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Determination of Amino Group Content on Nanosilicas with *p*-Aminobenzoic Acid Modified Glassy Carbon Electrode Using Copper(II) as Intermedia

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In the present work, a *p*-aminobenzoic acid (*p*-ABA) modified glassy carbon electrode (GCE) was developed to determine amino group content on γ-aminopropyltriethoxysilane modified nanosilica (AMNS) using copper(II) as intermedia by cyclic voltammetry. The method was based on the sensitive response of copper(II) on *p*-aminobenzoic acid modified glassy carbon electrode and the quantitative reaction of copper(II), 5-nitrosalicylaldehyde and surface amino group content on γ-aminopropyltriethoxysilane modified nanosilica. Results were found that the proposed method was of good reproducibility and accuracy and no significant differences from atomic absorption spectroscopy.

Key Words: *p*-Aminobenzoic acid, Copper(II), Glassy carbon electrode, Nanosilica.

INTRODUCTION

As an important surface modified nanomaterial, γ-aminopropyltriethoxysilane modified nanosilica (AMNS) had the high active aminopropyl which made it feasible to be applied in many areas like chemical engineering, material and bioengineering[1-4]. It was proved that AMNS's properties and applications were highly dependent on amino content on its surface[5,6]. So it was necessary to monitor the amino content on these nanoparticulates to ensure their reliability and satisfactory performance in engineering.

Many characteristic methods, such as Fourier transformation infrared spectrometry[7,8], X-ray photoelectron spectroscopy[9] and nuclear magnetic resonance[10,11], have been employed to investigate the structure, composition of modified layer, but results still could not meet the requirement[12]. Elemental analysis[11,13] was an efficient method to evaluate the amounts of C, N and H, but it always accompanied complicated sample preparation. Though gas chromatography[14] has been used for determining γ-aminopropyltriethoxysilane modified nanosilica, but it is still with many difficulties to determine amino group content on AMNS because of the inertia silica. Titration method was thought to be a simple and fast method. For example, Etienne *et al.*[15] adopted a pH metric titration to analyze amino group content of aminopropyl-grafted silica. Li *et al.*[16] also attempted to titrate amino content on AMNS in ethanol with thymol-blue as indicator. However, it seemed that

the accuracy and the reproducibility of the both methods were still unsatisfactory. Zhang *et al.*[17] analyzed the amino group content on AMNS through potentiometric titration using solid pH sensor, but the stability of electrode and reproducibility need further improvement.

Therefore, in the present work, *p*-aminobenzoic acid (*p*-ABA) modified glassy carbon electrode (GCE) was designed for amino group detection using copper(II) as intermediate. It was followed by reacting amino group content on AMNS with 5-nitrosalicylaldehyde first, then with copper(II) to generate insoluble complexes, after being centrifuged, the precipitate was dissolved with proper solvents and finally the mixture was employed for detecting copper(II) by cyclic voltammetry. The results indicated that this method was of reliability and accuracy and could be used for determining amino group content on AMNS. The optional conditions like solution's pH, supporting electrolyte and respond of copper(II) on modified glassy carbon electrode were also discussed.

EXPERIMENTAL

Cyclic voltammetry experiments were performed on a CHI 650 electrochemical station (CH Instruments, USA). A three-electrode system was employed with a bare or a *p*-ABA modified glassy carbon electrode (3 mm in diameter) as working electrode, an Ag/AgCl (saturated KCl) as reference electrode and a platinum wire as auxiliary electrode.

p-Aminobenzoic acid, analytical grade (> 99.9 %), was furnished from China Medicine (Group) Shanghai Chemical Reagent Corporation. γ-Amino-propyltriethoxysilane modified nanosilica was prepared by Henan Province Nanomaterial Engineering and Technological Research Centre. All the other chemicals were of analytical grade and high purity water was used throughout.

Pretreatment of γ-amino-propyltriethoxysilane modified nanosilica (AMNS): Accurately weighed AMNS (about 0.04 mmol amino group content) were dispersed among 5 mL 20 % ethanol-H_2O (v/v) solution in 10 mL polypropylene tubes and 2 mL copper(II) solution (prepared by diluting 3.372 g triethanolamine, 0.2050 g 5-nitrosalicylaldehyde, 1.20 mL 37 % acetaldehyde and 5.00 mL 4 % $CuSO_4$ solution to 50 mL with high purity water) was added into each tube. The tubes were sonicated for 3 min and then were shaken for 60 min. After centrifugation (10000 rpm) for 10 min the supernatant was removed and 10 mL H_2O was added to rinse the precipitate. This washing stage was carried out until no significant copper(II) was detected (using $K_4[Fe(CN)_6]$ as detection reagent). Then a little of HF solution was added to dissolve the precipitate and after evaporating the surplus HF away, several drops of HNO_3 was added. The resulting sample was finally dried with a water bath and then was dissolved in pH 3.1 0.1 mol L^{-1} $NaNO_3$ solution to 50.00 mL(denoted as solution A).

Preparation of *p*-aminobenzoic acid modified glassy carbon electrode: The *p*-aminobenzoic acid modified glassy carbon electrode was fabricated according to Liu *et al.*[18] and Cheng *et al.*[19]. The modified glassy carbon electrode were immersed in 0.1 mol L^{-1} KCl solution containing 5 mmol L^{-1} $K_3[Fe(CN)_6]$ and conducted cyclic voltammogram. Results were found the electrons were completely hindered, indicating the glassy carbon electrode has been modified by *p*-aminobenzoic acid successfully.

Measurement procedure: The three-electrode system was first scanned to a stable current in the blank solution, then was immersed in solution A (or a proper amount of copper(II) in pH 3.10 0.1 mol L^{-1} $NaNO_3$ for the condition selection and standard curve-protraction), after being kept for 0.5 h, the cyclic voltammograms were recorded between -0.6 and +1.0 V (*vs.* Ag/AgCl) at a scan rate of 0.1 V s^{-1}, respectively. Before the electrochemical measurements, all solutions were thoroughly deoxygenated by purging with pure N_2 for 10 min. All experiments were conducted at room temperature.

RESULTS AND DISCUSSION

Electrochemical behaviour of copper(II) on bare and modified glassy carbon electrode: Fig. 1 shows cyclic voltammograms of 1.0×10^{-4} mol L^{-1} copper(II) at bare and *p*-aminobenzoic acid modified glassy carbon electrode in 0.1 mol L^{-1} $NaNO_3$ solution (pH = 3.10). Comparing bare glassy carbon electrode, copper(II) yields a higher cathodic peak current (i_p) at about +0.027 V on the modified one. It suggested that the modification catalyzed the electrode for detecting copper(II). This was attributed to the preconcentration of copper(II) on modified glassy carbon electrode surface. As the *p*-ABA modified glassy carbon electrode surface was negatively charged[18], it could be readily acceptable that the copper(II) were accumulated on the COO^--terminated electrode. The
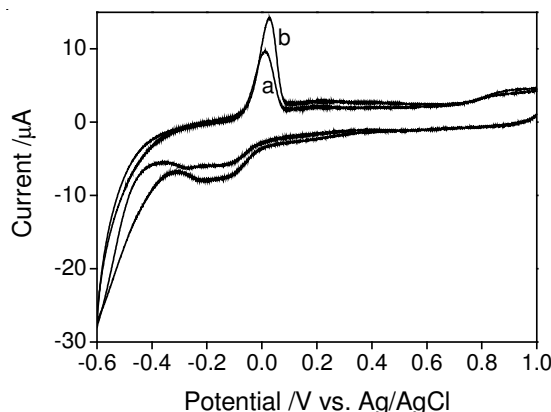

Fig. 1. Cyclic voltammograms of copper(II) on (a) bare and (b) *p*-aminobenzoic acid modified glassy carbon electrode
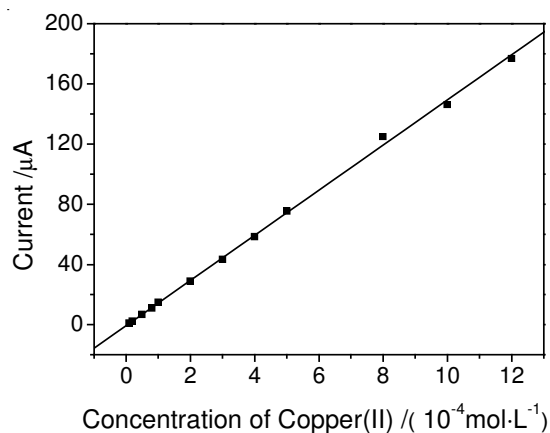

Fig. 2. Peak current *versus* various concentration of copper(II)

cathodic peak currents (i_p) *vs.* concentration of copper(II) (c) was found to be in good linearity over c between 1.0×10^{-5} and 1.2×10^{-3} mol L^{-1}, with regression equation $i_p = -0.4517 + 14.91c$ (Fig. 2), the correlation coefficient value of 0.9991 and detection limit of 5×10^{-6} mol L^{-1}, where i_p is in μA, c is in 10^{-4} mol L^{-1}.

pH plays an important role for recording cyclic voltammograms, because it not only affects the charged state of electrode surface but also the existing forms of copper(II) in solution. The effect of pH on the peak current of copper(II) on various electrodes had also been studied by Walcarius[20,21] and Arrigan[22], respectively. In this study, the cathodic peak current was found to be increasing rapidly with increasing pH from 1.8 to 2.3 and decreased gradually between 2.3 and 3.4 and then decreased sharply (Fig. 3). Liu *et al.*[18] has reported the surface pKa of the *p*-aminobenzoic acid modified electrode was 3.1. The highest peak current was found at pH around 2.3, under which the electrode surface was mainly dominated by COOH-terminal, with a small part of COO^--terminal, while the copper(II) mainly exist as cations. The highest peak current was not found out at the complete COO^--terminated surface. It indicated that the preconcentration of copper(II) onto the electrode surface might depend on complexation, not electrostatic force. To receive a reproducible result, in the present work, all experiments were conducted at pH 3.10 strictly, which could make every modified electrode have the same charged surface, thus the influence of pH was reduced.
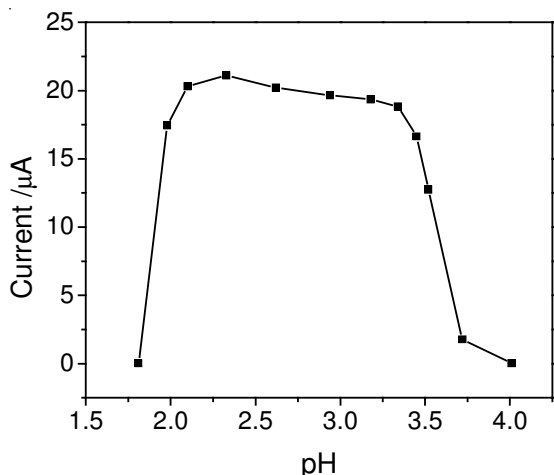
Fig. 3. Peak current *versus* pH in 1.37×10^{-4} mol L^{-1} copper(II) solution

Determination of copper (II): The reliability of the method was first validated by determining several copper(II) samples. The results were listed in Table-1. As can be seen, the average recovery of standard addition was 98.03 % which indicated that this method could be used for the determination of copper(II).

TABLE-1
DETERMINATION OF COPPER(II)

Sample	$c_{Copper(II)}$ (10^{-5} mol L^{-1})	Added (10^{-5} mol L^{-1})	Found (10^{-5} mol L^{-1})	Recovery (%)	Average ± SD (%)
1	5.280	5.357	10.18	95.7	
2	9.644	9.090	18.33	97.8	98.03±2.46
3	19.050	18.180	37.45	100.6	

Determination of amino group content on nanosilicas: γ-Amino-propyltriethoxysilane modified nanosilica samples were pretreated following by the proposed procedures and a proper amount of the result solution A was conducted cyclic voltammetry. The amount of amino group was calculated from the detected copper(II) and the linear equation. In order to confirm the accuracy of this method, atomic absorption spectroscopy (AAS) was carried out on a Z-2000 atomic absorption spectrophotometer (Japan) at the same time. Results were listed in Table-2. It illustrated that there was no significant

TABLE-2
AMINO AMOUNTS ON AMNS WITH DIFFERENT METHOD

Method	Amino amount (mmol g^{-1})	Average ± SD (mmol g^{-1})	RSD (%)
Proposed method	1.182 1.223 1.177 1.208 1.170	1.194±0.0261	2.19
AAS method	1.148 1.205 1.188 1.094 1.280	1.183±0.0690	5.84

difference between the both results. But compared with AAS method, the proposed method was of greater reproducibility. In addition, the proposed method was much simpler and more suitable for routine detection in laboratory.

Conclusion

A *p*-aminobenzoic acid modified glassy carbon electrode was fabricated and has been successfully developed for determination of amino content on nanosilica using copper(II) as intermediate. It was found that the accumulation of copper(II) onto modified electrode surface mainly depend on the complexation. The established method can be readily used to quantitatively determine the amount of amino on nanosilicas, with good reproducibility and accuracy. It was hoped that the results could provide the information about amino amount on APTES/nano-SiO$_2$, serving technical support for the development and application of this kind nanosilica.

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