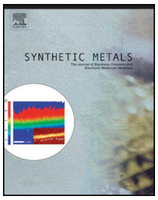
Synthetic Metals 196 (2014) 199–205

Contents lists available at ScienceDirect

Synthetic Metals

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



Preparation of conductive polyaniline/graphene nanocomposites via in situ emulsion polymerization and product characterization

Hossein Baniasadi, Ahmad Ramazani S.A. *, Shohreh Mashayekhan, Fariba Ghaderinezhad

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 5 April 2014
Received in revised form 3 August 2014
Accepted 6 August 2014

Keywords:
Polyaniline
Graphene nanosheets
Emulsion polymerization
Electrical conductivity

ABSTRACT

This work, which is a part of our ongoing studies on developing conductive scaffolds for nerve tissue engineering, reports synthesis of highly conductive binary-doped polyaniline nanoparticles and polyaniline/graphene nanocomposites. The samples were synthesized through chemical oxidation of aniline via in situ emulsion polymerization method in presence of hydrochloric acid and sodium dodecyl sulfate. Graphene nanosheets were also prepared via modified Hummer's method followed by chemical reduction using hydrazine monohydrate. Electrical conductivity measurements using a standard four-point probe technique with FTIR and UV–vis studies revealed that conductive binary-doped emeraldine salt polyaniline had been successfully produced. The results also showed that incorporation of less than 1 wt.% of graphene nanosheets into polymeric matrix had improved electrical conductivity of polyaniline from 2 to 7 S cm^{-1}. The SEM micrographs illustrated that the synthesized polyaniline had spherical morphology with particle size of 10–15 nm. The results of the investigated thermal properties showed that binary doping process and also incorporation of graphene into polymeric matrix had improved thermal stability of polyaniline main chains. Finally, this work supported proper morphological, electrical, and thermal properties of prepared PANI/graphene nanocomposites and their potential use in different biomedical applications such as tissue engineering, biosensor, controlled drug delivery systems, and surface coating.

1. Introduction

In recent years, conductive tissue engineering scaffolds have attracted much attention due to their special conductive properties [1]. Several studies have confirmed their great capacity for supporting and modulating the growth of various types of cells such as endothelial, nerve, bone and chromaffin cells [2,3]. These conductive scaffolds are usually obtained by incorporation of a biodegradable polymer as a matrix and an intrinsically conductive polymer as a conductive component.

Conducting polymers, extensively conjugated molecules, have π electron delocalization along their backbone which gives them unique optical and electrical properties. This characteristic causes them to act as a semiconductor or a conductor [4]. Some conductive polymers which are well known in the biomedical and tissue engineering applications include polyaniline, polythiophene and polypyrrole. They are used as the electroactive substrates for culturing electrically excitable cells such as neuron or muscle cells [5,6]. Polyaniline (PANI) is one of the most attractive conducting polymers among the known conducting polymers due to some of its characteristics including good environmental, thermal, and chemical stability, tunable conductivity switching between insulating and semiconducting materials, low operational voltage, facile synthesis, potentiality for practical applications and low cost [7,8].

Since PANI is non-biodegradable, non-flexible and non-processable, only very low amount of PANI should be used for producing conductive scaffolds. In addition, the particle size of PANI should be controlled within a proper range, i.e. less than 100 nm, in order that PANI particles can be easily excreted through circulatory systems after complete degradation of polymeric matrix [9]. Usually, two methods including chemical oxidation and electrochemical synthesis are employed for preparing PANI. Although prepared PANI via electrochemical synthesis generally has higher conductivity, this method is restricted by the size, shape and nature of the involved electrode. Therefore, this method cannot be used to prepare a large amount of PANI or to produce fine PANI powders; thus PANI used in conductive tissue engineering scaffolds is normally synthesized via the chemical oxidation method [9]. Furthermore, it is notable that emulsion polymerization is very

---

* Corresponding author at: Sharif University of Technology, P.O. Box 11365-8639, Tehran, Iran. Tel.: +98 216616 6405; fax: +98 216602 6405.
E-mail address: ramazani@sharif.edu (A. Ramazani S.A.).

http://dx.doi.org/10.1016/j.synthmet.2014.08.007
0379-6779/© 2014 Elsevier B.V. All rights reserved.

effective in producing polymer particles with the size in the range of 5–100 nm [10].

To improve electrical conductivity of PANI, conductive nanomaterials such as carbon nanotube and graphene nanosheets are usually used [11–13]. Graphene, a single layer of carbon atoms in a hexagonal lattice, has recently attracted much attention due to its novel electronic and mechanical properties [14]. It is usually prepared by reduction of its precursor-graphene oxide. Both graphene and graphene oxide sheets show very high mechanical properties with well biocompatibility and also have potential applications as biomaterials [15]. However, only graphene sheets show high electrical conductivity and can highly promote electrical conductivity of polymeric materials.

To produce highly conductive polymeric nanoparticles for ongoing researches on conductive scaffolds and their ability for neural cell proliferation, aniline was polymerized by the chemical oxidation method via emulsion polymerization in presence of chemically reduced graphene nanosheets. The results showed that spherical nanoparticles of polyaniline with the size of 10–15 nm had successfully produced and incorporation of small amount of graphene into polymeric matrix dramatically improved electrical properties of PANI. Hence, it can be a proper candidate for different biomedical applications especially fabrication of conductive scaffolds for nerve regeneration.

2. Experimental

2.1. Materials

Powdered flake of graphite was purchased from Dae-Jung Chemicals and Metals Co., Republic of Korea. The aniline monomer was obtained from Sigma–Aldrich, purified by vacuum distillation and kept under nitrogen in a refrigerator at 4 °C prior to use. Ammonium peroxydisulfate (APS) and sodium dodecyl sulfate (SDS) purchased from Sigma–Aldrich were used as the radical oxidant and emulsifier, respectively. Hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$) were purchased from Merck and were used as received.

2.2. Synthesis of graphene oxide and reduction to graphene nanosheets

Graphene oxide was prepared via modified Hummer's method and chemically reduced to graphene [16]. Synthesized graphene oxide was dispersed in water followed by adding aqueous KOH solution (1 N). KOH, a strong base, can confer a large negative charge through reactions with the reactive hydroxyl, epoxy and carboxylic acid groups on the graphene oxide sheets, resulting in extensive coating of the sheets with negative charges and K^+ ions. To produce a homogeneous suspension of reduced graphene, hydrazine monohydrate was added to KOH-treated graphene oxide.

2.3. Synthesis of polyaniline

Emeraldine salt polyaniline (PANI-ES) was synthesized by chemical oxidation via two methods: conventional emulsion polymerization to produce binary-doped PANI nanoparticles and homogeneous solution polymerization to produce single-doped PANI.

In conventional emulsion polymerization, 5.767 g SDS was dissolved in 90 ml HCl (1 M) containing 0.745 g aniline monomer in a three necked round bottom flask with vigorous stirring at room temperature under nitrogen atmosphere to obtain a uniform solution. After 30 min, 10 ml HCl (1 M) including 0.913 g APS as an oxidant was added dropwise into the reaction mixture in 20–30 min. During this period, the homogeneous milky reaction mixture was turned into bluish tint pronouncing polymerization proceeded. The stirring was continued for 6 h and then the reaction was allowed to proceed without agitation for 24 h at room temperature to complete polymerization. Excess amount of methanol was added into the system to stop the polymerization and to precipitate product by breaking the hydrophilic–lyphophilic balance of the mixture. The product was isolated by centrifuging for 20 min at 8000 rpm. The obtained cake was washed with methanol, acetone and water to remove unreacted chemicals, aniline oligomers and SDS. Finally, the synthesized binary-doped emeraldine salt PANI was dried in a vacuum oven at 50 °C for 48 h.

A homogeneous solution polymerization was also carried out with the same molar ratio of oxidant to monomer for comparison. The solution polymerization was stirred for 24 h at room temperature under nitrogen atmosphere, and obtained PANI was centrifuged with the same procedure described above. Obtained single-doped emeraldine salt PANI was dried in a vacuum oven at 50 °C for 48 h. Emeraldine base PANI (PANI-EB) was also prepared as a control by suspending prepared PANI-ES with constant stirring in 100 ml of NH_4OH (24%) solution in order to convert the polyaniline hydrochloride (emeraldine salt) to polyaniline (emeraldine base).

2.4. Synthesis of polyaniline/graphene nanocomposite

To prepare polyaniline/graphene nanocomposite, graphene was dispersed in 90 ml HCl (1 M)/monomer solution. The continuation of the process was similar to the PANI polymerization as described above. The amounts of graphene were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, and 1 wt.% of the monomer net weight. It should be mentioned that 1 M concentration was selected as the optimum concentration of HCl to dope according to the Thanpitcha et al. [17] report. Briefly, the enhancement of the electrical conductivity with increasing HCl concentration (from 0.1 to 1 M) is due to the increase of protonation degree of the imine group of PANI. At higher HCl concentrations (2–6 M HCl), a decrease in electrical conductivity occurs. This result is probably due to the over protonation of PANI chains causing a decrease in the delocalization length of PANI.

2.5. Characterizations

The Fourier transform infrared microscopy (FTIR) spectra were recorded using a Shimadzu FTIR spectrometer. All spectra were the average of 64 scans at a resolution of 4 cm^{-1}, from 500 cm^{-1} to 4000 cm^{-1} which were done at 25 °C.

The wide-angle X-ray diffraction (XRD) patterns were recorded using a X'pert PRO MRD, Philips, Netherlands using CuKa radiation ($\lambda = 1.5406$ Å) at a generator voltage of 40 kV and current of 40 mA. Scanning was done in 0.02° at a rate of 1°/s. The interlayer spacing (d_{001}) of graphene oxide was calculated in accordance with Bragg equation: $2d \sin\theta = \lambda$.

The transmission electron microscopic (TEM) images of graphene sheets were taken by Philips CM200 with an accelerating voltage of 200 kV. The samples were redispersed in deionized water and were sonicated for 5 min, then a droplet of graphene dispersion was cast onto a TEM copper grid and the solvent evaporated overnight at room temperature.

The conductivity measurements were performed using a standard four-point probe method at a constant current of 0.5 mA and ambient temperature. The dried PANI salt powder (and nanocomposites) was compressed into a disk of 13 mm in diameter with a hydraulic pressure at 3000 psi to measure the conductivity. Each measurement was repeated three times and the average values reported as the result.