Electrochimica Acta 272 (2018) 77–87

Contents lists available at ScienceDirect

Electrochimica Acta

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

Construction of layer-by-layer sandwiched graphene/polyaniline nanorods/carbon nanotubes heterostructures for high performance supercapacitors

Panbo Liu[*], Jing Yan, Xiaogang Gao, Ying Huang[**], Yiqing Zhang

MOE Key Laboratory of Material Physics and Chemistry Under Extrodinary Conditions, School of Science, Northwestern Polytechnical University, Xi'an 710129, China

ARTICLE INFO

Article history:
Received 26 February 2018
Received in revised form
14 March 2018
Accepted 31 March 2018
Available online 2 April 2018

Keywords:
Layer-by-layer heterostructures
Carbon materials
Polymer
Supercapacitors electrodes

ABSTRACT

Integrating polyaniline (PANI) with different dimensional carbon materials is considered as a promising strategy to solve the disadvantages of PANI electrodes, such as low rate capability and poor cyclic stability. In this work, a novel layer-by-layer sandwiched graphene/PANI nanorods/carbon nanotubes (G/PANI/CNTs) heterostructure has been synthesized. The morphology of the heterostructures has been characterized by XRD, Raman spectroscopy, N_2 adsorption-desorption, XPS, FESEM and TEM. The obtained new layer-by-layer sandwiched heterostructures exhibit intimate interface contacts, fully network-structured CNTs coating, dual physical supports and synergistic effects, which can effective host the electrochemical properties of PANI with the electrolyte and restrain the volumetric changes of PANI. As a result, the electrodes exhibit high specific capacitance (638 $F\,g^{-1}$ at 0.5 $A\,g^{-1}$), good rate capability (88.2% retention from 0.5 $A\,g^{-1}$ to 10 $A\,g^{-1}$) and long cycle stability (93% of the initial specific capacitance after 2000 cycles) when the amount of CNTs is 2 mg. Moreover, a possible mechanism for good performance of the layer-by-layer sandwiched heterostructures has been systematically studied. We believe that this strategy will open up an avenue for the rational design of sandwich structured electrodes for high performance supercapacitors and other electronic devices.

1. Introduction

Supercapacitors, known as electrochemical capacitors, have attracted wide attention as one of the most important energy storage devices over the past decades due to the high power supply (>10 $kW\,kg^{-1}$), long cycle life (>100,000 cycles) and high dynamics of charge propagation (within seconds) [1]. According to the mechanism, supercapacitors can be classified into two categories, electrical double layer capacitors and pseudocapacitors. Generally speaking, electrical double layer capacitors contain carbon materials with good electrical conductivity, in which the capacitive (non-faradic) develops from the pure electrostatic charges accumulated at the interface between the electrodes and the electrolytes [2–4]. Contrarily, pseudocapacitors include conducting polymers [5] and transition metal oxides [6–8], where the capacitive (faradic) relies on the reversible redox or Faradic charge-transfer reactions at or near the surface of the electrodes. As we known, the performance of supercapacitors is highly dependent on the electrode materials. Despite many significant advances have been achieved, some shortcomings, such as low specific capacitance in carbon materials, poor cycling stability and rate capability in conducting polymers, and low electrical conductivity in metal oxides, still limit their practical applications.

Polyaniline (PANI) is one of the most widely use electrode materials for supercapacitors because of the distinctive features, such as low manufacturing costs, facile synthesis, good environmental stability and high theoretical specific capacitance [9]. However, the practical application of single-phased PANI electrodes are limited by the low rate capability (the accompanied diminution of the electrical conductivity decay) and poor cycling stability (the large volumetric changes during the continuous charge-discharge processes, such as swelling, breaking and shrinkage). In order to address the above mentioned drawbacks, considerable achievements have been devoted to enhance the electrochemical

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: liupanbo@nwpu.edu.cn (P. Liu), yingh@nwpu.edu.cn (Y. Huang).

https://doi.org/10.1016/j.electacta.2018.03.198

performance of single-phased PANI electrodes by combining PANI with carbon materials, such as porous carbon [10,11], carbon fibers [12,13], carbon nanotubes [14,15] and graphene [16–18]. Among these carbon materials, graphene has been considered as one of the promising candidates due to its low costs, large surface area, superior mechanical property and relativity wide potential window [19]. For example, Wang et al. reported the first research on flexible graphene/PANI composite paper, the electrodes showed excellent flexibility and a stable specific capacitance of 233 F g^{-1} without apparent degradation over 1500 cycles [20]. However, the capacitance of the composite paper was mainly dominated by the pseudocapacitance of PANI, and the large surface area of graphene paper cannot be fully utilized due to the irreversible agglomerated layer structure and insufficient ion/electron transport, thus a low specific capacitance fading over cycling or at high rates was observed. In order to increase the capacitive performance, nanostructured PANI arrays covered on the surface of graphene should be considered, especially PANI nanostructures with ordered or aligned arrays, which can shorten diffusion pathway of the electrolyte ions for enhanced Faradic charge-transfer reactions and ensure high utilization of the active materials than the bulk materials [21–26]. Besides, the simultaneous achievement of both high specific capacitance and good rate capability can be realized by rational design of the electrode materials into desired architectures. Generally speaking, PANI nanostructures with ordered/aligned arrays on graphene sheets can be achieved by chemical polymerization or electrochemical polymerization of aniline in the presence of pre-prepared graphene sheets. A typical example is that highly-oriented PANI nanothorn arrays anchored on graphene by an in-situ polymerization, the electrodes delivered enhanced specific capacitance (595 F g^{-1} at 0.5 A g^{-1}) and good rate capability due to the large surface area, aligned PANI arrays and special 3D structures [23]. Except for layer structured graphene sheets, holey graphene framework is a new structure with a wide range of potential application in electrode materials. If PANI nanorod arrays coated on graphene nanomesh, the ultra-thin 2D planar structure together with the additional in-plane ionic channels can substantially accelerate the ions kinetics, thus making the electrodes for high rate capability [27].

Except for the above mentioned factors, the electrical conductivity is another important parameter to meet fast electron transport for the high rate redox reaction of PANI, but most of the reported graphene prepared by oxidation-reduction method usually results in low electrical conductivity, then wastes energy on unwanted inner resistance. The addition of carbon nanotubes (CNTs) into graphene-PANI is quite well acknowledge, that is, to improve the rate capability and cycling stability. The presence of CNTs not only provides open network structure to physically separate graphene sheets, but also acts as a “highway” for electron transport along the longitude direction and serves a crucial role in determining the ability of the electrolyte ions to access the entire structure, consequently, enhancing the electrochemical performance. In the past decades, the ternary composites can be designed or constructed by the physical mixing the solution of PANI-CNTs with graphene [28] or polymerization of aniline monomers in the presence of graphene-CNTs [29–34]. In the former one, the direct connection between different CNTs coated with a PANI layer is overlapped junctions by PANI-PANI contacts and not continuous, then electrons have to be transported through the overlapped contact, resulting in a relatively high contact resistance. In the second case, PANI anchored on a conductive network, such as physical mixing graphene and CNTs [31–33] or CNTs bonded on graphene [34], is beneficial for improving the electrochemical performance of the electrodes, but the performance, especially rate capability, is still unsatisfactory because the transfer of electrolyte ions to the surface of CNTs has been restricted to a certain degree. It is demonstrated that the layer-by-layer sandwiched graphene/PANI nanorods/carbon nanotubes heterostructures is an effective strategy to enhance the intimate interface contacts [35] and the dual effective interactions between the π-bonds of the aromatic rings of PANI and different dimensional carbon materials will effectively facilitate the electron transfer [36], and up to now, these sandwiched heterostructures have not been reported.

Inspired by the above thoughts, in this work, we reported a facile and low cost strategy to synthesize graphene/PANI nanorods/carbon nanotubes (G/PANI/CNTs) with layer-by-layer sandwiched heterostructures. The heterostructures exhibit intimate interface contacts between PANI and different dimensional carbon materials, fully network-structured CNTs coating, and strong dual physical supports and synergistic effects, which effectively increase the accessible contact area for electron/ions transfer and restrain the volumetric changes of PANI skeleton, thus improving the electrochemical performance. Different from the previous reports, the obtained heterostructures exhibited good specific capacitance, high rate capability, as well as long-term cycle stability as an binder-free electrodes for supercapacitors.

2. Experimental section

2.1. Materials

Carbon nanotubes (CNTs) were purchased from Nanjing Jicang nanotechnology Co., Ltd., other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Aniline (ANI) were distilled under reduced pressure and other reagents were used without further purification. Graphene oxide (GO) was synthesized by a modified Hummers method [37]. Graphene was prepared as follows: 250 mg of GO solids were placed into a Teflon autoclave with a capacity of 100 mL. After expelling out the air in the autoclave by Ar, the autoclave was sealed and heated at 250 °C for 10 h. After cooling to room temperature, graphene sheets were obtained.

2.2. Preparation of layer-by-layer sandwiched G/PANI/CNTs heterostructures

The layer-by-layer sandwiched graphene/PANI nanorods/carbon nanotubes heterostructures were carried out by an in-situ polymerization and top-down step, as schematically shown in Scheme 1. Firstly, 150 mg of graphene sheets were dispersed in 150 mL of HCl solution (1 mol/L) by sonication treatment until a homogeneous mixture was achieved, the mixture was cooled down to 0 °C under stirring, then 0.15 mL of aniline was added and stirred for 30 min, after that, 0.19 g of ammonium persulfate (APS) dissolved in 10 mL of HCl solution (1 mol/L) was added and the mixture solution was stirred for 24 h at 0 °C. The precipitates were washed by deionized water and ethanol several times until neutral and dried at 60 °C for 12 h in vacuum, the composites of graphene/polyaniline nanorods (G/PANI) were obtained, and the weight ratio of G and PANI in the composites was about 1:1. PANI nanorods anchored on the surface of graphene sheets can shorten ions diffusion path and facilitate the diffusion of electrolyte ions. Secondly, 200 mg of G/PANI was dispersed in 100 mL of ethanol by ultrasonication for 1 h, after stirring for 30 min, a slurry with different amount of CNTs was added dropwise and stirred for another 30 min, then the mixed solution was filtered by vacuum infiltration through a cellulose membrane and dried at 60 °C for 12 h in vacuum. For comparison, three kinds of G/PANI/CNTs with G/PANI unchanged and different addition of carbon nanotubes (1 mg, 2 mg and 5 mg) were obtained, named as G/PANI/CNTs-1, G/PANI/CNTs-2 and G/PANI/CNTs-3, respectively. From the illustration, it can be observed that a layer-