

Supporting information

Fabrication of dispersible graphene/gold nanoclusters hybrid and its potential application in electrogenerated chemiluminescence

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Materials and Chemicals

Graphite powder (KS-10), bovine serum albumin (BSA, 96-99%) and glutaric dialdehyde (GD) were purchased from Sigma, Chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was obtained from Shanghai Reagent Company (Shanghai, China), 3-aminopropyl-triethoxysilane (APTES) was obtained from Shuguang Chemical Co. (Nanjing, China), trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) was ordered from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China), Hydrogen peroxide (H_2O_2) solution (30 wt. % aqueous) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), 0.1 M phosphate buffered saline (PBS, pH 7.4) containing 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ and 0.1 M KCl was used as the electrolyte in electrogenerated chemiluminescence (ECL) analysis. Unless especially stated, reagents were all analytical grade and used without treatment. Aqueous solutions were prepared with ultrapure water from an Elix 5 Pure Water System ($>18\text{M}\Omega \cdot \text{cm}$, Millipore, USA).

Apparatus

UV-Vis absorption spectra were recorded using a UV-3600 spectrophotometer (Shimadzu, Japan), FT-IR spectrum was obtained on a Nicolet 6700 spectrophotometer (Nicolet, USA), and X-Ray diffraction (XRD) measurements were performed by an XRD-6000 powder diffractometer (Shimadzu, Japan). Photoluminescence (PL) spectra were obtained on a RF-5301PC spectrophotometer (Shimadzu, Japan). Atomic force microscopy (AFM) image was obtained in tapping mode on an Agilent 5500 (Agilent Technologies, Inc., USA). High-resolution transmission electron microscopy (HRTEM) images were taken using a JEOL 2010 electron microscope (JEOL Ltd., Japan). The ECL intensity was detected with a Model MPI-A Electrochemiluminescence Analyzer (Xi'an Remax Electronic Science & Technology Co. Ltd., Xi'an, China) with a configuration consisting of an indium-tin oxide (ITO) working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The emission window was placed in front of the photomultiplier tube (PMT) biased at 800-1000 V. The ITO electrodes with a working area of about $1\text{ cm} \times 1\text{ cm}$ were purchased from Kangdake Photoelectric Technique Ltd. Co. (60 Ω).

Preparation of the BSA-stabilized AuNCs and the graphene/AuNCs hybrid.

Red fluorescent BSA-AuNCs was prepared based on the reference.^[S1] For fabricating the graphene/AuNCs hybrid, graphene colloid stabled by ammonia was prepared beforehand according to the reference.^[S2] The concentration of the graphene was determined by UV-Vis spectroscopy and further determined by weight loss method. The optimal condition for the synthesis of the graphene/AuNCs hybrid was as follows: 500 μL of 1% (wt. %) HAuCl_4 added dropwise into 5 mL of 0.2 mg mL^{-1} graphene colloid solution. Then the solution was stirred at 60 $^{\circ}\text{C}$ for 2 h. The gained homogeneous solution was dark red. For functionalizing with carboxyl, after prepared with the graphene/AuNCs hybrid, 1 mL of 0.1 M freshly prepared sodium citrate added into the solution further. For morphology analysis, the hybrid was collected by centrifugation and rinsed with ultrapure water.

Section A: XRD patterns of (a) graphene and (b) graphene/AuNCs hybrid; FT-IR spectrum of the graphene/AuNCs hybrid functionalized with carboxyl

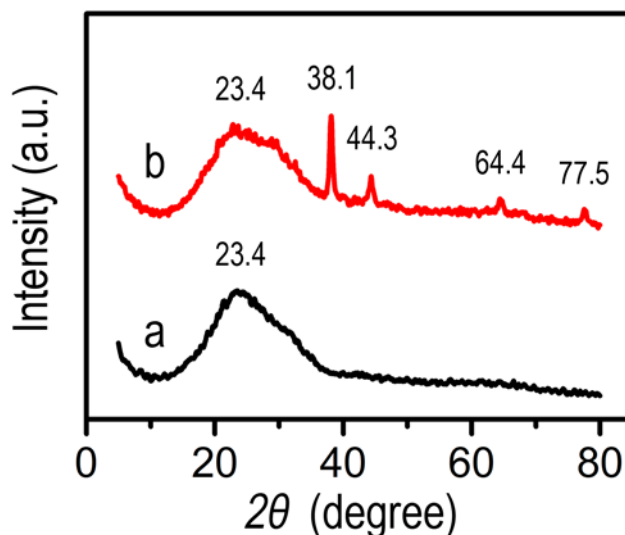


Fig. S1 XRD patterns of (a) graphene and (b) graphene/AuNCs hybrid.

In the XRD pattern, a broad peak focused at 23.4° was the characteristic peak of graphene (curve a). As for the graphene/AuNCs hybrid, it was clearly shown the Bragg angles of 38.1° , 44.3° , 64.4° and 77.5° , which corresponded to the (111), (200), (220) and (311) planes of AuNCs (curve b).^[S3]

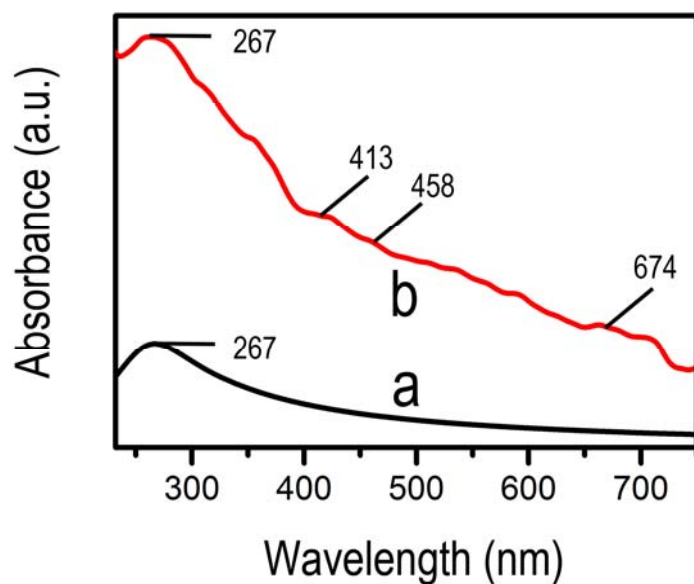


Fig. S2 UV-Vis absorption spectra of (a) graphene and (b) graphene/AuNCs hybrid.

For UV-Vis absorption spectra, the absorption peak at 267 nm shown in curve a and curve b can be ascribed to the characteristic peak of graphene.^[S2] As a typical absorption UV-Vis absorption spectrum of Au₂₅ has several distinct absorption peaks, and three of which appear at 670-690, 450, and 400 nm,^[S4-S5] the UV-Vis absorption peaks in curve b at 674, 458, and 413 nm identified the AuNCs on graphene were Au₂₅ clusters.

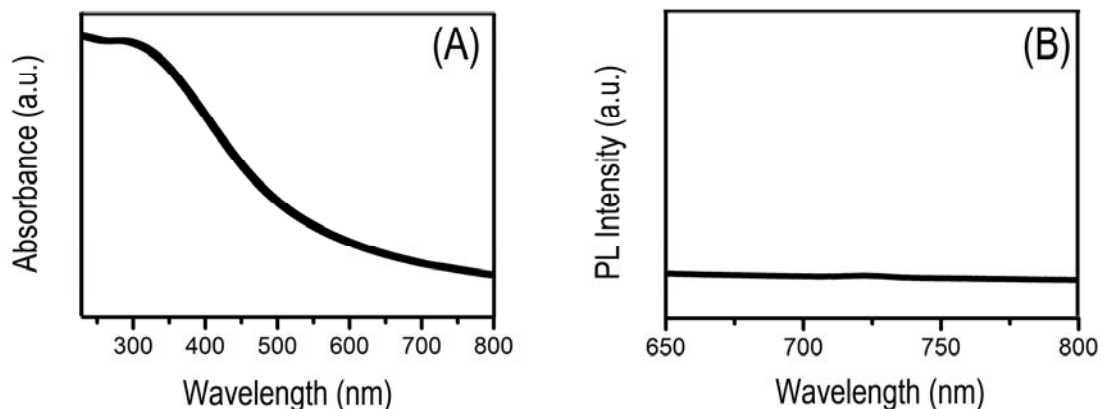


Fig. S3 (A) UV-Vis absorption spectrum and (B) photoluminescence spectrum of the product from ammonia as the reducing agent in the reduction of the gold ions.

In order to investigate effect of ammonia in the reduction of gold ions, the same amount of ammonia in the fabrication of graphene was used as the reducing agent to reduce HAuCl₄. No peak was observed in UV-Vis absorption spectrum, and also no emission peak was observed at 723 nm under the excitation light of 480 nm in PL spectrum. Therefore, ammonia could not reduce gold ions in this case.

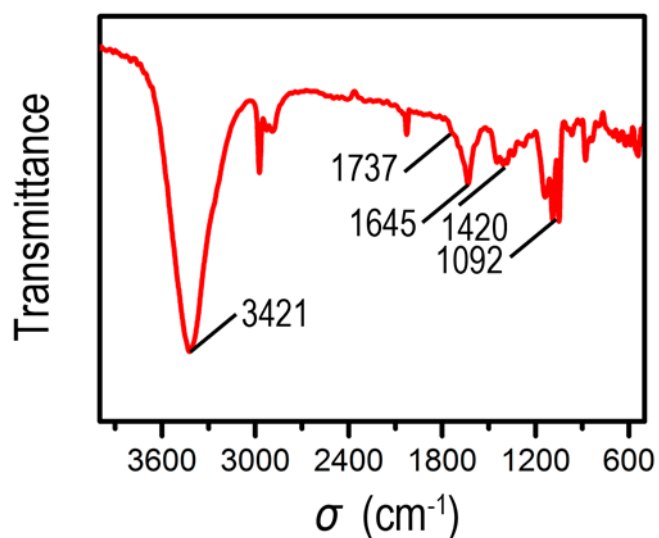


Fig. S4 FT-IR spectrum of the graphene/AuNCs hybrid functionalized with carboxyl.

The FT-IR spectrum of the graphene/AuNCs hybrid functionalized with carboxyl was obtained as shown in Fig. S4. It showed that the broad and distinct O-H stretching vibration was at 3421 cm^{-1} . The stretching peak focused at 1737 cm^{-1} ascribed to the C=O stretching peak, and the stretching peaks focused at 1420 cm^{-1} and 1092 cm^{-1} were derived from O-H and C-O stretching, respectively. All the results demonstrated that the carboxyl groups in sodium citrate molecules had attached to the hybrid.

Section B: Immobilization of the BSA-stabilized AuNCs or the graphene/AuNCs hybrid on ITO electrode

Constructing ITO modified electrode: The BSA-stabilized AuNCs electrode was prepared according to the reference.^[S6] For preparing the graphene/AuNCs hybrid electrode, after ITO electrode was cleaned according to the reference,^[S6] 20 μL of 4% (v/v) APTES in anhydrous ethanol was dropped onto the ITO electrode and dried in the air. After that, 20 μL (10 mM) graphene/AuNCs hybrid solution (the same amount and concentration as the BSA-stabilized AuNCs solution) was dropped on to the ITO electrode and dried in the air.

All the modified electrodes were thoroughly rinsed with water to remove the uncombined BSA-stabilized AuNCs or graphene/AuNCs hybrid prior to use.

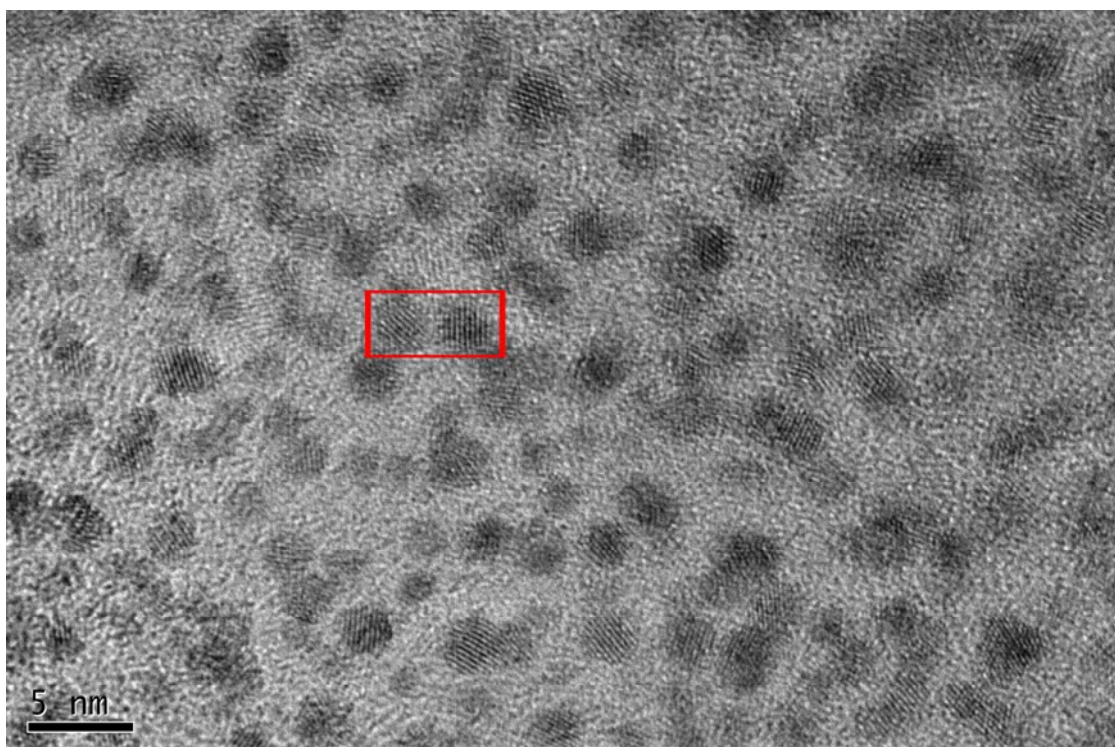


Fig. S5 HRTEM image of the graphene/AuNCs hybrid.

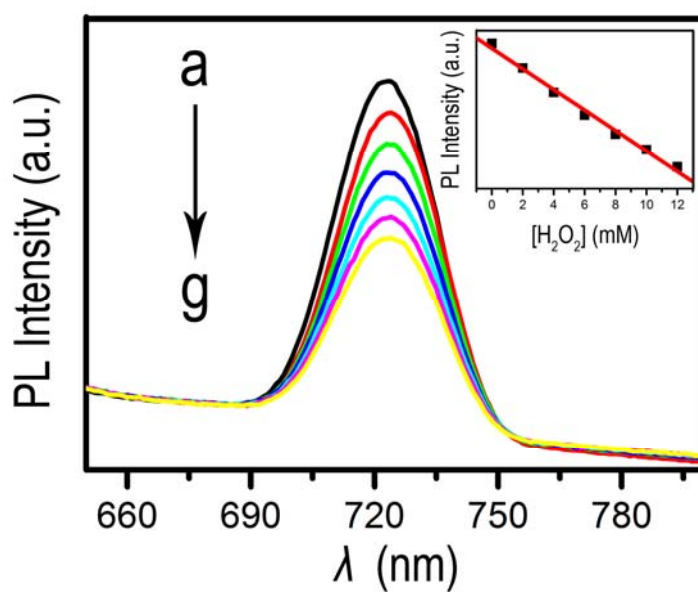


Fig. S6 Photoluminescence spectra of the graphene/AuNCs hybrid aqueous solution in the presence of different H_2O_2 concentrations: (a) 0 mM, (b) 2 mM, (c) 4 mM, (d) 6 mM, (e) 8 mM, (f) 10 mM and (g) 12 mM. Inset: The relationship of the response photoluminescence intensity *versus* the H_2O_2 concentration. $R = 0.996$.

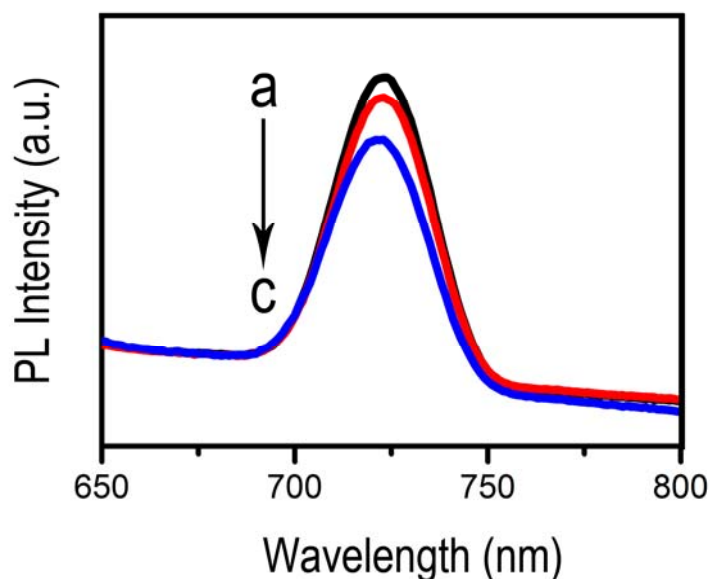


Fig. S7 Photoluminescence spectra of the graphene/AuNCs hybrid aqueous solution after fresh synthesis (a), after storage at room temperature for 1 month (b), and for 4 months (c).

In order to study the stability of the graphene/AuNCs hybrid, the optical property of the hybrid was investigated. Fig. S7 showed the photoluminescence spectra of the graphene/AuNCs hybrid aqueous solution after fresh synthesis (curve a), storage at room temperature for 1 month (curve b), and for 4 months (curve c), respectively. Under the excitation light of 480 nm, the emission peak at 723 nm did not change after the hybrid was stored for over 4 months, and the PL intensity was 93% after 1 month, and 77% after 4 months of the original intensity, respectively.

References

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