



Anodic stripping voltammetric determination of copper (II) ions at a graphene quantum dot-modified pencil graphite electrode

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Abstract

A simple and sensitive electrochemical sensor based on graphene quantum dot-modified pencil graphite electrode (GQD/PGE) was fabricated and used for highly selective and sensitive determination of copper (II) ions in nanomolar concentration by square wave adsorptive stripping voltammetric method. The sensing mechanism could be attributed to the formation of a complex between Cu^{2+} ions and oxygen-containing groups in GQDs which result in an increased SWV signal in comparison with the bare electrode. Optimization of various experimental parameters such as pre-concentration time, pre-concentration potential, pH, and buffer type which influence the performance of the sensor, was investigated. Under optimized condition, GQD-modified electrode has been used for the analysis of Cu^{2+} in the concentration range from 50 pM to 4 nM and a lower detection limit of 12 pM with good stability, repeatability, and selectivity. Finally, the practical applicability of GQD-PGE was confirmed via measuring trace amount of Cu (II) in water samples. The GQD/PGE surface could be regenerated by exerting more positive potentials than the stripping potential of the Cu (II) ion and then used for another deposition.

Keywords Graphene quantum dot · Electrochemical detection · Cu (II) ions · Adsorptive stripping voltammetry

Introduction

Copper is essential to all living organisms as a trace nutritional mineral because it involves the synthesis of hemoglobin, a variety of enzymes, and metabolism of the body [1–3]. However, copper deficiency or elevated levels of copper can bring about opposite health effects. For instance, copper deficiency can produce anemia-like symptoms or can affect the activity of enzymes and cell metabolism, while elevated levels of Cu^{2+} in the human body are a health risk of the kidneys, the liver, the central nervous system, and it can increase the blood pressure and the rate of respiration [4, 5]. The imbalance amount of copper ions can cause two classes of genetic diseases, namely Menkes and Wilson [6–8]. Due to physiological importance of copper and

wide usage of it in industrial and agricultural sectors, determination of copper in various matrices is very important and numerous analytical techniques have been used for the accurate and sensitive determination of trace quantities of copper including atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICPAES), inductively coupled plasma-mass spectrometry (ICPMS), UV spectrophotometry, fluorescence, and electrochemical methods [9–30]. Among these, electrochemical techniques have attracted extra attention because of many advantages such as simplicity, cost-effectiveness, and small instrumentation. Compared to other electrochemical procedures, stripping analysis method has high sensitivity and allows determination of trace amount of substances because of pre-concentrating of analytes at the surface of the working electrode.

Graphene quantum dots (GQDs), a new kind of carbon nanomaterials with features derived from both graphene and QDs, have attracted extensive consideration from researchers due to optical stability, good surface grafting, biocompatibility, low toxicity, and high electrical and thermal conductivity. GQDs with a great surface area and quick electron transferability are one of the best electrode modifiers which can increase the rate of electrochemical reactions

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and attracted more attention as electrode modifier [31–35]. Recently, Wang et al. developed graphene quantum dots as a fluorescent sensing platform for highly efficient detection of copper (II) ions [36]. Furthermore, novel conjugates of GQDs and gold nanoparticles (AuNPs) are synthesized and used for sensitive electrochemical detection of heavy metal ions [37]. In this work, we used GQD-modified pencil graphite electrode for electrochemical quantification of Cu^{2+} ions by applying anodic stripping analysis. As shown in Scheme 1, the pencil graphite electrode (PGE) modified by GQD formed a platform for the adsorption of Cu^{2+} which may be related to the oxygen-containing groups on the GQDs surface. This is the first usage of untreated graphene-type nanoparticles, GQD, for the simple, cheap, sensitive, and selective determination of copper ions with an excellent performance and low detection limit.

Experimental

Instrumentation and reagents

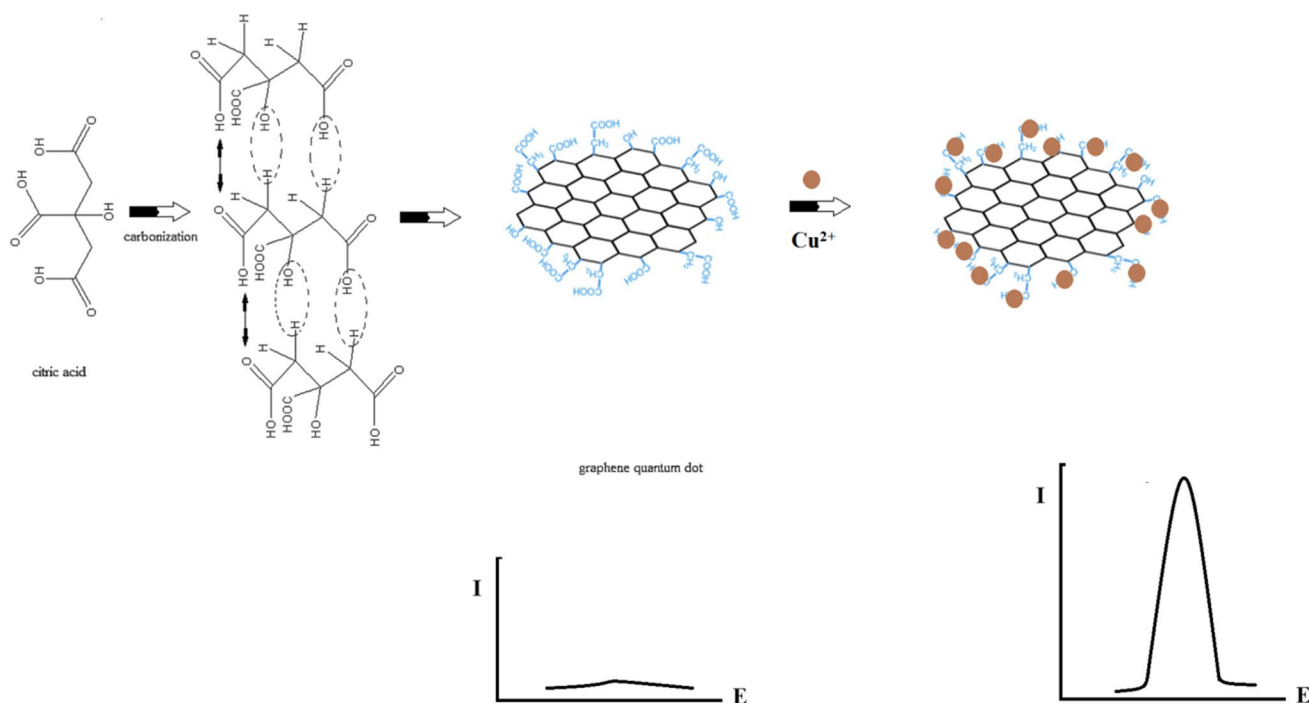
Electrochemical experiments were performed using AUTO-LAB PGSTAT 30 electrochemical analysis system and GPES 4.9 software package (Eco Chemie., the Netherlands). The utilized three-electrode system was composed of a modified pencil graphite electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode,

and a platinum wire as the auxiliary electrode. A digital pH/mV meter (Metrohm, pH Lab 827) was used for pH measurements, and an ultrasonic bath (KODO model JAC1002) was used for cleaning the electrode surface.

All solutions were prepared with deionized water. All chemicals were of analytical grade, purchased from Merck (Darmstadt, Germany), and used without further purification. The pencil graphite was obtained as pencil lead from Rotring Co. Ltd, Germany (R 505210 N), of type H. Dilute solutions of Cu^{2+} were prepared immediately before the use by diluting the stock solution with proper buffer. Metal ion solutions were prepared by dissolving appropriate amounts of their nitrate salts (Merck, Germany) in deionized water. GQDs were synthesized by pyrolyzing citric acid and dispersing the carbonized products into alkaline solutions [38]. The morphology of GQD was studied by TEM and AFM method.

Fabrication of the working electrode

The body of pencil lead was tightly coated with Teflon band. Electrical contact with the lead was achieved by connecting a copper wire to the metallic holder of the working electrode. The surface was polished on a weighing paper to a smooth finish and then sonicated in doubly distilled water. The GQD-modified electrode was fabricated by referring previous work of our research team [34]. Ten microliters of GQDs with the concentration 3 mg/mL was dropped on the



Scheme 1 Schematic representation of the preparation processes of Cu^{2+} ions sensor based on GQDs

surface of PGE and dried for 4 h at room temperature in a dark place. Then, the modified electrodes were rinsed with doubly distilled water.

Voltammetric measurements

Before determination, the modified electrode was immersed into the Cu^{2+} solution for adsorption with stirring under optimum potential and time, washed with doubly distilled water, placed in an electrochemical cell containing supporting electrolyte. Square wave stripping voltammetry was used to determine copper(II) from -0.3 to 0.3 V at a frequency of 15 Hz, an amplitude of 25 mV, a standing time of 40 s, and a step length of 4 mV. Prior to each measurement, the electrode was cleaned at 600 mV for 120 s to remove any deposit from the previous measurement.

Results and discussion

Characterization of GQDs

Figure 1a shows TEM images of GQDs. As can be seen, the synthesized GQDs are uniformly arranged. The morphology of the PGE and GQD/PGE was studied using SEM (Fig. 1b, c), and results represent the presence of numerous round-shaped prepared GQD on the electrode surface. The morphology of GQD was also studied by AFM method. As shown in Fig. 1S, the corresponding AFM image shows a single GQD monolayer thin film.

Electrochemical behavior of bare and GQD-modified electrode

Electrochemical behavior of bare and modified electrodes was studied by cyclic voltammetry with $10 \text{ mmol L}^{-1} \text{K}_3[\text{Fe}(\text{CN})_6]$ and 1 M KNO_3 as probe solution. Figure 2a shows cyclic voltammograms of the probe solution at bare and GQD-modified PGE. As shown in Fig. 2a, a pair of well-defined redox peaks was found at bare (curve a) and modified PGE (curve b). On GQDs/PGE, the peak potential separation (ΔE_p) decreased and the peak current increased obviously. Peak-to-peak separation decrease proves the fact that GQDs have higher electron transfer rate and electrical conductivity compared to bare PGE. The enhanced current response of GQDs/PGE attributed to the increase in the effective surface area of PGE upon the modification which is favorable for the design of a highly sensitive electrochemical platform.

In order to confirm the electrocatalytic activity of the bare and modified electrodes for the determination of Cu^{2+} , the electrochemical experiments were carried out in the absence and presence of Cu^{2+} (Fig. 2b). Results showed that these

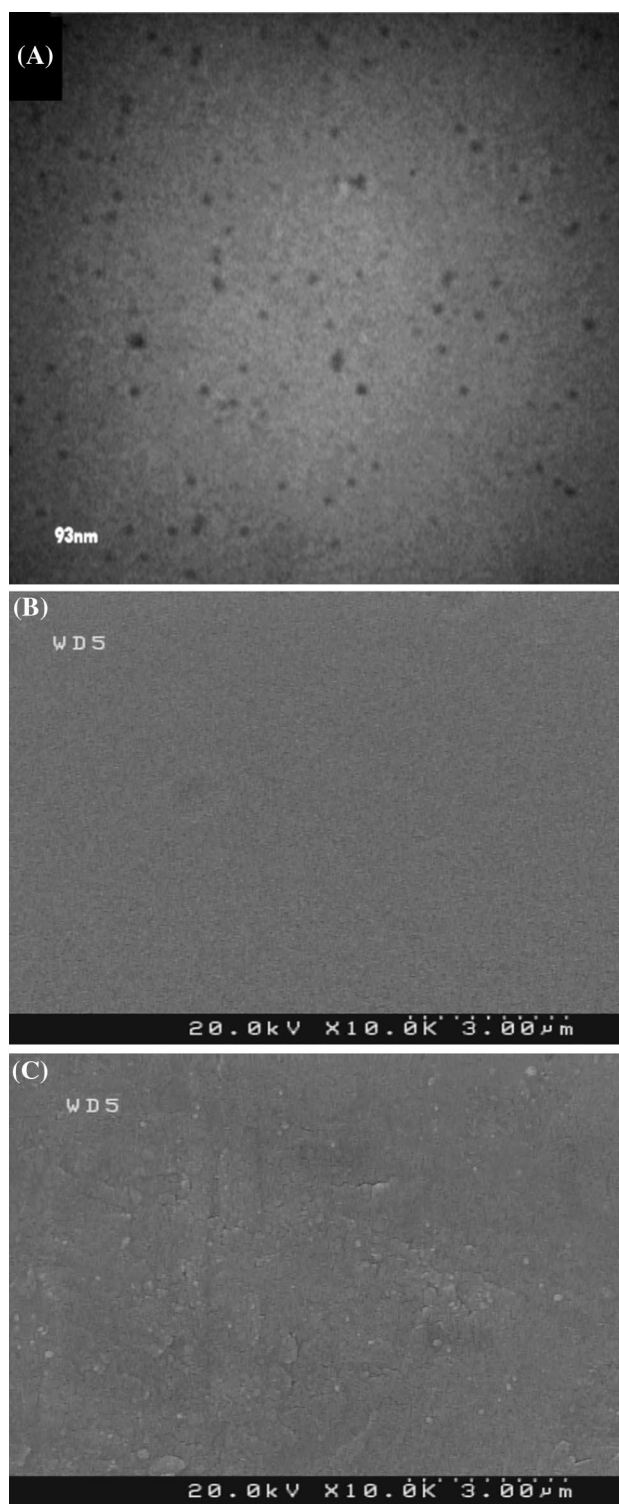


Fig. 1 a TEM image of GQD, Reprinted with permission from [34], and SEM images of b bare and c GQD-modified PGE

electrodes do not show any voltammetric feature (curves a and b) in the absence of Cu^{2+} ion. Upon dipping the electrodes into the $2 \mu\text{M Cu}^{2+}$ solution for 5 min, one pair redox

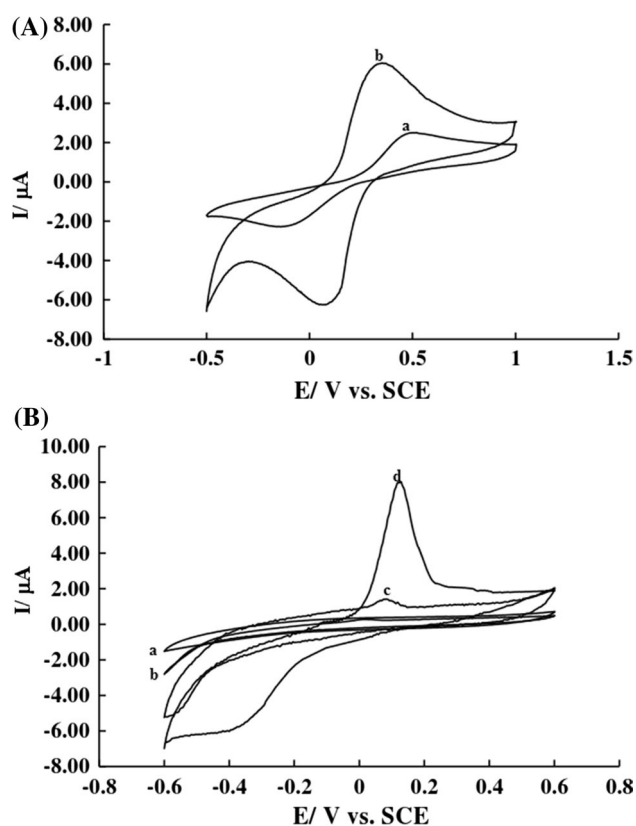


Fig. 2 **a** Cyclic voltammograms of (a) bare PGE, (b) GQDs/PGE in 10 mM K₃[Fe(CN)₆] solution containing 0.1 M KNO₃ at the scan rate of 50 mV s⁻¹; **b** cyclic voltammograms of bare (a, c) and GQD-modified (b, d) PGE in the absence of Cu²⁺ (a, b) and after immersion in 2 μM Cu²⁺ in PBS, pH 6 for 5 min, and return to the copper-free PBS (c, d); scan rate: 50 mV s⁻¹

peaks were observed at two electrodes due to the adsorption of Cu²⁺ on the electrodes, but GQD-modified electrode shows larger and better signal than unmodified electrode (curves c and d).

As shown in Scheme 1, these results might be related to that the oxygen-containing groups on the GQD surface can interact with Cu²⁺ ions and increase copper deposition on the electrode surface and also related to the high specific surface area, more active sites along the surfaces of GQD, and an increased electron transfer ability of GQD. Because of the above favorable characteristics, the parameters of voltammetric analysis, which affect the stripping signal of target metal ion, were studied and optimized in the following research.

Optimization of the conditions and analytical application

In order to get the maximum sensitivity for trace Cu(II) detection, the effect of following parameters was optimized:

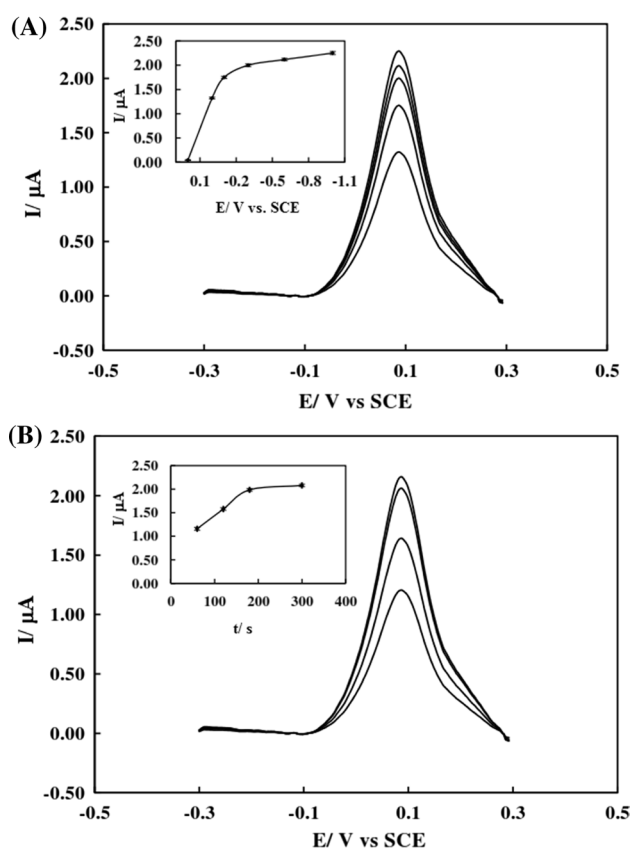


Fig. 3 Square wave voltammograms of GQD/PGE after immersion in 2 nM Cu²⁺ using various immobilization **a** potentials and **b** times; inset: variation of SWV response of GQD/PGE versus immobilization potential and time. Accumulation conditions: 2 nM Cu²⁺, pH 6, time 180 s at various potentials, or -0.3 V pre-concentration potential at various times with determination at copper-free PBS pH 5

(c) deposition potential; (d) deposition time; (e) buffer type and buffer pH value.

Effect of deposition potential and deposition time

One of the very important parameters for stripping analysis is deposition potential. Figure 3a depicts the deposition potential effect on the stripping peak signal of 2.0 nM Cu²⁺. Based on the achieved results, applying a negative potential favors the deposition of Cu on the electrode and maximum stripping peak current was observed for immobilization potential of -0.30 V. Therefore, a potential of -0.30 V was selected for subsequent works.

In stripping techniques involving an accumulation stage, the sensitivity usually depends on the deposition time, because of the increased amount of metal deposited on the electrode surface by increasing the accumulation time. For this reason, the modified electrodes were immersed in a 2 nM Cu²⁺ stirred solution for a different period of time (Fig. 3b). As it can be seen, the peak current was increased

as a function of pre-concentration time up to 180 s and remained constant between 180 and 600 s. No significant signals for analyte were observed without the deposition period. So, a 180-s accumulation time was used in the further experiments.

Effect of pH and electrolyte type

To reach high sensitivity and selectivity, the effect of pH value on the peak current was investigated and the best pH conditions for pre-concentration and determination steps were achieved around pH 6.0 and 5, respectively (Fig. 4a). The obtained results indicate that for pH values lower and higher than 6.0 in the pre-concentration step, the accumulated Cu decreases and may be due to the protonation of oxygen-containing groups on the GQDs surface or competition of OH^- with oxygen-containing groups on the GQDs

for Cu^{2+} ions in solution, respectively (Fig. 4a, curve a). In the stripping step, the largest peak current can be obtained at pH 5 (Fig. 4a, curve b). Therefore, pH 6 and pH 5 were used as optimum pH values in pre-concentration and determination steps, respectively.

To investigate the influence of the solution matrix on the extraction and determination steps of Cu^{2+} ions, the PBS, AcBS, and KNO_3 electrolytes were investigated. Results showed that determination buffer has no effect on the obtained signal, and because of the optimum pH of 5 for this step, we used acetate buffer solution in the determination step. For pre-concentration step, results (Fig. 4b) showed that maximum response was observed when 0.1 M PBS used as the buffer in this step. Therefore, 0.1 M PBS and 0.1 M AcBS were used as electrolytes in pre-concentration and determination steps, respectively.

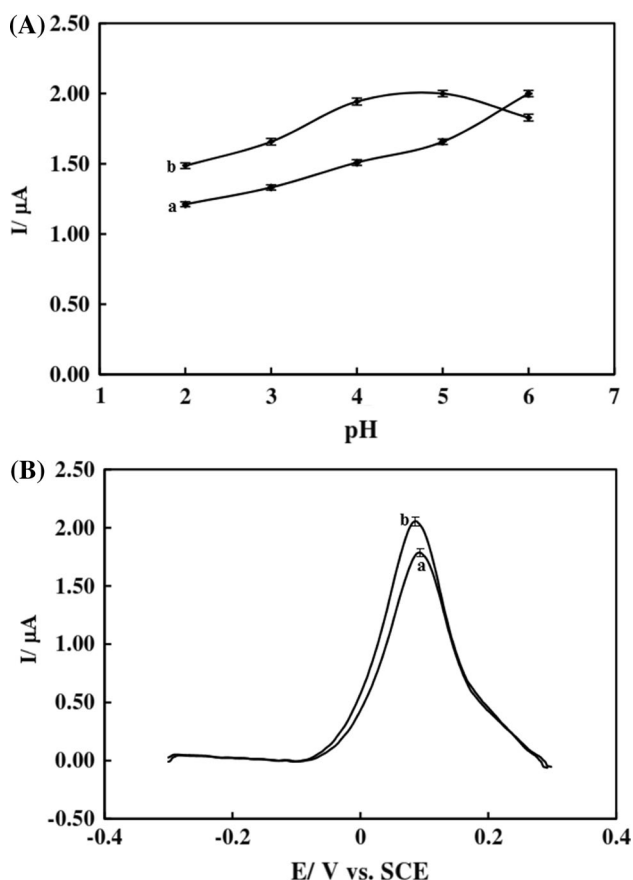


Fig. 4 Effect of solution pH at (a) accumulation step and (b) determination step on the SWV response of GQD-modified PGE. Accumulation conditions: 2 nM Cu^{2+} , time 180 s at -0.3 V with determination at pH = 5.0. Determination condition: copper-free PBS with accumulation at pH = 6; **b** Effect of adjusting pH buffer in accumulation step (a) 0.5 M KNO_3 + 0.1 M acetate, (b) 0.5 M KNO_3 + 0.1 M PBS on the SWV response of GQD/PGE. Accumulation conditions: 2 nM Cu^{2+} , pH 6, time 180 s at -0.3 V with determination at copper-free AcBS pH 5

Effect of scan rate

In order to study the nature of the electrode process occurring at the electrode surface, a series of voltammograms of 0.1 μM Cu (II) at various scan rates were also recorded. As shown in Fig. 5, both cathodic peak current and anodic peak current increase linearly with the increase in scan rate. This result confirms that the electron transfer reaction is surface-controlled redox system and Cu (II) adsorbed on the electrode surface.

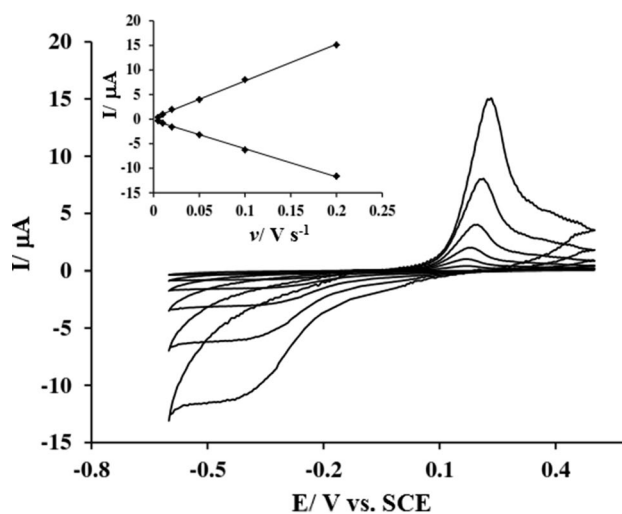


Fig. 5 Cyclic voltammograms of the GQD-modified electrode in 0.5 M KNO_3 + 0.1 M PBS containing 0.1 μM Cu^{2+} at various scan rates of 5, 10, 20, ..., and 200 mV s^{-1} (from inner to outer profiles), respectively; inset: plot of I_p versus v . Accumulation conditions: pH 6, time 180 s at -0.3 V with determination at copper-free AcBS pH 5

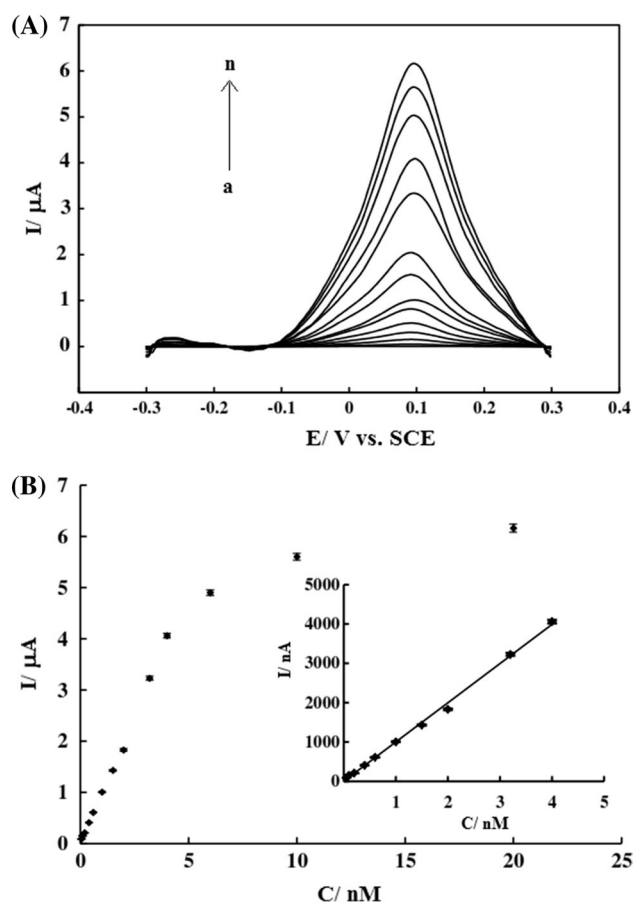


Fig. 6 **a** Differential pulse voltammograms of GQD-modified PGE after immersion in PBS containing Cu^{2+} with different concentrations of 0, 0.05, 0.1, 0.2, 0.4, 0.6, 1.0, 1.5, 2, 3.2, 4, 6, 10, 40 nM Cu^{2+} (from a to n), and **b** variation of SWV signal as a function of Cu^{2+} concentration; inset: calibration curve. Experimental conditions as Fig. 5

Calibration plots and detection limit

Figure 6 shows the SWV response of GQD/PGE after interaction with various concentrations of Cu^{2+} . Under the optimum analytical conditions, the sensor showed a linear range from 0.05 to 4 nM (inset of Fig. 6) with the linear correlation coefficient of 0.997. The sensitivity of the developed GQD/PGE was calculated as 997 AM^{-1} , and the detection limit was 0.012 nM based on a signal-to-noise ratio ($S/N = 3$). The comparison of the proposed electrode with other modified electrodes for Cu (II) detection is shown in Table 1. It can be seen that this method has the comparable detection limit for the Cu (II) detection with the simple electrode preparation procedure.

Interference study

The influence of various metal ions as potential interferences on the determination of copper (II) ions has been investigated by gradual addition of their standard solution to the electrochemical cell until a tolerated concentration causing a maximum relative error of $\pm 5\%$ in the voltammetric signal of Cu^{2+} is realized. In order to investigate the interference of some species including Pb(II), Zn (II), Cd (II), Bi(III), Ni (II), Co (II), and Mn(II) and Hg(II) on the determination of Cu^{2+} using the accumulation potential of -0.3 V at the concentration level of 2 nM, an extensive measurement was taken. It is found that the presence of (Pb^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+}), (Bi^{3+} and Mn^{2+}), and Hg^{2+} in the assay solution is tolerated with a concentration up to 50, 15, and 5 times of Cu^{2+} concentration, respectively, and determination error of Cu^{2+} in these conditions was lower than 5%.

Table 1 Comparison of the GQD-modified PGE with other modified electrodes as Cu (II) sensor

Electrode	Modifier	Technique	Linear range	Detection limit	References.
GCE	Chitosan–graphene	SWV	1–15 nM	0.43 nM	[26]
GCE	NH-rGO/β-CD	SWV	30 nM–100 μM	2.8 nM	[39]
Gold microelectrode	Sn film/gold nanoparticles	SWV	0.078–7.8 μM	31 nM	[40]
Glassy carbon electrode	Au nanoparticles	DPASV	0.3–1.4 μM	0.3 μM	[41]
Glassy carbon electrode	Antimony film		0.031–0.78 μM	7.8 nM	[42]
Glassy carbon electrode	Carbon nanotube thread	OSWSV	0.5–3.5 μM	0.27 nM	[43]
Boron-doped diamond electrode	None	SWV	2.5–100 μM	2.5 μM	[44]
Carbon fiber electrode	Nylon	ASV	0.125–468.7 μM	0.125 μM	[45]
Platinum ultramicrodisk electrode	None	CV	1550–6180 μM	20 μM	[46]
Glassy carbon electrode	[Polyallylamine hydrochloride–graphite oxide]	DPASV	0.5–50 μM	0.35 μM	[47]
Glassy carbon electrode	Diethylenetriamine penta-acetic/dopamine/iron oxide black	OSWV	0.005–100 μM	2.1 nM	[48]
Gold	Cysteamine-glutaraldehyde-L-lysine SAM	DPV	1 pM–1 μM	0.12 pM	[49]
PGE	GQD	SWASV	0.05–4 nM	12 pM	This work

Regeneration and repeatability of electrodes

One of the favorable characteristics of our electrode is its easiness in regeneration. Electrodes are easily regenerated by applying the positive potential of 0.6 V for 120 s to remove copper ions from the electrode surface. Based on the obtained results for studying the stability of modified electrode during repetitive stripping voltammetric experiments at the same modified electrode, each prepared electrode could be used for 23 determination experiment without apparent change in obtained results.

The reproducibility of the sensor was evaluated by the analysis of the same concentration of Cu^{2+} (2 nM) using five prepared GQD/PGE under the same conditions. All sensors exhibited close SWV signal, and a relative standard deviation (RSD) of 1.3% was achieved, which indicated that the reproducibility of the proposed sensor is acceptable. We checked long-term stability of the modified electrode by measuring the response of the Cu^{2+} from day to day. Results showed that there was no apparent decrease in the current response after 10-day storage, which indicates that the electrode has suitable storage stability.

Analysis of water

To evaluate the analytical reliability and application potential of the proposed sensor to real sample analysis, the GQD/PGE was used for the analysis of copper (II) under the optimized condition in tap water (has been taken from Urmia University) and synthetic water by direct analysis of the water with the modified electrode and the results are shown in Table 2. The attained results for measurement at three different concentrations (Table 2) indicate that the concentration of Cu^{2+} was accurately determined with the prepared electrode.

Table 2 Results of the determination of Cu^{2+} in synthetic water samples

Sample	Cu^{2+} added (nM)	Cu^{2+} found (nM)	Recovery (%)	RSD (%)
Synthetic water sample ^a	0.5	0.53	106	0.9
	1	1.01	101	1.2
	2	1.98	99	1.6
Tap water ^b	0	2.14	–	1.1
	2	4.32	104	1.6
	4	6.26	102	1.3

^aSynthetic samples containing other metal ions (nM): Mn^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Bi^{3+} : 5 nM, Hg^{2+} : 2.5 nM

^bTap water of Urmia University

Conclusions

We developed an electrochemical sensor based on GQD-modified pencil graphite electrode for the determination of the low concentration of Cu^{2+} ion by applying anodic stripping analysis. This is for the first time that untreated graphene-type nanoparticles, GQD, are used for the Cu^{2+} detection. The sensing mechanism could be attributed to the formation of complex between Cu^{2+} ions and oxygen-containing groups in GQDs which result in an increased SWV signal in comparison with the bare electrode. The results indicate that the prepared sensor has good reproducibility and stability, could meet the selective requirements for environmental application, and be sensitive enough to detect Cu^{2+} ions in environmental water samples.

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