



Effects of isomorphous substitution of a coordination polymer on the properties and its application in electrochemical sensing



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ABSTRACT

This work concerns the isomorphous substitution of coordination polymers (CPs) and its effect on the optical and electrochemical properties. The application of CPs in electrochemical sensing was studied as well. Isomorphous coordination polymers, $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ (tyr = L-tyrosine), where x (0–1) was controlled by the Co/Zn ratios of raw materials, were successfully synthesized via a hydrothermal method, as proved by XRD and EDS results. Their UV–vis DRS and fluorescence spectra change gradually along with the composition. Cyclic voltammograms of modified electrodes, $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n/\text{GCE}$, show that as more and more Zn replaced Co, the current signal decreases greatly and the potential shifts negatively. Much attention was paid to $[\text{Coty}]_n$ due to its highest sensitivity. Refreshable modified carbon paste electrode, $[\text{Coty}]_n\text{-CPE}$, was used to determine nitrite, and showed pretty good performance as evidenced by chronoamperometry. The response was made very fast within mere 5 s. The linear detection range was from 5.00×10^{-5} to 3.45×10^{-3} M, with sensitivity of $263.4 \text{ mA mol}^{-1} \text{ L cm}^{-2}$. The detection limit was found to be 2.00×10^{-5} M. The sensor also showed good antiinterference and reproducibility.

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1. Introduction

Metal–organic coordination polymers (MOCPs, or CPs), as tunable multifunctional materials, have attracted increasing research interest and found applications in many fields [1]. However, for CPs, the isomorphous substitution and the effects it has on the properties of CPs is a theme still poorly studied. Most of the few related works focused on the evolution of the specific surface area and the pore volume [2–5]. The effects of the composition on the structure flexibility, the magnetic property, and the thermal stability were also studied [2,6,7]. Sometimes, the substitution was limited [8]. In this work, isomorphous $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ ($x=1, 0.7, 0.5, 0.3$, and 0, tyr = L-tyrosine), without substitution limit, were successfully synthesized, and the effects of composition on the optical and electrochemical properties were studied.

Attention has been paid to the electrochemistry of CPs only recently [9]. Some CPs have found applications as battery materials, and few others in electrochemical sensing, where CPs acted as enzyme carrier [10] or enzyme-free sensors for hydrogen peroxide [11–13] or nitrite [14]. This work focused on the CP-based

electrochemical sensor for nitrite. Nitrite is common in environment, food, and physiological systems. It is noxious and may cause cancer. So its determination is very important and many determination methods have been developed [15]. Comparing with spectrophotometry [16] or chromatography [17], electrochemical sensing [18] is much simpler, faster, and cheaper. Many materials, such as transition metal-containing macrocyclic ligands [14,19], conductive polymers [20,21], metallic nanoparticles [22,23], and carbon materials [24], have been used in nitrite determination. Several CPs have also been used [25,26]. However, in most cases, only cyclic voltammetry of CP-based sensors were investigated, with no detailed performance data reported. In this work, chronoamperometry was also carried out and comprehensive performance data were given.

Organic ligands with conjugated structures are often fluorescent. For the CPs with this kind of ligands, fluorescence is usually remained, but the spectra changed somewhat. Optical properties of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ and their dependence upon the composition was investigated herein.

Transition elements have many unique properties, including redox activity. Amino acid ligands show biocompatibility, chirality, and diversity of coordination modes. The CPs consisting of transition elements and amino acid ligands are promising in many application fields, especially in the bio-related field. Reports on

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aminoacid-based CPs still mainly focused on the syntheses and structures [27–29]. Their magnetic [30] or fluorescent [31] properties were studied as well in some cases. We are trying to study the electrochemistry of these CPs and to find their applications in electrochemical biosensing. $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ reported herein show composition-depending fluorescence and electrocatalytic activity, and good performance in nitrite determination.

2. Experimental

All the reagents were of analytical purity and used as purchased without further purification.

$[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ ($x=1, 0.7, 0.5, 0.3, 0$) was synthesized hydrothermally following procedure similar to what had been reported previously [30]. Under magnetic stirring, aqueous NaOH solution (1.0 M) was added dropwise to the mixture of 20 mL of distilled water, 4 mmol of *L*-tyr (*L*-tyrosine), and 2 mmol of metal acetates (the Co/Zn molar ratio of which was 1/0, 0.7/0.3, 0.5/0.5, 0.3/0.7, or 0/1), to adjust the pH value to 9–10. The mixture was transferred into a 40 mL teflon-lined autoclave which was then kept in an oven of 150 °C for 1 day. After cooling to room temperature, the product was filtered, washed with distilled water, and air-dried under ambient conditions. All the obtained crystals of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ were purple with the exception of $[\text{Znty}]_n$, which was pale yellow. The crystals were ground in an agate mortar, if necessary, before used in characterizations or other experiments.

Powder X-ray diffraction (XRD) data were collected with an X'Pert MPD Philips diffractometer (Cu- $K\alpha$ radiation, $\lambda=1.54056 \text{ \AA}$). Energy dispersive analysis of X-ray spectroscopy (EDS) was performed using a Hitachi S-4100 field emission electronic microscope. UV–vis diffuse reflectance spectra (DRS) were recorded by a Tu-1901 double beam UV–vis spectrophotometer. Fluorescence emission/excitation spectra were recorded by a Perkin-Elmer LS-50B fluorescence spectrophotometer.

Modified electrode, $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n/\text{GCE}$ (glassy carbon electrode), was fabricated by casting 6 μL of the suspension of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ (13 mg/mL) onto the surface of pre-polished glassy carbon electrode (GCE, \varnothing 3 mm), following which 2 μL of nafion solution (1%) was cast. The modified carbon paste electrode (CPE), $[\text{Coty}]_n\text{-CPE}$, was fabricated as follows: 0.500 g of graphite powder and 0.050 g $[\text{Coty}]_n$ were mixed and ground in an agate mortar for 30 min; then 0.30 mL paraffin oil was added and the mixture was ground for another 15 min. The homogenized mixture was packed tightly into one end of a glass tube (with inner diameter of 5 mm). A copper wire was buried for electrical contact. The electrode surface of $[\text{Coty}]_n\text{-CPE}$ was polished with weighing paper. Bare CPE was fabricated following similar procedure.

All electrochemical experiments were conducted on a CHI660B electrochemical workstation with a conventional three-electrode electrolytic cell. GCE, KCl-saturated calomel electrode (SCE), and platinum wire served as working electrode, reference electrode, and counter electrode, respectively. The electrolyte used was 0.1 M phosphate buffer solution (PBS, pH 7.0), which was purged of oxygen by high purity nitrogen for at least 20 min beforehand. The chronoamperometry was performed at a constant potential of -1.0 V , upon successive addition of 0.2 M NaNO_2 into 4 mL N_2 -saturated PBS under continuous stirring.

3. Results and discussion

3.1. Characterization of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$

All of the as-prepared products with various Co/Zn atomic ratios have the same crystal structure. As shown in Fig. 1, their

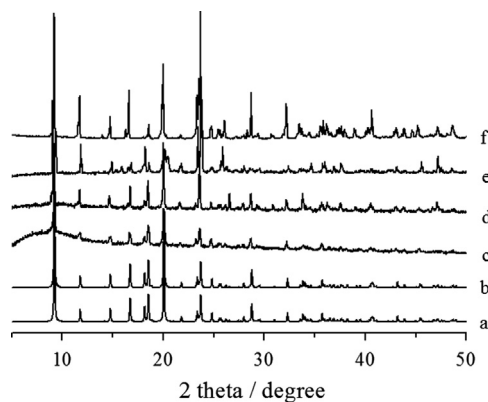


Fig. 1. The simulated XRD pattern of $[\text{CoTyr}]_n$ [30] (a) and the experimental XRD patterns of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ ($x=1, 0.7, 0.5, 0.3$, and 0 for b, c, d, e, and f, respectively).

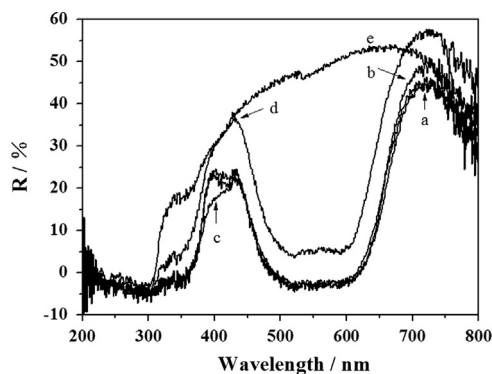


Fig. 2. UV–vis DRS of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ ($x=1, 0.7, 0.5, 0.3$, and 0 for a, b, c, d, and e, respectively).

XRD patterns are consistent with that simulated for $[\text{Coty}]_n$, which has been reported previously [30]. The crystal structure has been described in detail in the reference and would not be discussed here. The Co/Zn atomic ratios of products were very near to those of raw materials. As Co/Zn of raw materials decreased from 0.7/0.3 to 0.5/0.5, and then 0.3/0.7, the Co/Zn of products decreased from 0.66/0.34 to 0.53/0.47, and then 0.31/0.69, as evidenced by the EDS results. So we denoted the products by $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ ($x=1, 0.7, 0.5, 0.3$, and 0).

3.2. Optical properties of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$

To study the optical properties of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ and their dependence on the Co/Zn ratio, we investigated their UV–vis DRS and fluorescence spectra. From the DRS shown in Fig. 2, we can see that as the Co/Zn ratio decreases, the ratio of the reflections of two peaks at ~ 430 and $\sim 400 \text{ nm}$ (R_{430}/R_{400}) increases, the bands at about 330 and 550 nm also increase relatively. When x in $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ changes from 1 to 0.3, the spectrum changes gradually. But when x changes to 0 (i.e., $[\text{Znty}]_n$), the spectrum changes greatly and some peaks merge into broad bands. This result implies that the DRS of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ is mostly determined by Co component, and the doping of even a small amount of Co can cause great changes.

Fig. 3 shows the fluorescence spectra of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ and *L*-tyr, in solid state (3A) and in solution (3B), respectively. In solid state, the emission spectra of CPs and *L*-tyr are quite similar in peak wavelength and in shape, showing that the emission can probably be assigned to the intraligand ($\pi^* \rightarrow \pi$) transitions [32]. Meanwhile, the fluorescence intensities of $[\text{Co}_x\text{Zn}_{1-x}\text{tyr}]_n$ are higher than that of *L*-tyr. This may be due to the stabilization effect of coordination, which reduced the nonradiative transition

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