Colloids and Surfaces B: Biointerfaces 118 (2014) 72–76

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

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

Facile synthesis of soluble graphene quantum dots and its improved property in detecting heavy metal ions

Chengfeng Zhou[a,*], Wei Jiang[b,a], Brian K. Via[a,c]

[a] School of Forestry and Wildlife, Auburn University, Auburn 36849, USA
[b] Laboratory of New Fiber Materials and Modern Textile, The Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, PR China
[c] Department of Biosystems Engineering, Auburn University, Auburn 36849, USA

ARTICLE INFO

Article history:
Received 3 January 2014
Received in revised form 19 March 2014
Accepted 23 March 2014
Available online 30 March 2014

Keywords:
Graphene quantum dot
Cutting
Electrochemical detection
Heavy metal ions

ABSTRACT

An effective approach to produce graphene quantum dots (GQDs) has been developed, which based on the cutting of graphene oxide (GO) powder into smaller pieces and being reduced by a green approach, using sodium polystyrene sulfonate (PSS) as a dispersant and L-ascorbic acid (L-AA) as the reducing agent, which is environmentally friendly. Then the as-prepared GQDs were further used for the detection of heavy metal ions Pb^{2+}. This kind of GQDs has greater solubility in water and is more biocompatible than GO that has been reduced by hydrazine hydrate. The few-layers of GQDs with defects and residual —OH groups were shown to be particularly well suited for the determination of metal ions in the liquid phase using an electrochemical method, in which a remarkably low detection limit of 7×10^{-9} M for Pb^{2+} was achieved.

1. Introduction

Heavy metal pollution is a serious problem in nature due to the stability of metals at contaminated sites and high toxicity to the biosphere. Lead, cadmium and zinc are major heavy metal contaminants from industrial waste streams and being continuously added to the environment. Because of the extensive use of these metals and the hazardous effect to both humans and other organisms, the development of sensitive monitoring methods has become increasingly crucial. Therefore, a simple, sensitive and accurate analytical method for the detection of heavy metal ions is necessary. In recent years, with the development of new nanoscience and nanotechnology, many nanomaterial-based electrodes have been applied for the electrochemical determination. These electrodes are beneficial and can dramatically enhance the signal intensity of an electrochemical sensor and lead to ultrasensitive detection. To the best of our knowledge, the fabrication of novel electrochemical sensors using graphene-based materials to achieve sensitive, fast and facile detection has become a hot spot, and the work herein has not been replicated elsewhere.

Graphene-based materials are promising building blocks for future nanodevices owing to their superior electronic, thermal, and mechanical properties as well as their chemical stability [1]. However, currently available graphene-based materials produced by typical physical and chemical routes, including micromechanical cleavage [2], reduction of exfoliated graphene oxide (GO) [3], and solvothermal synthesis [4], are generally micrometer-sized graphene sheets (GSs), which limits their direct application in nanodevices. In this context, it has become imperative to develop effective routes for cutting large GSs into nanometer-sized pieces with a well-confined shape, such as graphene quantum dots (GQDs).

Most GQD-based electronic devices have been fabricated by lithography techniques, which can realize widths and diameters down to ca. 20 nm [5]. This physical approach, however, is limited by the need for expensive equipment and especially by difficulties in obtaining smooth edges. Alternative chemical routes can overcome these drawbacks. Moreover, surface functionalization can be realized easily and the preparation of carbon nanodots also has the similar results [6]. Very recently, Pan et al. [7] have developed a facile hydrothermal method for cutting preoxidized graphene nanosheets into ultrafine luminescent graphene quantum dots (GQDs). Subsequently, Li et al. [8] and Qu et al. [9] have developed preparation methods for luminescent GQDs by hydrazine hydrate reduction of polyethylene glycol (PEG) functionalized graphene oxide (GO) and electrochemical method, respectively. However,

* Corresponding author at: Forest Product Lab, School of Forestry and Wildlife, Auburn University, 520 Devall Dr., Auburn, AL, USA. Tel.: +1 334 844 1088.
E-mail addresses: chengfengzhou828@gmail.com, czz0024@auburn.edu (C. Zhou), weijiangqd@gmail.com (W. Jiang), BKV0003@auburn.edu (B.K. Via).

http://dx.doi.org/10.1016/j.colsurfb.2014.03.038
0927-7765/

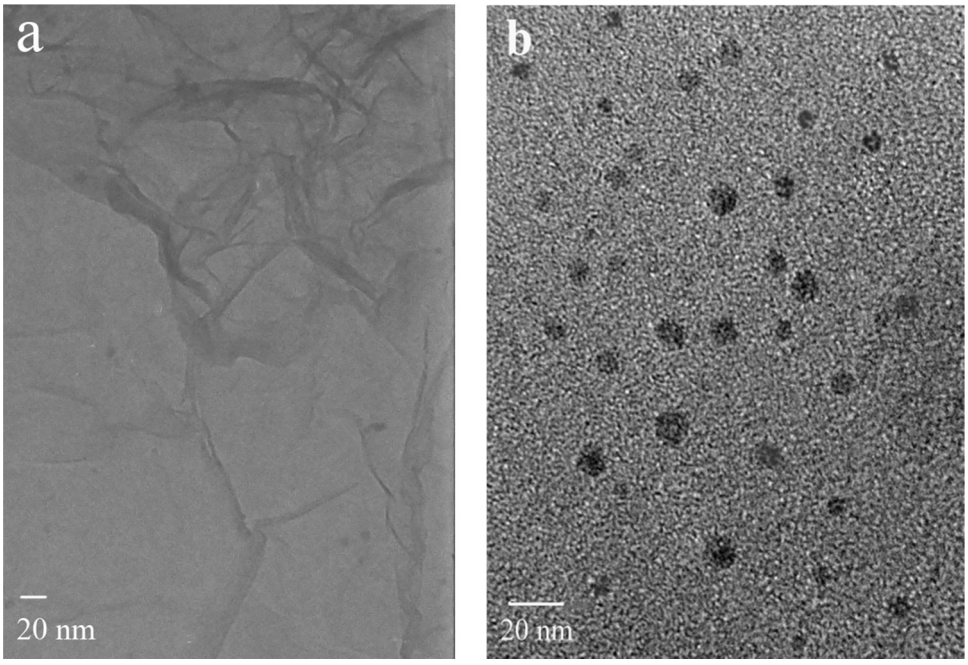

Fig. 1. Transmission electron microscopy (TEM) images of (a) pristine GO and (b) GQDs.

the hydrothermal method needs rigorous conditions, which is unsuitable for producing in quantity. Although, hydrazine was much more frequently used to reduce GO due to its high reduction efficiency [10–12,3,13,14], hydrazine and their derivatives are toxic and harmful to human as well as the environment. Zhang et al. [15] and Gao et al. [16] reported a green method to reduce GO with L-ascorbic acid (L-AA) in aqueous media, which is environmentally friendly. Meantime, L-AA possessed higher reduction efficiency concerning the electrical conductivity of the as-prepared chemically reduced graphene in comparison with such reductants as ammonia and potassium hydroxide, etc. [17]. If GO is highly reduced without surfactants, it will cause inevitable aggregation [18–20], making it difficult to be uniformly dispersed in solutions.

In our research, we present a simple and controlled method to well tune the lateral size of GO at the nanometer scale by periodic acid oxidation in a mild condition, and then the GO nanosheets were reduced by L-AA with surfactant of sodium polystyrene sulfonate (PSS) to obtain GQDs. The as-prepared GQDs showed an enhanced performance in the electrochemical sensing of heavy metal ions.

2. Experimental

2.1. Materials and synthesis

All chemicals and reagents used for experiments and analysis were analytical grade. Graphite oxide was synthesized from expandable graphite by a modified Hummers method [21]. Then graphite oxide (30 mg) was dispersed into deionized water (10 mL) followed by sonication for more than 3 h to obtain brown GO solution. Later, 15 g of periodic acid (H_5IO_6) were added into 10 mL of GO dispersion (concentration is 3 mg/mL) and the mixed solution was kept at 60 °C for 24 h. The precipitate was centrifuged out from solution at 15,000 rpm for 30 min, and then washed with deionized water until the supernatant was neutral. After that, PSS (0.1 g) was added into the above GO nanosheets solution (concentration is 1 mg/mL) and sonicated for 2 h. Finally, L-AA (250 mg) was added into the aqueous solution and stirred at 50 °C for 24 h. When the reaction ended, the color of the solution turned from yellow to dark black, which was a visual indication that the GO nanosheets were successfully reduced into GQDs. The resulting black suspension was filtered through a 0.22-μm microporous membrane. The colloidal solution still contained some large graphene nanoparticles (50–200 nm) that emitted weak blue fluorescence. So, the colloidal solution was further dialyzed in a dialysis bag (retained molecular weight: 3500 Da) overnight and GQDs that were strongly fluorescent through the bag were obtained. And the obtained GQDs solution was applied in the detection of heavy metal ions.

2.2. Characterization

TEM observations were performed on a Zeiss EM 10 Transmission Electron Microscope. FTIR spectra were recorded with a PerkinElmer spectrum 400 FT-IR/FT-NIR spectrometer within the wave range 750–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was carried out on KRATOS XSAM800 X-ray photoelectron spectrometer using Mg as the exciting source. UV–vis absorption and fluorescence spectra were recorded at room temperature on a Hitachi 3100 spectrophotometer and a F-96 spectrophotometer, respectively.

Anodic stripping voltammetry (ASV) experiments were performed using a CHI-660C electrochemical workstation with a conventional three-electrode cell. A glassy carbon electrode (GCE) and the modified electrodes were used as the bare and working electrodes. The auxiliary electrode was a platinum wire. All the potentials quoted in this work were referred to a saturated calomel electrode (SCE) as the reference.

2.3. Heavy metal ion detection procedure

A glassy carbon electrode (GCE) was polished with fine emery paper and chamois leather containing Al_2O_3 slurry (first 0.3 μm then 0.05 μm), then ultrasonically cleaned in distilled water, and dried in air for use. As-made GQDs was dispersed in water and then ultrasonicated to create a 1 mg/mL good-dispersion which was used immediately. The GQDs modified electrode (GQDs/GCE) was obtained by first sonicating GCE in nafion/ethanol (1%) solution for 5 min, then coating with GQDs dispersion (6 μL) on the GCE surface, and drying in air at room temperature.