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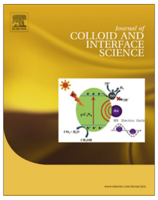

Temperature-dependent electrochemical capacitive performance of the α-Fe_2O_3 hollow nanoshuttles as supercapacitor electrodes

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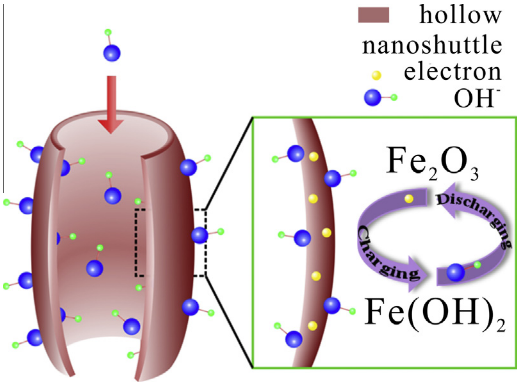
HIGHLIGHTS

- A-Fe_2O_3 have been rationally designed as supercapacitor electrode materials.
- Arrhenius-type equation was introduced to explain the charge storage mechanisms.
- The relationship between charge storage and the operating temperature was researched.

GRAPHICAL ABSTRACT



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ABSTRACT

The design and optimization of supercapacitors electrodes nanostructures are critically important since the properties of supercapacitors can be dramatically enhanced by tunable ion transport channels. Herein, we demonstrate high-performance supercapacitor electrodes materials based on α-Fe_2O_3 by rationally designing the electrode microstructure. The large solid–liquid reaction interfaces induced by hollow nanoshuttle-like structures not only provide more active sites for faradic reactions but also facilitate the diffusion of the electrolyte into electrodes. These result in the optimized electrodes with high capacitance of 249 F g^{-1} at a discharging current density of 0.5 A g^{-1} as well as good cycle stability. In addition, the relationship between charge storage and the operating temperature has been researched. The specific capacitance has no significant change when the working temperature increased from 20 °C to 60 °C (e.g. 203 F g^{-1} and 234 F g^{-1} at 20 °C and 60 °C, respectively), manifesting the electrodes can work stably in a wide temperature range. These findings here elucidate the α-Fe_2O_3 hollow nanoshuttles can be applied as a promising supercapacitor electrode material for the efficient energy storage at various potential temperatures.

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1. Introduction

With the increasing power demands of modern society and the emerging environmental concerns, it has become essential for the utilization of clean and renewable power source [1]. Many researchers have always been making study in the energy recycling and storage [2–4]. As a new class of energy storage device, supercapacitors have been extensively studied owing to their remarkable superiorities such as relatively large energy density, fast charge/discharge capability and reliable cycling stability [5,6]. According to the charge storage mechanism, supercapacitors can be classified as electrical double-layer capacitors (EDLCs) using porous carbon materials, pseudocapacitors using electroactive materials [7,8] and hybrid supercapacitor containing anode materials and cathode materials. Pseudocapacitors electrodes materials (metal oxides such as NiO, V_2O_5, $NiCoS_4$, MnO_2, Co_3O_4, and $CoMoO_4$) possess multiple accessible valence states and are commonly considered as suitable cathode materials [9–14]. However, these materials are severely restricted when served as the positive electrode materials due to the low hydrogen evolution potential in aqueous solution. Iron oxides own higher hydrogen evolution potential in aqueous solution in comparison to other metal oxides (e.g. MnO_2 or NiO), so that they can serve as the promising anode materials in asymmetrical ECs [15]. Apart from this, iron oxides have attracted much attention because of natural abundance, low cost, intrinsic safety and environmental friendliness [16].

It is well known that capacitance is associated with high electrochemical activity and the suitable structure for ionic transportation. Therefore many researches focus on tailoring Fe_2O_3 shape to improve the charge storage capacity such as nanorods, nanoparticles, cubic particles, worm-like mesoporous [16–22]. Such structures effectively shorten transmission path and accelerate ion insertion. However, there are no reports in the literature, dealing with the α-Fe_2O_3 hollow nanoshuttles as electrodes materials for supercapacitors. Besides that, the supercapacitors capacitive behaviors mainly depend on their electrodes, electrolytes and operating conditions. The influences of electrodes structures and electrolytes characteristics on the supercapacitor performance have extensively considered [23–24]. However, only few studies have been conducted regarding the potential behaviors of supercapacitors in different surroundings.

In this paper, we developed an iron oxide hollow nanoshuttles based supercapacitor electrode followed by investigating its temperature-dependent capacitance performance. The obtained products displayed excellent performance and operation stability over a wide range of working temperatures from 20 °C to 60 °C. The boosted performance highlights the important role of the thin-walled hollow nanoshuttles structure, which offers fast and efficient diffusion of the electrolyte ions into the active materials surfaces in storing and accumulating charge. Besides, the decline mechanism of the capacitance at higher discharge current density was discussed. According to the Arrhenius-type equation, the electrons could not be driven availably to leap over the higher barrier of the activation energy at the raised discharge currents. These development may trigger studies on α-Fe_2O_3 hollow nanoshuttles based supercapacitor electrodes for energy storage.

2. Experimental

2.1. Materials

Iron (III) chloride hexahydrate, sodium dihydrogenphosphate dihydrate, and sodium sulfate were obtained from Sinopharm Chemical Reagent Co. All chemicals used here were without any further simplification. Deionized water was used as solvent in all experiments.

2.2. Synthesis of α-Fe_2O_3 nanoshuttles

The hollow nanoshuttle-like α-Fe_2O_3 nanoparticles were prepared via a facile hydrothermal approach, followed by adding a solution of 0.02 M/L $FeCl_3{\cdot}6H_2O$ into a mixed solution which was consist of 5.5×10^{-4} M/L Na_2SO_4 and 2.5×10^{-4} M/L NaH_2PO_4. The resulting mixture was transferred to a Teflon-lined stainless-steel autoclave and heated at 220 °C for 24 h. The obtained solid was harvested by centrifugation, washed with water and ethanol three times, followed by drying at 50 °C overnight [25]. The working electrodes were fabricated by pressing mixtures of the as-prepared powder samples, acetylene black and polytetrafluoroethylene (PTFE) binder (weight ratio of 75:20:5) onto a nickel foam (1×1 cm^2) current collector.

2.3. Characterizations

Some α-Fe_2O_3 hollow nanoshuttles powders were pasted onto aluminum metal table with conductive adhesives for scanning electron microscopy (FESEM, FEI Quanta 3D) observations. X-ray diffraction patterns were carried out at room temperature using a Rigaku DMA-RB X-ray diffractometer with an incident X-ray beam ($\lambda = 1.5406$ Å) at 40 kV and 30 mA with Cu Ka radiation. Surface elements of electrode materials were examined by X-ray photoelectron spectroscopy (AXIS ULTRADLD), using Al Kα ($h\upsilon = 1486.6$ eV) as an exciting X-ray source. The electrochemical properties of the products were analyzed with cyclic voltammetry (CV) and charge–discharge measurements in a conventional three-electrode configuration employing an electrochemical workstation (SI 1287, Solartron Analytical). Electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 100 kHz to 10 mHz at open circuit voltage by applying a 5 mV signal. All the electrochemical measurements for electrodes were conducted in a 1 M KOH solution at room temperature.

3. Results and discussion

To realize high energy-dense supercapacitor electrodes, High-surface-area α-Fe_2O_3 hollow nanoshuttles were synthesized as supercapacitor electrodes. The formation mechanism of the nanoshuttles followed a preferential dissolution process, similar to that of hematite nanotubes. It underwent an evolution from capsule-shaped nanoparticles to short nanorods and then to hollow nanoshuttles. The detailed surface morphologies of the samples were imaged by FESEM. It could be clearly seen that the product was composed of many interconnected hollow nanoshuttle-shaped granules without aggregation (Fig. 1a), maintaining the uniform wall thickness of 30 nm and length of 100 nm respectively. Further, we performed high resolution transmission electron microscopy (HRTEM) analysis to understand the nanocrystals crystallinity. The image in Fig. 1b exhibited that the products with a lattice spacing of 0.25 nm corresponding to the (1 1 0) planes of iron oxide, verifying that the Fe_2O_3 particles with good crystallinity had been indeed produced.

The phase of the prepared-Fe_2O_3 was also determined by using powder X-ray diffraction (XRD) spectroscopy (Fig. 1c). Obviously, the peaks could be indexed to the hematite syn-Fe_2O_3 phase having a rhombo haxes structure (JCPDS Card No. 33-0664). No other peaks reflected that high-purity α-Fe_2O_3 hollow nanoshuttles were generated. The electronic structure of the α-Fe_2O_3 hollow nanoshuttles was further verified by XPS analysis. Two peaks centered at 710.8 and 724.6 eV in the high-resolution spectrum of Fe 2p (Fig. 1(d)) are related to the Fe 2p3/2 and Fe 2p1/2 spin–orbit peaks of Fe_2O_3 respectively, suggesting the Fe^{3+} ions are dominant in the product [17,21].