Journal of Alloys and Compounds 745 (2018) 370–377

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Electrophoresis deposition of flexible and transparent silver nanowire/graphene composite film and its electrochemical properties

Junyan Liu, Tinghui Jiang, Feng Duan, Gengzhe Shen, Xin He*, Weijia Yang, Ping Liang, Yunting Yue, Qiuming Lan, Jianhao Wu, Qingguang Zeng

School of Applied Physics and Materials, Wuyi University, Jiangmen 529020, Guangdong Province, PR China

ARTICLE INFO

Article history:
Received 17 January 2018
Received in revised form
17 February 2018
Accepted 19 February 2018
Available online 22 February 2018

Keywords:
Silver nanowires
Graphene
Flexible and transparent electrode
Electrochemical properties

ABSTRACT

Silver nanowire (Ag NW)/graphene composite films were fabricated on polyethylene terephthalate (PET) substrates using an electrophoresis method, making graphene sheets closely contact with NW networks. As electrophoresis voltage increased from −1 V to −10 V, the transmittance and sheet resistance of the composite film changed in the range of 64.8%–35.2% and 0.98 Ω/sq-6.61 Ω/sq (initial values are 75.7% and 0.77 Ω/sq). Combined advantages of two materials, the stability of the Ag NW film was greatly enhanced due to protection of the graphene layer, and the conductivity of the graphene electrode was remarkably improved ascribed to introduction of the interconnected networks. The areal and specific capacitance of the composite film increased from 1.22 mF/cm^2 to 7.6 mF/cm^2 and decreased from 108.4 F/g to 25.7 F/g at 100 mV/s in a 1 M $LiClO_4$ solution, as the electrophoresis voltage increased from −1 V to −10 V. Furthermore, the Ag NW/graphene composite film exhibited a good long-term cycling stability with 82.6% capacitance retention after 2500 cycles. Additionally, a symmetric supercapacitor using the Ag NW/graphene films as electrodes exhibited symmetric galvanostatic charge-discharge and similar CV curves under flat and bent conditions, indicating that the fabricated electrode could be considered as one of excellent candidates in flexible and transparent supercapacitors.

1. Introduction

In the recent years, flexible and wearable energy storage devices have attracted more and more interests [1–5]. Supercapacitor as one of next-generation power supplies exhibits many advantageous characteristics, such as high power density, fast power delivery, high rate capability and long service life [6–12]. Carbon based materials, such as activated carbon, mesoporous carbon, carbon nanotubes, graphene, have been extensively investigated as the electrodes in flexible supercapacitor due to their excellent electrical properties, large specific surface area, good mechanical properties and remarkable chemical stability and electrochemical properties [13]. Hence, these materials are regarded as comparatively promising electrodes for fully flexible supercapacitors. Recently, Kim et al. prepared a flexible supercapacitor based on reduced graphene oxide/single-wall carbon nanotubes composites, which exhibited the highest capacitance value of 52.5 F/g and retained 65% after 500 bending with 6000th galvanostatic charge/discharge cycles [14]. Sarac et al. obtained carbon nanofibers (CNFs) via an electrospinning technique. By utilizing different electrolyte, the specific capacitance values of CNF web were recorded between 204 F/g and 149 F/g [15]. Xiong et al. fabricated a three-dimensional reduced graphene oxide-carbon nanotube-polyaniline hybrid, which displayed a high specific capacitance of 741 F/g with a high energy density of 92.4 Wh/kg and power density of 6.3 kW/kg at the scan rate of 10 mV/s, as well as good stability with a retention ratio of 95% after 5000 cycles [16].

Although the carbon based materials have been widely utilized in the flexible supercapacitor, it is difficult to be further applied in transparent energy storage device due to their intense photo absorption in visible region. As well known, graphene sheets with thin thickness have been utilized in transparently conductive electrode [17,18]. However, in order to guarantee the film transparency, the utilized thickness and mass loading of the graphene sheets should be thin and little. In this case, the transparent electrode based on the pristine graphene sheets-based film usually exhibits poor electrochemical properties due to its large resistance, especially for the graphene prepared by a physical method. It is

* Corresponding author.
E-mail address: hexinwyu@126.com (X. He).

https://doi.org/10.1016/j.jallcom.2018.02.241
0925-8388/

mainly ascribed to the high grain boundary resistance between the sheets, which greatly limits the improvement of the device performance.

Therefore, we aimed to fabricate a flexible and transparent electrode based on the graphene sheets via a facile method, and obtain improved electrochemical properties. In this work, the Ag NW/graphene composite films were fabricated by an electrophoresis method. In the composite films, the Ag NWs could be considered as the bridges to connect the graphene sheets and provided effective electron transport pathways, greatly improving film conductivity. Meanwhile, the interconnected networks could also ensure the film transparency. When the electrophoresis voltage was set as −10 V, the Ag NW/graphene composite film with a transmittance of 35.2% and a sheet resistance of 6.61 Ω/sq exhibited a high areal capacitance of 7.6 mF/cm^2, and retained 82.6% capacitance after 2500 cycles. Compared to the pristine Ag NW film or graphene film, the electrochemical properties of the composite film was remarkably improved. Thus, the electrophoresis method is expected to fabricate composite films with effective contact between two materials, and the Ag NW/graphene film is one of promising electrodes in flexible and transparent supercapacitor.

2. Experimental sections

2.1. Preparation of the Ag NWs

The Ag NWs with high aspect ratio were prepared by a hydrothermal method [19,20]. Firstly, 3 mmol silver nitrate, 4 mmol glucose and 0.6 mmol ferric sulfate were respectively fully dissolved into 20 mL, 40 mL and 40 mL deionized water. After that, silver nitrate solution was dripped into the glucose solution, and then the ferric sulfate solution was introduced into the mixture. Following this, 4.5 g poly(vinyl pyrrolidone) (PVP, K30) was completely dissolved in the above solution. Finally, the resultant solution with a volume of 40 mL was sucked and transferred into an autoclave of 100 mL capacity, which was sealed and heated at 180 °C for 6 h. After the reaction, the precipitate with a gray-green color was washed by centrifugations with ethanol for several times.

2.2. Preparation of Ag NW/graphene composite film

Fig. 1a shows a schematic illustration of the fabrication process of the Ag NW/graphene composite films using an electrophoresis method. The detailed procedure is described as follows. Firstly, the conductive and transparent film was coated on PET substrate by pulling a glass rod over the Ag NW ethanol dispersion. Subsequently, the Ag NW film was laminated using a mechanical pressure of 10 MPa for 3 min to enhance the connection of the NWs and decrease the resistance of the percolation network. At the same time, 0.1 g physically prepared graphene powder purchased from TanFeng Graphene Technologies Ltd. was dispersed in a mixed solution consisting of 100 mL ethanol, 1 mL poly diallyldimethylammonium chloride (PDDA) and 2.019 g sodium dodecyl sulfate (SDS). The graphene layer was deposited onto the Ag NW film used as a cathode by the electrophoresis method. After drying the fabricated film at 50 °C, a flexible and transparent Ag NW/graphene composite film was obtained.

2.3. Fabrication of solid-state supercapacitor

Fig. 1b displays a schematic illustration of the fabrication process of a supercapacitor based on the Ag NW/graphene composite film. Firstly, the fabricated film was cut into a rectangle with an area of 2 cm × 4 cm for an electrode of supercapacitor, and then a copper conductive tape stuck to one side of the electrode. Following this, a pair of electrodes was oppositely placed using polyvinyl alcohol (PVA)/$LiClO_4$ blend as an electrolyte layer to fabricate a sandwich-structured supercapacitor. The device was treated at 50 °C for 4 h, making the electrolyte gel layer change to colorless. Finally, a mild pressure was applied on the device surface for 60 s to obtain a flexible and transparent supercapacitor.

2.4. Characterization

The nanostructures of the films were characterized using an X-ray diffractometer (XRD) (X'pert Pro MFD, Panalytical, Netherlands) with a Cu Kα radiation (λ = 0.154178 nm). Raman spectrum of the film was characterized utilizing a Raman spectrometer (Thermo Scientific™, DXR, USA) with a 633 nm laser as the excitation source. The surface morphologies of the transparent films were observed using a field emission scanning electron microscope (FESEM, Nova NanoSEM 430, FEI, USA). The microstructure of Ag NWs was carried out with a transmission electron microscope (JEOL, 2100 F, Japan). The transmittances of the films and devices were collected from a UV-VIS spectrophotometer (UV2550, Shimadzu, Japan). The sheet resistances of the films were recorded by a four-probe system (SZ-82, Suzhou Telecommunication, China). Cyclic voltammetry (CV), Nyquist plots and galvanostatic charge/discharge measurements of the composite electrodes and device were conducted using an electrochemical workstation (CHI 660e, CH Instruments Ins, USA).

3. Results and discussion

The graphene sheets modified by PDDA exhibits positive charge in the ethanol solution [21,22], and shows well dispersion due to the addition of SDS. In the electrophoresis system, the Ag NW film was used as a cathode. The charged graphene sheets moved towards it and covered onto the film surface under a given electrical field. Fig. 2a illustrates the mechanism diagram of the fabricating process. Under an electrical force, the positively charged graphene sheets were initially forced to move toward the negatively charged cathode. And then, the graphene sheets deposited onto the Ag NW film surface by releasing the charges, leading to tight contact between the graphene sheets and Ag NW networks [23–25]. The thickness of the graphene layer was dependent on the potential of the electric field and electrophoresis time.

Fig. 2b shows a typical Raman spectrum of the Ag NW/graphene composite film fabricated at the electrophoresis potential of −10 V for 1 min. There are two feature peaks at 1350 and 1592 cm^{-1}, corresponding to the D band and G band of graphene [26,27], respectively, indicating that the graphene layer can be effectively deposited on the Ag NW surface in a short time. Fig. 2c demonstrates XRD patterns of the pristine Ag NW film and Ag NW/graphene composite film fabricated at −10 V for 5 min. The standard card of metallic silver (JCPDF No. 65-2871) is provided for reference. Four diffraction peaks in the two films are observed at 38.07°, 44.30°, 64.48° and 77.42°, which can be assigned to the (111), (200), (220) and (311) reflections of the face centered cubic (*fcc*) structure of metallic silver, and the diffraction peaks of impurities or silver oxides were not observed. Similar peak positions in the XRD patterns of two samples suggest that there is no chemical reaction during the electrophoresis process, and the Ag NWs do not apparently be oxidized when it is used as a cathode.

Fig. 2d shows a typical SEM image of the pristine Ag NW film, displaying the Ag NWs have uniform diameter of approximately 50 nm, which further confirmed by a TEM image, as displayed in Figure S1a. Figure S1b presents a high resolution TEM image of single NW. The continuous lattice fringes reveal the crystal nature of the NW. The inset of Figure S1b shows that the distance of ten