One-step synthesis of Ag nanoparticles decorated graphene for application in electrochemical detection of Pb^{2+} and Cd^{2+} ions

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Here, the Ag nanoparticles decorated graphene (AgNP@GNs) were fabricated by combing liquid phase exfoliation with in-situ solvent reduction method. Furthermore, the electrochemical sensitivity toward Cd^{2+} and Pb^{2+} ions was also investigated in detail. This AgNP@GNs presented the excellent electrical properties (2.5×10^4 S/m), meanwhile showed high electrochemical detection ability toward Cd^{2+} and Pb^{2+}. The sensitivity of AgNP@GNs toward Pb^{2+} and Cd^{2+} was ca. 15.2μA/μM (or 1246.4μA/μg L^{-1}) and 0.09μA/μM (4.32μA/μg L^{-1}), respectively. The AgNP@GNs was also evaluated to electrochemical detection of Cd^{2+} and Pb^{2+} in real water, in which the recoveries (96~124%) were obtained. The work does not only provide a facile method to synthesize AgNP@GNs with good dispersion, but also showed good electrical properties for various applications.

1. INTRODUCTION

Ag nanoparticles (AgNPs) have attracted lots of interesting due to good electrochemical performance, antibacterial performance, large specific surface area and quantum dimension effect for various applications, such as optical materials, antibacterial materials, electrochemical sensor and so on [1]. The AgNPs were synthesized by chemical reduction method, in which the organic molecules were usually used to avoid the agglomeration and precipitation of AgNPs [2]. These organic molecules will reduce the physical or chemical property, restricting its practical applications. So, some supporting materials were reported for preparing AgNPs, such as conducting polymers [3], mesoporous silica [4], fiberglass [5], carbon materials (eg. carbon nanotubes, graphene) [6-7] and so on. Among these materials, graphene was a promising supporting material for the AgNPs due to high electrochemical

performance and large surface area. Therefore, there were some works reporting the synthesis of AgNPs decorated graphene for application in electrochemical detection. For example, the synthesis of AgNP/reduced graphene oxide (rGO) was reported for application in efficient nonenzymatic H_2O_2 biosensor [8]. The AgNP/GNs were prepared, in which the electrochemical detection toward chloride was investigated [9]. The AgNP/GNs was prepared for non-enzymatic H_2O_2 detection [10]. The AgNPs/modified GNs was also prepared for application in electrochemical detection toward nitroaromatic compounds [11]. The AgNP/rGO was prepared by phytoreduction for application in electrochemical detection toward nitrite [12]. Up to now, these preparation process of AgNPs/GNs or rGO required multistep and strong chemical reducing agents. Therefore, it is interesting to find a new preparation process of AgNP/GNs. In addition, the AgNP/GNs was few reported for electrochemical sensitivity to heavy metal ions in water.

Here, a facile one-step method was developed to prepare AgNP/GNs. Furthermore, the electrochemical detection toward heavy metal ions was investigated in detail. Here, the AgNPs and GNs were not only simultaneously synthesized by liquid phase exfoliation combing with in-situ solvent reduction method, but also exhibited excellent conductivity and electrocatalytic performance for various applications.

2. EXPERIMENTAL

2.1 Materials

Graphite was purchased from J&K Scientific. Silver nitrate ($AgNO_3$, 99%) was obtained from J&K Scientific. Ethanol (99%) and N, N-dimethylformamide (DMF, 99%) were obtained from Sinopharm Chemical Reagent Co. Ltd. Plumbi Nitrate ($Pb(NO_3)_2$, 99.9%) and Cadmium Nitrate ($Cd(NO_3)_2$, 99.9%) were obtained from China Institute of Metrology. Nitric Acid (HNO_3, 50%) Sodium acetate (NaAc, 99%), Ammonium Chloride (NH_4Cl, 99%), Ammonia ($NH_3 \cdot H_2O$, 35%), Sodium dihydrogen phosphate (NaH_2PO_4, 99%), Sodium hydrogen phosphate (Na_2HPO_4, 99%) were purchased from Tianjin Chemical Reagent Co. Ltd. Nafion solution (5%) was obtained from Aladdin.

2.2 Preparation of Ag nanoparticles decorated graphene nanosheets

Ag nanoparticles decorated graphene nanosheets (AgNP/GNs) was one-step preparation by in-situ reducing silver ions and liquid phase exfoliation of expanded graphite as shown in following.100 mg expanded graphite and 100 mg $AgNO_3$ were dispersed in 50mL DMF solvent under sonication for 1.5 h to form a stable AgNP/GNs dispersing solution. The AgNP/GNs products were purified by filtration, and then was further washed by ethanol for three times. Finally, the AgNP/GNs products were dried at 60℃ under vacuum condition. Pure graphene and silver nanoparticles were synthesized by the same method.

2.3 Characterization of structure

Crystal structure of samples was characterized by X-ray diffractomer (Rigaku D/max 2200PC) with Cu Ka radiation.

Micro-structure of samples was characterized by Transmission electron microscopy (TEM, JEOL JEM- 2100, Japan)

Structure of samples was characterized by Raman spectrometer (Jobin Yvon Labram HR800) with an excitation wavelength of 632.8 nm.

2.4 Procedure for electrochemical detection of Pb^{2+} and Cd^{2+} ions

The AgNPs@GNs modified glassy carbon electrode (AgNPs@GNs/GCE) was fabricated as shown in following. The GCE with 3.0mm diameter was firstly polished by ca.0.05 μm alumina dispersion solution and then washed by deionized water, Nitric Acid (10%) and ethanol. AgNP/GNs suspension was prepared by dispersing 10 mg AgNP/GNs composites in 2.0mL of deionized water containing 40.0mL of 5.0wt% Nafion solution with sonication for 10.0min. Finally, then, 8μL of the AgNP/GNs dispersion solution was coated on the surface of GCE and dried at room temperature for 60.0min.

PBS solutions (0.1M) were prepared as shown in following. Firstly, 0.1 M HAc and 0.1 M NaAc, 0.1 M NH_4Cl and 0.1 M $NH_3 \cdot H_2O$, 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 were prepared by mixing the deionized water and corresponding reagents. Secondly, above solutions were further mixed under mechanical Stirring for 60.0min.

Square wave anodic stripping voltammetry (SWASV) was characterized to evaluate electrochemical detection performance by the Shanghai Chenhua Electrochemical Work Station (CHI660D). Here, a three-electrode system was used, in which the Ag/AgCl electrode, platinum wire electrode and AgNPs@GNs/GCE were as acted as working, reference and counter electrode, respectively. The electrochemical detection voltage was controlled from -1.4V to 0.8V, in which frequency and quiet time were 25 Hz and 2 s, respectively. The GCE was treated by EDTA solution (0.1 M) under ultrasonic stirring for 2 min before next testing.

3. RESULTS AND DISCUSSION

Fig.1A shows the XRD patterns of pure GNs and AgNP@GNs. It clearly exhibited a strong peak at 26.5°, corresponding to (002) plane of graphite [13]. After liquid phase exfoliation, the intensity of (002) peak was clearly reduced and broader compared to pristine graphite, indicating a high degree of exfoliation [13-14]. In addition, some new weak peaks at 38.3°, 44.6°, 64.7° and 77.6° were observed for AgNP@GNs, which were assigned to (111), (200), (220), and (311) planes s of silver (JCPDS: 68-2871), respectively [2]. The result confirmed the formation of AgNP@GNs by present synthesis method. The above results were further confirmed by the Raman spectra (Fig.1B). Two peaks at 1355 cm^{-1} and 1580 cm^{-1} were obviously observed, which were assigned to D band and G band of graphene, respectively [13]. In addition, the ID/IG of GNs and AgNP@GNs was about 0.44 and 0.53, respectively. The

relatively low ID/IG indicated that present GNs showed few defects compared to rGO prepared by chemical solution method [14]. In a comparison, the higher ID/IG of AgNP@GNs was attributed to introduction of AgNPs adsorbed on surface of GNs compared to pure GNs. Here, the 2D peak at 2725 cm^{-1} was not only obviously observed, but also showed large I_{2D}/I_G. The result indicated the formation of graphene with few layers [15]. These results further indicated the formation of AgNP@GNs with few defects. As expected, the AgNP@GNs has excellent conductivity of 2.5×10^4 S/m due to the low defect on graphene. Furthermore, the conductivity was higher than that of rGO prepared by chemical solution method and similar with graphene prepared by liquid phase exfoliated method [14-15]. The result confirmed the formation of AgNP@GNs with good conductivity.
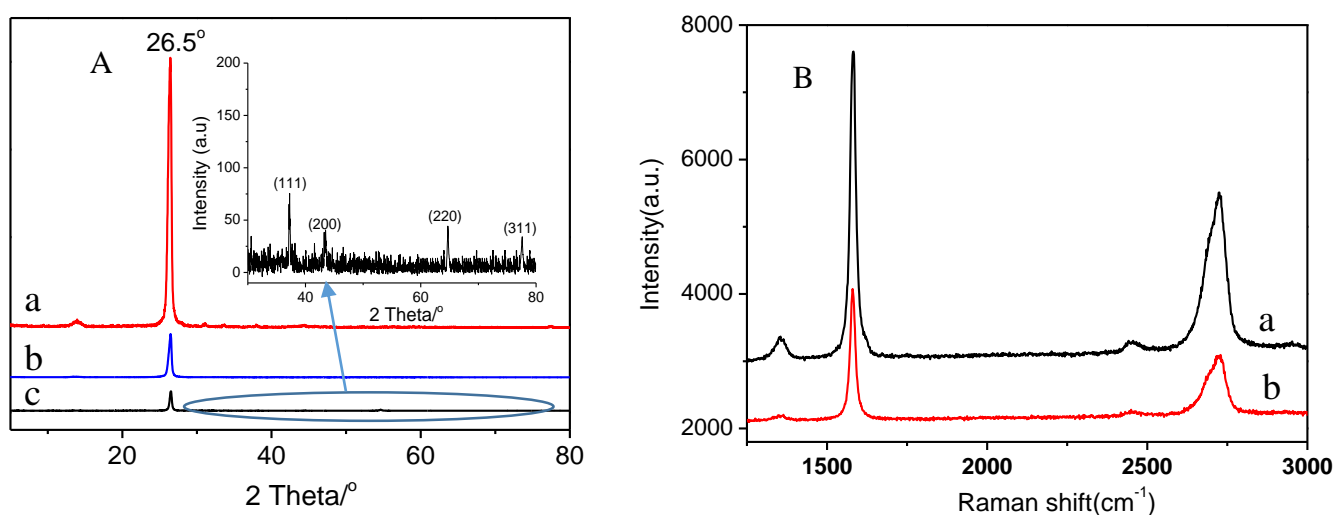

Figure 1. (A)XRD patterns of (a)graphite, (b)GNs and (c)AgNP@GNs; (B) Raman spectra of (a)GNs and (b)AgNP@GNs. The inset of A is enlarged XRD pattern of AgNP@GNs from 30º to 80º.

The micro-structure of pure GNs and AgNP@GNs was further characterized by TEM images as shown in Fig.2A and Fig.2B, respectively. It clearly showed a clean surface and folded layered structure for GNs. The result further confirmed the formation of GNs by present liquid phase exfoliation method. In a comparison, in addition to GNs, there were some nanoparticles on surface of GNs. The average size of these nanoparticles was about 12. 0nm.The morphology and layer thickness of AgNP@GNs were also determined by AFM as shown in Fig.2C. The thickness and lateral dimension of AgNP@GNs were in the range of 12.2~14.2 nm and about 0.75μm, respectively. These results further confirmed that the AgNP@GNs with uniform distribution could be prepared by one-step method.
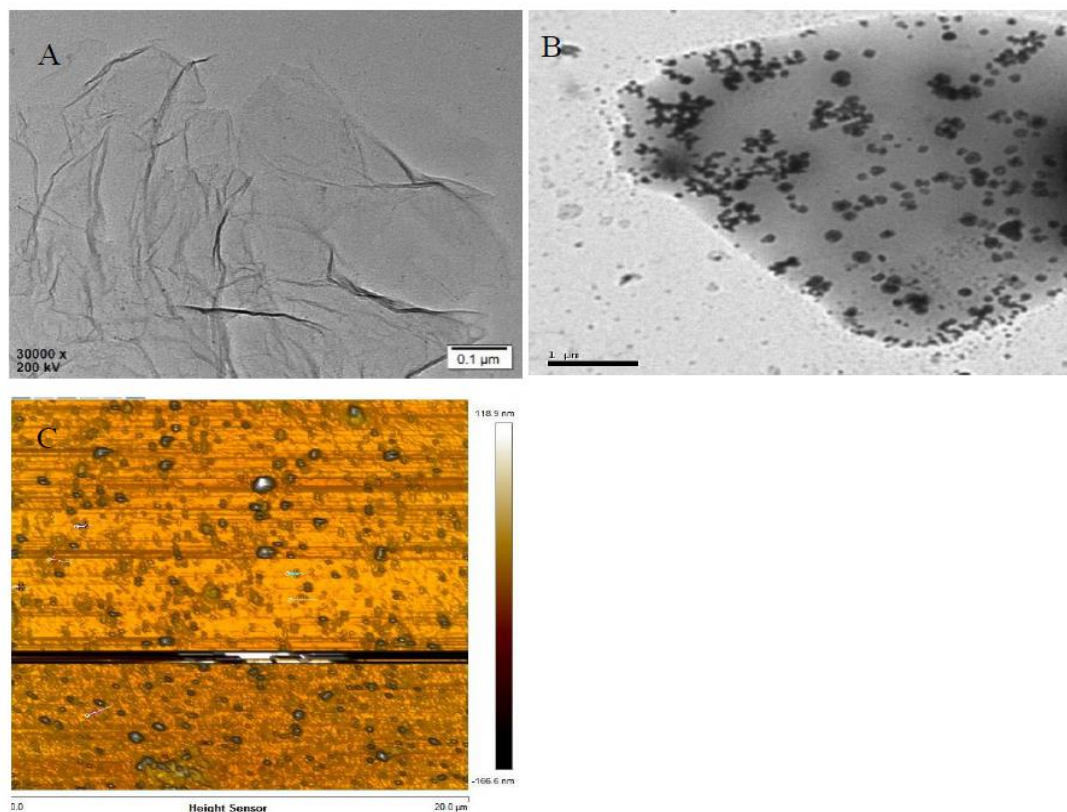
Figure 2. TEM images of (A) pure GNs and (B) AgNP@GNs, (C)AFM image of AgNP@GNs.

The testing condition of GNs, AgNPs and AgNP@GNs was firstly optimized for the electrochemical detection of Cd^{2+} and Pb^{2+} as shown in Fig.3. It clearly showed stripping currents for electrochemical detection of Pb^{2+} and Cd^{2+} in phosphate PBS buffer solutions as shown in Fig.3A and Fig.3B, respectively. The result indicated that phosphate PBS buffer solutions as electrolytes was a good choice for electrochemical detection of Cd^{2+} and Pb^{2+}. In addition, the effect of buffer solutions' pH on electrochemical sensitivity of AgNP@GNs toward Cd^{2+} and Pb^{2+} was also investigated. It was found that it showed highest stripping currents for electrochemical detection in pH=7. The result indicated that pH=7 was optimal for the electrochemical detection of Cd^{2+} and Pb^{2+}. Moreover, electrochemical sensitivity of GNs, AgNPs or AgNP@GNs toward Pb^{2+} and Cd^{2+} was further investigated and compared under optimal conditions as shown in Fig.3C and Fig.3D, respectively. The AgNP@GNs showed better electrochemical sensitivity compared to single AgNPs and GNs. The result was attributed to the synergistic effect of AgNPs and GNs. Firstly, the AgNPs suppressed the restack of GNs, meanwhile the GNs prevented the aggregate of AgNPs, providing a large electrochemical active surface. Secondly, the GNs mainly provided the active sites, meanwhile the AgNPs enhanced the conductivity of GNs.
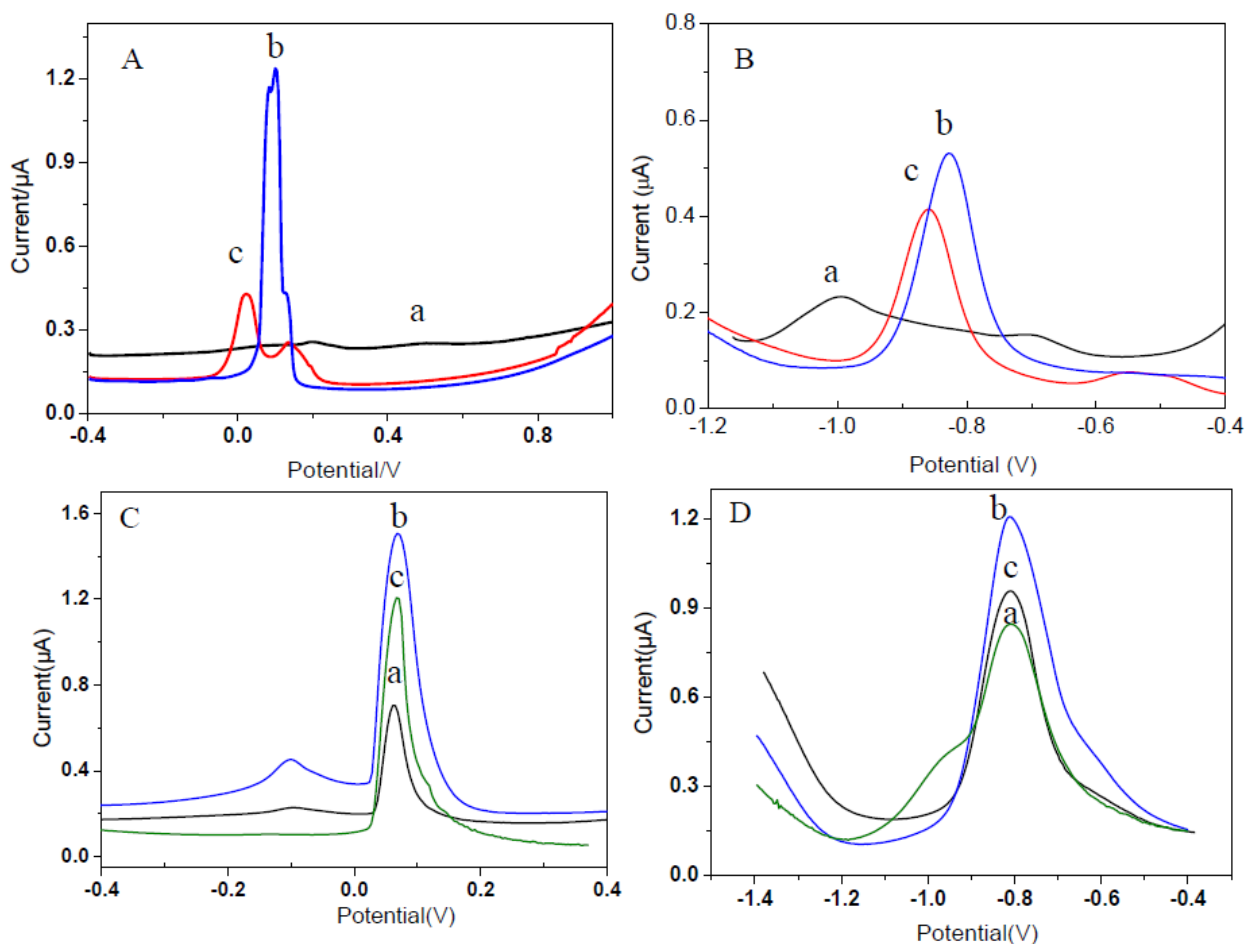
Figure 3. The electrochemical responses of AgNP@GNs toward to (A) Pb^{2+} and (B) Cd^{2+} in various pH aqueous solution of (a)3.0, (b) 7.0 and (c)11.0; The electrochemical responses of various materials toward to (C) Pb^{2+} and (D) Cd^{2+} in water (a)AgNP, (b) AgNP@GNs and (c)GNs.

The electrochemical sensitivity of AgNP@GNs toward Pb^{2+} and Cd^{2+} as a function of concentration were also investigated and the corresponding calibration curves were concluded in Fig.4. It was found that the stripping currents clearly increased with increasing in the concentration of Pb^{2+} and Cd^{2+} as shown in Fig.4A and Fig.4B, respectively. Furthermore, it clearly showed linear relationships between the largest current and the concentration of metal ions. $y=2.2+15.2x$ (Pb^{2+}, $R^2=0.945$) and $y=1.8+0.09x$ (Cd^{2+}, $R^2=0.980$) were observed as shown in Figs.4C and 4D, respectively. The sensitivity of AgNP@GNs on Pb^{2+} and Cd^{2+} was ca. 15.2µA/µM (or 1246.4µA/µg L^{-1}) and 0.09µA/µM (4.32µA/µg L^{-1}), respectively. The limit of detection (LOD) of AgNP@GNs toward Pb^{2+} and Cd^{2+} were calculated to be 5.2nM (0.43µg/L) and 0.5nM (0.024µg/L) according to LOD=3σ/k, respectively [19]. The limits of detection toward Pb^{2+} and Cd^{2+} were far lower than the target value (Pb^{2+}<0.01mg/L and Cd^{2+} < 0.005mg/L) required for practical application. The electrochemical detection performance of AgNP@GNs toward Cd^{2+} and Pb^{2+} was compared to other electrode materials based on GNs reported in previous works as shown in Table 1[20-26]. AgNP@GNs showed better comprehensive performance for electrochemical detection of Pb^{2+} and Cd^{2+}, such as wider linear range, lower LOD and higher

sensitivity. These results confirmed that present AgNP@GNs was a new good kind of electrochemically sensitive materials toward Pb^{2+} and Cd^{2+}.
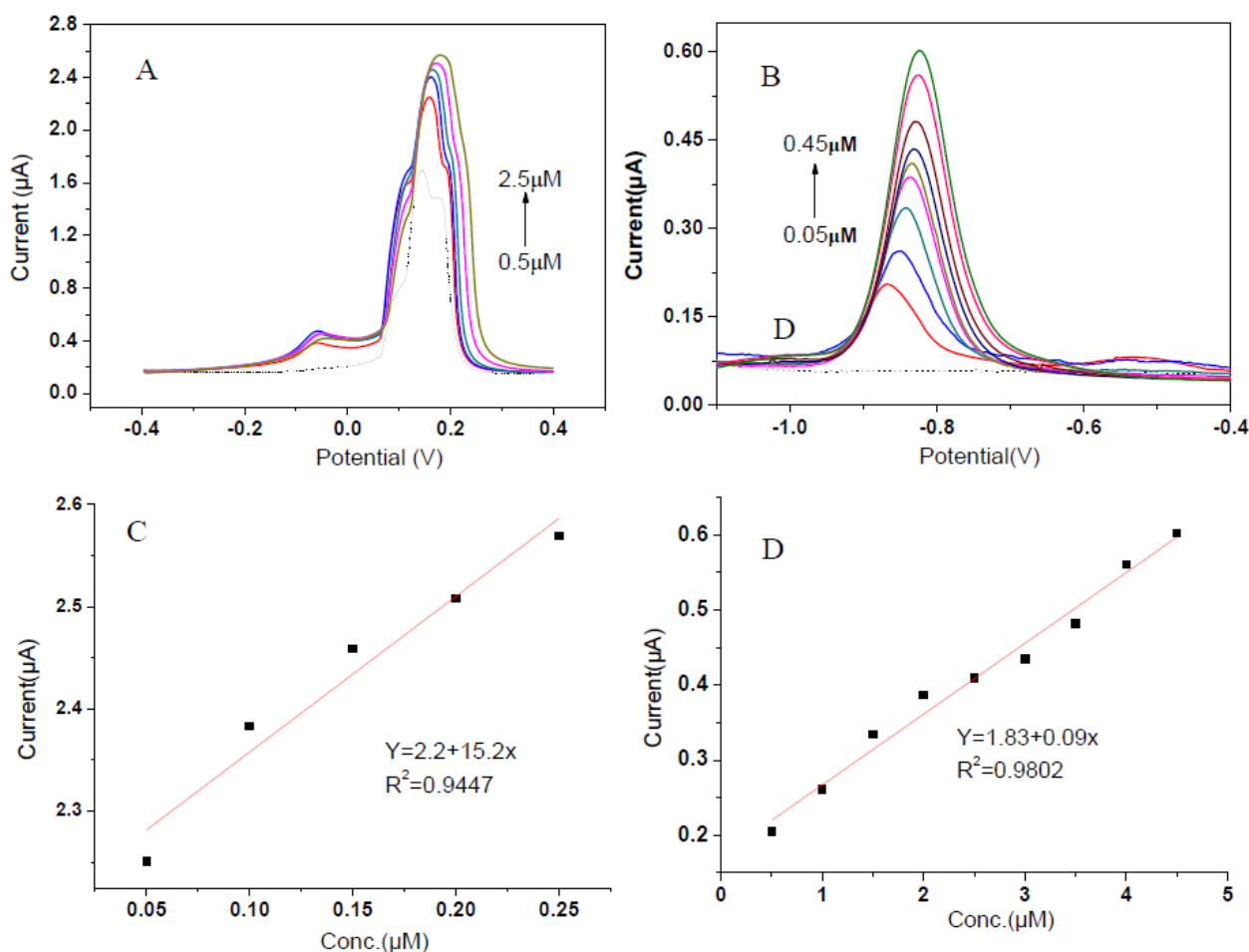

Figure 4. The electrochemical responses of AgNP@GNs toward to (A)Pb^{2+} and (B) Cd^{2+}; and corresponding calibration curves of AgNP@GNs toward to (C)Pb^{2+} and (D) Cd^{2+}.

Table 1. Eletrochemical detection of various materials based on GNs toward Cd^{2+} and Pb^{2+}.

Electrode materials	LOD (µg/L)		Linear range (µg/L)		Sensitivity (µA/µg L^{-1})		Ref
	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	
Ag@GNs	0.024	0.43	2.4~21.6	41~205	4.32	1246.4	This work
rGO	------	0.82	------	16.4~656	-------	1.15	[20]
rGO	1.2	0.20	10~50		0.2	0.4	[21]
SBDD@G	------	0.21	------	0~100		0.475	[22]
MWNT/Au@RGO	0.7	0.3	1~80		0.44	0.49	[23]
PANI@GN		0.005		0.2~20000		1.95	[24]
MWNT@G	0.2		1~50		0.41	0.445	[25]
Au/CD@GS	24.8	15.8	40~1200		0.03	0.04	[26]

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The electrochemical detection stability of AgNP@GNs toward Pb^{2+} and Cd^{2+} was further evaluated as shown in Fig.5A and Fig.5B, respectively. They showed the stripping currents toward Pb^{2+} and Cd^{2+} as a function of cycling time, which were slight changes within 10 cycling times. The standard deviation was about 0.3% and 3.8% for electrochemical detection of Pb^{2+} and Cd^{2+} within 10 cycling times, respectively. The result indicated that the AgNP@GNs had satisfactory stability. The selectivity of the AgNP@GNs toward Pb^{2+} and Cd^{2+} was further studied as shown in Fig.5C and Fig.5D, respectively. It was found that the stripping currents were slight change within ±2% for the electrochemical detection of AgNP@GNs toward Pb^{2+} and Cd^{2+} in the presence of 3μM interfering ions. The result indicated that the electrochemical detection was not affected by other interfering ions, and good selectivity. To further evaluate the practicability, the AgNP@GNs were used to electrochemical detection of Pb^{2+} and Cd^{2+} in tap water by standard addition method.
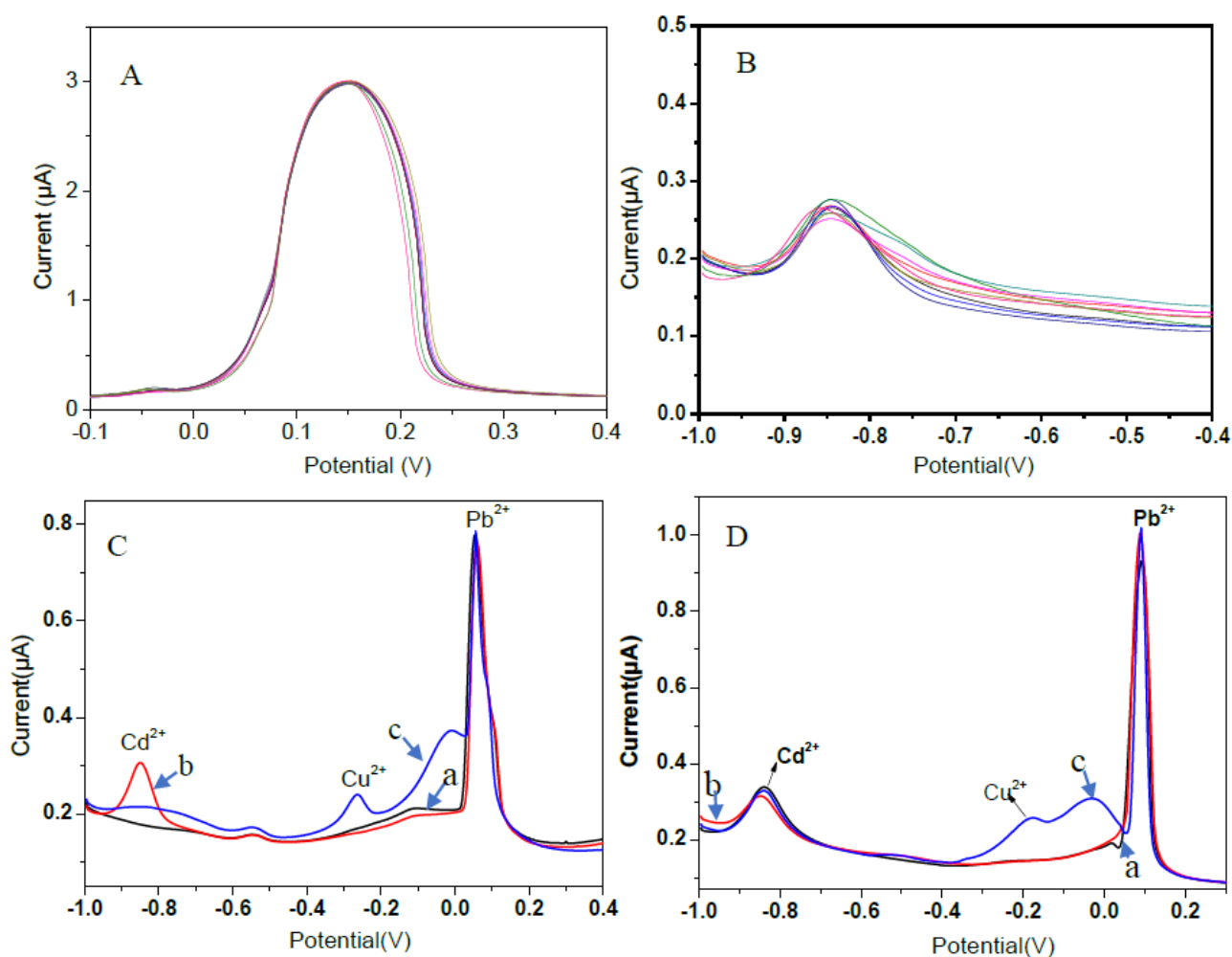

Figure 5. The reproducibility of the AgNP@GNs/GCE toward to (A) 1 μM Pb^{2+} and (B) 1 μM Cd^{2+}; (C) The selectivity of AgNP@GNs toward Pb^{2+} in aqueous solution containing various metal ions of (a)Pb^{2+}, (b) Pb^{2+}/Cd^{2+} and (c) $Pb^{2+}/Cd^{2+}/Cu^{2+}$; (D) The selectivity of AgNP@GNs toward Cd^{2+} in aqueous solution containing various metal ions of (a)Cd^{2+}, (b) Pb^{2+}/Cd^{2+} and (c) $Pb^{2+}/Cd^{2+}/Cu^{2+}$.

Table 2. Electrochemical detection of Cd^{2+} and Pb^{2+} in real water by AgNP@GNs/GCE.

Added Pb^{2+} /10^{-4} mol/L	Found Pb^{2+} /10^{-4} mol/L	Recovery /%	Added Cd^{2+} /10^{-4}mol/L	Found Cd^{2+} /(10^{-4}mol/L)	Recovery /%
0.50	1.12	124	1.00	1.09	118
1.00	1.59	118	1.50	1.54	108
1.50	1.99	98	2.00	2.08	116
2.00	2.48	96	2.50	2.47	94

The tap water was collected from our laboratory and were treated by filtering method. And then the buffer solution was added to above treatment tap water in a ratio of 1:2. The testing results were concluded in Table 2 and the nice recovery was obtained to be about 96.0%~124.0%. These results indicated that the AgNP@GNs were efficiently used to electrochemical detection of Cd^{2+} and Pb^{2+} in real water samples.

4. CONCLUSIONS

In this work, AgNPs@GNs was prepared by a new one-step method for application in electrochemical detection of Cd^{2+} and Pb^{2+}. It showed excellent sensitivity (eg. 15.2μA/μM) and limit of detection (eg.0.5nM). Furthermore, it also showed nice recovery of 96.0%~124.0% for electrochemical detection of Cd^{2+} and Pb^{2+} in real water. The work dose not only confirm the formation of AgNPs@GNs with good electrochemical detection performance, but also provides a new facile method of preparing AgNPs@GNs.

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