

# Self-assembled sulfonated $\beta$ -Cyclodextrin layer on gold electrode for the selective electroanalysis of dopamine

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**Abstract** Gold electrode with self-assembled *D,L*-cysteine grafted  $\beta$ -cyclodextrin sulfonic acid (Cys- $\beta$ -CD~SO<sub>3</sub>) layer was fabricated and used to investigate the electrochemical behavior of dopamine. The experimental results indicated that the self-assembled Cys- $\beta$ -CD~SO<sub>3</sub> layer modified gold electrode has selective electrochemical response to dopamine with high sensitivity and excellent tolerance of ascorbic acid, which is the most common accompanying component in biological samples. Dopamine could be accurately determined in the concentration range of 1–200  $\mu$ M in the presence of ascorbic acid of 5 mM. The relative standard deviation of 1.9% ( $n=5$ ) was achieved at a dopamine concentration of  $5 \times 10^{-5}$  M. The proposed sensor was successfully applied to the determination of dopamine in human blood serum samples.

**Keywords** Dopamine · Ascorbic acid · Sulfonation ·  $\beta$ -cyclodextrin · Self-assemble

## Introduction

Dopamine (DA) is a kind of natural catecholamine neurotransmitter. It has active reactivity and is widely distributed in the mammalian central nervous system for message transfer [1]. The decrease of dopamine in mankind nervous system could cause some serious diseases such as Parkinson's disease [2, 3], so the determination of dopamine plays an important role in the study of its physiolog-

ical mechanism and diagnosis of corresponding diseases and has attracted much attention from researchers since the electrochemical characteristics of DA were discovered in 1970s. However, in samples of animal and human body fluids, ascorbic acid (AA) exists as accompanying components with DA and its concentration is much higher than DA [4]. It makes the determination of DA using electrochemical methods difficult due to overlapping of their oxidization peaks as a result of the very similar redox potentials they have. The existence of AA gives rise to severe interference to the determination of DA. Therefore, finding selective ways for the determination of DA in the existence of AA has been an attractive research topic. Chemical modification of electrode is one of the powerful methods proposed for this purpose; examples include fabrication of selective membrane [5–8], utilization of derivatization reaction [9] and surface treatment of electrode with heat or laser [10]. Among these methods, modified electrodes based on the selective membrane have received more attentions. Since 1985, Nagyet had made electrode using Nafion [11] as a modifier to attract positively charged DA molecules while precluding negatively charged AA, the negatively charged polymer film modified electrodes have been reported largely. However, this kind of electrode usually suffers from slow response due to a smaller diffusion coefficient value in the film [12], whereas conducting polymer-modified sensors have hydrophobic surfaces that would adsorb proteins easily.

Since the methodology of self-assembled monolayers (SAMs) was first introduced by the research group of Sagiv [13], it has become true in many cases that molecules could be arranged according to people's expectation. Because self-assembled monolayers have well-organized structure and relatively high stability, SAMs are often used for photoelectrochemistry, chemical and biological sensors,

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surface modification of electrode for electrocatalysis, and the fabricating of sensitive membranes with biological and biomimetic affinities, etc. This methodology can render special and remarkable properties to electrodes and also broaden the possible application fields of electrochemistry [14–21]. SAMs modified electrodes were also proposed for the determination of DA [22–28].

Gold provides a platform for self-organized assemblies [29–35] for the detection of DA. It had been reported that different SAMs with negatively charged organosulfur compounds [12, 36, 37] attached on gold electrodes could selectively detect DA in the presence of AA due to the different electrostatic interactions between the self-assembled layer and AA. However, the responsible currents decrease significantly due to the hindrance of the dense layer on the electrode. So there is a need to further develop a highly sensitive method to detect DA.

$\beta$ -cyclodextrin, a cyclic oligosaccharide composed of glucopyranose units, has a conical cone structure owning hydrophobic interior and hydrophilic exterior, which contributes it to fabricating sensitive membranes for electrochemical sensors with some functions such as surface catalysis, concentrating of the analyte, and selective analysis [38–41].  $\beta$ -CD is often self-assembled onto electrode surfaces by the reaction of its hydroxyl with a thiol-containing molecule, through this way, several sensors based on  $\beta$ -CD have been constructed [42–47]. For example, electrodes with self-assembled monolayer of  $\beta$ -CD linked on gold surface by strong interaction between the grafted thiols on  $\beta$ -CD and gold atom was obtained [48].

In the present work, modified gold electrode with self-assembled Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  layer was obtained through the strong interaction between gold and thiol group incorporated into  $\beta$ -CD cavity. An electrochemical method was proposed for the selective detection of DA. Introducing sulfonic groups and carboxyl on  $\beta$ -CD was used for increasing the tolerance of ascorbic acid through the stereo effect and electrical repulsion of negative groups. Good selectivity toward DA was achieved by the prepared modified electrode. It is very suitable for the selective and sensitive determination of DA in the presence of AA in human blood serum samples.

## Experiments

### Apparatus

Electrochemical measurements were performed on a CHI660B electrochemical workstation (Shanghai Chenhua Instruments, Shanghai) connected to a personal computer, with a three-electrode system comprising a platinum wire as auxiliary electrode, a saturated calomel electrode as reference

electrode, and the Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  modified gold electrode as working electrode.

UV spectra were recorded with a TU-1901 UV/Vis spectrophotometer (Beijing Purkinje General Instrument). Infrared spectra was recorded with a FT-IR Paragon 500 spectrometer (Perkin Elmer, CO, USA). The  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were recorded on a Bruker Avance AV500 NMR spectrometer (Switzerland),  $\text{D}_2\text{O}$  was used as solvent. The elemental analyses were performed with a Perkin Elmer PE2400II Elemental Analyzer (USA). The other apparatus include a DZF-6020 vacuum drying oven (Yiheng Technology) and a THZ-82 shaker equipped with a water bath thermostat (Ronghua Instrument).

### Reagents

Pyridine (Merck analytical grade) was refluxed for 12 h in KOH solution, dried with solid CaO, and distilled before using. Analytical grade dimethyl formamide (DMF) was dried with solid CaO for several days and distilled before using.  $\beta$ -CD was recrystallized twice from water and dried for 12 h at 120 °C under vacuum. The other reagents, including dopamine hydrochloride, *D,L*-cysteine and *p*-toluene sulfonyl chloride, were of analytical grade and used without further purification. Redistilled water was used throughout the study.

### Synthesis of Cys- $\beta$ -CD- $\text{SO}_3\text{H}$

The solution of 0.5 g *p*-toluene sulfonyl chloride dissolved in 10.0 mL pyridine was slowly dropped into 10.0 mL pyridine solution containing 3.0 g  $\beta$ -CD with vigorous stirring under ambient temperature. After the mixture solution was stirred for 36 h, it was distilled under reduced pressure. The remaining solid was soaked into acetone for 5–6 min, then it was filtered, washed with acetone until pyridine was completely removed, then the resulting 6-OTs- $\beta$ -CD [49, 50] was dried under vacuum.

Solid KI was added to 6-OTs- $\beta$ -CD solution dissolved in DMF and nitrogen was bubbled in the mixture solution to eliminate the dissolved oxygen and then the flask was sealed and stirred at a high speed at temperature of 80–90 °C for 4 h. The reacted mixture was soaked in acetone for 10 min, filtered, and dried in the vacuum to obtain solid  $\beta$ -CD-I [51].

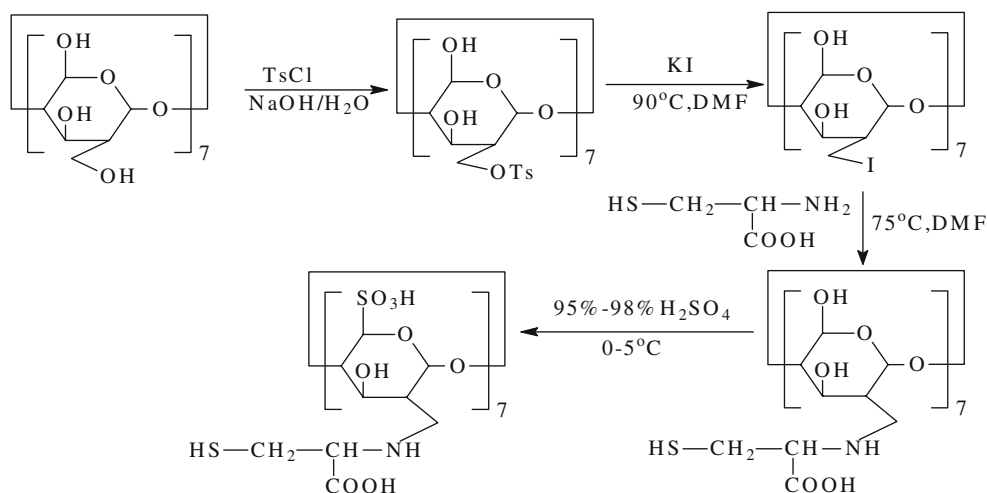
A solution of *D,L*-cysteine in  $\text{NaCO}_3$  was slowly dropped into a flask containing  $\beta$ -CD-I dissolved in DMF after oxygen removal through nitrogen bubbling. The reaction vessel was sealed and stirred with a high speed at 75 °C until the primary solution became dark red. The mixture was distilled under reduced pressure, then the remaining solid product was washed with acetone for three times and dried for 24 h to obtain *D,L*-Cys- $\beta$ -CD [51, 52].

A 30-mL volume of 80% (m/m)  $\text{H}_2\text{SO}_4$  solution and 10 g Cys- $\beta$ -CD were added sequentially into a 100-mL round bottomed flask and stirred for 2 h at 0–5 °C. The reacted mixture solution was poured into a beaker containing 500 mL water, then enough solid  $\text{CaCO}_3$  was added. After the reaction of the remained  $\text{H}_2\text{SO}_4$  with  $\text{CaCO}_3$  was completed, the mixture was filtered and washed with water. One hundred milliliters 95% (v/v) alcohol was added into the filtrate and waited until no more precipitate formed. The solution was filtered again and the filtrate of alcohol was adjusted to pH 10.5 using  $\text{NaCO}_3$  solution, filtered another time, filtrate was adjusted to nearly pH 7.0 with acetic acid and condensed carefully. Five hundred milliliters alcohol was added to the condensate to produce white precipitate and the mixture was filtered. The white precipitate was washed with alcohol, acetone and ethyl ether, respectively. Finally, it was dried under the vacuum to get white powder of (Cys- $\beta$ -CD~ $\text{SO}_3\text{H}$ )[53]. The whole synthesis procedure is schematically shown in Scheme 1.

#### Modification of gold electrode/glass carbon electrode

The bare gold electrodes were polished with 0.05  $\mu\text{m}$  polishing powder to smooth mirror before modification. Then it was rinsed with water, sonicated in absolute ethanol, 1:1 (v/v) nitric acid and water sequentially. After rinsing with water again, the polished electrodes were then electrochemically cleaned by cycling the potential between –0.3 and 1.5 V at the scan rate of 0.1 V/s in 0.10 M  $\text{H}_2\text{SO}_4$  until the constant background cyclic voltammogram for the bare gold electrode was obtained. Finally, the freshly pretreated gold electrode was immersed in water solution of Cys- $\beta$ -CD~ $\text{SO}_3\text{H}$  for 24 h for the formation of self-assembled layer on the electrode surface to obtain the Cys- $\beta$ -CD~ $\text{SO}_3\text{H}$  modified gold electrode. The electrode was rinsed with water to remove physically adsorbed species before use.

**Scheme 1** Synthesis procedure of D,L-Cys- $\beta$ -CD~ $\text{SO}_3\text{H}$



#### Procedures

The modified electrode, the platinum wire counter electrode, and the reference electrode were immersed in 0.05 M phosphate buffer solution (PBS, pH 6.0) in an electrochemical cell. A certain amount of the DA was added into the cell under stirring by a magnetic bar. The voltammograms were obtained by scanning from –0.30 to +0.70 V (vs. SCE). The anodic peak currents of DA were recorded. The amperometric measurements were performed at a potential of 0.5 V (vs. SCE), and current–time ( $I$ – $t$ ) curves were recorded.

#### Results and discussion

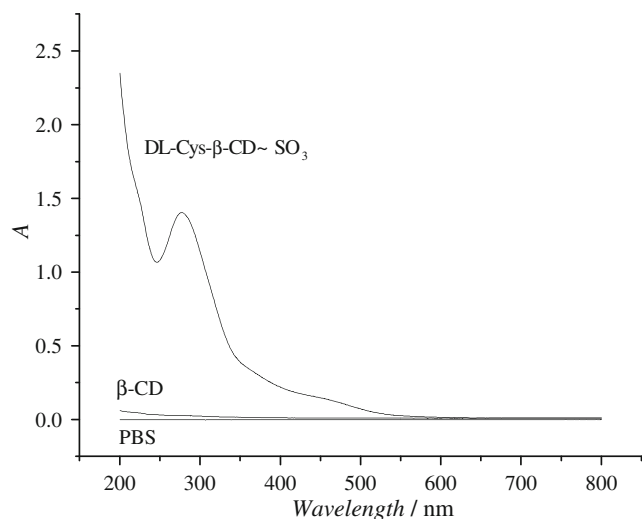
##### Structure characterization

The ultraviolet absorption spectra for Cys- $\beta$ -CD~ $\text{SO}_3$  and  $\beta$ -CD in the 200–800 nm region are given in Fig. 1.

There are absorption peaks that appeared at 280 nm and 246 nm for Cys- $\beta$ -CD~ $\text{SO}_3$ . The former is a strong peak generated from thiol groups; and the later is a weak one generated from amine groups. But no obvious absorption can be seen in the region from 200 nm to 800 nm for  $\beta$ -CD. This indicates that Cys was successfully linked onto  $\beta$ -CD.

Figure 2 is the infrared spectrum of Cys- $\beta$ -CD~ $\text{SO}_3$ . The characteristic peak of –OH at  $3,427\text{ cm}^{-1}$  indicates that only portion of –OH in Cys- $\beta$ -CD have participated the reaction of sulfonation. The characteristic peaks of –SH at  $2,368\text{ cm}^{-1}$ , – $\text{COO}^-$  at  $1,631\text{ cm}^{-1}$  and – $\text{NH}_2$  at  $1,459\text{ cm}^{-1}$  indicate that D,L-Cys has been linked to  $\beta$ -CD. The characteristic peak of – $\text{SO}_3\text{H}$  at  $1,377\text{ cm}^{-1}$  suggests that  $\beta$ -CD has been sulfonated.

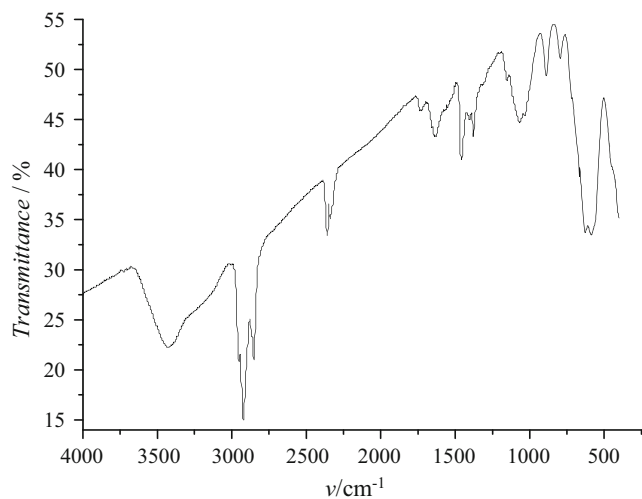
$^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectroscopy were used to confirm the structure of the molecules. The  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra are shown in Fig. 3.  $^1\text{H}$ NMR(500 MHz,  $\text{D}_2\text{O}$ - $d_6$ )  $\delta$  (ppm) relative to TMS at 8.37–8.39 and 1.83–1.96 respec-



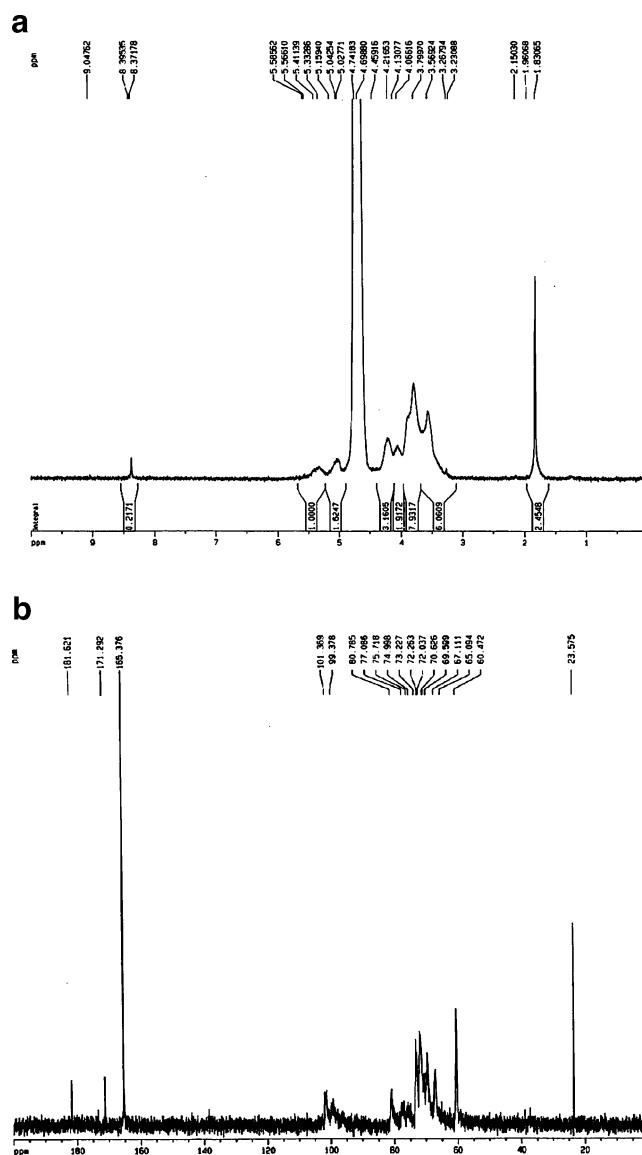
**Fig. 1** UV spectrum of  $\beta$ -CD- $\text{SO}_3\text{H}$ ,  $\beta$ -CD, and PBS; 2 mmol/L  $\beta$ -CD- $\text{SO}_3\text{H}$ , 2 mmol/L  $\beta$ -CD in 0.05 M PBS

tively indicates that  $-\text{NH}_2^+$  and  $-\text{SH}$  exist in Cys- $\beta$ -CD- $\text{SO}_3$ . The proton in  $-\text{SO}_3\text{H}$  and  $-\text{COOH}$  could be replaced by  $\text{Na}^+$ , so they could not be reflected in the spectrum. The  $\delta$  of other protons are respectively at 3.2–4.5 and 5.0–5.6.  $^{13}\text{C}$ NMR(125 MHz,  $\text{D}_2\text{O}-d_6$ )  $\delta$  (ppm) relative to TMS at 165.37, 101.37, and 23.57 respectively indicates that  $-\text{COO}^-$ ,  $-\text{O}-\text{CH}-\text{O}-$ , and  $-\text{CH}_2\text{SH}$  exist in Cys- $\beta$ -CD- $\text{SO}_3$ . The  $\delta$  of other carbons are respectively at 60.47–80.78.  $^1\text{H}$ NMR(500 MHz) and  $^{13}\text{C}$ NMR(125 MHz) spectral data indicate that L-Cys and  $-\text{SO}_3\text{H}$  were successfully linked onto  $\beta$ -CD.

The product was further purified by flash column chromatography on a silica gel using ether as the solvent to yield pure product as a white solid. Elemental analysis showed C 37.53%, H 5.24%, N 2.23%, and S 11.1% by weight, which indicated that only a of the hydroxy groups in  $\beta$ -CD is substituted.



**Fig. 2** FT-IR spectrum of Cys- $\beta$ -CD- $\text{SO}_3\text{H}$



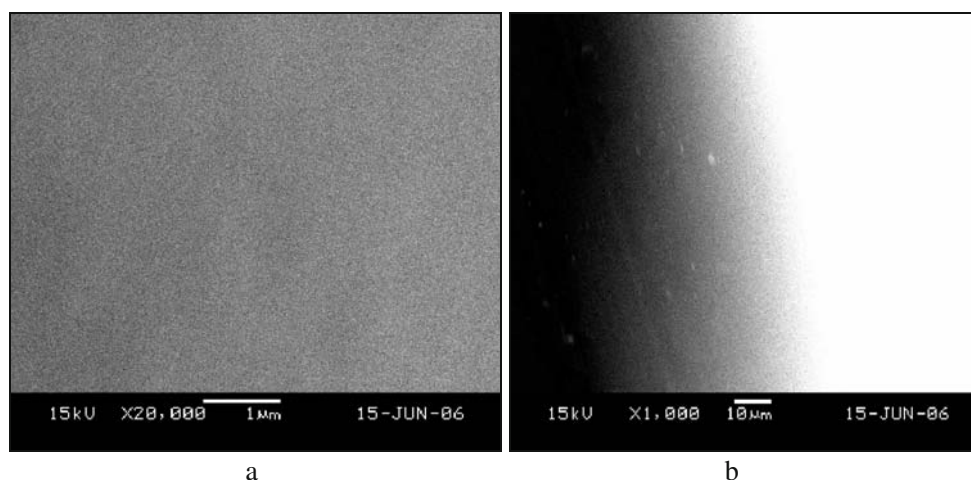
**Fig. 3** The  $^1\text{H}$ NMR (500 MHz) (a) and  $^{13}\text{C}$ NMR (125 MHz) (b) spectra of the product in  $\text{D}_2\text{O}$

The back-scattering electron images (BEI) of scanning electron microscope (SEM) of gold electrode surface with Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  are given in Fig. 4. Image (a) is the back scattering image of the modified electrode surface, the shadow area and bright area of (b) are modified layer and bare gold surface respectively. The comparison of the images suggests that Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  has self-assembled onto the gold electrode surface.

Cyclic voltammograms characteristics of modified electrode

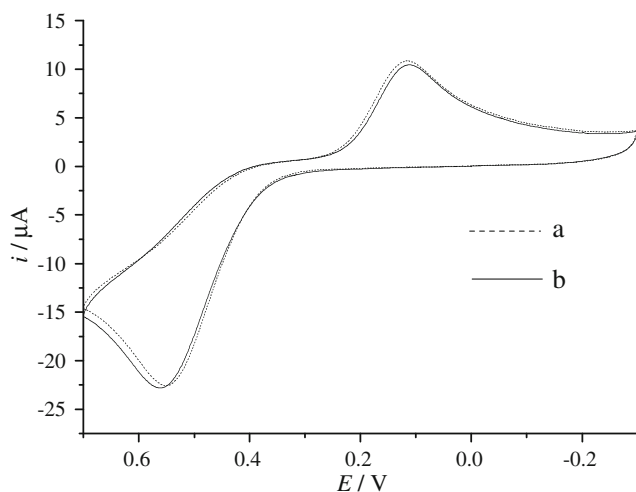
Figure 5 illustrates the curves of the cyclic voltammograms of DA on the Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  modified electrode (a) and on the bare gold electrode (b). In both (a) and (b), there are

**Fig. 4** The back-scattering electron images of Cys- $\beta$ -CD-SO<sub>3</sub>H modified gold electrode. **a** The back-scattering electron images of modified electrode surface; **b** BEI of the modified layer (*black area*) and non-modified layer surface (*white area*)



oxidization peak at 0.53 V and reduction peak at 0.13 V with almost same peak currents for both kinds of electrodes. This indicates that the reduction and oxidation of DA on the modified electrode is reversible and the self-assembled layer almost has no influence to the electrochemical response of the electrode towards DA.

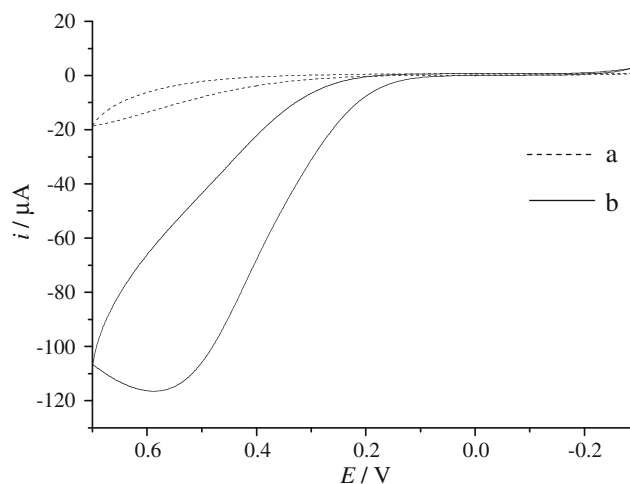
Figure 6 is the cyclic voltammograms of  $5 \times 10^{-4}$  M AA on Cys- $\beta$ -CD-SO<sub>3</sub>H modified electrode (a) and bare gold electrode (b). It is observed that the current of oxidization peak reaches  $-1.15 \times 10^{-4}$  A on the bare gold electrode, but only  $-0.2 \times 10^{-4}$  A on the modified electrode. The response currents of the electrode were recorded in the solutions containing DA and AA in fixed concentrations of  $2.5 \times 10^{-5}$  M and  $2.5 \times 10^{-4}$  M, over a pH range from 4.8 to 6.5, it was found that the currents ratios of the  $i_{DA}/i_{AA}$  remained almost unchanged over the pH range. The results indicate that the oxidation of AA on the modified electrode is negligible probably on account of the repulsion effect from negative sulfo groups and carboxyl groups.



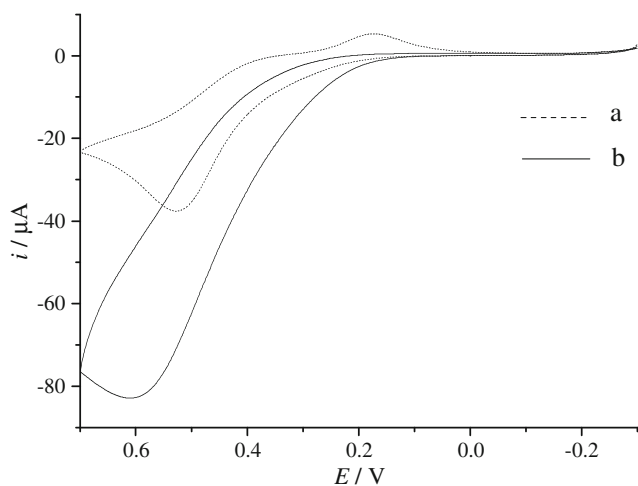
**Fig. 5** Cyclic voltammograms of DA ( $2.0 \times 10^{-5}$  M) on modified gold electrode (a) and bare gold electrode (b)

The cyclic voltammograms of the mixture of DA and AA on Cys- $\beta$ -CD-SO<sub>3</sub>H modified electrode (a) and bare gold electrode (b) are shown in Fig. 7. As can be seen that the oxidization peak current on the modified electrode (a) is only half of that on the bare gold electrode (b), indicating that the modified electrode can produce selective electrochemical response towards DA.

From Figs. 6 and 7, it can be concluded that the electrochemical behavior of DA and AA on modified electrode are independent from each other and the Cys- $\beta$ -CD-SO<sub>3</sub>H modified electrode can selectively response to DA. This suggests the possibility of the selective electrochemical detection of DA with the existence of AA. No evident oxidation peak was observed except a little increase of anodic current with increase of concentration of AA on the modified gold electrode. In our opinion, this effect can be attributed to the fact that the Cys- $\beta$ -CD-SO<sub>3</sub>H modified electrode carries negative charges. As it is known from literature, under the determination conditions, AA loses two electrons and two protons to produce the dehydroascorbic



**Fig. 6** Cyclic voltammograms of AA ( $5.0 \times 10^{-4}$  M) on modified gold electrode (a) and bare gold electrode (b)

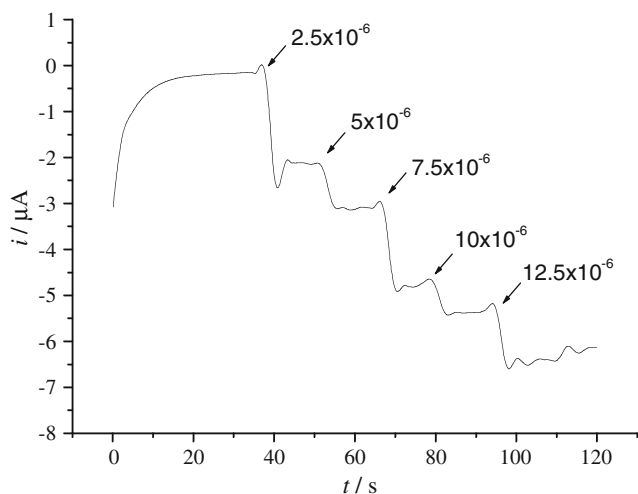


**Fig. 7** Total cyclic voltammograms of the matrix of DA ( $2.5 \times 10^{-5}$  M) and AA ( $2.5 \times 10^{-4}$  M) on modified gold electrode (a) and bare gold electrode (b)

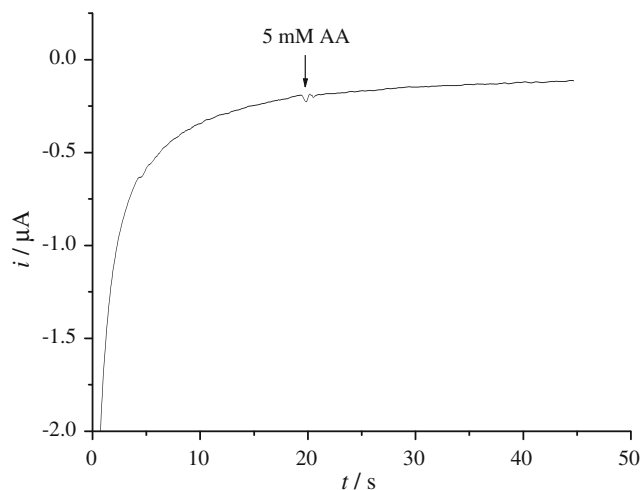
acid, so AA exists in the anionic form ( $pK_a$  4.1) in PBS buffer solution (0.05 M, pH 6.0), while DA ( $pK_a$  8.9) exists in the cationic form. The modified film can attract the cationic DA onto the electrode surface, but it is just opposite for anion AA.

#### Amperometric response of modified electrode

Figures 8 and 9 show the amperometric response curves of DA without and with the existence of AA on Cys- $\beta$ -CD- $SO_3H$  modified electrode respectively. It can be seen from Fig. 8 that the response currents increase linearly with the growth of DA concentration, which indicates that the self-assembled layer of Cys- $\beta$ -CD- $SO_3H$  is very suitable for the detection of DA. Figure 9 shows that there is little amperometric response for AA on Cys- $\beta$ -CD- $SO_3H$



**Fig. 8** The amperometric responses of DA on Cys- $\beta$ -CD- $SO_3H$  self-assembled monolayer modified gold electrode

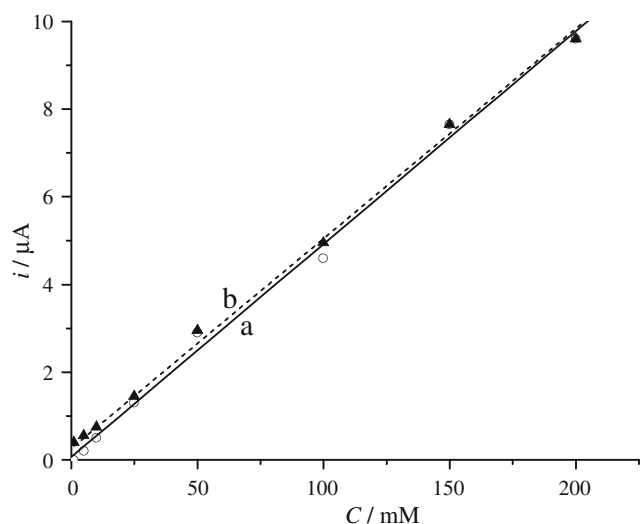


**Fig. 9** The amperometric response of AA on Cys- $\beta$ -CD- $SO_3H$  self-assembled monolayer modified gold electrode

modified electrode, indicating that the influence from AA on the response towards DA could be eliminated, probably because the linked Cys- $\beta$ -CD- $SO_3H$  hinders the permeation of AA in the solution.

#### Calibration curve of amperometric method

In Fig. 10, the calibration curve of DA (free of AA) with Cys- $\beta$ -CD- $SO_3H$  modified gold electrode as the working electrode is almost overlapped by the curve obtained in the presence of AA. Hence the electrochemical determination of DA in the range of 1–200  $\mu M$  with Cys- $\beta$ -CD- $SO_3H$  modified gold electrode as the working electrode is completely practicable when AA exists in sample solutions with concentrations up to 5 mM.



**Fig. 10** The calibration curves of DA (a) and DA+AA (b); AA, 5 mM

**Table 1** Analytical results of DA in spiked human blood serum samples

Serum samples	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ ) ( $n=5$ )	RSD (%)	Recovery (%)
S 1	20	19.67	2.3	98.4
S 2	20	20.71	3.3	103.6
S 3	50	51.32	1.9	102.6

### Interferences

The effects of other organic and inorganic species, coexisting with DA in the serum of healthy human adults, were also investigated. No interference was observed for glucose (500), uric acid (300), urea (200), adrenalin hydrochloride (500), carbamide (300), inosine phosphate (300), tryptophan (200), NaCl (10,000),  $\text{CaCl}_2$  (5,000),  $\text{FeCl}_3$  (250),  $\text{ZnCl}_2$  (2,000),  $\text{CuCl}_2$  (1,500), KCl (10,000), and  $\text{I}^-$  (1,000). Here the data in parentheses are molar ratios of the interfering compounds present in relation to  $2 \times 10^{-5}$  M of DA. It should be mentioned that the contents of these species in the serum samples are far below the tolerance limits listed above when the samples are diluted for the determination, which indicates that the new methodology enables reliable analysis of DA without interference of AA and other components present in serum samples.

### Reproducibility and lifetime of the sensor

To maintain the reproducibility of the Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  modified gold electrode and estimate the precision of determination, the electrode was renewed by soaking the modified electrode in the stirring solution of PBS (pH 6.0) for about 1 min after each measurement. The effectiveness of this regeneration process was evaluated by repetitive determination of  $5 \times 10^{-5}$  M DA, the average current was 2.6  $\mu\text{A}$  with a relative standard deviation of 1.9% ( $n=5$ ). Lifetime of the modified electrode was also investigated, the current responses did not apparently decrease within 20 measurements, 6% of decrease was found after the electrode was scanned for 30 times and only 10% of decrease occurred even after 50 measurements. On the other hand, the modified electrode retained 98.4% of its initial peak current response after 1 month of storage in PBS buffer solution (0.05 M, pH 6.0), this demonstrates a very good stability of the modified electrodes.

### Samples analysis

Human plasma samples obtained from six adult healthy volunteers were analyzed. The serum sample, an ultrafiltrate of plasma, was diluted tenfold with 0.05 M PBS

(pH 6.0) before determination. No dopamine was detected in the healthy blood. The samples were spiked with exogenous DA and analyzed again. The determination results are shown in Table 1. It can be seen that the recoveries and precision for samples were satisfying, suggesting that the proposed method offers reliable reproducibility and practicability.

### Conclusions

In the present investigation Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  modified gold electrode has been fabricated after self-assembling of Cys- $\beta$ -CD- $\text{SO}_3\text{H}$  on the gold electrode surface by the strong coordinate covalent bond between S atom and Au atom, which was also verified by structure characterization with UV, IR spectroscopy, and SEM. The modified electrode showed a selective response to DA. DA could be determined in the concentration range of 1 to 200  $\mu\text{M}$  when AA coexists in sample solutions up to 1 mM. The electrode offers attractive properties such as good reproducibility, high stability, high sensitivity, and wide linear range. The proposed method has demonstrated its practical application for rapid and precise assay of dopamine in practical samples with the existence of AA and other components.

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