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A study on the electrochemical behavior of hydroquinone at a nanometer cobalt/L-glutamate-modified electrode

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A new electrochemical sensor for hydroquinone (HQ) was prepared. The electrochemical sensor was modified by electrodeposition and electrochemical polymerization to modify nanometer cobalt (nano-Co) and poly-L-glutamic acid (poly-L-glu) on the surface of a glassy carbon electrode (GCE). Then, the electrochemical behavior of hydroquinone on the electrochemical sensor was investigated by cyclic voltammetry (CV). The experimental conditions were optimized from the aspects of electrolyte type, concentration, acidity, enrichment time and scanning speed. The experimental results showed that under optimized conditions the oxidation peak current has a good linear relationship with the concentration of hydroquinone in the range of 3.85×10^{-6} to 1.30×10^{-3} mol L⁻¹ ($R^2 = 0.9998$). Moreover, there was a low detection limit of 4.97×10^{-7} mol L⁻¹. When the sensor was used for the analysis of hydroquinone in water samples, the recoveries with satisfactory results were in the range of 97.2–102.6%.

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Introduction

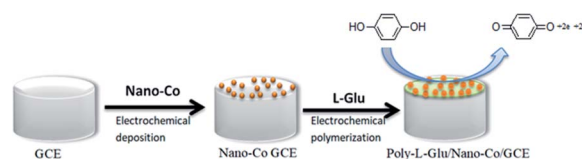
Hydroquinone (HQ, 1,4-dihydroxybenzene) is a phenolic compound naturally found in wood, tobacco smoke, coaltar, crude oil, and other materials.¹ It is widely used in dyes, cosmetics, anti-oxidants, and secondary coloring matter.² Due to its high toxicity and low degradation in the ecological environment, its presence in cosmetics, medicines, environment and human diet poses environmental pollution and toxic risks for the human health.^{3,4} The US Environmental Protection Agency (EPA) and the European Union (EU) have included hydroquinone in their lists of priority pollutants.⁵ According to the national standard of China (GB 8978-1996), the acceptable emission of phenolic compounds is 0.5 mg mL⁻¹ (0.00454 M).⁵

Up to now, numerous detection methods have been established to determine HQ, such as capillary electrophoresis,⁶ fluorescence,⁷ gas chromatography (GC),^{8,9} spectrophotometry,¹⁰ and high performance liquid chromatography (HPLC).^{11,12} These methods have the disadvantages of complicated processes, long time and high cost.⁵ The electrochemical method has attracted considerable attention since it has the merits of simple operation, fast response and low cost, which

offer the opportunity for portable, cheap and rapid methodologies.¹³

In recent years, electrochemical sensors with different modified electrodes have been successfully constructed, such as carbon-modified materials,^{5,14–16} organic matter-modified materials,^{17–20} metal-nanomaterials^{21–24} and other composite electrodes.^{25–34} However, the development of more reliable and sensitive electrochemical sensors for HQ is still one of the hot topics. Metal nanoparticles have the advantages of large specific surface area, high surface activity and high strength, which can improve the performance of electrochemical sensors.^{35,36} However, the adsorption of nano-Co on the GCE is unstable, and it needs to be combined with other materials to improve the stability. Amino acids have active sites and groups. The interactions between amino acids and metallic ions provide a better support for the performance of the sensor.

In this study, a simple and fast method for the determination of HQ at the nano-Co and L-glu-modified GCE is presented using electrodeposition and electrochemical polymerization sequentially (Scheme 1). The characteristics of the two modified



Scheme 1 Schematic representation of the preparation and application of the nano-Co/L-glu GCE.

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materials were combined to improve the conductivity and sensitivity of the electrode. The electrochemical behavior of HQ was investigated *via* cyclic voltammetry (CV), and the electrochemical conditions were optimized. A new electrochemical sensor was established for the determination of HQ with satisfactory results.

Experimental

Reagents and materials

HQ and L-glu were purchased from Kelong Chemical Reagent Factory in Chengdu. Cobalt nitrate was acquired from the second reagent factory in Shanghai. All the other chemicals were of analytical reagent grade and used without further purification.

Apparatus

Electrochemical experiments were performed on a CHI660E (Shanghai Chenhua Co., China) electrochemical workstation. The three-electrode system consisted of bare or modified GCE as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode in a saturated KCl solution. The surface characterization was observed *via* scanning electron microscopy (SEM) on a JSM-6460F, which was purchased from Japan Electron Optics Company.

Preparation of nano-Co/poly-L-glu/GCE

Before modification, the bare GCE was polished to be mirror-like with 0.03 μm alumina slurry, washed successively with anhydrous alcohol and deionized water in an ultra-sonic bath for 5 min. Then, it was potential cyclically scanned in the range from -0.1 V to $+0.5$ V in a 1×10^{-3} M $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution containing the 0.1 M KCl supporting electrolyte until a pair of well-defined redox peaks was observed.

First, the treated GCE was placed in a 3×10^{-2} mol L^{-1} cobalt nitrate solution, which was electrodeposited for 30 s at a constant potential of -0.9 V and dried at room temperature, which was denoted as nano-Co/GCE. Second, nano-Co/poly-L-

glu/GCE was synthesized from nano-Co/GCE in an L-glu solution (2×10^{-3} mol L^{-1}) by CV at a scanning rate of 100 mV s^{-1} in a potential range from -0.8 to -2.0 V. After 6 cycles of polymerization, the GCE was dried at room temperature. The obtained electrode was denoted as nano-Co/poly-L-glu/GCE.

Results and discussion

Characterization of the electrode

The SEM image of nano-Co/GCE (Fig. 1) displays the spherical size of the particles. Fig. 2 is the EDS of the modified nano-Co/GCE, which showed that nano-Co was modified on GCE.

Electrochemical behavior of HQ at different sensors

The electrochemical behavior of HQ on different modified electrodes was studied *via* CV, as shown in Fig. 3. It could be seen that the oxidation peak current at GCE (curve (a)) was the minimum, and the peak current of curve (d) significantly increased as compared to that of other electrodes, indicating that the modified material improved the catalytic effect. According to the Laviron formula $I_p = nFQv/4RT$, in which I_p is

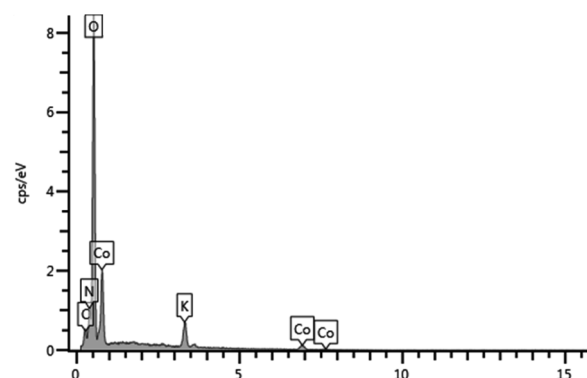


Fig. 2 The EDS images of the nano-Co electrode.

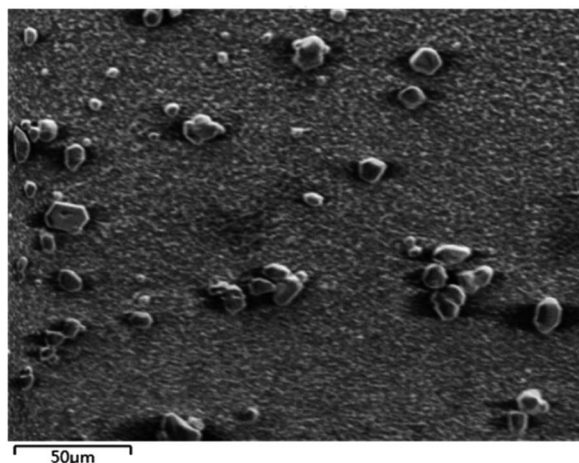


Fig. 1 The SEM images of the nano-Co electrode.

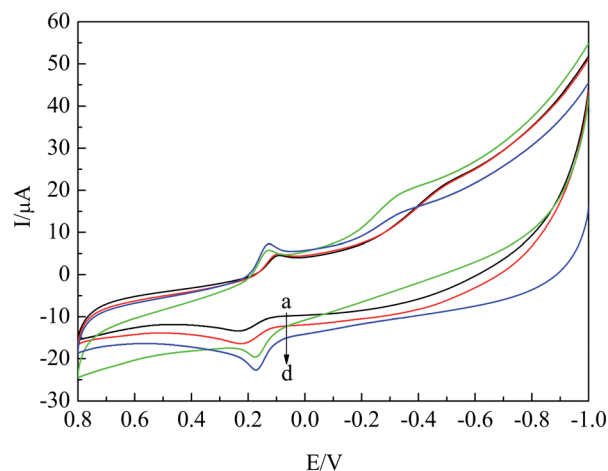


Fig. 3 CV curves of 2×10^{-4} mol L^{-1} HQ at GCE (a), poly-L-glu/GCE (b), nano-Co/GCE (c) and nano-Co/poly-L-glu/GCE (d) in 0.2 M PBS solution (pH = 7.0).

the peak current, n is the number of electrons transferred, F is the Faraday constant, Q is the electric quantity, ν is the scan rate, R is the gas constant, T is the temperature, and n was calculated to be 2.3, indicating that the number of electron transfer in the reaction of HQ on the modified electrode was about 2. Thus, the redox reaction of HQ on the nano-Co/poly-L-glu/GCE was a 2-electron reaction.

In addition, according to the Randles-Sevcik formula $I_p = 2.69 \times 10^5 n^{3/2} A c d^{1/2} \nu^{1/2}$, in which A is the electrode area, c is the concentration, D is the diffusion coefficient, ν is the scan rate, and the effective surface areas of nano-Co/poly-L-glu/GCE and the bare GCE were calculated to be 0.035 cm² and 0.025 cm² respectively, indicating that the effective surface area of the nano-Co/poly-L-glu/GCE was increased by 1.4 times. Based on the coaction of poly-L-glu and nano-Co, the effective area of the electrode increased and the catalytic capacity improved.

Optimization of the experimental parameters

Effect of the supporting electrolyte. Supporting electrolytes have direct effects on the chemical reactions of sensors and substances to be measured. The electrochemical behavior of HQ on the nano-Co/poly-L-glu/GCE in different supporting electrolytes was investigated using formic acid, sodium acetate and PBS solution as supporting electrolytes. The results are shown in Fig. 4, which states clearly that there are no peaks in the formic acid solution (curve (a)), but there are obvious redox peaks in the PBS solution (curve (c)), and the oxidation reaction is easier because of the more negative oxidation peak potential. Therefore, the PBS solution was chosen as the best supporting electrolyte in this experiment.

Effect of the solution pH. According to the reaction equation $C_6H_4(OH)_2 = C_6H_4O_2 + 2e^- + 2H^+$, we could find that hydrogen ions were produced in the reaction, therefore, HQ was greatly affected by the pH values of the solution. The effects of different pH PBS solutions (5.8, 6.0, 6.5, 7.0, 7.5, and 8.0) on the oxidation peak current and oxidation peak potential of HQ were studied

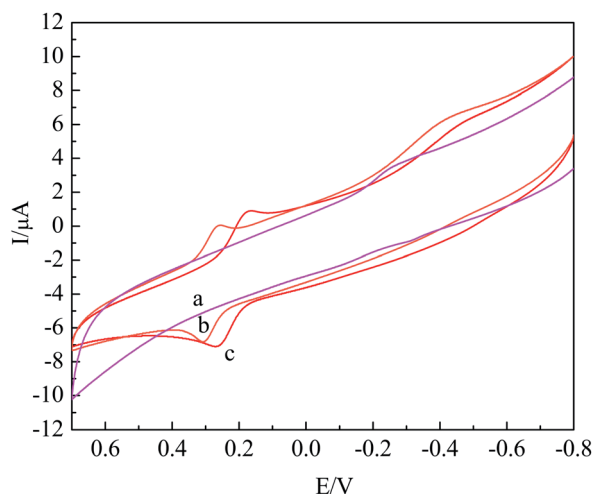


Fig. 4 CV curves of HQ on the nano-Co/poly-L-glu/GCE in formic acid (a), acetic acid-sodium acetate (b), PBS solution (c).

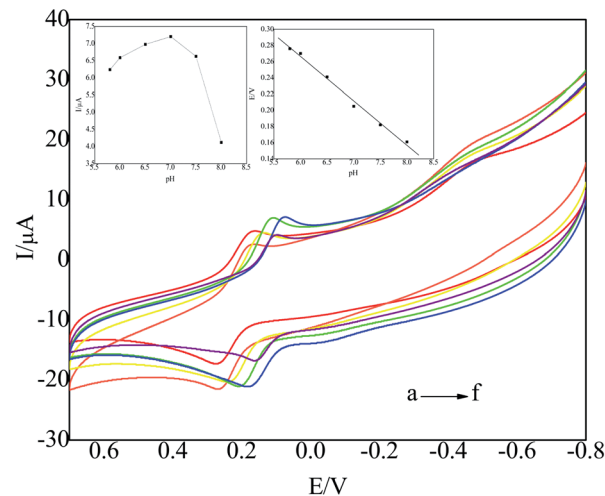


Fig. 5 CV curves of HQ on nano-Co/poly-L-glu/GCE at different pH values.

via CV. The CV curves are shown in Fig. 5. It can be seen that when the pH of the solution was 7.0, the current value of the oxidation peak reached the maximum (inset). Therefore, the optimum pH was 7.0. The main reason was maybe that there were a large number of active groups in amino acids, such as amino and carboxyl groups, and the electronegative oxygen and nitrogen atoms could form hydrogen bonds with the hydrogen atoms in hydroxyl groups in phenols, which accelerated the rate of the electron transfer. When the solution pH was high, the presence of large amounts of OH⁻ in the solution was more likely to form hydrogen bonds with hydrogen atoms in phenolic hydroxyl groups. However, when the solution pH was low, -NH₂ in the molecule of poly-L-glu acid was easily converted, which was not conducive to the formation of hydrogen bonds. In both cases, the nitrogen atoms in L-glu acid were difficult to participate in the formation of hydrogen bonds, which were not conducive to the reaction; therefore, the peak current decreased.

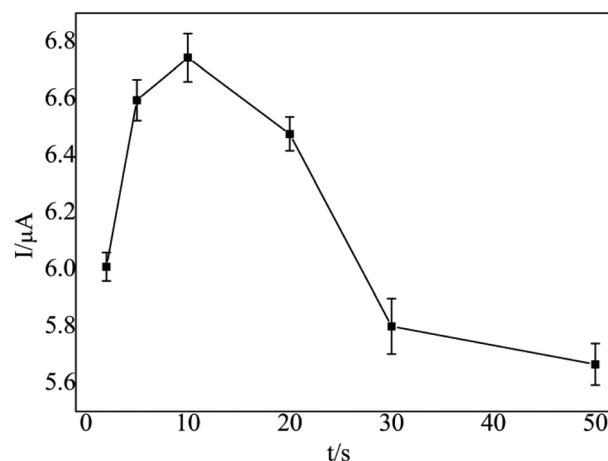


Fig. 6 The relationship between the oxidation peak current and accumulation time.



A good linear relationship between E_{pa} and pH was constructed with the linear regression equation as $E_{pa} = -0.0548\text{pH} + 0.5950$, and the correlation coefficient as 0.9905 (inset). The slope of the equation was -54.8 mV pH^{-1} , similar to -59 mV pH^{-1} , which indicated that the equal proton and equal electron reaction of HQ reacted on the sensor nano-Co/poly-L-glu/GCE.

Effect of the accumulation time. The relationship between the oxidation peak current and different accumulation time (2, 5, 10, 20, 30, and 50 s) was also investigated (Fig. 6). The results showed that the oxidation peak current of HQ increased with the increase in the accumulation time. However, when the accumulation time was longer than 10 s, the oxidation peak current of HQ decreased. This may be due to the saturation of the electrode surface. Therefore, the best accumulation time of this experiment was 10 s.

Effect of the scan rate. The scan rate dependence of CV for the nano-Co/poly-L-glu/GCE sensor is presented in Fig. 7.

It can be seen from Fig. 7 that the oxidation peak current of HQ increased with an increase in the scanning rate. The square root of the scanning rate had a good linear relationship with the oxidation peak current of HQ. The linear correlation coefficient was equal to 0.9922, and the linear regression equation was $I_{pa} (\mu\text{A}) = 0.5353v^{1/2} + 1.5919$ (inset), which showed that the redox reaction of HQ on the sensor was controlled by diffusion. However, in order to maintain the stability of the electrode, the reversibility of the redox reaction and to reduce the influence of the background current, 100 mV s^{-1} was chosen as the scanning rate of the experiment.

Effect of the polymerization cycles. The relationship between the oxidation peak current of HQ and the number of different polymerization cycles (1, 2, 4, 6, 9, and 12) was investigated (Fig. 8). With the increase in the number of polymerization cycles, the peak current of the oxidation of HQ first increased and then decreased. The reason was maybe that with an increase in the polymerization cycles, the thickness of L-glutamic acid on the electrode surface increased, which made the reaction point and oxidation peak current increase; however, with an increase in the film thickness, the electron transfer rate

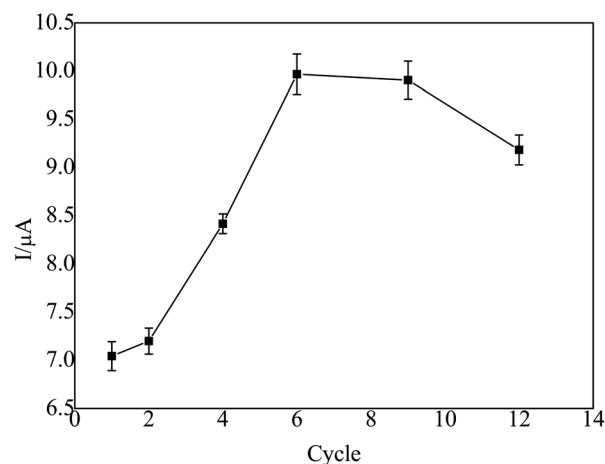


Fig. 8 Diagram of the relation between the oxidation peak current and the number of polymerization cycles.

was blocked and the transfer time was prolonged, which were not conducive to the reaction. In this experiment, when the number of polymerization cycles was 6, the oxidation peak current of HQ was the largest; therefore, the best choice for this experiment was 6 cycles of polymerization.

Calibration curve

Under the optimum experimental conditions, the CV method was used to determine HQ. The CV curve of the oxidation peak current of HQ with varied concentrations was obtained, as shown in Fig. 9.

The oxidation peak current of HQ had a good linear relationship with its concentration in the range from 3.85×10^{-6} to $1.30 \times 10^{-3} \text{ mol L}^{-1}$, which is shown in the inset of Fig. 9. The linear regression equation was $I (\mu\text{A}) = 3.5556c (10^{-4} \text{ mol L}^{-1}) - 0.1100$ ($R^2 = 0.9998$). The detection limit was as low as $4.97 \times 10^{-7} \text{ mol L}^{-1}$.

There were numerous reported methods for the detection of HQ using different modified electrodes as sensors, but as

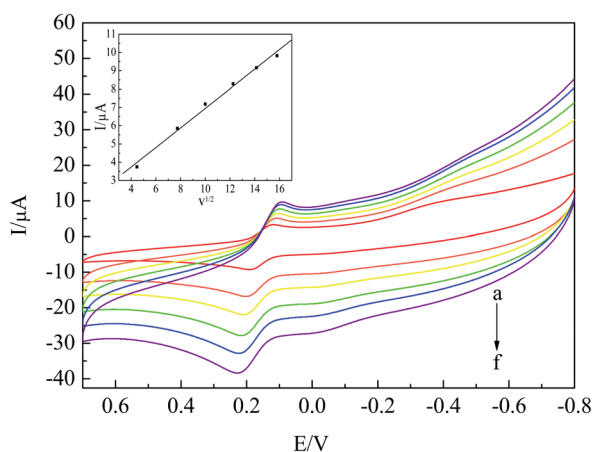


Fig. 7 CV curves of HQ on nano-Co/poly-L-glu/GCE at different scanning rates from (a) to (f) as 20, 60, 100, 150, 200 and 250 mV s^{-1} .

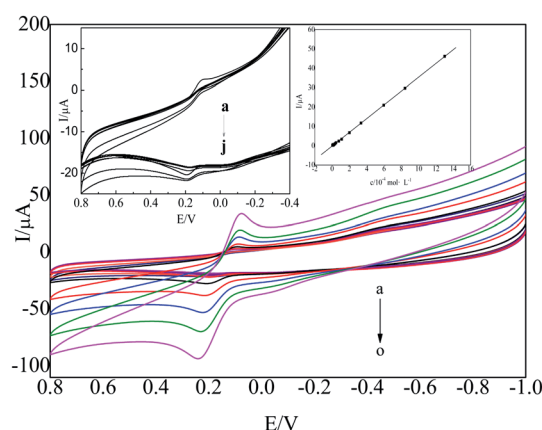


Fig. 9 CV curves of HQ with different concentrations at the nano-Co/poly-L-glu-modified electrode.

Table 1 Comparative results for the detection of HQ with different modified electrodes as the sensors

Electrode	Linear range/mol L ⁻¹	Detection limit/mol L ⁻¹	Method	literature
Meso-Co ₃ O ₄ -modified electrode	1.0×10^{-6} to 5.0×10^{-4}	1×10^{-7}	Differential pulse voltammetry (DPV)	23
Graphene–chitosan-modified electrode	1.0×10^{-6} to 3.0×10^{-4}	7.5×10^{-7}	Differential pulse voltammetry (DPV)	34
p-Phenylalanine-modified electrode	1.0×10^{-7} to 1.4×10^{-4}	1.0×10^{-6}	Differential pulse voltammetry (DPV)	37
Poly glutamic acid-modified electrode	5×10^{-6} to 8×10^{-5}	1×10^{-6}	Differential pulse voltammetry (DPV)	38
Co ₃ O ₄ /MWCN-modified electrode	1.0×10^{-6} to 8.0×10^{-4}	5.6×10^{-6}	Differential pulse voltammetry (DPV)	39
GR–P4VP-modified electrode	1.0×10^{-7} to 1.0×10^{-5}	8.1×10^{-9}	Differential pulse voltammetry (DPV)	40
Poly L-glutamic acid/nano-cobalt-modified electrode	3.85×10^{-6} to 1.30×10^{-3}	4.97×10^{-7}	Cyclic voltammetry (CV)	This method

Table 2 Results for the detection of HQ using the same modified electrode as the sensor

Number	Sample content/mol L ⁻¹	Scalar addition/mol L ⁻¹	Measurements/mol L ⁻¹	Recovery rate of standard addition/%
1	1.80×10^{-4}	2.88×10^{-5}	2.09×10^{-4}	100.7
2	1.80×10^{-4}	5.75×10^{-5}	2.39×10^{-4}	102.6
3	1.80×10^{-4}	1.42×10^{-4}	3.18×10^{-4}	97.2

compared to the results of other sensors (Table 1), the linear range of nano-Co/poly-L-glu was wider or the detection limit of nano-Co/poly-L-glu was lower.

Analytical performance

When the nano-Co/poly-L-glu/GCE sensor was continuously scanned for 8 times in the 2×10^{-4} mol L⁻¹ HQ solution, the relative standard deviation (RSD) was 1.9%, and the oxidation peak potential did not shift during continuous scanning, indicating that the electrochemical sensor had a good stability. The relative standard deviation (RSD) in the intra-day analysis was 2.3% and that in the inter-day analysis was 3.5%, indicating that the poly-L-glu/nano-Co/GCE electrode presented high reproducibility. To investigate the selectivity of this experiment under the optimized conditions, ascorbic acid (2×10^{-4} mol L⁻¹), resorcinol (2×10^{-4} mol L⁻¹), catechol (2×10^{-4} mol L⁻¹) and L-phenylalanine (2×10^{-4} mol L⁻¹) were added into the HQ solution, respectively, and the results showed that there was no interference in the determination of HQ, which indicated that the sensor prepared by nano-Co/poly-L-glu had good selectivity.

Analytical application

In order to evaluate the validity of the proposed method, the nano-Co/poly-L-glu/GCE was applied for standard addition recovery experiments for simulated water samples, as shown in Table 2. The recoveries calculated from Table 2 ranged from 97.2% to 102.6%, which showed that the electrochemical sensor based on nano-Co/poly-L-glu had a good application prospect for HQ detection.

Conclusion

Nano-Co/poly-L-glu modified GCE was prepared by the electro-deposition and electrochemical polymerization of nano-Co and poly-L-glu. It provided a new idea for the preparation of novel electrochemical sensors for HQ. The electrochemical sensor based on the modified electrode could not only effectively reduce the potential difference of HQ, but could also significantly increase the response current. The sensor has the advantages of simple fabrication, low cost, good reproducibility and selectivity. Therefore, the nano-Co/poly-L-glu electrochemical sensor has a good application prospect in the detection of HQ.

Conflicts of interest

There are no conflicts to declare.

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