



# Multi-shelled $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres for high-rate supercapacitors

Zhiwei Nie<sup>†</sup>, Yaping Wang<sup>†</sup>, Yifang Zhang and Anqiang Pan<sup>\*</sup>

**ABSTRACT** Hollow structured metal oxides are extensively studied in energy storage and conversion systems. In this work, we report the fabrication of multi-shelled Fe<sub>2</sub>O<sub>3</sub> microspheres with nanospindles assembly on its exterior shell. The  $\beta$ -FeOOH precursor nanospindles were firstly grown on the surface of carbon microspheres to produce  $\beta$ -FeOOH@carbon composites, which were later converted into multi-shelled Fe<sub>2</sub>O<sub>3</sub> microspheres by calcination in air. As electrode material for supercapacitors, the multi-shelled Fe<sub>2</sub>O<sub>3</sub> microspheres exhibit high capacity and good rate capability. The electrode delivers the specific capacitances of 630 and 510 F g<sup>-1</sup> at the current densities of 1 and 5 A g<sup>-1</sup>, respectively.

**Keywords:** nanospindle, multi-shells, hollow microspheres, Fe, supercapacitors

## INTRODUCTION

Hollow nano-/microstructures are extensively studied in energy storage and conversion systems due to their structural advantages [1,2]. In particular, hollow nano-/microstructures with complex structures have attracted more attention recently, which are expected to further tailor the properties for different applications [3,4]. To date, different preparation strategies, such as Ostwald-ripening formation mechanism and template-assisted approaches have been reported for the construction of multi-shelled hollow structures [5–7]. Although Ostwald-ripening formation mechanism is commonly reported in the solvothermal or hydrothermal process, it is still a challenge to obtain uniform hollow structures [5,8]. Template-assisted formation of hollow microspheres is believed a more reliable strategy for the synthesis of hollow structured materials [9]. Among the available templates, such as silica [3,10,11], polystyrene [12] and carbon microspheres [9,13,14], carbonaceous microspheres [15] are preferred due to their

large functional groups on the surface and easy removal by calcinations in air. Recently, Lai *et al.* [16] reported the synthesis of multi-shelled metal oxide microspheres with controlled morphology using carbonaceous microspheres as hard templates. The liquid solutions were absorbed into the carbonaceous microspheres first and converted into multi-shelled microstructures during the hard template removing process. The feasibility of fabricating multi-shelled microstructures from carbonaceous microspheres is well demonstrated, as comparing with other hard templates, such as silica and polystyrene. However, the surface is always smooth and no structural engineering of the exterior shell is reported.

Recently, low cost Fe<sub>2</sub>O<sub>3</sub> has attracted much attention as electrodes for asymmetric supercapacitors because of the high theoretical specific capacitance and suitable negative working window. However, the rate of capability and energy density are limited by its poor electrical conductivity. To date, many strategies have been developed to improve their electrochemical performance, including making nanostructure and incorporating carbon materials. For instance, a specific capacitance of 264 F g<sup>-1</sup> was observed for a three-dimensional Fe<sub>2</sub>O<sub>3</sub>/graphene composites [17]. More recently,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hollow nanoshuttles have been developed with a capacitance of 249 F g<sup>-1</sup> at a discharging current density of 0.5 A g<sup>-1</sup> [18]. However, their high rate performance needs further improvement.

Herein, we reported a facile synthesis of nanospindle-assembled Fe<sub>2</sub>O<sub>3</sub> hollow microspheres with multi-shells, where carbonaceous microspheres were employed as hard templates. The  $\beta$ -FeOOH nanospindles were grown on the surface of the carbonaceous microspheres firstly to form core-shell structured composites, which were converted into multi-shelled Fe<sub>2</sub>O<sub>3</sub> hollow microspheres with sub-

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sequent annealing process in air. As electrode material for supercapacitor, the multi-shelled Fe<sub>2</sub>O<sub>3</sub> hollow microspheres exhibit high capacity and good rate capability.

## EXPERIMENT SECTION

### Materials synthesis

All the solvents and chemicals were of reagent grade and used without further purification. The carbonaceous sphere templates were hydrothermally synthesized according to the previous report [19]. In a typical synthesis, 5 mg carbon spheres were dispersed into 20 mL FeCl<sub>3</sub>·6H<sub>2</sub>O (0.12 mol L<sup>-1</sup>) solution by ultrasonication and the obtained solution was heated in an oil bath under magnetically stirring at 75°C for 5 h. The obtained materials were centrifuged and washed by deionized water for several times. After drying at 80°C overnight, the dried materials were annealed in air at 400°C for 2 h with a temperature ramping rate of 0.5°C min<sup>-1</sup>.

### Structural characterization

The crystal structure of the products was characterized by the powder X-ray diffraction (XRD, Rigaku D/max2500) using Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) and scanned in the range between 10° and 80° (2 $\theta$ ) with a step size of 0.02°. The morphologies and structures of the obtained samples were observed by scanning electron microscopy (SEM, FEI Nova NanoSEM 230) and transmission electron microscopy (TEM, JEOL JEM-2100F). The calcination process was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10°C min<sup>-1</sup> in air.

### Electrochemical measurements

The electrochemical performances of the multi-shelled  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres were recorded by a three-electrode system, which is composed of a working electrode, a Pt foil counter electrode and an Hg/HgCl reference electrode. The hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres, acetylene black and polyvinylidene fluorides (PVDF) in a weight ratio of 8:1:1 were dissolved in *N*-methylpyrrolidone (NMP) to make the slurry, which was later coated on a nickel foam and dried in a vacuum oven at 60°C for 12 h to make the working electrode. The mass loading is about 0.5 mg cm<sup>-2</sup>. 2 mol L<sup>-1</sup> KOH aqueous solution was used as the electrolyte. Cyclic voltammetry (CV) measurements and the constant current charge-discharge were performed on an electrochemical workstation (CHI660C, Shanghai). The specific capacitances were calculated according to the charge/discharge test and the following equation:

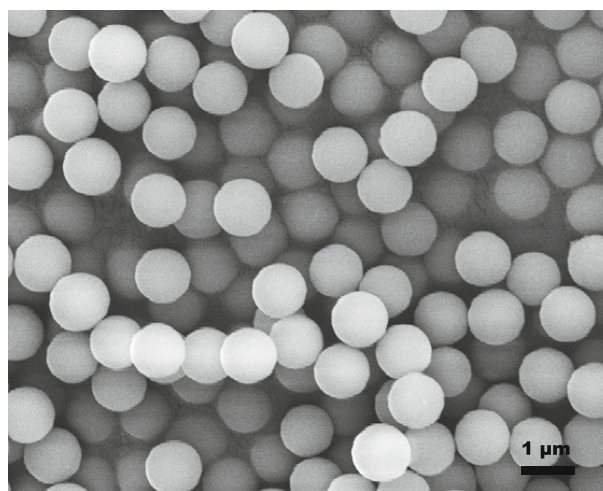
$$C = \frac{I\Delta t}{M\Delta V},$$

where  $C$  (F g<sup>-1</sup>) is the specific capacitance,  $I$  (A) represents the discharge current,  $\Delta t$  (s) is the discharging time,  $\Delta V$  (V) is the voltage window, and  $M$  (g) is the mass of active materials.

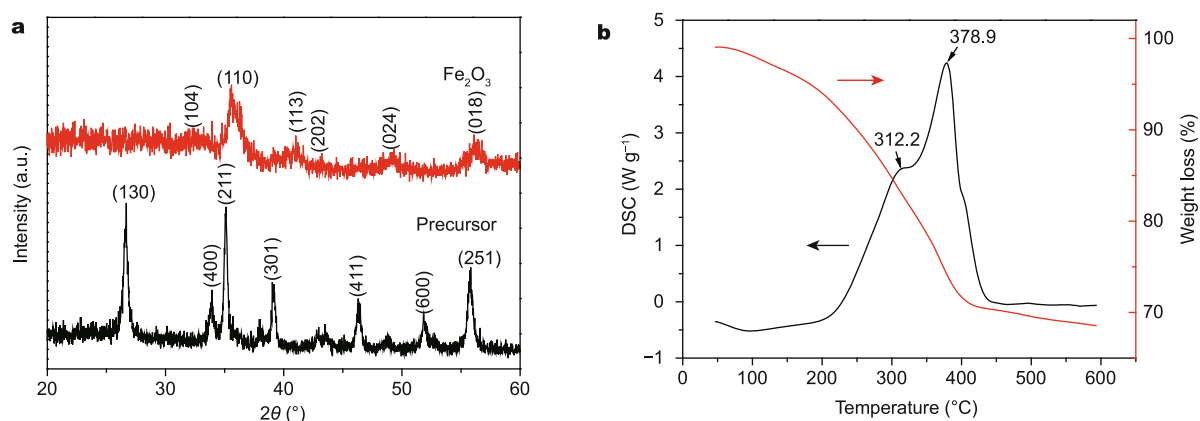
## RESULTS AND DISCUSSIONS

Fig. 1 shows the SEM image of the solvothermally prepared carbon microspheres, which demonstrates the good homogeneity of the carbonaceous microspheres with a diameter about 1  $\mu$ m. The selection of carbon microspheres as hard templates was attributed to their large functional groups on their surface and the easy removal of carbon during the calcination process [19, 20].

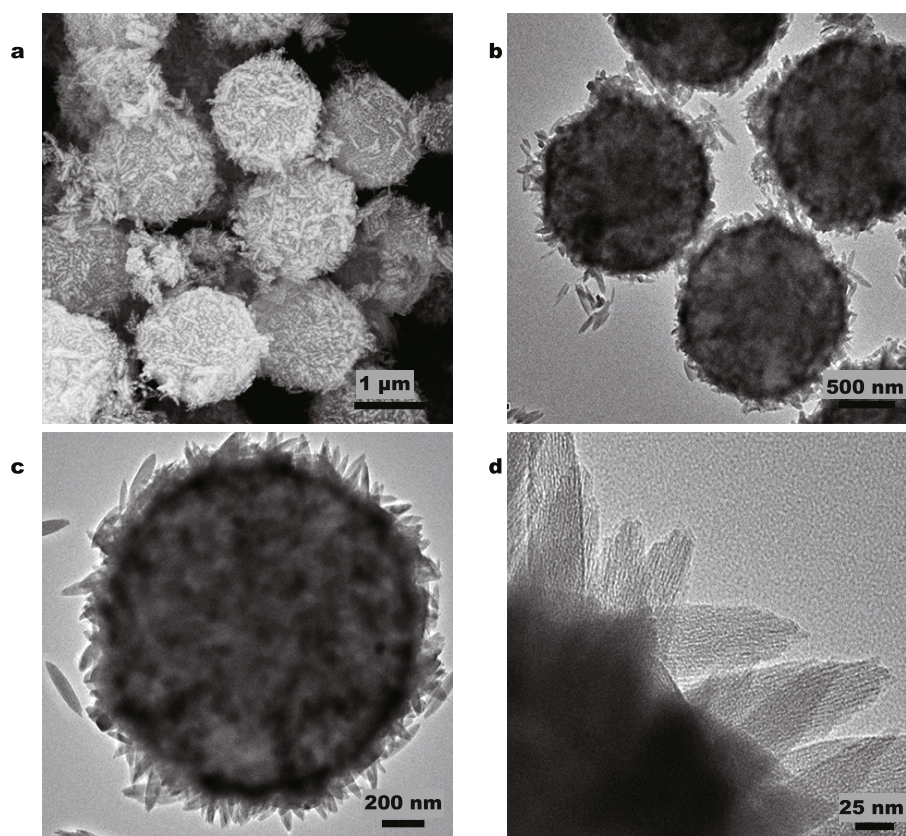
The XRD is employed to study the crystallinity and phases of the solvothermal product and its calcination product. Fig. 2a shows the XRD patterns for both precursor composite and the final product. After solvothermal treatment, the  $\beta$ -FeOOH can be obtained. The result indicates the species of Fe<sup>3+</sup> ions in the solution is converted into  $\beta$ -FeOOH in the solvothermal process. No extra XRD peaks are detected, which demonstrates the high purity of  $\beta$ -FeOOH and the amorphous feature of the carbon microspheres in the solvothermal prepared composite precursor. After annealing in air at 400°C for 2 h, the FeOOH is converted into hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS No. 33-0664). In order to further study the phase transition process, TGA and DSC experiments were carried out. As shown in Fig. 2b, the gradual weight loss below 220°C is caused by the evaporation of the physically or chemically



**Figure 1** SEM image of the carbon microspheres fabricated by hydrothermal method.



**Figure 2** (a) XRD patterns of the precursor (black) and its annealed product (red); (b) TGA and DSC results of the precursor with a temperature ramp rate of  $10^{\circ}\text{C min}^{-1}$ .



**Figure 3** SEM (a) and TEM (b, c and d) images of the  $\beta\text{-FeOOH@CS}$  precursor. CS stands for carbon spheres.

absorbed water in the precursor. The small exothermic peak at  $312^{\circ}\text{C}$  can be attributed to the phase transition from  $\beta\text{-FeOOH}$  to  $\alpha\text{-Fe}_2\text{O}_3$ . And the high exothermic peak and corresponding large weight loss at  $378^{\circ}\text{C}$  are ascribed to the removal of carbon microspheres. The result indicates that at relative high temperature ( $>378^{\circ}\text{C}$ ), the  $\beta\text{-FeOOH}$

can be converted into  $\alpha\text{-Fe}_2\text{O}_3$  and the carbonaceous microspheres can be removed.

The morphologies of the solvothermal products and its calcination product were studied by SEM and TEM. The SEM image (Fig. 3a) reveals the  $\beta\text{-FeOOH}$  nanospindles are uniformly coated on the surface of the carbon spheres.

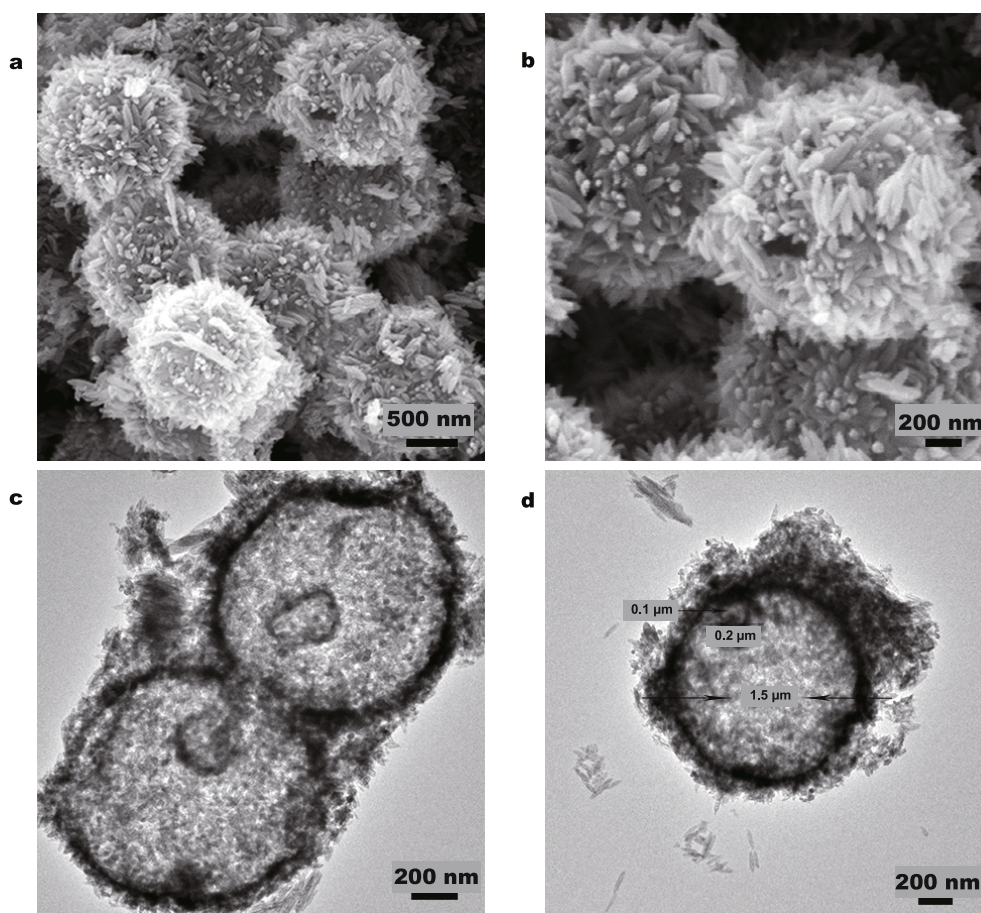


The preferential growth of FeOOH nanospindles on the carbon spheres can be attributed to the large amount of functional groups on the surface of the carbon spheres, which function as the nucleation sites for the particle growth. The TEM images (Figs 3b–d) reveal the spherical structure of the  $\beta$ -FeOOH@CS with a diameter of 1.5  $\mu\text{m}$  and the exterior shell is composed of the  $\beta$ -FeOOH nanospindles, which has a uniform size of 200 nm in length.

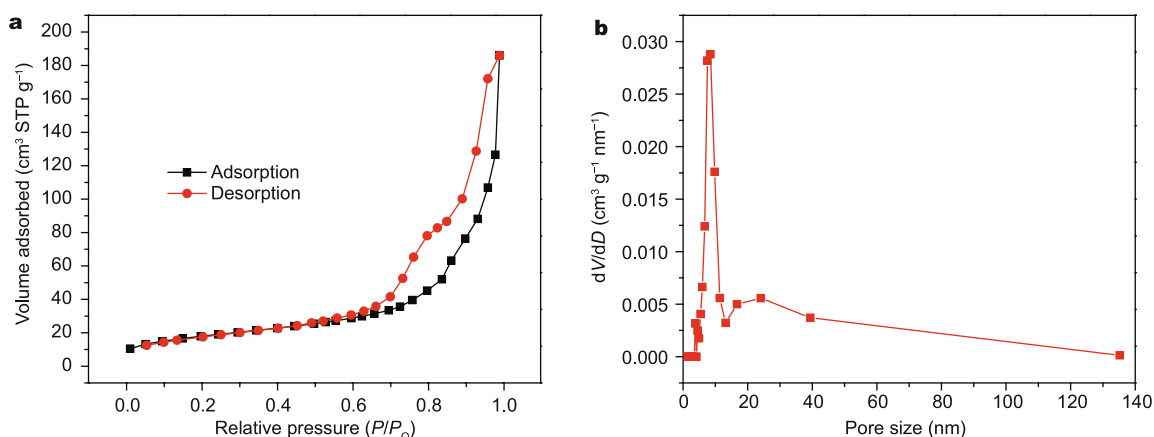
Multi-shelled hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres can be obtained after annealing the solvothermal product in air at 400°C for 2 h with a heating ramp rate of 0.5°C min<sup>-1</sup>. After calcination, the nanospindles assembled shells can still be observed (Fig. 4a) and the broken microsphere reveals the hollow interior of the microsphere (Fig. 4b). The TEM image confirms the hollow feature of the microspheres. Moreover, the multi-shells within the microspheres are also detected. The diameter of the exterior shell is similar to the diameter of the carbon template microspheres and the interior shell is about 200 nm in diameter. Moreover, some

hollow microspheres are found to have triple shells with the corresponding diameters of 1.5, 0.2 and 0.1  $\mu\text{m}$ , respectively. The formation of the multi-shells can be explained as follows: when subjected to calcinations in air, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> surface layer is formed first and the template material is partly removed, meanwhile the remained carbon sphere with a small amount of residue iron ions becomes the template for generating another shell. In this way, the multi-shelled structure is prepared.

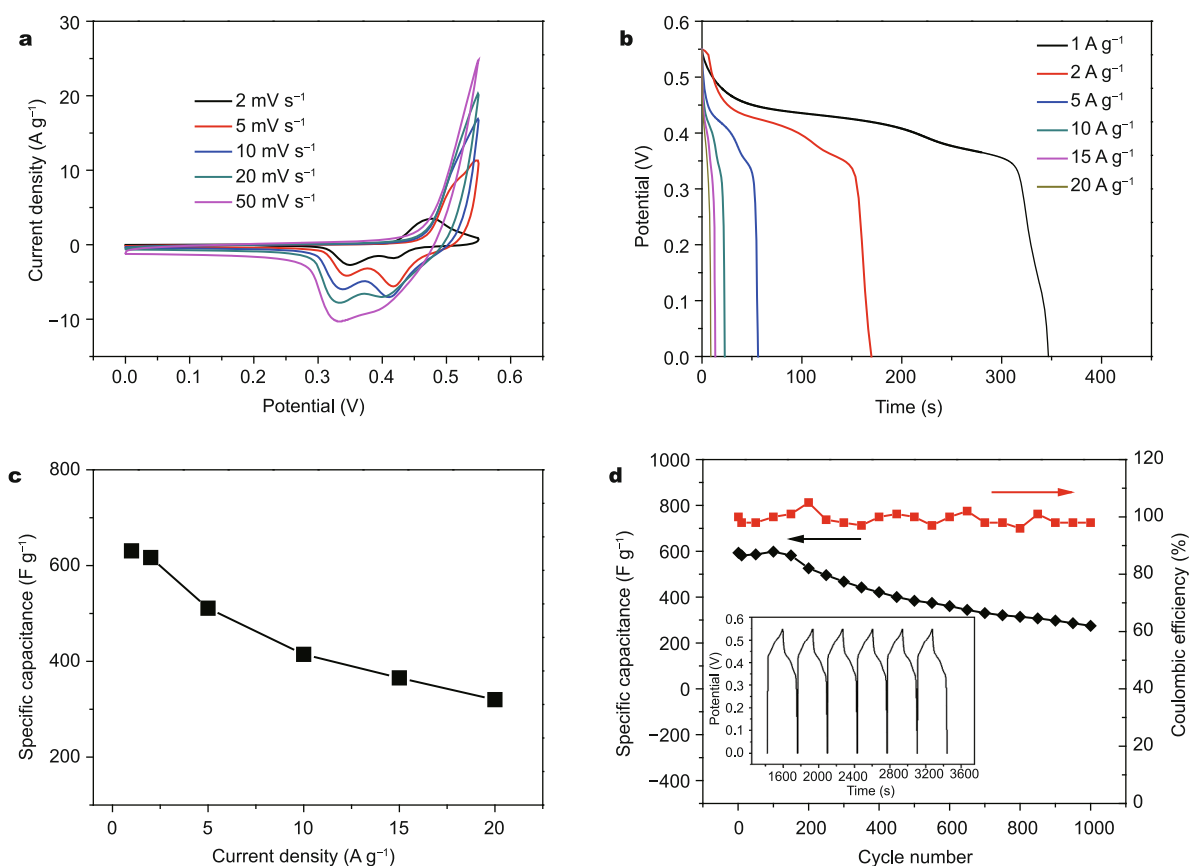
Fig. 5 shows the nitrogen adsorption-desorption isotherm and the pore size distribution for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres. The isotherm curve is of typical IV type, which indicates the mesoporous feature of the microspheres. According to the Brunauer-Emmett-Teller (BET) method, the hollow-structured  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microsphere has a high surface area of 79.9 m<sup>2</sup> g<sup>-1</sup>. Fig. 5b shows the pore size distribution of the electrode, which indicates the majority of the pores are about 10 nm. The relative large pores allow the good penetration of electrolyte in the electrode materials, ensuring the good wettability of the electrode



**Figure 4** SEM (a and b) and TEM (c and d) images of the nanospindle-assembled hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres.



**Figure 5** Nitrogen adsorption-desorption isothermal curve (a) and pore size distribution (b) of the hollow-structured  $\alpha$ - $\text{Fe}_2\text{O}_3$  microspheres.



**Figure 6** (a) CV curve of the hollow  $\alpha$ - $\text{Fe}_2\text{O}_3$  microspheres at different scan rates; (b) discharge curve and the corresponding specific capacitances at different discharge currents; (c) rate performance of the  $\alpha$ - $\text{Fe}_2\text{O}_3$  microsphere electrodes; (d) cycling performances of the hollow  $\alpha$ - $\text{Fe}_2\text{O}_3$  microspheres at  $2 \text{ A g}^{-1}$ . Inset: the corresponding charge/discharge curves of 5–10 cycles.

material.

The electrochemical performance of the obtained product as the working electrodes for supercapacitors was tested. Fig. 6a shows the CV curves in a potential range

between 0 and 0.55 V at different scan rates of 2, 5, 10, 20 and  $50 \text{ mV s}^{-1}$ , respectively. As expected, a change in the hysteresis of the cathodic and anodic peaks can be observed with the steady increase in scan rate, which can

be attributed to the larger polarization at higher rates. Fig. 6b shows the galvanostatic discharge curves at different current densities. Two plateaus are clearly observed on the discharge curve, which can be explained by the two-step reduction process [21]. The result is in good accordance with the CV result. Upon cycling, the coulombic efficiency is very close to 100%, which indicates the good reversibility of the electrode. The rate performance of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hollow microspheres is shown in Fig. 6c. The electrode delivers the specific capacitances of 631, 617, 511, 415, 365 and 320 F g<sup>-1</sup> at the current densities of 1, 2, 5, 10, 15 and 20 A g<sup>-1</sup>, respectively. The obtained capacitance is much higher than many previous reports. For instance, Sethuraman and coworkers [22] reported the synthesis of mesh-like Fe<sub>2</sub>O<sub>3</sub>/C nanocomposite, which showed a specific capacitance of 295 F g<sup>-1</sup> at the current density of 0.5 A g<sup>-1</sup> in the potential range of -0.4 to 0.5 V. Yang and coworkers [23] synthesized porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> grown on graphene by a simple hydrothermal method. When investigated the electrochemical performance as a supercapacitors electrode material, it delivers a specific capacitance of 343.7 F g<sup>-1</sup> at a current density of 3 A g<sup>-1</sup> in a three-electrode system. The result shows the advantages of multi-shelled  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hollow microspheres compared with other iron-carbon composite materials or other morphologies. The good rate capability and high specific capacitance can be attributed to the multi-shelled structures of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hollow microspheres. The multi-shelled microspheres can enlarge the contact area between electrode and electrolyte, allowing the fast ion diffusion and electron transportation. Fig. 6d shows the cycling behavior of the electrode material at the current density of 3 A g<sup>-1</sup>. The electrode material delivers a specific capacitance of 600 F g<sup>-1</sup>, which is quite stable for the initial 200 cycles. However, the long-term cycling stability of the as-prepared Fe<sub>2</sub>O<sub>3</sub> hollow microspheres is not quite satisfactory. The capacity decreases to 300 F g<sup>-1</sup> after 1000 cycles. Further electrochemical performance improvement is under investigation, such as carbon coating or Al<sub>2</sub>O<sub>3</sub> coating.

## CONCLUSIONS

In summary, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanospindles assembled hollow microspheres with multi-shelled interior structure are successfully synthesized using carbon spheres as hard templates. The  $\beta$ -FeOOH nanospindles are easily coated on the carbon spheres by a low-temperature solution route. The multi-shelled hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres can be obtained by calcination in air. The excellent electrochemical performance of this material shows that it is an interesting

and unique candidate for supercapacitor.

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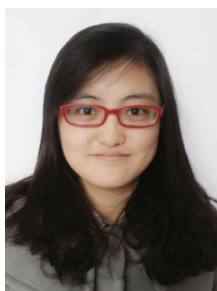
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**Author contributions** Nie Z and Wang Y carried out the main experiment and wrote the article; Zhang Y participated in the data discussion; Pan A conceived and supervised the project.

**Conflict of interest** The authors declare that they have no conflict of interest.



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## 多层壳结构 $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>中空微球用作高倍率超级电容器的研究

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**摘要** 中空结构的金属氧化物在能源储存和转化系统中已被广泛研究. 本文报道了纳米纺锤自组装的多层中空 $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>微米球.  $\beta$ -FeOOH前驱体纳米锤首先在炭球表面沉积生长得到 $\beta$ -FeOOH@炭球复合材料, 然后在空气中烧结移除模板, 转变为多层中空 $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>微米球. 该材料用作超级电容器的电极材料具有高容量和良好的倍率性能. 该电极在1和5 A g<sup>-1</sup>的条件下, 可以释放630和510 F g<sup>-1</sup>的比放电容量.