

Preparation of Mn-modified Porous Carbon Microspheres

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Abstract. Mixed / composite oxides of transition metals with microsphere structures have promising potentials for different applications but their preparation still remain a big challenge. Herein, a facile hydrothermal method was developed to construct Mn-modified porous carbon microspheres. The composition of the porous carbon microsphere structure can be adjusted by controlling the composition of the precursors using glucose and MnO₂ as raw materials. The precursors were heat-treated at 120°C, 150°C, and 180°C, respectively. The samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy (XPS). The optimum conditions of the measurement is 180 °C for 24 h and the specific surface area of as – prepared porous carbon microspheres is 93 m²/g. The improvement of mixed / composite oxides of transition metals preparation with a morphology of carbon-coated spherical materials exhibit a great potential application in new materials field.

1. Introduction

Mixed / composite oxides of transition metals with porous carbon microsphere structures are ideal candidates to improve Lithium ion batteries (LIBs) performance [1-4]. The addition of carbon into the composite could enhance the integrated conductivity notably, contributing to higher utilization of active material and better rate capability [5-7]. Carbon materials have been widely used in electrical double layer capacitor electrodes because of good electronic conductivity and chemical stability. High-surface-area microporous carbons (e.g. activated carbons) exhibit high capability for charge accumulation at the electrode–electrolyte interface, which contributes to large capacitance. While mesoporous carbons are favorable for high transportation speed of electrolyte ions, and thus show better charge–discharge rates, especially under high loading current density. Besides, porous carbon microspheres with regular morphology and adjustable porosity and diameter can decrease the resistance of ion diffusion, and the package porosity among carbon spheres benefits the generation of ion buffer reservoirs and reduces ion diffusion distance. Thus, it is desirable to design and fabricate micro and mesoporous carbon microspheres with regular geometry and well-developed pore structure for tailoring high performance electrodes to be used in electrical double layer capacitors. Meanwhile, carbon spheres are widely applied in catalyst supports, lubricants, additives for reinforced plastics and rubbers, electrode materials in fuel cells, and supercapacitors, as well as anodes in Li-ion batteries [8-10].

In this work, we report the simple preparation of Mn-modified Porous Carbon Microspheres via one-pot hydrothermal method. The hydrothermal time and temperature have been investigated and the morphology of microspheres has been studied with different instruments.

2. Experimental

All reagents were purchased from Aladdin. All reagents were analytical reagent (AR) grade and were used as-received without further treatment. Mn-modified porous carbon microspheres were prepared via one-pot hydrothermal method using glucose and MnO_2 as raw materials. Briefly, glucose and MnO_2 were mixed in a distilled water, which was transferred to a Teflon-lined autoclave and heated to a temperature of 120 °C, 120 °C and 180 °C, respectively, for 12 h, 18 h and 24 h, respectively. After cool down, the resulting slurry was filtered and washed in ethanol and distilled water. The powder obtained after filtering and water - ethanol wash was vacuum-dried and carbonized at 550 °C for 6 h in nitrogen condition.

Surface area measurements were obtained from an ASAP 2420 surface area analyzer (Micromeritics, USA) with the Brunauer–Emmett–Teller (BET) method. The samples were evacuated at 90°C for 1 h and at 250°C for 6 h before they were measured in a nitrogen atmosphere. The as-prepared samples were characterized by X-ray diffraction (XRD, Ultima IV X-ray diffractometer, Rigaku, Japan) with CuK α radiation ($\lambda = 1.54 \text{ \AA}$). The morphologies of the OM-CAs were observed via scanning electron microscopy (SEM, TESCAN MAIA3, USA) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The surface compositions of samples were obtained via X-ray photoelectron spectroscopy (XPS, PHI5600 Physical Electronics).

3. Results and discussion

Nitrogen adsorption–desorption isotherms at 77 K for Mn-modified porous carbon microspheres is shown in Figure 1. As seen in Figure 1, the isotherms exhibit a hysteresis loop shape in accordance with type IV hysteresis according to the IUPAC classification scheme. As listed in Table 1, when the hydrothermal time is up to 24 h, the sample exhibits a highest specific surface area, up to 93 m^2/g . The long hydrothermal time is beneficial for the formation of carbon microspheres.

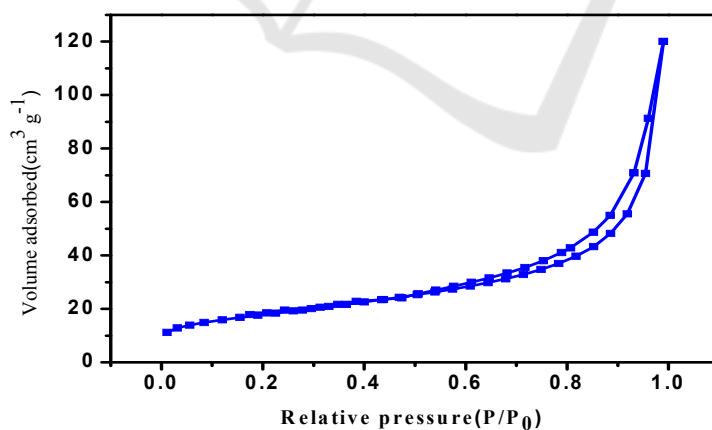


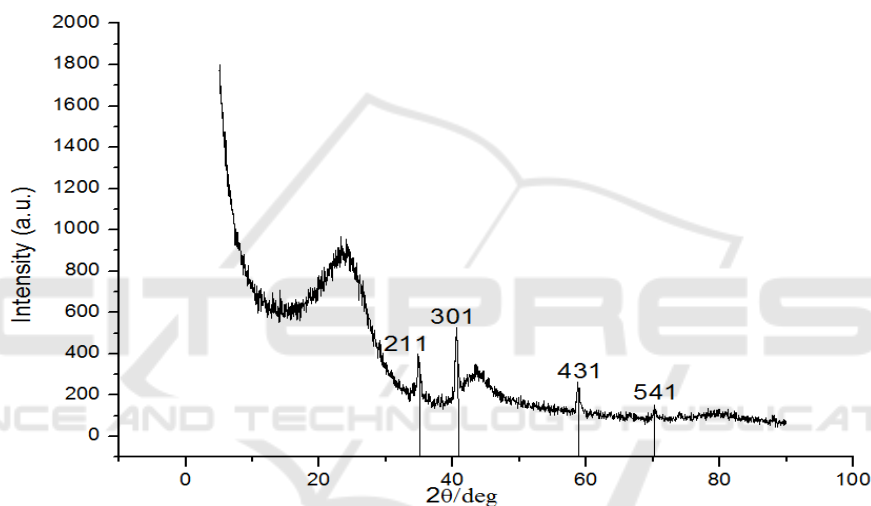
Figure 1. Nitrogen adsorption–desorption isotherms of as – prepared sample.

Table 1. The specific surface area (S_{BET}) of all samples.

Entry ^a	Time (h)	S_{BET} (m^2/g)
1	12	45
2	16	56
3	20	72
4	24	93

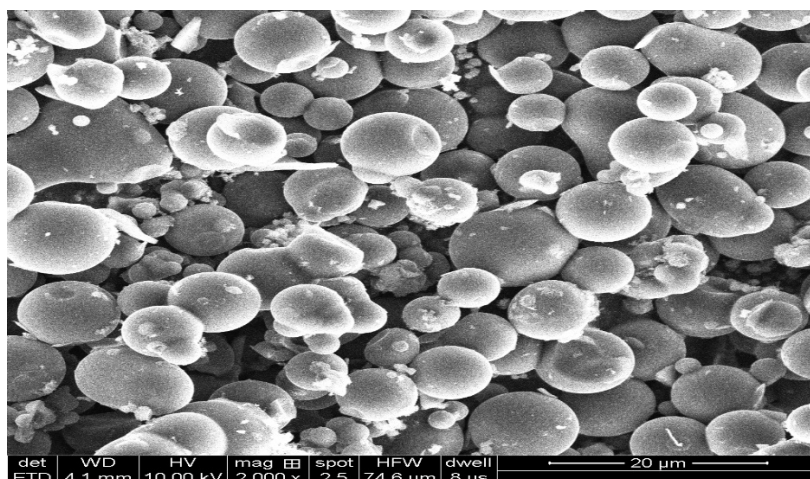
a: the hydrothermal temperature is 180 °C

XRD pattern of sample prepared under 180 °C for 24 h is presented in Figure 2. As shown in Figure 2, the curves clearly exhibits two diffraction peaks at a 2θ of 24° and 42°, which are attributed to the planes (002) and (100), respectively. This result implies that the composite is composed of graphite carbon and amorphous carbon. (211), (301), (431), and (541) are attributed to Mn_2O_3 , which implies the presence of Mn.

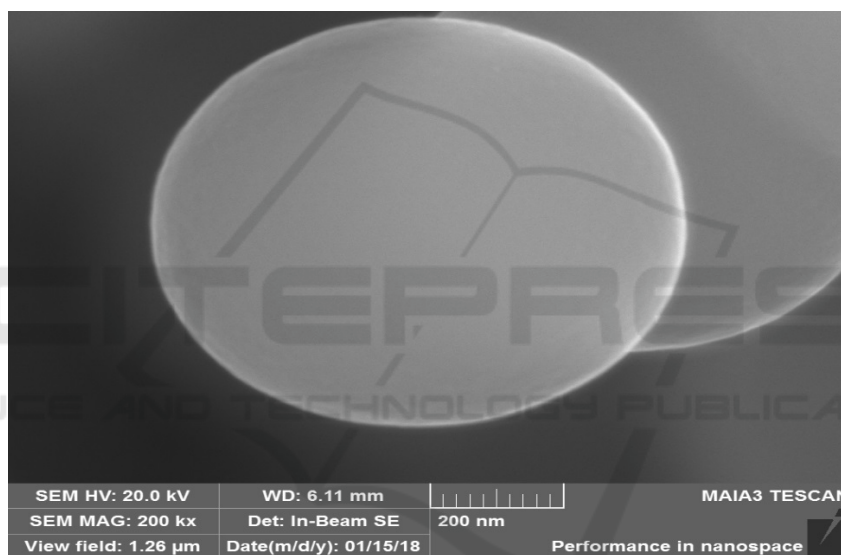
**Figure 2.** XRD patterns of as – prepared sample.

The SEM and TEM images of sample prepared under 180°C for 24 h are shown in Figure 3. As presented in Figure 3 (a), porous carbon microspheres can be clearly seen. Meanwhile, as seen in Figure 3 (b and c), metal oxides uniformly stick to the surface of carbon microspheres. As shown in TEM images, manganese oxides are very noticeable. Metal lattice fringe can be clearly observed in Figure 3 (f), which proved the metal oxides were Mn_2O_3 .

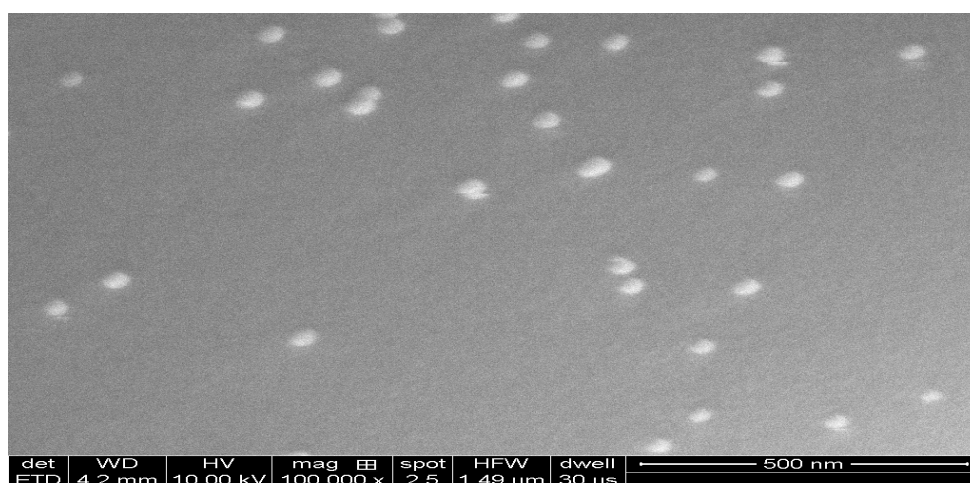
The XPS spectrum of sample prepared under 180 °C for 24 h is shown in Figure 4. As seen in Figure 4 (a), sample prepared under 180 °C for 24 h mainly contains C, O, and Mn elements. As shown in Figure 4 (b), Csp^2 and Csp^3 peaks are located at 284.6 eV and 285.3 eV, respectively. The 285.9 eV (C-O bonds), 287.4 eV (C=O bonds) and 289.1 eV (O-C=O bonds) peaks are obviously observed in the C 1s spectrum. Three peaks were clearly observed in the O 1s spectrum, and they are assigned to the C=O bonds (531.0 eV), COOH bonds (532.0 eV) and C-O-C bonds (535.0 eV), respectively. This result implies the presence of bulk oxygen-containing groups on the surface of the as-prepared carbon aerogels. In the Mn 2p spectrum, the peaks at 641.8 eV and 653.4 eV were easily distinguished.



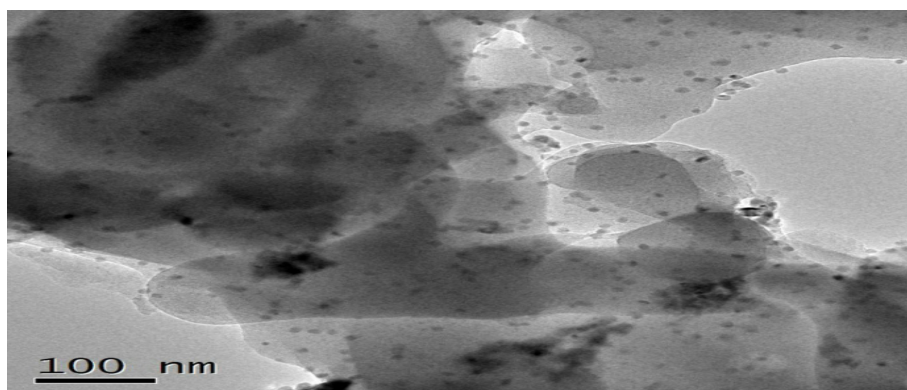
(a)



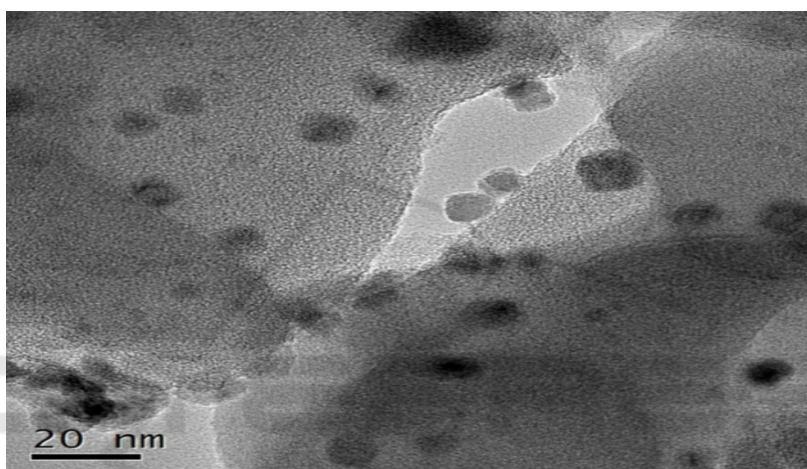
(b)



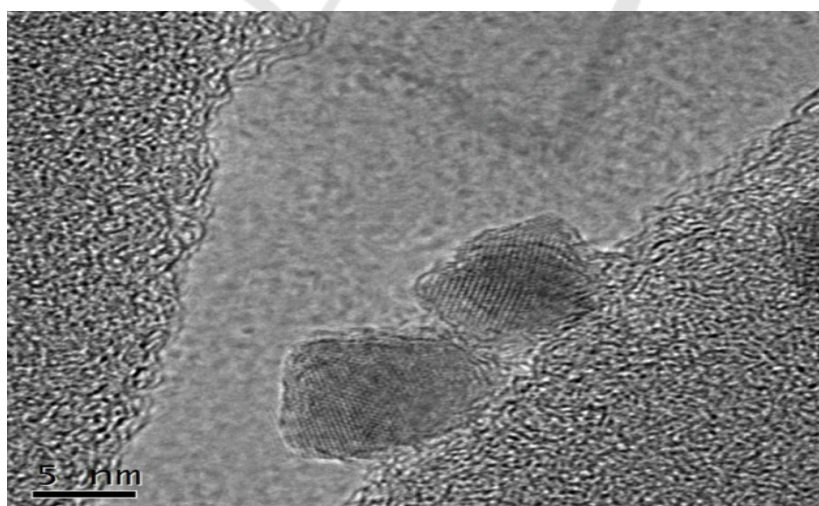
(c)



(d)



(e)



(f)

Figure 3. (a) SEM and (b) TEM images of as – prepared samples.

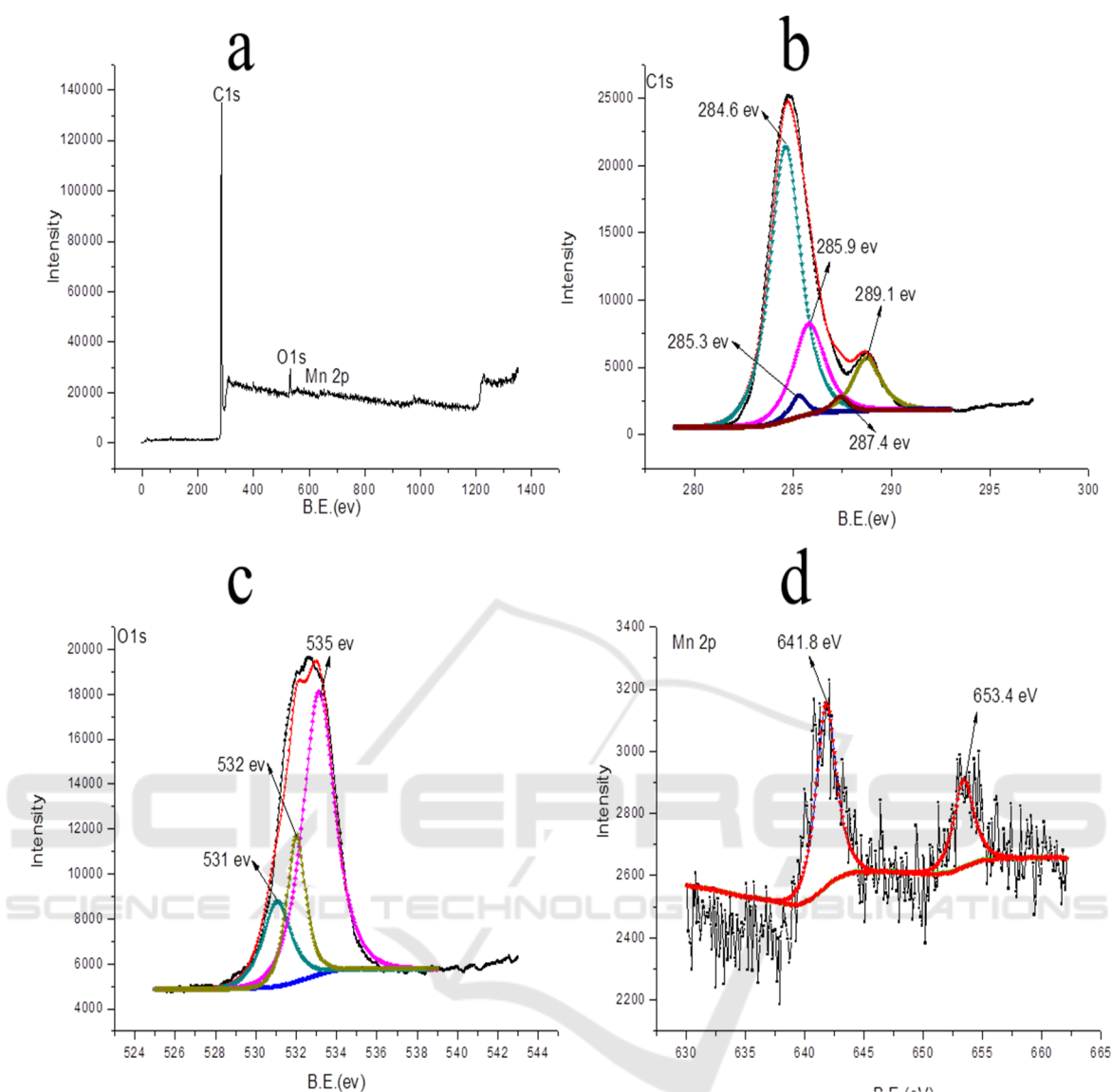


Figure 4. XPS spectra: (a) full-scan spectrum (b) C 1s, (c) O 1s, and (d) Mn 2p peak.

4. Conclusions

In summary, Mn-modified porous carbon microspheres have been synthesized by a facile method. The porous carbon microspheres exhibited a high specific surface area, up to 93 m²/g. The optimal preparation condition is 180°C for 24 h. Our facile strategy has made it possible to optimize the electrode conjugation of future energy storage devices and can also be extended to synthesize other metal oxides carbon microspheres materials with excellent performance.

Acknowledgments

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