



Synthesis of new copper nanoparticle-decorated anchored type ligands: Applications as non-enzymatic electrochemical sensors for hydrogen peroxide



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ABSTRACT

In this work, copper nanoparticles (CuNPs) decorated on two new anchored type ligands were utilized to prepare two electrochemical sensors. These ligands are made from bonding amine chains to silica support including SiO₂-pro-NH₂ (compound I) and SiO₂-pro-NH-cyanuric-NH₂ (compound II). The morphology of synthesized CuNPs was characterized by transmission electron microscopy (TEM). The nano-particles were in the range of 13–37 nm with the average size of 23 nm. These materials were used to modify carbon paste electrode. Different electrochemical techniques, including cyclic voltammetry, electrochemical impedance spectroscopy and hydrodynamic chronoamperometry, were used to study the sensor behavior. These electrochemical sensors were used as a model for non-enzymatic detection of hydrogen peroxide (H₂O₂). To evaluate the abilities of the modified electrodes for H₂O₂ detection, the electrochemical signals were compared in the absence and presence of H₂O₂. From them, two modified electrodes showed significant responses vs. H₂O₂ addition. The amperograms illustrated that the sensors were selective for H₂O₂ sensing with linear ranges of 5.14–1250 μmol L⁻¹ and 1.14–1120 μmol L⁻¹ with detection limits of 0.85 and 0.27 μmol L⁻¹ H₂O₂, sensitivities of 3545 and 11,293 μA mmol⁻¹ L and with response times less than 5 s for I/CPE and II/CPE, respectively. As further verification of the selected sensor, H₂O₂ contained in milk sample was analyzed and the obtained results were comparable with the ones from classical control titration method.

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1. Introduction

Influential roles of hydrogen peroxide (H₂O₂) have been recently reported in many fields, such as biochemistry, clinical chemistry, and industrial chemistry. H₂O₂ is a by-product of several oxidative metabolic pathways [1], so the relationship of H₂O₂ with human health is therefore greatly attended [2]. Various diseases, including cancer, cardiovascular disorders, and Alzheimer's disease have been related to the presence of H₂O₂ [3]. Thus, determination of H₂O₂ is of practical importance in clinical and biochemistry researches [4–8]. H₂O₂ is also released into the environment in either large or small quantities resulting in wide applications of it in various industrial processes, for example, as the oxidizing, bleaching or sterilizing agents in packaged materials [9–11]. In addition to the remaining value of H₂O₂ from sterilizing process, H₂O₂ has been intentionally added to raw milk to protect it against bacteria. However excess of H₂O₂ can cause some deleterious problems on the nutritional value of milk and consumer health. Consequently, determination of present H₂O₂ in milk was considered as our objective in this work. Various methods have been reported to monitor H₂O₂, such as

spectrofluorometry, spectrophotometry, chemiluminescence, chromatography, and electrochemistry [12–18].

Among the different techniques involving H₂O₂ detection, electrochemical sensors have been substantially developed due to their operational simplicity, low cost, high sensitivity and selectivity, and the possibility of electrode modification with different types of nano-materials [19–50]. Electrochemical sensors for H₂O₂ determination are basically classified into two major types: enzymatic and non-enzymatic modified sensors. Although enzymatic sensors are highly sensitive and selective, they can be affected by temperature, pH, moistness, and incompatible species like charged detergents [51]. Thus, the development of non-enzymatic sensors has become a trend. Among the enzyme-free sensors, nano-based sensors have been developed.

Metal nanoparticles (MNPs) have represented different physical and chemical properties compared to corresponding bulk ones. This fact can be resulted from considerable differences in their surface area to volume ratios [52]. To improve some difficulties of MNP suspensions, including aggregation, recovery, and separation, immobilization of MNPs on the various supports such as silica, carbon nanotubes, clay and titanium dioxide has been reported [53–57]. In this category of supports silica because of high surface area, inertness and low cost could be also used as a support for bonding of organic groups immobilized by MNPs [57,58].

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In this work, two new electrochemical sensors on the basis of copper nanoparticles decorated anchored-based ligands were studied. The synthesized products were characterized using Fourier transform infrared (FT-IR) spectroscopy and transmission electron microscopy (TEM). The electrochemical characterizations of these sensors were investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Moreover, hydrodynamic chronoamperometric analysis of H_2O_2 in the ultra-high-temperature (UHT) milk was investigated by these new sensors. The detection limit and sensitivity of these modified electrodes were comparable to those recently reported by other reported works.

2. Experimental

2.1. Chemicals

Copper nitrate ($\text{Cu}(\text{NO}_3)_2$), silica (SiO_2), graphite, glucose, sucrose, glutamic acid, calcium nitrate, tetrahydrofuran (THF), toluene and paraffin oil were provided from Merck. Ascorbic acid, uric acid, dopamine, tartaric acid, and hydrogen peroxide were purchased from Sigma-Aldrich. All other reagents were of analytical grade and used without further purification. Phosphate solutions (PS, 0.1 mol L^{-1}) were prepared at various pHs by addition of sodium hydroxide to phosphoric acid. The water used throughout all experiments was double distilled water.

Three ultra-high-temperature (UHT) milk samples were supplied from three dairy companies, including Mihan, Pegah, and Sobhgah (Iran). The milk samples were pretreated by filtering the contained proteins.

2.2. Apparatus

All electrochemical measurements were recorded using an Autolab electrochemical analyzer, Model PGSTAT-30 potentiostat/galvanostat (Eco-Chemie, Netherlands) controlled by a microcomputer. General purpose electrochemical system (GPES, version 4.9, Eco Chemie B.V., Utrecht, The Netherlands) and frequency response analyzer (FRA, Chemie B.V., Utrecht, The Netherlands) were employed for data processing. Electrochemical studies were accomplished using a conventional three-electrode system, which the working, auxiliary and reference electrodes were modified carbon paste electrode (CPE), Pt-rod and $\text{Ag}/\text{AgCl}/3.0 \text{ mol L}^{-1} \text{ KCl}$, respectively. All electrochemical experiments were recorded when the surface of the electrodes were stabilized by 20 cycles of potential from -1.0 to $+1.0$ (V vs. Ag/AgCl). Cyclic voltammetric (CV) experiments were carried out in various pH solutions of PS at a scan rate of 100 mV s^{-1} . The amperometric measurements were performed at a hydrodynamic electrode by successive addition of H_2O_2 solution. Electrochemical impedance spectra (EIS) were performed with a frequency range of 0.01 Hz to 100 kHz and the amplitude wave potential of 10 mV , in a $10.0 \text{ mmol L}^{-1} \text{ Fe}(\text{CN})_6^{3-}$ solution in the presence of $0.10 \text{ mol L}^{-1} \text{ KCl}$, as a probe. All these electrochemical measurements were performed under ambient temperature.

Fourier transform infrared spectra were conducted on a FT-IR spectrometer (Jasco, FT/IR-680 Plus) at $400\text{--}4000 \text{ cm}^{-1}$ when the samples were premixed with KBr as pellets. The composition of the synthesized products were investigated by an elemental analyzer (GmbH Vario EL V5.19.11, CHNS mode). Transmission electron microscopy (TEM) images were acquired to monitor the size and morphology of the formed particles under an acceleration voltage of 150 kV with a TEM (TECNAI, Model F30, USA). The size distribution of the particles was determined using image analysis of TEM images. Digimizer software (version 4.1.1.0) and SPSS statistics (version 17.0) were employed for the image analysis.

2.3. Procedure

2.3.1. Synthesis of $\text{SiO}_2\text{-pro-NH-cyanuric-NH}_2$

The strategy for synthesis of silica-based anchored type ligands was summarized as follows: activation of silica was performed by heating at $500 \text{ }^\circ\text{C}$ for 3 h. Afterwards the mixture of the activated SiO_2 and 3-amino propyl trimethoxysilane were refluxed in toluene during 24 h. The synthesized product was named " $\text{SiO}_2\text{-pro-NH}_2$ ". 0.80 g of this product and 1.10 g of cyanuric chloride were stirred for 24 h at $0 \text{ }^\circ\text{C}$ in THF. This product was assigned as " $\text{SiO}_2\text{-pro-NH-cyanuric-Cl}$ ". $\text{SiO}_2\text{-pro-NH-cyanuric-Cl}$ was reacted with 1,2-ethylenediamine in CCl_4 for 24 h at $60 \text{ }^\circ\text{C}$. The obtained product was named as " $\text{SiO}_2\text{-pro-NH-cyanuric-NH}_2$ ". Each step was followed by filtering, washing and drying under vacuum. The steps of synthesis were monitored using FT-IR spectroscopy.

2.3.2. Formation of Cu-decorated $\text{SiO}_2\text{-pro-NH}_2$ (compound I)

1.00 g of $\text{SiO}_2\text{-pro-NH}_2$ was stirred in 20.0 mL of water until thoroughly dispersed. 10.0 mL of $\text{Cu}(\text{NO}_3)_2$ solution ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) was slowly added to the former dispersion during 13 h. Copper ions were reduced to copper nanoparticles (CuNPs) by addition of NaBH_4 (0.1 mol L^{-1}) under inert atmosphere of nitrogen gas. This product was washed off and dried under vacuum atmosphere.

2.3.3. Formation of Cu-decorated $\text{SiO}_2\text{-pro-NH-cyanuric-NH}_2$ (compound II)

In the same way as compound I, 1.00 g of $\text{SiO}_2\text{-pro-NH-cyanuric-NH}_2$ was thoroughly dispersed in distilled water. Then, $\text{Cu}(\text{NO}_3)_2$ solution was added drop by drop to the mixture. After that, CuNPs were formed by addition of NaBH_4 solution to the former mixture. The final product was washed off and dried under vacuum atmosphere.

2.3.4. Preparation of the modified carbon paste electrode (CPE)

The modified carbon paste electrodes were prepared by thoroughly blending graphite powder, compound I or compound II, and paraffin oil with a weight ratio of 6:1:3 (w/w). Afterwards, the electrical connection was provided by passing a copper wire through the paste. In the same way, the unmodified electrode was prepared by mixing graphite powder with SiO_2 instead of the compounds I and II. The CPEs were polished with a piece of weighing paper until the surface of electrodes became uniform.

3. Results and discussion

3.1. Characterization of synthesized compounds

The synthesized compounds were characterized using five various techniques including CHNS analysis, FT-IR, TEM, CV, and EIS. Using CHNS analysis, the elemental compositions of compounds I and II were respectively obtained by the molar ratio of 1:3.4:0.3 and 1.7:4:1, corresponded to C:H:N.

The synthesis steps were monitored by FT-IR spectroscopy, as shown in Fig. 1A. The FT-IR spectra were plotted in the wavenumber range of $400\text{--}4000 \text{ cm}^{-1}$. In spectrum (a), the absorption band of 1100 cm^{-1} was owing to the stretching vibration of Si–O–Si and the band located at $3200\text{--}3500$ implicated the stretching vibration of hydroxyl groups of SiO_2 . In spectrum (b), the corresponding bands of $2921\text{--}2940$ and $2840\text{--}2870 \text{ cm}^{-1}$ were in consequence of the stretching modes of $-\text{CH}_2-$, and the band located at $1590\text{--}1620 \text{ cm}^{-1}$ shows the N–H bond. In spectrum (c), cyanuric ring could be characterized by the absorptions located in the range of $1500\text{--}1700 \text{ cm}^{-1}$, which presented the existence of aromatic function in the product structure. At last, the bonding of ethylenediamine to the former structure was confirmed by appearing the stretching mode of N–H in 3000 cm^{-1} and 1610 cm^{-1} , as seen in spectrum (d). As shown in spectrum (e), the connection of copper to anchored type ligand was characterized

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