



Graphene quantum dots functionalized gold nanoparticles for sensitive electrochemical detection of heavy metal ions



Siong Luong Ting^{a,b}, Shu Jing Ee^{a,b}, Arundithi Ananthanarayanan^a, Kam Chew Leong^b, Peng Chen^{a,*}

^a School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, Singapore 637457, Singapore

^b GlobalFoundries Singapore, 60 Woodlands Industrial Park D Street 2, Singapore 738406, Singapore

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ABSTRACT

Graphene quantum dots (GQDs) are emerging zero dimensional materials promising various novel applications due to their extraordinary physicochemical properties. In this work, novel conjugates of GQDs and gold nanoparticles (AuNPs) are synthesized and used for sensitive electrochemical detection of heavy metal ions (Hg^{2+} and Cu^{2+}). Ultralow detection limit (0.02 nM with $S/N = 6.25$ for Hg^{2+} and 0.05 nM with $S/N = 4.81$ for Cu^{2+}) and high sensitivity (2.47 $\mu\text{A}/\text{nM}$ for Hg^{2+} and 3.69 $\mu\text{A}/\text{nM}$ for Cu^{2+}) have been achieved.

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1. Introduction

Contamination of heavy metal ions (e.g., mercury) is of serious concern to human health. Accumulation of mercury ions (Hg^{2+}) poses many dangerous issues such as renal and neural problems [1,2]. According to US Environment Protection Agency, the safety limit of Hg^{2+} in water is as low as 10 nM to avoid potential health problems [3]. It is of a great challenge to detect such trace amount. Electrochemical sensing provides possibilities for rapid, sensitive, and on-site detection of heavy metal ions [4].

Graphene, a two-dimensional single-atom-thin carbon crystal-line sheet, has been widely used for electrochemical sensor development owing to its high electrical conductivity, large surface area, wide electrochemical potential window, chemical stability, biocompatibility, and highly tunable properties by chemical modification or heteroatom doping [5,6]. Recently, graphene quantum dots are emerging as a new class of zero dimensional materials [7,8], promising novel applications in bio-imaging [9], optical sensing [10]. Optical detection of Hg^{2+} [11] and Fe^{3+} [12] has been demonstrated using GQDs. For electrochemical sensing, GQD modified graphite electrode has been used for sensitive detection of ssDNA molecules [13]. GQDs have also been covalently

assembled on gold electrode for electrochemical sensing of hydrogen peroxide [14].

Gold nanoparticles (AuNP) have been widely employed for sensor development including electrochemical sensors [15]. For examples, AuNP decorated carbon nanotubes [16] and AuNPs conjugated with thymine containing oligonucleotides [16] have been used to electrochemically detect the low presence Hg^{2+} ions. It has also been demonstrated that hybridizing AuNPs with graphene oxide sheets can enhance the performance of electrochemical detection [17]. In this work, GQDs are functionalized onto cysteamine-capped gold nanoparticles for electrochemical detection of Hg^{2+} with a detection limit of 0.02 nM, using anodic stripping voltammetry (ASV) method. The sensor can also detect Cu^{2+} at a concentration as low as 0.05 nM.

2. Experimental

2.1. Reagents and Apparatus

All chemicals are purchased from Sigma Aldrich. Electrochemical measurements were carried out with CHI 660D electrochemical workstation (CH Instruments Inc.) using the three-electrode system consisting of a platinum counter electrode, standard calomel electrode (SCE) as the reference, and GQD-AuNP modified GCE as the working electrode (0.071 cm^2). The electrode surface morphology and X-ray energy dispersive spectrometry (XRD) of

* Corresponding author.

E-mail address: chenpeng@ntu.edu.sg (P. Chen).

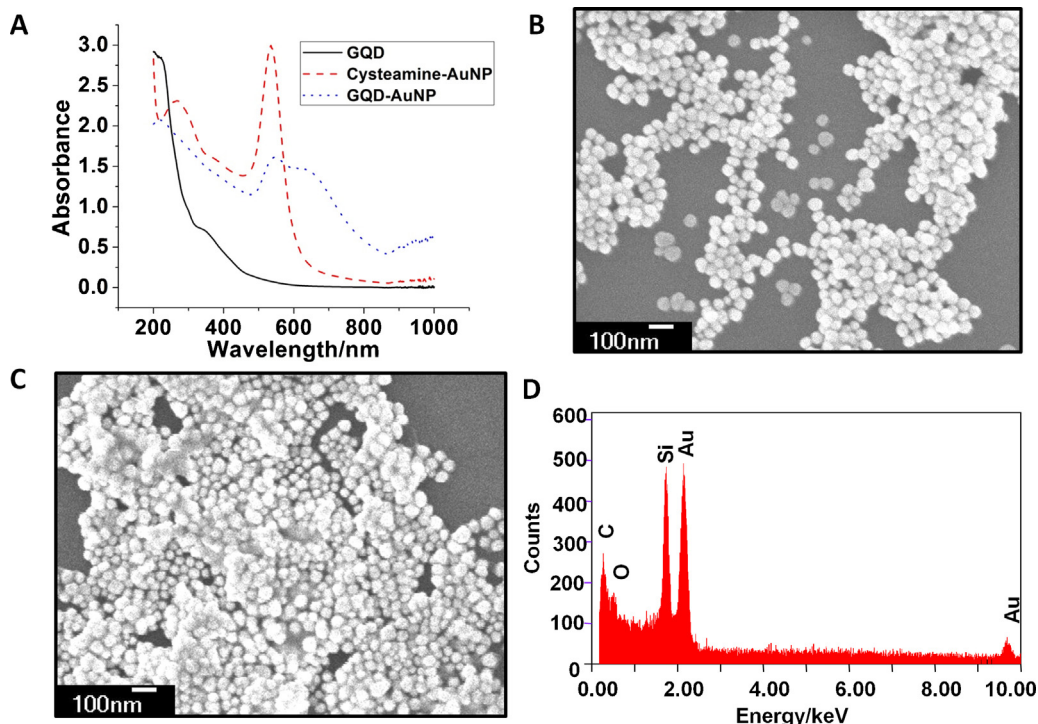


Fig. 1. (A) UV-vis spectra. (B) Scanning electron micrographs (SEM) of AuNPs drop-casted on glassy carbon electrode (GCE). (C) SEM of GQD-AuNPs on GCE. (D) Energy dispersive spectroscopy.

the sample were examined using field emission scanning microscope (JEOL JSM-6700F). UV-vis and Fourier transform infrared spectroscopy were obtained from a Shimadzu UV-vis spectrophotometer and a PerkinElmer Spectrum GX FTIR system, respectively.

2.2. Synthesis of GQD-AuNP conjugates

GQDs were synthesized as previously described [18]. Briefly, CX-72 carbon black was refluxed in concentrated nitric acid for 24 h, followed by centrifugation (7000 rpm). The supernatant was then fully dried and re-dissolved in deionized water to defined concentrations. Cysteamine-capped AuNPs were synthesized via chemical reduction of gold chloride solution [19]. In brief, 40 mL of HAuCl₄ (1.42 mM) and 400 μ L of cysteamine (213 mM) were mixed and stirred for 20 min in dark. 10 μ L of NaBH₃ was added with continuous stirring in dark for 10 min. The obtained cysteamine-AuNP solution (5 mL) was then mixed with GQD solution (5 mL at 2 mg/mL), followed by addition of 40 mg ethyl (dimethylaminopropyl) carbodiimide (EDC) with shaking for 1 h. The solution was then centrifuged at 10k rpm for 10 min to obtain the sediment. This process is repeated for 5 times to thoroughly remove the excess GQDs. Finally the sediment was re-dispersed into 1 mL of deionized water.

2.3. Preparation of modified electrode

The glassy carbon electrode was first polished using alumina powder, followed by thorough washing (with ethanol and deionized water) and sonication. After blow-drying using nitrogen gas, 3 μ L of prepared GQD-AuNPs solution was drop-casted onto the electrode surface and left to dry 30 min. The electrode was further dried in vacuum for another 10 min. Finally, 3 μ L of 5% nafion solution was drop-coated onto the modified electrode as the proton exchange membrane and protection layer.

2.4. Anodic Stripping procedure

Preconcentration of the electrode was performed by immersing the electrode in the electrolyte (0.1 M HCl) containing the target analyte (Hg²⁺ or Cu²⁺) at a defined concentration, with -0.2 V applied for 120 s. Anodic stripping was carried out using square wave voltammetry at frequency of 40 Hz, amplitude of 20 mV and potential increment step of 4 mV.

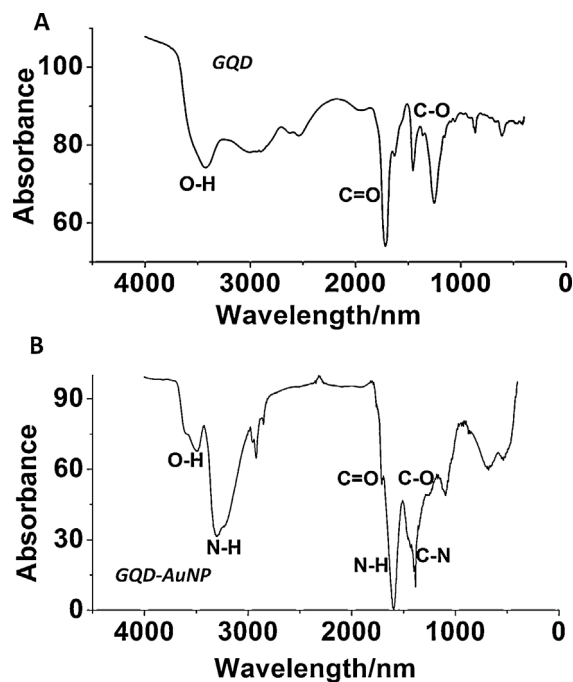


Fig. 2. FTIR spectra of GQD (A) and GQD-AuNP (B).

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