Chemical Engineering Journal 341 (2018) 102–111

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Tetsubo-like α-Fe_2O_3/C nanoarrays on carbon cloth as negative electrode for high-performance asymmetric supercapacitors

Dezhi Chen[a,*], Shuai Zhou[a], Hongying Quan[b,*], Ren Zou[a], Weimin Gao[a], Xubiao Luo[a], Lin Guo[c,*]

[a] Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, School of Environmental and Chemical Engineering, Nanchang Hangkong University, Nanchang 330063, China
[b] School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang 330063, China
[c] Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing 100191, China

HIGHLIGHTS

- Tetsubo-like α-Fe_2O_3/C nanoarrays on carbon cloth was prepared.
- The α-Fe_2O_3/C nanoarrays on carbon cloth can be used as free-standing electrode.
- The α-Fe_2O_3/C electrode delivered 430.8 mF cm^{-2} at a current density of 1 mA cm^{-2}.
- The asymmetric supercapacitor exhibited a high energy density of 0.56 mWh cm^{-3} in $NaSO_4$/CMC gel electrolyte.

ARTICLE INFO

Keywords:
Supercapacitor
Negative electrode
α-Fe_2O_3
Carbon cloth
Gel electrolyte

ABSTRACT

To explore novel negative electrode materials with high special capacitance for high-performance asymmetric supercapacitors, in this article, α-Fe_2O_3/C nanoarrays on carbon cloth with tetsubo-like structure was synthesized as a free-standing negative electrode for supercapacitor. The characterizations indicated that these α-Fe_2O_3/C nanoarrays are hollow structure and composed of α-Fe_2O_3 nanocrystals and carbon nanoparticles. In addition, there are plenty of mesopores existed between these α-Fe_2O_3 nanocrystals and carbon nanoparticles. Due to the hollow porous structure of α-Fe_2O_3/C nanoarrays and the presence of carbon nanoparticles not only in favor of accelerating the transport of electron and ion in α-Fe_2O_3/C electrode, but also increasing the active sites for energy storage, the as-synthesized α-Fe_2O_3/C electrode delivered much enhanced electrochemical performance including a high specific capacitance up to 430.8 mF cm^{-2} and 391.8 F g^{-1} at a current density of 1 mA cm^{-2}, good rate capability with a capacitance retention of 73.2% of capacitance retention at 10 mA cm^{-2} and great cycling stability with only 8.2% capacitance loss after 4000 cycles at a scan rate of 200 mV s^{-1}. By using α-Fe_2O_3/C as negative electrode and MnO_2 as positive electrode, an asymmetric supercapacitor was assembled to examine the electrochemical performance of α-Fe_2O_3/C in-depth. Benefit from the unique design of the α-Fe_2O_3/C electrode, the asymmetric supercapacitor exhibited a high energy density of 0.64 mWh cm^{-3} at the power density of 14.8 mW cm^{-3} in 1 M Na_2SO_4 electrolyte and 0.56 mWh cm^{-3} at the power density of 16.8 mW cm^{-3} in Na_2SO_4/CMC gel electrolyte. These satisfactory results prompt the as-fabricated hollow porous α-Fe_2O_3/C to use as a promising negative electrode material for high-performance supercapacitors.

1. Introduction

Supercapacitors have been widely concerned as one promising energy storage device for the future use in consumer electronics because of their fast charging/discharging speed, high power density, excellent circulation stability and low-cost [1]. However, compared with the battery, the relatively low energy density still seriously restricts the practical application of supercapacitors [2,3]. According to the equation of $E=\frac{1}{2}CV^2$, the enhancement of energy density (E) can be achieved by increasing the special capacitance (C) of electrode materials, enlarging the working voltage or both. For enlarging the working voltage, an effective method is to design asymmetric supercapacitors (ASCs) consisting of a negative electrode and a positive electrode, wherein the working voltage can be extended well by using the

* Corresponding authors.
E-mail addresses: chendz@nchu.edu.cn (D. Chen), quanhongying@nchu.edu.cn (H. Quan), guolin@buaa.edu.cn (L. Guo).

https://doi.org/10.1016/j.cej.2018.02.021
Received 18 November 2017; Received in revised form 20 January 2018; Accepted 5 February 2018
Available online 06 February 2018
1385-8947/

different potential windows of two electrodes, thereby significantly increasing the energy density [4,5]. Furthermore, the alternative method to enhance the capacitance of the electrodes is to construct ingenious structure with nano-sized or hybrid architectures through multi-strategies [6–13]. Therefore, enormous efforts have been devoted on the development of negative electrodes and positive electrodes possess high capacitance with novel morphologies [14–16].

Although the great progress has achieved in the research of cathodes, the achievements in high-performance negative electrodes is relatively slow, which inhibited the promotion of ASCs with high energy density. In the previous studies, carbon-based materials are the most intensively studied materials for negative electrode in ASCs due to their low cost, abundance, and high specific surface area, as well as high electronic conductivity and excellent cycling stability. However, their intrinsically low special capacitances and low energy density derived from the predominant energy storage mechanism of EDLCs are major drawbacks [17–19]. Other kinds of negative electrode materials, such as metal oxides/hydroxides and conductive polymers possess higher capacitance and energy densities than carbon-based materials, owing to their capacitance mainly rely on a pseudocapacitive charge-storage mechanism. Therefore, many efforts in the field have been devoted to developing pseudocapacitive negative electrode material with high special capacitance and high energy density [20,21]. Among those negative electrode materials, α-Fe_2O_3 particularly attracted extensive attention as prospective candidate due to their remarkable merit of earth-abundance, environment compatibility, stable crystal structure high theoretical capacitance, and wide negative working potential [4,20,22,23]. However, α-Fe_2O_3 suffers from the drawback of poor conductivity, which causes inferior capacitance performance especially the rate capability and power density, and severely suppressed the application of α-Fe_2O_3 as negative electrodes for high-performance ASCs [4,23]. Therefore, it is very meaningful to improve the electrochemical performance of α-Fe_2O_3 from the viewpoint of enhancing the intrinsic electronic conductivity of α-Fe_2O_3, and explore novel α-Fe_2O_3-based electrodes with accessible area to the electrolyte and short transport path for ions and electrons for high-performance ASCs.

Inspired by the remarkable achievement in nanoscience and nanotechnology, various kinds of α-Fe_2O_3 with nano-sized morphologies were designed, which offer notably improvement in terms of the utilization of active materials. Recently, the fabrication of α-Fe_2O_3 nano/micro-structures directly grown on current collector could effectively improve conductivity and accelerate ion diffusion, resulting in high storage capability. Mai and Wang et al. [20] reported amorphous α-Fe_2O_3 nanotubes grown on flexible carbon fabric for the first time. When the flexible materials used as negative electrode and α-MnO_2 nanowires grown on carbon fabric as positive electrode, the assembled novel flexible ASC device exhibited a high energy density of 0.55 mWh cm^{-3} and good rate capability in the extended operating voltage window of 1.6 V. In addition, constructing α-Fe_2O_3 hierarchical nano/microstructures combined with conductive materials is considered a very promising approach to further improve the electronic conductivities of α-Fe_2O_3 negative electrode. For example, α-Fe_2O_3 nanoneedles on ultrafine nickel nanotube arrays (NiNTAs@Fe_2O_3) were fabricated on the Ti foil by Xu and Xia et al. [4]. The as-fabricated NiNTAs@Fe_2O_3 negative electrode possessed a highly capacitance (418.7 F g^{-1} at 10 mV s^{-1}), matching well with the similarly built NiNTAs@MnO_2 nanosheet positive electrode, and the ASCs exhibited an excellent maximum energy density of 34.1 Wh kg^{-1} at the power density of 3197.7 W kg^{-1} in aqueous electrolyte and 32.2 Wh kg^{-1} at the power density of 3199.5 W kg^{-1} in quasi-solid-state gel electrolyte. Lu et al. [24] prepared the α-Fe_2O_3@PANI core–shell nanowire arrays on carbon cloth, and the fabricated ASCs displayed a high volumetric capacitance of 2.02 mF cm^{-3}, a high energy density of 0.35 mWh cm^{-3} at a power density of 120.51 mW cm^{-3}, and good cycling stability. Hu et al. [23] constructed hierarchical tectorum-like α-Fe_2O_3@PPy nanoarrays on carbon cloth, which exhibited a high areal capacitance of 382.4 mF cm^{-2} at a current density of 0.5 mA cm^{-2} and excellent reversibility. The solid-state asymmetric supercapacitor consisting of α-Fe_2O_3@PPy NAs and MnO_2 electrodes achieves a high energy density of 0.22 mWh cm^{-3} at a power density of 165.6 mW cm^{-3}. Despite all these achievements, the facile scalable fabrication of high-performance α-Fe_2O_3 negative electrode for ASCs remains a challenge. To improve the conductivity and built fast electron and ion pathways simultaneously, herein, we developed a novel strategy to prepare tetsubo-like α-Fe_2O_3/C nanoarrays on carbon cloth as a free-standing negative electrode in this work, and the α-Fe_2O_3/C nanoarray was hollow and composed of α-Fe_2O_3 nanocrystals and carbon nanoparticles. The as-synthesized hollow α-Fe_2O_3/C nanoarrays presented a high capacitance of 430.8 mF cm^{-2} and 391.8 F g^{-1} (based on the mass of α-Fe_2O_3/C) at a current density of 1 mA cm^{-2}. By using α-Fe_2O_3/C nanoarrays as the negative electrode and MnO_2 as the positive electrode, a flexible asymmetric supercapacitor was fabricated and showed a high energy density of 0.64 mWh cm^{-3} at the power density of 14.8 mW cm^{-3} in aqueous electrolyte and 0.56 mWh cm^{-3} at the power density of 16.8 mW cm^{-3} in solid-state gel electrolyte. The impressive results indicated that the synthesized α-Fe_2O_3/C is a promising negative electrode material for high-performance supercapacitors.

2. Experiment section

2.1. Synthesis of the α-Fe_2O_3/C nanoarrays on carbon cloth

First, core–shell ZnO@ZIF-8 nanoarrays were grown on carbon cloth (WOS1002, 4 cm × 4 cm, 12.5 mg cm^{-2}) using a reported method [10]. In a typical experiment, 0.3920 g of $Zn(NO_3)_2{\cdot}6H_2O$, 0.1838 g of HMTA and 2 mL of ammonia were dissolved in 70 mL distilled water under continually magnetic stirring for 30 min. Then the obtained homogeneous solution was transferred into the 100 mL autoclave liners and the carbon cloth was vertically immersed into the reaction solution and keeping sealed under 90 °C for 24 h. After the reaction, the carbon cloth coated with a white product was washed by deionized water and ethanol for several times and obtained the ZnO nanoarrays on carbon cloth. Then, the obtained carbon cloth coated with ZnO nanoarrays was transfer into a 25 mL Teflon-lined stainless-steel autoclave containing a mixed solvent of DMF/H_2O (16 mL, 3:1 of v/v) with 2-methylimidazole (0.1642 g, 2.0 mmol), and keep sealed under 70 °C for 24 h, the white product of core–shell ZnO@ZIF-8 nanoarrays on carbon cloth was collected and washed by fresh DMF and ethanol for several times, and then the ZnO@ZIF-8 nanoarrays were annealed at 650 °C in N_2 gas for 2 h to prepare ZnO@ZnO/C nanoarrays. Finally, the ZnO@ZnO/C nanoarrays on carbon cloth were placed into a 50 mL of aqueous solution containing 0.3 g of $Fe(NO_3)_3{\cdot}9H_2O$ and kept at room temperature for 2 h. After the complete reaction, the sample was taken out, and drying naturally, followed by annealed at 400 °C in air atmosphere for 30 min to obtain the final product of α-Fe_2O_3/C nanoarrays on carbon cloth. The loading mass of α-Fe_2O_3/C nanoarrays is about 1.1 mg cm^{-2}. For comparison, bare hollow α-Fe_2O_3 nanoarrays on carbon cloth was fabricated by the same method without ZIF-8, and the loading mass of bare α-Fe_2O_3 nanoarrays is about 1.3 mg cm^{-2}.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) operating at 40 mA and 40 kV. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were obtained using Quanta-450 field-emission scanning electron microscopy and JEM 2100 transmission electron microscopy, respectively. Scanning transmission electron microscope (STEM) and the corresponding EDX mapping images were obtained on a FEI Talos F200X transmission electron microscopy. The specific surface areas and pore size distributions were studied by nitrogen adsorption-desorption isotherms, which were obtained on a