Journal of Electroanalytical Chemistry 760 (2016) 113–118

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Investigation of the antioxidant activity of electrosynthesized polyaniline/reduced graphene oxide nanocomposite in a binary electrolyte system on ABTS and DPPH free radicals

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ARTICLE INFO

Article history:
Received 31 July 2015
Received in revised form 28 October 2015
Accepted 15 November 2015
Available online 1 December 2015

Keywords:
Polyaniline
Reduced graphene oxide
Antioxidant activity
Free radical scavenging
Impedance spectroscopy

ABSTRACT

This study investigated the effect of supporting electrolytes with different molar ratios of inorganic (KCl) and organic salt (*p*TSA) on antioxidant activity of polyaniline/reduced graphene oxide (PAni/r-GO) nanocomposite electrosynthesized on composite 2B graphite pencil in 1 M H_3PO_4 to scavenge 1,1-diphenyl-2-picrylhydrazyl (DPPH) and 2,2-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS) free radicals. The synthesis of PAni/r-GO nanocomposite was accomplished by cyclic voltammetry. The FT-IR and the electrochemical impedance spectroscopy (EIS) confirmed that the presence of KCl in the medium increased the degree of conductivity of polyaniline. In addition to this, the charge transfer resistance (Rct) value of synthesized composite in the presence of KCl is much smaller than that synthesized in the presence of *p*TSA; besides, the UV–vis spectra demonstrated the antioxidant activity of composite through reaction with free radicals in methanol solution. This indicated that both DPPH and ABTS eliminate increase in the presence of PAni/r-GO nanocomposite electrosynthesized with *p*TSA. Thus, scavenging of DPPH and ABTS radicals becomes more efficient when the amount of *p*TSA supporting electrolyte in the synthesis of PAni/r-GO nanocomposite is increased.

1. Introduction

A number of studies have been conducted to determine the antioxidant activity of natural compounds [1,2]. Since the evaluation of natural antioxidant increased considerably among scientific community, the scavenging of epidemiological disease decreased significantly, especially in cardiovascular diseases and cancers [3–9]. The effective influence of this natural oxidant is indicated in phenolic compound, which is known as hydrophilic antioxidant. A closer look at polyphenol compound reveals that they are used as conducting polymers for biomedical applications, a good illustration of this is polyaniline; hence, in order to improve the electrical conductivity of PAni, a conductive nanomaterial such as carbon nanostructure is used [10–13]. Graphene, a single layer of carbon atoms usually prepared by reduction of graphene oxide has attracted much attention due to its high electronic and mechanical properties [14]. As a result, aniline polymerization in the presence of small amounts of graphene nanoplates showed that the PAni electrical properties dramatically improved [15]. PAni/r-GO nanocomposite material has been recently used for energy application [16–18] but the antioxidant activity of this materials generally react with 1,1-diphenyl-2-picrylhydrazyl (DPPH) and 2,2-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS) free radicals in methanol [19–26]. The purpose of this study was to evaluate the antioxidant activity of electrosynthesized PAni/r-GO nanocomposite in a binary electrolyte system on ABTS and DPPH free radicals.

2. Experimental

2.1. Materials

Graphene nanoplatelets (Gr) (99.5%, thickness 2–18 nm 32 Layers, USA); Potassium chloride (KCl) and *para*-toluene sulfonic acid (*p*TSA) (Fluka Chemicals, Switzerland); *N*,*N*-di-methylformamide (DMF) and methanol (MeOH) (BDH Chemicals, UK); phosphoric acid (H_3PO_4), 2,2-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS) (Sigma Chemicals, USA) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) (Sigma Chemicals, USA) were used as received. Aniline (Ani) (Sigma Chemicals, USA) was distilled under nitrogen atmosphere at reduced pressure. The resulting colorless liquid was kept in the dark at 5 °C. Potassium ferricyanide ($K_3[Fe(CN)_6]$) (Shanghai No. 1 Reagent Factory, China) and potassium ferrocyanide ($K_4[Fe(CN)_6]$) (Shanghai Heng Da Chemical Co. Ltd., China) were used as received. All aqueous solutions were freshly prepared using ultra-pure water from Milli-Q plus (Millipore Corp., USA).

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http://dx.doi.org/10.1016/j.jelechem.2015.11.021
1572-6657/

2.2. Equipment

The electrochemical synthesis and characterization of PAni/r-GO nanocomposite were carried out with CompactStat potentiostat (Ivium Technologies, Netherlands) by a computer equipped with the IviumSoft software package. FTIR spectrophotometer System 2000 (Perkin Elmer, USA) and UV–visible spectrophotometer V-500 (JASCO, Japan) were used for structural analysis and characterization measurements. The three-electrode cell consists of a modified electrode as working electrode 2B pencil graphite (1.8 mm diameter) (Staedtler Lumograph, Germany) and a Pt electrode was used as the counter electrode against a pseudo Ag/AgCl reference electrode.

2.3. Procedure

The electrosynthesis of PAni/r-GO nanocomposite on the surface of composite 2B pencil graphite was performed in 10 mL solution mixture of 50 mM Ani, 0.1 mg Gr, 1 M H_3PO_4(solvent),1 M KCl and 0.2 M *p*TSA (supporting electrolyte) at different molar fractions by the Cyclic voltammetry method, with the potential between −0.2 and +1.0 V vs. Ag/AgCl, scan rate 100 mV s^{-1}, under OFN atmosphere and at 25 ± 2 °C.

The EIS of PAni/r-GO nanocomposite in 1 M H_3PO_4 containing $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ was measured at an applied potential of 0.25 V, frequency of 100 kHz to 10 MHz and amplitude of 10 mV.

Antioxidant capacities of PAni/r-GO nanocomposite in the scavenging of DPPH and ABTS free radicals were investigated. 4 mL of freshly prepared 8×10^{-5} M DPPH in MeOH was reacted with 1 mg of the investigated compounds. The solutions were stirred and their maximum absorbance was obtained at 516 nm after 30 min [27]. The ABTS was prepared according to the method of Roberta Re [25,28,29]. 7 mM of ABTS was diluted in 2.45 mM of potassium persulfate solution. ABTS radical cation ($ABTS^{\bullet+}$) was produced by allowing the mixture to stand in the dark at room temperature for 12–16 h before use. 1 mg of the investigated compounds reacted with 4 mL $ABTS^{\bullet+}$ which was diluted with MeOH to get the absorbance of 0.80 ± 0.02 at 734 nm after 15 min.

3. Results and discussion

3.1. Electrochemical synthesis

The cyclic voltammograms for growth of PAni has previously been reported [30]. In this study (Fig. 1), the cyclic voltammograms of synthesized PAni/r-GO nanocomposite in 1 M H_3PO_4 containing 1 M KCl supporting electrolyte has been indicated. The CV is cycled up to 20 cycles. The anodic peak O in the first forward scan is as a result of the monomer radical reaction. However, the cathodic peak is not always observed on the reverse scan. This demonstrates that the radical cation is quickly involved in the subsequent chemical reaction in the time scale (scan rate) used. Overall, this is an irreversible electrode process [31]. The deposition process is due to the shift of anodic and cathodic peaks to positive and negative potentials, this shows that the electrode process for oxidation states of PAni is quasi-reversible by extending scans [31,32]. The three pairs of redox peaks in the potential range of −0.2 to +1.0 V were observed [32–35]. The first redox flow in the potential range of −0.2 to +0.3 V (denoted as O_a/R_a) corresponds to the interconversion of leucoemeraldine (LE) to emeraldine salt (ES) [33,35,36]. The second redox flow at potentials above +0.6 V (denoted as O_c/R_c) is due to oxidation of ES to the pernigraniline (PN) (fully oxidized form) and vice versa [35,37]. Those in the potential range of 0.3 to 0.6 V (denoted as O_b/R_b) are attributed to benzoquinone (Bq) species (oxidation of segments of the PAni chain), which disappear after several successive scans [35,37].

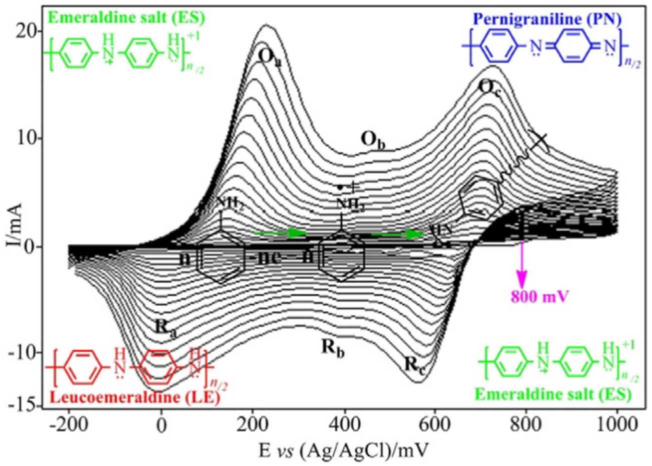

Fig. 1. The CVs of 50 mM Ani and 0.1 mg Gr in 1 M H_3PO_4 containing 1 M KCl at a scan rate of 100 mV s^{-1} for the 1st to 20th cycle.

The cyclic voltammograms of synthesized PAni/r-GO nanocomposite was conducted in 1 M H_3PO_4 in a binary electrolyte system, 1 M KCl and 0.2 M *p*TSA with different molar fractions: 1.0, 0.02, 0.0.5,0.8 and 0.0 (Fig. 2a to e). This indicates that the first and third redox sharp peaks of PAni/r-GO nanocomposite were observed in the presence of KCl supporting electrolyte (Fig. 2a) and there is only one single peak in electrolyte solution containing *p*TSA (Fig. 2e). This is as a result of the oxidation process in weak acid solutions [38], it seems that the presence of KCl helps to increase the dielectric constant of the solution. Consequently, the acidity of the medium is increased [39]. Thus, the acidic ability of *p*TSA was increased with KCl in aqueous medium. It also shows that the synthesized PAni/r-GO nanocomposite with KCl can increase the current of redox peaks. Furthermore, a green film of PAni in the medium containing KCl and *p*TSA which support electrolytes on the working electrode was observed; while the green film disappeared in electrolyte solution with *p*TSA. It is evident that the existence of first and third redox peaks in CVs shows the best quality of electrosynthesized PAni/r-GO nanocomposite [40].

3.2. Structural analysis

The FTIR spectra of PAni/r-GO nanocomposite are shown in Fig. 3. Similarity between the three curves with little differences in the width of the peak is very obvious. The vibrational band at 1602 and 1494 cm^{-1} can be attributed to quinoid (Q) and benzenoid (B) ring [41–43]; the appearance of the peaks at 986 and 1142 cm^{-1} are as a result of aromatic rings in-plane and out-of-plane C–H bending, respectively [41,42,44]. The broad bands at 875 and 495 cm^{-1} correspond to phosphate ions [45,46]. The infrared characteristic absorption bands in 1304 and 1242 cm^{-1} are due to the Q and B rings in C–N stretching of emeraldine base (EB) [47–49]. The ratio of the intensity of bands of Q and B is a measure of the degree of oxidation of the polyaniline film. The fully reduced form with the 0 ratio, the ratio between 0.5 and 1 is for the protoemeraldine form; 1 for the partially oxidized form and over 1 for fully oxidized form. The medium with organic salt has polyaniline in the oxidized form ($Q/B > 1$). Furthermore, medium containing inorganic salt ($Q/B \sim 1$) has partially oxidized polyaniline, which probably is B as its most stable form.

The intensity of UV–vis absorption band of the PAni/r-GO nanocomposite illustrates the availability of mid-gap state due to charge transfer in a conducting polymer. The PAni/r-GO nanocomposite prepared in the presence of different molar ratio of KCl and *p*TSA resulted in three absorption peaks which are 340, 450 and 800 nm (Fig. 4a–e) [50,51]. The high absorption intensity at 340 nm corresponds to the $\pi \rightarrow \pi^*$ electronic transition in the B ring of the reduced non-conducting LE [50,52]. The absorption peaks at 450 nm and to a lesser extent at 800 nm are related to the ES phase of PAni. The peak can be attributed to the polaronic and bipolaronic transitions of aniline unit in the PAni/r-GO