

Manganese Oxide/Mesoporous Carbon Spherical Composite: Study on Its Enhanced Catalytic and Electrochemical Performance

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Abstract-Manganese oxide/mesoporous carbon (MnO_2/MCs) spherical composites were prepared by hydrothermal method. The resorcinol and potassium permanganate were used as carbon source and manganese source, respectively. The morphology and pore character of the carbon materials were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and nitrogen adsorption-desorption. The measurements show the sample with the corresponding spherical morphology and mesoporous structure. By controlling the concentration of potassium permanganate, various amount of manganese in carbon/manganese oxide can be obtained. The composite was employed as the support of Au catalyst for CO oxidation. Different amount of gold has been deposited on the as-synthesized carbon sphere/manganese oxide, and the activity and stability of Au catalyst after sintered at 300°C has been tested. The 8%Au/ MnO_2/MCs -46 catalyst had obvious deactivation on stream after 65h reaction time at the reaction temperature of 185°C . Meanwhile, the sample further used as the supercapacitor electrode materials for electrochemical performance test. The specific capacitance of the MnO_2/MCs -30 electrode is as high as 275 F g^{-1} at 0.5 A g^{-1} .

Keywords-sphere; template; manganese oxide; CO oxidation; electrochemistry;

I. INTRODUCTION

In the past decade, the global warming and fossil energy sharply reduced has led to lots of efforts in developing low cost, safe and environmentally friendly energy sources[1-4]. Supercapacitors has received considerable attention, owing to their high power density, long cycle life and fast charging-discharging rates[5-7]. Carbon-based materials, including conducting polymers[8,9] and transition metal oxides have been widely used as electrode materials for supercapacitors. MnO_2 also has been study on supercapacitor and CO

oxidation. Owing to its poor electrical conductivity, MnO_2 was incorporated into conductive matrixes(such as carbon material) to overcome drawback[10,11].

In this paper, we report MnO_2/MC spherical composite through a facile method to synthesis. Using the sample as the support of catalyst which is used for CO oxidation and using nickel foam with deposited sample as the working electrode which is used for Electrochemical measurements.

II. EXPERIMENTAL SECTION

2.1 Materials

Ammonia aqueous, ethanol, potassium permanganate, hexadecyl trimethylammoniumchloride (CTAC), tetraethyl orthosilicate (TEOS), were purchased from shanghai Titan Co. All chemicals were used as received without any further purification.

2.2 Synthesis

Synthesis of manganese oxide/mesoporous carbon spherical composite: For the typical synthesis of the mesoporous carbon spheres, CTAC (0.25g) and ammonia aqueous solution (NH_4OH , 0.4g, 25wt%) were first dissolved in a mixture of ethanol (6g) and water (20g) which were stirred for 30min. Subsequently resorcinol (0.2g) and tetraethyl orthosilicate (TEOS) (0.4g) and formaldehyde solution (0.44g) were added to the reaction solution and stirred for 24 h at 30°C . The solid product was recovered by centrifugation and air-dried at 80°C over night. The carbonization was carried out in a tubular furnace under N_2 atmosphere at 300°C for 2h and at 600°C with a ramp rate of 1°C min^{-1} to make sure carbon spheres precursors completely converted subsequently. The carbon spheres and KMnO_4 (30mg, 50mg, 70mg, 100mg) was further dispersed in water and stirred for 2h.

The mixture was placed in a 40ml Teflon-sealed autoclave and maintained at 180°C for 40min. The product were washed with deionized water and ethanol, followed by drying at 60°C for 12h. The silica template was removed by 2M NaOH solution at 80°C for 24 h. Then samples were washed with deionized water and ethanol, followed by drying at 60°C for 12 h. The content of MnO₂ in the three MnO₂/MCs composites was estimated to be 25%, 30%, 35% and 46% by TG test, respectively. And the composites were then denoted as MnO₂/MCs-25, MnO₂/MCs-30, MnO₂/MCs-35 and MnO₂/MCs-46, respectively.

To load gold nanoparticles, 0.5g of MnO₂/MCs-46 was dissolved into 30g of water and 10ml, 50ml and 80ml of 0.243mmol/L HAuCl₄·3H₂O was also dropped into the solution. The pH value was adjusted to 7 using 1.0 M NaOH, and the solution was heated to 75°C. The mixture was stirred for 2h, after which the precipitates were separated by centrifugation and washed four times with water. The product was dried at 40°C and was calcined at 300°C for 2h to obtain the as-synthesized catalyst. The catalyst were then denoted as 1%Au/MnO₂/MCs-46, 5%MnO₂/MCs-46, 8%MnO₂/MCs-46, respectively.

2.3 Electrochemical Measurements

Electrochemical measurements were conducted on a computer-controlled potentiostat (CHI 660E, CH Instrument, USA) with a three-electrode electrochemical cell. The standard three-electrode electrochemical cell was fabricated using nickel foam with deposited sample as the working electrode, platinum wire as the counter electrode, and Hg/HgO as the reference electrode. The fabrication of working electrode, a mixture containing active materials (80wt%), acetylene black (10wt%), and polytetrafluoroethylene (PTFE; 10 wt%) were well mixed to form a homogeneous slurry. The slurry was then pressed onto a nickel foam with an area of 1cm² and followed by drying at 120°C for 10h. The mass loading of the active material was about 5mg. All the electrochemical measurements were carried out at 25°C using a 6M KOH electrolyte. The potentials for electrochemical measurements are reported relative to a Hg/HgO reference electrode and the potential window for cycling was confined between -1.1V and -0.1V. The gravimetric specific capacitance C_g was calculated according to the following equation using the discharge portion of the charge–discharge curves:

$$C_g = I \Delta t / m \Delta V = I / m K \quad (1)$$

where I, Δt, ΔV, m, and K are the applied current, discharge time, voltage change, the mass of active material, and the slope of the discharge curve, respectively.

2.4 Characterization

Scanning electron microscopy (SEM) images were taken by a Hitachi S3400 scanning electron microscope. X-ray scattering (XRD) measurements were taken on a Panalytical X'Pert Diffractometer using Cu Kα radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 system. Before measurements, the samples were degassed in a vacuum at 200°C for at least 10h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size

distributions were derived from the adsorption branches of isotherms, and the total pore volumes (V) were estimated from the adsorbed amount at a relative pressure P/P₀ of 0.995.

III. RESULTS AND DISCUSSION

The SEM image of mesoporous carbon spheres (Figure 1a.) was found that the morphology is spherical and partical size is about 300nm. Figure 1b shows the morphology of MnO₂/MC spherical composite is also spherical and partical size is about 500nm. MnO₂/MC spherical composite with bigger partical size illustrates MnO₂ doped on the surface of MCs.

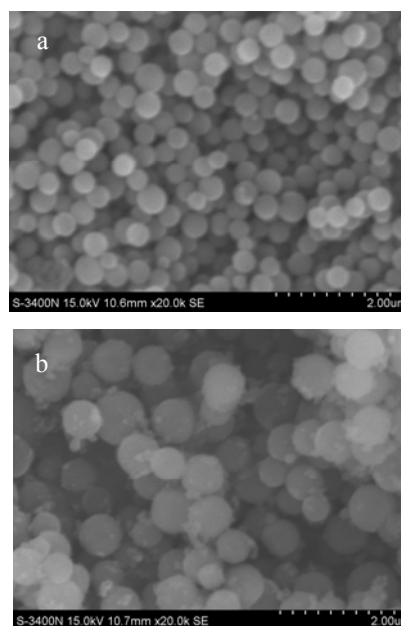


Figure 1. SEM images of (a) mesoporous carbon sphere (MCs) without MnO₂ and (b) MnO₂/mesoporous carbon spherical composite (MnO₂/MCs).

Wide angle XRD patterns of MnO₂/MCs and Au/MnO₂/MCs are shown in Figure 2. Seen from the Figure 2, there are typical diffraction peak of MnO₂ (2θ = 12.38°, 24.90°, 35.61°, 36.97°, 41.90°, JCPDS 43-1456) corresponding to its Birnessite structure. Au/MnO₂/MC spherical composite has typical diffraction peak of Au (2θ = 38.19°, 44.45°, 64.59°, 77.69°, JCPDS 04-0784) and the diffraction peak of Mn_xO which obtained by MnO₂ and MCs taking place.

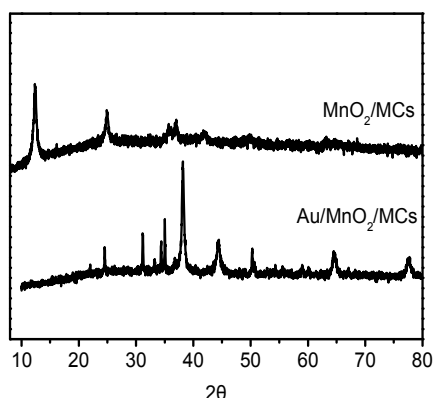


Figure 2. XRD pattern of MnO_2/C and $\text{Au}/\text{MnO}_2/\text{C}$

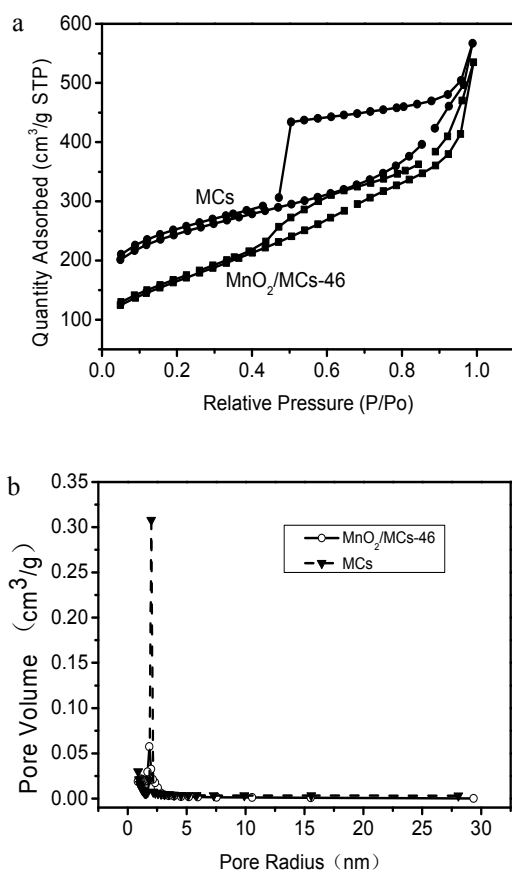


Figure 3. Nitrogen adsorption-desorption isotherms of (a) $\text{MnO}_2/\text{MCs-46}$ and MCs and BJH pore size distribution of (b) $\text{MnO}_2/\text{MCs-46}$ and MCs

Figure 3 gives the N_2 sorption isotherms (Figure 3a) and BJH pore size distribution plots (Figure 3b) of $\text{MnO}_2/\text{MCs-46}$ and MCs, the isotherms exhibit the same type IV adsorption behavior. The interpolation of pore size distribution reveals a uniform pore size. The surface area of MCs and $\text{MnO}_2/\text{MCs-46}$ is $806\text{m}^2\text{g}^{-1}$ and $588\text{m}^2\text{g}^{-1}$, pore volume is $0.877\text{cm}^3\text{g}^{-1}$ and $0.827\text{cm}^3\text{g}^{-1}$ from the BET method and BJH method. The BJH pore size of MCs and $\text{MnO}_2/\text{MCs-46}$ is 4.3nm and 5.6nm , respectively. The

surface area and pore volume of $\text{MnO}_2/\text{MCs-46}$ reduced can be attributed to the deposition of MnO_2 nanoparticles.

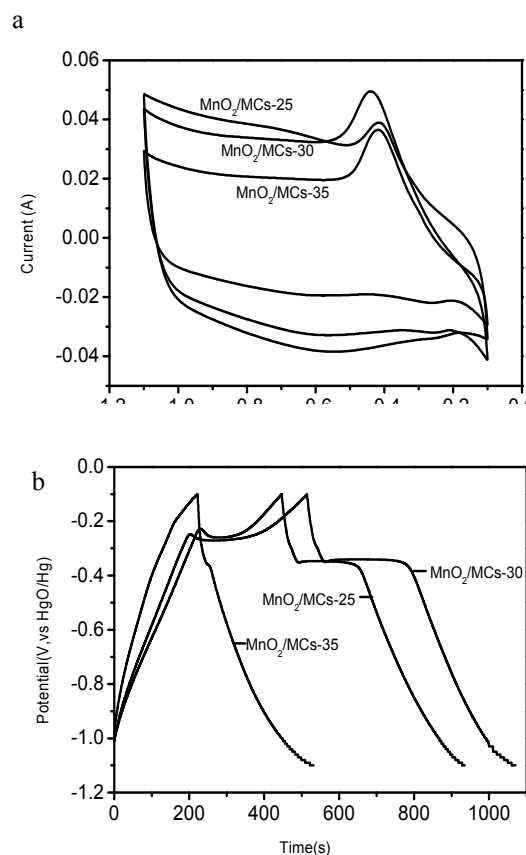


Figure 4. Electrochemical performance of the supercapacitors: (a) CV curves of $\text{MnO}_2/\text{MCs-25}$, $\text{MnO}_2/\text{MCs-30}$, $\text{MnO}_2/\text{MCs-35}$ at the scan rate of 50mV/s and (b) charge-discharge curves of $\text{MnO}_2/\text{MCs-25}$, $\text{MnO}_2/\text{MCs-30}$, $\text{MnO}_2/\text{MCs-35}$ at a current density of 0.5 A/g .

Figure 4a exhibits the cyclic voltammograms of $\text{MnO}_2/\text{MCs-25}$, $\text{MnO}_2/\text{MCs-30}$, $\text{MnO}_2/\text{MCs-35}$ electrodes at a scan rate of 50mVs^{-1} in 6M KOH electrolyte. $\text{MnO}_2/\text{MCs-25}$, $\text{MnO}_2/\text{MCs-30}$, $\text{MnO}_2/\text{MCs-35}$ electrodes show the absence of oxidation and reduction peaks ranging from -1.1 to -0.1V , suggests that the supercapacitor is charged-discharged at a pseudo constant rate over the complete voltammetric cycles. Among MnO_2/MCs electrodes, $\text{MnO}_2/\text{MCs-30}$ with the highest integrated area in the cyclic voltammograms shows the electrochemical capacitance is largest. Figure 4b shows the galvanostatic charge-discharge curves of $\text{MnO}_2/\text{MCs-25}$, $\text{MnO}_2/\text{MCs-30}$, $\text{MnO}_2/\text{MCs-35}$ electrodes at a loading current density of 0.5Ag^{-1} in 6M KOH solution. These curves are symmetric, suggesting good reversibility. The specific capacitance of the $\text{MnO}_2/\text{MCs-30}$ electrode is as high as 275Fg^{-1} at 0.5Ag^{-1} , much higher than that of $\text{MnO}_2/\text{MCs-25}$ (245Fg^{-1}) and $\text{MnO}_2/\text{MCs-35}$ (155Fg^{-1}). Suggesting that $\text{MnO}_2/\text{MCs-30}$ sample is an optimum candidate for supercapacitor electrode application.

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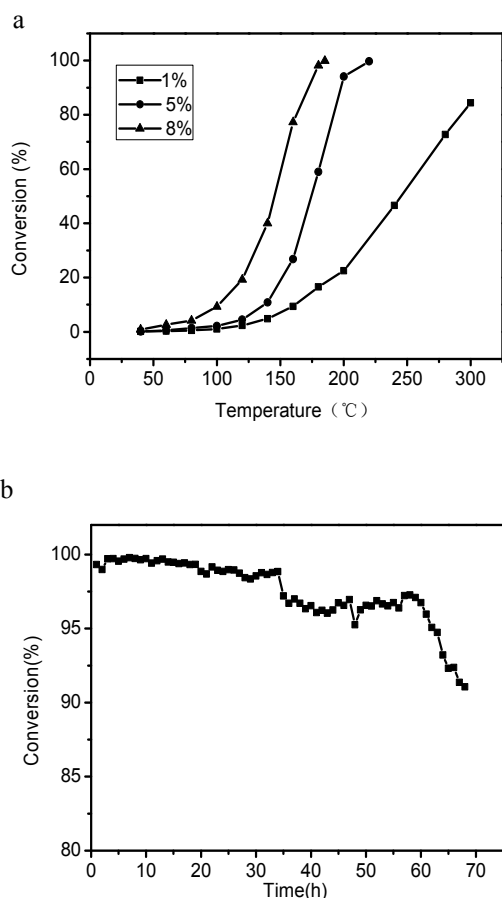


Figure 5.(a) CO conversion curves of 1%Au/MnO₂/MCs-46, 5%Au/MnO₂/MCs-46, 8%Au/MnO₂/MCs-46, (b) Stability of 8%Au/MnO₂/MCs-46 as a function of time on stream.

Futhermore, the MnO₂/MCs-45 was employed as Au catalyst support for CO oxidation, and the result are shown in Figure 5. Various Au amount (1,5,8%) was loaded on support, and was tested in a function of the temperature. The high loading of Au NPs have high activity in CO oxidation. The catalytic stability was tested as shown in Figure 5b. The catalyst had obvious deactivation on stream after 65h reaction time at the reaction temperature of 185°C.

IV. CONCLUSIONS

MnO₂/MC spherical composite was prepared by hydrothermal method have good electrochemical performance. The specific capacitance of the MnO₂/MCs-30 electrode is 275Fg⁻¹ at 0.5Ag⁻¹ in 6M KOH solution. MnO₂/MCs composite is good for supercapacitor electrode application. MnO₂/MC spherical composite was used as support of Au catalyst. The catalyst is active and stable, studying on CO oxidation. MnO₂/MC spherical composite promotes the study process in electrochemistry and CO oxidation.

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