



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^a, Hui-Ting Chen^b, Kuang-Chan Hsien^c, Chi-Yu Lu^d, Po-Yu Chen^{a,*}

^a Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

^b Department of Fragrance and Cosmetic Science, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

^c School of Pharmacy, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

^d 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– 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 H_2O_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 H_2O_2 determination is, therefore, important.

Due to its convenience, sensitivity, selectivity, and immediate response, electrochemical detection of H_2O_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 H_2O_2 detection [6–9]. While interference is regularly encountered because of the high overpotential of H_2O_2 oxidation, determining H_2O_2 by reduction successfully diminishes the interferences. Noble metals show noticeable catalytic activity to H_2O_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 H_2O_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 CuCl_2 or CuSO_4 , which were used for preparing IL-carbon paste electrodes via our previously developed one-step method for highly selective reduction of H_2O_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 μl 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 (P.-Y. Chen).

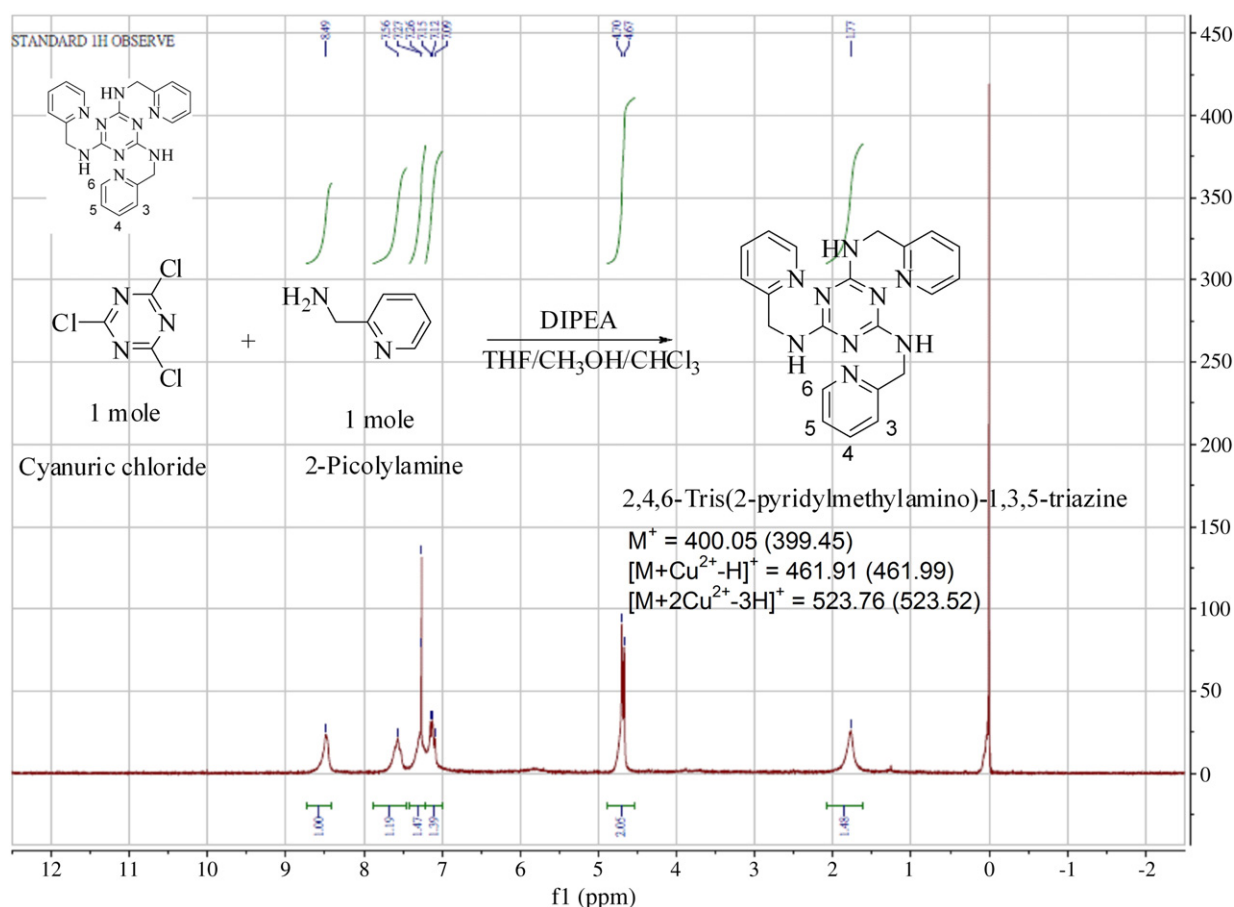


Fig. 1. Reaction scheme, NMR spectrum, and m/z values (from MALDI-TOF MS) of TPMATA.

ways were used to fix TPMATA–copper complexes to the IL-GP/SPCE. One is immersing the IL-GP/SPCE into TPMATA–CuCl₂ or TPMATA–CuSO₄ aqueous solutions (IL-GP-TPMATA–CuCl_{2(ads)} or –CuSO_{4(ads)}/SPCE) and the second is dissolving TPMATA and CuCl₂/CuSO₄ in IL, which is directly used to prepare the electrodes (IL-GP-TPMATA–CuCl_{2(IL)} or –CuSO_{4(IL)}/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 CuSO₄ in water, indicating the formation of TPMATA–Cu²⁺ complexes. Previous paper [26] shows that TPMATA reacts with three Cu²⁺ ions to form metal-organic frameworks (MOFs) accompanied with the removal of proton of the amino groups. Thus three Cu²⁺ 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, CuSO₄, 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 CuSO₄ confirms that a coordination compound was formed. The IL-GP-TPMATA–CuSO_{4(ads)}/SPCEs were prepared by immersing the IL-GP/SPCE in the similar TPMATA–CuSO₄ aqueous solutions where copper complex was fixed onto the electrode by physical adsorption. IL-GP-TPMATA–CuSO_{4(ads)}/SPCE, however, has low sensitivity towards H₂O₂ reduction. Increasing the concentration of TPMATA–CuSO₄ 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)₂. The increment of OH[−] concentration should result from the protonation at the amino groups of TPMATA, leading to the release of OH[−] 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–CuCl₂ or –CuSO₄ in IL. Presumably, the TPMATA–CuSO₄ complex in IL has a similar coordination structure as in water due to the similar $d-d$ transition absorption (650 nm). The TPMATA–CuCl₂ in IL, however, has different color and UV–vis spectrum, indicating the different coordination structure which may result from the participation of Cl[−] ions in coordination. Fig. 2c demonstrates that IL-GP-TPMATA–CuCl_{2(IL)}/SPCE exhibits the highest reduction current of H₂O₂, indicating that the anions of the cupric salts significantly contribute to the electrocatalytic activity. This behavior results from the different coordination environments of Cu²⁺ while different cupric salts are used. The inset A shows the magnified dashed curve of IL-GP-TPMATA–CuCl_{2(IL)}/SPCE. The reversible redox waves correspond to the Cu(II)/Cu(I) couple. Therefore, the catalytic reduction of H₂O₂ at the electrode should result from the reaction between Cu(I) and H₂O₂ [23]. Based on the scan rate-dependent experiments, the Cu(II)/Cu(I) was a surface-confined reaction. However, the H₂O₂ 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)