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Enhancement of electrogenerated chemiluminescence of luminol by ascorbic acid at gold nanoparticle/graphene modified glassy carbon electrode

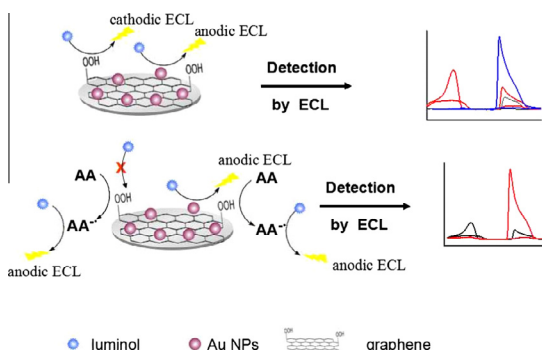
Yongping Dong^{a,*}, Tingting Gao^a, Ying Zhou^a, Xiangfeng Chu^a, Chengming Wang^{b,*}^a School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China^b Hefei National Laboratory for Physical Science at the Microscale, University of Science and Technology of China, Hefei 230026, China

HIGHLIGHTS

- Gold nanoparticles/graphene composite modified electrode is prepared.
- Luminol exhibits excellent electrogenerated chemiluminescence (ECL) at the modified electrode.
- Ascorbic acid could greatly enhance luminol ECL at the modified electrode.
- Ascorbic acid could be sensitively detected based on its enhancing effect on luminol ECL.

GRAPHICAL ABSTRACT

Gold nanoparticle (GNP) and gold nanoparticle/graphene (GNP/GR) modified electrodes were prepared. GNP/GR could enhance anodic luminol ECL slightly and enhance cathodic luminol ECL significantly. Ascorbic acid could be detected sensitively at the GNP/GR/GCE based on its enhancing effect of anodic luminol ECL.



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ABSTRACT

Gold nanoparticle/graphene (GNP/GR) nanocomposite was one-pot synthesized from water soluble graphene and HAuCl_4 by hydrothermal method and characterized by TEM, Raman spectroscopy, XRD, XPS, UV–vis spectroscopy, and electrochemical impedance spectroscopy (EIS). Electrogenerated chemiluminescence (ECL) of luminol was investigated at the GNP/GR modified glassy carbon electrode (GNP/GR/GCE) and the GNP modified glassy carbon electrode (GNP/GCE) in aqueous solution respectively. The results revealed that one strong anodic ECL peak could be observed at ~ 0.8 V at two modified electrodes compared with that at the bare electrode. The intensity of the anodic ECL at the GNP/GR/GCE is weaker than that at the GNP/GCE, which should be due to the synergic effect of the enhancing effect of gold nanoparticles and the inhibiting effect of graphene on anodic luminol ECL. One strong cathodic ECL peak located at ~ -0.8 V could be observed at the GNP/GR/GCE but not at the GNP/GCE, which should be result from the adsorbed oxygen at the graphene film. In the presence of ascorbic acid, the anodic ECL at the GNP/GR/GCE was enhanced more than 8-times, which is more apparent than that at the GNP/GCE. Whereas, the cathodic ECL peak was seriously inhibited at the GNP/GR/GCE. The enhanced ECL intensity at the GNP/GR/GCE varied linearly with the logarithm of ascorbic acid concentration in the range of 1.0×10^{-8} to 1.0×10^{-6} mol L^{-1} with a detection limit of 1.0×10^{-9} mol L^{-1} . The possible ECL mechanism was also discussed.

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* Corresponding authors. Tel.: +86 555 2311807, +86 551 63606447.

E-mail addresses: dongyp@ahut.edu.cn (Y. Dong), chmwang@ustc.edu.cn (C. Wang).

Introduction

Graphene is a one-atom-thick planar sheet of sp^2 -bonded carbon atoms that are densely packed in a honey-comb crystal lattice. Since Geim and Novoselov first exfoliated single-layer graphene from graphite, explosion of interest has occurred to both the theoretical and experimental scientists [1]. Graphene is widely used in electrochemical applications due to its large electrical conductivity, large surface area, unique heterogeneous electron transfer rate, and low production costs [2–5]. Different techniques have been performed to obtain graphene sheets such as epitaxial growth by ultra high vacuum graphitization, chemical oxidation of graphite and further reduction, chemical vapor deposition, and solvothermal synthesis with pyrolysis [6–10]. Recently, electrochemical techniques are alternatively used to produce graphene flakes because they are simple, economic, non-destructive, environmentally friend, operate at ambient temperature and pressure, and provide thickness control by adjusting the electrode potential [11–15]. However, the individual graphene sheets have a tendency to restack due to strong van der Waals interaction. Insertion of the metal nanoparticles into the graphene sheets is proven to be very effective in preventing such restoring. The hybridization of graphene with metal nanoparticles can not only provide an effective strategy for enhancing the functionality of materials but also further maximize high activity on the surface of graphene sheet [16]. Numerous studies have focused on the synthesis and applications of graphene/inorganic nanocomposite materials [17–25]. However, undesirable excessive reducing agents used in these methods both increase the cost in mass production and possibly remain and contaminate the synthesized materials. Therefore, it is of great interest to look for a simple and environmentally friendly approach for synthesis of graphene sheet-metal NPs composites.

Ascorbic acid, also known as vitamin C, acts as an antioxidant against a variety of diseases and is indispensable for life, health, and daily physical activities. Because of the biological and technological importance of AA, studies have been pursued to establish rapid and sensitive methods for the reliable determination of AA. Up to date, various analytical techniques including spectrophotometric, flow injection analysis, chromatography, and electrochemistry have been developed to study the ascorbic acid content in food, drugs and plants [26–31]. Electrogenerated chemiluminescence (ECL) is a special form of chemiluminescence in which light emission is generated by electrolysis. ECL has been applied in many analytical areas due to its versatility, simplified optical setup, reproducibility and high sensitivity [32]. However, to the best of our knowledge, only several ECL methods have been developed to determine ascorbic acid and luminol ECL has not been used in the detection of ascorbic acid [33–35].

It was reported that sodium citrate could be used as reducing and stabilizing reagent for Pt nanoparticles deposition on graphene film and the obtained nanoparticle-graphene nanosheets exhibited a better electrochemical activity than graphene sheet [36]. Therefore, in the present paper, water soluble graphene was prepared through electrochemical method. Then gold nanoparticle/graphene (GNP/GR) nanocomposite was synthesized by using sodium citrate as reducing and stabilizing reagent. The ECL behavior of luminol was investigated on the gold nanoparticle/graphene nanocomposite modified electrode and strong cathodic ECL emission was obtained. Ascorbic acid exhibited good enhancing effect on anodic luminol ECL and apparent inhibiting effect on cathodic luminol ECL, which could be used in the detection of ascorbic acid with high sensitivity.

Experimental sections

Chemicals and apparatus

Luminol was obtained from Sigma Chemical Co. (USA) and used without further purification. Chloroauric acid (HAuCl_4), sodium

citrate, and ascorbic acid was obtained from Sinopharm Chemical Reagent (Shanghai, China). The concentration of stock solution of luminol was 0.01 mol L^{-1} by dissolving luminol in 0.1 mol L^{-1} NaOH and stored in the refrigerator. Other chemicals were analytical grade or better and double distilled water was used throughout. The stock standard solution was used to prepare working standard solutions daily by suitable dilution. Phosphate buffer solutions (PBS 0.1 M) with different pHs were prepared with Na_2HPO_4 and NaH_2PO_4 , and the pH was adjusted with 0.1 mol L^{-1} NaOH and H_3PO_4 .

The electrochemical measurements were recorded with CHI 660D electrochemical workstation (Shanghai CHI Instruments Co., China). The ECL emission measurements were conducted on a model MPI-B electrochemiluminescence analyzer (Xi'an Remax Electronic Science & Technology Co. Ltd., Xi'an, China) at room temperature, and the voltage of the PMT was set at -800 V in the process of detection. All experiments were carried out with a conventional three-electrode system, including a modified GCE as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively. A commercial 5 ml cylindrical glass cell was used as ECL cell, and it was placed directly in the front of the photomultiplier tube (PMT). Transmission electron microscopy (TEM) was performed with JEOL model 2000 instrument operating at 200 kV accelerating voltage. The UV-vis absorption spectra were obtained on a Shimadzu UV-3600 spectrophotometer (Shimadzu, Japan). The fluorescence measurements were carried out on Edinburgh FLS920P fluorescence spectrometer (Edinburgh Instruments Ltd., UK). Raman spectra were recorded on a Renishaw inVia Raman microscope (excited with an Ar^+ line at 514 nm). X-ray photoelectron spectral (XPS) experiments were operated on a K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific Co., USA). X-ray powder diffraction (XRD) was performed on a Shimadzu XD-3A diffractometer with $\text{Cu K}\alpha$ radiation.

Synthesis of graphene by electrolytic exfoliation

The electrochemical synthesis of water soluble graphene was performed according to the literature [37]. Poly(sodium-4-styrenesulfonate) (PSS, $M_w = 70,000$) was dissolved in double distilled water to form the electrolyte (0.001 M). Two graphite rods were placed in an electrolysis cell filled with the electrolyte. A constant potential of 5 V was applied to the two graphite electrodes. After 20 min electrolysis, black product gradually appeared at the positive electrode. The exfoliation continued for 4 h. Then the product was taken from the electrolysis cell. The dispersion was centrifuged at low speed (1000 rpm) to remove large agglomerates. The obtained graphene suspension is very stable in nature and is used in the synthesis of gold nanoparticles/graphene colloid.

Synthesis of GNP/GR colloid

Gold nanoparticles with a diameter of 16 nm were prepared as follows: A 50 mL portion of HAuCl_4 ($10^{-2}\%$ w/w) solution was heated to boiling. While stirring vigorously, 1 mL of trisodium citrate ($1 \text{ wt}\%$) was added rapidly. The solution was maintained at the boiling point for 15 min , during which time a color change from gray to blue to purple was observed before a wine-red color was reached [38]. The obtained gold nanoparticles were stored in the refrigerator. During the preparation of gold nanoparticles, different amount of graphene was added in the above solution, and gold nanoparticle/graphene colloid was obtained. The resulting gold nanoparticles and gold nanoparticles/graphene colloids were characterized by transmission electron microscopy (TEM), XPS, XRD, UV-visible spectroscopy, and Raman spectroscopy.

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