Nano-MgO prepared via templating on biodegradable filter paper

1 | INTRODUCTION

Nano-MgO has attracted widespread attention because of its potential technical applications in the fields of catalysis [1], battery [2], hazardous waste treatment [3], antimicrobial agents [4] and so on. Up to now, MgO nanomaterials with different morphologies have been prepared by several methods, including chemical deposition method [5], combustion method [6], solid phase method [7], spray pyrolysis method [8], hydrothermal method [9] etc. In recent years, biological template method has been widely used in the preparation of nanomaterials due to its advantages such as low-toxicity, low-energy, and safety [10] compared with other preparation methods.

Many nano-materials were successfully fabricated using various biological templates such as plant fibres [11], tissues [12] and microorganisms [13]. Filter paper is a biological template that can be used to make a variety of inorganic nanomaterials [14], and is both biodegradable and a common filtering tool in the laboratory. It is composed of micron-level cotton fibres and has holes with different pore sizes. This structure is important for controlling the shape of the materials being fabricated. From this viewpoint, the filter paper template method has become one of the key technologies for preparing multi-hole, high surface area materials, which has attracted the attention of scientific researchers. For example, Zhang Qingshuang et al. [15] demonstrated the successful synthesis of photo-catalytic nano-TiO2 using filter paper. Zhou Shuaikun et al. [16] used quantitative filter paper as a template to prepare nano-SnO2 materials by impregnation and calcination, and applied them to dye-sensitized solar cells. Huang Baojun et al. [17] successfully prepared micro-nano Fe2O3 with biological morphology by using FeCl3 as the starting material, quantitative filter paper as a template through impregnation and calcination. Chen Feng et al. [18] used filter paper as a template to synthesize CeO2 fibres with microscopic morphology and uniform distribution of nanoscale pores. However, until now, the research on the preparation of nano-MgO using qualitative filter paper as template is rarely reported. In this work, we propose a method of synthesizing nano-MgO by filter paper templating.

2 | EXPERIMENTAL SECTION

2.1 | Materials and chemicals

Mg(CH3COO)2·4H2O (AR), ethyl alcohol absolute (AR), quick and medium qualitative filter papers (Φ7 cm), methylene blue (AR).

2.2 | Experimental method

The quick and medium qualitative filter papers were cut into small squares (1 × 1 cm), washed two or three times with deionized water, and then dried at 80 °C and cooled down to room temperature. About 4 g filter paper was immersed in 100 mL of Mg(CH3COO)2·4H2O ethanol solution and allowed to stand for 12 h. Then, the immersion liquid was discarded and the soaked filter paper was dried at 80 °C for 2 h. Finally, the filter paper was heated from room temperature to 650 °C in a muffle furnace and held for 2 h to obtain a white product.

2.3 | Characterization methods

X-ray diffraction (XRD, BRUKER D8 ADVANCE): operating under a voltage of 40.0 KV and a current of 40.0 mA with Cu-Kα radiation, the recording range of 2θ was 20–80°. FSEM (Carl Zeiss AG): the acceleration voltage was 10–12 KV and the magnification was 8000–200,000. Energy dispersive X-ray analysis (EDS, Carl Zeiss AG) combination with scanning electron microscope (SEM). Transmission electron microscopy (TEM, JEM 2100F): the acceleration voltage was 200 kV and the magnification was 1,500,000. Thermo gravimetric analysis (TG, NETZSCH STA F449): operating at the high purity N2 atmosphere, from 30 to 650 °C with a heating rate of 10 °C/min. Fourier transform infrared spectroscopy (FTIR, PerkinElmer): in the wavenumber range of 4000–600 cm⁻¹. Brunner-Emmet-Teller (BET, ASAP 2020 V4.03 H): sample pretreatment for 2 h at 300 °C.
FIGURE 1  Schematic diagrams of preparing MgO with Mg(CH₃COO)₂⋅4H₂O ethanol solution. (a) Without template, (b) addition of quick qualitative filter paper template, (c) addition of medium qualitative filter paper template

FIGURE 2  (a) SEM images of quick qualitative filter paper templates, (b) SEM image of medium qualitative filter paper templates

3  RESULTS AND DISCUSSIONS

3.1  Characterizations of MgO prepared with different filter paper templates

Two different types of filter paper templates, quick (Q) and medium (M) qualitative filter paper templates, were selected for these experiments. As can be seen from the SEM images (Figure 2(a,b)), both filter papers were composed of a 3D interwoven fibre network with holes on the surface, and their pore sizes are different. Before the experiment, TG tests were first performed on precursor Mg(CH₃COO)₂⋅4H₂O and filter papers. Since the trend of TG curves observed for quick and medium qualitative filter papers were almost the same, here only one TG curve is given, and it is represented by the name of the filter paper. Both curves were measured in an N₂ atmosphere from 30 to 600 °C at a heating rate of 10 °C/min. It can be seen that Mg(CH₃COO)₂⋅4H₂O experienced two weight loss (Figure 3). The first loss in the range of 30–100 °C was attributed to the loss of free water and bound water of Mg(CH₃COO)₂⋅4H₂O, which was about 40%. The second loss between 100 and 350°C was caused by the gradual decomposition of Mg(CH₃COO)₂ into MgO. As the temperature exceeded 500 °C, the mass did not further decrease, which indicates that the precursor Mg(CH₃COO)₂⋅4H₂O completely decomposed into MgO. For filter paper, the weight loss in the temperature range from 30 to 100 °C was not obvious, which may be caused by the evaporation of absorbed CO₂ and H₂O [19]. From 100 to 500 °C, the filter paper template gradually decomposed into CO₂ and H₂O. Above 500 °C, most of the filter paper templates were decomposed. Therefore, it can be determined that the temperature of the calcination experiment should be between 500 and 650 °C. It was found in the experiment that when the precursor solution was used, the removal temperature of the template shall be increased to 650 °C, which was due to the temperature difference caused by the template adsorbing the precursor solution.

XRD results (Figure 4) show that the position and strength of all the diffraction peaks of the products are consistent with that of MgO (PDF#45-0946), whether it was prepared by rapid or medium qualitative filter paper templates, and there are no peaks of other impurities. SEM images (Figure 1) display that
compared to the product prepared without a filter paper template, the product prepared by the filter paper template was well dispersed and uniform in particle size. However, the particle size of the product, MgO(M), prepared by medium qualitative filter paper template was significantly smaller than that of the product, MgO(Q), prepared by quick qualitative filter paper template, which is directly measured through the SEM images in Figure 1(b,c) using Nano Measurer. Therefore, the medium qualitative filter paper was selected as the template for nano-MgO preparation. FTIR (Figure 5) results reveal that a strong and wide absorption occurred within the range of 500–630 cm$^{-1}$, indicating that the product has strong infrared absorption capacity. The stretching vibration of Mg─O bond at 623.09 cm$^{-1}$ [20] confirmed the formation of nano-MgO, and agreed well with the XRD results. Moreover, no other characteristic absorption peaks of organic groups were observed, which proved that the filter paper template had been completely decomposed and pure nano-MgO had been formed under this calcination condition.

The influence of Mg(CH$_3$COO)$_2$•4H$_2$O concentrations on the product was investigated. The XRD patterns of the synthesized MgO(M) from different concentrations of Mg(CH$_3$COO)$_2$•4H$_2$O are shown in Figure 6. All diffraction peaks of MgO(M) were consistent with the JCPDS Card #45-0946, which can be indexed as a cubic phase of MgO with space group Fm3m (225). The peaks at 2θ values of 36.9, 42.8, 62.2, 74.6 and 78.6° correspond to the crystal planes of (111), (200), (220), (311), (222) of crystalline MgO, respectively. XRD pattern of 0.005 mol/L Mg(CH$_3$COO)$_2$•4H$_2$O showed a low intensity of the diffraction peaks of MgO, providing proof of poor crystallinity of MgO. When the concentration of the impregnating solution was increased to 0.01 mol/L, the intensity of the peaks increased sharply, indicating good crystallinity of MgO. With further increase of the concentration of impregnating solution, the diffraction peaks did not widen and the intensity did not change much, and no other heterophase diffraction peaks were observed. As evidenced by FTIR spectrum (Figure 5), there is no C=C vibration absorption peak at 1634 cm$^{-1}$, which proves that the template was completely removed from the product. EDS result (Figure 7) shows that the atomic ratio of MgO was 1:1. Here, the carbon came from the conductive adhesive used for analysis, and Pt was caused by sample’s spraying in sample test [21]. These results mean that high purity MgO can
Figure 8 SEM photos of MgO(M) prepared from (a,b) 0.005 mol/L, (c,d) 0.01 mol/L Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution.

Figure 9 SEM photos of MgO(M) prepared from (a,b) 0.02 mol/L, (c,d) 0.03 mol/L Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution.

Figure 10 SEM photos of MgO(M) prepared from (a,b) 0.04 mol/L, (c,d) 0.05 mol/L Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution.

Figure 11 TEM photos of MgO(M) prepared from 0.03 mol/L Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution. (a) Scale bar = 50 nm, (b) scale bar = 500 nm, (c) scale bar = 5 nm and (d) SAED pattern.

Figures 8–10 give the surface morphologies of MgO(M). The local magnification of Figure 8(b) shows that the particles exhibited a ‘loose’ morphology and the average particle size was calculated to be 20 nm by measuring Nano Measurer. It is interesting to find that the morphology of MgO fibres gradually formed when the concentration of Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution increased from 0.01 (Figure 8(c,d)) to 0.03 mol/L (Figure 9). The surfaces of MgO fibres (Figure 9(c)) were smooth, with an average width of 100 nm, indicating the micro-morphology of filter paper can be reproduced completely. Each fibre was made up of a large number of interconnected MgO nano-particles about 20 nm in size. When the concentration of Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution increased from 0.04 to 0.05 mol/L (Figure 10), the fibre structure was broken, the surface of the fibre was rough, and grain adhesion and blurred three-dimensional structure can be observed. This may be due to the increased concentration of Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution and the excessive amount of MgO particles adhering to the fibre, which causes the fibre structure to be ‘crushed’. In summary, when the concentration of precursor solution was 0.03 mol/L, MgO(M) fibres could replicate the microstructure of the media qualitative filter paper very successfully.

It can be seen from Figure 11(a) that the particle size of MgO(M) is 20 nm. Figure 11(b) shows the TEM image of MgO(M), where the obvious pores are confirmed by the obvious
electron density difference. From Figure 11(c), the lattice fringe spacing of MgO(M) was calculated to be 0.20 nm, which is the same as the MgO crystal plane spacing of (200). According to the analysis of Gatan Digital Micrograph software, the diffraction rings correspond to the (200) and (220) crystal faces of MgO, and the MgO are polycrystalline according to the diffraction pattern (Figure 11(d)). There is no impure phase, which is consistent with the results of XRD. This verifies that the filter paper template has been completely removed during the calcination process.

3.3 Products particle size calculation

According to the XRD results (Figure 6), the particle size of MgO(M) prepared from 0.03 mol/L Mg(CH$_3$COO)$_2$·4H$_2$O ethanol solution calculated by Scherrer equation (Equation (1)) was about 13 nm. However, SEM (Figure 9(d)) shows that the average particle size was about 20 nm. The inconsistency between the two results was due to the size effects. It is known that when the particle size decreases to 25 nm, it is difficult to calculate the exact particle size by using the Scherrer equation, which also indicates that the product is polycrystalline [22]. Therefore, the particle size analysis was here based on direct SEM and TEM observation, using Nano Measurer.

$$D = \frac{x\lambda}{\beta \cos \theta}$$

(1)

where ($\theta$) is the deadening of the peak at a particular diffraction angle; ($D$) is the crystalline domain size; ($\beta$) is the width of the peak at half of its height; ($\lambda$) is a consistent; ($k$) is typically considered to be 0.9 [23].

3.4 Nitrogen adsorption-desorption test of product

As shown in Figure 12, the hysteresis loop at high relative pressure indicates the presence of pores in the product of MgO(M). These pores are caused by the slit left after the template was removed and the gas escape during the calcination process in the preparation of MgO(M). This is consistent with the TEM results. The average pore diameter of the product was 13 nm. The specific surface area (SSA) was 68.28 m$^2$/g. This meets the requirements of the general catalyst carrier for the surface area of nano-materials.

3.5 Growth mechanism

Biological templating is a preparation method operating on the premise that some inorganic non-metals have good compatibility with natural biological templates. There are a large number of hydroxyl groups on the surface of qualitative filter paper fibres, which provide a suitable positioning point for metal oxide pre-

3.6 Photocatalytic activity

The photocatalytic activity of MgO was carried out by its photocatalytic degradation of methylene blue solution. The degradation rate of methylene blue at different times was estimated using Equation (2).

$$D\% = \frac{A_0 - A_t}{A_0} \times 100\%$$

(2)

where $A_0$ and $A_t$ are the absorbance of methylene blue solution measured by a UV-visible spectrophotometer at 663 nm before and after degradation, respectively; $D\%$ is the degradation rate. Figure 14 shows the effect of MgO(M) prepared by template and MgO prepared without template on the degradation rate of methylene blue. Under the same experimental conditions, the degradation rates of methylene blue of MgO(M) reached the constant after 180 min of sunlight, which was 50–57.4% higher than that of MgO prepared without template. This indicates that nano-MgO prepared by medium qualitative filter paper template has higher catalytic activity.
This is attributed to the higher specific surface area and pore structure of MgO(M), which increases the contact probability between MgO and organic molecules, thus improving the photocatalytic activity.

4 | CONCLUSION

In summary, the medium qualitative filter paper template was successfully used to fabricate nano-MgO, and the micro morphology of the filter paper was successfully replicated. The MgO fibres were approximately 100 nm in width and composed of small particles with an average particle size of 20 nm. Its SSA was 68.28 m²/g. The prepared nano-MgO was used in the degradation reaction of methylene blue, and it was found that its catalytic effect was stronger than that prepared without a template. This provided a feasible scheme for the green preparation of nano-MgO and could also be used for the preparation of other nanomaterials.

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