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Rational design and application of molecularly imprinted sol–gel polymer for the electrochemically selective and sensitive determination of Sudan I

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ABSTRACT

An electrochemical strategy on the basis of rationally designed molecularly imprinted sol–gel polymer embedded with gold nanoparticles (AuNPs) is developed for the specific and sensitive determination of Sudan I. The rationally designed sensing Sudan I imprinted sol–gel was prepared by mixing Sudan I with 3-aminopropyltriethoxysilane, tetraethoxysilane, chitosan, and AuNPs, followed by copolymerization and extraction of the template molecules. The hybrid forming membrane was characterized by SEM and FTIR-ATR, and used for the linear sweep voltammetric (LSV) determination of Sudan I in water/ethanol solutions. The LSV responses exhibited high sensitivity and selectivity, as discriminated from Sudan I analogues. Under optimal experimental conditions, LSV peak currents were linearly proportional to the concentrations of Sudan I in the range from 0.1×10^{-7} to 1.0×10^{-5} M, with a detection limit of 2.0×10^{-9} M. The strategy is generally applicable in developing sensitive, selective, and moreover, reusable electrochemical sensors for quantitative determination of electroactive species.

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1. Introduction

Molecular imprinting polymers (MIPs) possess the obvious advantages such as the easy and cheap preparation, the flexibility in choosing copolymerizable monomers and the tailorability in functionalities comprising the binding cavity wall, making MIPs a broad application in the fields such as separations, chemical sensing and catalysis [1–5]. Considerable attention has been drawn on recent developments like use of organically modified silane as precursors for the synthesis of hybrid molecularly imprinted polymers by a sol–gel method to construct thin MIP films, since it is favorable in controlling of the thickness, porosity, and surface area, providing the selectivity and diffusion comparable and even better than other polymer-based films [6,7].

The performance of a MIP is characterized by its high rebinding capacity and specificity, and various factors including the choice of polymerizable ingredients and the reaction conditions should be carefully weighted in the synthesis of a MIP [8,9]. In the electrochemical sensing application, besides the factors mentioned, high mass transportation efficiency and charge conductivity for a MIP are also necessary. Several studies have proposed the hybridization of MIPs with conductive nanomaterials to overcome the sensitivity related limitations of rebinding capacity and conductivity. Gold nanoparticles (AuNPs) has been frequently used in elaborating bisoensors because as one hybrid component in the sensing layer AuNPs can render the biosensor with improved conductivity and surface-to-volume ratio [10]. The application of gold nanoparticles in construction of electrochemical biosensors has shown enhanced analytical performance.

Using conductive MIPs for the electrochemical determination of Sudan I is one proper embodiment in its application. Sudan I is a member of Sudan azo-dyes and has been widely used in many fields such as household commodities, textile, and plastics [11,12], because of its bright and vivid colors that improve the luster of commercial products. Evidences have shown Sudan I is toxical and it has been classified as a category 3 carcinogen [13]. The use of Sudan I as foodstuff or animal feed additives is forbidden. However, illegal use has been occasionally reported, posing serious risks to public health. Analytical screening methods are needed for the fast identification and quantification of such banned additives [14]. Due to the inherent electrochemical activity of Sudan I, it is possible to find suitable electrode conditions for the simple and fast electrochemical determination. Up to date, activated glassy carbon electrode [15] and calcium montmorillonite modified carbon paste electrode [16] have been reported for the sensitive determination of Sudan I in spiked samples, but the selectivity is still problematic. The present work aims at the rational design and application of molecularly imprinted sol–gel polymer for the electrochemically selective and sensitive determination of Sudan I. Besides the common monomers APTES and TEOS are used, chitosan and AuNPs are

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chosen as adhesive component and conductive component respectively. Addition of chitosan in MIPs [17] is believed to improve the membrane stability while the use of gold nanoparticles is intended to increase the membrane conductivity [18] and surface roughness [19]. Further consideration in the use of chitosan is its polyhydroxyl and polyamino structure that will be favorable in improving the selective non-covalent interaction in cavities.

Thus the Sudan I imprinting sol-gel polymer was prepared by mixing Sudan I with APTES, TEOS, chitosan, and AuNPs, and subsequent copolymerization. After extracting the template molecules, the hybrid membrane was characterized by SEM and FTIR-ATR, and used for the linear sweep voltammetric (LSV) determination of Sudan I in water/ethanol solutions. The choice and quantity of copolymerizable monomers and additives, as well as the solvent conditions in the preparation, are rationally weighted and optimized. As demonstrated in this work, the sensor can be used for Sudan I determination with high selectivity in a linear range from 0.1×10^{-7} to 1.0×10^{-5} M, with a detection limit of 2×10^{-9} M. Its application in the spiked sample analysis has also been tested.

2. Experimental

2.1. Reagents

Tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) and chitosan (95% deacetylation) were purchased from Sigma–Aldrich (St. Louis, USA) and used as received. Sudan I–IV and Gold (III) chloride hydrate (g mL^{-1}) were purchased from Treechem Co. (Shanghai, China). The solution of AuNPs with 5–10 nm in diameter was prepared according to the reported method [20] and stored in a brown bottle at 4 °C. Acetate buffer and other chemicals were of analytical grade. Aqueous solutions were prepared with double distilled water.

2.2. Preparation of imprinting and imprinted polymers

The preparation of silica sol–gel polymer was conducted on the basis of a rational design and optimization. Thus various effective factors including the choice of monomers, additives were well weighted in the preparation process. Typically the molecularly imprinted sol–gel with embedding AuNPs (MIP/AuNP) was prepared according to the following procedure. Firstly, 200 μL of 0.1 M Sudan I in ethanol was mixed with 800 μL of APTES. The mixture was magnetically stirred for 30 min, and then 6 mL of 0.5 mg mL^{-1} chitosan solution, 1.2 mL of aqueous AuNPs solution and 1.8 mL of TEOS were added. After 10 min of stirring, the mixture was incubated for 10 h at 60 °C for cohydrolysis and co-condensation until a homogeneous gel was formed. The imprinting sol–gel polymer was extracted by adding 50 mL of ethanol and 15 mL of 1.0 M HCl under magnetic stirring for 2 h to remove the template Sudan I. After this extraction procedure, additional duplicate extractions were conducted to ensure the complete removal of the template molecules, which was verified by HPLC analysis.

2.3. Characterization of imprinting and imprinted films

The surface morphologies of the molecularly imprinting and imprinted polymers were examined by a JEOL-JSM-6700F scanning electron microscope, and the accelerated voltage was 5.0 kV. ATR-FTIR characterization was conducted at ambient temperature (21 ± 2 °C) using a Tensor 27 FTIR spectrometer with a microscope Hyperion ATR (object-lens with Germanium crystal) (Bruker Optics) and a liquid nitrogen cooled MCT detector.

2.4. Preparation of the sensor

A 3.0 mm diameter glassy carbon electrode (GCE) was polished to mirror using the BAS-polishing kit with 0.3 and 0.05 μm Al_2O_3 pastes successively and electrochemically treated using a reported method [21]. The electrode surface as treated was in rich in hydroxyl and carboxyl, providing a hydrophilic surface that favors the spin coating of the gel polymer with easy and homogeneity. The pretreated GCEs were spin-coated by placing 10 μL of the imprinted sol–gel polymer, holding for 30 s, and then spinning at 4000 rpm for 60 s. The electrodes were put into a glass vial, air-dried overnight. The as prepared electrode was used as the sensor and referred as MIP/AuNPs/GCE.

2.5. Electrochemical characterization and measurement

Electrochemical measurements were performed on a Bio-Analytical System (BAS, cv-50w, USA) with a conventional three-electrode system comprising platinum wire as auxiliary electrode, saturated calomel electrode (SCE) as reference and the above prepared sensor as the working electrode. The MIP/AuNPs/GCE was incubated in the ethanolic solution of 1.0×10^{-5} M Sudan I for 20 min at 25 °C. Then the electrode was transferred to a 2-mL electrochemical cell containing 0.2 M acetate buffer solution. The Linear sweeping voltammograms was recorded between −0.3 and −0.9 V at a scan rate 50 mV s^{-1}. Control experiment s were also performed using non-imprinted polymer modified GCE (NMIP/AuNPs/GCE) and imprinted sol–gel coated GCE without the hybridization of AuNPs (MIP/GCE) as the working electrodes. The measurements were carried out in non-deoxygenated solutions at room temperature. Each experiment was replicated fourfold.

2.6. Spiked ketchup sample analysis

As a demonstration of the utility of the prepared MIP sensor, a spiked ketchup sample was used, because real samples such as ketchup and hot chilli powder were tried and no Sudan I contaminant was found at present. The spiked ketchup sample was prepared as follows: 10.0 g ketchup was exactly weighed, and then known amount of Sudan I in 20 mL ethanol was added. After 20 min ultrasonication, the mixture was filtrated and the liquid phase was collected in a 100.0 mL volumetric flask. The treatment was repeated three times, and the filtrates were combined and diluted to volume with ethanol. The serial spiked sample solutions with different Sudan I concentrations were analyzed with the MIP/AuNPs/GCE sensors as the same procedure described in the electrochemical measurement section. The Sudan I concentrations were validated by comparing with the result from HPLC.

3. Results and discussion

3.1. SEM and FTIR-ATR characterization of the molecularly imprinting and imprinted film

Scanning electron micrograph was applied to characterize the surface morphology of the Sudan I molecularly imprinting (before the template extraction) and imprinted (after the template extraction) films coated on glassy carbon electrodes. As shown in Fig. 1(a), the imprinting film is uniform and homogeneous, demonstrating the excellent interfacial compatibility between the electrochemically pretreated GCE surface and the sol–gel polymer film. The visible AuNPs in 5–10 nm diameters are nearly monodisperse and uniformly distributed on the surface as seen from the top of the film. After extracting the template molecules, a richly hierarchical morphology was produced as seen in Fig. 1(b). This phenomenon probably stems from the facts that the exposed AuNPs were washed

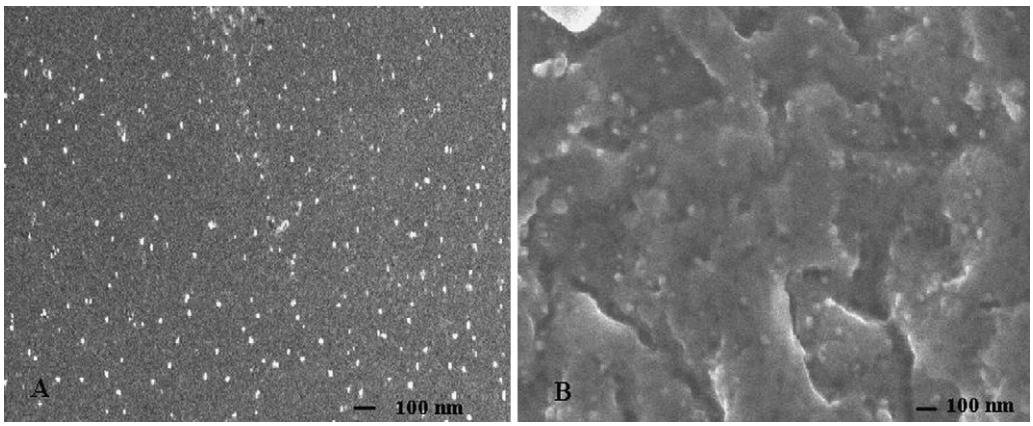

Fig. 1. SEM images of the surface morphology of the Sudan I molecularly imprinting (a) and imprinted (b) films coated glassy carbon electrodes.

off and the polymer surface was swelled and etched by the exacting reagent (the mixture of hydrochloric acid and ethanol) during the extraction process. It is undoubted the real surface area is greatly increased after this extraction procedure. The hierarchical structure in the imprinted film is beneficial for improving the rebinding efficiency of the binding cavities toward Sudan I molecules. Another feature of the imprinted film is the discernable gold nanoparticles embedded and evenly distributed in the hierarchical structure. It is expected that the embedded gold nanoparticles will promote the charge transfer in the redox reaction at the sensor interface.

For further comparisons between the molecularly imprinting and imprinted films, FTIR-ATR measurements were conducted. Fig. 2 shows the spectra of pure Sudan I (a), Sudan I imprinting film (b) and imprinted film (c), respectively. It can be seen pure Sudan I shows the characteristic bands of benzene at 1500 cm^{-1} and 1600 cm^{-1} and the absorption band of its –OH at 3400–3500 cm^{-1}. For the Sudan I imprinting and imprinted films, the common bands at 1000–1200 cm^{-1} and at 1654 cm^{-1} are attributed to the saccharide structure of chitosan and its amido group (CO–NHR) [22]. The band around 1064 cm^{-1} indicates Si–O–Si stretching vibrations, confirming the existence of an extensive silicate network in the film [23]. The broad band due to the stretching vibration of $-NH_2$ and –OH groups from chitosan, modified sol–gel silica particles, and the template Sudan I can be observed at 3400–3500 cm^{-1}. The distinct difference between the spectra of imprinting and imprinted films is the characteristic bands of Sudan I at 1500 cm^{-1} and 1600 cm^{-1}, which are discernable for the imprinting film but disappeared for the imprinted film, indicating that Sudan I has been completely extracted from the sol–gel polymer film.

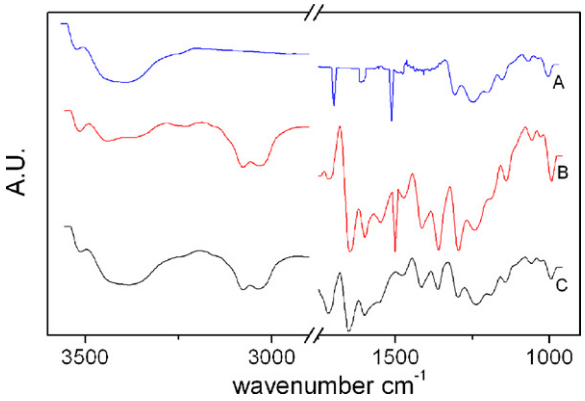

Fig. 2. ATR-FTIR spectra of pure Sudan I (a), Sudan I imprinting film (b) and imprinted film (c).

3.2. Electrochemical behavior of Sudan I at MIP/AuNPs/GCE

Sudan I is an aromatic azo compound, at a proper voltage, it can be electrochemically reduced into the hydrazo compound via a two-electron and two-proton reduction process as demonstrated in the literature [15].

After the imprinted film modified electrode was soaked in the Sudan I containing solution, the sensor electrode was characterized with cyclic voltammetry. An irreversible cathodic peak appeared at ca. −0.570 V, and the peak current was proportional to the scan rate in the range from 5 to 300 mV s^{-1} (Supplementary data, Fig. SI), suggesting the electrode reaction was a surface-confined irreversible reduction process. Linear sweeping voltammetry (LSV) was used for the electrochemical determination of Sudan I pre-collected by the MIP/AuNPs/GCE sensor, and the potential range from −0.3 to −0.9 V was applied.

Before the incubation, as clearly evidenced from Fig. 3, no peak was observed when MIP/AuNPs/GCE (curve a) was placed in the electrolyte of 0.2 M acetate buffer (pH 4.5) containing 20% (v/v) ethanol. After incubation of the MIP/AuNPs/GCE sensor in Sudan I solution, the LSV response exhibited an apparent reduction peak at −567 mV (curve d). As comparison, the non-imprinted sol–gel polymer coated GCE (NMIP/AuNPs/GCE) exhibits only a small signal at −580 mV (curve b). This small response is presumably attributed to a small amount of Sudan I non-specifically adsorbed toward the non-imprinted sol–gel polymer.

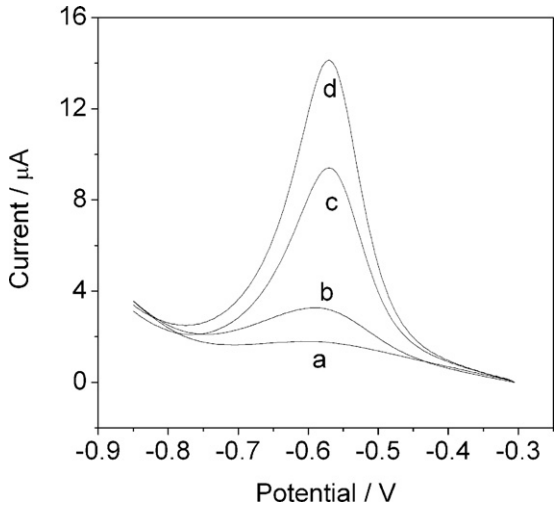

Fig. 3. LSV responses of the MIP/AuNPs/GCE without incubation in Sudan I solution (a), NMIP/AuNPs/GCE (b), MIP/GCE (c) and MIP/AuNPs/GCE (d) after incubation in 1.0×10^{-5} M Sudan I solution.

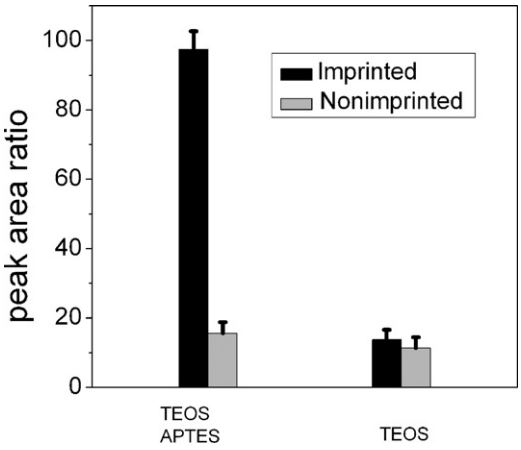

Fig. 4. Influence of functional monomers on the specific binding of Sudan I.

The hybridization of AuNPs has a direct effect on the current response of the sensor. When the molecularly imprinted sol–gel polymer was not hybridized with AuNPs (referred as MIP/GCE), the MIP/GCE displays a reasonable response (curve c), but much lower than that of the MIP/AuNPs/GCE sensor (curve d). This phenomenon means that AuNPs can improve the conductivity of the sensing interface and play a key role in mediating electron transfer between the rebinding species and electrode. Another factor possibly stems from the surface area increase due to the embedding AuNPs in the matrix, resulting in a higher binding capacity.

3.3. Rational design and optimization of the molecularly imprinted sol–gel polymer

3.3.1. Influence of functional monomers

The role of functional monomers in sol–gel films is to assist the creation of the specific binding cavity by leaving interacting chemical functions after the polymerization, which is situated within the cavity in an optimal position for rebinding, similar to the active site in an enzyme [24]. The influence of functional monomer APTES on the binding ability of imprinted films was explored using the HPLC method. Steady-state binding capacities of Sudan I toward the imprinted and non-imprinted films in the presence and absence of APTES functional monomer, respectively, were measured, after incubation of the respective films in 1.0×10^{-6} M Sudan I solution for 24 h. The amounts of bound Sudan I was analyzed by extraction and subsequent quantitative analysis by HPLC. As shown in Fig. 4, for the non-imprinted films, only nonspecific binding is observed; whereas for the imprinted films, strong specific binding is ascertained. In the cases of imprinted films, APTES in the gel polymer increases the binding capacity up to 60%, suggesting APTES has an enhanced synergistic effect for the specific rebinding of Sudan I.

3.3.2. Influence of co-solvents

The effect of co-solvents on peak current of Sudan I was investigated. Due to the comparatively weak solubility of Sudan I in water, we have to choose a co-solvent to promote its solubility in the sol–gel solution. Experimental results indicate that Sudan I has a comparatively high solubility in ethanol, and additionally, ethanol is miscible with water and compatible well with all the sol–gel components in the sol–gel formation. Thus ethanol was selected as a co-solvent of water to dissolve Sudan I.

The impact of ethanol content on the electrochemical response sensitivity was investigated in the volumetric percentage range from 0 to 30% for ethanol in water. The reduction peak current gradually increased with increasing ethanol content and reached a maximum at 25%, as shown in Fig. 5a. Further increase of the ethanol content led to the decrease of peak current. This phenomenon is possibly attributed to the "squeezing out" effect, a common phenomenon in the molecular recognition process in term of the hydrogen bonding competition and solvophilic/solvophobic interactions among solvent molecules, template and the binding cavity [25]. In our case, when the volumetric percentage of ethanol is low, the Sudan I molecule will enter the binding cavity because of the solvophilic/solvophobic interaction. However, when the volumetric percentage of ethanol is higher than 25%, the Sudan I molecule will be squeezed out of the cavity since the hydrogen bonding competition of plenty of ethanol molecules.

3.3.3. Effect of pH

The influence of the solution acidity on the electrochemical behavior of Sudan I at MIP/AuNPs/GCE was examined in the mixture of 250 μL absolute ethanol and 750 μL acetate buffer of different pH, as illustrated in Fig. 5b. At pH 4.5, the LSV peak current reached a maximum value, which is chosen as the optimal pH for following experiments. The dependence of current on the buffer pH is presumably attributed to the necessary disturbance for the solvophilic/solvophobic balance mediated by protons in the solution. Another factor is protons are needed in the electrochemical reduction of Sudan I involved in the proposed mechanism.

3.3.4. Effect of the content of AuNPs

The ability to detect electrochemically the encapsulated redox probes in silica gel modified GCE electrodes was first shown by Collinson et al. [26], but the electrochemical responses were poorly shaped due to the inability of most of electroactive dopants to freely exchange electrons with the electrode. Gold nanoparticles in sol–gel sensing films have shown the ability to decrease the background current, amplify the electrochemical signal and accelerate the electron transfer rate [27]. The applied volumetric percentage of AuNPs suspension during the composite preparation is another important parameter. Fig. 5c displays the effect of AuNPs content on the amperometric response. With increasing the content of AuNPs, the current increased and trended to reach a maximum value. However, further increase of the AuNPs resulted in the decrease of peak current. This phenomenon is possibly attributed to the impairment from the increased AuNPs concentration toward the imprinted cavities and the increased double layer capacitance of the modified electrode. The volumetric percentage of AuNPs at 15% gave the maximum response and was used for preparation of the biosensor.

3.4. Electrochemical detection and selectivity verification

Fig. 6 displays the LSV peak current of Sudan I under the optimal experimental conditions. The peak current increased with the increasing concentration of Sudan I, linearly proportional to the concentration of Sudan I ranged from 0.1×10^{-7} to 1.0×10^{-5} M with a correlation coefficient 0.9978. The detection limit was 2.0×10^{-9} M based on the signal-to-noise ratio equal to 3.

Additionally, the analytical performance of the developed Sudan I sensor has been compared with that of other electrochemical sensors on activated GCE and montmorillonite calcium modified carbon paste electrode reported in the literatures [15,16,28]. The performance features are summarized in Table 1. As can be seen, the proposed sensor exhibit a wide linear range and low detection limit for Sudan I.

The utility of the prepared sensor in actual samples was demonstrated using spiked ketchup sample with different amounts of Sudan I, because ketchup samples is a possible source that uses Sudan I as additive. Results are summarized in Table 2. The recoveries were from 97.8 to 102.3%. The results indicate that the sensor based on the MIP/AuNPs/GCE system is accurate, precise and reproducible.

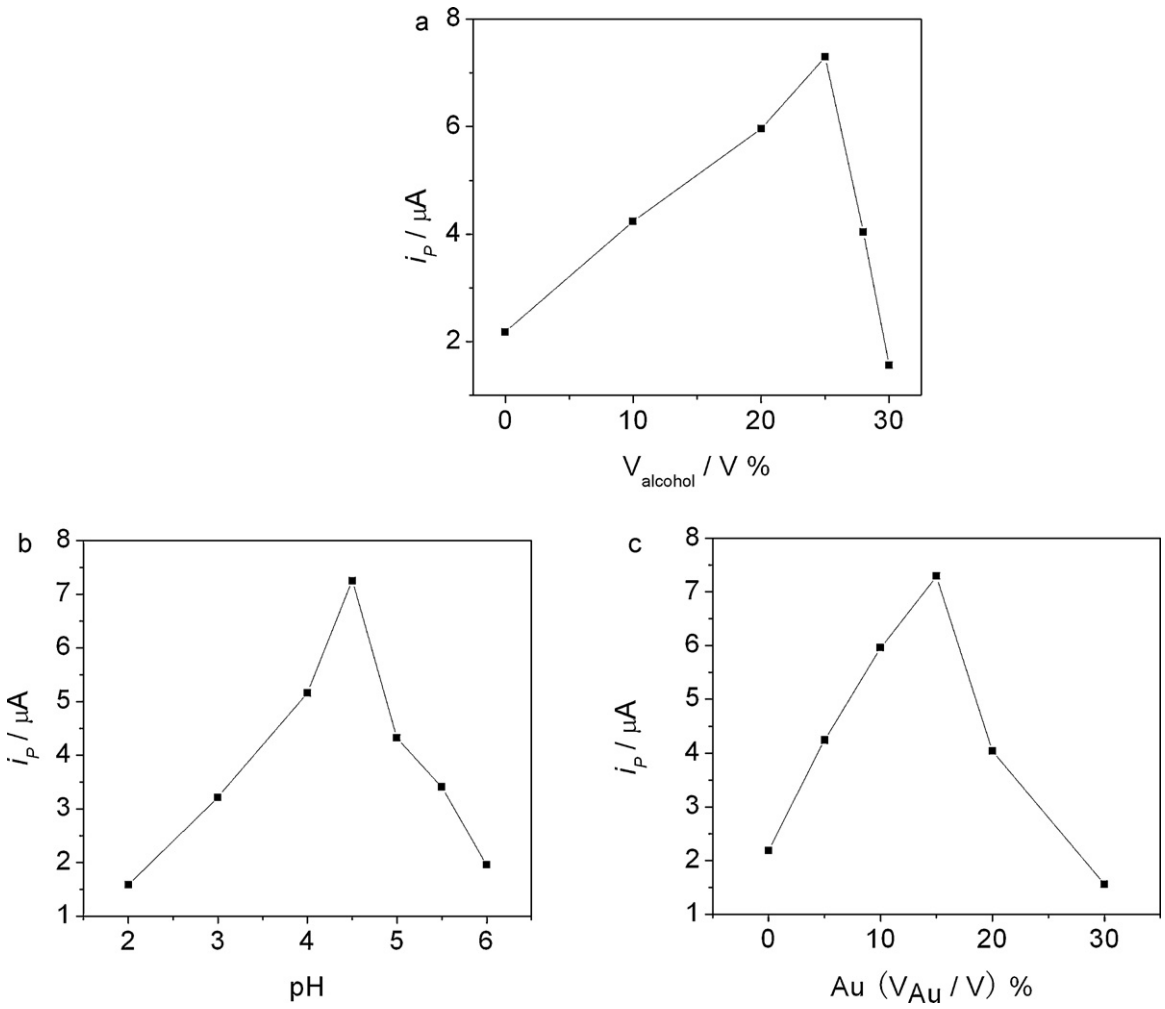

Fig. 5. Effect of different conditions on peak currents. (A) Ethanol content; (B) solution pH; (C) AuNPs content.

Table 1
Linear r with other electrochemical sensors.

Sensor fabrication	Linear range	Detection limit	Reference
Activated GCE	2.4×10^{-6} to 1.8×10^{-5} M	7.1×10^{-7} M	[15]
MMT-Ca modified CPE[a]	2.01×10^{-7} to 4.03×10^{-6} M	8.02×10^{-8} M	[16]
MWCNTs/GCE	6.0×10^{-7} to 7.5×10^{-5} M	2.0×10^{-7} M	[28]

[a] Calcium montmorillonite modified carbon paste electrode.

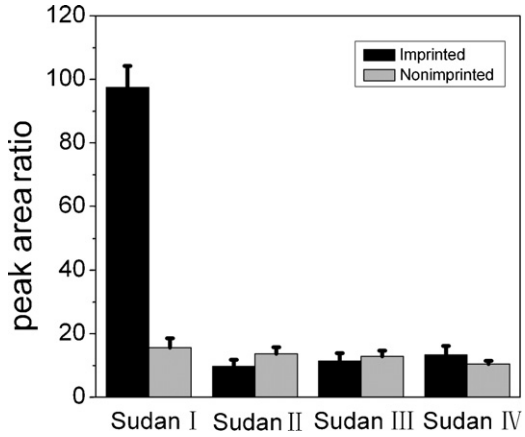

Fig. 6. The adsorption of Sudan I–IV to the imprinted and the non-imprinted films quantitatively analyzed by HPLC.

The selective recognition properties of imprinted and non-imprinted polymers toward the serial Sudan I–IV were investigated by immersing the polymer modified electrodes into the respective solutions at 1.0 μM for a fixed time. Then the bound Sudan compounds were extracted and subjected to quantitative analyses by HPLC. Results (Fig. 7) demonstrate that the adsorption capacity of imprinted polymer toward Sudan I was the highest among the adsorption capacities toward Sudan II–IV. On the other hand, the adsorption capacities of non-imprinted film toward Sudan I–IV

Table 2
Recovery study of Sudan I in spiked ketchup samples.

Sample	Taken (mol/L)	Found (mol/L)	Recovery (%)	RSD (%)
1	1.0×10^{-7}	0.98×10^{-7}	98.0	3.4
2	5.0×10^{-7}	4.71×10^{-7}	94.2	5.3
3	1.0×10^{-6}	1.02×10^{-6}	100.2	5.4
4	2.0×10^{-6}	2.04×10^{-6}	102.3	7.0
5	5.0×10^{-6}	4.89×10^{-6}	97.8	7.8

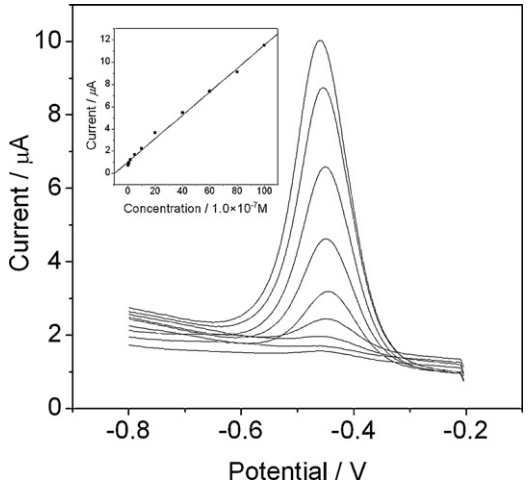

Fig. 7. The LSV responses of Sudan I with the concentrations ranged from 0.1×10^{-7} to 1.0×10^{-5} M. Inset: linear relationships between peak currents and Sudan I concentrations.

were almost the same due to the similar non-specific adsorption in these cases. The non-specific adsorption was consistent with that of imprinted film toward Sudan II–IV.

To further demonstrate the selectivity of the proposed sensor, interferences arising from other inorganic ions (PO_4^{3-}, Cl^-, SO_4^{2-}, and NO_3^-) and metal ions (Na^+, Cu^{2+}, Ag^+, Ca^{2+}) that are expected to coexist in real sample solution were tested for evaluating the selectivity of the determination of Sudan I with MIP/AuNPs/GCE. We found that 0.1 M of PO_4^{3-}, Cl^-, SO_4^{2-}, NO_3^- and Na^+, Cu^{2+}, Ag^+, Ca^{2+} solutions did not interfere with the determination of Sudan I at a concentration of 1×10^{-7} M. No perceivable change in the current was observed in comparison with the result obtained in the presence of Sudan I alone.

We believe that the high selectivity of the imprinted film toward Sudan I stems from the highly complementary effect of the formed cavity toward the template Sudan I in the molecular recognition process [29]. The highly complementary effect is based on the factors: the formed TEOS/APTES/chitosan gel network provides a geometric complementarity in the rigid cavity, while the amino group from APTES functions as additional binding site toward the template molecule. All the optimization procedures aforementioned are necessary and the optimized conditions can enhance the highly complementary effect.

4. Conclusions

In this article, we have shown the rational design and optimization of generally applicable silica sol–gel based molecularly imprinted polymers and the application in the electrochemical determination of Sudan I. Careful weighting of various effective factors including the choice and applied quantities of monomers and additives has been highlighted and it is demonstrated that the process is crucial for the construction of a selective and sensitive sensor. The rigid structure and APTES function provide the imprinted cavity with high affinity and specificity toward the template molecule. Gold nanoparticles embedded in the gel polymer render the sensing film conductivity. Although the detection limit for Sudan I in this work (2.0×10^{-9} M) is comparable with that of the HPLC/electrochemical detection (nearly 0.4×10^{-8} M) [30], but lower than that of the activated GCE determination (7.1×10^{-7} M) [15] and the montmorillonite calcium modified CPE determination (8.06×10^{-8} M) [16]. Moreover, the strategy may be used as a general platform that is applicable for the determination of other small electroactive molecules, as its flexibility on tuning the size and interfacial property of imprinted cavity with different molecules.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.01.047.

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