

Electrocatalysis for the hydrogen peroxide and nitrite at carbon paste electrode modified with a new zinc complex of 1-pentyl-1*H*-benzo[*d*][1,2,3]triazole

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Abstract A conductive carbon paste electrode (CPE) comprising a new zinc complex of $[\text{Zn}(\text{C}_{11}\text{H}_{15}\text{N}_3)_2\text{Cl}_2]$ and carbon powder was fabricated by the direct mixing method. The structure of $[\text{Zn}(\text{C}_{11}\text{H}_{15}\text{N}_3)_2\text{Cl}_2]$ was characterized by X-ray crystallography and elemental analysis. The electrochemical behavior and electrocatalysis of the new zinc complex modified CPE (Zn–CPE) have been studied in detail. This bulk-modified Zn–CPE displayed good electrocatalytic activity toward the reduction of the hydrogen peroxide and nitrite. The results are reproducible with a lower detection limit than reported currently using other modified electrodes. Also, this bulk-modified CPE exhibits remarkable long-term stability, simple preparation, and inexpensive material, which is important for practical application on electrochemistry sensors.

Keywords Crystal structure · Zinc complex · Bulk-modified carbon paste electrode · Electrocatalytic

Introduction

In recent years, the investigation of novel metal–organic frameworks represents one of the most active areas of material science and chemical research [1–5]. In these

materials, metal complexes have attracted much more attention not only for their interesting structures but also for the fact that they may be designed with specific functionalities in magnetic, optical properties, electronic conductivities and especially in electrochemistry and biosensors owing to their excellent electrocatalytic activity [6–8]. Electrochemical reactions catalyzed by metal complexes have received considerable attention during the past several decades [9, 10]. Most of those studies are focused on immobilizing the metal complexes using various techniques, such as electrochemical deposition, adsorption, and fabrication of multilayer ultrathin films [11]. A serious drawback in the application of these thin film-modified electrodes is their poor long-term stability; moreover, electrode surfaces cannot be renewed in the case of leakage, contamination, and passivation. Current chemically modified carbon paste electrodes are inexpensive and possess many advantages such as low background current, wide range of used potential, easy fabrication, and good performance comparison of traditional techniques [11–14]. In addition, renewing the surface of carbon paste electrodes avoids the contamination or deactivation of the surface between consecutive measurements [14]. The preparation of insoluble metal complexes and their application in electrode modification attracted the attention of many electrochemists. Up to now, only several research groups investigated the electrochemistry and electrocatalysis of transition metal complexes bulk-modified carbon paste electrode [15–19]. The idea of this work is to develop a new bulk-modified carbon paste electrode containing zinc complex of 1-pentyl-1*H*-benzo[*d*][1,2,3]triazole. Herein, we report the synthesis and crystal structure of $[\text{Zn}(\text{C}_{11}\text{H}_{15}\text{N}_3)_2\text{Cl}_2]$. The electrochemical properties of the title complex bulk-modified carbon paste electrode have been studied, and the Zn–CPE has electrocatalytic activities toward the hydrogen peroxide and nitrite in 0.1 M, pH 2, phosphates buffer solution (PBS).

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Experimental

Chemicals and measurement

All chemicals were of analytical reagent grade and used directly without further purification. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer (USA). Electrochemical measurements were performed on an Autolab PGSTAT-30 digital potentiostat/galvanostat (EcoChemie BV, Utrecht, The Netherlands). A three-electrode cell was used in the experiments. The working electrode was a modified CPE. The counter electrode was a platinum wire. The reference electrode was an Ag|AgCl|KCl (1 M), and all potentials reported in this work were measured versus this electrode (236.3 mV at 25°C). Supporting electrolytes used for electrochemical experiments were 0.1 M PBS (pH 2). All measurements were performed at room temperature (25±2°C).

The preparation and physical measurement of the title complex

Synthesis of $[\text{Zn}(\text{C}_{11}\text{H}_{15}\text{N}_3)_2\text{Cl}_2]$ Zinc chloride (136 mg, 1 mmol) and 1-pentyl-1*H*-benzo[*d*][1,2,3]triazole (378 mg, 2 mmol) were dissolved in 50 mL absolute alcohol. After 2 h, the white precipitate of $[\text{Zn}(\text{C}_{11}\text{H}_{15}\text{N}_3)_2\text{Cl}_2]$ was obtained by filtration. Recrystallization from acetonitrile gave a yield of 73.6%. The C, H, and N contents were determined by elemental analysis [anal. calcd for $\text{C}_{22}\text{H}_{30}\text{Cl}_2\text{N}_6\text{Zn}$ (%) C 51.33, H 5.87, N 16.32; found: C 51.31, H 5.88, N 16.33].

Reflection data and reflections for the unit cell determination were measured at 20°C using Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator. Empirical absorption correction was carried out using the SADABS [20] program. The structure of the title complex was solved by direct methods and refined by least squares on F_{obs}^2 using the SHELXTL [21] software package. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* [22].

Preparation of Zn-CPE

The traditional CPE was prepared by hand mixing of graphite powder with paraffin oil at a ratio of 70:30 (w/w) in an agate mortar. The procedure for the preparation of Zn-CPE was carried out according to [16]. Graphite powder (0.3 g) and the title complex (0.03 g) at a ratio of 10:1 (w/w) were mixed and ground together by agate mortar and pestle for approximately 30 min to achieve an even, dry mixture. To the mixture, 0.1 mL paraffin oil was added and stirred with a glass rod; then, the homogenized

mixture was used to pack 3-mm inner diameter glass tubes to a length of 0.8 cm. The electrical contact was established with the copper stick, and the surface of Zn-CPE was polished on a piece of weighing paper to get a mirror-like surface just before use.

Results and discussion

Crystal structure of the title complex

The molecular structure of the title complex was illustrated in Fig. 1. The Zn atom was four-coordinated and exhibited distorted tetrahedron geometry, and the coordination atoms were two nitrogen atoms from two ligands and two chlorine atoms. The two Zn–N bond lengths [2.040(3)–2.057(3) Å] were similar and consistent with those reported earlier [23]. Four angles of N–Zn–Cl were all larger than 100°; average angles are 106.86°. There was potentially weak C–H⋯Cl hydrogen bond intramolecular interaction; the donor and acceptor distance was 3.5182 Å for C(13)–H(13)⋯Cl(1). There were four types of π – π stacking interactions but no classic hydrogen bonds in the lattice. In the solid state, intermolecular interactions in this structure stabilized the crystal structure.

Electrochemical behavior of Zn-CPE

The electrochemical studies of the title complex modified CPE (Zn-CPE) were carried out in 0.1 M PBS (pH 2). The cyclic voltammograms (CVs) of a bare CPE (curve a) and Zn-CPE (curves b–f) were shown in Fig. 2. In the potential range –0.1 to –1.0 V, there was no redox peak at the bare CPE (curve a). While at the modified Zn-CPE, curve b had an obvious reduction peak at –0.678 V and one oxidation peak at –0.519 V when the scan rate was 0.05 V·s^{–1}, which indicated that the electrochemical behavior of the title complex on electrode was an irreversible process.

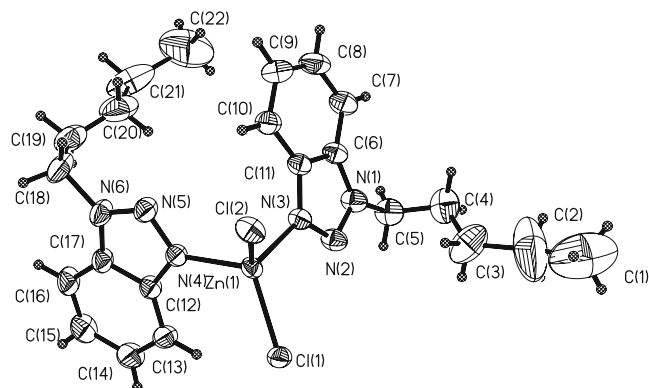


Fig. 1 ORTEP drawing of $[\text{Zn}(\text{C}_{11}\text{H}_{15}\text{N}_3)_2\text{Cl}_2]$ with partial atomic numberings

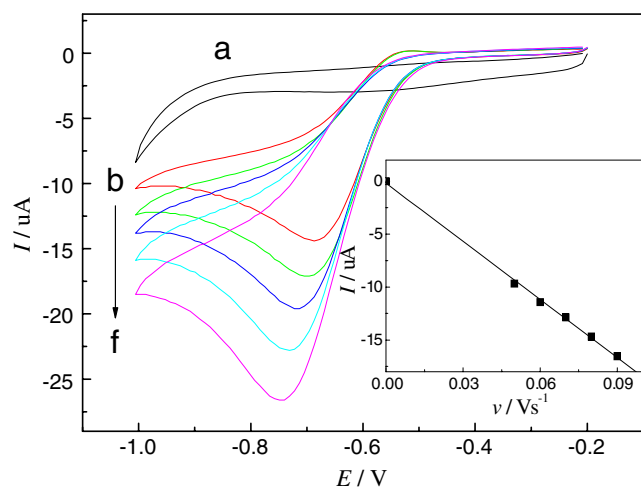


Fig. 2 CVs of the bare CPE (a) and Zn-CPE (b–f) in 0.1 M, pH 2, PBS. Scan rates (b–f) 0.05, 0.06, 0.07, 0.08, 0.09 $\text{V}\cdot\text{s}^{-1}$. Inset, the variation of peak currents vs. scan rate

Scan rates effect on the electrochemical behavior of the Zn–CPE can be seen from Fig. 2 (curves b–f). When the scan rate was varied from 0.05 to 0.1 $\text{V}\cdot\text{s}^{-1}$, the cathodic peak potentials shifted to negative direction with increasing scan rate. The plots of peak current versus scan rates were shown in the inset of Fig. 2; the cathodic currents were proportional to the scan rate, which were the characteristics of the surface adsorption-controlled process.

Electrocatalytic activity of the Zn–CPE

Electrocatalytic effect on reduction of hydrogen peroxide

Hydrogen peroxide is employed in pollution control, bleaching of textile and paper products, and in the processing of petrochemicals, minerals, food, and various products. Moreover, hydrogen peroxide is the product of various oxidases in countless biological reactions, and this fact has been used in the development of first-generation biosensors [24]. As is known, the electroreduction of hydrogen peroxide requires a large overpotential, and no obvious response was observed on a bare CPE [17].

The electrocatalytic activity toward H_2O_2 of Zn–CPE has been investigated in Fig. 3. Curve a was the cyclic voltammogram of the bare CPE in 0.1 M, pH 2, PBS with highest hydrogen peroxide concentration (2 mM), and there was no obvious response. With the addition of hydrogen peroxide (curves b–f), the reduction peak currents increased markedly, while the corresponding oxidation peak disappeared, which indicated that Zn–CPE had good electrocatalytic activity toward the reduction of hydrogen peroxide. This mechanism for the electrocatalytic action of Zn–CPE may be the electroreduction of Zn complex into elemental Zn, which could catalyze the reduction reactions,

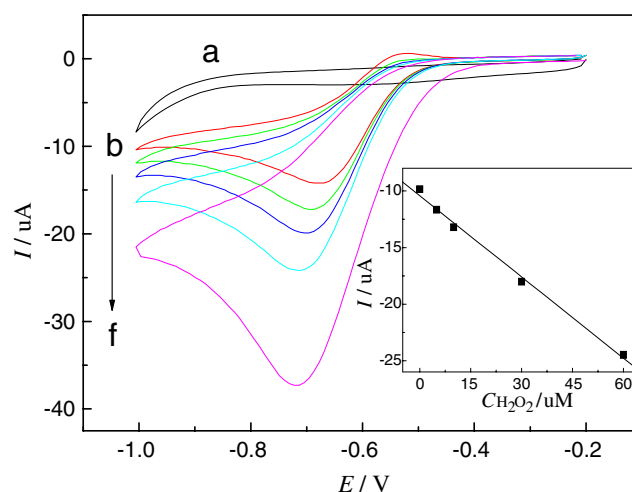


Fig. 3 CVs of a the bare CPE in 0.1 M, pH 2.0, PBS containing 2 mM H_2O_2 ; b–f Zn–CPE in 0.1 M, pH 2.0, PBS containing 0, 5, 10, 30, 60 μM H_2O_2 with the scan rate as 0.05 $\text{V}\cdot\text{s}^{-1}$. Inset, the variation of peak currents vs. H_2O_2 concentrations

especially when coupled to H^+ reduction yielding hydrogen, which is a strong reducing agent. The inset of Fig. 3 showed that catalytic current was found to be linear with hydrogen peroxide concentration in the range of 5–60 μM . The linear regression equation was $I_{pc} (\mu\text{A}) = -0.2923 C (\mu\text{M}) - 10.2$ with a correlation coefficient of 0.997, and the detection limit based on the signal-to-noise ratio of 3 was calculated to be 1.28 μM , which was much lower than reported currently [17].

Electrocatalytic effect on reduction of nitrite

Nitrite is a common pollutant from both agricultural and industrial sources. Many substrates such as porphyrins [25], heteropolyanion systems [14, 26] have been employed for

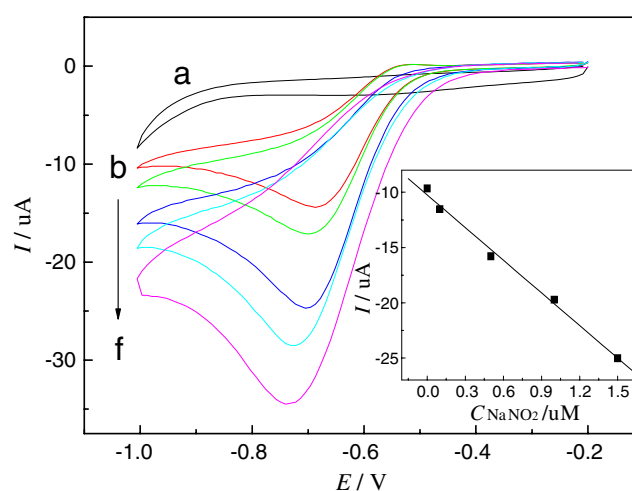


Fig. 4 CVs of a the bare CPE in 0.1 M, pH 2.0, PBS containing 2 mM nitrite; b–f Zn–CPE in 0.1 M, pH 2.0, PBS containing 0, 0.1, 0.5, 1.0, 1.5 μM nitrite with the scan rate as 0.05 $\text{V}\cdot\text{s}^{-1}$. Inset, the variation of peak currents vs. nitrite concentrations

the electrocatalytic reduction of nitrite in the past. As known, the electroreduction of nitrite requires a large overpotential, and no response is observed at a bare electrode [16].

In our experiment, we found that the Zn–CPE also displayed good electrocatalytic activity toward the reduction of nitrite, as shown in Fig. 4. Curve a was the cyclic voltammogram of the bare CPE in 0.1 M, pH 2, PBS with highest nitrite concentration (2 mM), and there was also no obvious response. Curves b–f indicated that Zn–CPE have good electrocatalytic activity toward the reduction of nitrite. With the addition of nitrite, the reduction peak currents increased. The process of electroreduction of nitrite at the surface of Zn–CPE was similar to that of the hydrogen peroxide. The inset of Fig. 4 showed that catalytic current was found to be linear with nitrite concentration in the range of 0.1–2 μM . The linear regression equation was $I_{\text{pc}} (\mu\text{A}) = -9.856C (\mu\text{M}) - 10.23$ with a correlation coefficient of 0.997, and the detection limit based on the signal-to-noise ratio of 3 was calculated to be 0.03 μM , which was much lower than reported currently using other modified electrodes [10, 17, 27].

Compared with other modified film electrodes, the title complex bulk-modified shows high stability. When the potential range was maintained in the same range, it was stable over 200 cycles at a scan rate of 0.05 $\text{V}\cdot\text{s}^{-1}$, and the current response remained almost unchanged. When the bulk-modified CPE was stored at room temperature for at least 2 months, the current response decreased only 2.3%.

Conclusions

In summary, a new complex of $[\text{Zn}(\text{C}_{11}\text{H}_{15}\text{N}_3)_2\text{Cl}_2]$ and the structure was characterized by X-ray crystallography. The electrochemical behavior and electrocatalysis of the new zinc complex modified CPE (Zn–CPE) have been investigated. This bulk-modified carbon paste electrode shows excellent electrocatalytic activity toward the reduction of the hydrogen peroxide and nitrite, and the results are reproducible with a lower detection limit than reported currently, which is suitable for the quantitative analysis of environmentally hazardous materials. The advantages of the bulk-modified Zn–CPE are its stability, excellent catalytic activity, high sensitivity, and simplicity of preparation in comparison with the other methods, which is important for practical application on electrochemical sensors.

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