Composite structure and enhanced photocatalytic activity in Mn–Co–Ni–O/LaMnO$_3$ microparticles

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Abstract
A series of Mn–Co–Ni–O/LaMnO$_3$ composite materials were synthesized through the sol-gel method. The structure of these powders changed from the spinel to a spinel–perovskite mixed phase as the content of LaMnO$_3$ increased from 0 to 50%. Meanwhile, some grains of composite material were refined to form many small particles and distributed among the porous microparticles. According to the absorption spectra of composite samples, the strong absorption structures appeared in visible ranges, especially between 400 and 730 nm. The photocatalytic degradation of tetracycline under the visible light irradiation indicated that the percentage of LaMnO$_3$ at 50% exhibited the highest degradation rate (70.2%) in 150 min. Its high photocatalytic activity was mainly due to the large surface area, strong visible light absorption and increased ratio of Mn$^{3+}$/Mn$^{4+}$ ions. These new micro-structured photocatalysts were expected to show considerable potential applications in the water treatment.

1. Introduction

With the acceleration of industrialization and urbanization, environmental pollution and energy shortage have become a serious social problem. Semiconductor-based photocatalyst is regarded as an efficient, green and promising solution to solve these crises [1]. Due to the unique electronic structures consisting of filled valence bands and empty conduction bands, some semiconductor materials can be used as photocatalysts for light-induced chemical transformations involving a series of redox reactions of photogenerated carriers in pollutant degradation [2]. However, the photogenerated carriers in the excited states are unstable and easy to recombine, resulting in low photocatalytic efficiency. Moreover, inappropriate band gaps lead to limited solar energy utilization, resulting in energy waste and reduction of catalytic efficiency. Therefore, the properties of photocatalysts and the efficiency of the utilization of light sources play an extremely important role in photocatalysis.

Since decades, many efforts have been made to improve the photocatalytic performances of photocatalysts, such as through textural design, doping, noble metal loading, forming semiconductor composites and exploring novel visible-light-induced photocatalysts [3–6]. Sun et al reported that compared to non-doped and singly doped photocatalysts, the light absorption performance of Co and Ni co-doped cryptomelane was significantly improved and the degradation rate of phenol was increased, mainly due to the increased specific surface area and the variations in the relative contents of Mn$^{4+}$/Mn$^{3+}$ ions [7]. Yao et al observed that Co–Mn oxides with large surface area have higher activity than the individual Co and Mn oxides for volatile organic compounds degradation due to the better redox property of Co–Mn material [8]. It can be concluded that polymeric transition metal oxides possess better photocatalytic performance than that of the monometallic oxide because of the multiple coordination numbers and oxidation states [9]. As a typical mixed transition metal oxide, Mn–Co–Ni–O spinel has multiple applications due to its low cost and environmental safety, such as thermistors, uncooled infrared detectors and magnetic materials [10]. Our previous studies demonstrated that the composite
thin film with strong optical absorption in the visible wavelength range could be obtained by compositing perovskite LaMnO$_3$ with Mn–Co–Ni–O [11]. It is well known that the enhanced absorbance, especially in visible light range, is conducive to promoting the photocatalytic activity. In this work, Mn$_{1.60}$Co$_{0.30}$Ni$_{0.40}$O$_4$/LaMnO$_3$ (MCN/LM) composite photocatalysts were synthesized and the characterized with regards to their structural, optical and photocatalytic properties to assess the potential for application.

2. Experimental

2.1. Preparation of MCN/LM photocatalysts
In order to extend the practical application of photocatalysts, an energy-efficient, environmentally friendly and low-cost synthesis is essential. Herein, MCN$_{(1−x)}$/LM$_x$ ($x = 0.1, 0.3, 0.5$) microparticles were synthesized by the sol–gel method with different composite ratio of two phases. For comparison, pure MCN ($x = 0$) was also included. Four samples were synthesized using the same procedure and labeled as S0, S1, S3 and S5, corresponding to $x = 0, 0.1, 0.3$ and 0.5, respectively. Analytical grade Mn(CH$_3$COO)$_2$·4H$_2$O (AR, 99%), Co(CH$_3$COO)$_2$·4H$_2$O (AR, 99%), Ni(CH$_3$COO)$_2$·4H$_2$O (AR, 99%), and La(NO$_3$)$_3$·6H$_2$O (AR, 99%) were chosen as raw materials according to the cation stoichiometric ratios. The chemicals were dissolved in glacial acetic acid under continuous magnetic stirring and the concentrations of the solutions were adjusted to 0.4 mol l$^{-1}$. The mixed solutions were then heated to 60 °C for 3 h to obtain a purple to brown viscous precursors. Finally, they were calcined at 750 °C in air for 2 h to obtain the desired samples.

2.2. Characterization of materials
The phase structures of prepared powders were identified by x-ray diffraction (XRD, Bruker D8). The morphology and element composition of samples were observed by scanning electron microscopy (SEM, Supra55VP, Zeiss) equipped with an energy dispersive spectroscopy (EDS). The specific surface area and N$_2$ adsorption-desorption were determined by Brunauer–Emmett–Teller analysis (BET, SA3100, Beckman Coulter). A desorption isotherm was used to determine the pore size distribution using the Barrett–Joyner–Halenda (BJH) method. Before the measurement, the samples were degassed at 200 °C for 2 h under vacuum. Ultraviolet-visible diffuse reflectance (UV–vis DR) spectra of samples were determined on Shimadzu SolidSpec–3700 spectrophotometer with an integral sphere employing BaSO$_4$ as the standard reference. All the samples were controlled at the same weight during the UV–vis DR measurement. The valence states of Mn ions were identified by x-ray photoelectron spectroscopy (XPS, Shimadzu AXIS-ULTRA DLD) with Al K$_\alpha$ radiation ($h\nu = 1486.6$ eV).

2.3. Evaluation of photocatalytic activities
Excessive use and release of drugs such as antibiotics into the environment is causing antibiotic-resistant genes and bacteria, which has become a serious health problem today. Among the various antibiotics used in human and veterinary medicine to treat bacterial infections, tetracycline (TC) is widely used. To achieve a sustainable ecosystem, there is an urgent need to remove TC from sewage. With this in mind, TC is selected as a probe molecule to evaluate the photocatalytic decomposition activity of MCN/LM samples.

For photocatalytic activity measurement, 30 mg of as-obtained sample was mixed with 100 ml TC aqueous solution (0.1 mol l$^{-1}$) in the tubular quartz reactor. The mixture was magnetically stirred to be homogeneous in dark for 30 min to establish adsorption equilibrium between the photocatalyst and TC. The photocatalytic reactions were stimulated under the radiation of a 300 W Xenon lamp (PLS–SXE300, Perfect Light Company, Beijing, China) at room temperature, and then the suspensions were centrifuged to remove sediment at 30 min intervals. The TC concentration before and after photo-degradation were determined through the UV–vis spectrophotometer at the maximum absorption of 357 nm. The photocatalytic degradation ratio (DR %) is calculated by the following formula:

$$DR\% = \left[1 - \left(\frac{A_t}{A_0}\right)\right] \times 100\%$$

where $A_0$ is the UV–vis absorption of the original TC solution when reached absorption equilibrium, while $A_t$ is the UV–vis absorption of degraded solution at certain times [12].

3. Results and discussion
The XRD patterns of MCN/LM powders with various compositions are shown in figure 1. All diffraction peaks are indexed to the cubic spinel structure (JCPDS No. 84–0542) for the pure MCN. The perovskite phases begin to appear in the composite samples, and the intensity of the peaks are continuously increased with increasing LM composition. The peaks assigned to the cubic spinel become weaker in intensity but the widths are broadened,
indicating that the average crystallite size of MCN becomes smaller. Besides the spinel structure, the diffraction peaks of the S1 sample are indexed to the perovskite-type cubic phase (JCPDS No. 75-0440). Interestingly, a phase transition to the rhombohedral structure (JCPDS No. 86-1227) occurs and new peaks appear as the content of LM continues to increase in the S3 and S5 samples. This may indicate that the Ni and/or Co have been partially embedded in the LM perovskite structure, leading to a distortion of the cubic-phase crystal lattice [11].

The XRD measurement reveals the composite samples are composed of mixed MCN spinel and LM perovskite grains. This is mainly due to the fact that the ionic radius of La is much larger than other ions and therefore cannot be embedded as dopant in the crystal of the spinel. The crystallite sizes of MCN in the S0, S1, S3 and S5 samples determined by the Scherrer equation from the spinel (311) peak are 32.9, 21.3, 20.3 and 16.8 nm, respectively. This suggests that average crystallite size of MCN spinel shrinks with more LM perovskite grains added into the materials. It is consistent with the previous findings that grain growth can be suppressed by the incorporation of LM [13].

According to EDS measurements, the constituent elements of samples are present at the expected levels. The atomic percent results for all samples are listed in table 1. As shown in figure 2, the EDS mapping analysis of the S5 sample indicates all cations are evenly distributed in MCN/LM composite.

Figure 3 displays SEM images of the pure MCN and composite MCN/LM microparticles. The morphology of pure MCN is almost irregular polyhedron and the surface of particle is very smooth, while composite samples show the porous structures in some particles. It is interesting to observe that without controlled formation process, the S5 sample has the quite different surface morphology and microstructure. The particles in the S5 sample are highly porous, with many small particles randomly distributed among microparticles. The sizes of 200 particles are measured in the low-magnification SEM images and the size distributions are calculated and presented in figure 4. The average particle sizes of S0, S1, S3 and S5 samples are 2.95, 2.78, 2.06 and 0.86 μm, respectively. For the S5 sample, the particles are significantly refined, indicating that smaller particles can be obtained by compositing the two phases at an appropriate proportion. More importantly, reducing the particle size of the photocatalyst will shorten the transfer path of the charge carriers, which leads to efficient carrier separation and improved photocatalytic performance [3].

Previous results have shown that adding La into MCN materials can reduce the average grain size and improves the density of individual grain [13]. The highly porous structures in this work seems to reduce the

Table 1. Atomic percentages of MCN/LM samples.

| Sample | Elemental % (Atom.) |
|--------|---------------------|
|        | Mn  | Co  | Ni  | La  |
| S0     | 52.68 | 31.73 | 15.39 | —   |
| S1     | 50.92 | 31.04 | 15.46 | 2.58 |
| S3     | 51.47 | 25.60 | 10.71 | 12.22 |
| S5     | 50.96 | 20.63 | 9.56  | 18.85 |

Figure 1. XRD patterns of MCN/LM powder samples.
density of the powder samples. However, it is worth noticing that one particle in images may consist of numerous grains, so it does not contradict the previous result. According to our results, when LM is added to the composite, the growth of MCN spinel is retarded and the crystallite size of MCN becomes smaller and smaller, resulting in smaller grains. On the other hand, with the densification of the composite grains, once the limit of compressive stress is exceeded, the small grains tend to detach from the cluster particles and adhere to the surface [11]. Another reason for the increase in stress is that the Jahn–Teller distortion occurs in LM lattices when the specific composite content is exceeded. These may explain the porous structure and fine grains in the S5 sample.

The specific surface areas of as-synthesized samples are investigated by using N₂ adsorption and desorption isotherms. As shown in figure 5, the isotherm of S5 sample is identified as the type IV with the H3 hysteresis loop in the IUPAC classification, indicating the co-existence of structural and interparticle meso- and macropores [14]. The corresponding pore size distribution confirm that it contains mesopores about 35 nm diameter. Meanwhile, the isotherms rising rapidly near \( P/P_0 = 1.0 \) further indicates the presence of macropores due to the interspaces between particles. However, almost no hysteresis loop can be found in other samples, especially for S1, indicating a small surface area and disappearance of pores [15]. The specific surface areas of S0, S1, S3 and S5 samples are calculated to be 2.0, 4.5, 6.8 and 16.2 m² g⁻¹. It can be concluded that the S5 sample exhibits relatively higher BET surface area due to the smaller particle size and the porous structure. In addition, particles with porous structures provide an abundant surface area for the contact between the materials and pollutants, which is of great significance in accelerating the adsorptive and photocatalytic reactions.

Figure 2. EDS mapping of (a) Mn, (b) Co, (c) Ni, (d) La and (e) EDS spectra of the S5 sample.
Figure 3. SEM images of MCN/LM microparticles.

Figure 4. Particle size distributions of MCN/LM samples.
The light absorption properties of MCN and composite MCN/LM materials have been confirmed by UV–vis DR spectroscopy measurements and depicted in figure 6(a). Compared to the pure MCN, composite samples exhibit stronger absorption intensity in the wavelength range of 300 to 900 nm. In addition, the S5 sample exhibits significant absorption enhancement in most visible wavelength ranges. This implies that light absorption would be more efficient in MCN/LM with pores and smaller particles.

For transition metal compounds, their valence and conduction bands responsible for the optical transitions are mainly consist of high-density \( d \)-states from transition metal ions, where an electron localized in and transferred to a neighboring ion through the optical excitation [16]. To understand the peak positions in the absorption spectra, the absorption coefficients of the S0, S1, S3 and S5 samples in their thin-film forms are used as reference, as shown in figure 6(b). The specific synthesis and testing methods are described in the literature [11]. First absorption structure between 300 to 450 nm can be ascribed to the charge transitions involving 2\( p \) electrons of oxygen ions and 3\( d \) electrons of Mn ions, i.e., \( \text{O}^{2-} (2p) \rightarrow \text{Mn}^{3+} (3d^4) \) [10]. With the increase of LM content, more Mn\(^{3+}\) ions are introduced into the composite system, thereby enhancing the absorption strength in the short wavelength range. The MnO\(_6\) octahedra in LM perovskite is cooperatively distorted due to Jahn–Teller instability of the Mn\(^{3+}\) ions, which is responsible for second absorption structure near 600 nm. The decrease in lattice symmetry caused by the perovskite structure can effectively promote the absorption of lattice vibrations [17], thereby improving the light absorption in the long wavelength range. According to the previous study, there is another absorption structure located at 730 nm, which is attributed to the \( d-d \) transition of Co\(^{3+}\)(\( t_{2g} \)) \( \rightarrow \) Co\(^{2+}\)(\( t_{2g} \)) [10]. The rhombohedral structure in the composite samples indicates that Co\(^{3+}\) cations in the MCN spinel can diffuse into the LM lattice to form LaCo\(_x\)Mn\(_{1-x}\)/LM, as the cobalt-doped sample shows a
rhombohedral structure [11, 18]. It can be inferred that the weakened absorption structure of the S5 sample around 700 nm may be due to a decrease in the Co content of the composite with increasing LM.

For LM, all Mn ions are nominally in a trivalent state, but sometimes non-stoichiometric LaMnO$_3$ compounds with Mn$^{3+}$ and Mn$^{4+}$ ions present in the structure can be obtained when prepared in air [19]. The presence of non-stoichiometric LaMnO$_{3+\delta}$ in these composites can be confirmed by the rhombohedral structures (S3 and S5 samples), which is due to the concentration of Mn$^{4+}$ ions greater than 21% (LaMnO$_{3.105}$) [19]. Since the amount of Mn$^{3+}$ in LaMnO$_{3+\delta}$ is greater than Mn$^{4+}$, the concentration of Mn$^{3+}$ in the composite should always increase with increasing LM. The valence variation of Mn ions in the composite can be confirmed further by the XPS measurements. The fitting results for the Mn 2p$_{3/2}$ orbitals of the S0 and S5 samples are shown in figure 7, and the corresponding binding energy and peak intensity data are listed in table 2. It is seen that the valence states of the Mn ions have a highly mixed state of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. After compounding, replacing MCN with LM can produce more Mn$^{3+}$ and Mn$^{4+}$ ions, but results in a higher ratio of Mn$^{3+}$/Mn$^{4+}$ ions. Notably, the amount and proportion of Mn$^{3+}$/Mn$^{4+}$ ion pairs have a significantly effect on the physicochemical properties of such materials.

The results of photodegradation of TC under visible light irradiation are shown in figure 8. The blank experiment shows that the TC is difficult to degrade without light and catalyst. Compared with the blank experiment, photocatalysts with ingredient ratios of LM from 0 to 50% exhibit significant photocatalytic degradation changes after 150 min of visible light exposure, corresponding to 32.3%, 40.3%, 50.5% and 70.2% of TC removal, respectively. As expected, the S5 sample shows much higher photo-degradation activity than that of other composite MCN/LM samples as well as pure MCN, which is indicative of the notable degradation ability of this kind of composite material. The enhancement of photocatalytic activity in composite microparticles indicates that even when combined with pure LM that without photocatalytic activity [4], the synergistic effect between MCN and LM can be obtained through the chemical composite synthesis for better photocatalytic performance.

There are many factors related to the enhancement of TC degradation by composite MCN/LM microparticles. The optical absorption behavior is an important one that influences the photocatalytic activity of photocatalysts. Considering the fact that the introduction of LM can significantly increase the visible light absorption during the photocatalytic process, it can promote formation of more pairs of photo-induced electrons and holes upon illumination. On the other hand, the porous structure and smaller particles can provide extra surface area and more active reaction sites. These porous channels will not only make the active surface accessible to the TC molecules for photocatalytic degradation, but also facilitate the efficient transfer of

| Sample | Mn 2p$_{3/2}$ binding energy (eV) | Mn 2p$_{3/2}$ peak intensity (%) |
|--------|---------------------------------|---------------------------------|
| Mn$_{1.56}$Co$_{0.36}$Ni$_{0.48}$O$_4$ | Mn$^{4+}$ | Mn$^{3+}$ | Mn$^{2+}$ | Mn$^{4+}$ | Mn$^{3+}$ | Mn$^{2+}$ |
| 643.3 | 641.9 | 640.4 | 25.95 | 23.94 | 50.11 |
| (Mn$_{1.56}$Co$_{0.36}$Ni$_{0.48}$O$_4$)$_{0.5}$/(LaMnO$_3$)$_{0.5}$ | Mn$^{4+}$ | Mn$^{3+}$ | Mn$^{2+}$ | Mn$^{4+}$ | Mn$^{3+}$ | Mn$^{2+}$ |
| 643.0 | 641.5 | 640.2 | 28.33 | 38.36 | 33.31 |

Figure 7. XPS spectra of Mn 2p$_{3/2}$ of the (a) S0 and (b) S5 samples (the black curves correspond to the experimental spectra and the color curves to the fitting results).

Table 2. The binding energy and peak intensity of Mn 2p$_{3/2}$ obtained from the XPS spectra.
the photogenerated carriers in two different structures during photocatalysis [20]. In addition, the growth of LM significantly reduces the proportion of electrophilic Mn$^{4+}$ ions in the composite material, which is more favorable for redox in photocatalytic reactions [9], thus the degradation of TC under the visible light by the S5 sample is enhanced. This result is consistent with the previous study that the enhanced degradation of phenol by cryptomelane can be obtained by an increase in the ratio of Mn$^{3+}$/Mn$^{4+}$ ions [7]. However, the small polaron mechanism used to describe hopping conduction for MCN spinel oxides may lead to a more complicated photocatalytic mechanism, which needs further investigation.

4. Conclusions

In summary, Mn$_{1.56}$Co$_{0.96}$Ni$_{0.48}$O$_4$/LaMnO$_3$ composite microparticles were synthesized through the sol-gel method and their structural, optical and photocatalytic properties were characterized. Due to the synergic effect of MCN and LM, the increasing concentration of LM in the composite system induced changes in the structures and morphologies, correspondingly leading to the variations in the optical and photocatalytic properties. In particular, the S5 photocatalyst showed relatively high efficiency in the visible light degradation of TC, which was mainly due to the large surface area, unique porous micro morphology, strong optical absorption in the visible wavelength range and the increase in the relative content of Mn$^{3+}$ in composite systems. These results imply that through the continuous research and improvement, the spinel–perovskite composite MCN/LM material will become a promising visible light catalyst.

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