

Based on Gold Nanoparticles-L-Tyr-Amino Functionalized Mesoporous Materials-Polyphenol Oxidase Modified Biosensor for the Detection of Resorcinol

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Nowadays, resorcinol (RC) has been widely applied in the chemical and pharmaceutical industries. However, the electrochemical detection technique of RC still features some significant drawbacks, for instance, a low sensitivity. Hence, in the present work, a glass carbon electrode was developed for the electrochemical detection of RC with good specificity and stability, through modifying the glass carbon electrode (GCE) by polyphenol oxidase (PPO), an NH₂-SBA-15 mesoporous material (NH₂-SBA-15), L-tyrosine (L-Tyr) and gold nano-particles (AuNPs). After being successively modified by AuNPs, L-Tyr, NH₂-SBA-15 and PPO, the constructed PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE was used to discriminate RC from ions and other common micromolecules, which showed a fairly good specificity and stability. The proposed electrochemical detection method features a linear range of from 0.5 to 21.0 μM with a LOD down to 0.15 μM, revealing a better sensitivity than the existing methods. It is worth mentioning that the proposed PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE has been successfully used as an electrochemical probe for the RC assay in domestic sewage.

Keywords Mesoporous material, resorcinol, nanomaterial, electrode

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Introduction

Resorcinol (RC), as one kind of traditional phenols, has a wide range of applications in chemical and pharmaceutical industries. It is an important raw material of many chemical products, such as dyes, rubbers, plásticos, cosmetics and pesticides.^{1,2} However, it has also been found that RC can induce many diseases, including headaches, kidney failure and tachycardia. In addition, since RC is difficult to degrade in the ecological environment, it has been recognized to be as a major pollutant in the detection of water environments by the Environmental Protection Agency (EPA) and the European Union (EU). Until now, various analytical approaches, including fluorescence,³ colorimetry,⁴ chemiluminescence,⁵ and high-performance liquid chromatography,⁶ have been developed for the detecting RC. Among these methods, the electrochemical approaches⁷ are reliable assay methods for accurately and quantitatively monitoring RC because of their low-cost and simple operation. However, the electrochemical approaches still feature some drawbacks, of which the most significant one is that the electrochemical response of RC is very weak to be detected. As a result, the research on electrochemical modifiers for improving the sensitivity of RS detection has attracted much attention.

Due to good biocompatibility, the high specific surface area, and the excellent electron-transfer capacity, the gold nanoparticles (AuNPs) serve as attractive nanometer materials

and electronic wire.^{8,9} Additionally, the high stability allows the AuNPs to be used as carriers for connecting with interesting mesoporous materials, which is especially important for immobilization of macromolecular proteins. Therefore, the AuNPs are widely used in the field of biosensors. For instance, AuNPs had been used as DNA sensors for biomarkers,¹⁰ and as functionalized sensors for small molecule substances.^{11,12}

Currently, mesoporous materials have been intensely pursued in chemical biology research because of their inherent characteristics, such as the desirable pore sizes (2 – 50 nm), which are similar to the size of a number of drugs, protease, and DNA.^{13,14} Moreover, mesoporous materials can provide a highly multifunctional platform for the adsorption, separation, and detection of biomacromolecules.^{15,16} Recently, increasing attention has been paid to the modification of mesoporous materials, which are assembled and loaded layer by layer to form new functional materials. SBA-15 is a typical kind of ordered mesoporous silica material, which has uniform hexagonal pores with pore sizes ranging from 5 to 15 nm and a high internal surface area of 400 – 900 m²/g.^{17,18} The mesoporous carbon material of FDU-15 has been applied to enhance the conductivity of the electrode to determine rutin,¹⁹ but the synthesis process of FDU-15 is still too complex. In order to develop a simpler and greener synthesis method, the SBA-15 was used in this experiment. More importantly, SBA-15 has a very good adsorption capacity to the PPO because the surface of silica is easy to be functionalized, which can tightly adsorb more enzyme molecules to the target substances.

In the present work, by combining the advantages of AuNPs and mesoporous materials, an efficient sensor was designed for

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the detection of RC in practical samples. In our strategy, the NH₂-SBA-15 mesoporous material with a strong adsorption capacity was prepared by using tetraethyl orthosilicate (TEOS) and (3-aminopropyl)-trimethoxysilane (APTMS). Polyphenol oxidase (PPO) was immobilized on the surface of NH₂-SBA-15 using the crosslinking agent glutaraldehyde (GA). The results reveal that: 1) AuNPs can promote electrical activity and improve the performance of the catalytic reaction; 2) NH₂-SBA-15 improves the electrochemical surface area and tightly adsorbs more enzyme molecules; 3) both AuNPs and NH₂-SBA-15 can increase the sensitivity of the fabricated electrode, which is beneficial for the sensitive determination of RC.

Experimental

Reagents and chemicals

Tetraethyl orthosilicate (TEOS, 98%), HAuCl₄·3H₂O (99.9%), 3-aminopropyl trimethoxysilane (APTMS), glutaraldehyde (GA), chlorhydric acid (HCl, 37%) and pluronic P123 (*M_w* = 5800, EO₂₀PO₇₀EO₂₀) were purchased from Sigma-Aldrich Co. Ltd. Other chemicals were purchased from Shanghai Chemical Reagent Co. Ltd. It should be noted that a phosphate buffer solution (PBS, 0.1 M) was used as the supporting electrolyte. All other chemicals and reagents were of A.R. grade and used without further purification. Prior to experiments, the solutions were purged with purified nitrogen for at least 15 min to remove oxygen. Milli-Q 18.2 MΩ water was used throughout the experiments.

Synthesis of NH₂-SBA-15 and the grafting of PPO

Ordered mesoporous silica materials of SBA-15 were synthesized according to a previously reported method.¹⁸ Under the acidic condition, the pluronic P123 triblock copolymer was used as structure-directing agent, and TEOS was used as silicon source. The reaction was intensely stirred at 40°C in a mixture with a composition of 4 g P123:130 g H₂O:20 mL 37% HCl: 8.5 g TEOS in a sealed system for one day, which was followed by crystallization for another day at 110°C. After filtration, washing and drying, the sample was calcined in a muffle furnace at 500°C for 6 h. At last, white SBA-15 was obtained.

Then, 2 g of SBA-15 was added in a 50-mL ethanol solution with 2 g APTMS. The mixture solution was evenly stirred for 24 h under a refluxing condition at 75°C. The as-prepared NH₂-SBA-15 mesoporous material was collected through filtering, washing and drying, successively.

About 200 mg of NH₂-SBA-15 was added into 2 mL of glutaraldehyde (GA) under stirring for 2 h. After centrifugation, the unreacted GA was removed by washing with PBS. The NH₂-SBA-15 modified by GA was added into 1 mL of a PPO (10 mg/mL) solution while reacting for 4 h. At last, PPO-NH₂-SBA-15 was obtained after centrifugation and rinsing by PBS.

Fabrication of PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE

The GCE (3 mm in diameter) was carefully polished with 1.0-, 0.3- and 0.05-μm alumina powder successively, which was followed by rinsing with ultrapure water. The polished electrode was sonicated in anhydrous ethanol, HNO₃-H₂O (v/v = 1:1), and ultrapure water for 2–3 min, respectively. Then, the cleaned GCE was pretreated by scanning from –0.35 to 1.70 V in 0.5 M H₂SO₄ at scan rate of 100 mV/s until stable singles were obtained. Finally, the electrode was rinsed with ultrapure water, and the surface of the electrode was dried with nitrogen.

The fabrication of PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE was performed as follows:

First, AuNPs were immobilized on the electrode surface by cyclic voltammetry in 0.2% HAuCl₄ of between 0 and 1.6 V at a scan rate of 50 mV/s. The electrode was then rinsed by ultrapure water and dried at room temperature. It was denoted as AuNPs/GCE.

Second, the electropolymerization of L-tyrosine was carried out on the electrode surface by cyclic voltammetry in a saturated L-tyrosine (L-Tyr) solution containing 0.1 M PBS (pH 6.0) between –0.5 and 2.0 V at a scan rate of 100 mV/s. Then, the electrode was rinsed with ultrapure water, and dried at room temperature. This was the fabrication of L-Tyr/AuNPs/GCE.

Finally, 6 mg of PPO-NH₂-SBA-15 was dissolved in 3 mL of 0.1 M PBS (pH 2.0). The mixture was then sonicated for 5 min. Further, 4.0 μL of a 2 mg/mL PPO-NH₂-SBA-15 solution was dropped onto the surface of the as-made L-Tyr/AuNPs/GCE to obtain PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE, which was dried in air for later use.

Anson's equation

$$Q(t) = \frac{2nFAcD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}$$

The surface area of the electrode can be calculated by the above Anson's equation,²⁰ where *A* is the electrochemical effective surface area of the working electrode, *c* is the substrate concentration of potassium ferricyanide (K₃[Fe(CN)₆], *D* is the diffusion coefficient (*D* is 7.6 × 10^{–6} cm²/s in K₃[Fe(CN)₆] solution), *Q_{dl}* is the charge for electric double layer (which can be eliminated by background), and *Q_{ads}* is the Faraday charge, other relevant letters have their usual significance.

Apparatus

The electrochemical experiments were carried out on a CHI 760B electrochemical workstation (Chenhua Instrument Company, Shanghai, China) with a conventional three-electrode. The working electrode, the reference electrode, and the counter electrode were the modified glass carbon electrode, the saturated calomel electrode, and the Pt wire electrode, respectively. Both cyclic voltammetry and chronoamperometry were performed in the PBS buffer solution. A small beaker with a volume of 10 mL was selected for electrochemical determination. All experiments were performed under room temperature (25°C) except for the additional instructions. The structures of NH₂-SBA-15 were characterized by field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan), transmission electron microscope (TEM, JEOL-2100, Japan) and using X-ray diffractometer (XRD, SA-HF3, Rigaku Corp. Japan).

Results and Discussion

Characterization of NH₂-SBA-15

The obtained NH₂-SBA-15 was characterized by field emission scanning electron microscopy (FESEM), the low-angle powder X-ray diffraction patterns (XRD), and the Fourier infrared absorption spectra (FTIR), respectively. As shown in Fig. 1A, NH₂-SBA-15 displayed the typical clavate twist structure. The SBA-15 and NH₂-SBA-15 showed well-resolved XRD peaks between 2θ = 0.5–6°, which are the (100) (110) and (200) planes of P6mm hexagonal symmetry (Fig. 1B). These diffraction peaks are characteristic peaks of SBA-15 with a hexagonal hole structure.²¹ According to nitrogen adsorption and the desorption curve (Fig. 1C), the specific surface area of the functionalized mesoporous material is 519 m²/g with a pore

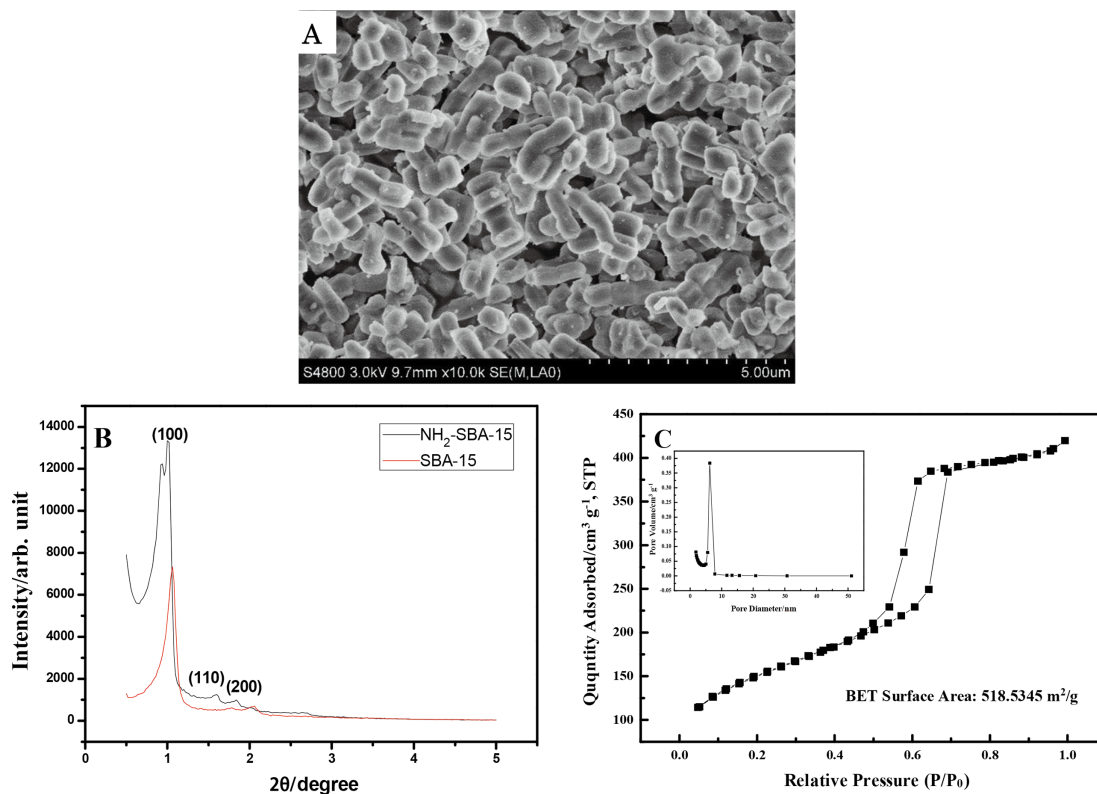


Fig. 1 FESEM (A), low-angle powder X-ray diffraction patterns (B), nitrogen adsorption-desorption isotherms (C) of NH₂-SBA-15.

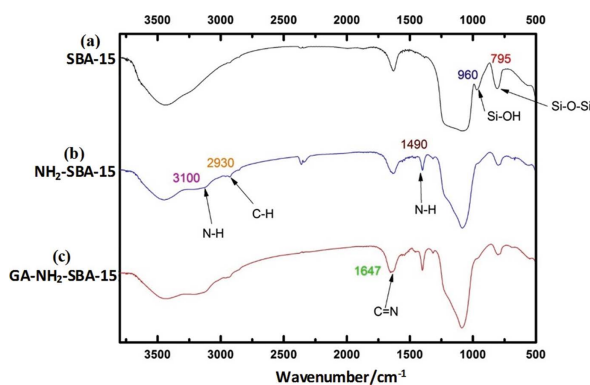


Fig. 2 Fourier infrared absorption spectra of NH₂-SBA-15.

diameter of about 7 nm (inset of Fig. 1C). These results indicate that SBA-15 still maintains a good void structure after being modified by amino group.

The FTIR spectra of SBA-15, NH₂-SBA-15, and glutaraldehyde (GA) modified mesoporous materials (GA-NH₂-SBA-15) are shown in Fig. 2. It was found that the characteristic peaks of the broad absorption peak and the bending vibration of the Si-OH group are clearly visible at 3000–3500 and 964 cm⁻¹, respectively (curve a). The peaks at 1080 and 796 cm⁻¹ indicate the asymmetric and symmetric Si-O-Si stretching vibration. All of these phenomena showed the successful fabrication of SBA-15. The absorption peaks at 1490 and 3100 cm⁻¹ indicate the existence of the N-H group (curve b), which indicated that the amino group was successfully modified on the SBA. From

curve c, the C=N absorption peak at 1647 cm⁻¹ is attributed to the reaction between the amino group of PPO and the carbonyl group of GA, which means the successful grafting of PPO.

Electrochemical behavior of PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE

The electrode was prepared by the following process *via* layer-by-layer assembly, where the bare GCE was successively functionalized to obtain AuNPs/GCE, L-Tyr/AuNPs/GCE, NH₂-SBA-15/L-Tyr/AuNPs/GCE, and PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE, respectively. Their impedance measurements were performed by electrochemical impedance spectroscopy (EIS) in 1.0 mM [Fe(CN)₆]^{4-/3-} containing a 0.1 M KCl solution. The electron-transfer resistance of Ret can be seen from the semicircle domains of the impedance spectra. As shown in Fig. 3A, the GCE is naked with a small Ret (curve a). When the AuNPs was deposited on the surface of the electrode, it caused a small semicircle in the 200 low-frequency region (curve b), which demonstrates that the AuNPs has the ability of promoting the electron transfer rate. The impedance in the high-frequency region increased after a modification of L-Tyr (curve c), which revealed that the L-Tyr could hinder the electron transfer on the electrode surface. The ordered mesoporous of NH₂-SBA-15 can increase the surface area of the electrode. In other words, they no longer hinder to the movement of small molecule of [Fe(CN)₆]^{3-/4-} between the electrode interface and the solution. Therefore, the impedance value of NH₂-SBA-15/L-Tyr/AuNPs/GCE was reduced (curve d) when NH₂-SBA-15 was modified on the electrode, and it was smaller than that of the GCE (curve a) and AuNPs/GCE (curve b). However, the biological macromolecular protein of PPO with the property of poor conductivity could induce the resistance of charge transfer (curve e). Hence, it could be found that the impedance value

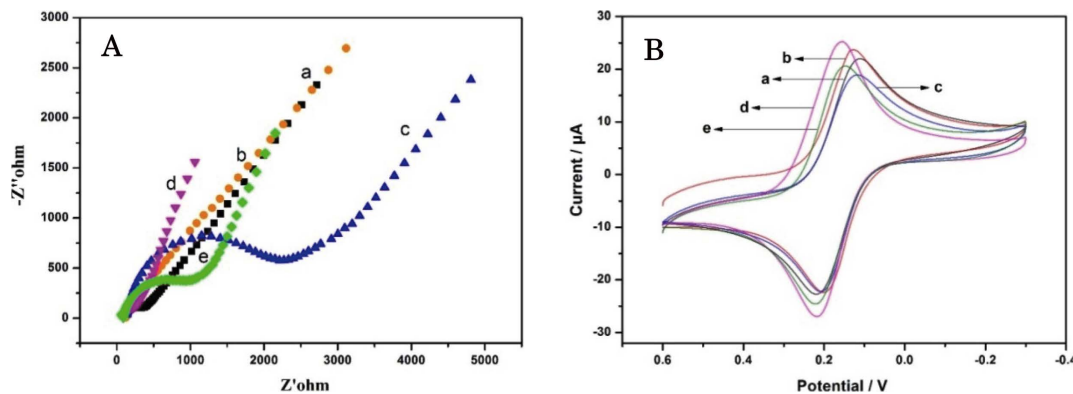


Fig. 3 (A) EIS and (B) CV curves of (a) bare GCE, (b) AuNPs/GCE, (c) L-Tyr/AuNPs/GCE, (d) $\text{NH}_2\text{-SBA-15/L-Tyr/AuNPs/GCE}$ and (e) $\text{PPO/NH}_2\text{-SBA-15/L-Tyr/AuNPs/GCE}$ in PBS buffer solution containing 1.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 0.1 M KCl.

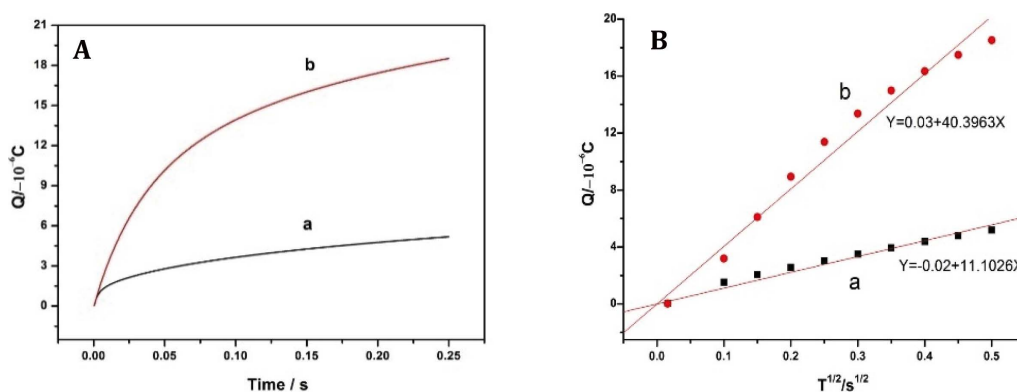


Fig. 4 (A) Plot of $Q-t$ curves for the (a) GCE and the (b) $\text{PPO/NH}_2\text{-SBA-15/Tyr/AuNPs/GCE}$ in 0.1mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution containing 0.1 mM KCl. Curve a stands for that in the blank solution. (B) Linear relationship of $Q-t^{1/2}$ on the (a) GCE and the (b) $\text{PPO/NH}_2\text{-SBA-15/Tyr/AuNPs/GCE}$.

increased when the PPO was modified on the electrode. In addition, the cyclic voltammograms (CV) were used to prove the successful preparation of electrodes once again (Fig. 3B). Obviously, the results of CV of the different modified electrodes remain highly consistent with R_{et} . When the value of R_{et} increases, the peak value of the corresponding CV curve goes down. Therefore, all of these results confirmed the successful construction of $\text{PPO/NH}_2\text{-SBA-15/L-Tyr/AuNPs/GCE}$ via the layer-by-layer assembly process.

To examine the effective electrochemical surface area of the bare GCE and $\text{PPO/NH}_2\text{-SBA-15/L-Tyr/AuNPs/GCE}$, the chronocoulometry was utilized according to Anson's equation.²⁰ Figure 4 depicts the effective surface area of the naked GCE, which was calculated to be 0.00105 cm^2 , while that of $\text{PPO/NH}_2\text{-SBA-15/Tyr/AuNPs/GCE}$ to be 0.00422 cm^2 . This result indicates that the surface area of the electrode was significantly increased after the modification of $\text{PPO/NH}_2\text{-SBA-15/Tyr/AuNPs}$, which led to a faster electron transport and electrochemical response to RC.

Determination of RC by different modified electrode

The electrochemical response of the electrode to the RC solution (0.1 mM) was investigated. As shown in Fig. 5, after incubation with RC, the bare GCE (curve a) displays an unobvious redox peak within the range of the electric potential

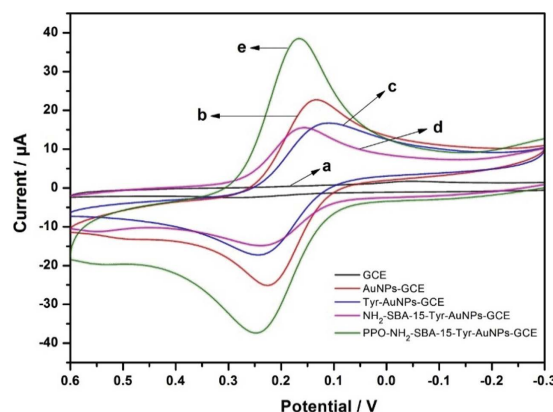


Fig. 5 CV curves of (a) bare GCE, (b) AuNPs/GCE, (c) L-Tyr/AuNPs/GCE, (d) $\text{NH}_2\text{-SBA-15/L-Tyr/AuNPs/GCE}$ and (e) $\text{PPO/NH}_2\text{-SBA-15/L-Tyr/AuNPs/GCE}$ in PBS (0.1 M, pH 6.0) containing 0.1 mM RC. Scan rate, 100 mV/s.

from -0.3 to 0.6 V , which means that the redox reaction was very weak on the surface of the electrode. However, the AuNPs/GCE (curve b) exhibits an enhanced peak current at an oxidation

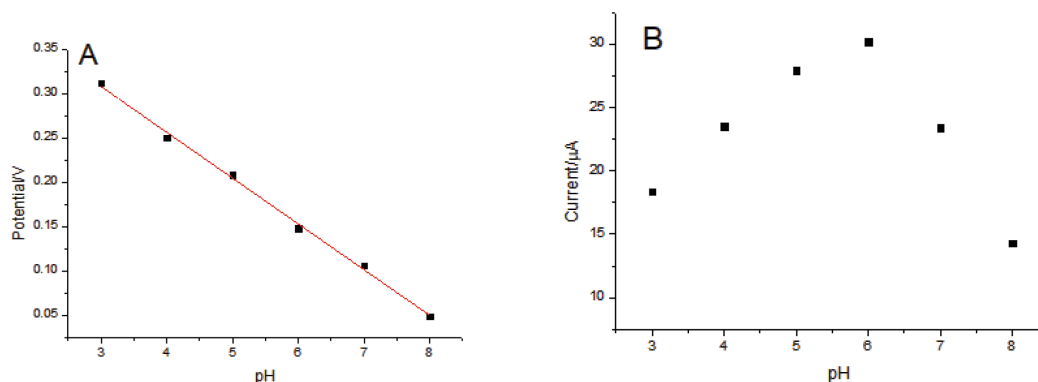


Fig. 6 (A) Cathode peak potential (E_{pc}) and (B) reduction peak current (I_{pc}) of PPO/ NH_2 -SBA-15/L-Tyr/AuNPs/GCE in 0.1 M PBS containing 0.1 mM RC at pH value of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0. Scan rate, 100 mV/s.

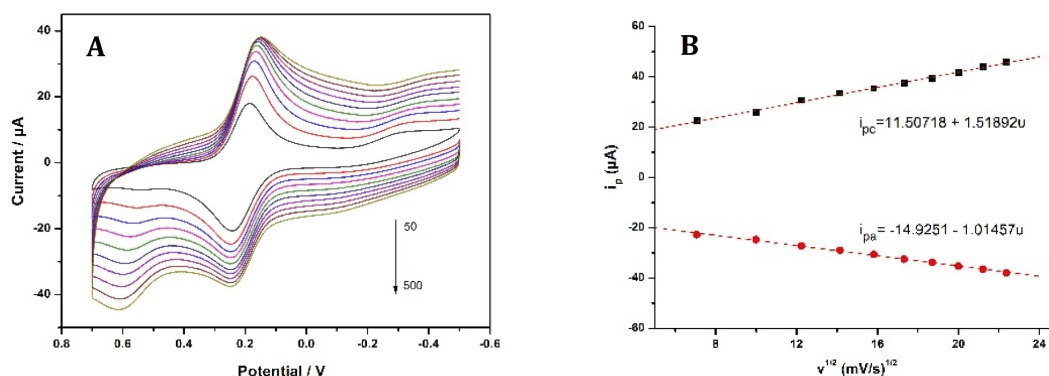


Fig. 7 (A) CV curves of 0.1 mM RC in 0.1 M PBS solution (0.1 M, pH 6.0) containing 0.1 M KCl at different scan rates: 50, 100, 150, 200, 250, 300, 350, 400, 450, 500 mV/s. (B) Calibration curve of the current vs. scan rates.

peak potential of 0.24 V in a PBS buffer solution (0.1 M, pH 6.0), which indicates a good electrochemical response of AuNPs to RC. After further modification of the layer of L-Tyr (curve c) and NH_2 -SBA-15 (curve d), both of the redox peak currents are decreased. Interestingly, after modifying of the layer of PPO (curve e), there was an obviously enhanced redox peak current of the PPO/ NH_2 -SBA-15/L-Tyr/AuNPs/GCE, which indicated that the layer-by-layer assembly could efficiently enhance the electrochemical response to RC. The results demonstrate that it is feasible to utilize PPO/ NH_2 -SBA-15/L-Tyr/AuNPs/GCE to detect RC.

Optimization of determination conditions

To obtain the optimum detection conditions, different experimental conditions, including the pH and scan rates, were investigated upon incubation with RC.

As shown in Fig. 6A, the peak current is positively correlated with an increasing pH value from 2.0 to 8.0. The peak potential shifts to a negative direction with the increase of the pH. The cathode peak potential (E_{pc}) is proportional to the linear regression equation for RC of $E_{pc}(V) = 0.463 - 0.0516 \text{ pH}$ ($R^2 = 0.9969$). The slope, 51.6 mV, is close to the theoretical value of 59 mV,^{22,23} which indicates that the ratio of the protons and electrons in the reaction is 1:1. The reduction peak current (I_{pc}) of RC reaches the maximum at a pH value of 6 in the range of 3–8. Therefore, the pH value of 6 is selected because of the

sensitivity of the determination.

Furthermore, the oxidation peak current increases linearly with an increasing root-square value with the scan rate increasing from 50 to 500 mV/s. This result indicates that the electrochemical reaction of RC on the electrode is a surface diffusion-controlled process, as shown in Fig. 7.

Sensitivity, stability and selectivity of the fabricated electrode To validate the sensitivity of the proposed assay, the chronoamperometric curves of PPO/ NH_2 -SBA-15/L-Tyr/AuNPs/GCE are depicted in Fig. 8 at a working potential of 0.24 V. The results reveal that the oxidation current gradually increased with an increased concentration of RC. Further, Fig. 8B shows a linear relationship between the current and the RC levels. The current features a good linearity with the concentration of RC varying from 0.5 to 21.0 μM , and with an R^2 value of 0.9993. The total response time was 5 s with a relative standard deviation of 2.7%. The limit of detection (LOD) at a signal-to-noise ratio of 3 for RC was 0.15 μM . A comparison between the proposed method and other electrochemical methods for the determination of RC is shown in Table 1. From Table 1, it can be seen that the proposed PPO/ NH_2 -SBA-15/L-Tyr/AuNPs/GCE has a comparatively lower detection limit and a widely linear range.

When the electrode was stored in a refrigerator at 4°C for about two weeks, the peak currents remained as 92.6%, suggesting a good stability of the constructed electrode. These results indicate that the developed electrode can be employed as

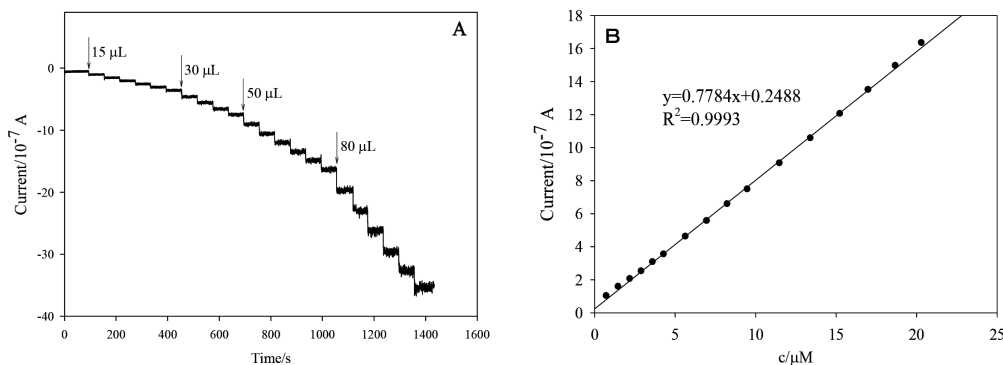


Fig. 8 (A) Amperometric response of PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE to RC at different concentrations in PBS buffer solution (0.1 M, pH 6.0) at working potential of 0.24 V. (B) Relationship between the current and RC levels.

Table 1 Comparison of the electrochemical method for the determination of RC

Electrode	Linear range/ μM	LOD/ μM	Reference
CoPC/PGE	1 – 100	0.72	24
Au-PdNF/rGo/GCE	2 – 100	0.7	25
NMC-G/GCE	3 – 200	1.0	26
SWCNT/GCE	0.4 – 10	0.3	27
MCNTs/GCE	5 – 80	1.0	28
PPO/NH ₂ -SBA-15/L-Tyr/AuNPs/GCE	0.5 – 21	0.15	This work

Table 2 Determination of RC in domestic sewage

Sample	Originally found by this method/ μM	Added/ μM	Found/ μM	Recovery, %	RSD, % (n = 6)
1#	1.0	1.5	2.47	98.8	0.6
2#	1.5	1.5	2.96	98.7	1.3
3#	1.5	1.5	3.03	101.3	0.5
4#	1.5	2.0	3.53	100.9	1.1
5#	2.0	2.0	4.08	102.0	2.0
6#	2.0	2.5	4.48	99.6	0.8

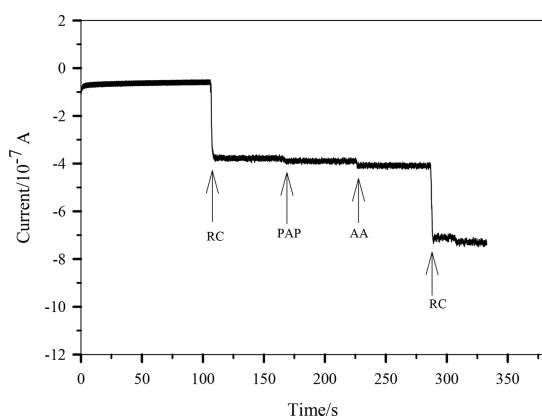


Fig. 9 Interference of different species (*p*-aminophenol, ascorbic acid) to the *I*-*t* curves for the determination of RC.

a potential candidate for the determination of RC.

To employ the modified electrode for the determination of RC in real samples, the effect of common interfering species including inorganic ions (data not shown) and micromolecules were investigated, as shown in Fig. 9. It was found that some common substances including glucose, hydroquinol, catechol, *p*-aminophenol (PAP), 1-nitroso-2-naphthol, phenol, *o*-aminophenol, 2,4-dichlorophenol and ascorbic acid (AA), even at 100 fold concentration, exhibited a negligible change in the response currents when they coexisted with RC. The good selectivity of PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE demonstrates the feasibility for discriminating RC from others in real samples.

Determination of RC in real samples

The proposed electrode was implemented for the determination of RC in domestic sewage. The RC with a known amount was added into the domestic sewage samples, and the results were obtained by the standard addition method. As shown in Table 2, the average recovery of RC varies from 98.7 to 102.0% with the standard deviation of less than 2.0%. The results declare the applicability of the prepared PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE for the determination of RC in domestic sewage.

Conclusions

In summary, an electrode of PPO/NH₂-SBA-15/L-Tyr/AuNPs/GCE for the electrochemical detection of RC was prepared. After successively modifying of AuNPs, L-Tyr, NH₂-SBA-15 and PPO on GCE, this constructed electrode was applied to the determination of RC with good sensitivity. The electrochemical method for the determination of RC had a linear range from 0.5 to 21.0 μM with the LOD down to 0.15 μM . Finally, the constructed electrode was employed in the RC assay of domestic sewage, and a satisfying results were achieved.

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