Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 67 (2005) 798–805

Talanta

www.elsevier.com/locate/talanta

Solid-contact potentiometric sensor for ascorbic acid based on cobalt phthalocyanine nanoparticles as ionophore

Kun Wang, Jing-Juan Xu, Kai-Shi Tang, Hong-Yuan Chen *

The Key Lab of Analytical Chemistry for Life Science, Department of Chemistry, Nanjing University, Nanjing, 210093, China

Received 31 December 2004; received in revised form 4 April 2005; accepted 4 April 2005
Available online 17 May 2005

Abstract

A novel solid-contact potentiometric sensor for ascorbic acid based on cobalt phthalocyanine nanoparticles (NanoCoPc) as ionophore was fabricated without any need of auxiliary materials (such as membrane matrix, plasticizer, and other additives). The electrode was prepared by simple drop-coating NanoCoPc colloid on the surface of a glassy carbon electrode. A smooth, bright and blue thin film was strongly attached on the surface of the glassy carbon electrode. The electrode showed high selectivity for ascorbic acid, as compared with many common anions. The influences of the amount of NanoCoPc at the electrode surface and pH on the response characteristics of the electrode were investigated. To overcome the instability of the formal potential of the coated wire electrode, a novel electrochemical pretreatment method was proposed for the potentiometric sensor based on redox mechanism. This resulting sensor demonstrates potentiometric response over a wide linear range of ascorbic acid concentration (5.5×10^{-7} to 5.5×10^{-2} M) with a fast response (<15 s), lower detection limit (ca. 1.0×10^{-7} M), and a long-term stability. Furthermore, microsensors based on different conductors (carbon fiber and Cu wire) were also successfully fabricated for the determination of practical samples.

Keywords: Solid-contact; Potentiometry; Cobalt phthalocyanine nanoparticle; Ascorbic acid; Redox mechanism

1. Introduction

As a classical field of electrochemical sensors, ion-selective electrodes (ISEs), or potentiometric sensors offer many advantages and have been widely used in many fields, including clinical diagnostics, industrial process control, environmental monitoring, and physiology [1,2]. Although potentiometric sensors have been regarded as a mature field where all important contributions had been made, recently, researches in this field are quite exciting, and a significant number of directions are emerged, because of the improved mechanistic understanding (e.g., various non-classical response mechanisms proposed), many new materials and concepts (e.g., molecular imprinting) employed, and so on [3,4].

For traditional potentiometric sensors with the internal solution, previous studies have shown that the internal solution is a major origin of primary ions contaminating the sample [5]. Although some remedies were adopted [6,7], the internal filling solution is still a major hindrance in the miniaturization of the devices. Thus, some new sensing systems, such as solid-contact electrodes, have been proposed [5,8,9]. Polymeric film containing electroactive species and other additives coated directly onto the surface of metallic or graphite conductors is a common method to fabricate the solid-contact electrodes. This type of sensors eliminated the internal filling solution provides new advantages, for instance, good mechanical stability, simplicity and possibility of miniaturization. They have been used as detectors in hydrodynamic separation systems (such as liquid chromatography, capillary electrophoresis and μ-TAS) [10] and flow injection analyzers [11]. However, a key disadvantage for solid-contact electrodes is that the formal potential is often unstable [12], which has been mainly attributed to the lack of a well-defined redox couple at the membrane-metal interface [13]. To obtain a thermodynamically defined electrochemical

---

* Corresponding author. Tel.: +86 25 83594862; fax: +86 25 83594862.
E-mail address: hychen@nju.edu.cn (H.-Y. Chen).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.04.015

interface between membrane and solid conductor, it has been suggested either to contact the conductor with the membrane via an intermediate polymer layer that is redox-active [13], or to use ISE membranes containing an appropriate redox-active component [14]. Besides, another disadvantage of these sensors is the polymeric membrane losing adhesion between the coating and the conductor. Thus, some alternative materials, such as sol–gel membrane matrix [15,16], carbon paste (CP) matrix [17,18], and electropolymerized conducting film [19], have been used as incorporating ionophores matrix.

Furthermore, for ISEs constructed by the conventional polymeric membrane, many additives (e.g., membrane matrix, plasticizer, and a small amount of other additives) are added in the polymeric membrane, while not all components are perfectly immobilized in the membrane [20]. Previous studies have indicated that exudation of plasticizer and leaching of dissolved ionophores may ultimately affect the performance of sensors, including the lifetime [21] and the selectivity [22]. In particular, it has been found that such component leaching induces a serious interfering response in vivo applications [23]. Recent studies have also showed that the leaching of plasticizer could induce a cross-contamination in microarray systems [24]. Thus, many solutions have been put forward to resolving these problems, and complicated procedures for grafting of various membrane components have been used to avoid leaching [25,26]. Plasticizer-free from the membrane has also been attempted with conventional polymers or photopolymers for ion-selective membranes [27–29], which are very advantageous to the miniaturization of ISEs.

Thus, as mentioned above, preventing the exudation of plasticizer and leakage of primary ion, and improving sensor rigidity are of interest to meet the requirement of miniaturization devices. In this work, we report a novel solid-contact electrode based on cobalt phthalocyanine nanoparticles as ionophore for potentiometric determination of ascorbic acid (Vc). Compared with previous reports, this proposed method presents some advantages: (i) Simple component of membrane and easy preparation procedure of modified electrode. The membrane is only composed of nanosized CoPc without any other auxiliary materials, which does not include polymer matrix, plasticizer, and other additives. The modified electrode could be prepared by simple drop-coating method. (ii) Low cost and excellent film-forming ability of material. The membrane material (nanosized CoPc colloid) is made from non-derivative cobalt phthalocyanine using a conventional ultrasonic dispersion reprecipitation in the surfactants solution. This nanosized CoPc colloid could form very firm, smooth and uniform film on the surface of the electrode. Previous studies have also used cobalt phthalocyanine derivatives for potentiometric determination of ascorbic acid [30,31]. However, these peripheral substitution derivatives require complicated synthesis process and expensive material cost. (iii) Solid-contact without the internal solution and easy miniaturization. (iv) Good performances of sensors. This kind of sensor shows a high selectivity for the ascorbic acid, as compared with many common anions, and a wide linear concentration range for the determination of ascorbic acid.

2. Experimental

2.1. Reagents and materials

L-Ascorbic acid and uric acid were purchased from Sigma and CoPc from Aldrich, and used as received without further purification. All other reagents are commercially available and of analytical grade. 0.1 M phosphate buffer solutions (PBS) with various pHs were prepared by mixing stock standard solutions of K_2HPO_4 and KH_2PO_4 and adjusting the pH with 0.1 M H_3PO_4 or K_3PO_4. All solutions were prepared with doubly distilled water.

2.2. Preparation of NanoCoPc colloid

NanoCoPc colloid was prepared as described previously [32] with a little modification. Briefly, 0.15 g CoPc was dissolved in 5 mL 98% concentrated sulfuric acid, the solution was then added drop by drop into a 300 mL aqueous solution containing 0.45 g hexadecyltrimethyl ammonium-bromide in an ultrasonic ice–water bath. The resulting transparent blue colloidal solution was ultracentrifugally separated. The obtained sedimentation was washed repeatedly to neutral with water, and dispersed with 300 mL water under ultrasonic as standby solution.

2.3. Preparation of the modified electrode

Prior to modification, a glassy carbon electrode (GCE, diameter 3 mm) was polished with sand paper followed by 1.0, 0.3, and 0.05 μm alumina slurry, respectively, then cleaned by successive ultrasonic treatment in baths with acetone (5 min) and double distilled water (10 min) to remove any residue on the surface of the electrode, and finally air-dried for use. The NanoCoPc colloid modified GCE (NanoCoPc/GCE) was prepared by drop-coating 20 μL of the NanoCoPc standby solution on the GCE followed by air-drying for 3–4 h. A smooth, bright and blue thin film appeared on the GC surface.

Cu microdisk electrode and carbon fiber electrode were fabricated as follows: 7 cm long glass capillaries (1.0 mm i.d.) were pulled with a vertical pipet puller (Shanghai Institute of Physiology, Shanghai, China) and the tips of these glass micropipets were carefully cut to about 400 μm i.d. A Cu wire with 3 cm long and 330 μm diameter was introduced into the tip of a glass capillary and epoxy was applied to fix the Cu wire. The other end of the wire was connected to a Cu lead by means of soldering tin and the capillary end was sealed with epoxy also; for carbon fiber electrode, a bundle of carbon fibers (ca. 8 μm diameter for single one) were introduced into the capillary. Epoxy was applied at the tip to seal the carbon fiber bundle with ca. 1 cm protruded from the tip. A copper wire was connected with the carbon fiber through carbon powder on the other end of capillary and then fastened with epoxy. The exposed carbon fiber bundle at the tip was cut. Prior to modification, the same pretreatment procedures as the mentioned above were made, and then 3.0 μL of the NanoCoPc standby solution was carefully drop-coated onto the surface of the carbon fiber or copper microdisk electrode.

All the modified electrodes were stored in a dry state at room temperature when not in use.

2.4. Apparatus

Potential measurements were made with a Model PXSJ-216 Ionalyzer (Shanghai Rex Instrument Factory, China). Potential–time measurements and cyclic voltammetric experiments of the electrodes were performed with an Autolab PGSTAT30 (EcoChemie, Utrecht, the Netherlands). For pH measurements, an Orion (ThermoOrion, USA) Model-868 with a conventional glass pH electrode was used. Scanning electron micrographs (SEM) were obtained with a Hitachi X-650 scanning electron microscope (Hitachi Ltd., Tokyo, Japan) at an acceleration voltage of 20 kV, and X-ray diffraction (XRD) experiments were performed on an X-ray diffractometer (Rigaku D/max-RA, Japan).

2.5. Potential measurements

Prior to measurement, the modified electrode was pretreated by electrochemical method as follows: it was electrooxidized in the bare solution at a constant potential of 0.6 V until a steady-state current was obtained about 50 s, and then soaked in 0.1 M PBS with the same pH value as the sample solution until a steady potential was obtained.

A two-electrode system comprising the modified electrode as the indicator electrode and a saturated calomel electrode (SCE) as reference one was employed for all electrochemical experiments. All the potentials given here were relative to SCE. All experiments were carried out in air-saturated and mild stirring 0.1 M PBS at 20 ± 0.1 °C, unless otherwise stated.

3. Results and discussion

3.1. Physical characterization

Cobalt phthalocyanine is one of the best-known synthetic porphyrin analogues. Much more highly catalytic property and biocompatibility combined with low raw material cost, makes it as a strong candidate for the development of novel sensor devices, such as glucose [33], ethanol [34], 2-mercaptobenzothiazole and 2-mercaptobenzothiazimidazole [35] etc. Unfortunately, only carbon paste embedding method has been used to fabricate these sensors, because it is difficult to firmly fix CoPc on the surface of the electrode without other auxiliary materials. Previous study has also showed the stability of the sensors based on carbon paste embedding method is rather poor, it may be caused by the decomposition of CoPc molecules and insufficient renewal of the electrode surface, because CoPc hardly diffuses from the bulk of carbon paste towards the electrode surface due to its infusibility in paraffin oil [36].

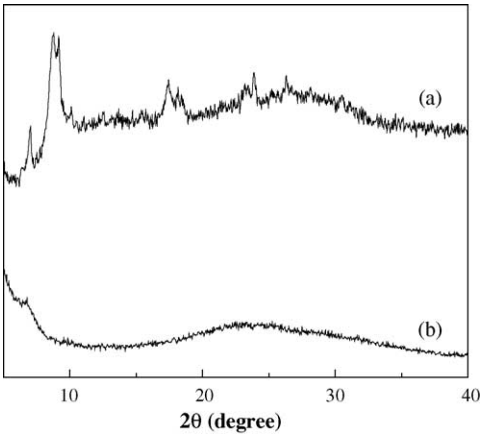

Fig. 1. X-ray diffraction patterns of (a) bulk CoPc dispersion and (b) CoPc nanoparticles.

Over the recent years, nanosized organic materials have received much more attention because of their unique physical and chemical properties [32,37,38]. In our previous work [39], nanosized CoPc colloid was successfully fabricated from non-derivative CoPc using a conventional ultrasonic dispersion reprecipitation in the surfactants solution. The X-ray diffraction patterns of bulk CoPc and nanosized CoPc are shown in Fig. 1, compared to the bulk CoPc that exhibits many sharp peaks, the NanoCoPc powder shows only two broad peaks, indicating a near amorphous state, which may be the result of the nanometer size effect. Because the number of CoPc molecules was very limited in every CoPc nanoparticle, they cannot stack up into a long-range ordered state, but only into a short-range ordered state, resulting in broad peaks in the X-ray diffraction pattern [38].

Fig. 2A shows the SEM image of the modified electrode prepared by conventional method coating with CoPc pyridine solution [40]. The crystallites of CoPc are distributed irregularly on the surface of the electrode, and it is easy to be removed by rinsing with water. Fig. 2B shows the SEM of the NanoCoPc film, which is very smooth and uniform without any cracking. The film strongly attached on the surface of the electrode without any shelling by rinsing continuously with water. It overcomes the disadvantage of easily desquamating from the surface of the electrode for the bulk cobalt phthalocyanine film, and provides a possibility to prepare a stable and long-term modified electrode. And also this kind of unique physical and chemical properties of nanosized CoPc colloid, namely excellent film-forming ability and strong adsorbability, will widen its application in many fields.

3.2. Response mechanism

As a kind of non-classical response mechanisms, namely, the potential response of membranes via redox reactions be-

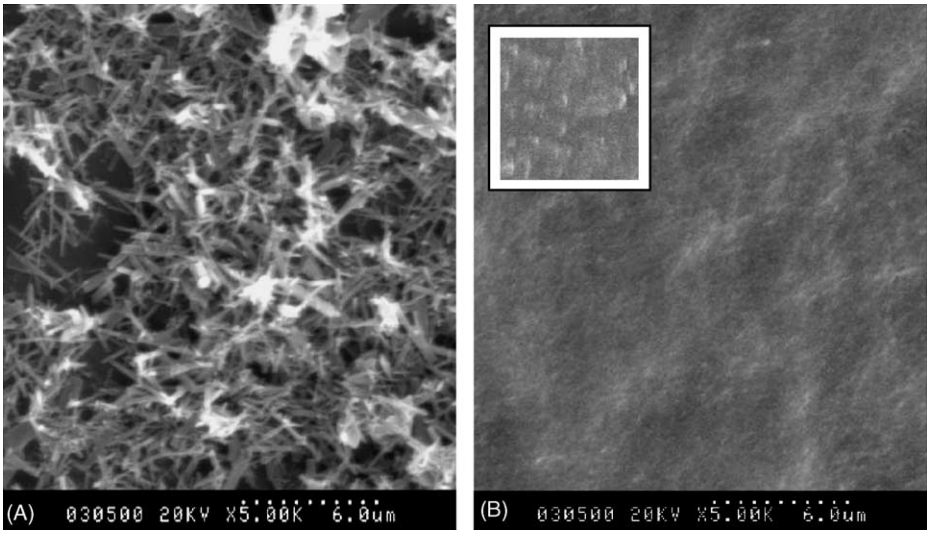

Fig. 2. SEM of the glassy carbon electrodes coated with (A) CoPc pyridine solution and (B) CoPc colloid (insert: 5×10^4).

tween the ionophore and the target ion, cobalt phthalocyanine derivatives [30,31], iron phthalocyanine [18] and other transition metal complexes [41] have been used as mediators for potentiometric determination of ascorbic acid. As we know, the direct oxidation of ascorbic acid by oxygen has been the object of many kinetic investigations due to its basic biochemical and potential significance, which is relatively slow without any catalyst present, especially at low pH [18,31].

The anodic peak potential of ascorbic acid at the NanoCoPc/GCE is at about +0.45 V (Fig. 3). Compared to the response of ascorbic acid at the bare GC electrodes, the NanoCoPc/GCE exhibits obviously higher current response towards ascorbic acid oxidation, and additionally a marked decrease (about 190 mV) in the oxidation peak potential of ascorbic acid, which implies that NanoCoPc modified electrode can electrochemically catalyze the oxidation of ascorbic acid. Thus, the potentiometric response mechanism for ascorbic acid of the modified electrode based on NanoCoPc could be similarly expressed as follows [18,31,35]:

$$\mathrm{Co(II)Pc} + \mathrm{Vc} \rightarrow \mathrm{Co(I)Pc} + \mathrm{Vc_{(ox)}} \tag{1}$$

$$\mathrm{Co(I)Pc} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow \mathrm{Co(II)Pc} + 2\mathrm{H_2O_2} \tag{2}$$

Potentiometric detection method based on a redox mediator represents a convenient way to measure the equilibrium potential of such a slow and irreversible reaction [42]. Here, [Co(II)]/[Co(I)] provides a reversible redox couple for measuring the equilibrium potential of the ascorbic acid-oxygen system. As can be seen from Eqs. (1) and (2), the potential of the electrode is determined by the concentration ratio of [Co(II)]/[Co(I)], which is a function of the ascorbic acid concentration under keeping the concentration of oxygen and other parameters at constants values. Fig. 4 illustrates a typical potential–time curve for the response of the modified electrode with sequential additions of ascorbic acid in air-saturated 0.1 M PBS (pH 7.0). Stable potential signals are obtained with a response time of less than 15 s at ascorbic

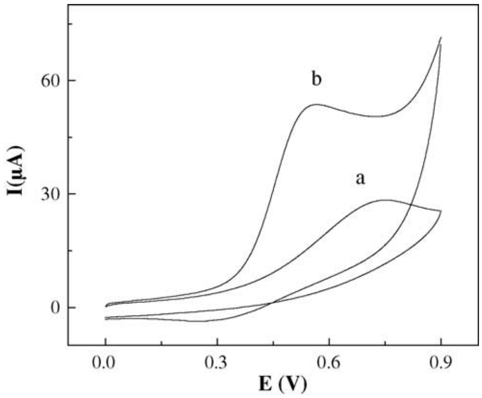

Fig. 3. Typical cyclic voltammograms for the oxidation of 0.1 mM ascorbic acid at (a) the bare, and (b) NanoCoPc modified glassy carbon electrodes at pH 7.0 in 0.1 M phosphate buffer solution at scan rate of 200 mV s^{-1}.

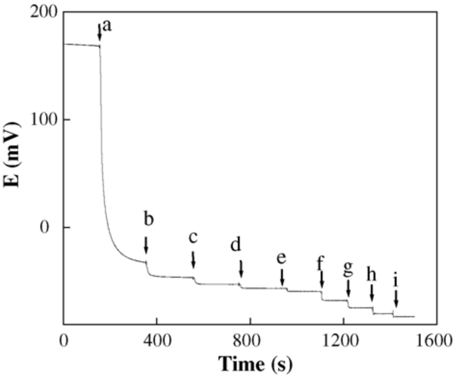

Fig. 4. Potential–time curve for the response of the NanoCoPc modified electrode to successive addition of ascorbic acid (a→e 0.1 mM increment each time and f→g 1 mM, respectively) to 10 mL 0.1 M stirred phosphate buffer solution, pH 7.0, at 20 ± 0.1 °C.

acid concentrations more than 1.0×10^{-4} M, showing a fast response of the modified electrode to ascorbic acid. Especially at low concentrations, e.g., 1.0×10^{-6} M, the electrode reaches an equilibrium reading within 50 s, the response is much faster than that the all-solid-state potentiometric sensor based on Ph_3SnCl (10 min for a concentration of 10^{-4} M ascorbic acid) [41], and the CoTTBPc electrode with the internal solution (4 min for 10^{-6} M ascorbic acid) [30], and similar with the carbon paste electrode based on embedding iron phthalocyanine (20 s for 4.0×10^{-5} M ascorbic acid) [18].

3.3. Optimization of dip-coating procedure

The preliminary studies indicated that the potentiometric response of the modified electrode was affected by the amount of NanoCoPc on electrode surface and smoothness of the membrane. The pretreatment of the bare GCE helped to prepare smooth and firm film of the NanoCoPc. Uncleaned surface of the electrode makes NanoCoPc conglomeratic easily and leads to unsmooth and non-uniform NanoCoPc film, which will affect the stability and lifetime of the modified electrode. So the pretreatment procedures of the bare GCE and microdisk electrode are necessary as stated in Section 2.

In order to evaluate the effect of the amount of NanoCoPc on electrode surface on the response, a series of the modified glassy carbon electrodes were prepared by drop-coating CoPc colloid solution on the surface of the bare glassy carbon electrodes. The responses of the different modified electrode were shown in Fig. 5. The results showed that the potential response to ascorbic acid increases with the increased of the amount of NanoCoPc on the electrode surface. The same response phenomena were observed for electrodes formulated with $Hg(DIDTC)_2$ in the polymer membrane [43] and coated with an electrodeposited cobalt tetramethylpyridoporphyrazine [31]. Once the coated CoPc colloid was more than 20 μL, the amount of coated NanoCoPc had no significant effect on the potential response of the modified electrode. So the modified electrode coated with 20 μL CoPc colloidal was used for further experiments.

3.4. Precondition and stability and reproducibility

In order to obtain a stable potentiometric response over a wide range of analyte concentrations, the preconditioning of the electrode is often required to conventional ISEs by soaking the electrode in a high concentration of the analyte ion for a reasonable time before measurements. However, it is another origin of primary ions contaminating the sample, which typically contains them in 1–10 mM concentrations in sensed layer [44]. Indeed, such preconditioning for the modified electrode has a significant negative influence on the potentiometric response characteristics, the modified electrode loses almost all of its ascorbic acid response after continuous soaking in 1.0 mM ascorbic acid solution for about 30 min (Fig. 6), which is consistent with the proposed redox response mechanism of the modified electrode based on NanoCoPc.

Moreover, the formal potential of solid-contact electrodes is often unstable, and varys among electrodes of the same type [12]. Therefore, the success of such electrodes often requires frequent calibration. Pretsch et al. [45] attributed this apparent instability to the changes in the electrolyte composition of a water layer between the metal and the membrane. The potentials became stable if a hydrophobic layer was deposited onto the metal, which suppressed the water film. However, Lever et al. [31,46] still observed a remarkable unstable potential response in solid-contact electrodes mediated by substitution cobalt phthalocyanine derivatives with a hydrophobic layer, they thought it was attributed to the thickness of ion-exchange membrane difficult to being controlled from one electrode to another [46]. Yu et al. [31] observed the same phenomenon even for the traditional potentiometric sensor with the internal solution based on substitution cobalt phthalocyanine derivative. But when cobalt phthalocyanine derivative was doped with oxidant, they obtained a stable potentiometric response

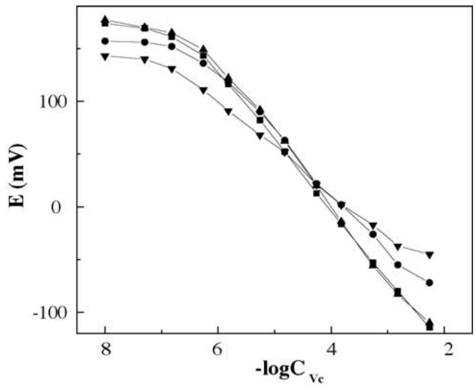

Fig. 5. Effect of the amount of NanoCoPc on the sensors' response, (▼) 10, (●) 15, (■) 20, and (▲) 25 μL CoPc colloidal standby solution coated on GC surface.

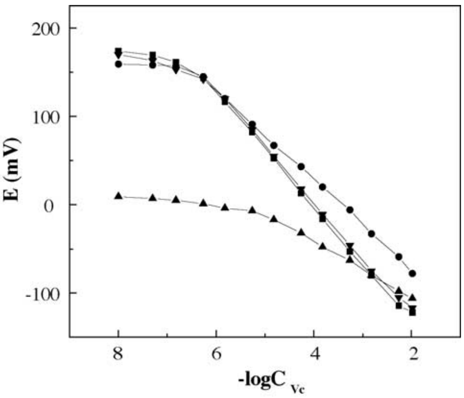

Fig. 6. Effect of electrode conditioning on the potentiometric respons of ascorbic acid sensor: (▲) soaked in 1.0 mM ascorbic acid solution for 30 min, (●) freshly prepared, (■) oxidation of constant potential at 0.6 V for 50 s, and (▼) the same as (■) after 1 month.

Table 1
Potentiometric response ranges in 0.1 M PBS with various pH values

pH	Slope (S.D.) (mV/decade)	Linear range (*M*)	Detection limit (*M*)	Initial potential (mV)
3.0	51.9 (±1.3)	5.5×10^{-7} to 1.5×10^{-2}	3×10^{-7}	268
4.0	53.2 (±1.4)	5.5×10^{-7} to 5.5×10^{-3}	2×10^{-7}	247
5.0	55.8 (±1.4)	5.5×10^{-7} to 5.5×10^{-3}	2×10^{-7}	223
6.0	61.7 (±1.4)	5.5×10^{-7} to 1.5×10^{-2}	1×10^{-7}	198
7.0	60.8 (±1.6)	5.5×10^{-7} to 1.5×10^{-2}	1×10^{-7}	179
8.0	44.5 (±0.9)	5.5×10^{-6} to 1.5×10^{-3}	8×10^{-7}	138

of the modified electrode to ascorbic acid. Taking the redox mechanism of the potential response into account, the surface concentration ratio of the oxidized and reduced form of the mediator is an important factor for making the potential stability. So a novel electrochemical precondition procedure was firstly proposed as described in Section 2. After this pretreatment, the stable potentiometric response of the NanoCoPc modified electrode to ascorbic acid was obtained (Fig. 6). When not in use, the modified electrodes were stored dry at room temperature for more than 1 month without remarkable loss of their original activity.

The relative standard deviation for a standard solution of 0.1 mM ascorbic acid was found to be 1.0% ($n = 5$) for the same modified electrode, and the fabrication reproducibility of five sensors, independently constructed based on the same bare electrode, shows an acceptable reproducibility with a relative standard deviation of 2.4% for the steady potential obtained at 0.1 mM ascorbic acid.

3.5. pH response and linear range

In general, the ISEs based on organometallic complexes are sensitive to pH, for these metals can form oxides and hydroxides at high pH. On the other hand, the distribution of predominant species (including $AscH_2$, $AscH^-$, and Asc^{2-}) of ascorbic acid is related to the pH value ($pK_1 = 4.04$ and $pK_2 = 11.4$) [41]. So it is important to study the effect of the solution pH on the properties of the ascorbic acid-sensitive electrodes based on NanoCoPc. Potentiometric response characteristics of the modified electrodes were obtained by using 0.1 M PBS in the pH range of 3.0–8.0 (Table 1). The potentiometric response of the modified electrode was sensitive to pH change. With the increasing solution pH, the initial response potentials of the modified electrode were shifted toward more negative values, which was evident that low pH values favored the oxidation of CoPc in the membrane phase to the charged form [47]. In a solution with a pH higher than 9.0, the potential response of the modified electrode was deteriorated, this behavior might be explained by an increased level of interference from OH^-. It was interesting to note that at low pH, the predominant species as protonated form existed in the solution, the modified electrode showed a linear response toward the ascorbic acid in a relatively wide concentration range.

As further application, the NanoCoPc modified microdisk electrodes based different conductors (carbon fiber and Cu wire) were fabricated. The relative standard deviation for a standard solution of 0.1 mM ascorbic acid was found to be 1.2% ($n = 5$) for the same modified electrode, and the fabrication reproducibility of five sensors, independently constructed based on the same bare electrode, showed a reproducibility with a relative standard deviation of 4.4% for the steady potential obtained at 0.1 mM ascorbic acid. The linear response range of the microsensors was from 5.5×10^{-6} to 5.5×10^{-2} with the slope of 61.2 mV/decade of ascorbic acid concentration in air-saturated 0.1 M PBS (pH 7.0) at $20 \pm 0.1\,^{\circ}C$.

3.6. Selectivity

The selectivity is clearly one of the most important characteristics of a potentiometric sensor, which represents the preference of a sensor for the response to primary ion over other ions (interfering ions) present in the solution. On the basis of the separate solution method [48], the results of potentiometric selectivity coefficients for the modified electrode are given in Table 2. These results reveal that the modified electrode exhibits fairly high selectivity to ascorbic acid over most of the common anions, only some redox species, such as iodine and oxalic give small interference. This behavior further supports the assumption that the electrode response is associated with a redox mechanism. Furthermore, the interfering effects of the physiological level of the tested compounds, such as uric acid (0.5 mM), acetaminophen (0.1 mM), glucose (5.6 mM), and cysteine (0.05 mM), were studied, respectively, in terms of the error of electrode potential readings for a 0.1 mM solution of ascorbic acid caused by the presence of corresponding interferents. Except for cysteine that shows an obvious error of the potential reading (16 mV), other tested compounds have no obvious influence on the potential reading (within

Table 2
Potentiometric selectivity coefficients for the common interferents in 0.1 M PBS (pH 7.0)

Interferent, *J*	log $K_{i,j}^{\text{pot}}$	Interferent, *J*	log $K_{i,j}^{\text{pot}}$
F^-	−4.76	$C_2O_4^{2-}$	−3.23
Cl^-	−4.71	HCO_3^-	−4.66
Br^-	−3.84	NO_2^-	−4.01
I^-	−3.01	$C_6H_5O_7^{3-}$	−4.16
NO_3^-	−4.67	SCN^-	−3.38
SO_4^{2-}	−4.80	CH_3COO^-	−4.51

Table 3
Determination of ascorbic acid in various real samples ($n = 5$)

Sample	Proposed method (mg/100 mL)		Reference method (mg/100 mL)	Relative error (%)	
	Electrode^A	Electrode^B		Electrode^A	Electrode^B
Pharmaceutical tablet	19.8	19.4	19.0	+4.2	+2.1
Vc injection	193	191	197	−2.0	−3.0
Orange drink	9.83	9.90	9.51	+3.4	+4.1

Note: Electrode^A and Electrode^B denote the NanoCoPc/GCE and Cu NanoCoPc modified microdisk electrode, respectively.

1–4 mV). This is a common phenomenon in all of the sensors prepared by many metalphthalocyanines (including Co, Fe, Ni, Mn, and etc.) and their derivatives.

3.7. Analytical application

In order to investigate the applicability of the proposed potentiometric method, the NanoCoPc/GCE and NanoCoPc/Cu microdisk electrodes were applied to the determination of various real samples (pharmaceutical tablet, Vc injection and orange drink). Pharmaceutical tablet was finely powdered with a mortar and pestle, and 200 mg of the powder was dissolved in 100 mL 0.1 M PBS (pH 7.0) under ultrasonic for 10 min. For the Vc injection, 1 mL of the injection was diluted to 100 mL, and orange drink was filtered as necessary before the determination. All the samples prepared were used for the determination of ascorbic acid content by potentiometric and spectrophotometric methods [49], and the results for various samples are summarized in Table 3. The matrix effect was studied by recovery experiments with known amounts of ascorbic acid. The recoveries attained were in the range of 96–103%.

4. Conclusions

The potentiometric detection of ascorbic acid using a solid-contact electrode based on NanoCoPc by the simple drop-coating method has been presented without any auxiliary materials, such as polymer matrix, plasticizer, and other additives. The solid-contact electrode yields fast and stable potential response to ascorbic acid in a broad range of concentrations (about five decades of concentration). Such an electrode is suitable for the direct determination of ascorbic acid concentration under ambient atmosphere. The novel precondition method provides the stable formal potential, avoiding frequent calibration of the traditional solid-contact electrode. And another interesting studies showed that the thin film prepared with the nanosized CoPc colloid by the simple coating method, provides a promising strategy for sensor miniaturization, and feasible application for the measurement in vivo and hydrodynamic separation systems, such as liquid chromatography, capillary electrophoresis and μ-TAS.

Acknowledgements

This project was financially supported by the National Natural Science Foundation (Grant no. 90206037, 20205007, 20475025) of China.

References

[1] J. Wang, Analytical Electrochemistry, Section Edition, John Wiley & Sons Inc., publication, 2001, p. 140.
[2] P. Bühlmann, E. Pretsch, E. Bakker, Chem. Rev. 98 (1998) 1593.
[3] E. Bakker, M.E. Meyerhoff, Anal. Chim. Acta 416 (2000) 121.
[4] E. Bakker, M. Telting-Diaz, Anal. Chem. 74 (2002) 2781.
[5] A. Michalska, J. Dumariska, K. Maksymiuk, Anal. Chem. 75 (2003) 4964.
[6] W. Qin, T. Zwickl, E. Pretsch, Anal. Chem. 72 (2000) 3236.
[7] A. Ceresa, T. Sokalski, E. Pretsch, J. Electroanal. Chem. 501 (2001) 70.
[8] P. Schnierie, T. Kappes, P.C. Hauser, Anal. Chem. 70 (1998) 3585.
[9] S. Shahrokhian, Anal. Chem. 73 (2001) 5972.
[10] L.J. Nagels, I. Poels, Anal. Chem. 19 (2000) 410.
[11] T. Dimitrakopoulos, P.W. Alexander, D.B. Hibbert, Electroanalysis 8 (1996) 438.
[12] W.-S. Han, M.-Y. Park, K.-C. Chung, D.-H. Cho, T.-K. Hong, Talanta 54 (2001) 153.
[13] P.C. Hauser, D.W.L. Chiang, G.A. Wright, Anal. Chim. Acta 302 (1995) 241.
[14] D. Liu, R.K. Meruva, R.B. Brown, M.E. Meyerhoff, Anal. Chim. Acta 321 (1996) 173.
[15] A. Jiménez-Morales, J.C. Galván, P. Aranda, Electrochim. Acta 47 (2002) 2281.
[16] K. Kimura, T. Sunagawa, S. Yajima, S. Miyake, M. Yokoyama, Anal. Chem. 70 (1998) 4309.
[17] Y.-K. Lee, J.-T. Park, C.-K. Kim, K.-J. Whang, Anal. Chem. 58 (1986) 2101.
[18] M.K. Amini, S. Shahrokhian, S. Tangestaninejad, V. Mirkhani, Anal. Biochem. 290 (2001) 277.
[19] D.T. McQuade, A.E. Pullen, T.M. Swager, Chem. Rev. 100 (2000) 2537.
[20] P.J. Missel, Langmuir 15 (1999) 7122.
[21] R.D. Armstrong, G. Horvai, Electrochim. Acta 1 (1990) 1.
[22] O. Dinten, U.E. Spichiger, N. Chaniotakis, P. Gehrig, B. Rusterholz, W.E. Morf, W. Simon, Anal. Chem. 63 (1991) 596.
[23] E. Lindner, V.V. Cosofret, S. Ufer, R.P. Buck, W.J. Kao, M.R. Neuman, J.M. Anderson, J. Biomed. Mater. Res. 28 (1994) 591.
[24] Y. Qin, S. Peper, A. Radu, A. Ceresa, E. Bakker, Anal. Chem. 75 (2003) 3038.
[25] D.N. Reinhoudt, J.F.J. Engbersen, Z. Brzozka, H.H. van den Vlekkert, G.W.N. Honig, H.A.J. Holterman, U.H. Verkerk, Anal. Chem. 66 (1994) 3618.

[26] K.C. Gupta, M.J. D'Arc, Talanta 52 (2000) 1087.
[27] Y. Qin, E. Bakke, Anal. Chem. 75 (2003) 6002.
[28] P. Sjoberg, J. Bobacka, A. Lewenstam, A. Ivaska, Electroanalysis 11 (1999) 821.
[29] L.Y. Heng, E.A.H. Hall, Anal. Chem. 72 (2000) 42.
[30] J. Li, M. Hu, R. Yu, Sens. Actuator B 30 (1996) 65.
[31] P. Janda, J. Weber, L. Dunsch, A.B.P. Lever, Anal. Chem. 68 (1996) 960.
[32] Y. Wang, K. Deng, L. Gui, Y. Tang, J. Zhou, L. Cai, J. Qiu, D. Ren, Y. Wang, J. Colloid Interface Sci. 213 (1999) 270.
[33] I. Rosen-Margalit, A. Bettelheim, J. Rishpon, Anal. Chim. Acta 281 (1993) 327.
[34] M. Boujtita, J.P. Hart, R. Pittson, Biosens. Bioelectron. 15 (2000) 257.
[35] S. Shahrokhian, M.K. Amini, I. Mohammadpoor-Baltork, S. Tangestaninejad, Electroanalysis 12 (2000) 863.
[36] F. Mizutani, S. Yabuki, S. Iijima, Anal. Chim. Acta 300 (1995) 59.
[37] X. Gong, T. Milic, C. Xu, J.D. Batteas, C.M. Drain, J. Am. Chem. Soc. 124 (2002) 14290.
[38] H.Z. Chen, C. Pan, M. Wang, NanoStruct. Mater. 11 (1999) 523.
[39] K. Wang, J.-J. Xu, H.-Y. Chen, Biosens. Bioelectron. 20 (2005) 138.
[40] C.A. Caro, F. Bedioui, J.H. Zagal, Electrochim. Acta 47 (2002) 1489.
[41] P.G. Veltsistas, M.I. Prodromidis, C.E. Efstathiou, Anal. Chim. Acta 502 (2004) 15.
[42] Y.I. Tur'yan, R. Kohen, J. Electroanal. Chem. 380 (1995) 273.
[43] I.H.A. Badr, M.E. Meyerhoff, S.S.M. Hassan, Anal. Chim. Acta 310 (1995) 211.
[44] J. Sutter, A. Radu, S. Peper, E. Bakker, E. Pretsch Anal. Chim. Acta 523 (2004) 53.
[45] M. Fibbioli, W.E. Morf, M. Badertscher, N.F. De Rooij, E. Pretsch, Electroanalysis 12 (2000) 1286.
[46] Y.-H. Tse, P. Janda, A.B.P. Lever, Anal. Chem. 66 (1994) 384.
[47] J.-Z. Li, X.-Y. Pang, R.-Q. Yu, Anal. Chim. Acta 297 (1994) 437.
[48] E. Pungor, K. Toth, A. Hrabeczy-Paall, Pure Appl. Chem. 51 (1979) 1973.
[49] Chinese Chemical Industry Committee, in: Chinese Pharmacopoeia, Second part, Chemical Industry Press, Beijing, 2000, p. 792.