Journal of Electroanalytical Chemistry 818 (2018) 26–34

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Electrochemical synthesis of polyaniline-exfoliated graphene composite films and their capacitance properties

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ARTICLE INFO

Keywords:
Graphene
Polyaniline
Chronoamperometry
Composite film
Specific capacitance

ABSTRACT

In this work, the graphene was synthesized by electrochemical exfoliation method, which was used to prepare the polyaniline-graphene composite film (PANI-GR) onto fluorine doped tin oxide (FTO) electrode by chronoamperometry technic at monomer oxidation potential 0.8 V vs. SCE. During the electropolymerization, the incorporation of the synthetized graphene into polyaniline matrix was assured by agitation of the electrolyte (10^{-2} M Ani/1 M H_2SO_4) containing different mass of graphene (1, 2 and 3 mg). By taking the advantages of the high conductivity of GR and the pseudocapacitance of PANI, the FTO/PANI-GR composite film was taken as an example for the application to the supercapacitor electrode materials. The morphology and structure of FTO/PANI and FTO/PANI-GR were characterized by different technics SEM, XRD, FTIR, Raman spectroscopy and UV–visible spectroscopy. The electrochemical performance was evaluated by cyclic voltammetry, galvanostatic charge-discharge tests and electrochemical impedance spectroscopy (EIS). The obtained specific capacitance for the PANI material alone is about 176.29 F g^{-1} this value was increased up to 305.57 F g^{-1} for the composite film PANI-GR 3 mg at 5 mV s^{-1}.

1. Introduction

Nowadays, conducting organic polymers are used in many technical applications especially in electrochemistry equipments like sensors, redox capacitors, catalysis and batteries [1–4]. Due to their high capacitance, conducting organic polymers represent the most important component of supercapacitor electrode [5,6]. Moreover, derivate carbon materials such active carbon [7], carbon nanotubes [8], and graphene [9–11] are known to be chemically stable and have large specific surface area. The latter features are so many targeted by searchers which that explain their use in supercapacitor electrodes. Thus, to produce high performance electrode materials, nano-composites conducting organic polymers and derivate carbon materials are undergoing deep investigations because of their interesting properties.

Within the same framework, graphene embodies a new element of carbon-based materials group represents the main constituent in several electrochemical devices such as supercapacitors. The expressed preference for the graphene is widely justified by its high electrical conductivity, mechanical strength, flexibility and effective working area [12]. The graphene witnesses significant stability during the charge–discharge process; however its specific capacitance (around 100–200 F g^{-1}) is proved to be limited by the stored energy mechanism mostly subsequent to the electric double-layer capacitance [13].

Among the processes leading to high quality graphene synthesis, the best way consist to proceed with direct exfoliation of graphite in solution, mainly electrochemical, sonochemical, and liquid-phase exfoliation [14–16]. In the opposite, the selected material rather required for pseudocapacitors, conducting organic polymers provides, in fact, high specific capacitance, nevertheless, they cause poor stability attributed to the Faradic mechanism [17]. In addition to the above-described characteristics, graphene may be combined with conducting organic polymer to form graphene/conducting organic polymer compound which is more electrochemically performant than pure graphene. The synergistic effects of each component that improve conductivity and increase electrochemical stability in the discharge process [18] explain the gain in performance shown by the graphene/conducting organic polymer. This stability as well as the high performance have been investigated in particular when combining conducting organic polymer with pure graphene such graphene/polyaniline [19–21], graphene/polypyrrole [22,23], and graphene/polythiophene composites

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https://doi.org/10.1016/j.jelechem.2018.04.016
Received 26 April 2017; Received in revised form 7 April 2018; Accepted 9 April 2018

[24,25] particularly focused on. Among the conducting organic polymers, PANI, due to its cost relatively low, simple synthesis process and significant specific pseudocapacitance, has witnessed positive features towards active electrode materials pseudocapacitors [26].In the light of the exposed deductions and features, composites of graphene/polyaniline have acquired a major interest in the electrochemical field [27]. To recall the outlines of the process, in their first step starting electrochemical synthesis of graphene/PANI composite films with high capacitance of 640 F g^{-1}, at 0.1 A g^{-1} [28]; Yan et al. produced a compound of graphene/polyaniline, in situ polymerization, with high specific capacitance of 1046 F g^{-1} at a scan rate of 1 mV s^{-1} relative to 115 F g^{-1} for pure PANI [29], figures due to the presence of graphene nanosheets that modify the structure of PANI. Yan Jun and co-produced an effective supercapacitor electrode made of graphene nanosheets, carbon nanotubes and PANI, following an easy chemical in-situ mode. The electrode thus obtained is characterized by high specific capacitance 1035 F g^{-1} at 1 mV s^{-1} [30].

In the present study, we develop a new and a facile method to synthesis the polyaniline-graphene composite film, in one-step by electrochemical way. The graphene has been prepared by the electrochemical exfoliation method which was characterized by X-ray diffraction and FTIR spectroscopy. The (FTO/PANI-GR) composite films were electrochemically prepared by chronoamperometry technic on a working electrode (FTO) which was immersed in electrolyte containing the graphene dispersed by stirring at different weight (1, 2 and 3 mg) in sulphuric acid 1 M as the supporting electrolyte and 10^{-2} M aniline as monomer. The composite films are characterized by scanning electronic microscopy, FTIR spectroscopy, Raman spectroscopy and UV–visible spectroscopy. The capacitance properties were evaluated by cyclic voltammetry and electrochemical impedance spectroscopy.

2. Experimental

Graphene was synthesized by the electrochemical exfoliation. Two high-purity graphite rods, placed parallel with a separation of 6 cm in ionic solution. The ionic solution was prepared by diluting 2.6 ml of sulphuric acid (Sigma-Aldrich; 98%) in 100 mL of deionized water. The electrochemical exfoliation process was carried out by applying different potential between both graphite electrodes (5 V for 5 min). To prepare the graphene sheet suspension, the exfoliated graphene sheets were collected with a 100 nm porous filter and washed with deionized water by vacuum filtration. After drying, they were dispersed in N,N-diméthyl formamide DMF (Sigma-Aldrich) solution by mild water-bath sonication for 5 min. To remove unwanted large graphite particles produced in the exfoliation, the suspension was subjected to centrifugation at 2500 rpm. Then, the centrifuged suspension can be used for further characterizations and film preparation. All of these electrochemical exfoliation experiments were performed at room temperature.

Electrochemical tests were performed at room temperature in one compartment cell by the use a PGZ-301 Voltalab coupled with a computer equipped with software (voltamaster 4) which makes it possible to select the electrochemical technique and to fix the desired parameter. The electrochemical measurements were performed in a three-electrode cell, the working electrode is fluorine doped tin oxide glass substrate (FTO) (from SOLEMS), the reference electrode is a saturated calomel electrode (SCE) and the auxiliary electrode is a platinum plate.

The FTO/PANI and FTO/PANI-GR (1, 2 and 3 mg) films were characterized by various technics. The X-ray analysis was performed using a Rigaku make powder X-ray diffractometer (model RINT 2100) with a CuKα radiation (λ = 1.54 Å). The UV–visible spectrums of different films were recorded using a Shimadzu UV-1800 UV–vis spectrophotometer. The FTIR transmittance spectra of films were obtained using Fourier transform infrared spectrometer (IRAFFINITY-1S Shimadzu). Raman scattering measurements were recorded at room temperature with a HORIBA scientific Lab RAM HR Evolution RAMAN SPECTROMETER operating with a laser excitation source emitting at 437 nm. The Electric conductivity of the samples was measured using a Kheithley 2400 electrometer with LUCAS LABS Model (PR04-8400) Field emission scanning electron microscopy micrographs were obtained by using a (FESEM, JEOL, JSM-6701F).

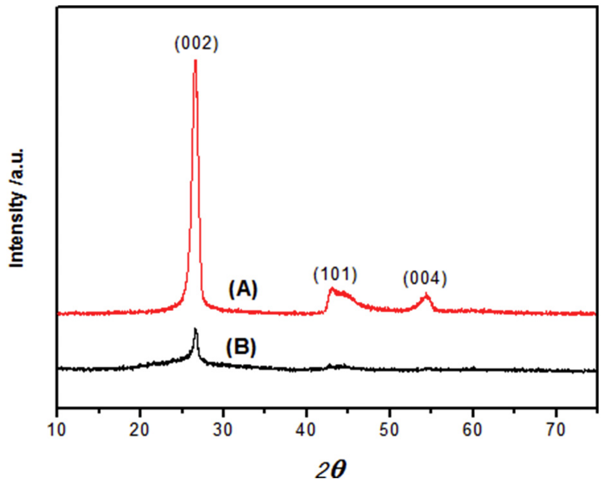

Fig. 1. XRD spectra of natural graphite (A) and graphene (B).

3. Results and discussion

The Fig. 1 represents the XRD patterns of graphite and graphene. So, in the XRD pattern of graphite powder (Fig. 1A) illustrates characteristics peaks of (002) at 26.50°, (101) at 42.31° and (004) at 54.60° with high intensity [31]. The powder of graphene (Fig. 1B) depicts a characteristic peak of (002) at 26.60° with weaker compared to graphite's peak. The decrease in the intensity of (002) plan peak indicates large exfoliation of graphite to graphene nanosheets [32]. The size of graphene nanoparticles estimation can be quantified by XRD in applying Debye–Scherrer's Eq. (1) as follows:

$$D = 0.\ 9\lambda/w\cos\theta \tag{1}$$

where D is the size of nanoparticle, λ is the wavelength used for XRD, w is the full width half maxima and θ is the peak position, in applying this formula, we have calculated the size of nanoparticles of graphene as 13 nm.

The electropolymerization of aniline was carried out by chronoamperometry method from 10^{-2} M aniline dissolved in 1 M H_2SO_4, with in an imposed potential of 0.8 V vs. SCE for 180 s period of time. The graphene sheets was added into to the solution (1, 2 and 3 mg) and dispersed by stirring. Then the polyaniline-graphene composite was deposited on the working electrode after end time, all tests were realized in the same conditions as that imposed for electropolymerization of aniline in absence of the graphene.

Chronoamperograms of preparation of films composite FTO/PANI (A), FTO/PANI-GR 1 mg (B), 2 mg (C) and 3 mg (D) during electropolymerization were shown in Fig. 2. The obtained curves are very similar to that obtained by G. Zotti and al [33]. Through the initial stage, the anodic current slightly decreases and then increases with the square of the electrolysis time. The slight decrease in the current is attributed to the formation of a uniform polyaniline film through the radical-coupling polymerization [34].

In radical-coupling polymerization, the current is controlled by the diffusion of aniline, and a slight current decrease is observed. In addition, the charging current of the electric double layer was subtracted from the current for the polymerization. It is interesting to find that even after the initial stage the anodic current continues to increase with the electrolysis time. The nucleation processes correspond to the first stage and in the second stage correspond to two dimensional growth