



## Short communication

# New copper complexes incorporated with the one-step preparation of ionic liquid carbon paste electrode for highly selectively reducing hydrogen peroxide



Hao Cheng<sup>a</sup>, Hui-Ting Chen<sup>b</sup>, Kuang-Chan Hsien<sup>c</sup>, Chi-Yu Lu<sup>d</sup>, Po-Yu Chen<sup>a,\*</sup>

<sup>a</sup> Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

<sup>b</sup> Department of Fragrance and Cosmetic Science, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

<sup>c</sup> School of Pharmacy, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

<sup>d</sup> Department of Biochemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

## ARTICLE INFO

## Article history:

Received 8 November 2013

Received in revised form 11 December 2013

Accepted 17 December 2013

Available online 27 December 2013

## Keywords:

Carbon paste  
Copper complex  
Electrocatalytic reduction  
Hydrogen peroxide  
Ionic liquid  
Modified electrode

## ABSTRACT

New copper complex compounds composed of 2,4,6-tris(2-pyridylmethylamino)-1,3,5-triazine (TPMATA) and  $\text{CuCl}_2/\text{CuSO}_4$  in water or ionic liquid (IL) were prepared. Two approaches were used to fix the copper complexes to the IL carbon paste electrodes through our previous one-step method. IL shows its advantage over the traditional organic binder paraffin oil because the electrodes demonstrated much higher activity towards hydrogen peroxide reduction. After introducing TPMATA– $\text{CuCl}_2$  dissolved in IL to the electrode, the electrode shows the best current response and selectivity to hydrogen peroxide reduction.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrogen peroxide is one of the most important analytes because  $\text{H}_2\text{O}_2$  is involved in various fields such as paper bleaching, food processing, textile industry, environmental analysis, cleaning products, minerals processing, oxidative stress study, fuel cell, and reactions of oxidases [1–5]. Developing the techniques of  $\text{H}_2\text{O}_2$  determination is, therefore, important.

Due to its convenience, sensitivity, selectivity, and immediate response, electrochemical detection of  $\text{H}_2\text{O}_2$  has its advantages over other techniques. Additionally, electrochemical apparatus is usually more compact than other instruments such as spectrophotometer. Consequently, electrochemical methods have been widely developed for  $\text{H}_2\text{O}_2$  detection [6–9]. While interference is regularly encountered because of the high overpotential of  $\text{H}_2\text{O}_2$  oxidation, determining  $\text{H}_2\text{O}_2$  by reduction successfully diminishes the interferences. Noble metals show noticeable catalytic activity to  $\text{H}_2\text{O}_2$  reduction but their high price encourages developing low-cost and efficient electrocatalysts such as electrodeposited-copper [10]. Another approach is using the copper complex compounds [11–16] which are potential electrocatalysts for preparing carbon paste electrodes. Carbon paste is

a convenient substrate for making composite electrode by simply mixing all components (including reactive materials) together [17]. Although ionic liquids (ILs) have demonstrated their advantages on electroanalysis [18,19] and are superior to paraffin oil as the binder in carbon paste [20], only few reports studied  $\text{H}_2\text{O}_2$  reduction at IL-carbon paste–copper complex electrodes [21–23], and these copper complexes were seldom employed in neutral condition and respond to different species, indicating lower selectivity.

Here we report new copper complexes composed of 2,4,6-tris(2-pyridylmethylamino)-1,3,5-triazine (TPMATA) and  $\text{CuCl}_2$  or  $\text{CuSO}_4$ , which were used for preparing IL-carbon paste electrodes via our previously developed one-step method for highly selective reduction of  $\text{H}_2\text{O}_2$ .

## 2. Experimental

TPMATA was prepared via the reaction shown in Fig. 1. THF/ $\text{CH}_3\text{OH}/\text{CHCl}_3$  was the solvent and HCl produced in the reaction was neutralized by diisopropylethylamine (DIPEA). The purified TPMATA and its copper complexes were analyzed by NMR and/or MALDI-TOF MS. 1-Butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)amide ionic liquid (BMP-TFSA IL) was prepared following the published procedures [24] and used as the organic binder for preparing carbon (graphite powder; GP) paste (IL-GP) using our previous one-step method [25]. Here, 300  $\mu\text{l}$  IL and 30 mg graphite were used. The paste (~1 mg) was spread onto screen-printed-carbon electrode (SPCE) to form the IL-GP/SPCE. Two

\* Corresponding author at: Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung City 80708, Taiwan. Tel.: +886 7 3121101x2587; fax: +886 7 3125339.

E-mail address: [pyc@kmu.edu.tw](mailto:pyc@kmu.edu.tw) (P.-Y. Chen).

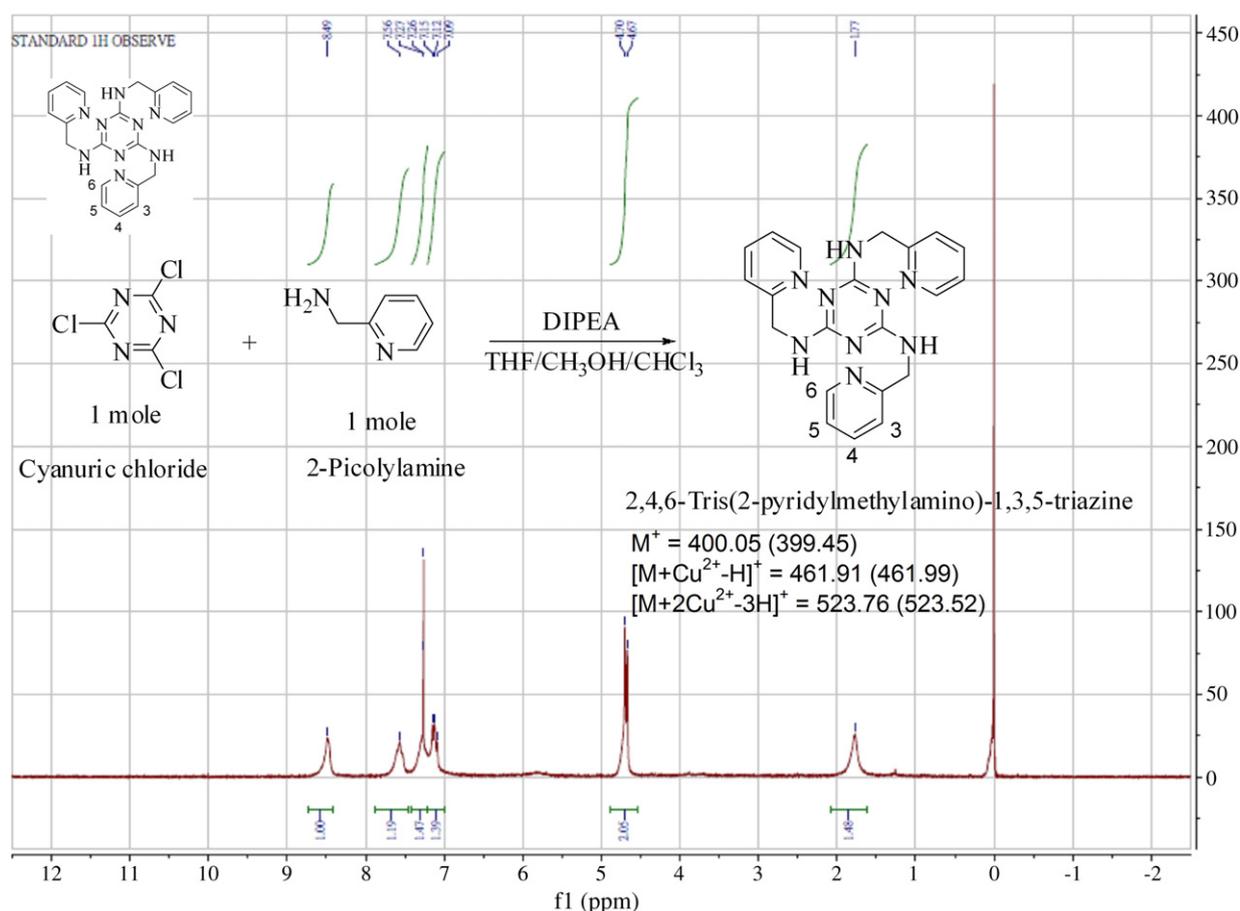


Fig. 1. Reaction scheme, NMR spectrum, and  $m/z$  values (from MALDI-TOF MS) of TPMATA.

ways were used to fix TPMATA–copper complexes to the IL-GP/SPCE. One is immersing the IL-GP/SPCE into TPMATA–CuCl<sub>2</sub> or TPMATA–CuSO<sub>4</sub> aqueous solutions (IL-GP-TPMATA–CuCl<sub>2(ads)</sub> or –CuSO<sub>4(ads)</sub>/SPCE) and the second is dissolving TPMATA and CuCl<sub>2</sub>/CuSO<sub>4</sub> in IL, which is directly used to prepare the electrodes (IL-GP-TPMATA–CuCl<sub>2(IL)</sub> or –CuSO<sub>4(IL)</sub>/SPCE).

Electrochemical experiments were performed with a CHI 621A electrochemical analyzer (CH Instrument) and a three-electrode cell was used where Ag/AgCl (NaCl saturated) and spiral Pt wire were respectively used as reference and counter electrodes. pH 7.4, 0.064 M Britton–Robinson (BR) buffer solution was used as the aqueous electrolyte.

### 3. Results and discussion

Fig. 1 shows the synthesis reaction and NMR spectrum of TPMATA. The molecular weight of TPMATA ( $m/z = 400.05$ ; numbers inside the parentheses are the theoretical molecular weight of the relevant species) was confirmed by MALDI-TOF MS. MS spectra indicated that  $[M + \text{Cu}^{2+} - \text{H}]^+$  ( $m/z = 461.91$ ) and  $[M + 2\text{Cu}^{2+} - 3\text{H}]^+$  ( $m/z = 523.76$ ) were produced after mixing TPMATA with three equivalents of CuSO<sub>4</sub> in water, indicating the formation of TPMATA–Cu<sup>2+</sup> complexes. Previous paper [26] shows that TPMATA reacts with three Cu<sup>2+</sup> ions to form metal-organic frameworks (MOFs) accompanied with the removal of proton of the amino groups. Thus three Cu<sup>2+</sup> ions are coordinated by one TPMATA. This was supported by our photometric titration experiments (data not shown). As a result, one equivalent of TPMATA and three equivalents of cupric salts were mixed to prepare the complex compounds.

Fig. 2a shows the UV–vis spectra of TPMATA, CuSO<sub>4</sub>, and their complex in the relevant solvents. The blue shift of the copper  $d-d$

transition (800 nm to 650 nm) upon the mixing of TPMATA and CuSO<sub>4</sub> confirms that a coordination compound was formed. The IL-GP-TPMATA–CuSO<sub>4(ads)</sub>/SPCEs were prepared by immersing the IL-GP/SPCE in the similar TPMATA–CuSO<sub>4</sub> aqueous solutions where copper complex was fixed onto the electrode by physical adsorption. IL-GP-TPMATA–CuSO<sub>4(ads)</sub>/SPCE, however, has low sensitivity towards H<sub>2</sub>O<sub>2</sub> reduction. Increasing the concentration of TPMATA–CuSO<sub>4</sub> can enhance the sensitivity but precipitates were formed while the concentration of TPMATA is higher than 8 mM. XRD analysis indicated that the precipitates contained Cu(OH)<sub>2</sub>. The increment of OH<sup>−</sup> concentration should result from the protonation at the amino groups of TPMATA, leading to the release of OH<sup>−</sup> from water. This behavior makes the system too complicated to be utilized. IL was thus used to prevent the formation of precipitates. Fig. 2b shows the UV–vis spectra of TPMATA–CuCl<sub>2</sub> or –CuSO<sub>4</sub> in IL. Presumably, the TPMATA–CuSO<sub>4</sub> complex in IL has a similar coordination structure as in water due to the similar  $d-d$  transition absorption (650 nm). The TPMATA–CuCl<sub>2</sub> in IL, however, has different color and UV–vis spectrum, indicating the different coordination structure which may result from the participation of Cl<sup>−</sup> ions in coordination. Fig. 2c demonstrates that IL-GP-TPMATA–CuCl<sub>2(IL)</sub>/SPCE exhibits the highest reduction current of H<sub>2</sub>O<sub>2</sub>, indicating that the anions of the cupric salts significantly contribute to the electrocatalytic activity. This behavior results from the different coordination environments of Cu<sup>2+</sup> while different cupric salts are used. The inset A shows the magnified dashed curve of IL-GP-TPMATA–CuCl<sub>2(IL)</sub>/SPCE. The reversible redox waves correspond to the Cu(II)/Cu(I) couple. Therefore, the catalytic reduction of H<sub>2</sub>O<sub>2</sub> at the electrode should result from the reaction between Cu(I) and H<sub>2</sub>O<sub>2</sub> [23]. Based on the scan rate-dependent experiments, the Cu(II)/Cu(I) was a surface-confined reaction. However, the H<sub>2</sub>O<sub>2</sub> reduction catalyzed by Cu(I) became diffusion-controlled, indicating an interfacial catalysis. Fig. 2c also indicates that

Download English Version:

<https://daneshyari.com/en/article/179057>

Download Persian Version:

<https://daneshyari.com/article/179057>

[Daneshyari.com](https://daneshyari.com)