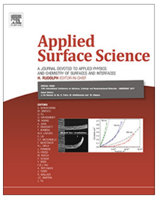
Applied Surface Science 450 (2018) 66–76

Contents lists available at ScienceDirect

Applied Surface Science

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



Full Length Article

Facilely prepared oxidized carbon Fiber@Co_3O_4@RGO as negative electrode for a novel asymmetric supercapacitor with high areal energy and power density

Weigang Wang, Yajun Liu, Mingqian Wang, Guohong Ren, Shishan Wu *, Jian Shen *

School of Chemistry and Chemical Engineering, Nanjing University, 163 Xianlin Avenue, Qixia District, Nanjing 210023, PR China

ARTICLE INFO

Article history:
Received 28 December 2017
Revised 27 February 2018
Accepted 9 April 2018
Available online 18 April 2018

Keywords:
Co_3O_4
RGO
Mutil-layer structure
Asymmetric supercapacitors

ABSTRACT

Supercapacitors, a promising kind of energy storage and transfer device for filling the gaps between traditional capacitors and lithium-ion batteries, are widely studied and used recently. A novel asymmetric supercapacitor was fabricated assembling Co_3O_4@RGO layer covered oxidized carbon fiber (OCF) and a mutil-layer OCF@Au@MnO_2@PIn electrode. The multi-layer structure of these electrodes and the synergistic effects among each component were confirmed and guaranteed outstanding electrochemical performances. This novel supercapacitor shows excellent electrochemical performances with a high areal energy density of 1.83 mWh cm^{-2} at an areal power density of 3.2 mW cm^{-2} and long cycling life of 91.75% capacitance retention after 5000 cycles. Thus, this kind of portable supercapacitor with high performances not only might be used commercially but also provides a strategy for designing high-performance electrodes for supercapacitors.

1. Introduction

An emerging kind of energy convert and storage device called supercapacitors (SCs) meets the great demands of developing renewable and sustainable electronic devices to mitigate the increasing energy problems, such as energy shortage and energy waste [1–3]. Supercapacitors possess the properties of high power density, outstanding cycling life, excellent rate capability and safety [4–6]. However, the relatively lower energy density of supercapacitors than commercialized batteries restricts the broader practical use of them in energy storage devices [7–9]. Therefore, intensive efforts have been committed to improving the energy density of SCs, including constructing nanostructured materials with high electrocapacitive performances as well as assembling supercapacitors with asymmetric electrodes (ASCs) [10,11]. Both of the methods could effectively improve the energy density of supercapacitances according to the formula of $E = 0.5CV^2$. Because nanostructured materials with high specific area and numerous active positions could achieve a high specific capacitance (C) and the ASCs usually hold a higher operation potential window (V) than symmetric supercapacitors [12,13]. Nowadays, materials composed of transition metal oxides, conductive polymers and carbonous materials could provide high power density and energy density simultaneously, and they are widely applied in high-performance supercapacitors [14,15].

Transition metal oxides like MnO_2, V_2O_5 and Co_3O_4 are extensively researched as faradaic pseudocapacitance electrode materials for high-performance supercapacitors due to their ultra-high theoretical storage capacity and outstanding redox reversibility in different electrolytes which are beneficial for providing high energy density. Among them, MnO_2 and Co_3O_4 show extremely high theoretical specific capacitance value of 1370 F g^{-1} and 3560 F g^{-1} respectively [16–18]. As reported, MnO_2 is environmentally friendly, low-cost and naturally abundant [19]. Notably, amorphous MnO_2 materials used in neutral aqueous based electrolyte like KCl solution show pseudocapacitive natures [20]. However, MnO_2 is typical positive electrode for KOH based batteries due to the complicated faradic reactions [21]. And Co_3O_4 with different structures, such as nanotube, nanopetal and nanosphere, could be synthesized via simple, controllable and reliable hydrothermal methods [22]. The spaces between those nanostructures could promote the diffusion of ions and electrolyte as well as increase the contact area between materials and electrolyte, which is beneficial for high electrochemical performances. Unfortunately, not only the poor electrical conductivity but also the structural instability of Co_3O_4 and MnO_2 could lead to the deviation of theirs practical specific capacitance from theoretical value, hindering the applications of pure nanostructured Co_3O_4 and MnO_2 in high-performance supercapacitors [23,24].

---

* Corresponding authors.
E-mail addresses: shishanwu@nju.edu.cn (S. Wu), 57jshen@nju.edu.cn (J. Shen).

https://doi.org/10.1016/j.apsusc.2018.04.092

To handle these problems, the electrodes fabricated by binder-free method like growing active materials on flexible and stable conductive substrates were researched [25,26]. Carbon cloth (CC) consisted of carbon fibers is regarded as a kind of prospective current collector and substrate for growing active materials because of its superior flexibility, light weight and excellent conductivity [27]. Moreover, the loose and cribriform structure of CC could effectively provide massive channels for ion diffusion and high contact area between the surface of materials and electrolyte. Furthermore, coating a layer of conductive polymer or carbonous material on the surface of transition metal oxides is another effective way to improve their performances and stability for the modified layer could not only prevent the degradation of metal oxides but also enhance the conductivity of them [28,29]. According to recent reports, polyindole (PIn) is a promising conductive polymer because of its high electric conductivity, excellent redox reversibility and superior thermal as well as structural stability [30].

In this work, CC was pre-treated by oxidation processes before used, and the product is called oxidized carbon fiber (OCF). MnO_2 and Co_3O_4 were grown onto the surface of OCF compactly by electrodeposition and solvothermal method respectively. Then a conductive polymer (PIn) shell covered OCF@Au@MnO_2 electrode was synthesized and used as the positive electrode for asymmetric supercapacitor while a RGO layer coated OCF@Co_3O_4 electrode was fabricated and used as the negative electrode. The electrochemical performances of OCF@Au@MnO_2@PIn and OCF@Co_3O_4@RGO electrodes and the fabricated asymmetric supercapacitor were investigated by various electrochemical methods and the superior results indicate that those electrodes cloud have broad applications in energy storage devices.

2. Experimental sections

2.1. Materials

CC was purchased from Hesen Co., Ltd (Shanghai, 160 g m^{-2}, the thickness is 360 μm). Indole monomer (Indole, AR), potassium permanganate ($KMnO_4$, AR), ammonium persulfate ($(NH_4)_2S_2O_8$, AR), manganese acetate tetrahydrate ($MnC_4H_6O_4{\cdot}4H_2O$, AR), sodium sulfate anhydrous (Na_2SO_4, AR), poly(vinylalcohol) (PVA, M_w=85000), concentrated nitric acid (HNO_3, 65%), concentrated sulfuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30%), graphite powder and cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, AR) were all procured from Sinopharm Chemical Reagent Co. (China). Furthermore, deionized water (DI) and analytical-grade chemicals were used for all synthesized processes without further purification.

2.2. Synthesis of oxidized carbon fiber (OCF)

The CC was pre-treated by oxidation processes before used as a substrate. Typically, CC was washed by ethanol, acetone and water in sequence to get rid of the hydrophobic and hydrophilic impurity. Afterwards, the cleaned CC (1 cm × 3 cm) was stirred in a mixed acid, which contains 20 mL concentrated HNO_3 and 30 mL concentrated H_2SO_4, at room temperature for 1 h. Then, 3 g $KMnO_4$ powder was added into the mixed acid slowly, keeping stirring for another 1 h at 35 °C. Subsequently, 100 mL of water was added into the solution and stirred for 3 h at 35 °C. In order to further oxidize the carbon cloth and remove the unreacted $KMnO_4$, H_2O_2 solution (30%) was added into the mixed solution until it became clear and no gas bubble produced. Finally, the obtained carbon cloth was cleaned with distilled water for several times and dried at 120 °C under air condition.

2.3. Synthesis of OCF@Co_3O_4@RGO electrode

The obtained OCF was soaked into 0.1 M $Co(NO_3)_2{\cdot}6H_2O$ ethanol solution and the Co_3O_4 shell was formed by solvothermal method under 140 °C for 12 h. Then the acquired OCF@Co_3O_4 was washed carefully by water and dried at 120 °C before it is used. Afterwards, the washed and dried OCF@Co_3O_4 electrodes were soaked in GO (20 mg/mL) aqueous solution, synthesized by a modified Hummer's method [31], to coat the Co_3O_4 architecture with GO sheets. Finally, the GO was reduced into RGO and the Co_3O_4 was activated simultaneously at different temperatures (300 °C, 400 °C, 500 °C and 600 °C) for 2 h under argon gas flow in a tubular furnace. Furthermore, the CV curves of OCF@Co_3O_4@RGO electrodes obtained at different temperatures are presented in Fig. S1b, where the electrode annealed at 500 °C shows a biggest closed curve. Thus, all the OCF@Co_3O_4@RGO and OCF@Co_3O_4 electrodes mentioned in the next content stand for the electrodes annealed at 500 °C.

2.4. Synthesis of OCF@Au@MnO_2@PIn electrode

Firstly, a thin layer of gold nanoparticles was deposited onto the surface of OCF using a sputter (model) with a current of 15 mA for 200 s. Then, the MnO_2 layer was wrapped onto the surface of OCF@Au fiber by electrodeposition method, where the OCF@Au electrode, a Pt foil (1 cm × 1 cm) and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively, and immersed in 0.1 M $MnAc_2$ and 0.1 M Na_2SO_4 aqueous solution with a constant potential of 1 V for different times (300 s, 900 s, 1800 s, 2700 s and 3600 s). The electrodeposition time of 2700 s was chosen as the optimal condition according to the results shown in Fig. S1a, where the OCF@Au@MnO_2 electrode synthesized by electrodepositing for 2700 s shows the biggest enclosed area with a relatively short time. And all the mentioned OCF@Au@MnO_2 electrode in the next content represent the electrode electrodeposited for 2700 s. Secondly, the washed and dried OCF@Au@MnO_2 electrodes were added into 20 mL ethanol solution, containing 40 mg indole monomer, and slowly stirred for 30 min. Then, 60 mL distilled water was added into the solution, keeping stirring for another 30 min. Subsequently, 20 mL initiator solution, containing 77.92 mg $(NH_4)_2S_2O_8$, was added to the mixed solution dropwise in 10 min and the whole solution continuously stirred for 12 h at 35 °C to complete the in-suit polymerization of indole monomer. Finally, the obtained OCF@Au@MnO_2@PIn electrodes were washed by water as well as ethanol for several times and dried at 120 °C in oven.

2.5. Fabrication of asymmetric supercapacitors (ASC)

KOH/PVA gel electrolyte was prepared at first by adding 6 g PVA into 60 mL KOH (4.5 g) aqueous solution, which was heated at 90 °C with vigorous stirring until the solution became homogenous gel. Subsequently, a supercapacitor was assembled by OCF@Au@MnO_2@PIn and OCF@Co_3O_4@RGO electrode with a nylon filter membrane (pore size = 0.22 μm) saturated KOH/PVA gel, which were used as the positive, negative electrode and separator, respectively. All the fabrication processes of OCF@Au@MnO_2@PIn// OCF@Co_3O_4@RGO ASC are illustrated in Fig. 1 directly and clearly. Furthermore, the photograph of prepared OCF@Au, OCF@Au@MnO_2@PIn, OCF@Co_3O_4, OCF@Co_3O_4@RGO electrodes and asymmetric supercapacitor are presented in Fig. S2.

2.6. Characterization

The morphologies and structures of the prepared electrodes were observed and recorded by scanning electron microscope