



Short communication

Amperometric determination of reduced glutathione with a new Co-based metal-organic coordination polymer modified electrode



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ABSTRACT

This communication reports a new 2-dimensional (2D) Co-based metal-organic coordination polymer (Co-MOCP) by a simple solvothermal synthesis, and exhibits the first use of Co-MOCP as an electrode material for the electrocatalytic oxidation of reduced glutathione (GSH). The GSH electrochemical sensor based on Co-MOCP showed a wide linear range from 2.5 μ M to 0.95 mM with the detection limit of 2.5 μ M for the determination of GSH. This work suggests that metal-organic materials would offer a promising candidate for the potential applications in electrocatalysis and electroanalysis.

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1. Introduction

Reduced glutathione (GSH) is an important biological thiol-containing small molecule, it plays a critical role in various biological processes including protection of cells against various oxidative stresses, xenobiotic metabolism, intra-cellular signal transduction, and gene regulation [1–3]. Moreover, the level of GSH in biological fluids is known to be directly linked to many human diseases, such as cancer, Alzheimer's, dementia, and cardiovascular disease [4]. Among the various analytical methods for GSH, electrochemical sensors are appreciated as an appealing method due to their high sensitivity and selectivity, easy of fabrication, and rapid response times. Recently, some electrochemical sensors for GSH have been developed by modifying traditional electrodes with various nanomaterials including noble metals and their alloys [5–7], metal oxide [8–10] and carbon materials [11–13]. However, developing new low-cost materials for GSH sensors is still one of the current challenging researches.

Metal-organic coordination polymers (MOCPs), an important kind of metal-organic materials with highly ordered structures and diverse compositions, have been widely used in gas storage, catalysis, separations, sensors, and fluorescent materials [14]. Nevertheless, the investigation of MOCPs in the field of electrochemistry is quite recent, such as electrolytes and electrode catalysts for fuel cells, lithium-ion rechargeable batteries, and supercapacitors [15]. Very recently, Wei et al. have exhibited the first application of Cu-based MOFs as electrocatalysts in oxygen reduction reactions [16]. Kulandainathan et al. also reported the electrocatalytic reduction of CO₂ at the Cu-based MOF film modified

carbon paste electrode [17]. In addition, some complex MOF composites exhibited excellent electrocatalytic activity towards the oxidation of L-cysteine (CYS) [18], hydrazine [19], H₂O₂ [20], methanol [21], and NADH [22]. Nevertheless, little effort has been paid on the exploitation of MOCPs as the electrode material for electrochemical GSH sensors. 1,3,5-Tris (1-imidazolyl) benzene (tib) is a typical imidazole-containing tripodal ligand with N donors, it is a good candidate for the construction of novel coordination architectures, and a series of one-, two-, and three-dimensional tib-based MOCPs have been reported over the course of the past ten years [23–28]. In the study, a new 2-dimensional (2D) MOCP with tib and transition element Co²⁺ (Co-MOCP) was designed and synthesized, which was first demonstrated as the electrode materials for the electrocatalytic oxidation of GSH.

2. Experimental

Co-MOCP, [Co(tib)₂]₂·2NO₃, was synthesized as follows. A mixture of 11.6 mg (0.04 mmol) Co(NO₃)₃·6H₂O, 11.0 mg (0.04 mmol) 1,3,5-tris (1-imidazolyl) benzene (tib), 13.2 mg (0.04 mmol) 1,1-biphenyl-3,3',4,4'-tetra carboxylic acid (H₄bptc), 1.0 mL DMA, 1.0 mL deionized water and HNO₃ (0.3 mL, 2.7 M in DMA) were sealed in a 20 mL vial, and then heated at 100 °C for 48 h. Block-shaped crystals were obtained in ca. 58% yield based on Co. IR data (see Fig. 1) (KBr pellet ν /cm⁻¹): 649(s), 767(s), 817(m), 927(s), 1069(s), 1237(s), 1381(s), 1497(s), 1615(s), 2420(w), 2740(w), 3042(s), 3134(s), and 3420(s). Crystallographic parameters for [Co(tib)₂]₂·2NO₃: hexagonal, *P*-31c, *a* = 11.443 (2) Å, *b* = 11.443 (2) Å, *c* = 15.227(3) Å, α = 90°, β = 90°, γ = 120°, *Z* = 2, *V* = 1726.8(5) Å³, ρ = 1.176 g/cm³, Goodness-of-fit =

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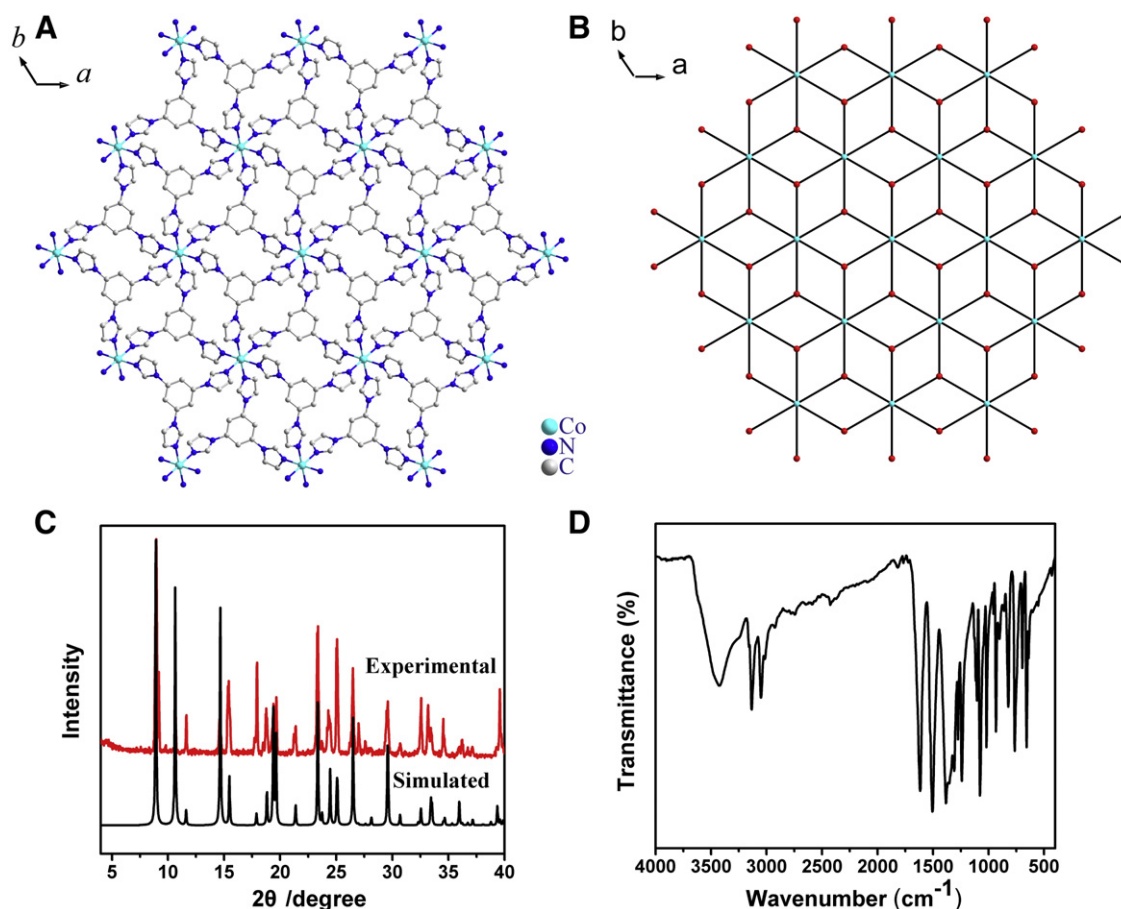


Fig. 1. (A) Illustration of the 2D structure of Co-MOCP (without guest molecules). (B) Schematic view of the *kgd* topology (the Co atoms represented as sky blue and tib ligands represented as red ball modes) (C) Powder X-ray diffraction patterns of the simulated and as-synthesized Co-MOCP. (D) IR spectrum of Co-MOCP.

1.049, $R1 = 0.0335$ ($[I > 2\sigma(I)]$) and $wR2 = 0.0963$ (all data) (squeeze).

IR spectrum was recorded in the range of $400\text{--}4000\text{ cm}^{-1}$ on a Nicolet Impact 410 FTIR spectrometer using KBr pellet. The suitable single crystal of Co-MOCP was selected for single-crystal X-ray diffraction analysis. The measurement was made on a Bruker Smart Apex-II CCD area detector by using graphite monochromated Mo- $K\alpha$ ($\lambda = 0.71073\text{ \AA}$). The crystal was mounted on glass fibers at room temperature. Cell parameters were refined by using the program Bruker_{SAINT}. The collected data were reduced by using the program Bruker_{SAINT} A, and the absorption corrections (multi-scan) were applied. The reflection data were also corrected for Lorentz and polarization effects. The structure was solved by direct method. Non-hydrogen atoms (except guest molecules) were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of ligands were calculated in ideal positions with isotropic displacement parameters. Guest molecules were highly disordered, and attempts to locate and refine the guest molecules peaks were failed. The diffuse electron densities resulting from the residual guest molecules were removed from the data set using the SQUEEZE [29] routine of PLATON and refined further using the data generated. X-ray powder diffraction (XRD) data was collected on a Rigaku 2550 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). A CHI 842C electrochemical workstation (Austin, TX, USA) was used to carry out all the electrochemical experiments with the conventional three-electrode system which was composed of Co-MOCP modified carbon paste electrode (CPE) (Co-MOCP/CPE) working electrode, platinum coil auxiliary electrode, and Ag/AgCl (saturated KCl) reference electrode. Bare CPE was prepared by mixing graphite powder and liquid paraffin with a ratio of 75:25 (w/w). A portion of the resulting paste was packed firmly

into a glassy tube (1.8 mm inner diameter) by utilizing a copper wire to make electrical contact. To prepare the Co-MOCP modified electrode, 2.0 mg of the as-prepared product was grinded to powder and dispersed in 1.0 mL water to give suspension by sonication. A 5.0 μL of the suspension was dip-coated onto CPE and the electrode was then dried in the atmosphere.

3. Results and discussion

X-ray crystallography study reveals that Co-MOCP crystallizes in the hexagonal space group of $P-31c$. The asymmetric unit of the framework contains one Co atom and two tib ligands. As illustrated in Fig. 1A, the Co atom adopts octahedral geometry coordinated by six N atoms from six different tib ligands. The six Co–N bond lengths in Co-MOCP are the same with $2.174(2)\text{ \AA}$ comparable to those reported compounds [30]. Each Co atom connects six tib ligands and every tib bridges three Co atoms to form a 2-D layered cationic Co(tib)₂ framework (Fig. 1A). Topological analysis method was used to simplify this structure, the tib ligand can be seen as a 3-connected node, and Co center can be seen as a 6-connected node, therefore, the whole framework can be simplified into a (3,6)-connected $(4^3)_2(4^6\cdot6^6\cdot8^3)$ -*kgd* layer in the *ab* plane (Fig. 1B). In order to check the phase purity of Co-MOCP, the X-ray powder diffraction (XRD) pattern was recorded at room temperature. As shown in Fig. 1C, the peak positions of the experimental and simulated patterns are in good agreement with each other, there are no other peaks in the bulk material powder diffraction pattern, indicating the pure phase of the product.

Fig. 2A shows the cyclic voltammograms (CVs) of Co-MOCP/CPE in the presence and absence of 5 mM GSH in pH 5.5 PBS. As it can be seen

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