



Graphene-cerium oxide/porous polyaniline composite as a novel electrode material for supercapacitor

Aijuan Xie, Feng Tao, Tie Li, Lu Wang, Sujie Chen, Shiping Luo*, Chao Yao

School of Petrochemical Engineering, Changzhou University, Changzhou 213164, PR China



ARTICLE INFO

Article history:

Received 30 October 2017

Received in revised form

8 December 2017

Accepted 26 December 2017

Available online 28 December 2017

Keywords:

Graphene

Cerium oxide

Porous polyaniline

Electrochemistry

ABSTRACT

In this study, a novel ternary nanocomposite, graphene-cerium oxide/porous polyaniline (rGO-CeO₂/porous PANI), was synthesized via in situ polymerization and electrochemical reduction methods. A series of characterization such as SEM, XRD, and FTIR for the as-prepared composites proved that the ternary nanocomposite with well-connected nanosheets and porous structure has been successfully synthesized. The electrochemical performance testing illustrated that the electrochemical capacitance of rGO-CeO₂/porous PANI nanocomposite could reach 454.8 F g⁻¹ at 1.0 A g⁻¹ when the mass ratio of CeO₂ and porous PANI was 1:4. And the specific capacitance retained 70.23% after 10000 cycles at a current density of 5.0 A g⁻¹ in 1.0 mol L⁻¹ H₂SO₄ electrolyte. In comparison to the other nanomaterials, the excellent electrochemical performance of rGO-CeO₂/porous PANI nanocomposite is attributed to good electrical conductivity and large specific surface area brought from graphene and porous PANI, energy density and better cycle life derived from CeO₂, and synergetic contribution among the three components. Thus, the rGO-CeO₂/porous PANI nanocomposite is a promising electrode material for supercapacitor.

© 2017 Published by Elsevier Ltd.

1. Introduction

In recent years, the development of recyclable and sustainable clean energy and environmentally friendly energy conversion and storage devices is one of the research hotspots. Supercapacitors are typical electrochemical storage devices available for advanced storage applications and energy conversion [1–3]. It has attracted considerable attention due to its good cycling performance and high power density, and so it has become potential applications in a variety of technologies such as portable devices, cellular phones, and hybrid electric vehicles [4–6]. The development of electrode materials is the main research about supercapacitors [4]. Current electrode materials include carbon materials (such as graphene [7] and carbon nanotubes (CNTs) [8]), metal oxides (such as MnO₂ [9], V₂O₅ [10]) and conducting polymers (such as polyaniline (PANI) [11], polypyrrole [12,13]). Graphene has been regarded as one of the best candidates for flexible electrode materials because of its many special performances such as good conductivity, excellent flexibility, and high accessible surface area [14–17]. However, the

graphene is facile agglomeration on account of strong π - π interactions between individual graphene sheets, and the specific capacitance of graphene-based materials is lower than that of the anticipated application [18,19]. Therefore, in order to overcome these defects, the graphene sheet has been combined with transition metal oxides or conductive polymers to prevent restacking of the sheets.

The metal oxides have been extensively used in supercapacitors due to the higher energy density and better cycle life than carbon materials and conducting polymers [13,20]. Nowadays, many metal oxides such as CeO₂, NiO, and La₂O₃ have been employed to increase electrocatalytic activity [21–23], in which CeO₂ has received remarkable attention because its cations can switch between +3 and +4 oxidation states and it can act as an oxygen buffer due to the ability of releasing oxygen reversibly of CeO₂ [24]. Nevertheless, the inherently poor electrical conductivity brought from CeO₂ can lead to insufficient capacitance and a big contact resistance [25]. One of the effective solutions is loading CeO₂ on highly conductive conducting polymer to improve its conductivity [13]. Among the various conducting polymers, PANI has the advantage of being coated easily by other materials and is frequently used as an electrode material due to the ease of polymerization in aqueous media, excellent specific capacitance, and low resistance [24,26]. However,

* Corresponding author.

E-mail address: shiping_luo@163.com (S. Luo).

the main drawback of using PANI as an electrode material for supercapacitor is its poor cycling stability [4,6]. Hence dispersing metal oxide into PANI particles and further combined with graphene is an attractive method to prepare graphene based ternary composite electrocatalysts [24]. The synergetic effect between graphene and transition metal oxides or conducting polymers can effectively enhance electrochemical performance [27–31]. To our knowledge, there are few reports on the graphene-based ternary composite using as supercapacitors. Consequently, in this research, porous PANI was first prepared by removing the attapulgite template due to the fact that porous PANI has better electrochemical performance than PANI based on our previous research [32]. Then the ternary rGO-CeO₂/porous PANI was obtained by ultrasonic mixing and electrochemical reduction methods. A series of characterization and electrochemical performance testing were carried out for the as-prepared composites. The research results revealed that the rGO-CeO₂/porous PANI exhibited better electrochemical performance than the other composites. Thus, the rGO-CeO₂/porous PANI composite as an electrode material for supercapacitors has a great future.

2. Experimental section

2.1. Material and sample preparation

All chemicals and reagents were analytical grade and were used without further purification before the synthesized process. Deionized water was used to prepare all the solutions. Graphene oxide (GO) suspension was synthesized from flake graphite (Linfeng Chemical Reagent Co., Ltd. (Shanghai, China)) by a modified Hummers method [33]. Porous PANI was prepared following the earlier work reported by our group [32]. CeO₂ nanoparticles were prepared according to the procedure adopted by Yang et al. [34]. Concisely, 3.0 mg mL⁻¹ (15 mL) urea and 0.2 mg mL⁻¹ (20 mL) cerium nitrate Ce(NO₃)₃·6H₂O was mixed under vigorous stirring, and the pH value of the solution was adjusted to 8–9 by ammonia water, then reacted at 80 °C for 2 h and aged at room temperature for 12 h. The resulting sediment was filtered and washed repeatedly with absolute ethanol and distilled water, then dried at 60 °C for 5 h followed by calcining at 400 °C for 1 h, thereupon CeO₂ nanoparticles were obtained. Next, different mass ratios of CeO₂/porous PANI were mixed together and sonicated for 2 h. 10 μL of 1.0 mg mL⁻¹ dispersion solution of CeO₂/porous PANI was dropped on the glassy carbon electrode (GCE) and then dried in air. Finally, 10 μL of 1.0 mg mL⁻¹ GO dispersion solution was overlaid onto the CeO₂/porous PANI modified electrode and dried again. The resulting composite modified electrode was reduced in 0.5 mol L⁻¹ H₂SO₄ about 10 min within potential window ranging from -1.4 to 0 V to obtain rGO-CeO₂/porous PANI. For comparison, graphene, porous PANI, and CeO₂/porous PANI modified GCE were also prepared by the same procedures as rGO-CeO₂/porous PANI. The whole fabrication process was depicted in Scheme 1.

2.2. Characterizations and electrochemical measurements

The isothermal N₂ adsorption/desorption of materials were measured at 77 K using Micromeritics Adsorption Instrument (ASAP2010, Micromeritics, American), and the pore volume was obtained from the N₂ desorption isotherm using Barrett–Joyner–Halenda (BJH) equations. Scanning electron microscope (SEM) images were acquired via a scanning electron microscope (JSM-6360LA, JEOL, Japan). Transmission electron microscopy (TEM) was performed with a transmission electron microscope working at 200 kV (JEM-2100, JEOL, Japan). X-ray diffraction (XRD) was carried out with an X-ray diffractometer with

Cu Kα radiation (D/Max 2500 PC, Rigaku Corporation, Japan). The fourier transform infrared spectroscopy (FTIR) spectrum was acquired using fourier infrared spectrometer (FTIR-8400S, Shimadzu, Japan). The conductivity of the materials was measured with a model SZT-2A four-probe instrument (Suzhou, China).

All electrochemical experiments were performed in a standard three electrode system using the CHI 660E electrochemical workstation (Huake 101 Putian Instrumental Co., Beijing, China). Solutions were freshly prepared before each experiment. A platinum foil (3.0 cm²) was used as the counter electrode, and the as-prepared nanomaterials as the working electrode. All the potentials were measured versus a saturated calomel electrode (SCE, 0.241 V versus RHE) electrode. The specific capacitance is obtained according to the following equation: $C_s = (I\Delta t) / (\Delta V m)$, where C_s is the specific capacitance (F g⁻¹), I is the constant discharge current (A), Δt is the discharge time (s), ΔV is charge voltage range, and m is the mass of the active materials of the electrode (g) [35].

3. Results and discussion

3.1. Characterization

3.1.1. BET analysis

For purpose of verifying the porosity and surface area of as-prepared porous PANI, the N₂ adsorption isotherms of porous PANI and PANI are displayed in Fig. 1. According to the IUPAC classification [36], the adsorption isotherms are typical IV curves with H1 type hysteresis loop, indicating the existence of a well-defined mesoporous structure of porous PANI. The desorption and adsorption isotherm of porous PANI has a larger hysteresis loop relative to PANI, implying there are rich pores in porous PANI but few in PANI. Meanwhile, the pore size distribution is illustrated in inset of Fig. 1. As can be seen, the pore diameters are concentrated in the range of 5–30 nm especially around 12.8 nm. Furthermore, the specific surfaces of porous PANI and PANI are 19.0 and 3.4 m² g⁻¹, respectively. It is evident that porous PANI has more mesopores and larger specific surface by contrast to pristine PANI, which is beneficial to the electrical conductivity of nanocomposites.

3.1.2. Morphology characterizations

SEM image was used to investigate the surface morphology of nanocomposites and the results were displayed in Fig. 2. It is very evident that CeO₂ (Fig. 2A) exhibits random nanoparticle shapes with size varying from tens of nanometers to hundreds of nanometers. Compared with pure PANI with bulk and smooth-faced nanoparticles in Fig. 2B, a relatively rough surface and abundant pore channels can be observed from porous PANI in Fig. 2C. Fractional nanoparticles are dispersed on the framework of the porous structure. Additionally, the three-dimensional net structure with more solid sense can be further observed, which offers many advantages as an electrode material for the electrocatalysts [24]. A typical morphology of graphene is presented in Fig. 2D, a good ultra-thin nanosheets with several nanometers in thickness is clear and distinct. The corrugated and curly nanosheets are well-connected and it is beneficial to the close combination of nanomaterials. Meanwhile, it can be noted that the CeO₂ nanoparticles cover irregularly on the both inside and outside of porous PANI by comparing Fig. 2E and C. Adjacent nanoparticles are stacked together to form agglomerates. Furthermore, a perfect combination among porous PANI, CeO₂, and rGO can be noticed in Fig. 2F, and the more clear image of rGO-CeO₂/porous PANI can be noticed in TEM image (Fig. 2G), where the rich pore, tiny nanoparticles and well-connected rGO-nanosheets are clearly visible and uniform distribution without agglomeration to form relatively regular porous-nanosheets feature, which helps the transmission of electrons.

Download English Version:

<https://daneshyari.com/en/article/6604628>

Download Persian Version:

<https://daneshyari.com/article/6604628>

[Daneshyari.com](https://daneshyari.com)