Contents lists available at ScienceDirect



Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Research paper

LaNi_{*x*}Fe_{1-*x*}O₃ ($0 \le x \le 1$) as photothermal catalysts for hydrocarbon fuels production from CO₂ and H₂O



(1)

Dongmei Zheng^a, Guohui Wei^a, Lijuan Xu^a, Qiangsheng Guo^b, Jianfeng Hu^c, Na Sha^{b,**}, Zhe Zhao^{a,d,*}

^a School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 201418, China

^b School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

^c School of Materials Scinece and Engineering, Shanghai University, 99 Shangda Road, Shanghai 200444, China

^d Department of Materials Science and Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

ARTICLE INFO

Keywords: LaNiO₃ LaFeO₃ Photothermal catalysis CO₂ reduction

ABSTRACT

LaNi_xFe_{1-x}O₃ perovskite compounds (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) were successfully synthesized by a sol-gel combustion method. The crystal structure, morphology, BET surface area, oxygen vacancies, band gap and catalytic properties of the catalyst were characterized in detail. The results showed that LaNi_{0.4}Fe_{0.6}O₃ compound exhibits the best photothermal catalytic performance. Under the same catalytic conditions (350 °C + Vis-light), CH₄ and CH₃OH yields are about 3.5 and 4.0 times, 1.8 and 2.1 times of that of LaFeO₃ and LaNiO₃. It was found that all the solid solutions possesses better catalytic properties than the pure end compounds. The doping of Ni lead to a significant modification with the quantity of oxygen vacancies and band gaps. These findings may further broaden the materials scope for photothermal conversion of CO₂ and H₂O.

1. Introduction

Recent years, the energy crisis and increasing anthropogenic emissions of Greenhouse gases are widely recognized as two of the primary causes of global environmental problems [1-6]. Carbon dioxide, one of the most severe environmental issues of recent years, has been identified as a potential contributor to ozone laver depletion in the stratosphere and a relatively strong greenhouse gas [7]. Thus, it is extremely important to transform CO2 into hydrocarbon fuel and then provided an alternative possibility for sustainable and clean energy development because it partly fulfills energy demands and would help to reduce atmospheric CO₂ [8,9]. Since Halmann discovered the photoelectrochemical reduction of CO2 into organic compounds in 1978 and Hiroshi and co-workers reported the photocatalysts reduction of CO₂ into organic compounds over suspending semiconductor particles in water [10], growing interest in the development of semiconductor photocatalysts. It's not high enough for practical use that the generation of CO and H₂ from CO₂ mostly [11]. Subsequently, a possible avenue for sustainable development is to use photocatalysts for the conversion of CO₂ into methane with the help of solar energy. A process involving only water and carbon dioxide is very promising as it can form a useful carbon cycle Eq. (1) [12,13].

 $CO_2+2H_2 \xrightarrow{Vis} CH_4+2O_2$

TiO₂ [14], Zn/TiLDH [15], Ru/NaTaO₃ [16], ZO₂@Cu-Zn-Al-LDH [17], SnNb₂O₆ [18] and so on have been studied extensively owing to its semiconductor material. But its band gap requires the use of ultraviolet energy to initiate the reactions, as its photocatalytic in the existence of some limitations. Further research of hydrocarbon fuels on thermal reactions with unique selectivity and high efficiency is still required. The simultaneous thermochemical reaction of CO₂ and H₂O with the oxygen deficient in material at a relatively low temperature can convert CO₂ into CH₄ efficiently. And the problem of catalytic carbon deposition has been solved. However, We combine photo and thermal processes to develop a new method called photothermal catalytic process, which unite the advantages of the photochemical and thermochemical catalytic processes in the form of CO₂ reduction to CO, C and O₂ while H₂O reduction to H₂ and O₂ in the same system [19,20] with a high-efficiency reaction rate.

In our earlier work, mesoporous WO₃ [20], the CH₄ evolution performance only reaches 21.42 μ mol g⁻¹ under thermal conditions, which is less than that under visible-light irradiation and thermal conditions (25.77 μ mol g⁻¹), the activity of m-WO₃ in the photocatalytic conversion of CO₂ with H₂O is not high enough for practical use. Furthermore,

E-mail addresses: shana@sit.edu.cn (N. Sha), zhezhao@kth.se (Z. Zhao).

https://doi.org/10.1016/j.jphotochem.2019.03.045

Received 16 November 2018; Received in revised form 7 March 2019; Accepted 27 March 2019 Available online 29 March 2019 1010-6030/ © 2019 Elsevier B.V. All rights reserved.

^{*} Corresponding author at: School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 201418, China. ** Corresponding author.

Xu et al has exploited $LaCo_xFe_{1-x}O_3$, nanoparticle which $LaCo_{0.6}Fe_{0.4}O_3$ has the best CH_4 evolution performance reaches 437.28 µmol g⁻¹ with showing better photocatalytic activity under a photothermal condition [21].

Perovskite-type oxides, with ABO3 formula, which have better photocatalytic activity are ascribed to the corner-shared BO₆ octahedron network that facilitates electron transfer [22,23]. Further, the large atoms at the A-site of ABO3 are responsible for the stabilization and more active behavior of the perovskite structure [24-26]. Therefore, advantages of them are applied to catalysis [27,28] and magnetoresistance devices [29,30]. Simultaneously, the valency and vacancy can be dominated due to their significant redox properties [31]. However. La-based catalysts could be the promising catalysts with excellent performance and low cost. In addition, LaFeO₃ as a function material plays a role in catalytic activity, which drawn great attention for its promising applicability in the utilization of solar energy and environment remediation [32-35]. Yet, there are still many problems in the utilization of photocatalysts, such as poor light absorbance and high recombination of photogenerated electron-holes pairs when band gap of 2.1 eV. Thus, various methods have been developed to overcome those problems and improve the photocatalytic activity [36,37]. Xu et al had exploited LaCo_{0.6}Fe_{0.4}O₃ nanoparticle for the best photocatalytic reduction of CO2, it absorbs in the visible region owing to possible variations in its band gap energy 1.68 eV. As we all know, the efficiency of the utilization of solar light is related to band gap of material, which also affect the photocatalytic activity [38]. It indicates that narrow band gap can largely improve the visible light absorptive quality and effectively restrain the recombination of photo generated electron holes pairs to exhibit a higher photocatalytic activity. Addition of photocatalysts have shown to prolong the time of recombination electrons-holes and then improve the lifetime of electron [39,40]. In this research, we can adjust the recombination of electrons-holes of LaFeO₃ by substituting partially Fe for Ni at B-site in our experiment.

In this paper, we focus on investigating the catalytic activity of dopant concentration, which photothermal reduction of CO_2 with H_2O vapor to CH_4 . At last, the influence of the nickel content for the perovskite microstructure on photothermal activity was revealed. It shows that an appropriate range of Ni-doping can facilitate the catalytic process. This discovery may further expand the materials scope of photothermal conversion and provide innovative insights into the catalysis of carbon dioxide reduction.

2. Experimental

2.1. Synthesis of catalyst

La(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O, Ni(NO₃)₃·6H₂O and citric acid were procured from Shanghai Titan chemicals Co, Ltd. These chemicals as raw material were directly used to compound series LaNi_xFe_{1-x}O₃ mixed-oxide perovskites, which was without any further purification treatment. In a typical experiment, the catalyst in accordance with the formula $LaNi_xFe_{1-x}O_3$ (with x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) were synthesized by the citric acid sol-gel method. The metal nitrate of 12.99 g La(NO₃)₃ 6H₂O of 0.03 mol and 12.12 g Fe(NO₃)₃ 9H₂O of 0.03 mol were added to the deionized water of 60 mL, and the molar ratio of nitrate to acid was 1:1.2. Adding 13.83 g anhydrous citric acid of 0.072 mol to the mixed solution, stirring and dissolving until a clarification solution is formed, heating the resulting solution in a water bath at 80°C until the sol is formed, and then moving to the oven for overnight drying at 120°C until the sol was completely dried, then sintered at 700°C for 7 h, and then the perovskite-type LaFeO₃ nanoparticles were obtained. According to the above synthesis method, a series of other doped LaNi_{0.2}Fe_{0.8}O₃, LaNi_{0.4}Fe_{0.6}O₃, LaNi_{0.6}Fe_{0.4}O₃, LaNi_{0.8}Fe_{0.2}O₃ and LaNiO₃ nanoparticles were synthesized by adjusting the amount of metal nitrate of Ni(NO₃)₃ 6H₂O, the raw material of Ni in position B, by the corresponding doping ratio.

2.2. Characterization of sample

The synthesized samples were characterized using X-ray diffraction (PAN alytical X'pert), their crystalline phases were determined by Cu Ka radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA. The XRD patterns were record in the range between 20°and 80° at the scan rate of 10°min⁻¹. The morphology and sizes of the products were investigated by using a scanning electron microscopy (SEM, JSM-7000 F). BET specific surface areas of the samples were performed by using a Micrometrics USA ASAP2020 instrument with adsorption-desorption of N₂ at 77 K, samples were degassed 2 h at 150°C. UV–vis diffuse reflectance spectra of the samples were measured in the range of 200–800 nm using SHIM-ADZU UV-3600 using spectral purity BaSO₄ as the reference. X-ray photoelectron spectroscopy (XPS) was characterized by an ESCALAB 250 instrument with Al Ka ($h\nu = 1486.6$ eV) source at a residual gas pressure of below 10⁻¹⁰ Pa. Mott-Schottky curves were measured using a three-electrode system on the CHI604E electrochemistry workstation

2.3. Catalytic measurements

The photothermal catalytic reduction of CO₂ was carried out with 100 mg of the sample powdered, which was uniformly placed at the bottom of a Pyrex glass cell. The whole catalysis reaction temperature was set at 350°C with visible light irradiation on (photothermal). The temperature control was realized by a heating jacket surrounded the quartz reactor. And the light source used was a 300 W Xe lamp equipped with a UV- light filter ($\lambda > 420$ nm). The light illumination intensity is measured using CEL-NP2000-2 Full Spectral Optical Power Meter. And the measured optical power density value is 145 mW/cm^2 . Vacuumed the reactor with the vacuum up to empty the air inside the reactor and then CO₂ (99.999 wt %) passed through the reactor at a flow rate of 27 mL/min for 5 min. The reaction was in a gas tight system, distilled water (0.3 mL) was injected into the system when the temperature above 120°C. In a period of insulation for 5 h, took samples per hour and qualitatively analyzed by GS-Tek (Echromtek A90) and quantitatively analyzed by gas chromatograph equipped with a hydrogen flame detector (FID). The quantification of CH₄ yield was based on the external standard and the use of calibration curve. method.

3. Results and discussion

3.1. XRD analysis

The crystal structure and phase purity of the LaNi_xFe_{1-x}O₃ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) were characterized by XRD and the results were shown in Fig. 1. According to the characteristic peaks of the perovskite LaFeO₃ and LaNiO₃, all the synthesized materials are with perovskite structure and no impurity phases can be identified from the XRD spectra. Furthermore, with partial substitution for Fe by Ni, we can see that the peak intensity of samples decreases and half peak width gradually widened. In addition, a clear crystal structure transition from orthorhombic Pnma (PDF #88-0641) to trigonal R-3c (PDF #88-0633) can be observed when x reached 0.6. Besides, the crystallite size determined by the Scherrer method is in the range of 22-35 nm (see Table1) and so no significant effect of x value on crystallite size can be defined. The results indicate change in unit cell parameters (a-c), This may be attributed to the difference in ionic radii of deferent cations causing crystal lattice contraction due to distortion of Fe/NiO6 octahedra or/and by mixed valence state of Ni in order to neutralize the charge imbalance.

3.2. BET surface area and pore structure analysis

N₂-sorption isotherms of LaNi_{*x*}Fe_{1-x}O₃ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) materials correspond to type-IV (see Fig. S2 SI), according to the IUPAC classification. However, the porous LaNi_{*x*}Fe_{1-x}O₃ exhibits a type-II



Fig. 1. XRD spectra of $LaNi_xFe_{1-x}O_3$ photocatalysts with different Ni-concentration synthesized at 700 $^\circ\text{C}.$

isotherm with a type-IV(a) hysteresis loop at high relative pressure (P/ P_0) range of 0.9–1.0, indicating the presence of macropores. Moreover, the specific surface area and the pore properties of the LaNixFe1-xO3 catalysts, with the different *x* values were listed in Table 2. All the synthesized catalyst materials possessed a specific surface area of 4-10 m²/g and it is rational to regard them as similar porous materials in the aspect of pore structure. The measured pore size and pore volume changed with *x* value, but no consistent tendency can be defined among the different materials. However, the difference in BET surface area can be a factor influencing the final photothermal catalytic performance, we will discuss this potential effect latter together with the catalytic performance of different compounds.

3.3. SEM analysis

The morphological features of the LaNi_xFe_{1.x}O₃ nanoparticles were characterized by SEM analysis, and the corresponding SEM results were shown in Fig. 2. As a result of Sol-gel combustion synthesis, it can be seen that the samples are all porous materials. Particle size expressed by these SEM images was rather similar between different compounds, which was also demonstrated by the previous XRD crystallite size analysis. However, with the increase of *x* value, the synthesized powder presented denser microstructure, which may affect the CO₂ gas transport during the photothermal catalysis process and hence potentially affect the catalytic results.

3.4. XPS analysis

As shown in Fig. 3, the chemical state and surface species of the $LaNi_xFe_{1-x}O_3$ catalyst were studied by XPS analysis. The survey spectra (Fig. 3d)) indicate that all of the peaks were ascribed to La, Fe, Ni, O and C elements and no peaks of other impurity elements were observed.

Journal of Photochemistry & Photobiology A: Chemistry 377 (2019) 182-189

Table 2
The surface properties of the catalysts were examined by BET surface area

x	Surface area (BET)(m ² /g)	Pore size(nm)	$Vp/cm^3 g^{-1}$
0.0	9.44	21	0.050
0.2	7.28	35	0.060
0.4	9.84	25	0.062
0.6	9.60	22	0.054
0.8	5.43	35	0.048
1.0	4.16	31	0.032

As shown in Fig. 3a) and b), the binding energies of both Ni and Fe show evidence of the coexistence of the least two oxidation states (+2 and +3), are consistent with the results of literature [41]. The Fe 2p peak fitting of the LaNixFe1-xO3 catalyst were performed for three components, Fe^{2+} , Fe^{3+} and the shake-up satellites reported by Liu [42]. For Fe $2p_{3/2}$, binding energy of 709.99 and 713.61 eV can be attributed to Fe^{2+} and Fe^{3+} respectively. Analogously, the characteristic binding energy peaks of for Ni 2p can be assigned to Ni 2p_{3/2} (Fig. 3a)). Binding energy of 854 and 856 eV [43] can be attributed to Ni²⁺ and Ni³⁺ respectively. Moreover, the presence of doublets characteristic of Ni 2p (Ni²⁺ and Ni³⁺) and Fe 2p (Fe²⁺ and Fe³⁺) (see Table 3) were common for all the studied compounds, thus substantial amount of oxygen vacancy can be expected. That the total valence of cation is much less than 6. Simultaneously, the oxygen stoichiometry (with a formal charge of -2) would change from LaNi_xFe_{1-x}O₃ to La-Ni_xFe_{1-x}O_{3-&}. Moreover, perovskite was ABO₃, the unit cell was changed, non-stoichiometry phenomenonin perovskites becomes very common, arising from oxygen deficiency especially. As shown in Table 3, it is possible to estimate the concentration of +2 ions for both Ni and Fe, but it is difficult to be used as a precise estimation due to the potential artifacts in data fitting. To further elucidate the information of the oxygen vacancy in various compounds, the O 1s spectra were analyzed carefully. All O 1s spectra shown in Fig. 3c) can be separated into three components with characteristic peaks at 528.37, 530.65 and 532.19 eV respectively. According to the previous results [44], they can be attributed to lattice, surface and adsorbed oxygen respectively. The presence of the surface adsorption oxygen (such as O^- , and O^{2-}) in XPS spectra is generally associated with the surface oxygen vacancies in perovskite oxides. Thus, the relative concentration of surface oxygen vacancies can be roughly estimated according to the relative intensity ratio (RIR) of O 1s (adsorption oxygen) /O 1s (lattice oxygen) (see Table 4). The calculated RIR values for the $LaNi_{0.4}Fe_{0.6}O_3$ sample were 1.69, which indicates the maximum quantity of oxygen vacancies [45]. Besides, the photothermal catalytic activities for CO₂ conversion with H₂O vapor to CH₄ over LaNi_xFe_{1-x}O₃ catalysts showed that the catalytic activity toward this reaction depends on $O_{ads}/O_{lattice}$ ratios. (see Table 4). It revealed that oxygen vacancies in oxide semiconductor photocatalysis play an important role in the photocatalysis. We tentatively hypothesize that oxygen vacancy can preferably adsorb the oxygen atom in CO2 and H2O molecule and thus enhance the asymmetry in their molecule structure and thus promote their disassociation and further reduced to hydrocarbon fuels, follow the DFT, the results suggest that the order of LaBO₃(B = Fe, Mn, Co, Ni)oxygen vacancy

Table 1

The XRD analysis results.

Samples(x)	Crystal structure	2-Theta(°)	d(121) (nm)	Unit cell a, b, c(nm)	Crystallite size(nm)
0.0		32.2394	0.2774	5.556, 5.560, 7.855	31
0.2	Orthorhombic Pnma	32.4055	0.2761	5.521, 5.548, 7.809	32
0.4		32.5968	0.2745	5.484, 5.514, 7.780	22
			d(110) (nm)	Unit cell $a = b$, $c(nm)$	
0.6		32.7458	0.2732	5.496, 13.381	28
0.8	Trigonal R-3c	32.7015	0.2736	5.472, 13.172	35
1.0		32.9597	0.2715	5.448, 13.187	27



Fig. 2. SEM images of LaNi_xFe_{1-x}O₃ powders synthesized by sol-gel combustion method at 700 °C for 2 h. a) x = 0, b) x = 0.2, c) x = 0.4, d) x = 0.6, e) x = 0.8, f) x = 1.

formation energies is Fe > Mn > Co > Ni(where the larger implies more difficult to form a vacancy), meanwhile, first-principles calculations revealed the oxygen vacancies play an important role in adsorbing oxygen by increasing the adsorption energy of H_2O and CO_2 in LaFeO₃ and LaNiO₃ [46–50]. properties of the LaNi_xFe_{1-x}O₃. The UV–vis diffuse reflectance spectra (DRS) are shown in Fig. 4a). It was interesting that only LaFeO₃ showed clear light absorption edge around 600 nm. All other compounds showed strong light absorption through the wavelength range of 200–800 nm, indicating that LaNi_xFe_{1-x}O₃ nanoparticles can respond to visible light for photocatalytic reaction.

3.5. UV-vis DRS analysis

To elucidate the influence of surface oxygen vacancies on the optical

In order to estimate the optical band gap (E_g) of the LaNi_xFe_{1-x}O₃ perovskties, we used the following equation to fit the Kubelka Munk function Eq. (2):



Fig. 3. The XPS spectra of a) Ni 2p, b) Fe 2p, c) O 1s and d) survey spectra of $LaNi_xFe_{1,x}O_3$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) prepared at 700 °C for 2 h.

Table 3

XPS binding energies relative to	the perovskites	LaNi _x Fe _{1-x} O ₃ .
----------------------------------	-----------------	--

	Ni2P(eV)	Fe2p(eV)
Catalyst(x)	Ni 2p _{3/2} (%)	Fe 2p _{3/2} (%) Fe2p _{1/2} (%)
0	Ni(³⁺)	710.03(66.22%) 723.51(66.50%)
	$Ni(^{2+})$	711.85(33.78%) 725.53(33.50%)
0.2	853.78(64.77%)	710.07(63.83%) 723.52(66.38%)
	855.10(35.23%)	712.66(36.17%) 725.42(33.62%)
0.4	854.26(64.56%)	709.73(63.12%) 723.33(65.72%)
	855.40(35.44%)	711.15(36.88%) 724.80(34.28%)
0.6	853.29(68.74%)	709.94(69.21%) 723.01(70.75%)
	854.40(31.26%)	712.90(30.79%) 725.03(29.25%)
0.8	854.16(68.83%)	710.09(70.91%) 723.59(69.41%)
	855.78(31.17%)	712.79(29.09%) 725.50(30.59%)
1.0	853.11(72.37%)	$Fe(^{2+}) Fe(^{2+})$
	854.72(27.63%)	$Fe(^{3+}) Fe(^{3+})$

Table 4

XPS O1 s analysis of the LaNi_xFe_{1-x}O₃ perovskites.

O 1 s(eV)	x = 0	x = 0.2	x = 0.4	x = 0.6	x = 0.8	x = 1.0
Lattice oxygen	54.28	43.38	35.60	39.83	39.98	45.48
Surface oxygen	37.04	50.33	60.04	59.47	55.83	50.62
Absorbed oxygen	8.68	6.29	4.36	0.7	4.19	3.90
Surface/Lattice	0.68	1.16	1.69	1.49	1.40	1.11

$$F(R) = \frac{(1-R)^2}{2R}$$
(2)

Which determines the extent of photon absorption of a semiconductor from its reflectance (R). Fig. 4b) represents Tauc plot (F(R) $*E^{1/n}$ vs. photon energy hv (eV) where n is 2 for indirect transition and n is 0.5 for direct transition. In our case, only n = 2 can lead to a reasonable fitting for the DRS spectra (see Fig. 4b)). All LaNi_xFe_{1-x}O₃ compounds were indirect semiconductor.

As indicated in Fig. 4b), all the solid solution compounds presented lower *Eg* than the two end compound, LaFeO₃ and LaNiO₃. *Eg* reached the lowest value of 1.56 eV when x = 0.4. Lower *Eg* will promise more efficient visible light absorption and thus potentially to be beneficial for the final photocatalytic performance. For detailed possible mechanism of this reduced band gap by changing x value will be discussed later.

3.6. Band structure analysis

As we all know, the electronic band gap energy of material is critical for its photocatalytic activity. Additionally, it is also important for samples to study the positions of conduction band (CB) and valence band (VB) in order to understand how the different hydrocarbon fuels will be formed by the photothermal catalysis. In most common sense, CB edges (E_{CB})can be approximated by the flat band which can be measured by Mott–Schottky plot, even such an approximation is not very precise. Combined with the band gap Eg obtained by Kubelka Munk function, it is very convenient to deduce the edge of VB (EVB). As show in Fig. 5a), the typical p-type semiconductor characteristics of LaNi_{0.4}Fe_{0.6}O₃ was revealed by observing the positive slope of the MS plot. (MS plots of other compounds were provided in SI). By calculating, the E_{CB} of $LaNi_xFe_{1-x}O_3$ nanoparticles with x value changing from 0 to 1 were about -0.313, -0.277, -0.250, -0.255, -0.268 and -0.273 V respectively and the E_{VB} of them were 1.717 V, 1.353, 1.31, 1.395, 1.502, and 1.527 V respectively. To get the possible catalytic reactions [Eqs. (3-5)] to thermodynamically proceed automatically, the E_{VB} should be always more positive than $E^{o}(H_2O/H^+)$ and E_{CB} should be more negative than $E^{\circ}(CO_2/CH_4)$ and $E^{\circ}(CO_2/CH_4)$ CH₃OH). As described above, it is rational to expect CH₄ to be the photothermal catalysis product. However, due to the lack of very precise estimation of the E_{CB} from the flat band approximation, it is not very definitive to exclude the possible formation of CH₃OH, which was actually observed in the final products in this study.

Except for the reduction of *Eg* by forming a solid solution between LaNiO₃ and LaFeO₃, it is also noteworthy to point out that mixed B-site with Ni and Fe will only introduce minor change in E_{CB} and rather tremendous modification with E_{VB} . As we already know that non-metal doping mostly introduce occupied orbitals above the energy of the valence band thus narrowing the band gap, it is rational to attribute the reduced *Eg* in LaNi_xFe_{1-x}O₃ (x = 0.2, 0.4, 0.6 and 0.8) to the extra oxygen vacancy resulted from the presence of Ni²⁺ and Fe²⁺.

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-(E^o_{ox} = 0.82V_{vs.}NHE)$$
 (3)

$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O(E_{red}^o = -0.24V_{vs.}NHE)$$
 (4)

$$CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O(E_{red}^o = -0.38V_{vs}NHE)$$
 (5)

3.7. Photothermal catalytic performance

Fig. 6a) and b) shows the amount of CH₄ and CH₃OH generation with the photothermal catalytic activity at different Ni-doping levels, which was evaluated under photothermal conditions at 350 °C and vislight irradiation for 6 h. In Fig. 6a) and b), we can find out that the catalytic activity increased greatly with Ni doping in B-site compares with LaFeO₃ perovskite. After 6 h for the reaction, the methane yield at different x values was in the order of 0.4 > 0.6 > 0.2> 0.8 > 1.0 > 0, as well as the methanol yield. The accumulated yield of methane and methanol under photothermal conditions after 6 h were 134.98, 374.92, 471.39, 422.69, 295.08, 259.20 $\mu mol\,g^{-1}$ and 3.85, 11.91, 15.50, 13.75, 19.11, 7.46 μ mol g⁻¹ respectively (see Table 5). Among them, LaNi_{0.4}Fe_{0.6}O₃ was clearly the best material for both CH₄ and CH₃OH generation. It was about 3.5 times and 4.0 times of those yields provided by LaFeO₃ and LaNiO₃. Look at all the solid solution compounds $LaNi_xFe_{1-x}O_3$ (x = 0.2, 0.4, 0.6 and 0.8), the catalytic production of them were always higher than pure by LaFeO₃ and



Fig. 4. UV-vis diffuse reflectance spectra of $LaNi_xFe_{1-x}O_3$ nanoparticle in different Ni rate a), plots of $(F(R)*E)^{0.5}$ versus photon energy of $LaNi_xFe_{1-x}O_3$ sample b).



Fig. 5. Mott-Schottky plots of LaNi_{0.4}Fe_{0.6}O₃ nanoparticle a). A schematic illustration of the band structure of LaNi_xFe_{1.x}O₃ nanoparticle b).



Fig. 6. CH₄ generation over the under visible light irradiation and heating condition at 350 °C a) and CH₃OH generation over the under visible light irradiation and heating condition at 350 °C b).

Photothermal catalytic activity and physical properties of the LaNi _x Fe _{1-x} O ₃ perovs	kites.

Sample(x) product	The first hour yield (µmol g^{-1}) CH ₄	CH ₃ OH	yield after 6 h (µmol g^{-1}) CH ₄	CH ₃ OH	Total yield (%) CH ₄ +CH ₃ OH	Selectivity (%) CH ₄	CH ₃ OH
0 0.2	89.06 225.78	2.06 7.45	134.98 374.92	3.85 11.91	0.25 0.68	97.23 96.92	2.73 3.80
0.4	291.47	10.10	471.39	15.50	0.86	96.82	3.18
0.6	243.72	8.86	422.69	13.75	0.77	96.85	3.15
0.8	162.92	5.85	295.08	19.11	0.54	97.00	3.00
1.0	142.22	4.44	259.20	7.46	0.47	97.20	2.80



Fig. 7. Catalytic results of co-catalysts in other report.

LaNiO₃. The existence of mixed transition metal ions at B-site is beneficial for the photothermal catalysis of CO_2 and H_2O to produce hydrocarbon fuels.

To be noticed, there is no metal co-catalysts were involved in this study. To be compared with other reported results (see Fig. 7, experimental conditions details in SI table S1) where similar photothermal catalysis was investigated, the studied non-metal perovskite oxides showed great promise for further improvement if the detailed catalysis mechanism can be elucidated in the future.

3.8. Mechanism of photocatalytic reduction of CO₂

In order to understand the reaction process, a possible catalytic mechanism of $LaNi_xFe_{1-x}O_3$ catalysts for the reduction of CO_2 to CH_4 and CH_3OH were shown in Fig. 8. The first is of the perovskite $LaNi_xFe_{1-x}O_3$ surface, creating electron–hole pairs [Eq. (6)], that surface can adsorb CO_2 and H_2O molecules as well. H_2O is also photoexcitation [Eq. (7)]. The adsorption of CO_2 on $LaNi_xFe_{1-x}O_3$ suggest that these interactions are not strong enough with stoichiometric, defect-free surfaces to sufficiently lower the barrier and enable transfer of conduction-band electrons. The interactions are much stronger at oxygen vacancy sites



Photo-thermal

Fig. 8. Schematic diagram of the combined photo- and thermal-catalytic reduction of CO₂ with H₂O vapor to CH₄ in one system over LaNi_xFe_{1,x}O₃ perovskites.

where a foreign oxygen atom can fill the vacancy. That may lead to the dissociation of CO₂ upon electron transfer and subsequent release of CO [Eq. (8)]. Furthermore, H₂O adsorbed on surfaces could spontaneously dissociate into an H atom and an OH group [Eq. (9)]. The adsorption not only spatially enables the transfer of photoexcited electrons to reaction species, but also alters the form of active species to lower the photon energy requirement for reactions. Notably, the CO intermediate may also undergo further reduction. Finally, the activated CO species would transform into CH₄ [Eq. (4)] through reacting with the formed atomic hydrogen on the surface via a photogenerated electron-induced multistep reduction process involving electron and proton transfer, C-O bond breaking, and C-H bond formation. However, the VB edge of all LaNi_xFe_{1-x}O₃ compounds is not negative enough for the production of CH₃OH [Eq. (5)] through photocatalytic reduction process. So we have to point out that the production of amount of CH₃OH was small in our study. Notably, surface Vo plays a very important role in the activation and dissociation of CO2 molecule on the surface of LaNixFe1-xO3. In summary, the photothermal catalytic activity of LaFeO₃ was enhanced by Ni-doping, which adjusted the band structure and reduced the band gap. These findings may be of importance for a variety of applications. Photocatalytic:

 $LaNi_xFe_{1-x}O_3 + hv \rightarrow e^- + h^+$ (6)

 $2H_2 O+ 4h^+ \rightarrow 4H^+ + O_2$

Thermochemical:

 $CO_2 + V_0 \rightarrow CO + O$ (8)

 $H_2O + V_0 \rightarrow H^+ + OH^-$ (9)

4. Conclusions

In summary, we successfully synthesized (x = 0, 0.2, 0.4, 0.6, 0.8, 0.6, 0.8)1.0) nanoparticles through the sol-gel combustion process. Their structure, phase, morphology, surface area and electronic structure were investigated by using XRD, SEM, BET and UV-vis. And the catalytic properties were characterized as well. Under photothermal reaction conditions, the sample manifest better catalytic performance for the reduction of CO₂ with H₂O vapor to CH₄ after Ni-doping in LaFeO₃. Therefore, the electronic structure of the material can be influenced by doping transition mental element, the oxygen vacancies and band gap have significant changes in our study by appropriate range of Nidoping, which facilitate more efficient light adsorption and potentially prevent the recombination of the electron holes pairs due to the better conductivity resulted from extra oxygen vacancies. Meanwhile, the

morphology and surface area of the sample have also changed. By contrast, the CH₄ and CH₃OH generation rate of LaNi_{0.4}Fe_{0.6}O₃ for the reduction of CO₂ with H₂O, under the same photothermal reaction conditions, were enhanced 3.5 and 4.0 times, 1.8 and 2.1 times better than LaFeO₃ and LaNiO₃. According to these results, we believe that the coexistence of Ni and Fe on B-site can promote the photothermal catalysis of CO₂ and H₂O. The working mechanism can be the enhanced light adsorption and the extra oxygen vacancies. The more detailed mechanism for this doping effect need more investigation to elucidate. The LaNi_xFe_{1-x}O₃ composites can work as highly active and stable visible-light-driven photocatalysts. This research will lead to new efforts in exploring more effective and inexpensive visible-light-driven photocatalysts.

Acknowledgements

The authors highly acknowledge the financial support of the National Key R&D Program of China (Nos. 2017YFB1103500 & 2017YFB1103502).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2019.03. 045.

References

(7)

- [1] R. Dhinesh Kumar, R. Thangappan, R. Jayavel, Synthesis and characterization of LaFeO₃/TiO₂ nanocomposites for visible light photocatalytic activity, J. Phys. Chem. Solids 101 (2017) 25-33
- [2] S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri, H. Alamdari, Perovskites as substitutes of noble metals for heterogeneous catalysis: dream or reality, Chem. Rev. 114 (20) (2014) 10292-10368.
- M. Mikkelsen, M. Jørgensen, F.C. Krebs, The teraton challenge. A review of fixation and transformation of carbon dioxide, Energy Environ. Sci. 3 (1) (2010) 43-81. [4]
- Y. Yamazaki, H. Takeda, O. Ishitani, Photocatalytic reduction of CO₂ using metal complexes, J. Photochem. Photobiol. C Photochem. Rev. 25 (2015) 106-137.
- [5] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light, Nat. Mater. 8 (1) (2009) 76-80.
- [6] O. Khaselev, A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting, Science 280 (5362) (1998) 425-427.
- [7] M. Hussain, P. Akhter, D. Fino, N. Russo, Modified KIT-6 and SBA-15-spherical supported metal catalysts for N₂O decomposition, J. Environ. Chem. Eng. 1 (3) (2013) 164-174.
- S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Photocatalytic CO2 re-[8] duction using non-titanium metal oxides and sulfides, ChemSusChem 6 (4) (2013) 562-577.

- [9] Q. Duan, J. Wang, C. Ding, H. Ding, S. Guo, Y. Jia, P. Liu, K. Zhang, Partial oxidation of methane over Ni based catalyst derived from order mesoporous LaNiO₃ perovskite prepared by modified nanocasting method, Fuel 193 (2017) 112–118.
- [10] H. Yoneyama, Y. Yamashita, H. Tamura, Heterogeneous photocatalytic reduction of dichromate on n-type semiconductor catalysts, Nature 282 (5741) (1979) 817–818.
- [11] J. Hawecker, J.-M. Lehn, R. Ziessel, Efficient photochemical reduction of CO₂ to CO by visible light irradiation of systems containing Re(bipy)(CO)₃X or Ru(bipy) 3²⁺-Co²⁺ combinations as homogeneous catalysts, J. Chem. Soc. Chem. Commun. 9 (1983) 536–538.
- [12] A. Olivo, V. Trevisan, E. Ghedini, F. Pinna, C.L. Bianchi, A. Naldoni, G. Cruciani, M. Signoretto, CO₂photoreduction with water: Catalyst and process investigation, J. Co2 Util. 12 (2015) 86–94.
- [13] S.S. Tan, L. Zou, E. Hu, Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO₂ pellets, Catal. Today 115 (1-4) (2006) 269–273.
- [14] L. Collado, A. Reynal, J.M. Coronado, D.P. Serrano, J.R. Durrant, V.A. Peña O'Shea de la, Effect of Au surface plasmon nanoparticles on the selective CO₂ photoreduction to CH₄, Appl. Catal. B 178 (2015) 177–185.
- [15] F. Sastre, C. Avelino, Garcila Hermenegildo. 185 nm photoreduction of CO2 to methane by water. Influence of the presence of a basic catalyst, J. Am. Chem. Soc. 134 (34) (2012) 14137–14141.
- [16] M. Li, P. Li, K. Chang, et al., Highly efficient and stable photocatalytic reduction of CO₂ to CH₄ over Ru loaded NaTaO₃, Chem. Commun. 51 (36) (2015) 7645–7648.
- [17] Q. Guo, Q. Zhang, H. Wang, et al., Core-shell structured ZnO@Cu-Zn-Al layered double hydroxides with enhanced photocatalytic efficiency for CO₂ reduction, Catal. Commun. 77 (2016) 118–122.
- [18] S. Zhu, S. Liang, J. Bi, et al., Photocatalytic reduction of CO₂ with H₂O to CH₄ over ultrathin SnNb₂O₆ 2D nanosheets under visible light irradiation, Green Chem. 18 (1) (2016).
- [19] M.N. Ha, G. Lu, Z. Liu, L. Wang, Z. Zhao, 3DOM-LaSrCoFeO₆₋₈ as a highly active catalyst for the thermal and photothermal reduction of CO₂ with H₂O to CH₄, J. Mater. Chem. A 4 (34) (2016) 13155–13165.
- [20] L. Wang, Y. Wang, Y. Cheng, Z. Liu, Q. Guo, M.N. Ha, Z. Zhao, Hydrogen-treated mesoporous WO₃ as a reducing agent of CO₂ to fuels (CH₄ and CH₃OH) with enhanced photothermal catalytic performance, J. Mater. Chem. A 4 (14) (2016) 5314–5322.
- [21] L. Xu, M.N. Ha, Q. Guo, L. Wang, Y. Ren, N. Sha, Z. Zhao, Photothermal catalytic activity of combustion synthesized $LaCo_xFe_{1-x}O_3$ ($0 \le x \le 1$) perovskite for CO_2 reduction with H_2O to CH_4 and CH_3OH , RSC Adv. 7 (73) (2017) 45949–45959.
- [22] K. Yu, S. Yang, C. Liu, H. Chen, H. Li, C. Sun, S.A. Boyd, Degradation of organic dyes via bismuth silver oxide initiated direct oxidation coupled with sodium bismuthate based visible light photocatalysis, Environ. Sci. Technol. 46 (13) (2012) 7318–7326.
- [23] Y. Qu, W. Zhou, Z. Ren, S. Du, X. Meng, G. Tian, K. Pan, G. Wang, H. Fu, Facile preparation of porous NiTiO₃ nanorods with enhanced visible-light-driven photocatalytic performance, J. Mater. Chem. 22 (32) (2012) 16471.
- [24] M. James, T. Tedesco, D.J. Cassidy, R.L. Withers, Oxygen vacancy ordering in strontium doped rare earth cobaltate perovskites Ln_{1-x}Sr_xCoO_{3-δ} (Ln=La, Pr and Nd; x > 0.60), Mater. Res. Bull. 40 (6) (2005) 990–1000.
- [25] G. Pecchi, C. Campos, O. Peña, Thermal stability against reduction of LaMn_{1-y}Co_yO₃ perovskites, Mater. Res. Bull. 44 (4) (2009) 846–853.
- [26] Y. Yang, Y. Sun, Y. Jiang, Structure and photocatalytic property of perovskite and perovskite-related compounds, Mater. Chem. Phys. 96 (2-3) (2006) 234–239.
- [27] R.K.C. de Lima, M.S. Batista, M. Wallau, E.A. Sanches, Y.P. Mascarenhas, E.A. Urquieta-González, High specific surface area LaFeCo perovskites—synthesis by nanocasting and catalytic behavior in the reduction of NO with CO, Appl. Catal. B 90 (3-4) (2009) 441–450.
- [28] Y. Wang, X. Cui, Y. Li, L. Chen, Z. Shu, H. Chen, J. Shi, High surface area mesoporous LaFe_xCo_{1-x}O₃ oxides: synthesis and electrocatalytic property for oxygen reduction, Dalton Trans. 42 (26) (2013) 9448–9452.
- [29] A.A. Saad, W. Khan, P. Dhiman, A.H. Naqvi, M. Singh, Structural, optical and magnetic properties of perovskite (La_{1-x}Sr_x)(Fe_{1-x}Ni_x)O₃, (x = 0.0, 0.1 & 0.2) nanoparticles, Electron. Mater. Lett. 9 (1) (2013) 77–81.
- [30] L. Chávez-Guerrero, B. Medina-Lott, R.F. Cienfuegos, M.A. Garza-Navarro,

R.N. Vannier, A. Ringuedé, M. Hinojosa, M. Cassir, Synthesis and characterization of $LaNi_xCo_{1-x}O_3$: Role of microstructure on magnetic properties, J. Rare Earths 33 (3) (2015) 277–281.

- [31] L. Liu, Y. Cheng, Z. Liu, M.N. Ha, Q. Guo, Z. Zhao, Thermochemical conversion of CO₂ into CH₄ using oxygen deficient NiFe₂O₄₋₈ with unique selectivity, RSC Adv. 6 (87) (2016) 83814–83819.
- [32] G. Iervolino, V. Vaiano, D. Sannino, L. Rizzo, P. Ciambelli, Production of hydrogen from glucose by LaFeO₃ based photocatalytic process during water treatment, Int. J. Hydrogen Energy 41 (2) (2016) 959–966.
- [33] L. Jing, Y. Qu, H. Su, C. Yao, H. Fu, Synthesis of high-activity TiO₂-Based photocatalysts by compounding a small amount of porous nanosized LaFeO₃ and the activity-enhanced mechanisms, J. Phys. Chem. C 115 (25) (2011) 12375–12380.
- [34] H. Su, L. Jing, K. Shi, C. Yao, H. Fu, Synthesis of large surface area LaFeO3 nanoparticles by SBA-16 template method as high active visible photocatalysts, J. Nanopar. Res. 12 (3) (2009) 967–974.
- [35] S. Farhadi, M.M. Amini, F. Mahmoudi, Phosphotungstic acid supported on aminosilica functionalized perovskite-type LaFeO₃ nanoparticles: a novel recyclable and excellent visible-light photocatalyst, RSC Adv. 6 (105) (2016) 102984–102996.
- [36] F. Ling, O.C. Anthony, Q. Xiong, M. Luo, X. Pan, L. Jia, J. Huang, D. Sun, Q. Li, PdO/ LaCoO₃ heterojunction photocatalysts for highly hydrogen production from formaldehyde aqueous solution under visible light, Int. J. Hydrogen Energy 41 (14) (2016) 6115–6122.
- [37] S. Wang, D. Chen, F. Niu, N. Zhang, L. Qin, Y. Huang, Hydrogenation-induced surface oxygen vacancies in BiFeO₃ nanoparticles for enhanced visible light photocatalytic performance, J. Alloys. Compd. 688 (2016) 399–406.
- [38] S. Li, L. Jing, W. Fu, L. Yang, B. Xin, H. Fu, Photoinduced charge property of nanosized perovskite-type LaFeO₃ and its relationships with photocatalytic activity under visible irradiation, Mater. Res. Bull. 42 (2) (2007) 203–212.
- [39] A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garcia, Photocatalytic CO₂ reduction by TiO₂ and related titanium containing solids, Energy Environ. Sci. 5 (11) (2012) 9217.
- [40] H. Shen, T. Xue, Y. Wang, G. Cao, Y. Lu, G. Fang, Photocatalytic property of perovskite LaFeO₃ synthesized by sol-gel process and vacuum microwave calcination, Mater. Res. Bull. 84 (2016) 15–24.
- [41] S. Mickevičius, S. Grebinskij, V. Bondarenka, B. Vengalis, K. Šliužienė, B.A. Orlowski, V. Osinniy, W. Drube, Investigation of epitaxial LaNiO_{3-x} thin films by high-energy XPS, J. Alloys. Compd. 423 (1-2) (2006) 107–111.
- [42] B. Liu, Y. Zhang, L. Tang, X-ray photoelectron spectroscopic studies of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃₋₈ cathode for solid oxide fuel cells, Int. J. Hydrogen Energy 34 (1) (2009) 435–439.
- [43] T. Maneerung, K. Hidajat, S. Kawi, K-doped LaNiO₃ perovskite for high-temperature water-gas shift of reformate gas: role of potassium on suppressing methanation, Int. J. Hydrogen Energy 42 (15) (2017) 9840–9857.
- [44] F. Puleo, L.F. Liotta, V. La Parola, D. Banerjee, A. Martorana, A. Longo, Palladium local structure of La_{1-x}Sr_(x)Co_(1-y)Fe_(y-0.03)Pd_(0.03)O_(3-delm) perovskites synthesized using a one pot citrate method, Phys. Chem. Chem. Phys. 16 (41) (2014) 22677–22686.
- [45] E. García-López, G. Marcì, F. Puleo, V. La Parola, L.F. Liotta, La_{1-x}Sr_xCo_{1-y}Fe_yO₃₋₈ perovskites: preparation, characterization and solar photocatalytic activity, Appl. Catal. B 178 (2015) 218–225.
- [46] Lee Y L, J. Kleis, J. Rossmeisl, et al., Ab initio energetics of LaBO₃(001) (B = Mn, Fe, Co, and Ni) for solid oxide fuel cell cathodes, Phys. Rev. B 80 (22) (2009) 308–310.
- [47] X. Liu, B. Cheng, J. Hu, et al., Study on adsorption of O₂ on LaFe_{1-x}Mg_xO₃ (010) surface by density function theory calculation, Appl. Surface Sci. 258 (22) (2012).
- [48] Pan C C, Y.H. Chen, N. Wu, et al., First-principle study of O vacancy on LaNiO₃ (001) surface, Int. J. Hydrogen Energy 41 (35) (2016) 15756–15763.
- [49] L. Sun, J. Hu, H. Qin, et al., Influences of Ca doping and oxygen vacancy upon adsorption of CO on the LaFeO₃, (010) surface: a first-principles study, J. Phys. Chem. C 115 (13) (2011) 5593–5598.
- [50] K. Zhu, T. Wu, M. Li, et al., Perovskites decorated with oxygen vacancies and Fe-Ni alloy nanoparticles as high-efficiency electrocatalysts for the oxygen evolution reaction, J. Mater. Chem. A (2017) 5.