Synthesis and characterization of $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ with enhanced visible light photocatalytic activities

Ying-ying Li^{a*}, Jin-zhou Li^b, Yong-chun Liu^a,

^a College of Chemistry and Chemical Engineering, Longdong University, Qingyang, 745000, China.

^b Department of Chemistry, Harbin Normal University, Harbin 150025, China

Abstract: A series of $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ photocatalysts with different content of cerium element have been synthesized by sol-gel method. The as-prepared products were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic activities of these $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ composites under visible-light irradiation were evaluated by the degradation of methyl orange (MO). The effect of important operational parameters such as catalyst amount, reaction temperature, irradiation time, and comparison of photocatalytic activity with different dyes including methyl orange, alizarin red, alizarin yellow, xylene orange were also studied. The results revealed that the $\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$ (LCNO) composites exhibited much higher photocatalytic activities than pure LaNiO_3 (LNO).

1. Introduction

Recently years, semiconductor photocatalysts have attracted enormous interest in cleanup of organic contaminants in effluent, because it is an inexpensive and convenient method which can totally mineralize dye molecules into H_2O and CO_2 . Unfortunately, most of these photocatalysts only function as a photocatalyst under UV light irradiation due to their wider band gap of 3.2 eV~4 eV [1,2]. Therefore, it has been a research challenge to explore photocatalytic materials that can utilize visible light ($420\text{ nm} < \lambda < 800\text{ nm}$) with a band gap of 2 eV. Perovskite oxides with the general formula ABO_3 have various crystalline structures and show special physical chemical properties, which can be used as photocatalysts for degradation of organic dyes under visible light irradiation [3-5]. However, there are still some drawbacks hindering their limited region of visible-light photoresponse, although many efforts have been made to improve the activity of perovskite oxides photocatalysts [6-8]. Therefore, much work needs to be done in order to identify structural parameters that help to improve available photocatalysts such as particle size, surface area, particle morphology, acid centers, and defects [9]. Among these parameters, defects in photocatalysts have been regarded as one of the most important impact factors on the photocatalytic activity. By chance, Perovskite oxides offer a promising matrix for the chemical substitution. Substitution in both A and B sites can change the composition and symmetry of the oxides and create cation or oxygen vacancies, which has a major influence on the band structures, as well as the photocatalytic behavior of these materials. Consequently, photocatalysts with ABO_3 -type perovskite structure

activated in the visible light region can be designed and prepared by substitution on both A and B sites [10]. Lanthanum nickelate (LaNiO_3), as one of the simplest perovskite oxides have received much attention owing to its good photocatalytic performance in organic contaminant decomposition under visible light irradiation. Several research groups have reported that LaNiO_3 -based photocatalysts can degrade organic pollutants under visiblelight irradiation [11-13]. But the activity of LaNiO_3 photocatalyst is not high enough to meet industrial use. So, it is necessary to modify the structure of photocatalyst in order to improve the photocatalytic activity. In this work, cerium was chosen as doping atom to substitute lanthanum atom in LaNiO_3 to prepare the novel $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ ($x = 0.2, 0.4, 0.6, 0.8$) photocatalysts, and methyl orange solution was employed as a simulated waste water to evaluate the photocatalytic degradation activity of the samples under sunlight irradiation. The photocatalysts reveal enhanced photocatalytic activities as compared to nonmodified LaNiO_3 .

2. Experimental section

2.1 Sample preparation

All chemical reagents in this work were analytical grade and used without further purification. Analytical-grade lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), ammonium cerium nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, nickel nitrate $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) were used as raw materials. The nitrates, with a metal molar ratio $\text{La} : \text{Ce} : \text{Ni} = 1-x : x : 1$, were solubilized in distilled water, and the solution

* Corresponding author: livingyinghx@163.com

was evaporated under agitation at 80°C until forming gel. After that, the gel was dried overnight in air oven. The powder was homogenized in an agate mortar and calcined at 700°C.

2.2 Analytical methods

Powder X-ray diffraction (XRD) was carried out with a BRUKER D8-ADVANCE X-ray diffractometer with Cu-K α radiation at a scanning rate of 0.3 °·s⁻¹ in the 2 θ range from 20° to 80°. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The field emission scanning electron microscopy (FE-SEM) images were taken on a JSM-6700F scanning electron microscope. The original and residue concentration of methyl orange in solution were analyzed via SHIMADZU UV-2500 UV-vis spectrophotometer. The spectra were collected in the 200~800 nm range at room temperature.

2.3 Photocatalytic experiment

The solar photocatalytic degradations were carried out from 10:30 am to 12:30 pm during autumn (September–October) under clear sky. The photocatalytic reactions were made in beakers (covered by transparent thin film) filled with a mixture of 20 mL fresh methyl orange solutions of different concentrations (10~50 mg·L⁻¹) and photocatalyst powder (0.3 g). During the reaction, the solution was magnetically stirred with magnetic stirrers. Samples (2 mL) were collected every 30 minutes from the beakers and analyzed to determine methyl orange concentration. Prior to analysis, samples were centrifuged to remove catalyst particles. The residue concentrations of methyl orange were analyzed via UV-vis spectrophotometer. The rate of decoloration (D) was calculated from the absorbency of methyl orange in solution before (A_0) and after (A_t) the photocatalysis reaction according to:

$$D = (A_0 - A_t) / A_0 \times 100\%.$$

3. Results and discussion

3.1 XRD and SEM

The powder X-ray diffraction patterns of unmodified and ceriummodified LaNiO₃ photocatalysts calcined at 700°C are shown in Figure 1. The powder X-ray diffraction patterns reveals that samples were well crystallized and all the diffraction peaks can be well indexed to the LaNiO₃ (JCPDS Card No. 34-1181) and La_{0.8}Ce_{0.2}NiO₃ (JCPDS Card No.34-1077), respectively. The ideal perovskite structure ABO₃ has a cubic symmetry and A atom is located at a three dimensional network 12 coordinate environment, which consists of regular BO₆ octahedra with 180° M–O–M. From a crystal chemistry point of view, as a matter of fact, LaNiO₃ adopts distorted structure and the decrease of tolerance factor (0.89: considering Shannon ionic radii) lowers the symmetry. In addition, a new diffraction peak

at 2 θ = 27.8° was observed in the XRD pattern when lanthanum atoms were substitutes partially by cerium atoms (shown in figure 1(2)). Simultaneously, the corresponding peaks of LCNO became weaker and wider compared with the XRD pattern of LNO, which is probably due to the local lattice distortion to a lower symmetry induced by the replacement of lattice atoms with the doped ones [14]. The appearance of such new peak can be assigned to the patterns of ceric oxide, indicating that the oxide is composed of two different phases [15]. In addition, the morphology of the LNO and LCNO samples were examined by FE-SEM (shown in Fig. 2). It can be clearly seen that the samples of LNO and LCNO oxide exhibit porous morphology with different pore size. And there is no significant difference between them. It can be concluded that cerium doping has little impact on the morphology of the LNO.

Fig. 1. XRD of the photocatalysts

Fig. 2. SEM of LaNiO₃ and La_{0.8}Ce_{0.2}NiO₃

3.2 Photocatalytic activities of photocatalysts under the sunlight irradiation

3.2.1 Effect of different photocatalysts on degradation of methyl orange

The photocatalytic activity of the as-prepared sample was first evaluated by the degradation of MO in aqueous solution. Figure 3 shows the UV-vis spectrum of MO solution degraded under different photocatalysts. Absorbance and decolourization rate of MO were also listed in Table 1 to illustrate the photocatalytic activities of catalysts. From Figure 3, it can be seen that the absorbance peaks of MO solution at 463 nm decreased significantly compared to MO original solution, which manifested the instability of MO to light irradiation. In addition, as is shown in table 1, only 18.14% MO can be photodegraded under visible light in the absence of catalysts and decolourization rate of MO catalyzed by LNO and LCNO systems are all higher than the blank test. Moreover, decolourization rate of MO catalyzed by LCNO systems increase at the beginning and then decrease with the increase of doping ratio of cerium element. $\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$ has the best catalytic activity and decolourization rate of MO can reach 91.19% under visible light in 2 h, which is 28.52% higher than LaNiO_3 . One possible reason for this photocatalytic activity enhancement of $\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$ is that a certain amount of cation or oxygen vacancies have been generated to maintain the electroneutrality by Ce^{4+} substituting La^{3+} . The existence of vacancies can slow down the recombination of the electron-hole pairs [16], so far as to improve the activities of catalysts.

Table 1 Absorbance and decolourizing rate of methyl orange degraded under different catalysts

samples Number	Absorbance (A_0)	Absorbance (A_t)	Decolourizing rate (%)
a	1.3389	0.1180	91.19
b	1.3389	0.2384	82.19
c	1.3389	0.4997	62.67
d	1.3389	0.6383	52.32
e	1.3389	1.0217	23.69
f	1.3389	1.0920	18.14

Fig. 3. UV-vis spectrum of methyl orange solution

3.2.2 Effect of photocatalyst amounts

Figure 4 shows that the photocatalytic degradation curve of normalized MO as a function of catalyst amounts. When the catalyst amounts was below $3 \text{ g} \cdot \text{L}^{-1}$, the photocatalytic activities increased with the increase of catalyst amounts. The decolourization rate of MO increased from 91.25 to 95.89% with the catalyst amounts increasing from 1 to $3 \text{ g} \cdot \text{L}^{-1}$ after irradiation for 120 min. However, when the catalyst amounts exceeded $3 \text{ g} \cdot \text{L}^{-1}$, the photocatalytic activities of samples decreased. Therefore, the optimal catalyst amounts for increasing the photocatalytic activity is $3 \text{ g} \cdot \text{L}^{-1}$. Reason for the mentioned results may be that the enhanced catalytic activities of photocatalysts could attribute to the increases of activity point by increasing the catalyst amounts. However, when the catalyst amounts reached a certain value, light shielding effect increased, resulting in a catalytic activity decreased.

Fig. 4. Decolourizing rate of methyl orange with different catalyst amounts

3.2.3 Effect of different temperatures

The influence of different temperatures upon the photodegradation rate of MO is shown in Fig. 5. It can be seen that experimental temperature also have effects on decolorization rate of MO solution, the catalytic activity of catalysts were enhanced as the temperature rising. When reaction temperature was 80°C , the decolorization rate can reach to 96.24% under sunlight irradiation for 2 h. The reason for the above results may be: when the experimental temperature increased, the thermal motion of the dye molecules in the solution were accelerated, the chance of dye molecules closing to the surface of the catalyst increased in per unit time, and lead to the catalyst activity increased.

3.2.4 Effect of sunlight irradiation time

Effect of sunlight irradiation time on decolorization rate of MO solution was also discussed (as is shown in Fig.6). Decolorization rate of MO solution catalyzed by LCNO can reach to 45.32% after reacting 20 mins, and the decolorization continued to raise with the increasing of time, but chang less at the end, which can illustrate that

the decolorization rate can reach maximum if reaction time is long enough.

Fig. 5. Decolourizing rate of methyl orange under different temperatures

Fig. 6. UV-vis spectrum and decolourizing rate of methyl orange solution under sunlight irradiation time

3.2.5 Photocatalytic degradation of different dyes

In addition, different dyes were chosen as the research targets in order to discuss the photocatalytic ability of LCNO. The decolorization rate of various dyes in the systems of LNO and LCNO were listed in table 2. It can be seen that both LNO and LCNO have photocatalytic activity to different dyes. But comparing the decolorization rate, the results reveals that decolorization rate of all kinds of dyes in $\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$ system were higher than that in LaNiO_3 system, although the structure and properties of dyes are various. Therefore, It can be concluded that photocatalytic activity of the LNO increased significantly after doping.

Table 2 The decolorization rate of various dyes in the systems of LaNiO_3 and $\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$

Dyes	Decolourizing rate (%)	
	LaNiO_3	$\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$
Methyl orange	62.67	91.19
Alizarin red	40.34	78.40
Alizarin yellow	43.73	88.73
Xylenol orange	55.43	82.82

3.3 Mechanism

Photocatalytic processes are based on electron/hole pairs generated by means of band gap radiation, which can give rise to redox reactions with species adsorbed on the surface of the catalysts^[17]. When Ce^{4+} ion replaced La^{3+} ion position in LaNiO_3 lattice, there will be additional charge, which need to compensate to maintain system electrically neutral through forming metal vacancy or separating out oxygen. Along with the doping percentage increased, lattice oxygen vacancy or metal vacancy concentration must be increased. So the photocatalytic activity of $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ will be gradually enhanced. When the vacancy concentration increases to a certain extent, randomization of space distribution reduced, which caused orderly arrangement in the vacancy, and result in catalyst activity declined. Therefore, photocatalyst will displace the highest photocatalytic activity at the best doping value. Moreover, Ce^{4+} doping can be seen as the insertion of donor and acceptor states to LaNiO_3 energy gap, and expand the light response range of catalysts. For the above catalytic reaction, the best doping value is 0.2, as $x > 0.2$, catalytic activity of catalyst decreased. The reason for the decrease of catalytic activity may be that when doping ratio greater than 0.2, the system will appear ceria phase. A small amount of CeO_2 could improve the activity activity through synergistic action between $\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$ and CeO_2 . But too much CeO_2 will weak skeleton structure of ABO_3 , and decrease the catalytic activity.

4. Conclusion

In summary, a series of novel $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ catalysts with excellent photocatalytic performance were successfully prepared through sol-gel method. Due to the doping of cerium, $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ showed substantial improvement in the photocatalytic activity for the degradation of dyes under visible light irradiation. Ce^{4+} doping can be seen as the insertion of donor and acceptor states to LaNiO_3 energy gap, which expand the light response range of catalysts, and promote the photocatalytic activity under visible light irradiation. Therefore, it is suggested that $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ catalysts are promising visible-light-driven photocatalysts for environmental applications.

Acknowledgement

This work was supported by The Key Discipline of Gansu Province and the project of science and technology department of Gansu province (No. 17CX1FM071).

References

1. N. Prastomo, N. H. Zakaria, G. Kawamura, H. Muto, M. Sakai. J. Eur. Ceram. Soc. 31, (2011)
2. W. Chen, C. Li, H. Gao, J. Yuan, W. Shangguan. J. Su. Int. J. Hydrogen Energy. 37, (2012)

3. J. Kong, T. Yang, Z. Rui. H. Ji. Catal. Today. 327, (2019)
4. Fresno, Jana, Reñones, Coronado, Serrano, Photochem. Photobiol Sci. 1, (2016)
5. R. Shi, J. Lin, Y.Wang, J. Xu, Y. Zhu. J. Phys. Chem. C: 114, (2010)
6. X. Zhang, J. Hu, Y. Cao, J. Xie, W. IChem. Eur. J. 24, 53 (2018)
7. J. Zhang, D. S. Zhao, J. L.Wang, L. Y. Yang. J. Mater. Sci. 44, (2009)
8. Kumar, Schuerings, Kumar, Kumar, Krishnan. Beilstein J. nanotechnology. 9, (2018)
9. C. Pana, J. Xua, Y. Chenb, Y. Zhua. Appl. Catal. B: Environmental. 115-116, (2012)
10. H. X. Chen, Z. X. Wei, Y. Wang, W. W. Zeng, C. M. Xiao. Mater. Chem. Phys. 130, (2011)
11. M. Khettab, S. Omeiri, D. Sellam, M. A. Ladjouzi, M. Trari. Mater. Chem. Phys. 132, (2012)
12. D. Aman, T. Zaki, S. Mikhail, S.A. Selim. Catal. Today. 164, (2011)
13. W. Qin, Y. P. Guo, B. Guo, M. Y. Gu. J. Alloys Compd. 513, (2016)
14. Y. Wang, Y. Wang, Y. Meng, H. Ding, Y. Shan. J. Phys. Chem. C: 112, (2008)
15. Y. Liu, L. Fang, H. Lu, Y. Li, C. Hu, H. Yu. Appl. Catal. B: 12012, 15–116: 245-251.
16. H. Kunioku, M. Higashi, O. Tomita, M. Yabuuchi D. Kato. J. Mater. Chem. 6, 7 (2018)
17. X.Shu, J.He, D. Chen. Ind. Eng. Chem. Res. 47, (2008)