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# Selective detection of copper ion in water by tetradentate ligand sensor

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## ABSTRACT

Tetradentate ligand, 3,5-bis(((2-hydroxynaphthalen-1-yl)methylene)amino)benzoic acid (3,5-BHNMABA), was synthesized for the selective detection of copper ion. The fluorescence of the ligand in solution was quenched about 72% by Cu(II) and about 18% by Fe(II), but it was scarcely influenced by the existence of other metal ions. The ligand was chemically bound on self-assembled monolayer on indium tin oxide electrode. The as-prepared electrode exhibited the electrochemical recognition ability for metal ions: Cu(II) could be selectively caught to 3,5-BHNMABA ligand on the electrode, but Fe(II) and other metal ions did not display electrochemical response. Results indicate the selective coordination linkage of Cu(II) with the ligand both in solution and on electrode, being different from other ions. It can be concluded that the 3,5-BHNMABA-functionalized electrode is a favorable sensor for the selective detection of Cu(II) in water.

## 1. Introduction

The environmental contamination by undesirable inorganic, organic and organometallic species is one of the serious issues faced by the world. Since metals are biologically nondegradable, they tend to be accumulated in various vital organs. Therefore, even if their concentrations are of only injection/exposure trace, diverse metal ions can lead effects during long term. Copper is an essential and necessary micronutrient for many plants and animals. Copper in the natural environment could be accumulated within the food chain. Drinking water can be a potential source on the condensation of Cu(II) because of its production and/or use in industries [1]. Then, high doses of copper in drinking water are hazardous to animals (including humans) and aquatic plants, where the cell membranes prevent the transport of materials across the cell walls [2–5]. The excessive intake of Cu(II) could injure human kidney, liver and other internal organs and increase blood pressure and respiratory rate [6,7]. Moreover, diseases have been found to closely relate to the disorder of Cu(II) metabolism [8]. Therefore, its maximum permissible limit in drinking water should not exceed $0.05\,g/cm^3$ [9]. Hence, rapid, simple and sensitive methods for the detection of copper are in great demand. The determination of Cu(II) has been performed using various analytical methods such as spectrophotometry, fluorescence, ion chromatography, inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma–atomic emission spectrometry (ICP–AES), atomic absorption spectrometry and electroanalytical techniques [10–18]. Some of these methods are either time-consuming or requiring highly designed and costly instruments. Thus, spectrophotometric, fluorescent and electrochemical sensors have attracted attention due to their high sensitivity, universal effectiveness and less cost.

Ion-selective sensors are the convenient and quick analysis tools to monitor metals. Thus, Cu(II) selective sensors based on copper chelates [19], oximes [20,21], 4-decyloxy-2-(2-pyridylazo)−1-naphthol [22], 4-phenylpiperazinecarbodithioate [23], and 3-(((5-ethoxy-benzenethiol)imino)methyl)-salicylic acid [24] have been reported. However, most of these sensors suffer from the restrictive characteristics of electrodes, *i.e.*, applicable concentration range, selectivity, response time, pH range and life time. It is known that Schiff base ligands can coordinate copper ions to form strong complexes with them, as these ligands can be used for exploiting the metal ions in aqueous solutions [25–27]. Therefore, in this paper, a selective Schiff base, 3,5-bis(((2-hydroxynaphthalen-1-yl)methylene)amino)benzoic acid (3,5-BHNMABA), was synthesized and the selective binding was identified among various metal ions in aqueous solutions by means of ultraviolet (UV)–visible absorption and fluorescence spectroscopy. This ligand was also bound chemically on siloxane self-assembled monolayer (SAM) on indium tin oxide (ITO) electrode, and the selective binding of metal ions from aqueous solutions was electrochemically investigated. To the

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best of our knowledge, there was no electrochemical study handling the selective sensing of Cu(II) among coexisting metal ions by means of the coordination with a 3,5-BHNMABA Schiff base ligand on ITO-based electrode.

## 2. Experimental section

### 2.1. Materials

Chemicals of 3,5-diaminobenzoic acid (99+%) and 2-hydroxynaphthalene-1-carbaldehyde (99+%) were purchased from Acros Organic, and 3-(aminopropyl)triethoxysilane (APTES), 3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) and methanol (99.5%) were purchased from Wako chemicals. An aqueous ammonium (35 v/v%) solution was obtained from Fisher Scientific Limited. $Pb(CH_3COO)_2{\cdot}3H_2O$, $Cu(CH_3COO)_2{\cdot}H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Cd(CH_3COO)_2{\cdot}2H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, $Hg(ClO_4)_2{\cdot}5H_2O$, $FeSO_4{\cdot}5H_2O$, $KNO_3$ and phosphate buffer were purchased from Sigma Aldrich. ITO substrate (8–12 Ω) was acquired from Delta Technologies, Ltd. All other supplied chemicals were of standard reagent grade quality.

### 2.2. Measurements

Measurements of UV–visible absorption and fluorescence spectra were carried out with Shimadzu UV-2200 and Hitachi F-7000 spectrophotometers, respectively. These measurements were performed using a 1 cm quarts cell or a modified ITO substrate. The static contact angle measurement was performed by using a conventional camera. Fourier transform infrared (FT-IR) absorption spectra were obtained using a Nicolet 6700 FT-IR spectrophotometer by a KBr pellet method. The $^1H$ NMR spectra were recorded on a Varian AMX 400 MHz instrument. The electrochemical measurements were performed on an electrochemical measurement system (HZ-3000, Hokuto Denko) at a scan rate of 50 mV $s^{-1}$ with a three-electrode cell consisting of modified ITO substrate as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode. The supporting electrolyte used was a phosphate buffer containing 0.1 M $KNO_3$ at pH 7.0, which was degassed by nitrogen bubbling. Stripping voltammograms were recorded on a universal electrochemical Zahner system. All the measurements were carried out at room temperature.

### 2.3. Synthesis of tetradentate ligand, 3,5-bis(((2-hydroxynaphthalen-1-yl)methylene)amino)benzoic acid (3,5-BHNMABA)

A methanol solution (20 mL) of 3,5-diaminobenzoic acid (2 mmol, 0.304 g) was added drop wise in a methanol solution (20 mL) of 2-hydroxynaphthalene-1-carbaldehyde (4 mmol, 0.723 g) at 40–50 °C with continuous stirring. After further continuous stirring for 2 h, the reaction mixture was cooled down to room temperature and left to stand overnight. The resulting precipitate (orange solid product) was filtered, washed with water several times, and dried in air. The crude solid was recrystallized from aqueous ethanol and dried on $CaCl_2$. Yield = 68%. Infrared absorption spectrum ($cm^{-1}$, KBr pellet): 3400 (O–H), 2900 (C–H), 1680 (C=N, C=O) and 1430 and 1280 (C–O, O–H). $^1H$ NMR (DMSO-$d_6$, $\delta$/ppm): 7.56–8.45 (d, 8H, Ar–H), 7.56–8.45 (q, 4H, Ar–H), 8.69 (s, 3H, Ar–H), 9.075 (d, 2H, HC=N), 10.39 (d, 2H, OH phenolic), 11.35 (s, 1H, OH carboxylic).

### 2.4. Preparation of solutions and modified-ITO electrodes

An acetone solution of 3,5-BHNMABA (1.0 mM) was diluted to 0.01 mM by 9:1 acetone:$H_2O$ (v/v) at pH 7.0. Aqueous solutions of metal ions were prepared at a concentration of 1.0 mM. For a solution of 3,5-BHNMABA (2 mL) in a quartz cell of 1 cm optical path length, an adequate amount of a solution of metal ion was gradually added. The mixed solution was provided for spectroscopic measurements.

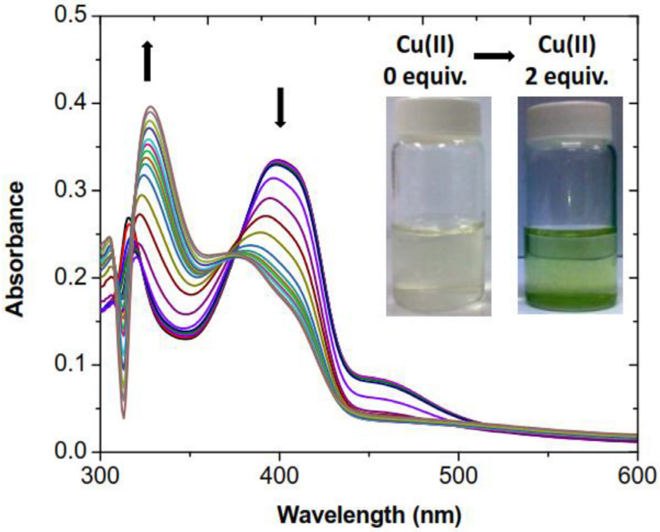

**Fig. 1.** UV–visible absorption spectra of 3,5-BHNMABA (10 $\mu$M) in acetone/water (9:1 v/v) upon the addition of 0–2 equivalent Cu(II).

The ITO electrode (0.5 × 1 cm size) was cleaned by sonication (10 min) and washed with acetone, ethanol and then water. The cleaned ITO electrode was treated with a solution of $H_2O_2/NH_4OH/H_2O$ (a ratio of 1:1:5 vol%) for 30 min at 60 °C to obtain the hydroxylated active surface on ITO and immersed in a toluene solution of APTES (2.0 vol%) at 70 °C for 48 h [28]. The prepared ITO/APTES electrode was then rinsed with toluene and dried under nitrogen. Then ITO/APTES electrode was immersed for 24 h in a solution of 3,5-BHNMABA ligand (1.0 mM) in the presence of EDAC for amidation reaction in order to covalently immobilize a COOH group of the legend onto amine group of APTES [29,30] on ITO electrode [28]. The resulting electrode was rinsed with water and dried by nitrogen gas flow. The ITO/APTES/3,5-BHNMABA-modified electrode was maintained in a closed vessel in a refrigerator before use. Contact angles for ITO, ITO/APTES and ITO/APTES/3,5-BHNMABA electrode substrates were 80° ± 0.4°, 67° ± 0.6° and 48° ± 0.4° respectively. The whole scheme of the procedure is shown in Supporting Information Fig. S1. For the electrochemical study, the stock solutions of metal ions (10 mM) in water were prepared from corresponding salts. All the other solutions were prepared using standard laboratory procedures.

## 3. Results and discussion

### 3.1. Selective detection of copper ion in a solution

The complexation capability of 3.5-BHNMABA with metal ions was investigated in acetone/water (9:1 v/v) by UV–visible absorption spectroscopy. The 3.5-BHNMABA exhibited strong absorption bands at 324 and 400 nm, being characteristic of $\pi$–$\pi^*$ and n–$\pi^*$ transitions of electrons, respectively [31]. The significant change was observed in the UV–visible absorption spectra upon the addition of 0–2 equivalent Cu(II) (Fig. 1), where the solutions varied the color from light orange to green. A band at 400 nm was weakened and a band at 324 nm was intensified with red shift to 328 nm, indicating the intramolecular charge transfer [31]. Although the similar variation on absorption spectra of 3,5-BHNMABA was observed

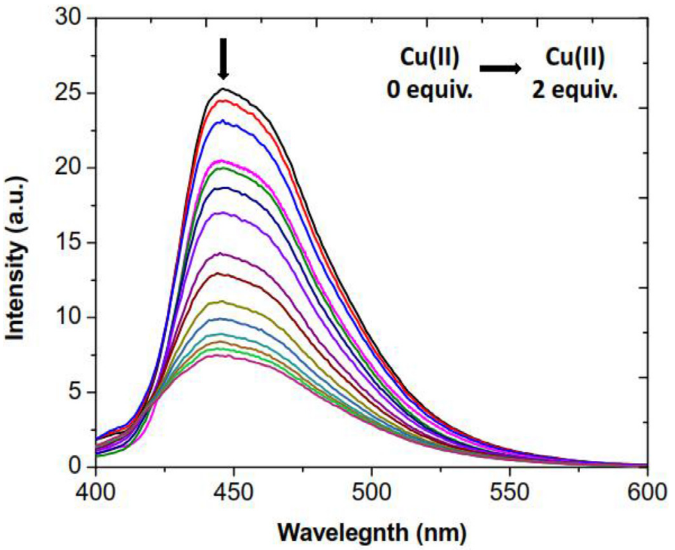

**Fig. 2.** Fluorescence spectra of 3,5-BHNMABA (10 $\mu$M) in acetone/water (9:1 v/v) upon the addition of 0–2 equivalent Cu(II). The excitation wavelength is 380 nm.

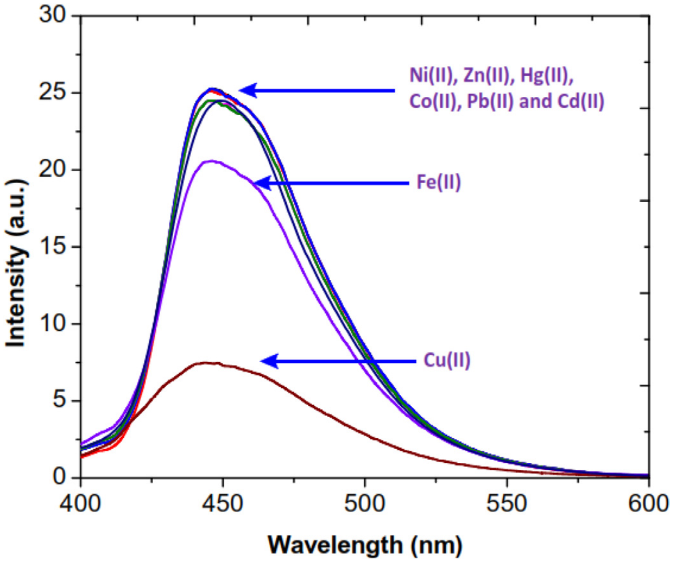

**Fig. 3.** Fluorescence spectra of 3,5-BHNMABA (10 $\mu$M) in acetone/water (9:1 v/v) upon the addition of Cu(II), Ni(II), Zn(II), Hg (II), Fe(II), Co(II), Pb(II) or Cd(II) (each 20 $\mu$M). The excitation wavelength is 380 nm.

even for the addition of Fe(II) (Fig. S2), the addition of Ni(II), Zn(II), and Hg(II) gave rise to less or negligible spectral variation in comparison with those of Cu(II) and Fe(II). (data is not shown). These results suggest the remarkable selectivity of 3,5-BHNMABA toward Cu(II) and Fe(II).

The complexation of 3,5-BHNMABA with metal ions in acetone/water (9:1 v/v) was also investigated by fluorescence spectroscopy. Fluorescence spectra of the 3,5-BHNMABA solution exhibited an emission band at 450 nm (at $\lambda_{\mathrm{ex}}$ 380 nm). Upon the addition of 0–2 equivalent Cu(II), the emission intensity at 450 nm decreased gradually, as shown in Fig. 2, since the formation of 3,5-BHNMABA-Cu(II) complex enhances the intramolecular charge transfer [31]. When the quenching behavior was compared among different metal ions (Fig. 3), Cu(II) showed the quenching effect (about 72%), and the effect was higher than Fe(II) (about 18%), but other metal ions did not quench definitely (less than 5%). These behaviors are qualitatively consistent with those of UV–visible absorption spectra. These results suggest the remarkable selectivity of 3,5-BHNMABA toward Cu(II) in solution.

### 3.2. Characterization of ITO/APTES/3,5-BHNMABA electrode

When 3,5-BHNMABA ligand was covalently immobilized on the ITO/APTES-modified electrode, the ITO/APTES/3,5-BHNMAB electrode exhibited strong absorption bands at 324 and 400 nm, and its fluorescence emission band at 380 nm excitation appeared at 450 nm (see Fig. S3), although no fluorescence band justifiably occurred from the APTES-modified ITO electrode. These spectroscopic behaviors are consistent with those of 3,5-BHNMABA in solution, indicating the successful immobilization of 3,5-BHNMABA on the ITO/APTES electrode. The consistency of spectra also suggests no electronic structural variation of 3,5-BHNMABA after the immobilization.

The electrochemical behavior of 3,5-BHNMABA-functionalized ITO/APTES electrode was examined by cyclic voltammetry (CV) in a phosphate buffered saline (PBS) at pH 7.0 containing $KNO_3$ supporting electrolyte and compared with ITO and APTES-modified ITO electrodes in Fig. S4. The ITO electrode showed a sensible cathodic peak response with a peak potential ($E_{\mathrm{pc}}$) at −0.62 V and a peak current ($I_{\mathrm{pc}}$) at −25 μA/cm$^2$. However, the modification of ITO surface with APTES did not change largely the cathodic peak potential but enhanced the peak current: an ITO/APTES electrode showed a cathodic response at$E_{\mathrm{pc}} = -0.64$ V and $I_{\mathrm{pc}} = -50$ μA/cm$^2$. It should be assumed that amino groups on APTES-modified ITO positively charge in aqueous solution and cause an easy electron transfer reaction on the electrode surface [32]. Meanwhile, on a CV of ITO/APTES/3,5-BHNMABA electrode, a cathodic peak potential at $E_{\mathrm{pc}} = -0.80$ V and a peak current at $I_{\mathrm{pc}} = -18$ μA/cm$^2$ were fairly lower than those of ITO/APTES electrode. It is supposed that after the immobilization of 3,5-BHNMABA on ITO/APTES electrode, the amide bond is formed between ligand and APTES so that positively charged amino groups are decreased.

### 3.3. Detection of metal ions on ITO/APTES/3,5-BHNMABA electrode

The detection of metal ions by ITO/APTES/3,5-BHNMABA-electrode was performed in PBS containing 0.1 M $KNO_3$ at pH 7.0. When the electrodes were immersed in a solution in the presence of 0.02 mM Cu(II), the bare ITO and ITO/APTES electrodes did not show any potential response for the detection of Cu(II) at a potential range of −1.0 to 1.0 V. Meanwhile, Fig. 4 revealed that the ITO/APTES/3,5-BHNMABA electrode displayed the oxidation and reduction potentials at $E_{\mathrm{pa}} = -0.12$ V, $E_{\mathrm{pc}} = -0.20$ V and $\mathrm{I}_{\mathrm{pa}} = 10.0$ μA/cm$^2$, $\mathrm{I}_{\mathrm{pc}} = -34.0$ μA/cm$^2$, respectively. The consequent redox peak potentials and currents correspond to changes of $\Delta E_{\mathrm{p}} = 0.08$ V and $\Delta I_{\mathrm{p}} = 44.0$ μA/cm$^2$.

The peaks can be assigned to result from the redox process of Cu(II), since the ITO/APTES/3,5-BHNMABA electrode did not exhibit any redox peaks in this potential range in the blank solution without Cu(II). The ITO/APTES/3,5-BHNMABA electrode can coordinate Cu(II) via two azomethine (>C–NH–) and two hydroxyl (–OH) groups at pH 7.0 (see Fig. 5). In the electrochemical reaction, an anodic peak in the CV is a reduction process corresponding to the variation of Cu(II) to Cu(I) and a cathodic peak is for an oxidation of Cu(I) to Cu(II). On the forward scan, the ITO/APTES/3,5-BHNMABA electrode exhibits an anodic peak potential ($E_{\mathrm{pa}}$) at −0.12 V and, on the reverse scan, an intense cathodic peak potential ($E_{\mathrm{pc}}$) is observed at −0.20 V. Therefore, the corresponding redox peaks are due to the two-way reaction of Cu(II) and Cu(I). The anodic peak of the Cu(II)/Cu(I) electron transfer couple is less intense than the cathodic peak of the Cu(II)/Cu(I) reduction couple. This phenomenon can be explained on the basis of the stability of Cu(II) and Cu(I), which depends highly on environment of solution.

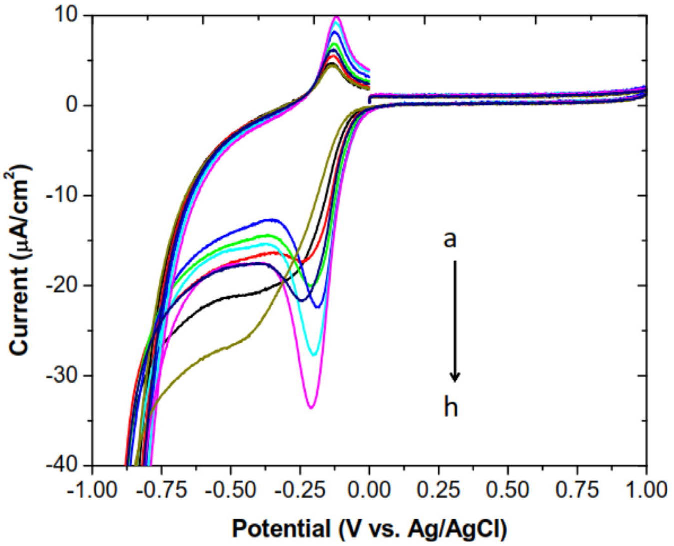

**Fig. 4.** Cyclic voltammograms on an ITO/APTES/3,5-BHNMABA electrode in 0.1 M PBS (pH 7.0) containing 0.1 M KNO$_3$ in the presence of Cu(II) from (a) 0.2 to (h) 26 $\mu$M. Scan potential: $-1.0$ to $+1.0$ V. Scan rate: 50 mV/s.

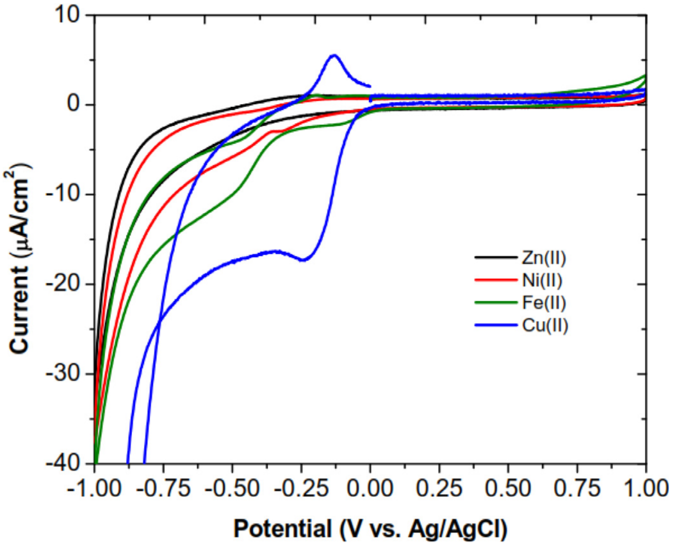

**Fig. 6.** Cyclic voltammograms on an ITO/APTES/3,5-BHNMABA electrode in 0.1 M PBS (pH 7.0) containing 0.1 M KNO$_3$ in the presence of Zn(II), Ni(II), Fe(II) or Cu(II) (each 10 $\mu$M). Scan potential: $-1.0$ to $+1.0$ V. Scan rate: 50 mV/s.

The stability at the aqueous atmosphere depends on the hydration energy of the ions, when they bind water molecules [33]. Cu(II) has a greater charge density than Cu(I) and, therefore, gives rise to stronger bond-releasing energy. On the other hand, Cu(I) is significantly stable in the presence of a complex-forming ligand and in nonaqueous media [34,35]. These results indicate that the copper ion coordinated on ITO/APTES/3,5-BHNMABA electrode generates a one-electron reduction/oxidation on electrode surface through an electrochemical mechanism as shown in Fig. 5. That is, the mechanism on the ITO/APTES/3,5-BHNMABA-electrode is

Cu(II) (in solution) + 3,5-BHNMABA (on ITO) → Cu(II)–3,5-BHNMABA (on ITO)

Cu(II)–3,5-BHNMABA (on ITO) + $e^-$ → Cu(I)–3,5-BHNMABA (on ITO)

Cu(I)–3,5-BHNMABA (on ITO) → Cu(II)–3,5-BHNMABA (on ITO) + $e^-$

Meanwhile, the concentration dependency of Cu(II) was investigated by cyclic voltammetry on the ITO/APTES/3,5-BHNMABA-electrode. The voltammetric current increased with the concentration of Cu (II) (Fig. 4). This indicates the existence of enough binding site for Cu(II) on the electrode.

CV study of various metal ions was investigated using ITO/APTES/3,5-BHNMABA electrode at the same condition as Cu(II). Fig. 6 shows the CV in the presence of Fe(II), Ni(II) and Zn(II) in comparison with Cu(II). Different from Cu(II), CV in the presence of Fe(II) displayed a weak cathodic peak at potential $E_{pc} = -0.50$ V and current $I_{pc} = -12.0$ µA/cm$^2$, which can be assigned to Fe(II) on electrode surface. Similarly, in the existence of Ni(II), the cathodic peak was observed at potential $E_{pc} = -0.50$ V and current $I_{pc} = -8.0$ µA/cm$^2$, and the addition of Zn(II) solution produced a peak at $E_{pc} = -0.60$ V and current $I_{pc} = -6.0$ µA/cm$^2$. However, these ions had weak cathodic peak currents against Cu(II). These results mention the remarkable selectivity of an ITO/APTES/3,5-BHNMABA-electrode toward Cu(II), and this mention is correlative to it from florescence in a solution system.

### 3.4. Selective detection of copper ion on ITO/APTES/3,5-BHNMABA electrode

Selective detection of Cu(II) was examined by cyclic voltammetry on the ITO/APTES/3,5-BHNMABA electrode. The experimental results described above indicate that the ITO/APTES/3,5-BHNMABA electrode possesses strong complex-forming and adsorption abilities, which could greatly improve the sensitivity of the detection of Cu(II). For this reason, here, CV on ITO/APTES/3,5-BHNMABA was examined under the coexistence of Cu(II), Ni(II), Fe(II) and Zn(II). Redox peaks of Cu(II) at $E_{pc} = -0.13$ V and $E_{pa} = -0.125$ V were intensified with increasing the concentration of Cu(II) in the range of 0.2–26 $\mu$M (Fig. 7), even if the concentration of Cu(II) is maximum

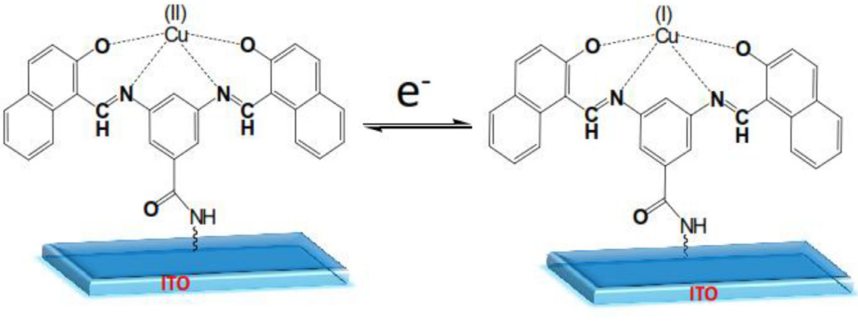

**Fig. 5.** Redox equation of copper ion on an ITO/APTES/3,5-BHNMABA electrode.

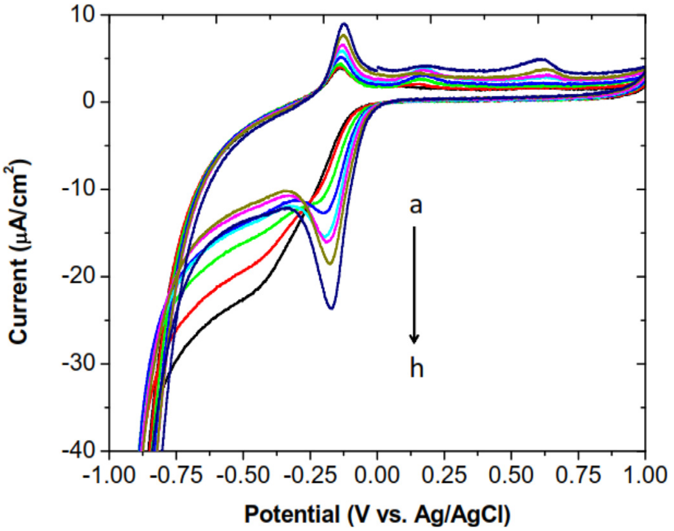

**Fig. 7.** Cyclic voltammograms on an ITO/APTES/3,5-BHNMABA electrode in 0.1 M PBS (pH 7.0) containing 0.1 M $KNO_3$ in the presence of Cu(II) from (a) 0.2 to (h) 26 $\mu$M. Coexisting metal ions: Ni(II), Zn(II) and Fe(II) (each 20 $\mu$M). Scan potential: −1.0 to +1.0 V. Scan rate: 50 mV/s.

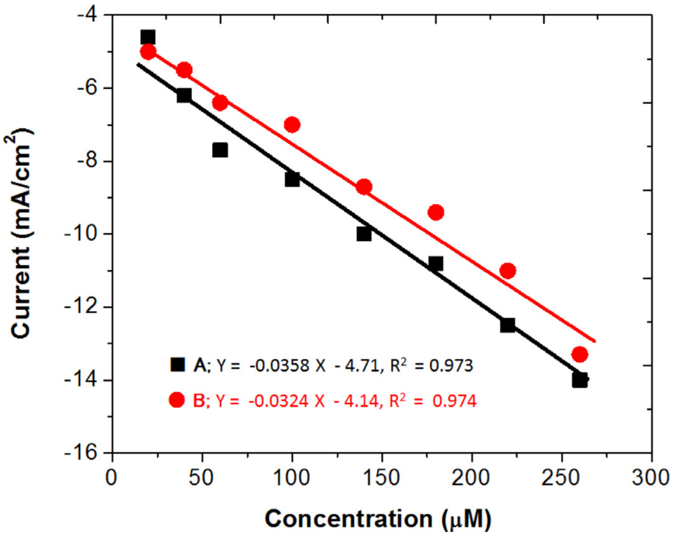

**Fig. 9.** The plot of stripping peak current as a function of concentration of Cu(II) (A) without and (B) with Ni(II), Zn(II), and Fe(II). Data comes from Figure S5. Linear regression equations with correlation coefficients are described in the figure.

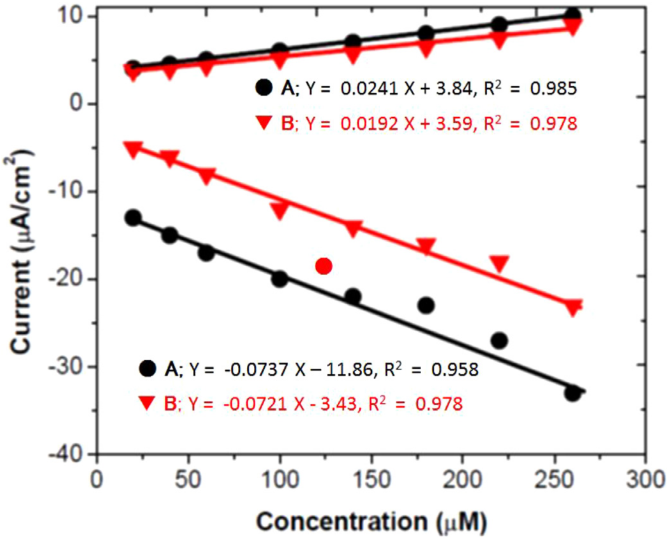

**Fig. 8.** The plot of redox peak current as a function of concentration of Cu(II) (A) without and (B) with Ni(II), Zn(II), and Fe(II). Data comes from Figs. 4 and 7. Linear regression equations with correlation coefficients are described in the figure.

100 times lower than that of additive metal ions (each 20 $\mu$M). This indicates the strong coordination of Cu(II) with the tetradentate ligand-loaded electrode and no influence of other metal ions on the binding of Cu(II). The CV in the coexistence of different metal ions (Fig. 7) can be compared to it without additive metal ions (Fig. 4). Fig. 8 shows the plot of the redox peak current as a function of the Cu(II) concentration from Figs. 4 and 7. Both anodic and cathodic peak currents ($I_{pa}$ and $I_{pc}$) linearly varied with similar slope against Cu(II) concentration, and their behavior was really inconsistence between solutions with and without additive metal ions.

Similar results were obtained even from stripping voltammograms recorded between −0.5 and 0.2 V. As shown in Fig. S5, no obvious stripping peak was observed on the ITO/APTES/3,5-BHNMABA electrode for a solution without Cu(II). In contrast, a stripping peak for Cu(II) was observed at −0.12 V on the ITO/APTES/3,5-BHNMABA electrode because of the abundant hydroxyl groups on the electrode, which can chelate with Cu(II) in the solution. Any additive peaks were not found even coexistence of Ni(II), Fe(II) and Zn(II), and the stripping peak current for both systems with and without additive ions linearly changed with the concentration of Cu(II) (Fig. 9). These results from cyclic and stripping voltammograms indicate that the coordination of Cu(II) on tetradentate ligand-loaded electrode is stoichiometric and that the ITO/APTES/3,5-BHNMABA electrode should selectively separate Cu(II) from the mixture with Ni(II), Zn(II) and Fe(II). Thus, the developed ITO/APTES/3,5-BHNMABA electrode is sensitive and selective to detect Cu(II) and, moreover, the present electrode possesses the specific coordination binding site of Cu(II), different from the modified ITO electrodes previously reported for the detection of metal ions (see Table S1).

## 4. Conclusions

The work in this paper describes a sensitive and selective ligand, 3,5-BHNMABA, as a sensor for Cu(II) in a solution and on a functionalized ITO electrode, which is easy to be fabricated. With a view to electrochemical characterization, the ITO/APTES/3,5-BHNMABA electrode was prepared chemically through the sequential functionalization process via self-assembled monolayer procedure. Spectroscopy and electrochemical analysis revealed that the 3,5-BHNMABA was successfully immobilized on an ITO electrode. The selective coordination of Cu(II) on 3,5-BHNMABA ligand was confirmed with fluorescence and CV techniques. The response of ITO/APTES/3,5-BHNMABA-electrode elucidated the electrochemical recognition of Cu(II) and showed its characteristic redox peaks even in the coexistence of other metal ions. Based on the obtained results, the present methodology provides an advanced assay for the detection of Cu(II) by means of the ITO/APTES/3,5-BHNMABA electrode, and it will contribute to the issue of sensing and removal. The detection limit of Cu(II) can be assumed at least 1 mg/$cm^3$ or less, and the preparation of electrode is not hard and less costly. Thus, the practicability of this assay tool for Cu(II) detection should be the subsequent matter of concern, including some issues like the mass production of the electrode and the fabrication of electrochemical analyzer device.

## Acknowledgments

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2017.01.009.

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