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Molecularly imprinted electrochemical sensor based on an electrode modified with imprinted pyrrole film immobilized on β-cyclodextrin/gold nanoparticles/graphene layer

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A novel molecularly imprinted electrochemical sensor was constructed for the sensitive detection of quercetin (Qu) based on glassy carbon electrode (GCE) modified with β-cyclodextrin (β-CD), gold nanoparticles(AuNPs) and graphene (GR). The molecularly imprinted polymers (MIPs), which were applied as the molecular recognition element, were prepared by electropolymerization using Qu as template and pyrrole as monomer. The fabrication conditions that affect the performance of the sensor, such as PH, pyrrole concentration, scan rate and scan cycles, were investigated. The sensor was characterized by cyclic voltammetry (CV), differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM). Under the optimized conditions, the sensor offered an excellent response for Qu, the linear response range was 1.0×10^{-9} to 1.0×10^{-6} mol/L (R=0.9998) with a detection limit of 1.0×10^{-10} mol/L. Moreover, the proposed sensor possessed good selectivity and stability, providing a promising tool for practical applications.

Introduction

Molecular imprinting technology (MIT) offers noticeable potential for biomolecular-based recognition due to its high recognition capacity to the template molecule, good chemical and thermal stability, reusability, and cost-effective fabrication. In the field of electrochemical sensor, molecularly imprinted polymers (MIPs) can not only accumulate template molecules on the electrode surface to enhance the sensitivity of sensors but also separate template molecules from the other analytes to improve the selectivity.[1-3] Up to now, molecularly imprinted electrochemical sensors (MIECSs) have been successfully used to detect many kinds of molecules.[4-6] For constructing imprinted electrochemical sensor, it is important to construct an efficient electrode surface for targets imprinting and electronic signal transfer. A variety of nanomaterials and nanocomposites were used to modify electrode to promote the effective surface area and the electron transfer rate of the electrode, leading to the improvement of the sensitivity and selectivity of MIECSs. [5, 7, 8]

Among the nanomaterials, Graphene (GR), a two-dimensional sheet of sp^2 conjugated atomic carbon, has enjoyed widespread attention owing to its ultra high specific surface area, unique electronic features, great mechanical strength, and good biocompatibility.[9-11] It is an ideal candidate to improve the effective surface area and the electron transfer rate of the electrode. Various graphene-based composites have been reported for the preparation of MIECSs. Gold nano-material possesses accurate quantum scale dimensions, wonderful conductivity and biocompatibility, which make it a good catalytic material for sensor.[10, 12, 13] Moreover, many researchers constructed multi-component MIECSs using multiple nanomaterials to improve the performance of sensor. For example, Lian et al. prepared electrochemical sensor based on gold nanoparticles fabricated molecularly imprinted polymer film at chitosan-platinum nanoparticles/graphene-gold nanoparticles double nanocomposites modified electrode for detection of erythromycin with good sensitivity.[14] Similar results can also be found in several other studies, including of the MIECSs based on a three-dimensional molecularly imprinted film for the determination of cefotaxime,[8] MIECSs based on ionic liquid-functionalized graphene for the detection of bovine hemoglobin,[15] sensor based on molecularly imprinted gold nanoelectrode ensembles for the detection of ovarian cancer marker.[16] The synergistic effects of these modified materials can promote the electrochemical response and the sensitivity of the sensor. Although the electrode modified material has been developed greatly, it still includes a range of shortcomings such as complicated preparation process, low binding capacity with template molecule and slow binding kinetics, etc.[17] As a consequence, we have a great interest in developing MIECSs based on a new kind of modified material which has excellent sensitivity and selectivity to the target molecule, and is prepared easily.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

β-Cyclodextrin (β-CD) is polysaccharides of glucose with a shape of a toroid and hollow truncated cavity, and the edge of the torus of the larger circumference contains chiral secondary hydroxyl groups. Due to the toroidal form with a hydrophobic inner cavity and a hydrophilic outer side, β-CD is well known for its high molecular selectivity and enantioselectivity to molecules of appropriate size and shape,[18, 19] such as cholesterol, steroids, peptides, amino acids and drugs protein.[20-23] Furthermore, β-CD was widely employed as recognition reagent for rebinding guest molecules with compatible size.[7] Because of the above characteristics, the combination of β-CD with MIPs could direct the selective imprinting polymerization and thus lead to the increase of the recognition cavities.[24] Therefore, β-CD was chosen as the recognition element and participated in building the molecularly imprinted sensors in this research. To the best of our knowledge, though it has been widely used in the preparation of molecularly imprinted sphere,[7, 18] its application to construct MIECSs is relatively few.

In this work, we incorporated both β-CD and AuNPs on GR to prepare a composite for modifying electrode (β-CD/AuNPs/GR/GCE)[25] before electropolymerization. During the synthesis process, $HAuCl_4$ was reduced into AuNPs, which combined with GR and β-CD respectively. The preparation procedure is easy and the resulting β-CD/AuNPs/GR composite can be easily purified, stored and redispersed in water without any further chemical treatment. Quercetin was chosen as the target molecule. It is a natural flavonoid usually existing in Chinese herbal medicine plants, which has anticancer, anti-allergic, anti-inflammatory and antiviral activities.[26-28] The size and shape of quercetin are compatible with the cavity of β-CD. With the aid of pyrrole, the method of electropolymerization was employed to synthesize MIPs for the construction of the imprinted electrochemical sensor (**MIPs/β-CD/AuNPs/GR/GCE)**. With the synergistic effects of MIPs, β-CD, AuNPs and GR, the MIPs/β-CD/AuNPs/GR/GCE exhibits fast rebinding dynamics, high selectivity and excellent sensitivity.

Experimental

Reagents and apparatus

Quercetin dehydrate were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Pyrrole was purchased from Fluka Chemical Reagent Co. Ltd. (Switzerland). Buffer solutions were prepared using Citric acid and sodium citrate in the pH range 3.0-6.0. Graphene was synthesized according to the methods mentioned in our reported work.[29] All other reagents were of analytical grade and without further purification. All solutions were prepared with doubly distilled water (DDW) throughout the experiment. All electrochemical measurements were performed on a CHI 660C electrochemical workstation (Shanghai, China). The classical three-electrode system consisted of a β-CD/AuNPs/GR based quercetin molecularly imprinted glassy carbon electrode (MIPs/β-CD/AuNPs/GR/GCE) as the working electrode, a potassium chloride (KCl)-saturated calomel electrode (SCE) as the reference electrode, and a Pt wire electrode as the auxiliary electrode.

Preparation of β-CD/AuNP/GR composite

The preparation of β-CD/AuNPs/GR composite was based on literature methods with modifications to a one-pot synthesis.[16] At first, 80 mg GO and 10 mg β-CD were added to 30 ml double-distilled water and stirred for a while. Then we dropped 300 μL ammonium hydroxide into the mixture to make an alkaline condition. After that, 2 ml 1% $HAuCl_4$ were mixed into the former solution, uniformed by ultrasonic oscillations and then heated at 60□ for 3 h. The product was separated by centrifugation, and then washed with double-distilled water for several times. Finally, the obtain β-CD/AuNPs/GR composite was dried under vacuum. For comparison, GR, β-CD/GR and AuNPs/GR composites were also disposed in similar procedures.

Preparation of β-CD/AuNPs/GR based electrode

At first, the as-prepared β-CD/AuNPs/GR was homogeneous dispersed into aqueous solution by sonication in 1.0 mL DDW for 30 min. Polished the glassy carbon electrode on the Suede by 0.1, 0.3, 0.05 μm Alumina polishing powder, rinsed it with DDW and then followed by sonication in ethanol and DDW. Then immersed the electrode in the 1.0 mol/L H_2SO_4 and scanned by cyclic voltammetry (CV) from -0.20 to +0.60 V for 20 cycles at the rate 100 mV/s to activate the electrode. Here after, rinsed the electrode with DDW and dried it with an IR lamp. Got 5.0 μl β-CD/AuNPs/GR aqueous solution by an appropriate pipette and dropped it carefully onto the surface of the GCE. Ensured the electrode still and dried under an IR lamp for about 1h to obtain the β-CD/AuNPs/GR modified GCE (β-CD/AuNPs/GR/GCE).

Fabrication of quercetin imprinted electrochemical sensor (MIPs/β-CD/AuNPs/GR/GCE)

At first, the as-prepared β-CD/AuNPs/GR/GCE was immersed into solution containing quercetin (1.0×10^{-4} mol/L), pyrrole (1.0×10^{-2} mol/L, pH = 7.0) and 0.1 mol/L KCl, followed by cyclic voltammetry (CV) at the scanning rate of 100 mV/s for 15 cycles under a potential from -0.2 V to 1.0 V to get the polymers modified β-CD/AuNPs/GR/GCE. After the electropolymerization, the polymers modified electrode was immersed into a solution of 0.5 mol/L NaOH, followed by cyclic voltammetry (CV) at the scanning rate 100 mV/s for 15 cycles under a potential from -0.2 V to 1.0 V to extract the template quercetin. Up to now, oxidized polypyrrole molecules layer were performed and the imprinting template molecule quercetin has been eluted. So the molecularly imprinted polymer electrode (MIPs/β-CD/AuNPs/GR/GCE) was obtained. As a contrast, β-CD/GR/GCE, AuNPs/GR/GCE, GR/GCE were disposed exactly as above and got modified imprinted electrodes respectively (MIPs/β-CD/GR/GCE, MIPs/AuNPs/GR/GCE and MIPs/GR/GCE).

Electrochemical measurements

All electrochemical measurements were performed on a conventional three-electrode electrochemical workstation. CV and EIS measurements to characterize the MIPs films were carried out in Citrate-Sodium citrate (C-S) buffer solution (pH=4.0) containing 5 mmol/L $[Fe(CN)_6]^{3-/4-}$. Immersed the MIPs/AuNPs/β-CD/GR/GCE into quercetin solution with different concentrations, and then incubated for 30 min to ensure quercetin molecule rebound by MIPs/AuNPs/β-CD/GR/GCE. DPV method was chosen for electrochemical determination of quercetin in C-S buffer solution (pH=4.0) from 0.0 to 0.4 V at a scan rate of 100 mV/s. All

electrochemical experiments were carried out at room temperature. Luteolin, primuletin and apigenin were chosen as control molecule to evaluate the selectivity of the MIPs/AuNPs/β-CD/GR/GCE. Experimental parameters were optimized according to the voltammetric response of quercetin in the solution.

Results and discussion

Characterization of the MIPs/β-CD/AuNPs/GR/GCE

The process of electropolymerization for MIPs/β-CD/AuNPs/GR/GCE was shown in Fig. S1. Along with the increase of cycle numbers, the anodic peak current at 1.0 V decreased gradually, which indicated the growth of polymeric film on the composite. Finally, the obtained current-voltage curve was stabilized, which indicated the prepared molecularly imprinted sensor was completed.

The surface morphologies of the GR, β-CD/AuNPs/GR, MIPs/β-CD/AuNPs/GR/GCE (with template molecules) and MIPs/β-CD/AuNPs/GR/GCE (without template molecules) were evaluated by scanning electron microscopy (SEM). As shown in Fig. 1A, GR shows a typically curved, layer-like structure with a fairly smooth surface. The surface image (Fig. 1B) of β-CD/AuNPs/GR showed clearly that there were many granules of AuNPs on the surface of composite with an average size of about 100 nm (amplified SEM image of AuNPs shown in the inset of Fig. 1B). With the electropolymerization of the MIPs, a layer of film was coated on the surface of β-CD/AuNPs/GR (Fig. 1C). Fig. 1D shows the morphologies of MIPs/β-CD/AuNPs/GR/GCE after remove the template molecule. Compared with Fig. 1C, it showed a rather rough and dense surface. And some pores were left in the MIPs layer to provide high-speed pathways for the template molecules transferring from solution to the sensor.

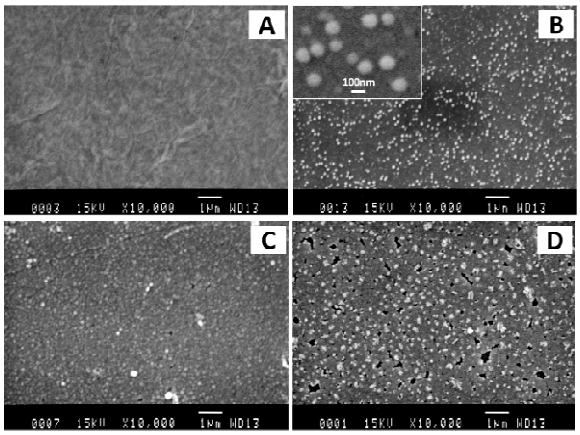

Fig. 1 SEM images of GR (A), β-CD/AuNPs/GR (B) (Inset: SEM images of β-CD/AuNPs/GR presented in 100nm scale), MIPs/β-CD/AuNPs/GR/GCE (with template molecules) (C) and MIPs/β-CD/AuNPs/GR/GCE (without template molecules) (D).

CV was used to investigate the processes of the modification of electrodes. CV was performed with a supporting electrolyte containing 5.0 mmol/L $K_3[Fe(CN)_6]$ and 0.1 mol/L KCl. As shown in Fig. 2, the redox peak revealed a reversible CV at the bare gold electrode (Curve d). After the electrode was modified with graphene, the peak current increased greatly (Curve c). It was due to the ultrahigh specific surface area and unique electronic features of graphene, which could improve the electrical conductivity of electrode. When β-CD/AuNPs/GR was used to modify electrode, the β-CD/AuNPs/GR/GCE exhibited a much higher current response (Curve a) due to the synergistic effects of the good electrical conductivity of GR and AuNPs and the biocompatibility of β-CD. As shown in Curve e, the CV of the MIPs before removing of the template molecule exhibited a pimping current response. The block of electropolymerization film to electrode can explain the phenomenon. As shown in Curve b, after removing of the template, the current response got an apparent increase. Because a large quantity of vacant recognition sites were released after removing of the template, the process of electronic transmission was improved.

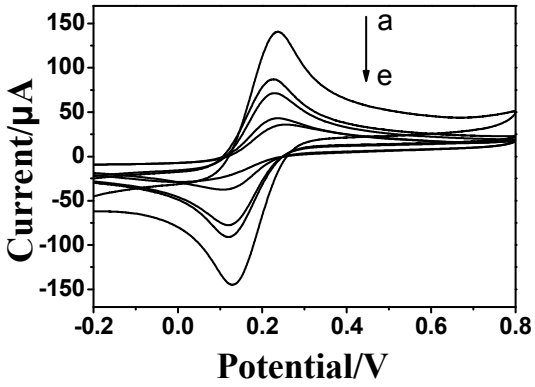

Fig. 2 CVs of the prepared process of electrode: (a) β-CD/AuNPs/GR/GCE, (b) MIPs/β-CD/AuNPs/GR/GCE (after removing of the template molecules), (c) GR/GCE, (d) GCE, (e) MIPs/β-CD/AuNPs/GR/GCE (before removing of the template molecules) in C-S buffer solution (pH=4.0) containing 5 mmol/L $K_3[Fe(CN)_6]$.

In order to investigate the influence of the modified materials to the process of electropolymerization, we measured the DPVs of different MIECSs (MIPs/GCE, MIPs/GR/GCE, MIPs/AuNPs/GR/GCE and MIPs/β-CD/AuNPs/GR/GCE) after 300 s' incubation in 10^{-6} mol/L quercetin soluton in 0.1 mol/L C-S buffer solution (pH=4.0). Fig. 3 showed that the MIPs/GR/GCE (curve c) produced a larger peak current of quercetin compared with the MIPs/GCE (curve d), which might result from the excellent electron transfer ability and larger surface area of GR. After the incorporation of AuNPs with GR/GCE, a higher peak current appeared (curve b) compared to that of MIPs/GR/GCE (curve c), which could be attributed to the wonderful conductivity and biocompatibility of AuNPs. Thus, the conductivity of the AuNPs/GR-modified electrode was greatly improved. After adding β-CD to the AuNPs/GR/GCE, the highest peak current of quercetin was obtained (curve a), which was probably due to the selective binding of quercetin by toroidal form of β-CD and the synergistic effect of graphene and AuNPs to immobilize more quercetin on electrode.

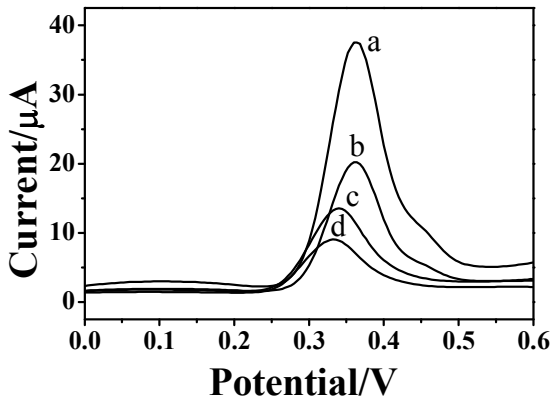

Fig. 3 DPVs of different electrodes (after binding MIECSs in 1.0 ×10^{-6} mol/L Qu solution) in C-S buffer solution. Electrodes: a. MIPs/AuNPs/β-CD/GR/GCE, b.MIPs/AuNPs/GR/GCE, c.MIPs/GR/GCE, d. MIPs/GCE.

The different electron-transfer resistance of various modified electrodes were investigated by electrochemical impedance spectroscopy (EIS) with $K_3Fe(CN)_6$ as the redox probe (Fig. 4). After β-CD/AuNPs/GR composite were immobilized on the surface of the GCE (curve b), the semicircle decreased distinctively compared to that of bare GCE (Curve a), indicating that β-CD/AuNPs/GR could accelerate the electron transfer between the electrochemical probe $[Fe(CN)_6]^{3-/4-}$ and the GCE, which was attributed to the significantly improved electrical conductivity of β-CD/AuNPs/GR films. After electropolymerization on the β-CD/AuNPs/GR films, the prepared MIPs/β-CD/AuNPs/GR/GCE (with template molecules) (Curve c) displayed an obvious increase in the interfacial resistance, implying the formation of the hindered pathway for the electron transfer within the polymers. As shown in curve d, the diameter of the semicircle was remarkably reduced, which could be attributed to the formation of imprinted sites after the extraction of template molecules, leaving channels for the penetration of $[Fe(CN)_6]^{3-/4-}$ through the MIPs film to the electrode for further oxidation. This result further verified the characteristics of the different modified electrode surface.

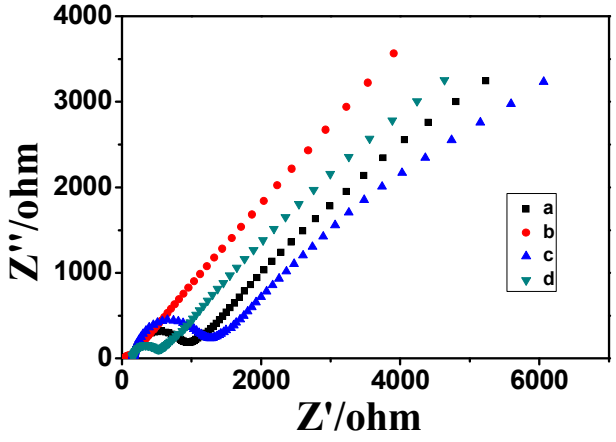

Fig. 4 EIS of a.GCE, b. AuNPs/β-CD/GR/GCE, c.MIPs/AuNPs/GR/GCE (with template molecules), d. MIPs/AuNPs/GR/GCE (without template molecules) in C-S buffer solution containing 5 mmol/L $K_3[Fe(CN)_6]$.

The optimization of the preparation conditions for MIPs/β-CD/AuNPs/GR/GCE

In order to fabricate an efficient sensor, different factors, including of pH of rebinding solution, monomer concentration, the scan cycles and scan rate, were investigated. The peak current responses of quercetin on MIPs/β-CD/AuNPs/GR/GCE by DPV were used to show the performance of the sensor.

Optimization of pH of rebinding solution

The pH of rebinding solution exhibited a significant effect on the electrochemical behavior of the imprinted sensor. MIPs/β-CD/AuNPs/GR/GCE was tested by DPV method in C-S buffer solution containing constant concentration of quercetin with the pH value ranging from 2.0 to 6.0. As shown in Fig. S2a, the current responses increased from pH 2.0-4.0, and then decreased from pH 4.0-6.0. The highest current was observed when the pH value was adjusted to 4.0. So we chose 4.0 as the proper pH in the preparation process of MIPs solution.

Optimization of pyrrole concentration

The monomer concentration plays an important role in the polymerization process of MIPs/β-CD/AuNPs/GR/GCE. It could affect not only the thickness of the polymer matrix but also the amount of imprinted molecule, which in turn influences the electrochemical behavior of the sensor. In order to find the optimal concentration of functional monomer, We prepared five MIPs sensors with different concentration of functional monomer (0.5 × 10^{-2}, 0.8 × 10^{-2}, 1.0 × 10^{-2}, 1.2 × 10^{-2} and 1.5 × 10^{-2} mol/L) and used them to detect 1.0× 10^{-4} mol/L quercetin, respectively. As shown in Fig. S2b, the peak current was tiny when pyrrole concentration was lower than 1.0 × 10^{-2} mol/L. The reason was that the less pyrrole reduce the capture of Qu during electropolymerization. A considerable decrease of the current response on MIPs/β-CD/AuNPs/GR/GCE was observed when the concentration of pyrrole was above 1.0 × 10^{-2} mol/L. The reason was that the electropolymerized film was too compact to elute template molecules and form imprinted caves in solution with high concentration of pyrrole. The highest peak current was observed when the concentration of pyrrole was 1.0 × 10^{-2} mol/L, which was chose as the optimal concentration of pyrrole for preparing MIPs/β-CD/AuNPs/ GR/GCE.

Optimization of scan rate and scan cycles

During the electropolymerization process, scan rate and scan cycles has big effect on the thickness and tightness of polymer film, which can influence the analytical performance of sensor. In this work, we designed a series of experiments to explore the optimum scan rate and scan cycles. As shown in Fig. S2c, the maximum current response was obtained at 100 mV/s. The reason was that it could form a tight polymer film at a lower scan rate, which made it difficult to remove template molecule from the polymer matrix leading to the decrease of imprinted sites. At a higher scan rate, a loose and rough film with a low recognition capacity was formed.

Thus, the optimum scan rate of electropolymerization was set to be 100 mV/s. As shown in Fig. S2d, when the number of cycles was fifteen, the current response to quercetin reached maximum. When the scan cycles were less than fifteen cycles, the imprinted polymer membranes were too thin to survive, which could lead to the decrease of current response. If the scan cycles were more than fifteen cycles, the current response decreased too. The reason was that the imprinted polymer membranes were too thick to elute the template molecules situated at the central area of the polymer membranes and decrease the number of recognition site to template molecule. Therefore, we chose fifteen cycles as the optimum scan cycles during the electropolymerization process.

Calibration curve

Under optimal conditions, the prepared MIPs/β-CD/AuNPs/GR/GCE was used to detection of Qu with different concentrations. As shown in Fig. 5, the current response on MIPs/β-CD/AuNPs/GR/GCE increased with increasing Qu concentrations from 5.0 ×10^{-9} to 1.0 × 10^{-6}mol/L. A good linear regression equation can be expressed as Ip(μA) = 2.4765 + 0.3176C (10^{-8} mol/L) (R = 0.9998). The limit of detection was 1.0× 10^{-10} M (the concentration when ratio of the signal to noise is 3). As compared to other sensors for detecting Qu, including of MIP/GO/GCE,[26] PAO/GR/GCE[29] and MIPs/CNTs/GCE,[30] this method possessed good sensitivity and a wide detection linear range, which could be used for sensitive detection of samples in wide concentrations. The excellent performances were resulted from the combined effect of β-CD, AuNPs and GR, which provided efficient electrode surface for targets imprinting and electronic signal transfer.

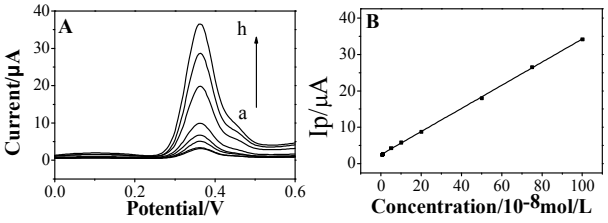

Fig. 5 DPV curves (A) and calibration curve (B) of the MIPs/AuNPs/β-CD/GR/GCE towards to different concentrations (from 5.0 ×10^{-9} to 1.0 × 10^{-6}mol/L.) of Qu in C-S buffer solution.

Selectivity, repeatability and stability of the sensor

The selectivity of the MIPs/β-CD/AuNPs/GR/GCE was tested *via* DPV using luteolin, primuletin and apigenin as interferents in the presence and absence of quercetin. As shown in Fig. 6, the addition of luteolin (b), primuletin (c) and apigenin (d) did not produce a strong change in current signal compared to quercetin alone (a). Furthermore, in the absence of quercetin, there were three tiny current response of MIPs/β-CD/AuNPs/GR/GCE to luteolin (e), primuletin (f) and apigenin (g). These results clearly indicated that the sensor was capable of selectively detecting quercetin in complex samples.

After Putting the prepared modified electrode into the condition with 4℃ covered with beaker for two weeks, we found that the surface of MIPs/β-CD/AuNPs/GR/GCE was still clean. A parallel determination of quercetin for 5 times by MIPs/β-CD/AuNPs/GR/GCE was carried out to get the RSD of 1.9%. Then five imprinted sensors was prepared using the same method and used to determine the quercetin with the same concentration, which got the RSD of 2.3%. The experimental results showed that the prepared MIPs/β-CD/AuNPs/GR/GCE had good repeatability. And the MIPs/β-CD/AuNPs/GR/GCE also exhibited good stability. In fact, as much as 95 % of the initial peak current was preserved after storage of the biosensor at 4 ℃ for 3, 7 and 15 days (Fig. S3).

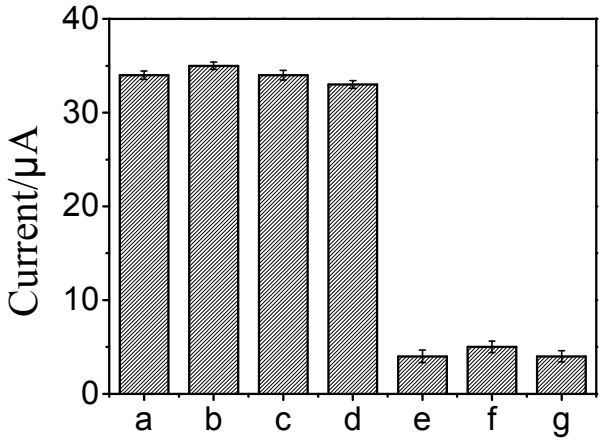

Fig. 6 The selectivity of MIPs/β-CD/AuNPs/GR/GCE for quercetin, luteolin, primuletin and apigenin. Experimental solutions are composed by: a. quercetin; b. quercetin and luteolin; c. quercetin and primuletin; d. quercetin and apigenin; e. luteolin; f. primuletin; g. apigenin. The concentration of each compound is 1.0×10^{-6} mol/L.

Determination of quercetin in real sample

In order to test the applicability and reliability of the imprinted sensor, the quercetin content in Compound Quercetin Tablets (20 mg/tablet) was determined using the proposed sensor. The recoveries were performed with the standard addition method. As shown in Table 1, measured results were satisfactory with the recoveries of 97.6-102.1%, suggesting that this sensor could be applicable for the determination of quercetin in pharmaceutical samples.

Table 1

Determination of quercetin in real pharmaceutical samples.

Sample	Added (μmol/L)	Founded (μmol/L)	Recovery (%)
1	0.000	0.000	
2	0.053	0.052	98
3	0.104	0.101	97.5
4	0.525	0.517	98.5
5	0.978	0.999	102.1
6	0.143	1.397	97.6

Conclusion

In this study, a novel MIPs/β-CD/AuNPs/GR/GCE with excellent selectivity and sensitivity for efficient detection of quercetin was successfully prepared. The synergistic effects of the specific structure of β-CD and the good electrical conductivity of AuNPs/GR were used to improve the current response and recognition capacity of the sensor. The MIPs/β-CD/AuNPs/GR/GCE showed low limit of detection, high selectivity and excellent stability towards quercetin determination. This strategy can be further expected to be used to fabricate various molecular imprinting-based sensors for advanced applications.

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