Materials Science and Engineering C 79 (2017) 55–65

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Synthesis of silane ligand-modified graphene oxide and antibacterial activity of modified graphene-silver nanocomposite

Soghra Fathalipour *, Mojtaba Mardi

Department of Chemistry, Payame Noor University, PO Box: 19395-3697, Tehran, Iran

ARTICLE INFO

Article history:
Received 25 July 2016
Received in revised form 26 January 2017
Accepted 4 May 2017
Available online 5 May 2017

Keywords:
Silane ligand
Ag nanoparticles
Modified graphene oxide
Antibacterial

ABSTRACT

In this research, a new type of chemically modified graphene oxide (GO) was synthesized based a silane ligand and then used as substrate and stabilizing for the synthesis of monodispersed and small Ag nanoparticles (NPs). First, ligand molecules were successfully grafted onto the surface of GO (LGO) and then, active groups of LGO could effectively interact with Ag ions. The reduction of Ag ions and LGO sheets was carried out by hydrazine under reflux. The resulted nanocomposite was fully characterized by different techniques. Furthermore, the antibacterial behavior of nanocomposite was studied against *E. coli* and *S. aureus*. The results showed that nanocomposite exhibits good antibacterial activity against *E. coli* and *S. aureus* and also *S. aureus* showed greater resistance than the *E. coli* strains against the LG/Ag nanocomposite.

1. Introduction

Recently, graphene (G) has received increasing attention due to its unique structural, surface properties, extraordinary electronic, thermal and mechanical properties [1–3]. The general method for the preparation of exfoliated graphene sheets is the combination of oxidation and sonication procedures, followed by chemical reducers [4,5]. In solution, obtained graphene sheets are aggregated due to strong Vander Waals interactions and it needs to decrease [6]. Graphene oxide (GO), a graphene derivative, consists of a basal plane with hydroxyl, epoxy, carbonyl and carboxylic groups [7,8]. The surface modification of graphene oxide sheets with classification of the organic chemical functionalization and then inserting of metal nanoparticles (NPs) among two-dimensional (2D) modified GO sheets through the reduction of metal precursors could inhibit the aggregation of graphene sheets [9–11]. On the other hand, the grafting of functional groups to graphene sheets also helps in dispersion a hydrophilic or hydrophobic media and this issue has crucial importance in their applications [12–16]. Extensive studies have been carried out on the surface modification of graphene sheets and the preparation of graphene-metal nanoparticles composites [17–20]. However, there are limits due to dispersibility, electrical conductivity and the experimental complications.

In recent years, silver-graphene nanocomposites have attracted much attention due to their potential applications in catalysis, nanoscale electronics, antibacterial, SERS substrates biomedical field and use in pharmaceuticals [21–26].

Silane organic compounds as a modifier of carbon based materials could produce nanomaterial with new chemical and physical properties [27–29]. Yang and coworkers prepared modified graphene via facile covalent functionalization of GO with 3-aminopropyltriethoxysilane and employed as reinforcing components in silica monoliths [30]. The resulting functionalized graphene sheets showed high dispersibility into water, polar solvents such as ethanol, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). Chemonne et al. linked chelating groups via a silanization reaction between N-(trimethoxysilylpropyl) ethylenediamine triacetic acid (EDTA-silane) and hydroxyl groups on GO sheets. The modified GO showed high adsorption behavior for pb (II) removal [31]. Yao and coworkers prepared also functionalized graphene by the reaction of N-(3-trimethoxysilylpropyl) diethylenetriamine with the hydroxyl groups of GO and then used as the template for Au nanoparticles (Au NPs). The resultant Au-G nanocomposite showed potential applications in SERS [9].

In this report, a new silane ligand (3,3′-bis-(3-triethoxysilylpropyl)-2,2′-dithioxo [5,5′] bithiazolidinylidene-4,4′-dione) has been used for the modification of GO. The silylation modification technique with this ligand on Al_2O_3 NPs has been previously reported by Hassanpoor et.al. [32]. The resulted Al_2O_3 nanoparticles were used in ultra-trace determination of arsenic species in environmental waters and food and biological samples.

The researchers would like to highlight in fact that this chelating ligand is a superior modifier for GO, and a new type of chemically functionalized graphene oxide sheets with chelating groups via a silanization reaction. On the other hand, it is believed that the silanization of GO with this ligand will be the best method to prepare the monodispersed Ag NPs due to several advantages that includes: (a) chemical reaction between the trialkoxy groups of silane ligand

* Corresponding author.
E-mail address: fathalipour@pnu.ac.ir (S. Fathalipour).

http://dx.doi.org/10.1016/j.msec.2017.05.020
0928-4931/

and the hydroxyl groups on the surface of graphene oxide that created the higher distance between the layers in the composites than pure GO and prevented from aggregation of GO sheets (b) modification provided a suitable environment for the presence the monodispersed Ag NPs with high density. Several active functional groups, such as carbonyl, thiol, thiocarbonyl, amide and hydroxyl groups in modified GO, could easily interact with Ag ions through strong and weak covalent binding to form the MGO/Ag+ complex and then chemical reduction of the complex with hydrazine monohydrate at reflux condition formed the LG/Ag nanocomposite.

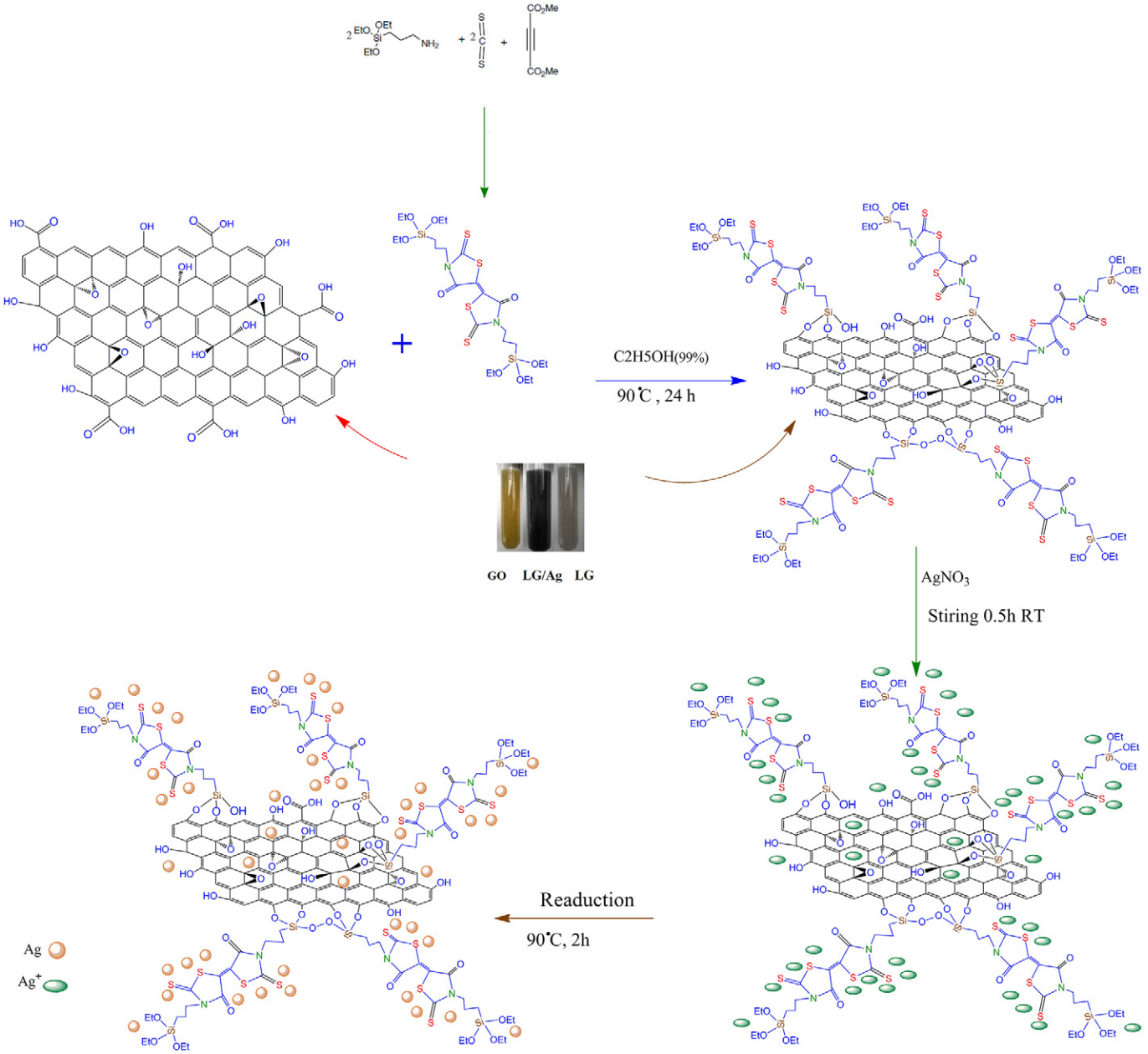
2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$), graphite, carbon disulfide (CS_2), dimethyl acetylene dicarboxylate (DMAD), 3-(triethoxysilyl) 1-propanamine (TEPA) were obtained from Merck and used as received without further purification. Deionized water was used during the samples.

2.2. Equipment

UV–Vis spectra were recorded by a PG Instruments T80 UV–Vis spectrophotometer with a scan range of 200–800 nm and NMR spectra were recorded with a Bruker DRX-250 AVANCE (Rheinstetten, Germany) instrument (300.1 MHz) with $CDCl_3$ as solvent. Besides, X-ray diffraction measurements were recorded by a Bruker-D8 ADVANCE 3000 X-Ray diffractometer based on Cu Kα radiation (Kα = 0.1542 nm) at a scanning rate of 10.0°/min, using a voltage of 40 kV and a current of 40 mA. Fourier Transform Infrared (FTIR) spectra were obtained on Shimadzu 8400 spectrometer. The Raman spectra were determined by Dispersive Raman Microscope (Bruker, Germany) in the range of 500–1800 cm^{-1} using a laser beam with wavelength of 785 nm. Morphology and particle sizes of composites were noticed using by transmission electron microscopy (TEM, Philips-CM 30). Energy-dispersive X-ray



Scheme 1. Schematic diagram to illustrate the preparation process of LG/Ag nanocomposite.