



# Self-assembled graphene and copper nanoparticles composite sensor for nitrate determination

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## Abstract

A new sensor based on decorated copper nanoparticles and self-assembled graphene was fabricated and exemplified with the determination of nitrate solutions. Traditionally, graphene is coated on the sensor by drop-casting, leading to poor adhesion between graphene and the sensor. The self-assembled graphene proposed in this paper not only have a firm connection with the substrate, but also provide a three-dimensional network structure for copper nanoparticles. Copper was found as an effective catalyst for nitrate reduction. The combination of copper nanoparticles and self-assembled graphene can greatly enhance the sensitivity. Thus, low detection limit of 7.89  $\mu\text{M}$  is obtained for nitrate, which to our knowledge, is among the lowest reported in the literatures. This method was employed for the determination of nitrate in lake water and the results were in good agreement with those obtained from a standard analytical procedure.

## 1 Introduction

Nitrate is a highly soluble ion which exists extensively in our environment. It is an essential nutrient for plants and the basic element that makes up amino acids (Crawford 1995; Nazoa et al. 2003). However, excess intake of nitrate can cause unnatural blooms of aquatic plants and algae, resulting in “red tides” and the death of fishes (Camargo et al. 2005; Lee 2006). Recent studies found that the concentration of nitrate also had an positive association with the incidence of colorectal cancer and non-Hodgkin lymphoma (Gulis et al. 2002). In addition, it is the main cause of blue baby syndrome for infants (Knobeloch et al. 2000). Thus, concern has been expressed about the increasing levels of nitrate ion in water. For the sake of ecological security and human health, World Health Organization (WHO) has suggested that nitrate concentration in ground water should be no more than 800  $\mu\text{M}$  (50 mg/L) (WHO 2008) and various techniques have been used to determine nitrate in natural water, soil and food.

Many laboratory analytical methods have been used to determine nitrate in environmental circumstances such as chromatography (Lopez-Moreno et al. 2016), Raman and molecular cavity emission (Sayer et al. 2003), fluorescence (Masserini and Fanning 2000) and flow-injection spectrophotometry (Kazemzadeh and Ensafi 2001). These methods can achieve low detection limits, but on the other hand, they are cumbersome, slow and expensive to use. The complex process and their massive size make them especially unsuitable for portable and online analysis. Commercialized portable sensors utilize ion-selective electrodes and test strips for nitrate detection in real water (Campanella et al. 1995). But ion-selective electrodes can hardly achieve low detection limits and the visual estimation of color change in test strips will decrease the sensitivity and accuracy of the results. Taking into account of these aspects, it is clear that the development of portable and highly sensitive sensors for nitrate determination are in great demand for environmental monitoring areas.

While spectroscopic instruments are difficult to reduce in size, electrochemical voltammetric techniques offer an alternative way to determine trace nitrate with micro sensors. Voltammetric methods depend on the reduction of nitrate and different materials, such as copper (Solak et al. 2000), lead (Genders et al. 1996), nickel (Bockris and Kim 1996), silver (Hu et al. 2013), boron-doped diamond electrodes (Ward-Jones et al. 2005) were used as the

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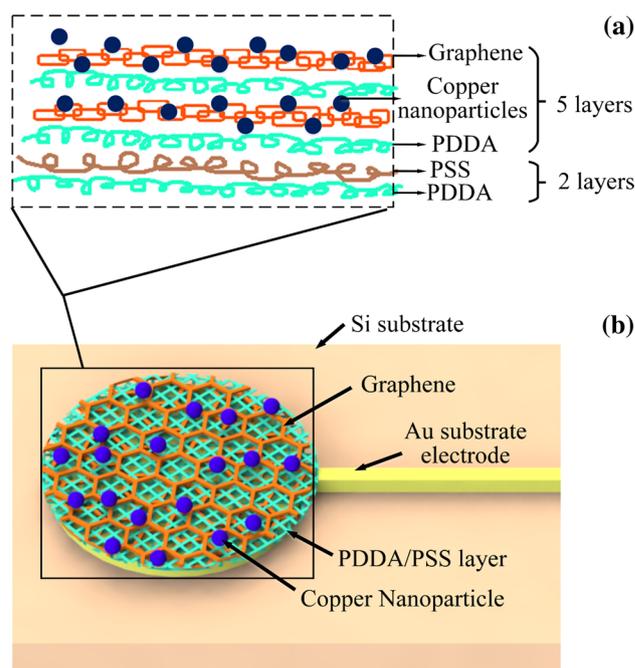
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working electrode for voltammetric analysis. Among these materials, copper was found as the most efficient one as it can catalyze the reaction of reducing nitrate to ammonia. Copper coated glassy carbon electrode and copper decorated boron-doped diamond electrode were both utilized to detect nitrate with fine limits of detection (Solak et al. 2000; Ward-Jones et al. 2005). However, as glassy carbon and boron doped diamond are expensive and difficult to manufacture, it is still not possible to make micro sensors with them. Fortunately, as copper is a solid material which can be evaporated or electroplated easily, micro-electro-mechanical systems (MEMS) technology gives more possibility of making copper into micro sensors. Stortini et al. (2015) have applied copper nanowire electrodes arrays for nitrate determination with linear sweep voltammetry and achieved detection limits as low as  $1.7 \mu\text{M}$ .

The layer-by-layer self-assembly technique is a simple and inexpensive way to form multilayer films with unique mechanical properties. In the self-assembly process, positively and negatively charged materials were assembled together through electrostatic force and a bilayer structure was formed. By repeating the assembly process, multilayer structures can be obtained. As many materials can be decorated with charged groups, a lot of functional materials were pretreated and incorporated within the multilayer structure (Shen et al. 2009). Among these materials were carbon nanotube and graphene. Graphene is a unique material with high surface area and high electrical conductivity (Huang et al. 2016). When self-assembled, graphene can form electrostatic three-dimensional structure which provides a stable and effective platform for sensing applications (Zhang et al. 2014). Thanks to its structure and intrinsic property, self-assembled graphene has been used in chemical sensors and biosensors with superb performance. For instance, Luo et al. (2013) used self-assembled hierarchical graphene and polyaniline nanoworm composites to fabricate supercapacitors and achieved high electrochemical capacitance. Liu et al. (2011) applied self-assembled graphene platelet–glucose oxidase nanostructures to glucose biosensing and low detection limit of  $20 \mu\text{M}$  was achieved.

In this paper, we propose an innovative sensor with decorated copper nanoparticles and self-assembled graphene to detect nitrate using differential pulse voltammetry (DPV). As shown in Fig. 1, different polymers and graphene nanoplatelets are deposited onto the working electrode by self-assembly. Positively charged Poly(diallyldiamine chloride) (PDDA) and negatively charged poly(sodium 4-styrene sulfonate) (PSS) layers are assembled on the substrate to offer firm connection between graphene and glass substrate. Copper could catalyze the reduction of nitrate (Solak et al. 2000) and PDDA/graphene layers are fabricated to form a conductive three-dimensional structure for copper



**Fig. 1** Sketch of the self-assembled graphene and copper nanoparticles composite sensor structure

nanoparticles, enlarging the reaction area of the sensor. Consequently, high sensitivity and low detection limit were achieved by this sensor. The analytical applicability of the sensor was explored by measuring the nitrate content in lake water and the results showed that this sensor had huge potential in environmental monitoring.

## 2 Experimental

### 2.1 Reagents

All the chemicals were purchased from Sigma-Aldrich unless mentioned specifically. Graphene (PureSheets MONO,  $0.25 \text{ mg/mL}$ ) solution was purchased from NanoIntegris Inc. Copper sulfate 5-hydrate was purchased from Mallinckrodt Baker Inc. to make copper nanoparticles. All low concentration nitrate solutions were prepared by diluting stock solution in buffer solutions.  $0.01 \text{ M HCl} + 0.1 \text{ M}$  sodium sulfate buffer was chosen as the supporting electrolyte for nitrate. All the solutions were prepared with DI water ( $18.2 \text{ M}\Omega \text{ cm}$ ) from a Milli-Q system (Millipore, Milford, MA, USA).

### 2.2 Apparatus

Four-inch silicon wafers ( $500 \mu\text{m}$  thick) were purchased from Silicon Quest International, USA. An Ag/AgCl ( $3 \text{ M KCl}$ ) (CH Instruments, Inc., TX, USA) was used as a

reference electrode instead of the gold pseudo reference electrode for more accurate results. Electrochemical measurements were performed by a CHI630C electrochemical workstation (CH Instruments, Inc., TX, USA), which is controlled by a computer. Scanning electron microscope (SEM) images were taken with Zeiss GeminiSEM 500 field emission scanning electron microscopy. Standard nitrate analysis procedure was performed with Hach DR1900 Portable Spectrophotometer (Hach Company, USA).

### 2.3 Device fabrication

As shown in Fig. 2a, the micro sensor is mainly integrated with three layers, including a substrate layer, a conducting layer, and a self-assembled graphene/copper nanoparticles composite (GCuNPs) layer. Microfabrication was utilized to pattern the three-electrode system layer on silicon substrate. Chromium/gold layers 50/200 nm thick were firstly evaporated on a clean wafer with a CHA sputter system. Subsequently, three-electrode system was patterned by photolithography and lift-off process. Next, graphene/copper nanoparticles layers were deposited by self-assembly technique (Zhang and Cui 2012). 1.5 wt% poly(diallyldiamine chloride) (PDDA) and 0.3 wt% poly(sodium 4-styrene sulfonate) (PSS) were prepared in DI water with 0.5 M sodium chloride buffer solutions to enhance the surface properties. As illustrated in Fig. 2b, PSS/PDDA layers were prepared by immersing the sensor in the above PDDA and PSS solutions for 10 min separately, then repeat once to form a bi-layers structure for charge enhancement. Graphene self-assembling was accomplished by immersing the working electrode area into PDDA solutions for 10 min and graphene solutions for 20 min, and then repeat for four repetitive cycles. DI water rinsing and nitrogen drying were added before immersing into the next solution. Later, the working electrode area was protected by photoresist spinning and lithography. Exposed self-assembled graphene was removed by oxygen plasma. Finally, the photoresist was removed and copper nanoparticles were electrodeposited on the sensor with 0.01 M  $\text{CuSO}_4$  solution at the potential of  $-0.2$  V.

### 2.4 Measurement procedure

A series of nitrate solutions, with concentrations ranging from 10 to 90  $\mu\text{M}$ , were prepared by diluting stock solutions in 0.01 M HCl + 0.1 M sodium sulfate buffer solutions. Fresh lake water sample was taken from the Lake Como (St. Paul, MN, USA). Filtration were operated to remove big particles and algae in lake water before analysis. Before analysis, the sensors were immersed in the nitrate solutions and dissolved oxygen was removed by purging nitrogen. Differential pulse voltammetric scan

(amplitude 50 mV; pulse width 0.05 s) was performed on an electrochemical workstation and the sensors were analyzed afterwards. Scanning signal from 0 to  $-1$  V was applied on the working electrode and the corresponding response was recorded.

## 3 Results and discussion

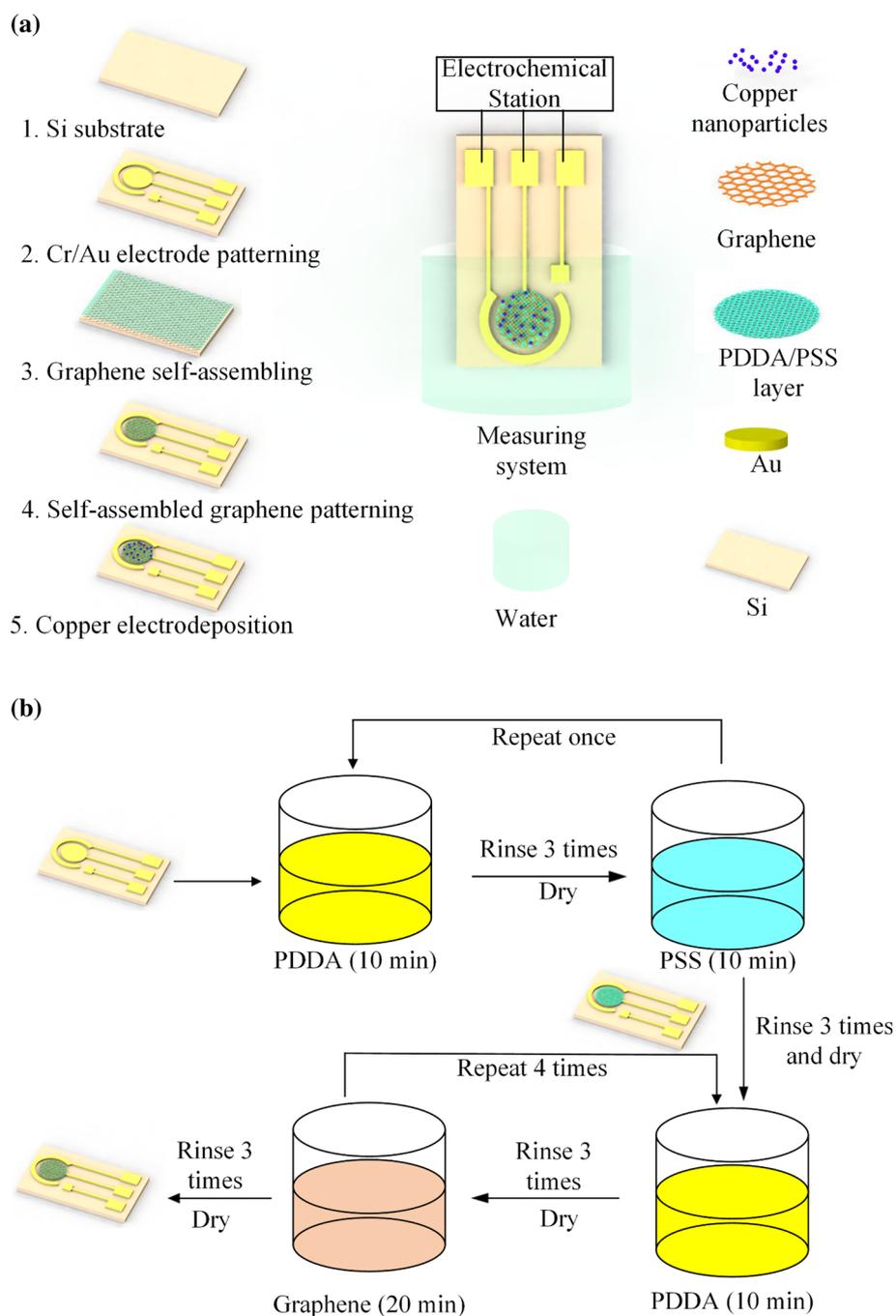
### 3.1 Morphology of a self-assembled graphene/copper nanoparticles composite Electrode

Most literatures use planar electrode for copper deposition. The copper film deposited on a planar electrode appeared to be compact and bright, which provided less surface area for the target ions to react. The lack of reaction sites will result in smaller output signal of the target reaction (Keawkim et al. 2013). The self-assembled graphene we proposed has particular advantages over surface area. The self-assembly procedure results in hierarchical nanostructures (Zeng et al. 2010) and provides a foam network for copper deposition, making it possible for copper nanoparticles to form a three-dimensional structure. In addition, graphene nanoplatelets exhibit many cracks and high surface roughness (Chandrasekaran et al. 2013), implying that the material could increase the electroactive surface area. Figure 3 shows the scanning electron microscope (SEM) image of copper nanoparticles from the electrode with and without self-assembled graphene. Figure 3a was captured from copper microparticles decorated planar gold electrode. Particles with the size ranging from 1 to 2  $\mu\text{m}$  were obtained. These particles were firmly connected with each other to form a compact surface. Figure 3b shows the surface of a self-assembled graphene/copper nanoparticles composite electrode. Growth of copper nanoparticles starts from the nucleation on the active sites of self-assembled graphene. As the active sites were relatively close to each other, the sizes of resultant copper nanoparticles were ranging from 200 to 500 nm. Smaller size increased the surface-to-volume ratio of the particles, which facilitated the catalytic reaction of nitrate. In addition, as graphene was layer by layer assembled, the lower layers could also take part in the reaction and contribute to higher output signal.

### 3.2 Effect of self-assembled graphene and copper nanoparticles on nitrate determination

To characterize the effects of copper nanoparticles and graphene on the sensing performance, a bare gold sensor, a copper nanoparticles decorated sensor and the proposed

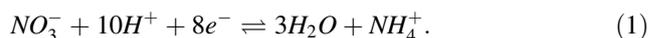
**Fig. 2** Illustration of the sensor's microfabrication process (a) and the self-assembly process (b)



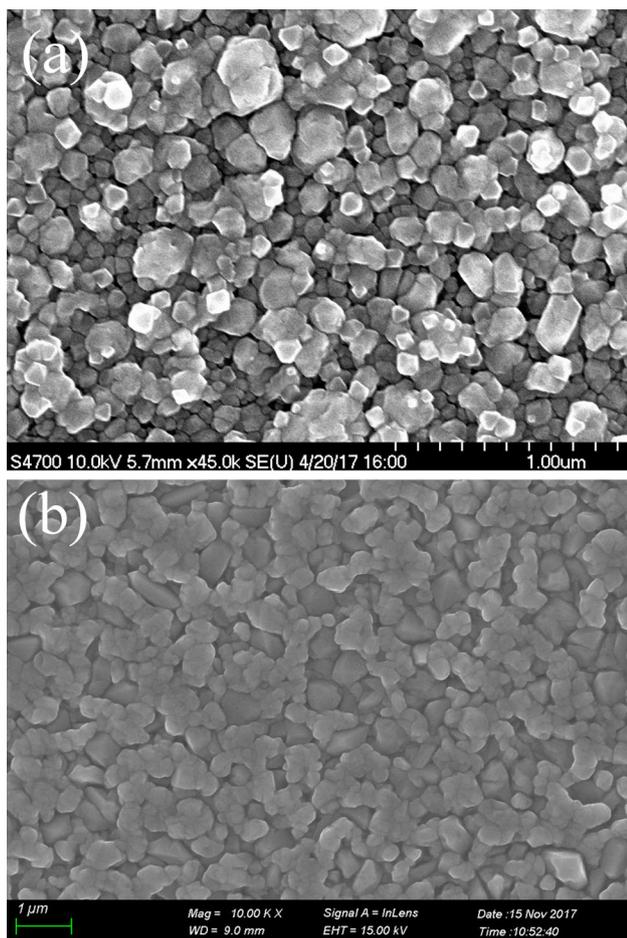
sensor were tested in a solution with 50  $\mu\text{M}$  nitrate, respectively. Differential pulse voltammetric responses were recorded when using the three sensors for nitrate determination.

As shown in Fig. 4, no conspicuous reduction peak for nitrate was shown when using the bare gold sensor, suggesting that nitrate reduction occurs at more negative potentials than  $-0.8$  V, which is outside of the window. When copper decorated sensor was used to detect nitrate, a curve with a reduction peak at the value of 5.06  $\mu\text{A}$  was

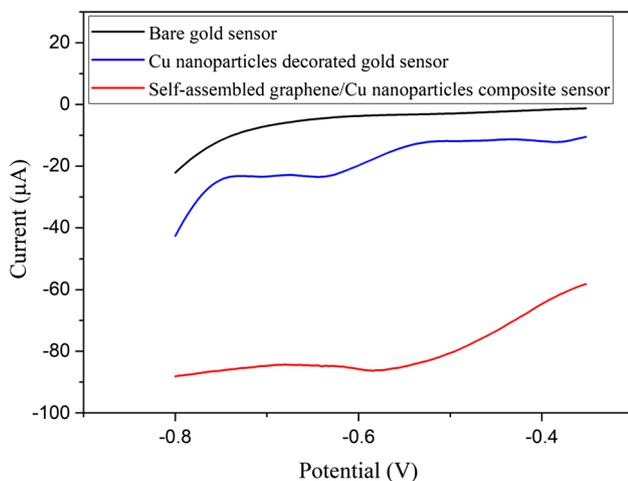
observed. This indicates that copper catalyzer is essential for the reduction of nitrate. Specifically speaking, in acidic environments, the exist of copper can catalyze the reduction of  $\text{NO}_3^-$  and then make Eq. (1) happen at less negative potentials (Carpenter and Pletcher 1995).



As shown in Fig. 4, when the proposed graphene and copper nanoparticles composite sensor was utilized, the responsive curve shows a peak with the value of 12.2  $\mu\text{A}$ ,



**Fig. 3** SEM image of copper nanoparticles decorated planar gold electrode (a) and the proposed self-assembled graphene and copper nanoparticles composite electrode (b)



**Fig. 4** Differential pulse voltammograms of 50  $\mu\text{M}$  nitrate solutions using bare gold sensor, copper nanoparticles decorated gold sensor and self-assembled graphene and copper nanoparticles composite decorated sensor

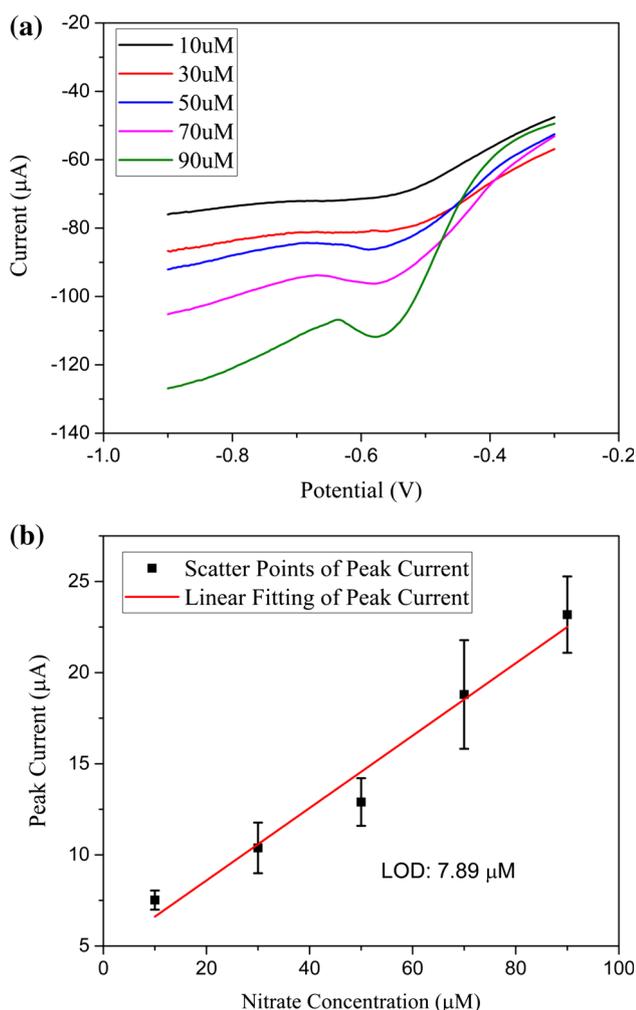
more than two times of the value from copper nanoparticles decorated sensor. This proves that self-assembled graphene can help enhance the reaction and contribute to higher output signals. Besides, after graphene was applied, the peak value of nitrate reduction shifted from  $-0.62$  to  $-0.58$  V, indicating that less negative potential was needed to reduce nitrate. The reduction of nitrate became easier and the catalytic property of the sensor was improved. This may owe to the nanostructure of graphene and reduced size of copper nanoparticle.

### 3.3 Differential pulse voltammetric analysis for quantitative determination of nitrate

Quantitative analysis is crucial for a sensor as it determines the concentration of a sample and the feasibility for mass production of a sensor. In this part, differential pulse voltammetry was chosen as the electrochemical technique for nitrate analysis as it can reduce background currents coming from interfacial capacitance and increase the signal-to-noise ratio of a sensor (Bard and Faulkner 1980). Stirring was avoided to eliminate the interferences caused by convection and dissolved oxygen. Nitrate sample solutions with the concentrations ranging from 10 to 90  $\mu\text{M}$  were prepared in 0.01 M HCl + 0.1 M sodium sulfate solutions. Differential pulse voltammetric measurements were performed and corresponding response from 10 to 90  $\mu\text{M}$  was obtained, as shown in Fig. 5a. Well-defined voltammetric peaks were observed at the peak potentials between  $-0.55$  and  $-0.58$  V versus Ag/AgCl reference electrode (3 M KCl). Reduction peaks of nitrate increased linearly with the concentration of nitrate increasing, indicating the sensor's suitability of quantitative analysis of nitrate preliminarily. Corresponding calibration curve was plotted with five repeated measurements at each concentration. As shown in Fig. 5b, fine linearity was achieved with high coefficient of variation due to the highly uniform microfabrication method. Limit of detection was calculated as  $\text{LOD} = 3\sigma/S$ , where  $\sigma$  is the standard deviation of measurement at 10  $\mu\text{M}$  ( $\sigma = 0.53$   $\mu\text{A}$ ) as a substitute for the buffer solution and S is the analytical sensitivity ( $S = 0.20$   $\mu\text{A}/\mu\text{M}$ ). Finally, detection limit of 7.89  $\mu\text{M}$  was achieved for nitrate, which is much lower than the guideline of 800  $\mu\text{M}$  offer World Health Organization. This low detection limit further proved the sensor's capability for trace nitrate determination.

### 3.4 Reusability of the self-assembled graphene/copper nanoparticles decorated sensors

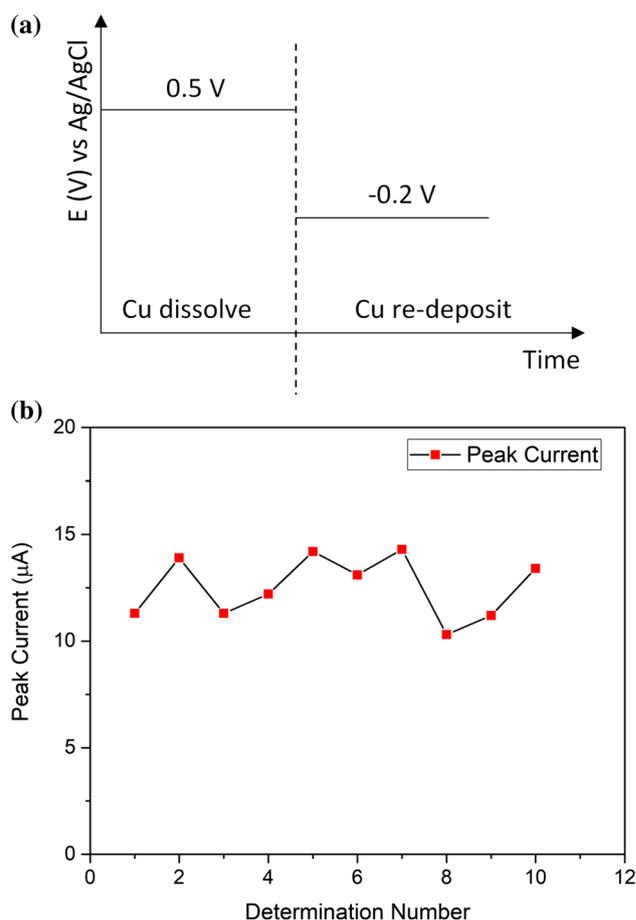
As reported in literature (Pletcher and Poorabedi 1979), nitrate can be reduced to ammonia, in accordance with



**Fig. 5** Differential pulse voltammograms of nitrate measured by the proposed sensor (a) and linear fitted calibration curve of nitrate from 10 to 90  $\mu\text{M}$  (b)

Eq. (1), on the surface of a fresh copper electrode. Copper electrode can be poisoned a few minutes after being made (Pletcher and Poorabedi 1979). Therefore, copper nanoparticles decorated sensors cannot be reused directly after one determination. Fresh copper nanoparticles must be redeposited before reusing the sensor for DPV analysis. Figure 6a shows the electrode pre-treatment procedure between two determinations when using the sensor for multiple tests. Copper nanoparticles were dissolved in the copper sulfate solution at 0.5 V for 30 s firstly and then redeposited at  $-0.2$  V to form a fresh copper nanoparticles layer.

Figure 6b reveals the results of ten determinations using the same graphene decorated sensor. Fresh copper nanoparticles were reformed before each determination. Nitrate solutions with the concentration of 50  $\mu\text{M}$  were analyzed. The peak current fluctuated randomly at an average value of 12.52  $\mu\text{A}$ . No upward or downward trend



**Fig. 6** Schematic representation of the copper surface pretreatment procedure (a) and current peak values as a function of time for determinations of 50  $\mu\text{M}$  nitrate solution with electrochemical pretreatment between two adjacent determinations (b)

was observed. It indicated that the result of a new graphene/copper nanoparticles decorated sensor can be reproduced by dissolving and redepositing copper nanoparticles. Thus we can conclude that the proposed sensor is reusable on conditions that fresh copper nanoparticles were reformed before analysis.

### 3.5 Real water determination

Increasingly serious environmental pollution and algae bloom situations demand in situ determination of nitrate. In this case, the proposed sensor has a great advantage over spectroscopic methods because of its portability and simple-to-use properties. As unknown ions and surface active compounds may interfere the determination procedure, the analysis condition in real waters is very critical and the possibility of using the proposed sensor for real water determination needs to be confirmed.

In order to investigate the reliability of using the proposed sensor for real water detection, nitrate standard

**Table 1** Nitrate determination in standard and real water solutions by using a standard procedure and the proposed sensor

Samples	Results from Hach spectrometer ( $\mu\text{M}$ )	Results from the proposed sensor ( $\mu\text{M}$ )
20 $\mu\text{M}$ nitrate solution	$20.78 \pm 1.04$	$21.8 \pm 2.5$
40 $\mu\text{M}$ nitrate solution	$41.05 \pm 0.90$	$38.8 \pm 3.5$
60 $\mu\text{M}$ nitrate solution	$60.03 \pm 1.00$	$55.3 \pm 3.0$
80 $\mu\text{M}$ nitrate solution	$81.05 \pm 0.73$	$78.2 \pm 3.5$
Lake water	$30.75 \pm 1.29$	$29.6 \pm 2.3$

solutions and waste water solutions were prepared and analyzed by the proposed sensor. As comparison, a standard spectroscopic method was also adopted to analyze the above samples. As shown in Table 1, standard nitrate solutions with the concentration of 20, 40, 60, 80  $\mu\text{M}$  were prepared as well as lake water samples. Fresh lake water samples were taken from Lake Como. Filtration was operated to remove big particles in lake water before analysis. Standard spectroscopic method was operated with Hach DR1900 Spectrophotometer. As shown in the resultant table, for nitrate standard solutions, both standard method and the proposed sensor got results close to the real concentration of the samples. This validates the reasonability of using spectrometer as a standard analysis method and proves that the proposed sensor is capable of determining standard nitrate solutions. As for lake water analysis, the mean nitrate concentration from the proposed sensor is 29.6  $\mu\text{M}$ , which is in good agreement with the result from standard method (30.75  $\mu\text{M}$ ). The consistency owes to the uniformity from the fabrication process. This preliminary result demonstrates that this sensor is reliable for nitrate determination of environmental samples such as lake water.

## 4 Conclusion

This paper reports a novel three-dimensional micro sensor for nitrate detection. Layer-by-layer self-assembled graphene and copper nanoparticles composite were used to improve the sensitivity of the sensor. Copper was proved as an excellent catalyzer for nitrate reduction and self-assembled graphene provided a three-dimensional foam network for copper nanoparticles. The mechanism of the sensor was studied and the morphology was investigated by scanning electron microscope images. A linear range from 10 to 90  $\mu\text{M}$  nitrate was observed and low LOD of 7.89  $\mu\text{M}$ , which is far below the WHO guideline, was achieved. The sensor was reusable when pre-treatment was applied before analysis. Finally, the results of real water detection were consistent with those from a standard process. Taking the advantages of low cost and small size into

account, this portable and high sensitive sensor holds great potential for environmental monitoring.

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