

## Graphene/Polyaniline Nanocomposite as an Electrochemical Sensor for Ultrasensitive Detection of Pb(II)

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This work describes the development of an electrochemical sensor for the ultrasensitive detection of Pb(II) using a graphene/polyaniline (GN/PANI) nanocomposite electrode prepared by a reverse-phase suspension polymerization technique in the presence of polyvinylpyrrolidone (PVP). The obtained GN/PANI nanocomposite was characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. The electrochemical behavior of lead ions ( $\text{Pb}^{2+}$ ) was determined by cyclic voltammetry and differential pulse voltammetry. The GN/PANI nanocomposite showed evidence of increased surface area under SEM. The GN/PANI-modified electrode exhibited high electrochemical conductivity, producing a four-fold increase in peak current (vs. the unmodified electrode). The largest current response was obtained when the weight fraction of graphene was 0.49%. A linear working range of  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-4}$  M was established between current and  $\text{Pb}^{2+}$  concentration with detection limits ( $S/N = 3$ ) of 0.06088 nM. The large specific surface area, satisfactory repeatability, long-term stability and simple synthesis promote the GN/PANI nanocomposite as a promising electrochemical sensor for the determination of  $\text{Pb}^{2+}$ .

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**Keywords:** Heavy metal; Reverse-phase suspension polymerization; Graphene/polyaniline nanocomposite; electrochemical sensor

### 1. INTRODUCTION

Heavy metals have long been recognized as a significant threat to kidneys, blood circulation and regeneration, and immune systems [1, 2]. Therefore, remarkable efforts have been made towards developing analytical methods, such as inductively coupled plasma (ICP), atomic emission spectrometry (AES) and atomic absorption spectroscopy (AAS) [3-5]. However, these methods are time-consuming, costly and highly specialized, which limit their application. Electrochemical sensing, as one of the most promising new methods, exhibits several advantages in testing heavy metal ions, owing to its instrumental simplicity, moderate cost, high timeliness, and in situ detection [6-8].

Therefore, electrochemical sensors have been considered as an efficient option in determining trace amounts of  $\text{Pb}^{2+}$ .

To improve the sensitivity of metal ion detection, a variety of electrode surface modified materials have been explored and researched. One common method has been to incorporate graphene (GN) on the working electrode due to its high specific surface area, outstanding electron transmission and extraordinary electrocatalytic activity [9-11]. Polyaniline (PANI) is one of the most intensively researched conductive polymer materials based on its variable structure, excellent electrochemical properties and good environmental stability [12]. Consequently, PANI has been applied to the fields of electronics, optics and electrochemistry [10, 13]. Therefore, graphene-based polyaniline (GN/PANI) composites have attracted widespread attention combining the compatible properties of both materials in recent years [14, 15].

Most GN/PANI nanocomposites are prepared by in-situ chemical oxidative polymerization. By controlling the reaction conditions, GN/PANI nanocomposites with different structures can be obtained [13]. The addition of polyvinylpyrrolidone (PVP) by a method called reverse dropping prevents the agglomeration of nanoparticles during the synthesis, thereby uniformly dispersing the particles in the solution [16]. Here, GN/PANI nanocomposites were prepared using the reverse dropping method with PVP.

Herein, GN/PANI nanocomposites were investigated as an enhanced material for a glassy carbon electrode (GCE) to set up a sensor for the ultrasensitive determination of  $\text{Pb}^{2+}$ . First, we prepared graphene by using a hydrothermal reduction method. Then, GN/PANI nanocomposites were synthesized by the reverse dropping method. The electrochemical behaviors of  $\text{Pb}^{2+}$  at the GN/PANI/GCE, GNs/GCE and bare GCE were investigated. Differential pulse voltammetry (DPV) was used to study the limit of detection and applied to analyze the actual water samples with satisfactory results.

## 2. MATERIALS AND METHODS

### 2.1 Materials and reagents

Graphite oxide was obtained from Alfa Aesar Tianjin Chemical Co., Ltd. Ammonium persulfate, aniline monomer and PVP were purchased from Sigma-Aldrich (St. Louis, MO), and N,N-dimethylformamide (DMF) was obtained from the Tianjin Kemiou Chemical Reagent Co., Ltd. Potassium ferricyanide, potassium dihydrogen phosphate and dipotassium hydrogen phosphate were from the Sinopsin Group Chemical Reagent Co., Ltd. A 10 mM phosphate buffer saline (PBS, pH 7.40, 0.10 M  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  and 0.10 M KCl) was used as the buffer solution. All chemical reagents were of analytical grade and could be used directly without further treatment. Milli-Q ultrapure water was used during all experiments.

### 2.2 Synthesis of GN/PANI composites

Graphite oxide was reduced into graphene by a hydrothermal method. GN/PANI nanocomposite was prepared according to a previous report by N. Ruecha. et al. [17]. To prepare the

GN/PANI nanocomposite with 0.49% graphene, 2.0 g of aniline monomer was dissolved in 1 mL of concentrated HCl and diluted to 10.0 mL, then graphene (10 mg) was added and sonicated for 2 h to obtain a uniformly dispersed solution (solution I). A total of 1.0 g of ammonium persulfate (APS), 2.0 g of polyvinylpyrrolidone (PVP), and 0.8 mL of concentrated HCl were dissolved in 90.0 mL of ultrapure water and magnetically stirred for 30 minutes in an ice water bath to obtain solution II. Solution I was slowly added dropwise to solution II and continuously stirred for 4 h to obtain a dark green suspension. The suspension was filtered through a 0.22  $\mu\text{m}$  microporous membrane and rinsed with distilled water and ethanol until the filtrate was colorless and transparent and then dried in a vacuum oven at 65  $^{\circ}\text{C}$  for 24 h. The GN/PANI composite was then obtained for the next step. The nanocomposites with different proportions of graphene were prepared by adjusting the amount of aniline monomer added.

### 2.3 Preparation of the GN/PANI/GCE or GN/GCE

4 mg of GN/PANI and 10 mg of PVP were dissolved in 5 mL of DMF to obtain a GN/PANI solution with a concentration of 0.8 mg/mL. 5  $\mu\text{L}$  of GN/PANI solution was pipetted onto the surface of the polished GCE, and dried under infrared light to obtain a GN/PANI modified glassy carbon electrode (PANI/GN/GCE). Preparation of the GN modified electrode (GN/GCE) was performed as described above.

### 2.4 Characterization and detection apparatus

The microstructures of GN, PANI and GN/PANI were observed by a scanning electron microscope (Model Hitachi S-4800, Japan). The chemical structure information was investigated using Fourier transform infrared (FT-IR) spectrophotometry (Perkin Elmer Spectrum, PerkinElmer Corp., USA). All electrochemical characterizations and detections, including cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were conducted in a three-electrode setup using a CHI660D electrochemical workstation (Shanghai Chenhua Limited, China). This three-electrode system in the experiment used the bare and the modified glassy carbon electrode (3 mm in diameter) as the working electrode, respectively. A saturated calomel electrode and a Pt wire electrode were used as the reference and counter electrode, respectively. All electrochemical measurements were carried out in 5 mL of 10 mM PBS (pH 7.40) containing different concentrations of  $\text{Pb}^{2+}$  solution.

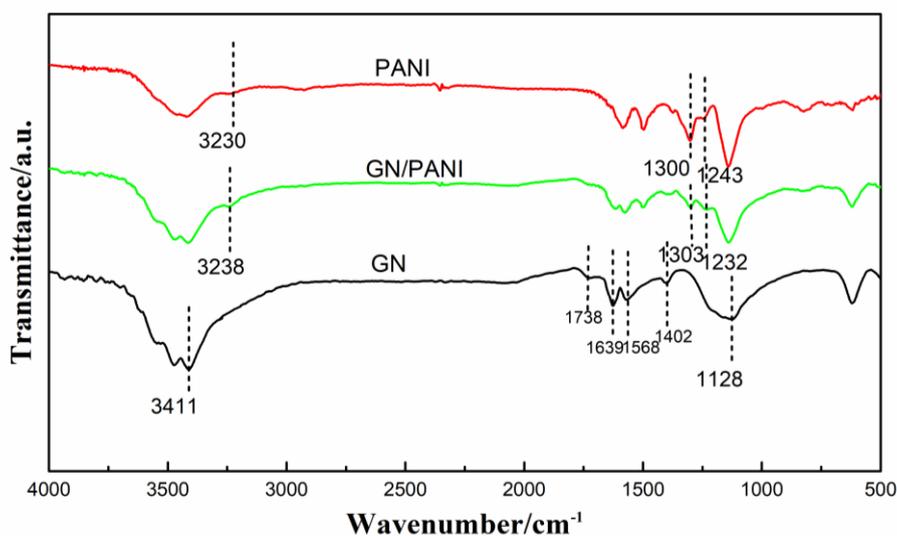
## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of the GN/PANI

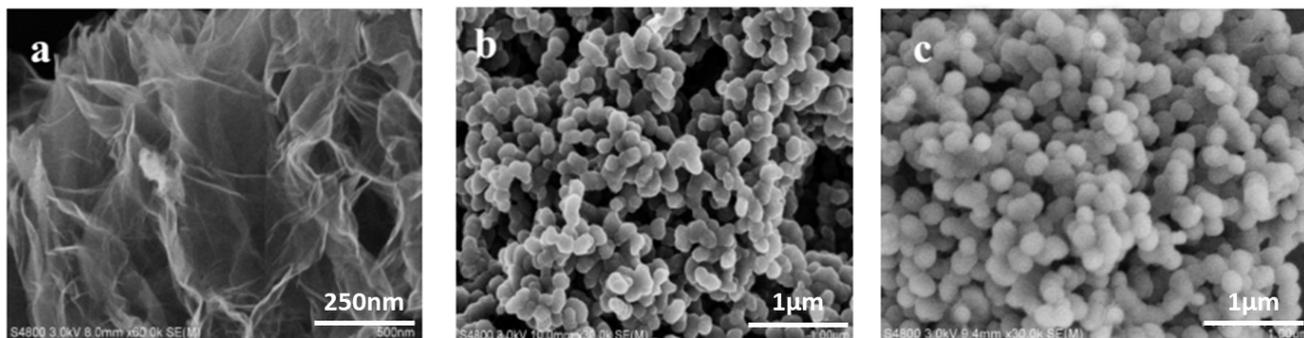
The FT-IR spectra of GN, PANI and GN/PANI composite, shown in Fig. 1, were studied. GN showed three characteristic peaks at 1738, 1402 and 1128  $\text{cm}^{-1}$ , which correspond to the vibration peaks of the C = O stretching in COOH, the C-O stretching in C-OH and C-O-C functional groups,

respectively [19,20]. The peak of GNs at  $1639\text{ cm}^{-1}$  indicated the vibration of  $\text{C}=\text{C}$  stretching. The peak at  $1568\text{ cm}^{-1}$  was mainly due to the vibrations of symmetric stretching of  $-\text{CH}_2$ . The peak at  $3411\text{ cm}^{-1}$  represents the vibrations of  $-\text{OH}$  [19, 21]. It was shown that the GN has abundant oxygen-containing functional groups and could be used for the in situ adsorption of the pyrrole monomers in the process of polymerization. The characteristic peaks at  $1243$ ,  $1300$  and  $3230\text{ cm}^{-1}$  correspond to the vibrations of  $\text{N-H}$ ,  $\text{C-N}$  and benzene ring, respectively. The spectrum of GN/PANI contained characteristic peaks of both GN and PANI, however, the deviations from the characteristic peaks for GN/PANI at  $1232$ ,  $1303$  and  $3238\text{ cm}^{-1}$  can be attributed to molecular interaction between graphene and PANI [22, 23]. These results proved that a composite particle of PANI and graphene was formed.

Fig. 2 shows the SEM image of GN, PANI, and PANI/GN on a glassy carbon electrode. As indicated in Fig. 2(a), the GN consisted of large-scale crumpled sheets and multiple sheets were laminated together to form a multilayer structure, which greatly increased the effective surface area of the electrodes. Fig. 2(b) shows that PANI was granularly stacked. When GN was combined with PANI, as shown in Fig.2(c), a more regular and uniform spherical microstructure was obtained with an average particle size of  $210 \pm 8\text{ nm}$ , which provided more active sites for  $\text{Pb}^{2+}$  attachment.



**Figure 1.** FTIR spectrum of GN, PANI and GN/PANI composite

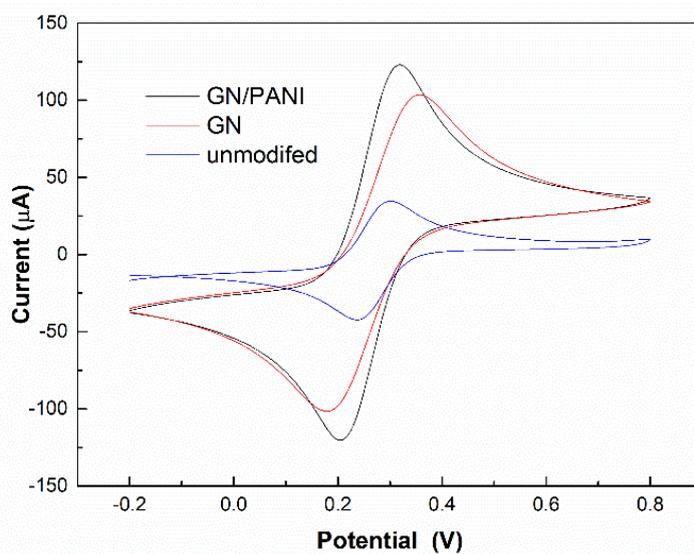


**Figure 2.** SEM images of (a) GN, (b) PANI and (c) GN/PANI composite

### 3.2. Electrochemical behavior on modified and unmodified electrodes

The performance of modified and unmodified electrodes (Fig. 3) was investigated by cyclic voltammetry of 1mM  $K_3[Fe(CN)_6]$  solution at scan rates of 100 mV/s. Compared with the cathodic peak current on the GCE ( $I_{pc}$ ) of 34.62  $\mu A$  and the anodic peak current ( $I_{pa}$ ) of -42.26  $\mu A$ , the redox peak current on the GN/GCE ( $I_{pc}=103.4 \mu A$  and  $I_{pa}= -101.6 \mu A$ ) significantly increased. The large specific surface area and high conductivity of GN favor the electron transfer of  $[Fe(CN)_6]^{3-/4-}$  on the electrode surface [24]. As expected, GN/PANI/GCE exhibited the largest anodic and cathodic currents ( $I_{pc}=122.9 \mu A$  and  $I_{pa}= -120.2 \mu A$ ).

According to the Randles-Sevcik equation,  $I_{pa} = 2.69 \times 10^5 AD^{1/2} n^{3/2} v^{1/2} C$  [25], where  $n$  refers to the electron-transfer number,  $A$  is the surface area of the electrode,  $D$  is the diffusion coefficient,  $C$  is the concentration of  $[Fe(CN)_6]^{3-/4-}$  and  $v$  is the scan rate, the electroactive surfaces of the electrodes can be calculated. For this work,  $D=6.30 \times 10^{-6} \text{ cm}^2/\text{s}$ ,  $n=1$ ,  $v=100 \text{ m}\cdot\text{s}^{-1}$  and  $C=1 \text{ mM}$ . The active surface areas of the bare GCE, GN/GCE, and PAN/GN/GCE were calculated to be 0.20, 0.47 and 0.56  $\text{cm}^2$ , respectively. This indicated that the synergy between the graphene and PANI improved the conduction pathway on the electrode surface. Moreover, the peak potential difference ( $\Delta E_p$ ) of the GN/PANI ( $\Delta E_p=0.114 \text{ V}$ ) decreased compared to the  $\Delta E_p$  of GN modified electrodes ( $\Delta E_p=0.180 \text{ V}$ ), further indicating that the presence of PANI partly enhanced the rate of interfacial electron transmission.

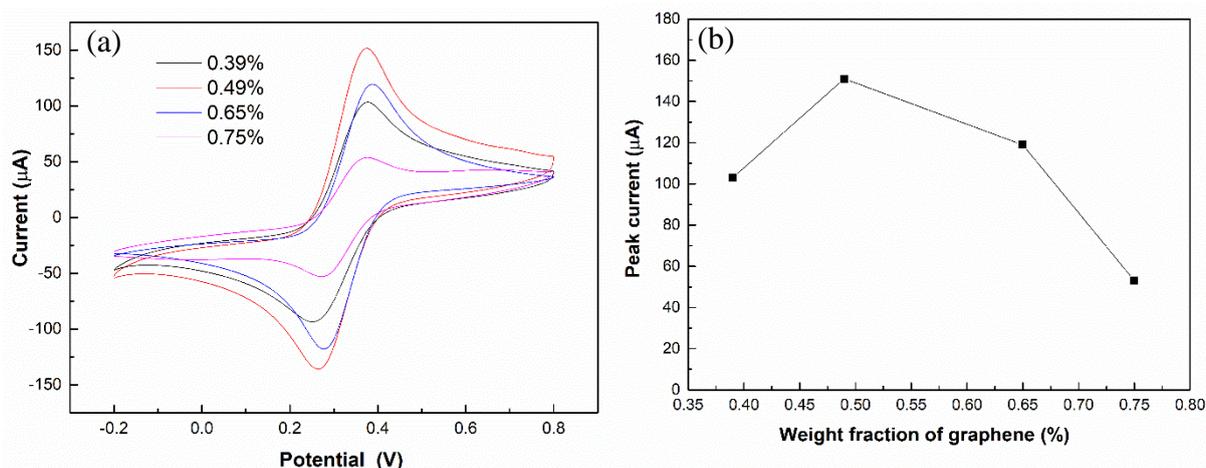


**Figure 3.** Cyclic voltammogram of 1 mM  $K_3[Fe(CN)_6]$  solution (scan rate:  $100 \text{ mV}\cdot\text{s}^{-1}$ ) measured on an unmodified electrode, or electrodes functionalized with GN or GN/PANI composites.

### 3.3. Effect of the content of graphene on the detection of $Pb^{2+}$

The influence of the relative content of GN and PANI was studied by cyclic voltammetry. As shown in Fig.4, the relative content of graphene and polyaniline has a great influence on the peak

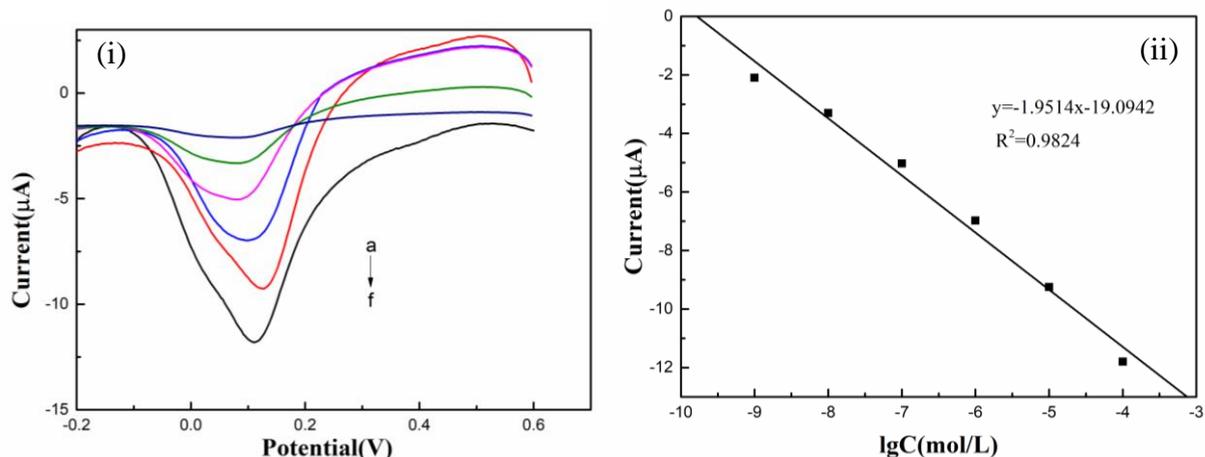
current of the electrode. When the content of graphene reaches 0.49% (weight fraction), the maximum peak current of  $\text{Pb}^{2+}$  appears. This is due to the superior electrical conductivity of GN dispersed in PANI, which promotes the doped/dedoped process of the PANI material and improves the diffusion and migration rate of  $\text{H}^+$  in PANI molecular chain[26,27]. As the content of graphene increased further, the peak currents decreased. It indicates that appropriate addition of graphene can promote the exchange of electrons. However, too large of an addition affects the conductivity of the electrode and weakens the current response. Therefore, a modified composite material with 0.49% graphene was used as the electrolyte for  $\text{Pb}^{2+}$  in all voltammetric determinations.



**Figure 4.** (a) Cyclic voltammograms of GN/PANI composites with different weight fractions of graphene in PBS (pH: 7.40) containing  $1 \times 10^{-6}$  M  $\text{Pb}^{2+}$  (scan rate:  $100 \text{ mV} \cdot \text{s}^{-1}$ ) and the (b) plot of peak current vs. the weight fraction of graphene.

### 3.4. DPV response of GN/PANI/GCE for the detection of $\text{Pb}^{2+}$

Under the selected conditions, the electrochemical property of GN/PANI modified GCE for  $\text{Pb}^{2+}$  detection was investigated by DPV because of its high sensitivity [27, 28]. To detect very low levels of  $\text{Pb}^{2+}$ , peak currents of the varying concentrations of  $\text{Pb}^{2+}$  using electrodes modified with GN/PANI are shown in Fig. 5. The peak current of  $\text{Pb}^{2+}$  increases linearly with its concentration in the range of  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-4}$  M. The liner equation is  $i_p (\mu\text{A}) = -1.6460 - 0.1179 \lg C (\text{M})$ , where the correlation coefficient is 0.9966,  $i_p$  is the oxidative peak current in  $\mu\text{A}$  and  $C$  is the concentration of  $\text{Pb}^{2+}$  in M. The limit of detection (LOD) for  $\text{Pb}^{2+}$  is estimated to be 0.06088 nM (S/N=3) (Fig. 6(ii)). As shown in Table 1, this work is compared with reported studies on detecting  $\text{Pb}^{2+}$ . The proposed sensor in this work exhibited a broader linear range and is 3 orders of magnitude larger than most, which may be ascribed to the synergistic effects between PANI and GNs:



**Figure 5.** (i) DPV of GN/PANI/GCE in 0.1 M PBS with different concentrations of Pb<sup>2+</sup>: (a)  $1.0 \times 10^{-4}$ , (b)  $1.0 \times 10^{-5}$ , (c)  $1.0 \times 10^{-6}$ , (d)  $1.0 \times 10^{-7}$ , (e)  $1.0 \times 10^{-8}$  and (f)  $1.0 \times 10^{-9}$  M; (ii) plot of the peak current vs. the concentration of Pb<sup>2+</sup>.

**Table 1.** Comparison of the proposed method with some of the reported determinations of Pb<sup>2+</sup>

Modified electrode	Liner concentration range(μg/L)	Detection limit(μg/L)	Ref.
Nafion/G/PANI nanocomposite	1-300	0.1	[17]
CNTs	5-150	1	[29]
CNT arrays (CNT thread)	1-4	1.5	[13]
PPY-rGO	1-150	$9.4 \times 10^{-3}$	[30]
GN/PANI	$0.2-2.0 \times 10^4$ ( $1.0 \times 10^{-9}$ to $1.0 \times 10^{-4}$ M)	0.01218 (0.06088 nM)	This work

### 3.5. Modified electrode repeatability and stability

The repeatability of the electrochemical sensor was investigated at a  $1 \mu\text{M}$  concentration of Pb<sup>2+</sup>. Five GCEs were modified by GN/PANI independently, and they yielded a mean current response of  $6.98 \mu\text{A}$  with a relative standard deviation of 2.4%. To investigate electrode performance after periods of extended storage, a prepared modified electrode was stored in a refrigerator for 10 days. After being placed, it was tested by DPV technology, and its response was basically consistent with the initial response. The good long-term stability could be due to the inherent stability of PANI and the strong interactions between GN and PANI. It can be concluded from the results that the GN/PANI has good repeatability and stability.

### 3.6. Analysis of Pb<sup>2+</sup> in actual water samples

To evaluate the practical application of the constructed sensor, the modified GCE was applied to the analysis of Pb<sup>2+</sup> in actual samples and recovery studies were performed. As shown in Table 2,

the recoveries were found to be in the range of 98.0 – 102.4%. The good recoveries of the samples suggest that this method is well suited for application to the detection of  $Pb^{2+}$  in actual water samples.

**Table 2.** The determination of  $Pb^{2+}$  in actual water samples (n=3).

Sample	Added concentration (nM)	Measured concentration (nM)	Recovery%
Tap water 1	10.0	9.8±0.3	98.0%
Tap water 2	20.0	19.9±1.1	99.7%
Tap water 3	50.0	51.2±2.7	102.4%

#### 4. CONCLUSION

In summary, a facile and reinforced electrochemical sensor based on GN/PANI was established by reverse-phase suspension polymerization. The high conductivity and large surface area of the GN/PANI nanocomposite improved the electrochemical sensitivity. When the mass fraction of GN was 0.49%, the peak current reached the maximum value. Under optimal conditions, detection limits below 0.1 nM and wide linear ranges (>4 orders of magnitude) were obtained for Pb(II). The GN/PANI nanocomposite reinforced electrode was then used to measure  $Pb^{2+}$  in actual water and showed good repeatability and stability. These results demonstrate that the GN/PANI based electrode is a low-cost alternative to the determination of heavy metals.

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