

Synthesis of MnO₂ nanowires on cordierite honeycomb ceramics by in-situ deposition method

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Abstract: The thin layer of MnO₂ nanowires with a three-dimensional (3D) porous network structure is uniformly supported on the surface of cordierite honeycomb ceramic (CHC) monolithic substrate by the in-situ deposition method. A series of characterizations of scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and ZETA potentiometric analyzer were used to determine the optimal preparation conditions. Firstly, the MnO₂ prepared in acid medium reveals the most suitable nanowire morphology and crystal structure. Secondly, compared to alumina sol adhesive, the nanocellulose sol adhesive is more favorable to uniformly disperse MnO₂ nanowires on CHC surface, due to the strong electrostatic repulsion between nanocellulose sol and MnO₂ nanowire. Thirdly, a medium MnO₂ adding content in the precipitating solution is more beneficial to form a thin 3D network structure with appropriate pore size distribution on CHC substrate, which allows gas feedstocks or products to freely pass through and fully contact with the active component of MnO₂ nanowires.

Introduction

Manganese oxide (MnO₂) is constructed by the basic unit of [MnO₆], which can form many nanostructures with different morphologies, such as wires, sheets and rods, and with different crystal structures, such as α -, β -, δ - or γ - MnO₂, just by controlling the synthesis conditions in hydrothermal method [1]. Meanwhile, because MnO₂ samples with different nanostructures always exhibit lots of special and excellent physical and chemical properties, they have been used in the fields of water treatment[2], catalysis[3] and supercapacitor[4]. But nowadays in industrial applications, the MnO₂ powder is usually easy to lose, which limits its extensive application.

Cordierite honeycomb ceramic (CHC) has many advantages of good thermal shock, low air resistance, high transforming efficiency and low cost, which makes it be widely used as monolithic supporters or carriers in the field of environmental protection [5, 6]. Moreover, the CHC as substrate has been used to load the active components, such as noble metals or transition metal oxides, in order to prevent their loss in the removal reaction of volatile organic compounds[7]. Herein, the α -MnO₂ nanowires were firstly synthesized, and then loaded on the surface of CHC to form a three dimensional (3D) porous network structure by an in-situ deposition method.

Experimental

MnO₂ nanowires were synthesized by hydrothermal method using KMnO₄ as main precursor mixed with other precursors in different media: ① NaOH and ethanol in base medium; ② MnCl₂·4H₂O in neutral medium; ③ CH₃COOH (HAc) in acid medium. The precursor mixtures were transferred to a 50ml Teflon-lined stainless steel autoclave and maintained at 140°C for 24 h. Finally the collected precipitates were dried at 60°C for 12h after washing by water and ethanol.

CHC substrate with the shape of 4×4×20mm were used as monolithic substrate. Firstly, the as-synthesized MnO₂ nanowires were mixed with different adhesives and DI water to form precipitating solution. Then the CHC substrate was impregnated into the precipitating solution under

stirring. After 3h, the obtained products (denoted as MnO_2/CHC) were washed with DI water and dried at 80°C overnight. The whole schematic of the MnO_2/CHC preparation by in-situ deposition method was shown in Fig.1.

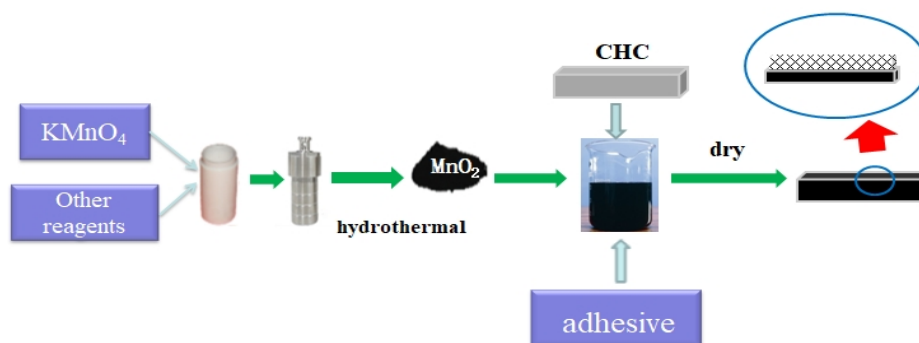


Fig.1 Schematic illustration of MnO_2/CHC prepared by in-situ deposition method.

The samples were analyzed by scanning electron microscopy (SEM, JSM-7001F) and X-ray powder diffraction (XRD, D8ADVANCE) operated with $\text{Cu K}\alpha$ radiation. The values of zeta potential were obtained by Zeta PALS/90plus analyzer.

Results and discussion

From the SEM images (Fig. 2a-c), it is shown that MnO_2 nanowires in different media can be fabricated into different shapes. In base medium, some MnO_2 nanowires tended to stick together to form a slice shape (in Fig. 2a). In neutral medium, some MnO_2 nanowires got together at one end to form the shape like a bunch of flowers (Fig. 2b). Only in acid medium, MnO_2 nanowires can exist one by one without obvious collaboration and congestion (Fig. 2c). Further from XRD pattern in Fig. 2d, all the diffraction peaks of MnO_2 sample prepared in acid medium can be indexed to $\alpha\text{-MnO}_2$ phase (JCPDS 44-0141).

As shown in Fig. 3a and b, MnO_2 nanowires can be uniformly distributed and form a porous network structure on the surface of CHC substrate while using nanocellulose sol as adhesive. However, when using alumina sol as adhesive, MnO_2 nanowires tended to stick together shoulder to shoulder on the CHC surface in Fig. 3d. For further study, zeta potential values were revealed in Fig. 3e. It can be found that the zeta potential values of MnO_2 nanowires, nanocellulose sol and alumina sol were -19.94 , -16.85 and $+19.69\text{mV}$ respectively. That means alumina sol and MnO_2 nanowires are easy to be attracted by electrostatic attraction, which is not favorable to disperse nanowires uniformly on the CHC. In contrast, there is electrostatic repulsion between nanocellulose sol and MnO_2 , which is beneficial to scatter MnO_2 nanowires evenly on the CHC surface. In a word, the results suggest that using nanocellulose sol as adhesive is more suitable to form a 3D porous network structure of MnO_2 on the CHC substrate surface.

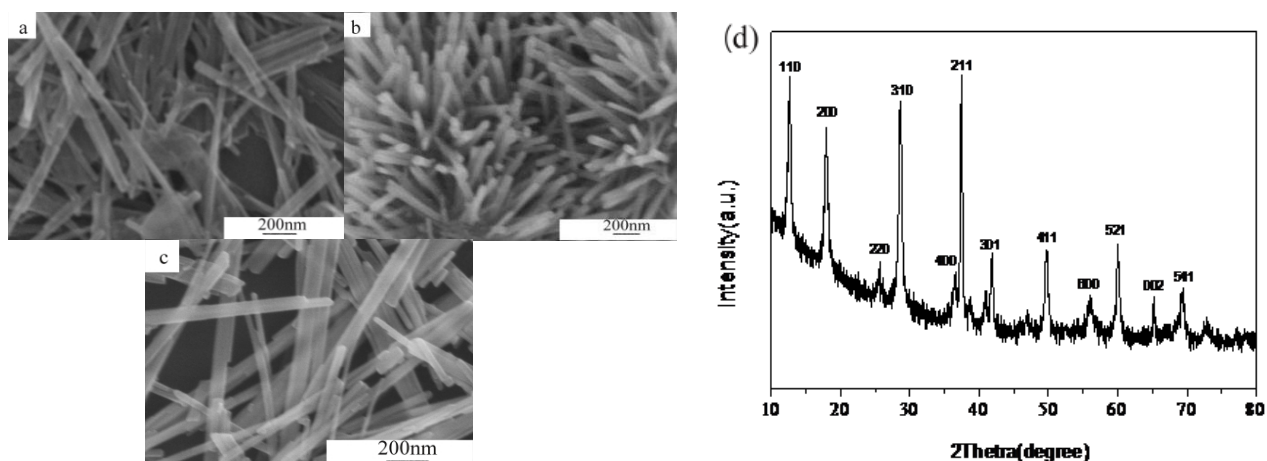


Fig. 2 SEM images of MnO_2 nanowires synthesized by hydrothermal method in different media of (a) base, (b) neutral, and (c) acid medium; (d) XRD pattern of MnO_2 nanowires synthesized in acid medium by hydrothermal method.

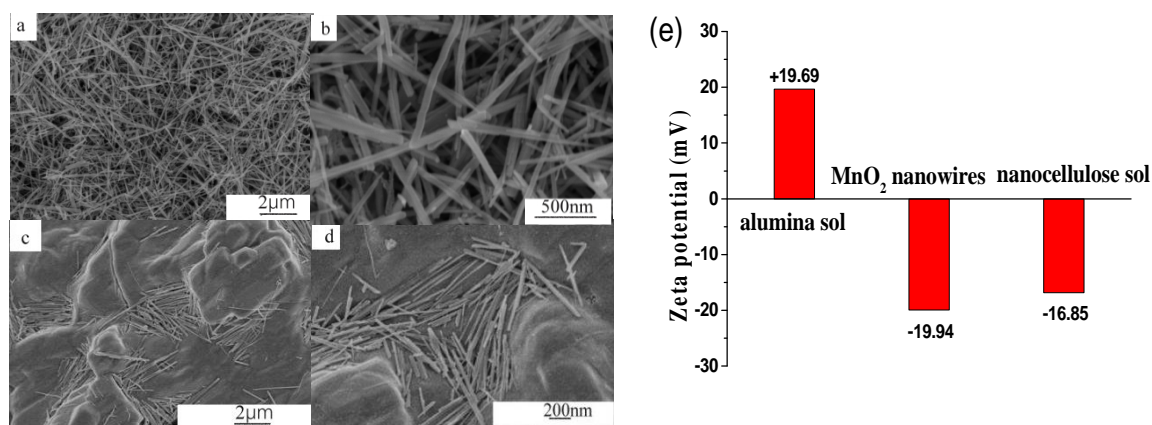


Fig. 3 SEM images of MnO_2/CHC samples using different adhesives of (a,b) nanocellulose sol and (c,d) alumina sol; (e) Zeta potential values for pristine MnO_2 nanowires, nanocellulose sol and alumina sol.

The SEM images of MnO_2/CHC samples prepared from different MnO_2 adding contents by using cellulose sol as adhesive, are shown in Fig. 4. For the MnO_2/CHC prepared from low MnO_2 adding content of 0.12 wt.%, MnO_2 nanowires cannot fully cover the whole CHC surface. While increasing the MnO_2 adding content to 0.18 wt.% to prepare MnO_2/CHC , it can be seen that MnO_2 nanowires completely covered the CHC surface and formed a thin 3D network structure with appropriate pore size distribution (in Fig. 4b). Such a thin 3D porous network structure might be beneficial to allow gas feedstocks or products to freely pass in and out, so as to fully contact with the active component of MnO_2 nanowires. But further increasing to the adding content of 0.26 wt.% to prepare MnO_2/CHC , as shown in Fig. 4c, the 3D network of MnO_2 nanowires on the CHC surface was too thick, which causes that the pore size in this network is too narrow to let macromolecular gas get through freely. As a result, in order to make MnO_2 nanowires form a thin 3D porous network on CHC substrate, the most suitable adding content of MnO_2 component is 0.18 wt.%.

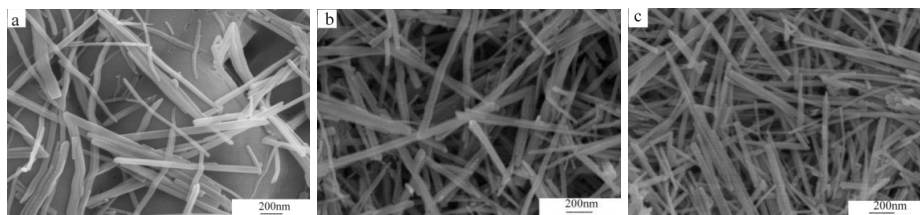


Fig. 4 SEM images of MnO_2/CHC samples prepared from different MnO_2 adding contents of (a) 0.12 wt.%, (b) 0.18 wt.%, and (c) 0.26 wt.%

Conclusions

A thin 3D MnO_2 porous network structure of MnO_2 is supported on the surface of CHC substrate uniformly by the in-situ deposition method. The result suggests that MnO_2 prepared in acid medium reveals the most suitable nanowire morphology and crystal structure. As the result of the strong electrostatic repulsion between nanocellulose sol and MnO_2 nanowire, the nanocellulose sol adhesive is more beneficial to uniformly distribute MnO_2 and form porous network structure on CHC surface in comparison with alumina sol adhesive. To form pore size in MnO_2 network suitable for macromolecular gas get through freely, the optimal adding content of MnO_2 component is 0.18 wt.%. The results indicate that as-prepared MnO_2/CHC might have the potential applications in environmental protection, especially air purification.

Acknowledgements

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