

Molecularly imprinted TiO₂ thin film using stable ground-state complex as template as applied to selective electrochemical determination of mercury

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Abstract

Molecular recognition sites for mercury ions were imprinted in TiO₂ film using stable ground-state complex of 1-amino-8-naphthol-3,6-disodium sulfonate (ANDS) and mercury ions as template. The complex ratio between mercury ions and ANDS was estimated to be 2:1. Compared with the controlled and pure TiO₂ electrodes, the imprinted electrode revealed selectivity towards the imprinted ions. Linear calibration plots for mercury ions were obtained and the regression equation was $I_p (\mu\text{A}) = 4.29 \times 10^{-7} + 19.40 [\text{Hg}^{2+}]$ with a detection limit of 3.06×10^{-9} mol/l. The imprinted electrode could be used for more than 1 month. Recoveries were calculated at both high and low concentrations, with a mean recovery of 99.6%.

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1. Introduction

Interest in the molecular imprinting technology (MIT) has surged greatly since theophylline MIPs were reported by Mosbach et al. [1]. The molecularly imprinted materials include traditional cross-linked organic polymers and some novel ones, such as electropolymerization, self-assembling monolayers and inorganic materials [2–6]. Generation of imprinted sites in these novel materials highlight a way to eliminate the diffusion barriers of the association between target analytes and recognition sites and to improve electrical communication between recognition sites and transducers [7–10]. These characters are fully exhibited also by inorganic macromolecular imprinted materials, such as TiO₂. The imprinted inorganic macromolecular polymer and recognition sites are highly stable and selective toward the analytical substrates [11,12]. This meets the sensors' requirements

and can be used as idea materials to construct sensitive elements.

Currently, two general strategies have been suggested to generate imprinting sites. One is covalent approach [13,14], where the aggregates in solution prior to polymerization are maintained by reversible covalent bonds. The other is noncovalent approach [15,16], where the pre-arrangement between the templates and the functional monomers is formed by noncovalent means, such as H-bonds, electrostatic interaction, hydrophobic effect and metal coordination interactions. Compared with the covalent approach, the latter method is used more widely due to the following merits: versatile and avoiding complicated synthesis and chemical cleavage steps. In contrast to single templates, applications of compound templates are rarely reported [17]. It is well known that formation of stable ground-state complex through strong interaction between fluorescent substances and ions may cause increase/decrease of fluorescence [18–24]. This is very similar with the imprinting process to form multifunctional compounds between templates and monomers.

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Thus, a stable ground-state complex as template is attempted to generate imprinted sites in inorganic materials in this paper.

As we know, it is effective to generate sites with shape selectivity in TiO₂ thin film through coordination interaction between carboxyl and titanium(IV) [7,25–27]. Pogorelova et al. described formation of recognition sites achieved through the coordination interaction between phosphate radical and hydrosulfide group together with titanium(IV) in TiO₂ film [28]. Considering the similar interaction between phosphate radical and titanium(IV), we used 1-amino-8-naphthol-3,6-disodium sulfonate (ANDS) and mercury ions to form stable ground-state complex, which was then used as templates to induce congregation of TiO₂ particulates in sol–gel process. Mercury ions with relatively small size were easily washed away, recognition sites would be achieved through coordination interaction and size effect of template ions. In this work, formation of stable ground-state complex, imprinting technology and electrochemical response on TiO₂ imprinted thin film will be reported.

2. Experimental

2.1. Apparatus and material

Amperometric measurements were carried out using Potentiostat/Galvanostat Model 283 (EG&G Princeton Applied Research) controlled by the M270 software. A three-electrode configuration containing a homemade graphitic working electrode ($S=0.50\text{ cm}^2$), an SCE reference electrode and a Pt counter electrode was used for electrochemical measurements. All potentials are reported versus the SCE reference at room temperature. For the ultraviolet measurements, an ultraviolet–visible spectrophotometer of Model UV-2102 (Unico instrumental Co., Shanghai) was used. Acetate buffer solution was used as refer solution in this case (wavelength: 200–500 nm; slit: 2 nm; scan precision: 3 nm).

Mercury nitrate and other nitrates are of analytical grade. Acetate buffer solutions were prepared by adjusting 0.10 mol/l sodium acetate to the desired pH with the addition of 0.10 mol/l glacial acetic acid. Mercury nitrate and other nitrates for analysis were prepared with acetate buffer solutions of pH 4.7. Doubly distilled water was used throughout.

2.2. Formation of ground-state complex of ANDS and mercury ions

Prepare a series of mixed solutions containing 5.00×10^{-5} mol/l ANDS and variable concentrations of mercury ion ranging from 6.67×10^{-6} to 1.00×10^{-3} mol/l. The absorption spectra were recorded from 200 to 500 nm. The complexing ratio was estimated by curve fitting.

2.3. Preparation of imprinted TiO₂ thin film by sol–gel technology

Under constant stirring, 1 ml diethyleneglycol were added into 8 ml of isopropanol and then dense nitric acid was added to adjust the solution to pH 2. To the above solution, 1 ml of titanium(IV) isopropoxide dissolved in 3 ml of isopropanol was added. The resulting solution was slowly hydrolyzed under constant stirring at room temperature for 4 h. To the aforementioned solution, 5 ml of acetate buffer solution containing 10 mmol/l ANDS and 5 mmol/l Hg²⁺ was added. The resulting pH value was about 2–3 and the final concentrations of titanium(IV) isopropoxide and ANDS were about 2 and 3 mmol/l, respectively. The mixed solution was stirred for another 2 h and kept for 5 days to ensure titanium(IV) isopropoxide to hydrolyze. With solvent volatilizing slowly, a dark yellow TiO₂ suspension sol was finally obtained.

A polished graphitic electrode was immersed in the solution for 20 min and dried in air and then heated in oven at 85 °C for 5 h. Then the electrode was treated with 0.10 mol/l HClO₄ solution and then washed by doubly distilled water to remove the mercury ions. Thus, an electrode modified with TiO₂ imprinted thin film was made. For comparison, a controlled TiO₂ film was prepared with ANDS instead of the stable ground-state complex and a pure TiO₂ film was also made according to the same sol–gel method.

2.4. Electrochemical measurements

The graphitic electrode modified with imprinted TiO₂ film was immersed in a acetate buffer solution of pH 4.7 and cycled between +0.80 and –0.80 V at 100 mV/s. Different volumes of mercury ions were added and the response was recorded with the blank corrected. Linear sweep voltammetry (LSV) was chosen as an effective way to record the responses on the imprinted electrode. The responses on the controlled and pure TiO₂ electrodes were also studied. After each measurement, the electrode was immersed in 0.10 mol/l HClO₄ to remove mercury ions.

3. Results and discussions

3.1. Formation of stable ground-state complex

A series of solutions containing 5.00×10^{-5} mol/l ANDS and different concentrations of mercury ions exhibited different UV-absorbance spectrum (Fig. 1). It could be seen that ANDS in acetate buffer solution had much strong absorbance peaks at 236, 344 and 359 nm. After addition of mercury ions, peaks at 344 and 359 nm were depressed, while two new strong peaks appeared at 263 and 431 nm. The peak at 236 nm became weaker and blue-shifted firstly, and then became stronger and red-shifted with concentration of mercury ions increased. The intensity of the absorbance spectrum changed gradually at four wave bands, and three isoabsorptive points

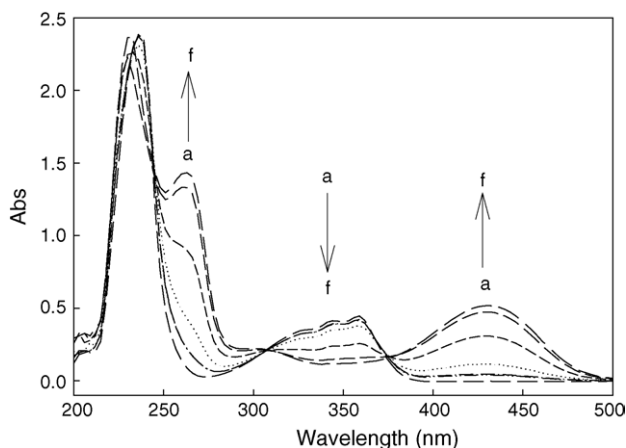


Fig. 1. UV spectra. The concentration of ANDS is 5.00×10^{-5} mol/l, the concentration of mercury ions is: (a) 0 mol/l; (b) 5.00×10^{-5} mol/l; (c) 1.00×10^{-4} mol/l; (d) 2.00×10^{-4} mol/l; (e) 4.00×10^{-4} mol/l; (f) 8.00×10^{-4} mol/l.

existed at 245, 308 and 374 nm. It could be observed by naked eyes that the color of the solutions changed from lilac to yellow. It was in agreement with the result of fluorescence spectrum, in which fluorescence quenching was observed because mercury ions absorbed some part of excitation energy of ANDS (not given). This explained that strong and complexing interaction occurred between mercury ions and ANDS, and stable ground-state complex was formed with its own characteristic absorbance spectrum.

The formation of the ground-state complex seems to depend on the interaction between ANDS and mercury ions. One can write:



A represents ANDS. According to the law of mass action, the corresponding apparent equilibrium constant K can be expressed as the following:

$$K = \frac{[\text{A}_n(\text{Hg}^{2+})_m]}{[\text{A}]_f^n [\text{Hg}^{2+}]^m} \quad (2)$$

$[\text{A}_n(\text{Hg}^{2+})_m]$, $[\text{A}]_f$ and $[\text{Hg}^{2+}]$ are the concentrations of respective species in solution. To indicate the degree of association between ANDS and Hg^{2+} in the solution, a parameter, α is defined as the ratio of free and total concentration of ANDS:

$$\alpha = \frac{[\text{A}]_f}{[\text{A}]_t} = \frac{\text{A}}{\text{A}_0} \quad (3)$$

A_0 is the absorbance of ANDS in acetate buffer solution and A is the absorbance of ANDS when mercury ions were added, Eq. (2) can then be expressed as:

$$K = \frac{([\text{A}]_t - [\text{A}]_f)}{n[\text{A}]_f^n [\text{Hg}^{2+}]^m} \quad (4)$$

According to Eq. (3), Eq. (4) can be converted to the following equation:

$$K = \frac{(1 - \alpha)}{n\alpha^n [\text{A}]_t^{n-1} [\text{Hg}^{2+}]^m} \quad (5)$$

Then the relationship between α and mercury concentration $[\text{Hg}^{2+}]$ can be expressed as:

$$\frac{\alpha^n}{(1 - \alpha)} = \frac{1}{nK[\text{Hg}^{2+}]^m [\text{A}]_t^{n-1}} \quad (6)$$

We assume that absorbance at 344 nm is only caused by free ANDS and stable ground-state complex causes no absorbance at this wavelength. Thus, absorbance peak at 344 nm was chosen to investigate complexing ratio of ANDS and mercury ions.

The functional relationship between α and the concentration of mercury ions is governed by different m , n and K . Changing the ratio of $m:n$ from 1:3 to 3:1 and adjusting the overall apparent equilibrium constant K can change the curvatures of fitting curves. The curve fitting for coordination of ANDS and mercury are shown in Fig. 2. The real lines represent different fitting curves corresponding to different ratios of $m:n$, and the hollow circles are the experimental data obtained. It can be seen, mercury ions yields a fairly good fit to curve 4. This suggests a 2:1 mercury ions/ANDS complexing ratio with a reasonable apparent equilibrium constant of $6.08 \times 10^6 \text{ l}^2 \text{ mol}^{-2}$. This indicates that one ground-state complex molecule is composed by one ANDS molecule and two mercury ions.

3.2. Preparation of the imprinted TiO_2 film

In the present paper, titanium(IV) isopropoxide was firstly slowly hydrolyzed at pH 1–3. The stable ground-state com-

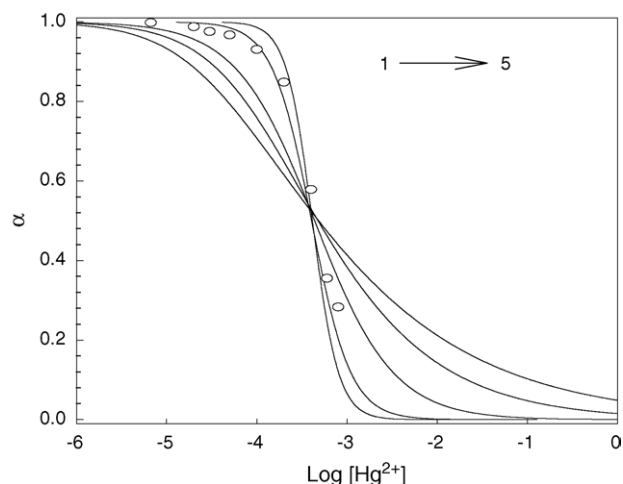


Fig. 2. The parameter values (α) as a function of $\log [\text{Hg}^{2+}]$. The experimental data were calculated from Eq. (6). The circles are experimental observed data points: (1) $m:n = 1:3$, $K = 1.50 \times 10^{12} \text{ l}^3 \text{ mol}^{-3}$; (2) $m:n = 1:2$, $K = 5.37 \times 10^7 \text{ l}^2 \text{ mol}^{-2}$; (3) $m:n = 1:1$, $K = 2.58 \times 10^3 \text{ l mol}^{-1}$; (4) $m:n = 2:1$, $K = 6.08 \times 10^6 \text{ l}^2 \text{ mol}^{-2}$; (5) $m:n = 3:1$, $K = 1.41 \times 10^{10} \text{ l}^3 \text{ mol}^{-3}$.

plex of ANDS and mercury ions was then added in when small particulated center was formed in the sol solution. Further hydrolysis of titanium(IV) isopropoxide was induced around the center by the two sulfonate groups of ANDS. Then the solution was kept in air for 5 days, and the solvent slowly volatilized. Finally, the sol system condensed further more and became viscous, clear and dark yellow. If the templates and titanium(IV) isopropoxide were added together rather than by the above-mentioned method, the templates might be embedded in the particulated TiO_2 , resulting in incomplete removal of mercury ions. If the solution was not aged for enough time, the solution was not viscous enough. Therefore, in order to achieve an imprinted film with good performance, the solution was aged for 5 days before casting onto a graphite surface as a film. The treatment of the film with $0.10 \text{ mol/l HClO}_4$ solution aimed to wash the templates out, while ANDS still remained in the imprinted film. Thus, cavities with specific size and shape in the TiO_2 film were created, which exactly matched the template molecules.

3.3. The electrochemical response toward mercury ions on the imprinted film

The prepared TiO_2 sol–gel solution was spitted on the graphitic electrode surface and then cycled in black acetate solution after dryness. The oxidation peak of Hg^{2+} at $+0.35 \text{ V}$ and redox peaks of ANDS at -0.05 and -0.35 V were observed, which confirmed complexing templates were embedded in the TiO_2 material. After the imprinted electrode was washed with $0.10 \text{ mol/l HClO}_4$ solution, the oxidative peak of mercury ions disappeared, while the peaks of ANDS still remained. This indicates mercury ions can be removed from the porous sol–gel film. However, ANDS, which is larger in size, is withheld in the TiO_2 material through coordination interaction between sulfonate groups and titanium(IV).

The cyclic voltammograms recorded in the presence of mercury ions on the imprinted, controlled and pure TiO_2 electrodes in acetate buffer solutions are shown in Fig. 3. On the controlled electrode, a small oxidative peak is seen at about $+0.60 \text{ V}$ when the concentration of mercury ions reaches $1.00 \times 10^{-4} \text{ mol/l}$. On the imprinted electrode, a significant oxidative peak of mercury ion appears at about $+0.35 \text{ V}$. Compared with that on the controlled electrode, the oxidation potential of mercury ions shifts positively on the imprinted electrode. While on the pure TiO_2 electrode, no response toward the mercury ions is observed. It confirms that recognition sites for the target analyte are tailored in TiO_2 film, mercury ions are embedded during preparing process.

Mercury ions may react with ANDS after they are captured by the imprinted film. With increase of scan numbers, the oxidative peak current of mercury ions decrease and shift negatively (not shown). Yet, the oxidative peak currents of ANDS decrease at -0.35 V and increase at -0.05 V . Here, ANDS act as an electron donor and mercury ions act as an electron receptor. It can be proposed reasonably, after enter-

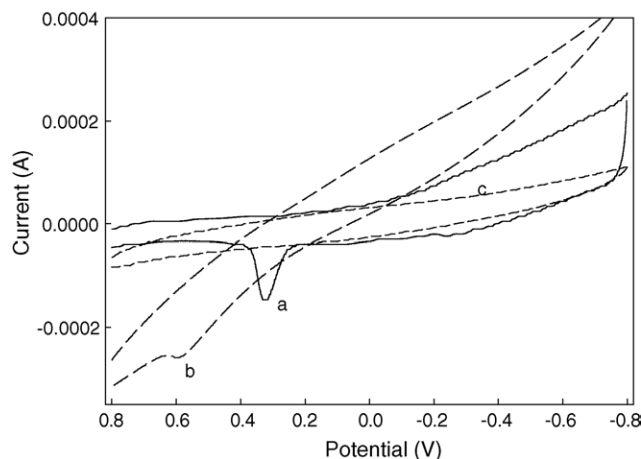


Fig. 3. The CV responses of: (a) $1.00 \times 10^{-5} \text{ mol/l Hg}^{2+}$ on the imprinted TiO_2 film electrode; (b) $1.00 \times 10^{-4} \text{ mol/l Hg}^{2+}$ on the controlled TiO_2 film electrode; (c) $1.00 \times 10^{-4} \text{ mol/l Hg}^{2+}$ on the pure TiO_2 film electrode; pH 4.7; scan rate: 100 mV/s .

ing into the recognition sites, mercury ions might catalyze oxidation of ANDS and then be reduced. So, only an oxidative peak of mercury ions is observed. After 10 scans, the oxidative peak current of ANDS decreases too.

In our experiment, the oxidative peak current of mercury ions increases linearly with increasing scan rate from 10 to 400 mV/s . The equation could be expressed as: $I_p = 5.99 \times 10^{-7} + 5.60 \times 10^{-6}(v)^{1/2}$ ($r = 0.9975$). This indicates that the redox reaction of mercury ions on the imprinted TiO_2 imprinted film is a diffusion-controlled process [29].

The effect of conditioning time in $1.00 \times 10^{-6} \text{ mol/l Hg}^{2+}$ solution on its anodic peak current at the imprinted electrode was investigated (not shown). The oxidation peak current increases rapidly within 3 min and levels off after 4 min. From the point of view of rapid response of sensor, response time of 4 min was selected for the assay of Hg^{2+} . Linear sweep voltammetry was used to record the responses. After each measurement, the electrodes were treated with $0.10 \text{ mol/l HClO}_4$ to remove mercury ions from the membrane phase. The oxidation peak current of mercury ions increased gradually with increasing concentration of mercury ions from 1.00×10^{-8} to $1.60 \times 10^{-6} \text{ mol/l}$ and became saturated above $1.80 \times 10^{-6} \text{ mol/l}$ (seen in Fig. 4). Linear calibration plot is obtained in the concentration range for mercury ions as one can see from Fig. 5a. The regression equation is: $I_p (\mu\text{A}) = 4.29 \times 10^{-7} + 19.40 [\text{Hg}^{2+}]$ with a correlation coefficients of 0.9984. The detection limit defined as the concentration corresponding to a signal three times the noise level of the background was $3.06 \times 10^{-9} \text{ mol/l}$. The response of mercury ions on controlled electrode was also studied (shown in Fig. 5b). Because the controlled film was also porous with only ANDS added, mercury ions could enter into the holes in some part. Compared with the response on the imprinted electrode, it was much weaker on the controlled electrode. It can be deduced that metal ions (templates) really play an important role in the formation of recognition cavi-

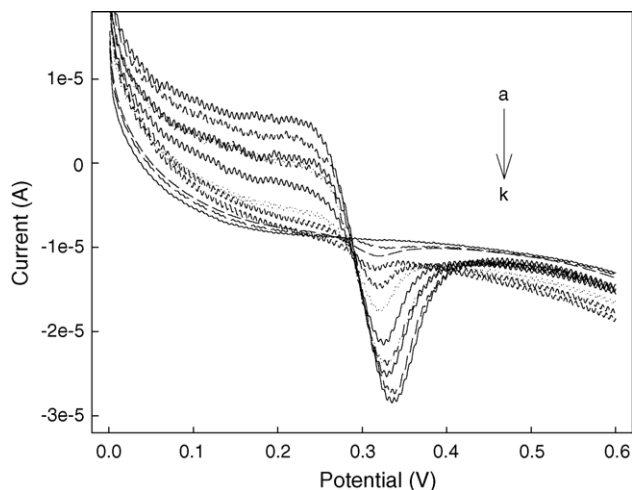


Fig. 4. LSV response of Hg^{2+} on the imprinted TiO_2 film. The concentration of Hg^{2+} is: (a) 0 mol/l; (b) 5.00×10^{-8} mol/l; (c) 1.00×10^{-7} mol/l; (d) 3.00×10^{-7} mol/l; (e) 5.00×10^{-7} mol/l; (f) 7.00×10^{-7} mol/l; (g) 9.00×10^{-7} mol/l; (h) 1.10×10^{-6} mol/l; (i) 1.30×10^{-6} mol/l; (j) 1.60×10^{-6} mol/l; (k) 1.80×10^{-6} mol/l.

ties. Moreover, it was observed that the peak potential shifted positively with the concentration of mercury ions increasing. A proportional relationship between the concentration and potential existed.

3.4. The selectivity of the imprinted film

The influence of interference was evaluated by measuring the peak current changes of 20 mmol/l Hg^{2+} , Cu^{2+} , Ag^+ , Pb^{2+} and Ni^{2+} on the imprinted and controlled electrodes, respectively. The results are plotted in Fig. 6. One can see that the sensitivity of the controlled electrode follows the sequence: Cu^{2+} , Ni^{2+} , Hg^{2+} , Pb^{2+} and Ag^+ . On the imprinted electrode, the selectivity to mercury ions was enhanced greatly. From

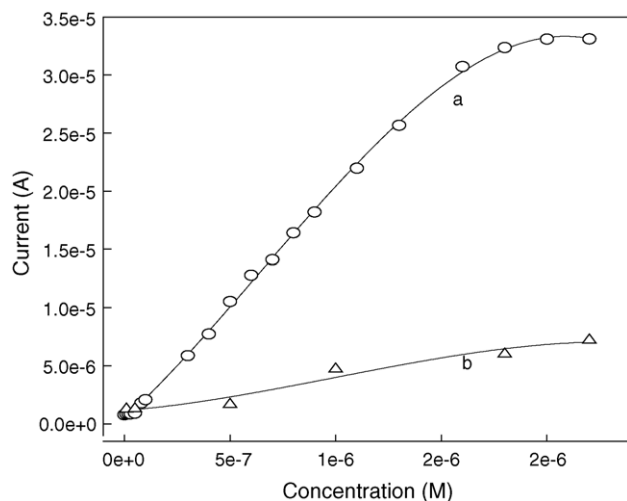


Fig. 5. Calibration curves for Hg^{2+} on: (a) the imprinted electrode and (b) the controlled electrode.

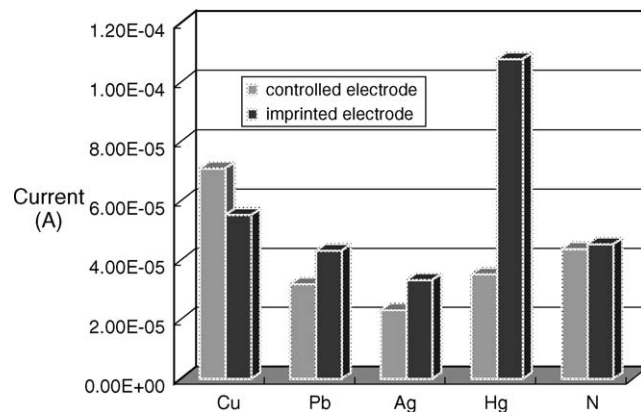


Fig. 6. The peak current response of 2.00×10^{-5} mol/l Hg^{2+} on the imprinted TiO_2 film electrode and controlled TiO_2 film electrode.

these experiments, it can be proposed that the recognition sites are organized according to the size and stereochemical structure of mercury ions in the imprinted film, which in turn optimized the diffusion of the target ions. The mercury ions can react with ANDS through coordination interaction after permeating the recognition sites and catalyzes the oxidation of ANDS. Though other metal ions can enter into the porous imprinted film in some extent, no available interaction is observed between the ions and recognition sites. The formation of recognition sites for mercury ions may be attributed to the coordination interaction between mercury ions and ANDS, together with the $\text{Ti}-\text{OH}$ group in the TiO_2 film.

3.5. Reversibility, reproducibility and lifetime

It is desirable that the imprinted inorganic material is stable and reversible during the washing and assay process. The same concentration of Hg^{2+} were detected more than five times, the relative standard deviation (R.S.D.) is less than 5%. Recovery experiments were carried out with calibration curve method. Acceptable recoveries are obtained at both high and low concentrations as shown in Table 1. The results suggest that it is feasible to apply the proposed method to detect mercury ions selectively.

When the sol system was aged enough, different imprinted films were made using the same electrode. The R.S.D. response value to Hg^{2+} is less than 15% ($n = 3$). When differ-

Table 1
Recovery experiment

Added (10^{-7} mol/l)	Found (10^{-7} mol/l)	Recovery (%)
0.65	0.64 ± 0.01	98.5
3.11	3.04 ± 0.01	97.8
4.05	3.85 ± 0.01	95.1
6.47	6.87 ± 0.04	106.2
8.58	8.73 ± 0.10	101.8
11.60	11.38 ± 0.13	98.1

ent electrodes were considered, the phenomenon of catalysis, response and selectivity was also observed.

The current response on the imprinted electrode remained 90% of the initial response if it was stored in air at room temperature. And the imprinted electrode could be used for more than 1 month, if used every day, for more than 200 assays if being stored in diluted mercury ion solutions.

4. Conclusion

A stable ground-state complex was formed by mercury ions and ANDS with 2:1 mercury ion/ANDS complexing ratio. The stable ground-state complex used as compound template could induce congregation of particulated TiO₂ during the sol–gel process. The imprinted TiO₂ material was treated with HClO₄ to wash out mercury ions. ANDS with larger size remained in the TiO₂ material through the coordination interaction between sulfonate groups and titanium(IV). Thus, the imprinted sites for mercury ions were generated in the TiO₂ material. Compared with the results obtained on the controlled and pure TiO₂ electrodes, the response on the imprinted electrode indicated that mercury ions played an important role in the formation of recognition cavities, and the selectivity for mercury ions on the imprinted electrode was greatly enhanced. The response became stable within 4 min. The linear range was from 1.00×10^{-8} to 1.60×10^{-6} mol/l with a detection limit of 3.06×10^{-9} mol/l. The inorganic imprinted film prepared is stable and can be used for more than 200 times.

Acknowledgements

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