Journal of Electroanalytical Chemistry 751 (2015) 15–22

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

A study on the pseudocapacitive behavior of polyluminol/graphene nanocomposite

H. Heli [a,b,*], A. Parsa [a], N. Sattarahmady [a,b,c]

[a] Nanomedicine and Nanobiology Research Center, Shiraz University of Medical Sciences, Shiraz, Iran
[b] Department of Nanomedicine, School of Advanced Medical Sciences and Technologies, Shiraz University of Medical Sciences, Shiraz, Iran
[c] Department of Medical Physics, School of Medicine, Shiraz University of Medical Sciences, Shiraz, Iran

ARTICLE INFO

Article history:
Received 19 December 2014
Received in revised form 23 April 2015
Accepted 18 May 2015
Available online 19 May 2015

Keywords:
Polyluminol
Poly(5-amino-2,3-dihydro-1,4-phthalazinedione)
Graphene
Nanocomposite
Pseudocapacitor
Synergism effect

ABSTRACT

A nanocomposite of polyluminol (poly(5-amino-2,3-dihydro-1,4-phthalazinedione)) and reduced graphene oxide nanosheets was electrochemically synthesized, characterized by scanning electron microscopy, X-ray diffraction and electrochemical methods, and its pseudocapacitance behavior was investigated. The excellent supercapacitive properties of the nanocomposite arising from both the electrical double layer capacitance of graphene nanosheets and pseudocapacitance of polyluminol resulted from a synergistic effect of the complementary properties of graphene and polyluminol. The nanocomposite presented a specific capacitance of 218.7 F g^{-1} at a discharge current of 0.55 A g^{-1}. The nanocomposite was kept >99% of the initial capacitance after 1000 charge/discharge cycles.

1. Introduction

Electrochemical supercapacitors as battery-complementary devices have been studied in recent years. These devices have the main advantages of high power density, wide thermal range and operating potential window, highly reversible charge-storage and cycling and delivery capabilities. Moreover, supercapacitors are rugged, reliable and maintenance-free and they can be charged very rapidly. Electrochemical supercapacitors store energy via charge separation at the electrode/electrolyte interface in electrical double layer capacitors, or through reversible faradaic reactions in pseudocapacitors. Among the supercapacitors, pseudocapacitors are mainly fabricated using transition metal oxides [1–3], phosphites and phosphates [4,5] and hexacyanoferrates [6], polyoxometalates [7], ferrites [8], hydrotalcites [9], conducting polymers [10–13] and their composites with carbonaceous materials [14–16]. Electronically conducting polymers have good conductivity, low band-gap, high surface area, and high capacitance with a high rate of charge transfer kinetics. In this regard, development of novel composites of conductive polymers with remarkable pseudocapacitive properties is highly desirable.

Graphene is a single layer of carbon packed in honeycomb lattice. It represents the unique properties of superior mechanical properties, high thermal and electrical conductivities and high surface area [17,18]. It has a wide range of applications in various tools and devices such as sensors [19–21], solar cells [22], batteries [23], and supercapacitors [10–12,24]. In the supercapacitor applications, graphene supports active redox materials providing both the electrochemical double-layer capacitance and the highly reversible pseudo-capacitance. This leads to enhancement in the overall capacitance of the composite material and reduces self-discharge [11,12,25–27].

Luminol is a strong chemiluminescence compound, and an efficient electrogenerated chemiluminescence system employed for bioanalysis [28–31]. On the other hand, electropolymerization of luminol occurs similar to aniline [32] through linkage of $-NH_2$ group of one luminol molecule to para-carbon atom of another one [33]. Polyluminol, as a conducting polymer [34], has been employed for fabrication of various sensors and biosensors [35–38]. It has also been synthesized as co-polymers with aniline [33,39,40], benzidine [41] and neutral red [42], and as composites with carbon nanotubes [43], polyoxometalate [44], flavin adenine dinucleotide [35], ZnO [37], and gold nanoparticles [45].

In the present research, a nanocomposite of polyluminol/graphene was synthesized on the electrode surface. To the best of our knowledge, the synthesis of polyluminol/graphene

* Corresponding author at: Nanomedicine and Nanobiology Research Center, Shiraz University of Medical Sciences, Shiraz, Iran.
E-mail addresses: hheli7@yahoo.com, heli@sums.ac.ir (H. Heli).

http://dx.doi.org/10.1016/j.jelechem.2015.05.022
1572-6657/

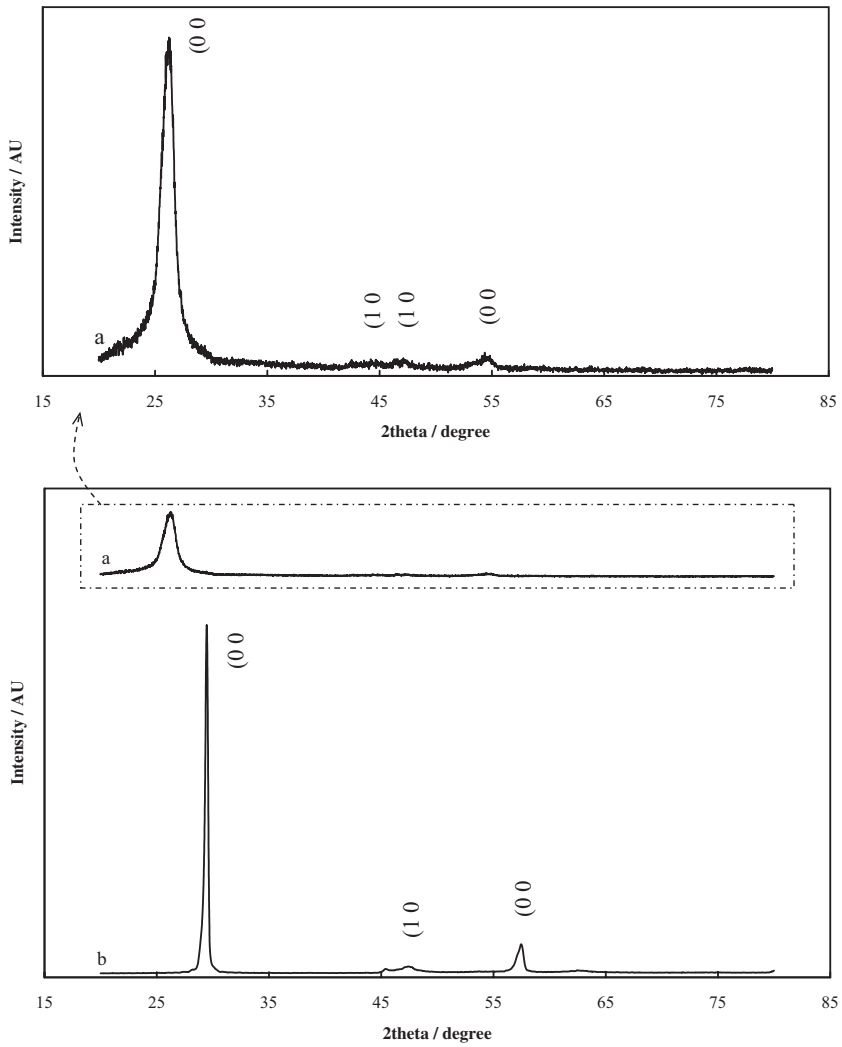

Fig. 1. X-ray diffraction patterns of the pristine graphite and the synthesized RGONS.

nanocomposite has never been approached. This nanocomposite represented an interesting pseudocapacitive behavior due to a synergistic effect of graphene and polyluminol.

2. Experimental

2.1. Materials

All chemicals were of analytical grade from Merck or Sigma and used without further purification. Redistilled water was used throughout the work.

2.2. Synthesis of reduced graphene oxide nanosheets (RGONS)

RGONS were synthesized using graphite powder based on a modified Hummer's method [11,19–21,46]. In a typical synthesis process, 2.0 g graphite (with a size of <50 μm) was dispersed into 140 mL concentrated H_2SO_4, and 1.0 g $NaNO_3$ was added to the mixture on an ice bath. Then, 6.0 g $KMnO_4$ was slowly added to the mixture and stirred for 2 h to fully oxidize graphite into graphite oxide (GO). Afterwards, the mixture was diluted with water. Then, a 5% H_2O_2 solution was added to the mixture until the color of the mixture changed to brilliant yellow. The suspension was filtered and the obtained GO was thoroughly washed with water. Then, GO was re-dispersed in water and exfoliated to graphene oxide nanosheets using an ultrasonic bath for 3 h. The suspension gradually evolved into a brown solution during the ultrasonication and GO was transformed into nanosheets. Finally, the exfoliated GO was reduced to RGONS by refluxing the GO suspension with hydrazine hydrate for 2 h. During the reflux process, the solution color turned into dark black. The obtained RGONS was filtered, washed by water and ethanol, and dried in an oven at 80 °C.

2.3. Electrode preparation

Glassy carbon (GC) electrode of 2.0 mm diameter was firstly polished by 50-nm alumina powder on a polishing microcloth using glycerin as a lubricant. Then, the electrode was sonicated in a 1:1 water:ethanol mixture for 5 min in an ultrasound bath. In order to prepare the GC/RGONS electrode, RGONS was firstly dispersed in acetone (10 mg in 1 mL) using ultrasound and 10 μL of the suspension was dropped on the GC surface and remained to dry at room temperature. In order to prepare the GC/polyluminol (GC/PL) electrode, the GC electrode was transferred to a 1.0 mmol L^{-1} luminol dissolved in 0.1 mol L^{-1} sulfuric acid solution (electropolymerization solution). Potential in the range of 100–900 mV (vs. Ag/AgCl) in a regime of cyclic voltammetry was applied to the GC electrode for 100 cycles at a potential sweep rate of 100 mV s^{-1}. To prepare the GC/RGONS–PL electrode, the GC/RGONS electrode was transferred to the