Construction of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ /attapulgite nanocomposite for photo-SCR of NO_x at low temperature

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Abstract: $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ /attapulgite (ATP) nanocomposite was prepared by a sol-gel method. The structures and physicochemical properties were investigated by X-ray diffraction (XRD), Transmission electron microscope (TEM), UV-visible diffused reflectance spectroscopy (UV-vis) and X-ray photoelectron spectroscopy (XPS). $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ /ATP nanocomposite was used as catalyst for photo-assisted selective catalytic reduction (photo-SCR) of NO under visible light irradiation. The impact of the various Mn doping fraction on the NO conversion was investigated. Results indicate that $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ remains as a perovskite solid solution supported uniformly on the ATP surface when x is less than 0.4. When x is beyond 0.4, LaMnO_3 phase co-precipitates with the perovskite $\text{LaFe}_{0.6}\text{Mn}_{0.4}\text{O}_3$ and forms coherent heterojunction of LaMnO_3 / $\text{LaFe}_{0.6}\text{Mn}_{0.4}\text{O}_3$ on ATP. The photocatalytic de NO_x activity of the composite material is the highest when $x = 0.6$ and the NO conversion reaches as high as 85% even under room temperature.

Keyword: attapulgite; nanocomposite; perovskite; photo-SCR; denitrification; heterostructure

1. Introduction

Nitrogen oxides (NO, NO₂) are widely known as one of the primary air pollutants which are harmful for the ecosystem and human health in terms of respiratory diseases, acid rain, photochemical smog and solid particles PM_{2.5}. Therefore, the NO_x pollution abatement becomes an imperative challenge. For several decades, selective catalytic reduction (SCR) with NH₃ has been recognized as an alternative strategy which is extensively used to remove NO_x [1]. However, there are still some drawbacks including high temperature window (300 °C -400 °C), low conversion capacity of NO_x and generation of by-products. Therefore, developing efficient and low temperature catalyst is of great significance.

In recent years, photocatalysis including photo-oxidation, photo-decomposition, and photo-selective catalytic reduction (photo-SCR) [2, 3] has become an innovative and promising technology which takes advantage of sunlight to eliminate environmental pollutants [4-7]. For instance, a number of efforts have been put aiming for photocatalytic oxidation denitrification [8-11]. However, nitrates are easy to form on the surface of the material in photo-oxidation and difficult to remove which adhere strongly to the material. Accumulation of nitrates to a substantial concentration may cause corrosion of catalytic material thus reducing the activity. Therefore, it needs to be washed with deionized water and then regenerate under calcination [12]. Photo-reduction which directly decomposes NO_x to N₂ is another option [13-16]. However, the conversion rate of nitrogen oxide in this case is very low and far to reach the requirement of practical application. Alternatively, the photo-SCR

approach is attracting a great interest in air purification which can effectively remove volatile organic compounds and NO_x [17, 18], due to the mild reaction conditions, less secondary pollution, low energy consumption, etc [19]. Current photo-SCR materials are focused on semiconductors, which has attracted great attentions as it holds great promise to address the worldwide energy and environmental issues. Tanaka group has studied TiO_2 for photo-SCR de NO_x under UV and visible-light irradiation. Interestingly they found that photo-SCR of NO took place over TiO_2 even under visible light due to the formation of donor band from N 2p level by NH_3 adsorption to Lewis acid sites and direct excitation [20,21]. However, higher activity under high-GHSV conditions is largely required in terms of practical application when such in situ doping approach is adopted [22]. In order to improve the activity of the photocatalysts driven by visible light, a series of dye sensitized TiO_2 have been developed, however stability of the dye is not enough due to the photo-induced decolorization effect [23,24]. Therefore, developing visible light driven photocatalyst with high stability is a great challenge to improve the photo-SCR system.

As known as a p-type semiconductor material, some of perovskite (ABO_3) have narrow bandgap and good photoresponse to visible light [25]. It has received great scientific interest owing to its flexible structure and remarkable photocatalytic properties. In the ideal structure of rare earth perovskites, larger cations of the A type are surrounded by 12 anions in a cub-octahedral coordination, and smaller cations of the B type are surrounded by 6 anions in an octahedral coordination [26]. Due to the flexible alternation of A or B site by band gap engineering, ABO_3 perovskite has been widely studied in photocatalysis area, such as photoreduction of CO_2 [27], photocatalytic decomposition of water [28, 29], photocatalytic degradation of dyes [30, 31]. Zhang et al. [32-34] have studied the denitrification activity of B-site cation

doped LaFeO_3 with different elements and find that doped catalysts enhance the catalytic efficiency. However, the perovskite particles are prone to aggregate due to its large particle size. More attention has been taken on the preparation of supported photocatalyst which immobilize semiconductor with various supports to address the above issues [35-37]. As a natural clay material, ATP has been known as a species with special lath-like or fibrous morphology composed of hydrated magnesium aluminum silicate [38]. It has been an ideal support because of its high-specific surface area as well as abundant active sites [39], making it own good physical adsorption capacity of the gas molecules [40]. In our previous work, we have successfully synthesized a series of ATP supported CeO_2 with various metal dopings [40, 41]. To the best of our knowledge, there has been no report on rare earth perovskite catalyst for NO_x removal by photo-SCR strategy.

In the present work, we use ATP as the support to load $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ rare earth perovskite by facile sol-gel method. The B site cation of LaFeO_3 can be substituted by adequate Mn cation, which is expected to generate new precipitated phase to form the coherent heterojunction with original solid solution when the doping content reaches a certain proportion. The composite-activity on the photo-SCR removal of NO is investigated with tuned molar fractions of Mn to elaborate the factors determining the activity of photo-SCR of NO.

2. Experimental

2.1. Materials

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$ were provided by Sinopharm Chemical Reagent Co., Ltd., China. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was purchased by Shanghai Xinbao Fine Chemical Factory. ATP was supplied by Jiangsu Nanda Zijin Technology Group Co., Ltd. (Changzhou, China). $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and $(\text{CH}_2\text{OH})_2$ were purchased from

Chinasun Specialty Products Co., Ltd., Jiangsu. All reagents were analytical grade reagents without further purification.

2.2. Synthesis of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$

An appropriate amount of aqueous solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and citric acid were dissolved in deionized water and dispersed by ultrasonic wave, which was added 3 ml of ethylene glycol and the purified ATP after a few minutes. It was followed by stirring at 80 °C in temperature magnetic stirrer to obtain a wet gel. The wet gel was placed in a thermostatic drum wind at 80 °C for 12 h to obtain a dry gel, followed by calcination in muffle furnace and heated to 600 °C at the rate of 2 °C /min for another 2 h to obtain the $\text{LaFeO}_3/\text{ATP}$ nanocomposites. A series of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ nanocomposites with the incorporation of Mn were synthesized in the same way, and the molar fractions of Mn ions in the current synthesis were adjusted from 0.1-0.9. Subsequently the final products were granulated and sifted through a 20–40 mesh sieve for characterization of the morphology characterization and catalytic activity.

2.3. Characterization

The transmission electron microscopy (TEM) characterization was recorded on a transmission electron microscope using a JEOL–2100 coupled with a Gatan 832 CCD operating at 200 kV. The X-ray diffraction (XRD) analyses was carried out with an X-ray diffractometer on a Rigaku D/MAX-2500PC diffractometer using Cu $K\alpha$ radiation which is recorded for 2θ range between 5° and 80° at a scan rate of 0.02°/s. The Fourier-transform infrared (FT-IR) spectra were recorded on a Spectrum 100 spectrometer (PE, USA). The UV-Vis diffuse reflectance spectra (DRS) of the obtained catalysts were carried on a UV-Vis spectrometer (Thermo Nicolet Evolution

500) which equipped with an integrating sphere. The binding energy of the elements was measured by X-ray photoelectron spectroscopy (XPS) with a Quantum 2000 Scanning ESCA Microprobe instrument using AlK α . The Photoluminescence (PL) spectrum was carried on a Fluorescence photometer (LS45) with the excitation wavelength of 300nm. The C 1s signal was set to a position of 1486.6 eV. The electronic structure calculations based on density functional theory (DFT) were performed by using the Vienna ab initio simulation package (VASP). Projector-augmented wave (PAW) potentials were adopted to present the interaction of the valence electrons with the ionic cores. The electron paramagnetic resonance spectra were obtained using a Bruker EMX10/12 apparatus. Before the EPR measurements, the sample was heated in air and evacuated for 30 min at 400°C. The g values and the relative amount of radical species were determined using a Mn marker. EPR spectra of NH₂ radical were obtained by illumination of catalyst with adsorbed NH₃. As a light source, a 500 W Xenon lamp equipped with UV cut-off filter was used.

2.4. Photo-SCR of NO performance

This experiment was carried in the photo-SCR deNO_x reactor (Fig 1) consistent with PFD-5000 light-heat fixed bed reactor provided by Huasi Instrument Co., Ltd. (Hunan, China) and KM9106 flue gas analyzer purchased by Kahn International Co., Ltd. A space velocity (SV) of 50000 h⁻¹ is calculated by the total gas flow rate of 150 ml/min. The inlet gas composition was as follows: 1000 ppm NH₃, 1000 ppm NO and 3 vol% O₂ with N₂ as balance gas. The light source is a 200-1000W xenon lamp that can simulate sunlight. Two open windows on both sides of the reactor chamber are conducive to the light source irradiation. Two ZJB380 UV-filters are placed at both ends of the window to cut off the light whose wavelength is lower than 420 nm. The

concentration of gas was by flue gas analyzer recorded once every 5 minutes during the reaction.

The N_2 selectivity and NO_x conversion [42] in the reaction are calculated as follows:

$$NO_x \text{ conversion} = \frac{[NO+NO_2]_{inlet} - [NO+NO_2+N_2O]_{outlet}}{[NO+NO_2]_{inlet}} \times 100\%$$

$$N_2 \text{ selectivity} = \left(1 - \frac{2[N_2O]_{outlet}}{[NO_x]_{inlet} + [NH_3]_{inlet} - [NO_x]_{outlet} - [NH_3]_{outlet}} \right) \times 100\%$$

Where $[NH_3]_{inlet}$, $[NO]_{inlet}$, $[NO_x]_{inlet}$ and $[NO_2]_{inlet}$ represent the NH_3 , NO , NO_x and NO_2 concentration in the inlet gas respectively, $[NH_3]_{outlet}$, $[NO]_{outlet}$, $[NO_x]_{outlet}$, $[NO_2]_{outlet}$ and $[N_2O]_{outlet}$ represent the NH_3 , NO , NO_x , NO_2 and N_2O concentration in the outlet gas respectively.

Fig 1 Schematic for the photo-SCR de NO_x instrument

3. Results and discussion

3.1. XRD analysis

Fig. 2 shows the XRD patterns of the synthesized $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ ($x = 0-1$) catalysts. No peaks for ATP species can be observed in XRD patterns of the $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ ($x = 0-1$) catalysts after 600 °C calcination which indicates that the original structure of ATP is not maintained, and all $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0-1$) are attributed to perovskite-type crystalline structure. With the increasing of doping amount, the main peaks has a progressive shift to higher angles, which is due to the fact that the Mn^{2+} (0.067 nm) radius is larger than Fe^{3+} (0.064 nm) radius. Some species of Mn^{2+} enter into the lattice of LaFeO_3 consequently leading to lattice distortion and the tolerance factor value t of the crystal structure is decreased. In addition, there is a transition from the orthogonal phase to rhombic phase which LaFeO_3 is of orthogonal phase [43] and LaMnO_3 is of rhombic phase [44]. It should be noted that the main peak of rare earth perovskite decreases from $x=0.1$ to $x=0.3$ and then increases when $x>0.4$. When the doping amount of Mn ion is 0.3, the peak intensity of perovskite is the weakest, implying that all Mn^{2+} ions enter into the crystal lattice of LaFeO_3 completely and generate $\text{LaFe}_{0.7}\text{Mn}_{0.3}\text{O}_3/\text{ATP}$ without other precipitation. On the contrary, when doping amount of Mn ion is beyond 0.4, the main peak of perovskite remains unchanged with the absence of shifting of two-theta angle and has a gradually enhancement of crystallinity with further increase of doping amount suggesting that there appears a new precipitation [45]. Since the characterization peaks of pure LaMnO_3 and LaFeO_3 in XRD are very close, Raman characterization is necessary to provide further evidence to determine the status of new precipitated phase because Raman spectroscopy is more surface sensitive compared with XRD.

Fig 2 XRD patterns of ATP and $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ ($x=0.1-0.9$)

3.2. Raman spectroscopy

Fig. 3 shows the Raman spectra of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ with various x doping. The peak at around 631 cm^{-1} corresponds to the characteristic peak of LaFeO_3 as reported by Barbero [46]. However, when x is beyond 0.4, the band at 675 cm^{-1} corresponding to LaMnO_3 becomes stronger which is agree well with the above results of XRD. With the increase of x , the band around 635 cm^{-1} decreases suggesting that the Mn ion is entering into the LaFeO_3 structure leading to the formation of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ solid solution. It should be noted that there is a progressive peak shift to the higher wavenumber when x is from 0.3 to 0.8, indicating that structural distortions increase because of the change in lattice constant by Mn which is consistent with XRD analysis. The band of ATP situates at approximately 1500 cm^{-1} which is therefore not included because there is an order of magnitude weaker than those in Fig.3. Although the XRD analysis only indicates the formation of solid solution, the Raman data shows the formation of LaMnO_3 phase in addition to that of

LaFeO₃, which may be due to the difference in the surface sensitivity of these methods.

Fig 3 Raman spectra of LaFe_{1-x}Mn_xO₃/ATP with various x doping

3.3. TEM analysis

Fig. 4 shows the TEM morphology of LaFe_{1-x}Mn_xO₃/ATP with various x doping. It can be seen that the nanoparticles of rare earth perovskite are dispersed on the surface of ATP uniformly. Results suggest that the doping of Mn ion does not significantly alter the morphology of composite. The high-resolution TEM image (HRTEM) of LaFe_{1-x}Mn_xO₃/ATP clearly shows the evolution of crystallization status. Without doping as shown in Fig.4b, the lattice spacing of nanoparticles on the ATP surface is 0.278 nm which corresponds to the (121) planes of LaFeO₃. When x=0.3 shown in Fig.4c, the corresponding HRTEM of the LaFe_{1-x}Mn_xO₃ solid solution nanoparticles in the composite shows that the lattice distance of the (121) plane is decreased to 0.272 nm. Interestingly, when x is beyond 0.4, the lattice spacing of 0.240 nm corresponding to the (121) planes of LaMnO₃ appears in addition to the

original (121) planes of solid solution, suggesting the formation of coherent heterojunction structure of rare earth perovskite as shown in Fig. 4d-h, which is consistent with the XRD results. Apart from the Cu element from the copper grids, four elements of La, Fe, Mn and O are evidenced in EDS spectrum as shown in Fig 4i, which indicates successful preparation and loading of perovskite nanoparticles.

Fig 4 TEM of ATP and LaFe_{1-x}Mn_xO₃/ATP: (a) ATP, (b) x=0, (c) x=0.3, (d) x=0.4, (e) x=0.5, (f) x=0.6, (g) x=0.7, (h) x=0.8, (i) EDS of LaFe_{0.4}Mn_{0.6}O₃/ATP

3.4. UV-vis analysis

The UV-vis spectra of LaFeO₃/ATP, LaFe_{0.6}Mn_{0.4}O₃/ATP, LaFe_{0.4}Mn_{0.6}O₃/ATP and LaMnO₃/ATP are shown in Fig.5 respectively. It can be seen that the pure LaMnO₃/ATP has very less adsorption in the visible range. On the contrary, the pure LaFeO₃/ATP composites have an obvious adsorption band in the visible range. The visible light response capability of composite material has been significantly improved after doping LaFeO₃/ATP with Mn ion, and the adsorption edge in the

visible range is extended to 480 nm correspondingly. According to the above analysis results, the heterojunction structure is formed by $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ and precipitated LaMnO_3 when the doping ratio of Mn ion reaches 0.4. The composite material of $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ almost reaches the highest adsorption edge of 610 nm because it may decrease the band gap of composite with the Mn ion doped into the lattice of LaFeO_3 whose band gap is lower than LaMnO_3 , which leads to the formation of optimal $\text{LaMnO}_3/\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ heterostructure.

Fig 5 UV-vis spectra of $\text{LaMnO}_3/\text{ATP}$, $\text{LaFe}_{0.6}\text{Mn}_{0.4}\text{O}_3/\text{ATP}$, $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ and $\text{LaFeO}_3/\text{ATP}$

3.5. XPS analysis

Fig.6a shows the survey scan spectrum of $\text{LaFeO}_3/\text{ATP}$ and $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$. La, Fe, O, and Mn peaks are shown in Fig. 6a which is consistent with the results of EDS. There should be two kinds of oxygen on the surface of the catalyst of $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$. It is obvious that the two peaks of O 1s with binding energies at 529 eV and 531 eV correspond to crystal lattice oxygen (O_L) and adsorbed oxygen (O_A) of the catalyst [47-49]. As shown in Fig. 6b, O 1s peak of $\text{LaFeO}_3/\text{ATP}$ with

binding energies around 529 eV can be assigned to crystal lattice oxygen (O_L) of the catalyst. However, the peak intensity of adsorbed oxygen (O_A) of $LaFeO_3/ATP$ is weaker than that of $LaFe_{0.4}Mn_{0.6}O_3/ATP$, which suggests that adsorbed oxygen (O_A) on the surface of pure $LaFeO_3/ATP$ is rare. It can be seen that the peaks at around 835 eV and 852 eV corresponding to $La\ 3d_{5/2}$ and $La\ 3d_{3/2}$ in the Fig 6c show dual peaks, which can be assigned to La^{3+} oxidation state of the composites according to the report by Li et al [50]. A binding energy shift of $LaFe_{0.4}Mn_{0.6}O_3/ATP$ toward lower binding energy takes place compared with $LaFeO_3/ATP$ due to the substitution of Fe by Mn which results in the change of the structure. Fig. 6d shows the Fe 2p XPS spectrum of $LaFeO_3/ATP$ and $LaFe_{0.4}Mn_{0.6}O_3/ATP$. There appear two peaks around 711 eV and 724 eV respectively corresponding to Fe $2p_{3/2}$ which is attributed to characteristic peaks of Fe^{3+} in composite surface [51, 52], signifying the presence of Fe^{3+} on the surface both in $LaFeO_3/ATP$ and $LaFe_{0.4}Mn_{0.6}O_3/ATP$. And the peak of $LaFe_{0.4}Mn_{0.6}O_3/ATP$ is weaker than the counterpart of $LaFeO_3/ATP$ suggesting the incorporation of Mn ion. The Mn 2p XPS spectrum of $LaFe_{0.4}Mn_{0.6}O_3/ATP$ is shown in Fig 6e which can be found that the peak at around 641eV corresponds to the signals of Mn $2p_{3/2}$ and the peak at around 654eV corresponds to the signals of Mn $2p_{1/2}$, respectively. Siwach.et al [53] has pointed out that the peak with binding energies around 641eV corresponds to Mn^{3+} on the surface of $La_{0.7-x}Mm_xCa_{0.3}MnO_3$ ($0.0 \leq X \leq 0.45$), suggesting the presence of Mn^{3+} in the structure of $La_{0.7-x}Mm_xCa_{0.3}MnO_3$ ($0.0 \leq X \leq 0.45$). Therefore, it can be concluded that Mn ion exists in the form of Mn^{3+} in $LaFe_{1-x}Mn_xO_3/ATP$ nanocomposite likewise.

Fig 6 XPS spectra of LaFeO₃/ATP and LaFe_{0.4}Mn_{0.6}O₃/ATP (a) survey scan, (b) O 1s, (c) La 3d, (d) Fe 2p, (e) Mn 2p

3.6. PL analysis

Fig.7 shows the photoluminescence (PL) spectra of LaFe_{1-x}Mn_xO₃/ATP (x=0.1, 0.2, 0.4, 0.6, 0.8, respectively) which demonstrate the influence of Mn doping on PL emission. It can be seen that the intensity increases along with x increasing from 0.1

to 0.4 but significantly decrease from 0.4 to 0.6. As is known that PL emission presents the reflection of recombination of photo-excited electrons and holes. In other words, the weaker intensity of PL reveals lower recombination rate [54], suggesting that the separation of the photo-generated charges is not improved when the doping amount is less than 0.4 whereas the $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ has the highest separation efficiency.

Fig 7 PL emission spectra of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ ($x=0.1, 0.2, 0.4, 0.6, 0.8$)

3.7. Photo-SCR deNO_x activity and stability analysis

Fig.8 shows the photo-SCR activity and stability of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ with various x doping where triplicate experiments are carried out for each test with the relative deviation generally less than 5%. It can be observed that the pure ATP has almost no activity in terms of denitration and the photocatalytic activity of pure $\text{LaMnO}_3/\text{ATP}$ is very weak. NO_x conversion presents a rising trend with the increasing of Mn doping from 0.1 to 0.6 and the NO_x conversion rate approaches 85% when doping amount of x is 0.6. It should be noted that with the amount of Mn ion

continuing to increase to 0.7, NO_x conversion rate of the sample decrease for instead. Furthermore, the photocatalytic activity of pure LaMnO₃/ATP shows the lowest activity except bare ATP. In combination with the above analysis, LaFe_{1-x}Mn_xO₃ on the ATP is assumed to form solid solution and can increase the light response range to some extent when the doping amount is less than 0.4. However, the separation efficiency of the photo generated electron-hole is not improved. When the doping amount is beyond 0.4, the coherent heterostructure of LaFe_{1-x}Mn_xO₃/ATP is formed in favor of electron-holes separation as shown in Fig.7 which leads to improve the efficiency of photo-SCR deNO_x. However, on the contrary, with further doping amount beyond 0.6, the over precipitates of LaMnO₃ may hinder the adsorption of light and may jeopardize the well-formed heterojunction, which result in the reduced catalytic efficiency.

Fig 8 Photo-SCR conversion rate of LaFe_{1-x}Mn_xO₃/ATP with various x doping

3.8. On-off response performance of light irradiation

Fig. 9 shows the on-off response for the photo-SCR activity under visible-light irradiation over the LaFe_{0.4}Mn_{0.6}O₃/ATP photocatalyst which are tested three times at

each time with the deviation less than 5%. It can be observed that the conversion of NO is about 10% without visible-light irradiation which may be attributed to the absorption of ATP matrix, on the contrary, it significantly increases to 83% under visible-light irradiation, manifesting the function of the $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ as a visible-light-driven photocatalyst for the photo-SCR of NO. It is worth mentioning that with the increase of irradiation time, the conversion of NO increases slightly. This phenomenon is different with the previous report whereas the conversion of NO rate decreases slightly with the increase of irradiation time, which may be due to the instability of sensitized porphyrin derivative under photoirradiation [22,23]. In other words, the perovskite oxides constructed on the ATP support may benefit the photo-stability.

Fig 9 Conversion of NO during several on/off cycles of visible-light irradiation over the $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ photocatalyst

3.9. N₂ selectivity analysis

Fig.10 shows N₂ selectivity curves of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ with various x doping which are tested three times with the deviation less than 5%. It can be found that N₂

selectivity of pure $\text{LaFeO}_3/\text{ATP}$ and $\text{LaMnO}_3/\text{ATP}$ are only 40% and 66%, respectively. N_2 selectivity is increased with the increase of the doping amount gradually because of the heterojunction structure which promotes photogenerated electron-hole separation. An obvious increase can be noted with an increase of the Mn content from 0.4 to 0.6, whereby the $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ affords a maximum N_2 selectivity of nearly 100%. With the increasing of doping amount beyond 0.6, N_2 selectivity of sample decreases. This phenomenon can be rationalized that when the doping amount of Mn reaches maximum, the excess precipitation of a LaMnO_3 phase on one hand may decrease the acidic sites on the ATP surface inhibiting the NH_3 adsorption, on the other hand may destruct the coherent heterostructure both of which lead to the emerging of by-product N_2O consequently reduces the N_2 selectivity [22].

Fig 10 N_2 selectivity of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ with various x doping

3.10. EPR analysis

Fig.11 shows the EPR spectra of $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ recorded under various conditions. Fig. 11a is the EPR spectrum of $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ after introduction of

NH₃ in the dark and Fig. 11b is the EPR spectrum of LaFe_{0.4}Mn_{0.6}O₃/ATP under irradiation with a 500 W Xenon lamp equipped with UV cut-off filter. The EPR spectrum is centered on a single line of g=2 whereas the feature near g=4.3 is due to Fe³⁺ and become weaker in Fig.11b which indicates that Fe³⁺ decreases [55, 56]. New signals are observed at g=2.007, 2.009 and 2.021 in Fig.11b which may be ascribed to the generation of NH₂ radical under photoirradiation [22]. This phenomenon has also been identified by S.Yamazoe et al. who proves that NH₂ radical is formed on TiO₂ under photoirradiation as an intermediate [20,57].

Fig 11 EPR spectra of LaFe_{0.4}Mn_{0.6}O₃/ATP (a) after introduction of NH₃ in the dark (b) under photoirradiation .

3.11. Photo-SCR deNO_x mechanism

The band edge positions of LaFeO₃ and LaMnO₃ in this study are estimated according to the following formulas [58, 59].

$$E_{VB} = \chi - E_e + 0.5E_g$$

$$E_{CB} = E_{VB} - E_g$$

Where E_{VB} represents the valence band (VB) edge potential, E_{CB} represents the conduction band (CB) edge potential, E_g represents the band gap of the semiconductor, E_e represents the energy of free electrons of the hydrogen (~ 4.50 eV) and χ represents the absolute electronegativity of the semiconductor. The CB and VB of LaFeO_3 corresponding to 0.03eV and 2.13eV, and the CB and VB of LaMnO_3 correspond to -0.29eV and 2.24eV which are calculated by the band gap of LaFeO_3 [60] and LaMnO_3 [41] respectively, suggesting that the VB edge potential of LaMnO_3 is more positive than that of LaFeO_3 , while the CB edge potential of LaMnO_3 is more negative than that of LaFeO_3 [61]. In order to predict the bandgap structure of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$, we conduct DFT calculations by using VASP. The computational models of the LaFeO_3 and Mn doped unit crystal cell are shown in Fig. 12a and Fig. 12b respectively. There is wide band gap of 2.1 eV and high CB and VB level which is 0.02eV and 2.12eV in ideal LaFeO_3 as direct bandgap semiconductor in Fig.12c. However, after doping with Mn at $x=0.3$, the LaFeO_3 is changed to indirect bandgap semiconductor and the levels are comparatively narrowed as shown in Fig.12d. What is more, the CB and VB position of solid solution $\text{LaFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$ become 0.11 eV and 2.08 eV which is located between that of the original LaFeO_3 , making the charge carriers transporting between solid solution and LaMnO_3 more easily [62]. This obviously indicates that the introduction of Mn into LaFeO_3 as a constituent element is an effective way for engineering the band edges of the valence band as well as the conduction band.

Fig.12 Computational model of the LaFeO_3 unit crystal cell (a) and $\text{LaFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$ solid solution (b). Atoms: green—La, brown—Fe, red—O, brown wrapped by yellow—Mn. DFT calculated electronic band structures of the LaFeO_3 (c), $\text{LaFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$ solid solution (d)

According to the above analysis, the mechanism of photo-SCR of NO is put forward in Fig. 13. In the first Step, NH_3 is adsorbed on Lewis acid site of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ based on enrichment effect of ATP which has been identified in our previous work [63]. Secondly, $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ and LaMnO_3 are excited under visible light where photogenerated electrons on the conduction band of LaMnO_3 directly transfer to the conduction band of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$, which hinders the recombination of electron-hole pairs. Subsequently the photogenerated electrons coming from LaMnO_3 and remained in the conduction band of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ reduce Fe^{3+} to Fe^{2+} . On the other side the holes in the valence band of LaMnO_3 transfer to the valence band of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$,

which lead to forming more photogenerated holes which are captured by the NH_2 -species developed from NH_3 adsorbed on the surface of $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ to produce NH_2 radical. In the third Step, NH_2 radical is attacked by NO and produces NH_2NO intermediate [64,65]. In step 4, the unstable intermediate NH_2NO is decomposed into N_2 and H_2O quickly [66]. Finally, Fe^{2+} is re-oxidized to Fe^{3+} by adsorbed O_2 . The reaction is continued as shown in the following cycle.

Fig 13 Schematic mechanism of photo-SCR of NO by $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ catalyst

4. Conclusions

$\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ catalysts with various Mn doping are successfully prepared, where adequate doping of Mn expands the visible absorption range of perovskite species. The LaMnO_3 phase co-precipitates and forms the heterojunction structure of $\text{LaMnO}_3/\text{LaFe}_{0.6}\text{Mn}_{0.4}\text{O}_3$ on the surface of ATP when the doping amount reaches 0.4, which facilitates the separation of photo-generated electrons. The $\text{LaFe}_{0.4}\text{Mn}_{0.6}\text{O}_3/\text{ATP}$ catalyst demonstrates the highest NO conversion of 85% and nearly 100% N_2 selectivity, which exhibit remarkable catalytic performance at room temperature as compared with the $\text{LaMnO}_3/\text{ATP}$ and $\text{LaFeO}_3/\text{ATP}$. This work paves a promising avenue aiming to the industrial denitration application.

Acknowledgements

This work was supported by the National Science Foundation of China (51674043, 51478285), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Jiangsu Technology Support Program (BE2014100, BE2015103, BE2016654) and Jiangsu International Cooperation Project (BZ2015040). We also appreciate Prof. Yuanming Huang for his work on DFT calculations.

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