Contents lists available at ScienceDirect

Applied Surface Science

Full Length Article

A facile and green preparation of reduced graphene oxide using *Eucalyptus* leaf extract

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ABSTRACT

In this paper, a green and facile synthesis of reduced graphene oxide (GO) by *Eucalyptus* leaf extract (EL-RGO) was investigated, which was characterized with ultraviolet-visible spectroscopy (UV), Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Thermal gravimetric analysis (TG). *Eucalyptus* leaf extract also play both reducing and capping stabilizing agents prepared EL-RGO as shown a good stability and electrochemical properties. This approach could provide an alternative method to prepare EL-RGO in large-scale production. Moreover, the good electrochemical property and biocompatibility can be used in various applications. In addition, the merit of this study is that both the oxidized products and the reducing agents are environmental friendly by green reduction.

1. Introduction

Graphene, a two-dimension hexagonal form sheet of sp^2-hybridized carbon nanostructures, has becoming one of the materials in nanoscale science and technology. It has been widely investigated for many fields such as nanoelectronics, sensors, nanocomposites, battery, suppercapacitors, and hydrogen storage, owing to its excellent mechanical, electrical, thermal, and optical properties [1–4]. The challenge of finding an effective route to synthesize the high quality monolayer graphene has attracted the attention. Various techniques have been used to prepare graphene, including micromechanical exfoliation, [5] chemical vapor deposition, [6,7] epitaxial growth [8] and chemical route via reduction of graphene oxide (GO) [9–12]. Among these methods, the chemical reduction of GO with reducing agent has trends toward the greatest potential for industrialization owe to it has the advantages of low-cost and easy accessibility [10], so far, numerous reducing agent such as hydrazine and its derivatives [11], sodium borohydride [13], lithium aluminium hydride [14] and hydroquinone [9] have been used to convert GO to reduced graphene oxide (RGO). However, those chemical reducing agents are highly toxic and dangerously, leading to impact on the ecosystem. Moreover, chemical

agents the hazardous waste generated by the chemical reduction significantly increase the cost. In addition, graphene are prone to aggregate when reducing GO in aqueous solution using chemical agents without adding any cosolvent. As a result, all those problem of graphene by chemical method limits its applications.

Graphene has a potential for microbial fuel cells and biomedical application, including tissue engineering, drug delivery, bioimaging due to their biocompatibility [15]. Therefore, new approaches need to be explored for effective reduction of GO sheet to stable graphene by utilizing environmentally friendly reducing agents at mild reaction conditions. In recent years, there have been developed some environmental-friendly methods for reduction of GO. For example, an environmental friendly method to produce graphene utilizing vitamin C as the reductant and amino acid as the stabilizer was established [16]. Zhu et al. successfully produced graphene nanosheets with graphene oxide as precursor and reducing sugars as reducing agent [17]. Wang et al. reported that the soluble graphene can be synthesized via the tea solution reduction of graphene oxide [18]. However, those environmentally friendly methods for reducing GO are required with a natural biomass.

Eucalyptus is a kind of fast-growing endemic trees in Fujian province, China. In our previous study, it demonstrated that aqueous leafs extracts of *Eucalyptus* was used as a reducing and stabilization agent for iron nanoparticles (Fe NPs) synthesis [19]. In this work, we report an environmentally friendly approach to reduction of graphene oxide by using *Eucalyptus* leaf extract

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as a reducing. As a primary study, the reduced graphene oxide (EL-EGO) by leafs extracts of Eucalyptus was characterized by ultraviolet visible spectroscopy (UV-vis), Raman spectra, X-ray diffraction (XRD), scanning electron microscope (SEM), atomic-force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and Cyclic voltammetry (CV).

2. Experimental

2.1. Materials and chemicals

Graphite powder (8000 mesh, purity 99.95%) was obtained from Aladdin Reagent Co. Ltd., Shanghai, China. Concentrated sulfuric acid (H_2SO_4, 95–98%) was purchased from Hengyang city kaixin chemical reagent co., LTD. Potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%) and anhydrous ethanol (CH_3CH_2OH, 99.7%) were provided by Guangdong guanghua Sci-Tech co., LTD. All the chemicals were analytically grade and were used as received without further purification. All aqueous solutions were prepared with deionized water. Dried Eucalyptus leaves were collected from a local farm in Minhou (Fuzhou, China).

2.2. Preparation of GO by oxidizing the graphite powder

GO was prepared by oxidizing the graphite powder in a mixture of concentrated H_2SO_4 and $KMnO_4$ via the modified Hummers method [20,21]. The brief procedures are described as follows. Firstly, 2 g of graphite powder was added into a beaker containing 35 mL of 98% H_2SO_4 and stirred at room temperature for 2 h on a magnetic stirrer. Secondly, 6 g of $KMnO_4$ was gradually added into the above beaker by maintaining the temperature below 20 °C with gentle stirring. Then the mixture solution was heating in a temperature-controlled water bath kettle at 35 °C for 4 h. The resulting solution was diluted by adding 90 mL of distilled water and vigorous stirring with magnetic stirrer for 1 h. Then a dark brown suspension was obtained. The suspension was further treated by adding 30% H_2O_2 solution dropwise until the color of the solution became brilliant yellow. The resulting GO suspension was washed with 5% HCl solution to remove excess of manganese salt, then further filtered and washed with 0.45 μm filter to remove the residual acid until the pH value of rinse water become neutral. Then the purified GO was diluted in water and effectively dispersed in an ultrasonic cleaner. Thus a stable dispersion of GO solution was obtained. Finally, the resulting solution of GO was freeze-dried for 48 h.

2.3. Preparation of Eucalyptus leaf extract

A 200 mL aqueous solution containing 2 g milled eucalyptus leaves was prepared and heated at 80 °C. After 1 h, the mixture was filtered with 0.45 μm filter to obtain the extract and the filtrate was stored at 4 °C [22].

2.4. Preparation of the EL-RGO based on Eucalyptus leaf extract reduction

The reduction of prepared GO was performed as follows: 10 mg of GO was dispersed in 20 mL of distilled water by sonication for 30 min. Then 5 mL of Eucalyptus leaf extract (EL) was added into the above prepared solution. The final solution was kept in electro-thermostatic water bath at 80 °C for 8 h. Then, the products were washed and filtered with ethyl alcohol and distilled water several times until a clear solution was obtained. Finally the products were dried by vacuum freeze dryer to get EL-RGO.

2.5. Characterization

Morphology of the GO and EL-RGO were determined by field emission scanning electron microscope (FESEM, JEOL, JSM-S4800) and Multimode atomic-force microscopy (AFM) equipped with a Nanoscope IIIa Controller system (Veeco instruments, Santa Barbara, CA). The surface oxidation states were measured using a Thermo ESCALAB 250 Xi X-ray photoelectron spectroscopy (XPS, VG Scientific Co., UK) with an Al Kα X-ray radiation (1486.6 eV) for excitation. The ultraviolet visible spectroscopy (UV-vis) absorption spectroscopy was conducted with a UV–vis reflective spectrophotometer (UV1902, Phoenix, Shanghai, China) over the wavelength range from 190 to 800 nm at atmospheric pressure and room temperature to indicate the electronic absorption spectra. Thermogravimetric analysis (TGA) was carried out using a TA Q600 thermal analyzer (SDT Q600,TA Instrument Co., USA) under a nitrogen atmosphere, over a temperature range of 30–1000 °C with a heating rate of 10 °C min^{-1}. Raman spectra were recorded with LabRAM HR-800 high resolution Raman spectrometer (Horiba Jobin Yvon Co., Longjumeau, France) using a YAG Laser (λ = 532). The X-ray diffraction (XRD) pattern of powdered samples were characterized by using PANalytical X'pert PRO with a Cu Kα radiation (λ = 0.15418 nm, 40 KV and 40 mA). Cyclic voltammetry (CV) experiments were performed with a CHI 660 B electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd.).

2.6. Electrochemical measurements

The cell of CV experiment was carried out in a conventional three electrode system with a supporting electrolyte of 0.5 mol L^{-1} H_2SO_4. The working electrodes including an Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wires as counter electrode, and the bare and modified glassy carbon electrode (GCE) as working electrode. First, GCE (3 mm in diameter, 0.07065 cm^2 geometric area) was polished with alumina slurry (particle size: D50: 0.5–0.7 μm) sequentially and then ultrasonic washing in deionized water and ethanol for a few minutes, respectively. The GCE was dried and purged with nitrogen gas for 10 min before each test. The electrodes were pretreated in a separated cell containing 0.5 mol L^{-1} H_2SO_4 to remove any possible surface contaminants and to ensure catalysts' activity before each CV measurement. Then, a total of 5 μL of GO or EL-RGO (0.2 g/mL) was dropped on the pretreated GCE surface and dried at room temperature to form GO or EL-RGO modified GCE. The CV curves are investigated in the potential region of −0.1 ∼ 0.6 V at a scanning rate of 50 mV s^{-1}.

3. Results and discussion

3.1. Characterization

Since the reduction of GO results in a great change in its microstructure and properties, it is directly observed to judge the reducing effect of reduction process. First, on completion of reduction process, a visible change in the color of EL-RGO from the reactant, as shown in Fig. 1, indicating of the reaction and form the new compounds [23]. The reduction in colloid state by chemical reduction usually results in a black precipitate from the original brownish-yellow suspension, which probably results from an increase in the hydrophobicity of the material caused by a decrease in polar functionality on the surface of the sheets [11,12]. Therefore, the change in color to black can be an obvious visible characteristic to exposure the reduction of graphene oxide by Eucalyptus leaf extract.