Fe$_2$O$_3$ hollow sphere nanocomposites for supercapacitor applications

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Abstract. Nanomaterials have attracted increasing interest in electrochemical energy storage and conversion. Hollow sphere Fe$_2$O$_3$ nanocomposites were successfully prepared through facile low temperature water-bath method with carbon sphere as hard template. The morphology and microstructure of samples were characterized by X-ray diffraction (XRD) and Scanning electron microscope (SEM), respectively. Through hydrolysis mechanism, using ferric chloride direct hydrolysis, iron hydroxide coated on the surface of carbon sphere, after high temperature calcination can form the hollow spherical iron oxide materials. Electrochemical performances of the hollow sphere Fe$_2$O$_3$ nanocomposites electrodes were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge. The Pure hollow sphere Fe$_2$O$_3$ nanocomposites achieves a specific capacitance of 125 F g$^{-1}$ at the current density of 85 mA g$^{-1}$. The results indicate that the uniform dispersion of hollow ball structure can effectively reduce the particle reunion in the process of charging and discharging.

1. Introduction

Supercapacitor is becoming a significant option of new energy to meet world's fossil energy crisis because of high power cycle long life, fast charge and discharge, high efficiency, non-pollution, wide temperature scope, and high security[1-3]. Supercapacitors can be used in electronics, smart grids, new energy vehicles, wind and solar power systems[4]. Moreover, In new energy vehicles, supercapacitors can be used in conjunction with secondary batteries to conserve energy and protect the battery. Supercapacitors are a new type of energy storage device in between conventional capacitors and chemical mains, called dielectric capacitors and electrochemical capacitors[5-7]. Electrodes and electrolyte are both vital to its performance which are also the main concern improved and optimized. Therefore, the development of suitable electrode materials and electrolyte solutions is the main direction of the improved supercapacitor[8-11].

In recent years, researchers have developed a variety of electrode materials, which can roughly be divided into three categories, carbon electrodes, metal oxide, and conducting polymers. Among them, the carbon electrode material with high specific surface area and good electrical conductivity and wide pore size distribution and other advantages. For the past few years, metal oxides have been proved with good electrochemical performance. Conductive polymer is good at electrical conductivity, small internal resistance, and high specific capacity advantages[10-16].

As we know, nanomaterials including inorganic nanometer hollow ball morphology oxide, have unique structure, high specific surface area, and show a broad application prospect in the lithium ion battery, solid oxide fuel cells, etc[9,13-16]. The synthesis of large scale and high permeability nano-
hollow microspheres will be useful for applications in related fields. Here, we give a research preliminarily about a hollow sphere Fe$_2$O$_3$ nanocomposites for supercapacitor application synthesized by a facile hard template method.

2. Experimental section

2.1. Preparation of carbon microspheres
Dissolve a certain amount of glucose in deionized water and add the appropriate ethanol as dispersant, stir until completely dissolved. Shift this solution to the high-pressure reaction kettle, put the stainless steel with PTFE into the oven of 60°C for 8h. At last put the product within the drying oven temperature of 60°C over night after centrifugal separation and washing by deionized water and ethanol several times.

2.2. Process of preparation of iron oxide hollow microspheres
Typically, certain mount of prepared carbon sphere were dispersed in 50ml 0.05, 0.1, 0.15, 0.2 mol/L ferric chloride solution under ultrasonic condition at 70°C for 30min. High speed centrifuge centrifugal separation was used to remove the supernatant fluid. The above process was repeated three times with deionized water and ethanol washing to remove the unreacted iron ion and other ions residual. At last, the sample was placed in drying oven over night at 60°C. Grind to powder and get the precursors C/Fe$_2$O$_3$. Calcination under N$_2$ protection to remove the carbon and gets the Fe$_2$O$_3$ hollow ball.

The sample was tested by the Frontier Fourier transform infrared spectroradiometer, produced by the American PE company, and the vibrational graph of the functional group was obtained. Sample preparation by KBr tabletting method with test range of 400 cm$^{-1}$-4000 cm$^{-1}$.

The Empyrean X-ray diffractometer produced by the Dutch panaco company, was used to determine the structure of the sample crystal phase. Parameters are as following: the target of Cu K$_{\alpha}$, $\lambda=0.15418$ nm, test voltage 40.0 kV, test current 40.0 mA, scanning step 0.026261°. Scanning Angle: 10.00°- 90.00°.

The microstructure of the powder sample was observed by JSM-6360LV scanning electron microscope, which was produced by JEOL company of Japan.

2.3. Electrode preparation
Soak the glassy carbon electrode in nitric acid for 1 minute, each one minute with ethanol, acetone and ultra-pure water. Disperse the samples ultrasound in anhydrous ethanol, and then drop it on the glassy carbon electrode with a syringe, drying, the dry electrode under normal temperature.

In 6 mol/L KOH solution by electrochemical work station of Fe$_2$O$_3$ electrode electrochemical performance test. Electrochemical performance test of the classic three electrode system was used with the Pt electrode as counter electrode, saturated calomel electrode (SCE) as the reference electrode, nickel oxide electrode as working electrode. Cyclic voltammograms test scanning voltage range of 0~0.7 V, constant current charge and discharge test is 0.6 ~ 0.6 V voltage window.

3. Results and discussion

3.1. SEM and IR representations of carbon sphere
As shown in figure 1a, SEM image for carbon ball can be seen. From the diagram, the sample morphology of carbon materials are globular structure, morphology of a single, uniform dispersion, diameter range in 300-400 nm. The diameter of the ball is more uniform, and there is no mass reunion.
Figure 1. SEM image (a) and IR spectrum (b) of the as-synthesized carbon spheres.

The infrared spectrum of carbon sphere is shown in figure 1b. The peaks appeared from 3000 cm\(^{-1}\) to 3750 cm\(^{-1}\) corresponds to the absorption peak of the hydroxyl group. At the same time the carbonyl (C=O) vibration absorption peak red moved to 1703 cm\(^{-1}\) and widened, indicating the presence of the hydrogen bonds in the molecule; 1617 cm\(^{-1}\) corresponds to the vibration of conjugate olefins; The presence of 1500 cm\(^{-1}\) and 1300 cm\(^{-1}\) is likely to vibrate for the benzene ring. By the possibility of the existence of the above functional groups shows that carbon ball retained a large number of functional groups of the glucose molecules, and glucose in the hydrolysis process may produce a certain degree of aromatization, because in the process of hydrothermal sugar molecules between intermolecular dehydration crosslinking reaction, and dehydration, carbide forming carbon-carbon bond and double bond, makes the product part, carbide purpose of preparation of carbon microspheres.

Figure 2. XRD pattern of the as-synthesized iron oxide.
Figure 3. SEM images of as-prepared iron oxide calcined at 450℃ with precursor concentration of 0.05(a), 0.1(b), 0.15(c), and 0.2 mol l⁻¹(d).

Figure 4. IR spectrum of as-prepared iron oxide (a) and the sample calcined at 450℃ (b).
3.2. XRD, SEM and IR of Fe$_2$O$_3$.

The XRD representation can understand the material and crystalline structure of the material, and figure 2 shows the X-ray powder diffraction pattern of Fe$_2$O$_3$ hollow spheres. XRD spectrum in 2 theta = 24.13°, 33.15°, 35.61°, 39.27°, 40.85°, 43.51°, 49.47°, and 54.08° appear strong characteristic peak, the peak just corresponding rhombic type hexagonal crystal characteristic diffraction peak of α-Fe$_2$O$_3$ with crystal cell parameters for a=5.036, b=5.036, c=13.749, and space group for R=3c(167)[17]. This shows that in the process of heat treatment, in addition to organic kernel has been removed, the amorphous shell under high temperature and crystallization, forming crystalline good α-Fe$_2$O$_3$ hollow sphere.

Figure 3 is a representation of the SEM electroscopy for the preparation of C/Fe$_2$O$_3$ materials for the experiment. As shown in figure 3a, the diameter of the ball is about 500 nm in diameter before the sample roasting. The surface of the sphere is coated with tiny particles of about 30 nm. After the sample is roasting, the α-Fe$_2$O$_3$ hollow ball is formed, as shown in figure 3b. Empty core ball surface there are still small particles, its relative to the unburned samples increases slightly, but the particle size distribution is more even and size between 50 ~ 80 nm, empty core ball surface can be clearly observed between small particles of porous structure. These holes make the material in the process of forming the electrode material to ensure the effective mass transfer.

Figure 4 is an infrared spectrogram for the material before and after roasting. Since the pre-calcined substance is C/Fe$_2$O$_3$, the absorption peaks in figure 4a correspond to the groups of the carbon spheres and the groups of the Fe$_2$O$_3$. Compared to figure 1b, we know that peak of 3390 cm$^{-1}$ corresponds to the absorption peak of the hydroxyl group; At the same time the carbonyl (C=O) vibration absorption peak red moved to 1706 cm$^{-1}$ and widened, indicating the presence of the hydrogen bonds in the molecule. Peak of 1614 cm$^{-1}$ corresponds to the vibration of conjugate olefins. The existence of the 1292 cm$^{-1}$ peak may be the vibration of the benzene ring skeleton. After 3 h calcination at 450 °C(Figure 4b), peaks of 559 and 479 cm$^{-1}$ correspond to Fe-O groups of α-Fe$_2$O$_3$ expansion and bending vibration characteristic peak.

3.3. Electrochemical properties of Fe$_2$O$_3$.

We tested the material for electrochemical properties. Fe$_2$O$_3$ capacitive material because more valence, such as Fe (II), Fe (III) to shift between, under a variety of current density values of Fe$_2$O$_3$ material charge and discharge performance was tested in KOH solution, as shown in figure 5. The e-t curve shows an obvious uniform symmetry, and the result shows that the charge and discharge of the Fe$_2$O$_3$ material is reversible. The quality of the sample is calculated by the following calculation: CCPS = I ∆t/(m ∆V), the ∆V/∆t in the form is calculated by the slope of the discharge curve. We have a capacitor value of Fe$_2$O$_3$ hollow sphere about 90, 107, 110, 125, 106 F g$^{-1}$ at the current density of 3.5, 2.8, 1.8, 0.7, 0.4 mA cm$^{-2}$.

![Figure 5](image-url)  
**Figure 5.** Cyclic voltammetry curves at different scan rates (a) and galvanostatic charge/discharge curves with different charge/discharge current densities (b) for the electrode.
4. Conclusions

With hard template method iron oxide hydroxide particles out of the hollow sphere, the sphere shell is composed of nanoparticles, sphere is relatively loose, the size of about 600 nm. The synthesis of hollow sphere morphology of iron oxide used in supercapacitor, in KOH electrolyte solution. Almost symmetry E-t curve shows the charge and discharge of reversible Fe₂O₃ materials. Capacitance performance of Fe₂O₃ hollow sphere material can be further improved by doping such as activated carbon for supercapacitor electrode materials.

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