In situ synthesis of metal oxide nanostructures on flexible SiO$_2$ nanofibrous membrane for environmental application

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Abstract. Formaldehyde (HCHO), as a primary carcinogen, may cause severe health problems in light of its wide applications in the indoor decorations. Nowadays, catalytic oxidation proves to be the most promising method to remove HCHO. By virtue of its environment-friendly and cost-efficient advantages, manganese dioxide (MnO$_2$) has attracted enormous attention in HCHO removal. In this work, flexible silica dioxide (SiO$_2$) nanofibrous membrane (NFM) was fabricated by an electrospinning technique and MnO$_2$ nanoparticle was successfully loaded on SiO$_2$ (MnO$_2$@SiO$_2$) nanofibrous membranes (NFMs) through liquid phase synthesis. Scanning electron microscope (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) were used to characterize the material. MnO$_2$@SiO$_2$ NFMs exhibited great catalytic oxidation activity for HCHO. This research provides a simple and effective method for the development of transition metal oxides (TMOs) for HCHO degradation at room temperature and the composite MnO$_2$@SiO$_2$ material is expected to be used for air purification.

1. Introduction

Nowadays, air quality is closely related to human health because people stay indoors most of the time. HCHO belongs to the most typical and persistent indoor air pollutions currently and its main sources include building materials, furniture and decoration materials. Long-term exposure to HCHO can lead to a series of health problems, such as headaches, dizziness, allergic fatigue and irritation of eyes, throat, and nose, and even lead to leukemia$^{[1]}$. Presently, there are generally two methods for the removal of HCHO: the traditional physical adsorption and the catalytic oxidation method. Activated carbon adsorption and other traditional physical adsorption technologies transfer HCHO from the gas phase to the solid phase to absorb HCHO without completely degrading it. When the materials reach the maximum adsorption capacity, the adsorbent will leak from the materials into the air again, causing secondary pollution. However, the catalytic oxidation method can convert HCHO into carbon dioxide and water at ambient conditions, among all techniques, it is regarded as the most hopeful technology for removing HCHO. Catalytic oxidation catalysts are mainly divided into earth-abundant transition metal oxides (TMOs) catalysts and noble metal catalysts. However, the scarcity and high cost greatly restrict the widespread use of the noble metal-based catalysts. TMOs, especially MnO$_2$, have been extensively studied to remove HCHO, with regard to sufficient quantity and low cost$^{[2],[3]}$. Currently, most of the catalytic materials used are in the form of powder or granules, facing the problem of high cost of separation from the reaction medium and easy to cause secondary pollution. Nanofibers prepared by electrospinning are considered to be an ideal carrier due to their controllable, highly porous structure.
and large specific surface area. Binders are normally applied to combine the powder and substrates firmly, nevertheless, certain active sites will be shielded, resulting in reduced catalytic activity. Therefore, it’s very important to develop heterogenous catalysts that are highly active and easy to use.

2. Experimental

2.1. Fabrication of flexible SiO$_2$ NFM

Typically, the SiO$_2$ NFM was prepared by electrospinning and annealing procedures. First of all, the Si sol was obtained by blending TEOS and H$_2$O in a mass ratio of 1:1, then rapidly adding H$_3$PO$_4$ with vigorously stirring for 8 h. Meanwhile, PVA was respectively dissolved in H$_2$O and obtained 10 wt% PVA solution at 80°C. To obtain the last precursor solution, the as prepared Si sol and the 10% PVA solution were equally mixed and stirred for another 8 h. Afterwards, the nanofibers were deposited on the cylinder by a DXES-4 electrospinning device at the temperature of 24 ± 2 °C and relative humidity maintained of 42 ± 4%. Eventually, the inorganic-organic hybrid membrane was heated to 800 °C in air on a muffle resistance furnace with the temperature rising rate of 6°C min$^{-1}$, and then the flexible SiO$_2$ NFM was obtained.

2.2. Synthesis of flexible MnO$_2$@SiO$_2$ NFMs

The MnO$_2$@SiO$_2$ NFMs were fabricated through liquid phase synthesis through in-situ growing MnO$_2$ nanoparticles on the SiO$_2$ NFM, and the detailed synthesis pathway of MnO$_2$@SiO$_2$ NFMs was shown in Figure 1. Firstly, KMnO$_4$ and MnSO$_4$ were respectively dissolved in 100 ml deionized water and obtained 40 mmol/L KMnO$_4$ solution and 56 mmol/L MnSO$_4$ solution. After that, the SiO$_2$ NFM was first immersed into MnSO$_4$ solution for 3 minutes and then taken out for washing by deionized water, then the material was transferred to KMnO$_4$ solution for another 3 minutes, and then taken out for washing by deionized water again. After 5 synthesis cycles, the MnO$_2$@SiO$_2$ NFMs material was prepared by placing it in an oven at 80°C for 2 hours to dry.

$$2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

![Figure 1](image)

Figure 1 Schematic diagram of the process for synthesizing MnO$_2$@SiO$_2$ NFMs.

2.3. Characterization

SEM was applied to observe the morphologies and microstructures of the obtained material. The crystal structure of the resultant material was characterized by XRD. And the surface chemical states of the final materials were performed by XPS.

2.4. Catalytic activity evaluation

The removal efficiency of HCHO with MnO$_2$@SiO$_2$ NFMs was tested under static condition, which was carried out with the relative humidity at 68 ± 2% and the temperature at 24 ± 2 °C. The synthetic sample with a size of 20 × 20 cm$^2$ was placed in a 10 L plexiglass reactor to test its HCHO removal activity, typically. The initial concentration of HCHO in the reactor is about 200 ppm. And the concentration of
HCHO was detected by a BSQ-BCH20 handheld pump suction HCHO detector. Pure SiO2 NFM without MnO2 loading was used as a comparison group for HCHO removal test in the same way. The conversion rate of HCHO was calculated as follows:

\[ \text{HCHO concentration(\%)} = \frac{C_t}{C_0} \times 100\% \]  

(1)

\( C_0 \) is the original HCHO concentration, and \( C_t \) means the concentration at different times after the start of experiment.

3. Results and discussion

3.1. Characterizations of MnO2@SiO2 NFMs

The morphology evolution of SiO2 NFM and MnO2@SiO2 NFMs are shown by SEM in Figure 2 (a). Initially, the fibers of SiO2 NFM is smooth and exhibited ultra-large ratios and the average diameter is ~250nm. Figure 2 (b) shows that after 5 cycles, MnO2 was grown on the SiO2 NFM.

![Figure 2](image_url)

Figure 2 (a) SEM images of SiO2 NFM, (b) SEM images of MnO2@SiO2 NFMs. The inset are the corresponding low-resolution images.

XRD patterns of SiO2 NFM and MnO2@SiO2 NFMs was shown in Figure 3 (a). Comparing with XRD patterns of SiO2 NFM, new weak diffraction peaks at 37.1° and 66.8° assigned to 100 facet and 110 facet which belong to MnO2 appeared on MnO2@SiO2 NFMs. It is shown that MnO2 is poorly crystallized.

Subsequently, XPS was used to characterize the surface chemical composition and the valence states of surface elements. XPS survey spectrum of MnO2@SiO2 NFMs was displayed in Figure 3 (b). Figure 3 (c) revealed the Mn2p XPS spectra shows two main peaks at 641.7 and 653.5 eV, which attributing to the Mn2p3/2 and Mn2p1/2.\(^{[5]}\) The Mn 2p spectra of the sample which were shown in Figure 3 (c) were curve-fitted by two peaks: the first peak at 641.5 eV corresponded to Mn\(^{3+}\), the second at 642.8 eV assigned to Mn\(^{4+}\).\(^{[6]}\) The content of Mn\(^{3+}\) is more than that of Mn\(^{4+}\), which is consistent with the result of XRD. The result of XRD shows that the crystallinity is poor, which makes the material more vacancies, and finally leads to the lower valence of Mn. The O 1s spectra of MnO2@SiO2 were deconvoluted into three peaks at 529.2, 531.2 and 532.5 eV, which were assigned to the lattice oxygen (O\(_{\text{lat}}\)), oxygen vacancies (O\(_{\text{vs}}\)), and adsorbed oxygen (O\(_{\text{ads}}\)).\(^{[7]}\) According to the reports, the O\(_{\text{vs}}\) plays an significant role in decomposition of HCHO at room temperature.\(^{[8]}\)
3.2. Activity for HCHO decomposition

The catalytic efficiency of the samples was assessed at room temperature. As can be seen from Figure 4, SiO$_2$ NFM almost shows no detectable activity towards removing HCHO, which means that there is no chemical reaction with HCHO molecule or physical adsorption on the pure SiO$_2$ NFM. For MnO$_2$@SiO$_2$ NFMs, the concentration of HCHO declined dramatically in the first 0.5 h, and then tends to be gentle. The removal efficiency of HCHO reached 90.5% at 2h.

Figure 3  (a) XRD patterns of SiO$_2$ NFM and MnO$_2$@SiO$_2$ NFMs. XPS spectra of MnO$_2$@SiO$_2$ NFMs: (b) survey spectra, (c) Mn 2p spectra, and (d) O 1s spectra.

Figure 4  Comparison of SiO$_2$ NFM and MnO$_2$@SiO$_2$ NFMs for removing HCHO.
4. Conclusions
In conclusion, flexible SiO$_2$ NFM was fabricated by an electrospinning method and MnO$_2$ nanoparticle was successfully loaded on SiO$_2$ NFM through liquid phase synthesis and MnO$_2$@SiO$_2$ NFMs were obtained. SEM, XRD, and XPS analyses proved that the MnO$_2$ which was loaded on SiO$_2$ NFM is poorly crystallized. The as-prepared MnO$_2$@SiO$_2$ NFMs material exhibited high activity to decompose HCHO at room temperature. Therefore, the prepared MnO$_2$@SiO$_2$ NFMs have excellent potential application in decomposing HCHO with the following advantages such as simple preparation, good flexibility, high activity, low cost and reliable safety at room temperature.

Acknowledgments
This work was financially supported by the National Key R&D Program-Science and Technology Winter Olympics Key Special Project (No. 2019YFF0302105) and the Natural Science Foundation of Shanghai (No. 19ZR1401100).

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