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Electrochemical performances of silver nanoparticles decorated polyaniline/graphene nanocomposite in different electrolytes

Saptarshi Dhibar, Chapal Kumar Das*

Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur, 721302, India

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ABSTRACT

In the present study, a simple, inexpensive and novel synthetic procedure was used for the preparation of Silver-Polyaniline/Graphene [Ag-PANI/Gr] nanocomposite as superior supercapacitor electrode material. The probable interaction of Ag with PANI and Gr were characterized by Fourier transform infrared, UV–visible, and Raman spectroscopies. The formation of Ag nanoparticles in the PANI coated Gr sheets were confirmed by morphological study. The maximum specific capacitance of 591 F/g has been achieved for the nanocomposite at 5 mV/s scan rate in 1 M KCl electrolyte. The nanocomposite also attained superior energy as well as power density. Here, both Ag nanoparticles and Gr take part for the increment of specific capacitance of the nanocomposite. The nanocomposite showed enhanced electrical conductivity of 5.17 S/cm and also reached nonlinear current-voltage characteristics. The higher thermal stability also observed for the nanocomposite. Depending on those superior properties the Ag-PANI/Gr nanocomposite can be used for supercapacitor electrode material.

1. Introduction

The world is now facing a serious energy problem described by growing energy costs and reducing production capacities for oil and gas. Significant efforts have been committed to the expansion of alternative energy storage/conversion devises in response to supply depletion. In the past few years, research into supercapacitors has experienced an enormous growth due to their high specific capacitance, pulse power capabilities, long cycle life, fast charge and discharge rates, low internal resistance, high power densities, and sustainable features [1–6]. Due to these special properties supercapacitors are considered to be the most-promising energy-conversion/storage systems to manage future energy-storage requirements. They are more advantageous where long cycle life and the high power density are highly required, such as in mobile electronic devices, hybrid electric vehicles, memory backup systems, large industrial equipment, and military devices [7,8]. According to charge storage mechanism, supercapacitors are classified into two distinctive parts. First one is the electric double-layer capacitance (EDLC) that occurs from pure electrostatic attraction between the charge surface of the electrode and the ions, for example the capacitance provided by porous carbon materials [9]. Second one is the pseudocapacitance that obtained from a Faradic reaction of the electro-active materials with the electrolyte ions, such as the capacitance contributed by transition metal oxides [10] or electronically conducting polymers [11].

Conductive polymers such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and their derivatives have been widely studied in supercapacitors. Out of these conducting polymers, PANI is considered one of the most promising candidates due to its high capacitive characteristics, ease of synthesis and comparatively low cost [12,13]. But PANI restricts practical applications because of poor cycling life. Nowadays, researcher has resolved those problems and provides an innovative route to fabricate PANI-based hybrid composite with superior performance as electrode materials [14,15].

Graphene (Gr), a two dimensional monolayer of sp^2-bonded carbon atoms has received a rapidly growing research attention due to its unique electronic and mechanical properties [16–19]. Gr has drawn extensive research interest in the areas of fabricating electronic and energy storage devise, transparent electrodes, sensors, high strength composite materials, anticorrosion coatings, and electromagnetic shielding materials [20,21]. By easy chemical processing of graphite, the graphene-based materials can be simply obtained. Therefore, over the past few years, much attention has given on the potential using of graphene-based materials for

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* Corresponding author.
E-mail address: chapal12@yahoo.co.in (C.K. Das).

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supercapacitor [22,23]. Introduction of various nanoparticles into a graphene-based matrix is an important study for the investigation of their properties and applications. Among these various nanoparticles, silver (Ag) nanoparticles have attracted much more research attention due to their wide applications and unique properties in biosensing, catalysis, chemical sensing, electronics, and photonics [24–27]. It is also well known fact that the incorporation of the Ag nanoparticles into the conducting polymer matrices improves the optical, mechanical, thermal, conducing and electrochemical properties.

In recent years, the nanocomposites based on Ag nanoparticles decorated on Gr surface are reported by various research groups by different synthetic procedure with their different applications. Shanmugharaj et al. synthesized graphene-silver nanoparticles hybrids using eco-friendly microwave radiation and characterized the electrochemical performances [28]. A facile and green approach is reported by Yuan et al. to synthesized Gr-Ag nanocomposite using sodium citrate as the reducing agent and checked their surface plasmon resonance property and antibacterial activity [29]. Wang et al. reported Gr-Ag nanocomposite prepared by one-pot reduction of both Ag^+ and graphene oxide, and studied their electrochemical oxidation of methanol in alkaline solution [30]. Gao et al. prepared the paper like Gr-Ag nanocomposite films synthesized by in-situ reduction of graphene oxide films with Ag^+ using ascorbic acid and investigated their mechanical and electrical properties [31]. Yu et al. prepared Gr-Ag nanocomposite by in-situ using ascorbic acid as green reducing agent and checked their electrochemical detection of halide [32]. Hsu et al. fabricated the Ag/rGO nanocomposite as a surface-enhanced Raman scattering (SERS) substrate with high enhancement factor (EF) and homogeneity [33]. Li et al. reported a facile strategy to fabricate hair-like nanoarchitectures made up by ultrafine MnO_x nanowires entrapped with ultrafine Ag nanoparticles synthesized by in situ reaction between Ag nanowires and $KMnO_4$ and investigated their electrochemical behavior [34]. Zhang et al. prepared Gr-Ag nanocomposite in aqueous solution by using tannic acid and polyphenol as reducing agent and checked their surface enhanced Raman scattering and electrochemical properties [35]. The application of GO-Ag nanocomposite in photocurrent generation has been demonstrated by Tian et al. [36]. Liu et al. designed and successfully fabricated the microsupercapacitors based on the $rGO/MnO_2/Ag$ nanowire ternary film [37]. Zhi et al. developed ordered mesoporous carbon (OMC) based highly conductive and flexible electrodes for supercapacitor, employing 3D Gr foam as flexible and conductive scaffold and Ag nanowires as conductive reinforcing agent [38]. Vanitha et al. prepared $Ag/CeO_2/rGO$ ternary nanocomposite synthesized by facile hydrothermal method and investigated as electrode materials for supercapacitors application [39]. The EMI shielding efficiency and the electrical conductivity of the polyaniline composite filled with Gr-Ag was investigated by Chen at el [40]. Sawangphruk et al. prepared Gr-Ag-PANI nanocomposite coated on flexible carbon fiber paper and investigated their electrochemical properties [41]. Zhang et al. synthesized rGO-Ag nanocomposite by one-step photochemical reaction method and checked their catalytic activity [42]. Therefore we have seen that there are several works done by numerous research groups on Gr-Ag or GO-Ag and Gr-Ag-PANI nanocomposite, although the synthesis of Ag nanoparticles by using dodecylbenzenesulfonic acid (DBSA) and silver nitrate ($AgNO_3$) in the presence of PANI and Gr is not yet done. In one of our previous study we have synthesized Ag nanoparticles decorated PANI/MWCNTs nanocomposite for supercapacitor electrode materials [43]. More interestingly we want to know how Gr, Ag nanoparticles and PANI effects on the electrochemical properties. So, our main motivation of this work to fabricate Ag nanoparticles decorated PANI-Gr nanocomposite for next generation supercapacitor electrode materials.

Herein, we report Ag nanoparticles decorated PANI/Gr [Ag-PANI/Gr] nanocomposite synthesized by a simple and inexpensive in-situ oxidative polymerization technique using ammonium persulfate (APS) as an oxidizing agent in presence of DBSA and $AgNO_3$ and investigated as electrode material for next generation supercapacitor electrode material. The electrochemical performances of the electrode material was analyzed by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) analysis with a two-electrode system in two different aqueous electrolytes. The chemical interaction, morphological characteristics, electrical properties and thermal stability of the nanocomposite, was also investigated.

2. Experimental section

2.1. Materials used

The monomer, aniline, ammonium persulfate $[(NH_4)_2S_2O_8]$, H_2SO_4, HNO_3 and dimethylformamide (DMF) used in this study was provided by Merck, Darmstadt, Germany. Dodecylbenzenesulfonic acid (DBSA) and silver nitrate ($AgNO_3$) were purchased from Sigma–Aldrich, Bangalore, India. Graphene was supplied from Sinocarbon Materials Technology Co. Ltd., China. To remove the impurities, the graphene sheets were treated with mixed acid (H_2SO_4 and HNO_3). Cetyltrimethylammonium bromide (CTAB) used in the study was obtained from Loba Chemie Pvt. Ltd., Mumbai, India.

2.2. Synthesis of Ag-PANI/Gr nanocomposite

The Ag-PANI/Gr nanocomposite was synthesized by in-situ oxidative polymerization technique. The synthetic procedure of the nanocomposite was the same as our previous study [43]. Briefly, 1.24 g of cetyltrimethylammonium bromide (CTAB) and 50 mg of Gr were taken in 150 ml of double distilled water and sonicated for 45 min at room temperature. 100 ml of 0.01 M $AgNO_3$ solution was taken in a round-bottom flask and stirred for 30 min at room temperature. Into this solution, 0.01 M DBAS solution was added and stirred for another 15 min. The well-dispersed suspension of Gr solution was then added slowly to the $AgNO_3$ solution and stirred for 30 min. Then the pre-cooled solution of 0.01 M aniline was added to the above solution and stirred for 8 h at room temperature. Subsequently, 0.01 M APS solution was added drop wise to the above solution to initiate the polymerization process. The monomer and the oxidizing agent ratio were kept as 1:2. Then the entire solution was stirred for another 8 h at room temperature and kept at 0–5 °C for overnight to complete the polymerization process. Afterward, the greenish black precipitate was filtered and washed with ethanol and double distilled water for many times to remove the un-reacted monomer. Then, the product was vacuum-dried at 80 °C for 24 h to get the Ag-PANI/Gr nanocomposite. The schematic representation of the synthesis technique of the nanocomposite is illustrated in Fig. 1.

2.3. Characterization

The Fourier transform infrared (FTIR) spectrum was recorded using a NEXUS 870 FT-IR (Thermo Nicolet) instrument in the range from 400 to 4000 cm^{-1}. By using a Perkin–Elmer, Lambda 750 spectrophotometer, the UV–visible spectra of the nanocomposite was recorded. UV–visible spectroscopy analysis was executed by dissolving the electrode materials in DMF solvent and the spectrum