



Full Length Article

Decorative reduced graphene oxide/C₃N₄/Ag₂O/conductive polymer as a high performance material for electrochemical capacitorsJavad Shabani Shayeh^{a,*}, Hadi Salari^{b,*}, Azar Daliri^c, Meisam Omidi^a^a Protein Research Center, Shahid Beheshti University, GC, Tehran, Iran^b Department of Chemistry, College of Sciences, Shiraz University, Shiraz, Iran^c Department of Chemistry, Sharif University of Technology, Tehran, Iran

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ABSTRACT

Here in, reduced graphene oxide/g-C₃N₄/Ag₂O nano structure (RGO/CAO) was decorated through a facile and simple chemical method. After that RGO/CAO nano structure combined with poly aniline electrochemically to form a composite electrode. Several physicochemical techniques were applied to characterize the composite electrode such as X-ray Diffraction (XRD), Fourier Transform Infra-Red spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Furthermore, several electrochemical techniques were used to study the performance of composite electrode as an electrochemical capacitor. Results show that RGO/CAO nano structure distributed on the surface of poly aniline filaments uniformly and specific capacitance of composite electrode increased from 105F/g for poly aniline to 175F/g for composite electrode. Increasing the conductivity of composite electrode is another advantage of using of RGO/CAO nano structure in the structure of poly aniline electrode. For study the stability of composite electrode during continues cycles, the composite electrode conducted for 1000th cycles and results show the good stability of composite electrode over consecutive cycles.

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1. Introduction

Electrochemical capacitors that often called super capacitors are one of the energy storage devices that attracted many attentions due to their unique properties [1,2]. Filling the gap between batteries and ideal capacitors by higher power to first and higher energy against the latter is the noticeable character of super capacitors [3,4]. Study the materials improvements for super capacitors manufacturing is one of the most important research fields in recent years [5]. Carbon materials [6], metal oxides [7] and conductive polymers [8,9] are major classes of materials which employed in super capacitors. Using each material lonely has many defect points, such as low specific capacitance, low conductivity and poor stability during continues charge – discharge cycles [10]. Combination of different types of materials and forming new composite electrodes, can solve these problems. Conductive polymers due to their physicochemical structures can prepare a suitable platform for other nano materials and enhance the nano materials specific surface area in composite electrode structure. Increasing the stabil-

ity of electrodes through continues cycles is another advantage of using nano materials in the structure of conductive polymers [11–14]. Nano materials can connect the polymer filaments together and enhance the mechanical stability of composite electrodes [15,16]. The method for synthesis of composite electrodes is another important factor for study the super capacitors. Composite materials could be prepared via chemical and electrochemical methods. In chemical procedure, an initiator such as ammonium per sulfate (APS), added to the solution contained monomer and nano materials. Simple procedure and high mass of composite materials are the benefits of using chemical synthesis but the synthesis procedure is not controllable and high magnitude of nano materials is needed [17,18]. In electrochemical synthesis, an electrochemical signal act as an initiator and free radicals are produced on the surface of electrode. The controllable synthesis and low nano materials consumptions are the benefits of using electrochemical technique for nano composites synthesis. Furthermore, in chemical synthesis, the composite materials must be dried for weighting and characterization. During these procedures, materials morphologies are changed which could be a weakness for this method [19]. Graphene is one of carbonaceous materials that is very interested due to high surface area, electrical conductivity, chemical stability and etc. Decoration of nano materials on the

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surface of graphene sheets can improve their properties [20–22]. There are many reports about the nano materials that decorated on the surface of graphene [23,24]. The superior properties of graphitic C_3N_4 ($g-C_3N_4$) as well as high nitrogen content and facile production methods cause $g-C_3N_4$ be an important candidate for coupling with graphene to facilitate the electron transferring as an conductive mixture. In this work, we synthesized the reduced graphene oxide/ $g-C_3N_4$ /silver oxide nanostructure and it's composite with poly aniline. Increasing the super capacitive performance of composite electrode against polymeric one is the goal of this procedure.

2. Material and methods

2.1. Synthesis of $g-C_3N_4$

The $g-C_3N_4$ was synthesized by direct pyrolysis of thiourea at 550 °C. 5 g of thiourea put into a crucible with a cover and heated to 550 °C in static air at a ramp rate 15 °C min^{-1} . Then for 4 h, the sample kept up at 550 °C [25]. After cooling to room temperature the obtained white yellow powder grounded into a fine powder.

2.2. Synthesis of graphene oxide (GO)

Modified Hummers' method was applied for preparation of GO [26]. 1 g graphite powder and sodium nitrate added to concentrated sulfuric acid in an ice bath with vigorous stirring. After 30 min stirring in room temperature, potassium permanganate added slowly to mixture and the brown color will be appeared. 50 ml water added to mixture and then stirred for 24 h. For complete oxidation process, the hydrogen peroxide added drop by drop to mixture and after 2 h stirring, the precipitate washed several times with HCl 5 wt% and water several times. The product (GO) dried at 80 °C over a night.

2.3. Synthesis of reduced graphene oxide (RGO)

Chemical reduction was used for RGO synthesise [27,28]. 100 mg of GO added to 100 ml of DI water and the mixture sonicated for 2 h. The reduction process followed by adding 20 ml hydrazine and reflux at 70 °C for 2 h.

2.4. Synthesis of RGO/Ag₂O

0.03 g of RGO and 20 ml of DI water sonicated for 1 h at room temperature. 0.48 g sodium hydroxide added to mixture and stirred for 3 h. Then 10.5 ml of Silver Nitrate solution (0.1 M) added dropwise and the mixture stirred in absence of light for 1 h. The obtained product washed with DI water and dried in oven at 80 °C for 6 h.

2.5. Synthesis of RGO/ $g-C_3N_4$ /Ag₂O

15 mg of RGO and 15 ml of DI water sonicated for 90 min at room temperature. 0.17 g of Silver Nitrate dissolved in 1 ml of concentrated ammonia and added to RGO solution and pH adjusted to 7.3 by dilute nitric acid. In other vessel, 0.03 g of C_3N_4 and 20 ml of DI water sonicated for 120 min and after adding 0.48 g of sodium hydroxide, the mixture stirred for 3 h. This mixture appended to RGO solution slowly and sonicated for 60 min. The obtained mixture stirred vigorously for 24 h at 70 °C. The black powder filtered and washed several time with DI water and ethanol and dried in an oven at 80 °C for 12 h.

2.6. Composite electrode preparation

PANI/RGO/CAO composite was synthesized electrochemically by cyclic voltammetry in solution of 0.03 M ANI in H_2SO_4 1 M, 0.2 wt%. RGO/CAO and 0.005 M of sodium dodecyl sulfate (SDS) that was dispersed in solution by sonication. PANI electrode was synthesized in same solution without YAG nano particles. Polymerizations were conducted by 10 cycles at the sweep rate of 50 mV/s. The mass of PANI films was approximated assuming a current efficiency for the electro polymerization process of 100%, using Faraday's law.

2.7. Apparatus

Electrochemical experiments were carried out by an Auto lab General purpose System PGSTAT 30 (Eco-chime, Netherlands). A conventional three electrode cell with a glassy carbon electrode with the area of 0.03 cm^2 as working electrode, Platinum wire and an Ag/AgCl reference electrode (Argental, 3 M KCl) were used as counter and reference electrode respectively. The EIS experiments were conducted in the frequency range between 100 kHz and 15 mHz with perturbation amplitude of 5 mV. Morphological investigations of the polymeric films were carried out by using SEM (Philips XL 30 and KYKY-EM3200) and transmission electron microscopy (TEM, Philips Tecnai G220, operated at 120 kV). X-ray diffraction patterns were obtained from an X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu-K α monochromatized radiation source and a Ni filter.

3. Results and discussion

Fig. 1 presents layered and wrinkled morphology of RGO/CAO. As can be seen, Ag₂O nano particles distributed uniformly on the surface of RGO sheets by the average size of 40 nm. Distribution of nano particles on the surface of RGO sheets caused to increasing the active surface area of nano particles (Fig. 1a, b). As illustrated in (Fig. 1c, d), surface of PANI filaments covered by RGO/CAO uniformly. Distribution of RGO/CAO nano structures caused to increase the surface of composite materials and furthermore, these nano structures can connect the polymer filaments together that increase the mechanical stability of composite electrode.

For investigation of surface composition and chemical states of elements in RGO/ $g-C_3N_4$ /Ag₂O nanostructure, X-ray photoelectron spectroscopy (XPS) was applied. The presence of C, N, O and Ag was detected by XPS scanning of the hetero structure (Fig. 2). After deconvolution of C1s spectra, three main peaks appeared at 285.3 eV, 286.8 eV and 288.8 eV. The peaks at 285.3 eV and 286.8 eV are corresponded to sp^2 hybridized graphitic carbon and residual terminal carboxylic group at the edge of graphene [29,30]. The peak located at 288.8 eV is related to carbon which attend in $g-C_3N_4$ aromatic rings as N=C=N [31]. The peak with binding energy of 398.5 eV is related to the sp^2 hybridized nitrogen in triazine rings (pyridinic-N). Bridging Nitrogen in pyrolic and graphitic structure are assigned to the peak at 399.7 eV and 401.3 eV respectively [32]. Deconvolution of O1s spectra demonstrates two peaks at 530.0 eV and 533.0 eV. The former is ascribed to Ag–O bonding in silver oxide structure, while the latter is hydroxilic or carboxylic oxygen in graphene (C–O). The photoelectron peaks centered at 368.1 eV and 374.0 eV are associated with $3d_{5/2}$ and $3d_{3/2}$ of silver highlighting that silver is presented in structure as ion in silver(I) oxide [33,34]. It should be noted that shifting of binding energy in all elements is due to electronic interactions between organic parts of heterojunction and silver[35].

Fig. 3a presents the XRD patterns of RGO/Ag₂O, C_3N_4 -Ag₂O, RGO/ $g-C_3N_4$ /Ag₂O, PANI and PANI/RGO/CAO samples. As

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