combination of visible light and ultrasonic (Vis+US) in photosonocatalytic activity achieved maximum



performance in degrading methylene blue (MB) as organic pollutant model. In the present study, catalyst performance was improved by synthesizing $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite using the sol-gel method. TiO_2 's influence on the photosonocatalytic activity of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite was assessed using different irradiation sources: UV light and ultrasonic (UV+US) and visible light and ultrasonic (Vis+US). The main factors influencing photosonocatalytic activity are investigated and discussed below.

2. Experimental details

Chemicals: All chemicals were of analytical grade and were used without further purification. Reagents included $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, titanium dioxide (TiO_2), and sodium hydroxide (NaOH), (Merck).

Catalyst preparation: LaMnO_3 nanoparticles were first prepared following our procedure in previous work [9]. $\text{LaMnO}_3/\text{TiO}_2$ with different molar ratios (1:0.1, 1:0.3, and 1:0.5) were synthesized using the sol-gel method [10], involving the following steps. First, 0.00125 mol TiO_2 was dissolved in 30 mL distilled water under the influence of a magnetic stirrer. Then, 0.00125 NaOH was dissolved in 65 mL distilled water and added to the mixture (solution A). Next, solution A was stirred and heated to a temperature of 80°C . Meanwhile, the prepared LaMnO_3 nanoparticle was dissolved into 30 mL a distilled water (solution B). Solution B was then mixed with solution A under the continuous influence of a magnet stirrer at 80°C for 2 hours. The final product was allowed to stand for one night at room temperature and then heated at 120°C for an hour in vacuum conditions.

Characterization: The crystal structure was obtained using X-ray diffraction (XRD) spectroscopy (Rigaku Miniflex 600) with monochromatic $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.54060 \text{ \AA}$), operating at 40 kV and 20 mA in the range 10 – 90° . The XRD pattern was then analyzed using the MAUD program and the Rietveld method for obtaining crystal structure and lattice parameters. Magnetic characteristics were measured using an Oxford Type 1.2 T vibrating sample magnetometer (VSM) (from 0 to ± 1 Tesla). Optical characteristics were measured using a UV-Vis diffuse reflectance spectrophotometer.

Photosonocatalytic activity: Methylene blue (MB) was chosen as a model organic pollutant. For present purposes, MB degradation was executed using $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite as catalyst and a combination of light and ultrasonic irradiation, known as photosonocatalysis. This photosonocatalytic procedure was described in detail in our previous work [9], using a Hitachi UH5300 UV-visible spectrophotometer for measurement. Moreover, in this work, the photosonocatalytic were monitored using different irradiation sources: UV light and ultrasonic (UV+US) and visible light and ultrasonic (Vis+US). MB degradation percentage was measured as C_t/C_0 , where C_t is the MB concentration at a specified time following irradiation and C_0 is the earlier concentration of MB after reaching adsorption–desorption equilibrium. To identify the main active species in MB degradation, chemical compounds such as di-ammonium oxalate, sodium sulfate, and tert-butyl alcohol were used as hole, electron, and hydroxyl radical scavengers. To check its stability, the catalyst was reused 4 times.

3. Results and discussion

The crystal structure of the sample was studied using XRD spectroscopy. Figure 1(a) shows the diffraction pattern of $\text{LaMnO}_3/\text{TiO}_2$ samples with different molar ratios, as well as the diffraction patterns of TiO_2 and LaMnO_3 . The dominant diffraction pattern of the $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite was that of orthorhombic LaMnO_3 [11–12]. The diffraction peak at 2θ 25.2° confirmed the presence of the tetragonal structure in the anatase phase of TiO_2 [7]. There was no impurity phase in the diffraction pattern of the $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite. Table 1 summarizes lattice parameter values for the diffraction pattern of the sample obtained by the Rietveld refinement method and crystal size values calculated using Scherrer's formula [13].

VSM measurement was used to investigate the magnetic properties of samples. Figure 1(b) shows the magnetic saturation of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposites with different molar ratios. All samples showed ferromagnetic behavior at room temperature. The results also confirm that magnetic saturation were influenced by the presence of TiO_2 , and that magnetization decreased with increased TiO_2 molar ratio. This decrease in magnetization with increased TiO_2 molar ratio may be caused by the decrease of LaMnO_3 mass in the presence of TiO_2 as non-magnetic material. TiO_2 is also known to have diamagnetic

characteristics, which may reduce dipolar interaction of the $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite [10]. Magnetic saturation values for $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite are summarized in table 1.

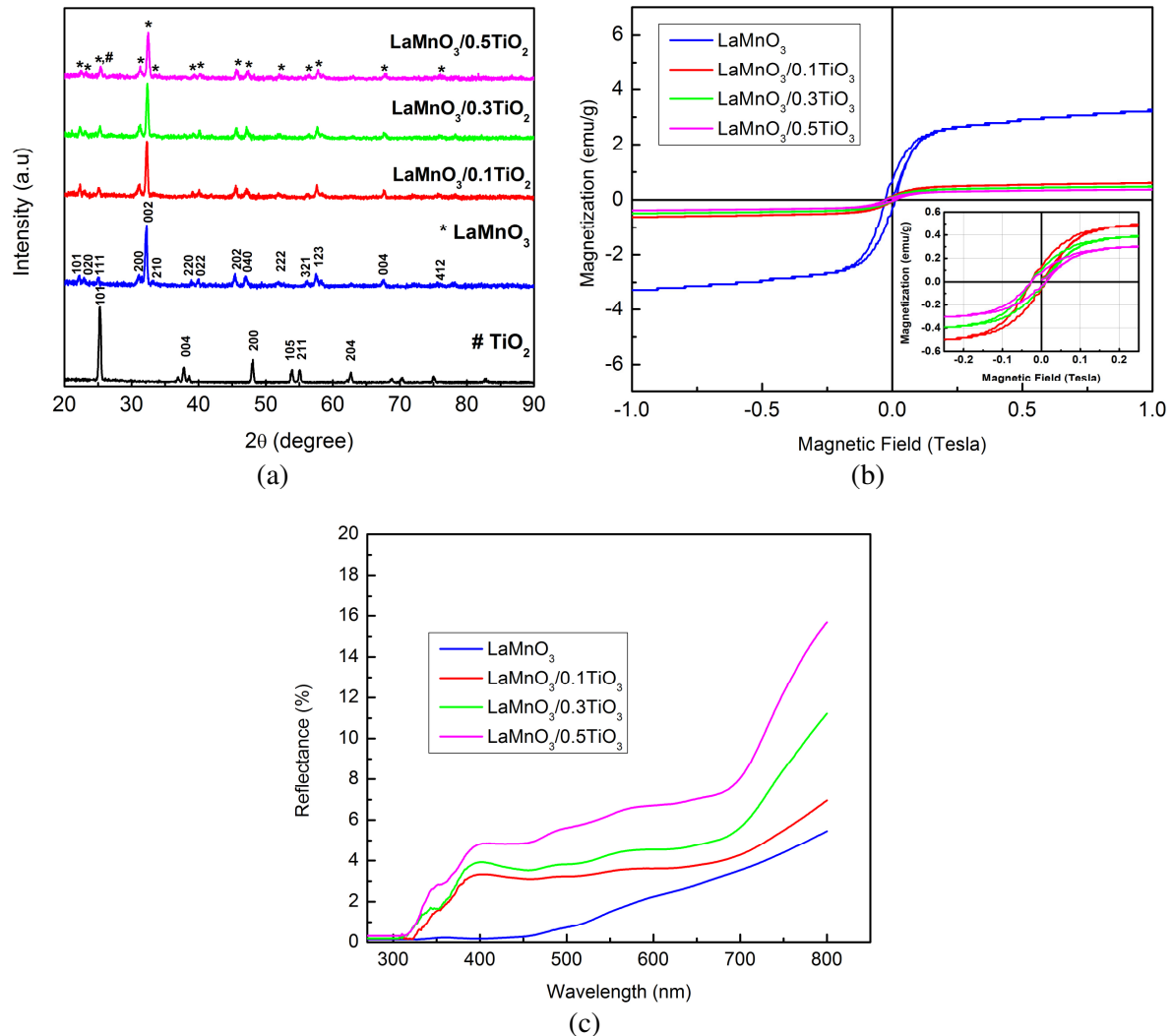


Figure 1. (a) XRD pattern; (b) VSM spectra; and (c) UV-Vis reflectance spectra of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposites with different molar ratios.

Table 1. The lattice parameter, grain size $\langle D \rangle$, magnetic saturation (M-S) and optical gap of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite.

| Sample | Lattice Parameter LaMnO_3 | | | Lattice Parameter TiO_2 | | $\langle D \rangle$ LaMnO_3 (nm) | $\langle D \rangle$ TiO_2 (nm) | M-S (emu/g) | Optical gap (eV) |
|----------------------------------|---------------------------------------|--------|--------|-------------------------------------|--------|---|---|----------------|------------------------|
| | a (Å) | b (Å) | c (Å) | a=b (Å) | c (Å) | | | | |
| LaMnO_3 | 5.7419 | 7.7215 | 5.5403 | - | - | 44 | - | 3.20 | 1.24 |
| $\text{LaMnO}_3/0.1\text{TiO}_2$ | 5.7382 | 7.7187 | 5.5430 | 3.8215 | 9.4850 | 24 | 23 | 0.60 | 1.48 |
| $\text{LaMnO}_3/0.3\text{TiO}_2$ | 5.7269 | 7.6995 | 5.5321 | 3.7824 | 9.5055 | 23 | 22 | 0.48 | 1.59 |
| $\text{LaMnO}_3/0.5\text{TiO}_2$ | 5.7136 | 7.6787 | 5.5176 | 3.7685 | 9.4907 | 20 | 21 | 0.36 | 1.62 |

Optical characteristics of the samples were studied using UV-Vis diffuse reflectance spectroscopy (DRS). Figure 1(c) shows the UV-Vis reflectance spectra of LaMnO_3 and $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite with variation of molar ratio. Extrapolating the curve using Kubelka-Munk analysis [14] provided the optical band gap value of each sample. These values are summarized in table 1. The results indicate that the adsorption capacity of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite is in the range of visible light radiation. Additionally, optical band gap value was found to increase with the molar ratio of TiO_2 . The increase in optical band gap value would be expected to increase the response of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite light in the UV light radiation.

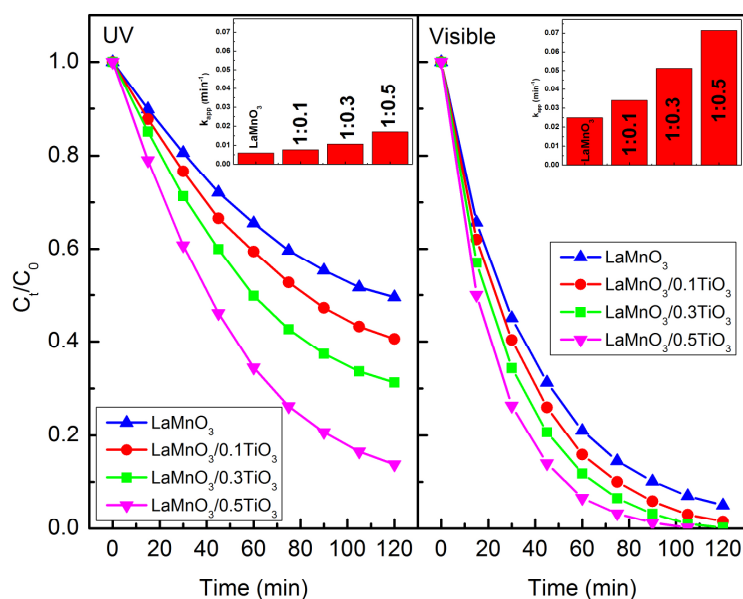


Figure 2. The photocatalytic activity of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite with different molar ratios of TiO_2 under UV (left) and Visible (right) light irradiation. The inset shows MB degradation rate using $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite.

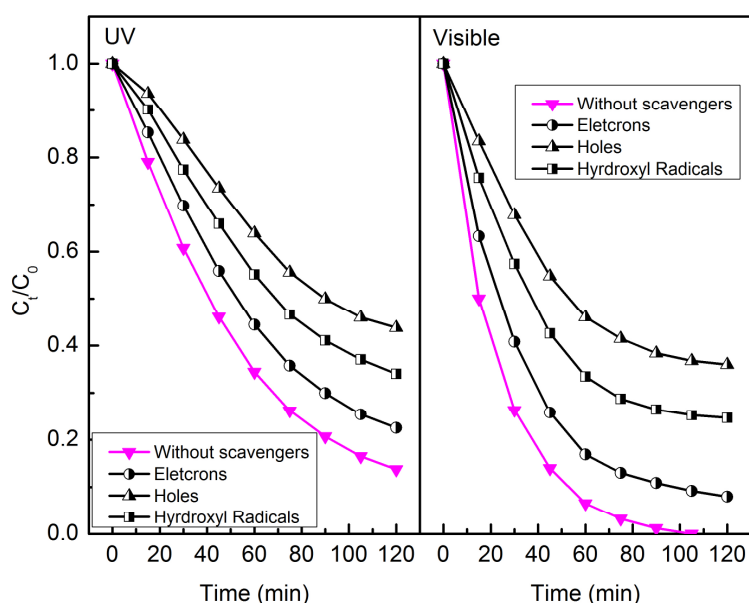


Figure 3. The effect of scavengers on photocatalytic degradation of MB using $\text{LaMnO}_3/0.5\text{TiO}_2$ nanocomposite.

The photosonocatalytic activity of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite was used to degrade MB as model organic pollutant under different light irradiation sources, combining UV light and ultrasonic (UV+US) and visible light and ultrasonic (Vis+US). Figure 2 shows the photosonocatalytic activity of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite with different molar ratios. For comparison, the photosonocatalytic activity of LaMnO_3 nanoparticle is also shown. The results demonstrate that the presence of TiO_2 in the nanocomposite also increases the photosonocatalytic activity of LaMnO_3 nanoparticles. Increased TiO_2 molar ratio increases the photosonocatalytic activity of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite in both UV+US and Vis+US. The highest degradation was obtained using $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite with molar ratio 1:0.5. The inset in figure 2 shows MB degradation rate using $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite, calculated by a pseudo-first order kinetics model [15], in which $\ln(C/C_0) = k_{\text{app}} t$. The results show that photosonocatalytic activity using Vis+US irradiation was faster than when using UV+US irradiation; this may be caused by the greater LaMnO_3 content as a catalyst of visible light. The optical gap values for the nanocomposite also confirmed its absorption capacity in the range of visible light irradiation.

In general, photosonocatalytic activity was influenced by catalyst interaction with ultrasonic and light waves. The increase of photosonocatalytic activity following combination of the two wave interactions was described in our previous work [9]. The influence of different light irradiation on catalyst interaction can be described as follows. Light waves can influence photosonocatalysis by forming electrons and holes. The electrons in conduction band interact with oxygen (O_2) molecules to form superoxide radicals ($\bullet\text{O}_2^-$), and holes in the valence band interact with water molecules to form hydroxyl radicals ($\bullet\text{OH}$). Superoxide radicals and hydroxyl radicals are known as strong reductor and oxidator agents and can degrade the complex chemical bonds of organic pollutants. It follows that the time needed for electrons and holes to recombine is strongly influenced by photosonocatalytic activity [16]. In the nanocomposite, using visible light as irradiation source, electrons in the conduction band of LaMnO_3 did not return directly to the valence band but were first transferred to the conduction band of TiO_2 . In this way, the recombination of electrons and holes can be inhibited, and photosonocatalytic activity is seen to increase by comparison with the performance of the LaMnO_3 nanoparticle alone. The opposite was found to occur when UV light was used as irradiation source. At that moment, electrons from the TiO_2 conduction band did not return directly to the valence band but were transferred to the conduction band of LaMnO_3 , inhibiting the recombination of electrons and holes, and increasing photosonocatalytic activity.

The present study also sought to identify the most influential factors in photosonocatalytic activity by adding several kinds of different scavenger. The degradation of methylene blue due to the existence

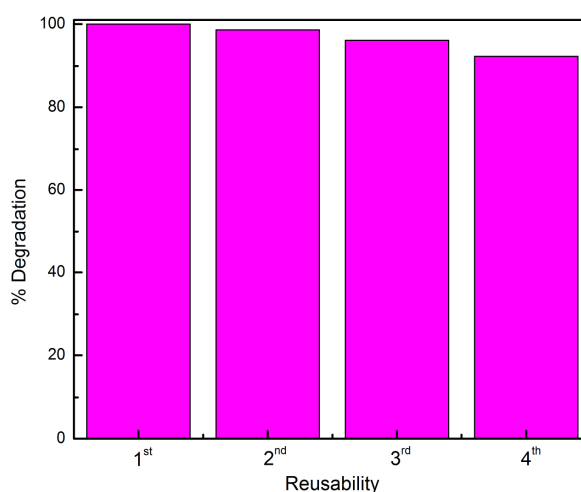


Figure 4. The reusability on the photosonocatalytic degradation of MB using $\text{LaMnO}_3/0.5\text{TiO}_2$ nanocomposite

of $\text{Na}_2\text{S}_2\text{O}_8$, di-ammonium oxalate, and tert-butyl alcohol as scavengers of electrons, holes, and hydroxyl radicals is shown in figure 3. The use of di-ammonium oxalate as a hole scavenger inhibited MB degradation rate, indicating that holes played the most important role in photosonocatalytic activity. Catalyst stability during degradation is shown in figure 4. Reused 4 times, 1:0.5 $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite using Vis+US irradiation succeeded in degrading 92% of MB, indicating the good stability of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite as catalyst.

4. Conclusions

The use of $\text{LaMnO}_3/\text{TiO}_2$ nanocomposite's photosonocatalytic activity to degrade methylene blue was successful using both UV+US and Vis+US irradiation. The incorporation of TiO_2 on the nanocomposite increased the photosonocatalytic activity and successfully extended the response of catalyst to the ultraviolet light region. The use of $\text{LaMnO}_3/\text{TiO}_2$ in nanocomposite form plays an important role in the improvement of photosonocatalytic performance by reducing electron-hole recombination.

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