



# Monodisperse carbon microspheres derived from potato starch for asymmetric supercapacitors



Qiang Ruibin, Hu Zhongai\*, Yang Yuying, Li Zhimin, An Ning, Ren Xiaoying, Hu Haixiong, Wu Hongying

Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, China

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## ABSTRACT

Uniform and monodisperse carbon microspheres (MCMs) are synthesized via a catalyst-free and hydrothermal process by following a high temperature carbonization, in which potato starch is used as raw material. The morphology and microstructure of the as-obtained samples are characterized using SEM, TEM, XRD, Raman, FTIR and BET. TEM image shows that the products consist of carbon microspheres with a mean diameter of about 250 nm. BET specific surface area of MCMs is up to  $456 \text{ m}^2 \cdot \text{g}^{-1}$ . Furthermore, the supercapacitive performances of the MCMs are investigated by cyclic voltammogram (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS). The experimental results indicate that the MCMs exhibits not only high specific capacitance of  $245 \text{ F} \cdot \text{g}^{-1}$  and good rate capability (the specific capacitance at  $10 \text{ A} \cdot \text{g}^{-1}$  is 61% of that at  $1 \text{ A} \cdot \text{g}^{-1}$ ), but also excellent cycle stability (no obvious capacitance decay after 4,000 cycles at  $3 \text{ A} \cdot \text{g}^{-1}$ ). An asymmetric electrochemical capacitor is assembled by using the obtained MCMs as negative electrode and reduced graphene oxide (RGO) as positive electrode. The as-assembled MCMs//RGO capacitor can cycle reversibly in a voltage of 0–1.5 V and give a high energy density of  $21.5 \text{ Wh} \cdot \text{kg}^{-1}$  at a power density of  $759 \text{ W} \cdot \text{kg}^{-1}$ .

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## 1. Introduction

During the past decade, carbon-based supercapacitors have been widely applied in the fields of vehicles (especially electric vehicles, hybrid vehicles, and special heavy-duty vehicles), electric power, railways, telecommunications, consumer electronics products and emergency power supplies [1–2]. According to the energy storage mechanism, carbon-based supercapacitors are classified as electrical double-layer capacitors (EDLCs) that arise from the separation of electronic and ionic charges at the electrode–electrolyte interface. Electrode material is a key factor to affect the electrochemical properties of EDLCs. Therefore, development of high performance electrode materials is of great importance for fundamental advances in EDLCs application.

Currently, activated carbons (ACs) have attracted much interest during the development of carbon-based supercapacitors because of their large surface area, low cost, non-toxicity and easy processability. However, the current bottlenecks in the supercapacitors prepared by ACs are still low energy storage density and restricted rate capacity [3]. Other types of carbon materials such as carbon

nanotubes (CNTs) and graphene with outstanding electrochemical and surface properties are also considered that there are some disadvantages to their application in supercapacitors: CNTs provide smaller surface area and lesser micropores content than conventional ACs, resulted in insufficient capacitance [4–7]; graphene usually suffers from agglomerating and restacking in the electrode processing owing to Vander Waals interaction, which leads to their “theoretical” capacitance is hard to display completely because of the loss of effective surface area that are inaccessible by the electrolyte, wetting deficiencies of solutions on electrode surface [8]. Because of the limited availability and expense of these materials, therefore, development of new cost-effective and environmentally friendly carbon materials is still needed.

Recently, numerous research activities have shifted to innovative carbon-based electrode materials, including carbon microspheres, glassy carbons, mesoporous carbon, onions, fullerenes [9–10], coin-like hollow carbons, macroflowers, colloidal spheres, nanofibers and so on [11–13]. Among these carbon materials, carbon microspheres (CMSs) is a candidate for outstanding electrode material of supercapacitors and Li-ion batteries owing to their high packing density, good liquidity and high specific surface area [14–17]. Besides, the pores and channels among the spherical particles may remain open and favor diffusion of species

\* Corresponding author.

during the electrochemical processes [18]. Carbon microspheres have been prepared by various methods, such as chemical vapor deposition, pressure carbonization, mixed-valence oxide-catalytic carbonization, and reduction of carbides with metal catalysis [19].

Nowadays, agricultural byproducts and renewable plant resources have become excellent carbon sources of preparing carbon-based materials. For instance, Kurniawan et al. developed a subcritical water carbonization method to synthesize sugar-derived carbon microspheres (CMSs), the sample possesses the highest specific capacitance (about 179.2 F·g<sup>-1</sup>) at a current density of 1 A·g<sup>-1</sup> [20]. Wang and co-workers reported a method to synthesize phosphorus- and nitrogen-co-doped glucose derived microporous carbons, the resultant samples exhibit a specific capacitance of 183.8 F·g<sup>-1</sup> at the current density of 50 mA·g<sup>-1</sup> [21]. Zhao et al. reported a three-step route to synthesize potato starch-based activated carbon spheres (PACS), in which the high specific capacitance of 335 F·g<sup>-1</sup> is obtained at current density of 50 mA·g<sup>-1</sup> [22]. Recently, Wang et al. fabricated porous carbon spheres (PCS) through a facile hydrothermal method by using glucose as a carbon precursor, the PCS exhibits a high specific capacitance of 260 F·g<sup>-1</sup> at 0.5 A·g<sup>-1</sup> [23]. Yang et al. prepared micro-mesoporous carbon spheres by hydrothermal carbonization of carrageenan and the carbon spheres present high specific capacitance of 230 F·g<sup>-1</sup> at a current density of 1 A·g<sup>-1</sup> [24]. However, as a cheaper and more available polysaccharide, potato starch is rarely used as green carbon sources to synthesize uniform and monodisperse carbon microspheres (MCMSs) through a hydrothermal method. In this paper, we report a simple and efficient hydrothermal method to synthesize uniform and monodisperse carbon microspheres (MCMSs) on a large scale by using potato starch as starting materials. The preparing processes without involving any chemicals render this method green and productive. The electrochemical measurements in either three-electrode or two-electrode system indicate that MCMSs have excellent capacitive performance and a promising potential in applications of negative electrode of asymmetric supercapacitors.

## 2. Experimental

### 2.1. Preparation of MCMSs

Highly dispersed carbon microspheres were synthesized by a facile hydrothermal method followed by high temperature carbonization under nitrogen atmosphere. In a typical synthesis, 2 g potato starch powder was dispersed in 100 mL distilled water with magnetically stirring for 5 h, afterward, the mixture solution was transferred to a Teflon-lined stainless steel autoclave (150 mL in volume) and hydrothermally treated at 180 °C for 16 h. After the autoclave was cooled to room temperature naturally, the dark precipitates were filtered and washed with distilled water and ethanol several times and dried in a vacuum at 60 °C for 12 h. This as-synthesized sample was marked as MCMSs-180. It was loaded into tube furnace and heated in nitrogen stream (flowrate = 10 mL·min<sup>-1</sup>) at 900 °C for 2 h with a heating rate of 4 °C·min<sup>-1</sup>. The resultant sample was marked as MCMSs-900.

### 2.2. Materials characterization

The morphology of samples are characterized by using field emission scanning electron microscopy (FESEM; ULTRA plus, Germany), and transmission electron microscope (TEM; JEOL, JEM-2010, Japan). The structure and component information of samples was examined by X-ray diffraction (XRD; D/Max-2400, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) operating at 40 kV, 100 mA, Raman spectrum (BRUKER RFS 100/S, Germany) with the 514.5 nm line of an argon laser, and the Fourier transform infrared

spectroscopy (FTIR) spectrum. Brunauer–Emmett–Teller (BET) was measured by N<sub>2</sub> physisorption at –196 °C using a Micromeritics ASAP 2010 instrument.

### 2.3. Electrochemical measurements

In order to evaluate the electrochemical performance of the as-prepared samples, we used a glassy carbon electrode with a diameter of 5 mm as current collector. The working electrode was fabricated by dispersing mixtures (5.88 mg) of the as-prepared samples and acetylene black (weight ratio of 85:15) in 1 mL of Nafion (0.25 wt%) and then the above suspension of 5  $\mu$ L was dropped onto the glassy carbon electrode using a pi-pet gun and dried at room temperature. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge tests of active electrode materials were performed in a three-electrode system, in which platinum foil and Hg/HgO electrode were used as counter electrode and reference electrode, respectively, in 1 M KOH solution electrolyte. In order to test further the electrochemical performance of the material, an asymmetric supercapacitor was fabricated by two active material electrodes, where MCMSs and RGO were served as negative electrode and positive electrode, and glass fiber was served as separator respectively. All of the above electrochemical measurements were carried out by using a CHI860D electrochemical working station.

#### 2.3.1. Related Formula

The specific capacitance ( $C$ , F·g<sup>-1</sup>) of a single electrode in the three-electrode configuration is respectively calculated from the charge/discharge curves and the CV curves by using the formula: [25,26]

$$C = \frac{i \cdot t}{\Delta V} \quad (1)$$

$$C = \frac{\int i \cdot dV}{2\nu \cdot \Delta V} \quad (2)$$

where  $i$  (A·g<sup>-1</sup>) is current density,  $t$  (s) is the discharge time,  $\Delta V$  (V) is the applied potential window and  $\nu$  (mV·s<sup>-1</sup>) is the potential scan rate.

The mass ratio ( $R$ ) between the positive and the negative electrodes in the two-electrode configuration is expressed as follows: [27,28]

$$R = \frac{m_+}{m_-} = \frac{C_- \cdot \Delta V_-}{C_+ \cdot \Delta V_+} \quad (3)$$

where  $m_+$  and  $m_-$  are the mass,  $C_+$  and  $C_-$  are the specific capacitance, and  $\Delta V_+$  and  $\Delta V_-$  are the potential window for the positive and negative electrodes, respectively.

The total capacitance ( $C$ , F), average specific capacitance ( $C_s$ , F·g<sup>-1</sup>), power density ( $P$ , kW·kg<sup>-1</sup>), and energy density ( $E$ , Wh·kg<sup>-1</sup>) of the cell in the two-electrode configuration are calculated from the galvanostatic charge–discharge curves by using the formula: [29,30]

$$C = \frac{I \cdot t}{\Delta V} \quad (4)$$

$$C_s = \frac{4 \cdot C}{M} \quad (5)$$

$$E = \frac{0.5C(\Delta V)^2}{3.6} \quad (6)$$

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