



Synthesis of metal–organic frameworks derived nanocomposites for superoxide anion radical sensing and cell monitoring upon oxidative stress



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ABSTRACT

In this work, Co_3O_4 nanoparticles (NPs) with an average diameter of about 30 nm were synthesized using MOFs as a template. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) investigation showed that Co_3O_4 nanocrystals embedded in mesoporous graphitic carbon layer/multiwalled carbon nanotubes (MWCNTs) uniformly. The structure of the final nanocomposite (denoted as $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$) was further confirmed by X-ray diffraction (XRD), Raman spectra and Brunauer-Emmett-Teller (BET) techniques. As a result, electrochemical study demonstrated that the $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$ modified glassy carbon electrode exhibited excellent electrochemical activity toward the reduction of $\text{O}_2\cdot^-$ with a super wide linear range from 5.00×10^{-12} to 1.00×10^{-4} M and very low detection limit (LOD) of 1.67×10^{-12} M (S/N = 3). Importantly, three kinds of stimulants were selected to monitor the flux of $\text{O}_2\cdot^-$ released from living cells. By using phorbol 12-myristate-13-acetate as optimal stimulus, the novel non-enzymatic $\text{O}_2\cdot^-$ sensor can detect $\text{O}_2\cdot^-$ release from cancer cells, which has the great potential application in clinical diagnostics to assess oxidative stress of living cells.

1. Introduction

As a by-product of oxidative metabolism in living organisms, superoxide anion ($\text{O}_2\cdot^-$) has been widely studied as a common representative of reactive oxygen species (ROS) due to its critical roles in several pathological conditions including atherosclerosis, hypertension, inflammation and postischemic myocardium [1]. Besides, the relationship between $\text{O}_2\cdot^-$ concentration and human health has also attracted great attention [2]. Therefore, the practical significance of monitoring $\text{O}_2\cdot^-$ in physiological environments with wide dynamic linear range has been well acknowledged in the past decades.

Compared with electron spin resonance [3], chemiluminescence [4], spectrophotometry [5], chromatography methods [6], electrochemical method is considered as one of the most promising strategies due to its simplicity, fast response, low detection limit, and easy of use. Especially, enzyme-based electrochemical biosensors (such as superoxide dismutase (SOD), a specific enzyme for $\text{O}_2\cdot^-$ dismutation, immobilized in the various kinds of functionalized electrodes) have always been the research highlights. Nevertheless, the relatively high cost, limited lifetime and the critical operating situation limit their applicability [7,8]. Therefore, non-enzymatic $\text{O}_2\cdot^-$ sensors have received keen interest and need to be developed rapidly.

In this respect, various functional materials such as noble metals and metal oxides have been extensively investigated as the candidates for the development of effective enzyme-less sensors [9–11]. Our group has utilized AgNPs combination with L-cysteine functionalized carbon nanotubes (Cys-MWCNTs) nanocomposites as the support for sensitive and selective $\text{O}_2\cdot^-$ detection [12]. Recently, Co_3O_4 -based electrochemical sensors have attracted considerable attention because of their excellent electrocatalytic performance toward ROS oxidation [13–15]. It is generally believed that the electrocatalytic performance of Co_3O_4 can be influenced by various factors such as size, surface-to-volume ratio, and level of crystallinity. Hence, it is very important to prepare the matrix for dispersed Co_3O_4 highly [16].

Metal–organic frameworks (MOFs) are a rapidly growing class of porous material with well-defined channels and cavities of regular size and shape that are easily tunable on the nanometer scale [17–19]. Thanks to the periodic arrangement of metal nodes and organic motifs in MOF scaffolds, it has reported that MOFs are novel pyrolytic precursors to obtain nonprecious-metal electrocatalysts with the homogeneous distribution of metal nanoparticles (NPs) and in situ formed porous carbon layer [20–23]. What's more, the formed porous carbons layer can encapsulate the metal NPs, creating a very strong interaction/contact between the metal and the carbon. These fascinating properties

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of MOFs make them an ideal template for synthesizing nanoscale materials. Zeolitic imidazolate framework-9 (ZIF-9) is a chemically robust and thermally stable MOF material, which can be selected as the cobalt-based MOF precursor to synthesize nanoscale metal oxides [24,25]. Nevertheless, the organic ligands from ZIF-9 cause poor water solubility and electron conductive property, restricting their applications [19]. Therefore, it is strongly desired to find pathways for overcoming above obstacle.

Carbon nanotubes (CNTs), as another typical nanomaterial, have been widely used in electrochemical sensors since they possess relatively large surface area, excellent electric conductivity, high chemical stability and strong adsorptive ability [26]. In this work, MWCNTs are used as a special substrate in ZIF-9 to solve the problem above. As a result, the as-prepared hybrids (denoted as $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$) are featured with homogeneous distribution of Co_3O_4 NPs and well defined mesopores, showing excellent electrochemical activity toward $\text{O}_2\cdot^-$ determination.

The aim in this article is to fabricate a novel non-enzymatic sensor for the determination of $\text{O}_2\cdot^-$ by utilizing ZIF-9 as a template. By combining the advantages of MWCNTs and $\text{Co}_3\text{O}_4@\text{C}$, the designed sensor exhibited excellent performance toward $\text{O}_2\cdot^-$ with super wide linear range, low detection limit and excellent reproducibility. More importantly, using the optimal stimulus, it can monitor the $\text{O}_2\cdot^-$ release from living cells under both the external stimulation and the normal condition. Thus, this work has the great potential application in clinical diagnostics to assess oxidative stress of living cells.

2. Experimental section

2.1. Apparatus

Scanning electron microscopy (SEM) images were obtained, using a JSM-6701F system (Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken from a JEM-3010 transmission electron microscope (JEOL Co., Ltd., Japan). X-ray powder diffraction (XRD) measurements were carried out at room temperature and performed using a Rigaku D/max-2400 diffractometer with Cu-K α radiation as the X-ray source in the 2θ range of 10–80°. Raman spectra were recorded on a Renishaw inVia Raman microscope system with 632.8 nm laser excitation. Specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and pore sizes by the Barrett–Joyner–Halenda (BJH) methods using the Tristar II 3020 instrument.

Electrochemical measurements were performed on a CHI660C electrochemical workstation (Austin, TX, USA) with conventional three-electrode system. A bare or modified glassy carbon electrode (GCE, $d = 3.0$ mm) was employed as working electrode. A platinum electrode and a saturated calomel electrode (SCE) were served as the auxiliary and reference electrode. All potentials given in this paper were referred to the SCE. Electrochemical impedance spectroscopy (EIS) experiments were performed on Multi-potentiostat (VMP2, Princeton Applied Research, USA). Ultraviolet-Visible spectroscope (UV–vis, EVOLUTION 220, Thermo Scientific) was used to detect the concentration of $\text{O}_2\cdot^-$ obtained from the KO_2 stock solution. Before each electrochemical measurement, solutions were thoroughly deoxygenated by bubbling nitrogen through the solution for at least 20 min to remove dissolved oxygen.

2.2. Reagents

The multi-walled carbon nanotubes (MWCNTs) used (diameter: 20–40 nm, length: 1–2 μm , purity: $\geq 95\%$) came from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). Benzimidazole, Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and KO_2 were obtained from Aladdin Industrial Inc. Dimethyl Sulphoxide (DMSO) and *N,N*-dimethylformamide (DMF) were purchased from Beijing Chemical Works

(Beijing, China). 18-crown-6 was bought from Energy Chemical (Shanghai Chemical Industries, Ltd.). 4 Å molecular sieve was obtained from Tianjin Kernel Chemical Industries, Ltd. (Tianjin, China). Superoxide dismutase (SOD), Phorbol 12-myristate-13-acetate (PMA), Zymosan A and 3-[(3-cholamidopropyl)dimethylammonio]-1-propane-sulfonate (CHAPS) were bought from Sigma-Aldrich (USA). A 0.2 M phosphate buffer solution (PBS, pH 7.0) comprising NaH_2PO_4 and Na_2HPO_4 was used as the supporting electrolyte. A physiological PBS solution containing KH_2PO_4 (1.76 mM), Na_2HPO_4 (10.14 mM), NaCl (136.75 mM), and KCl (2.28 mM), was mainly used for washing of PC12 cells and observing the release of $\text{O}_2\cdot^-$ from cells. Other chemicals were all of analytical grade, and the solutions were prepared by doubly distilled water.

2.3. Fabrication of $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$ nanocomposite

2.3.1. Synthesis of MOF

Preparations of ZIF-9 was carried out according to the procedure described elsewhere [25]. In brief, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.84 g) and benzimidazole (0.68 g) were dissolved in 72 mL of DMF in a 100 mL glass flask and sonicated to ensure homogeneity. The flask was heated at 130 °C with a heating rate of 5 °C min^{-1} in an oven for 36 h followed by slow cooling to room temperature at 0.4 °C min^{-1} . The purple crystal were collected via centrifugation and washed with DMF several times and dried under vacuum.

2.3.2. Synthesis of MOF-MWCNTs

The synthesis of MOF-MWCNTs was performed in the following manner. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.84 g) and benzimidazole (0.68 g) were dissolved with DMF (72 mL) in a 100 mL glass flask. Different mass ratios of MWCNTs (5, 10, 20, 30, 40 and 50 wt%: based on the total mass of solid materials above) were added to the mixtures. After continuous sonicating 1 h at room temperature, the vessel was sealed and heated up to 130 °C with a heating rate of 5 °C min^{-1} in an oven for 36 h followed by slow cooling to room temperature at 0.4 °C min^{-1} . The purple-grayish crystals were collected, centrifuged and washed with DMF and dried under vacuum.

2.3.3. Synthesis of $\text{Co}_3\text{O}_4@\text{C}$ and $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$

The above prepared MOF and MOF-MWCNTs were transferred into a tube furnace and exposed to a flow of argon (30 mL min^{-1}) for 1 h. Afterward, the furnace was heated to 700 °C at a heating rate of 3 °C min^{-1} for 2 h and cooled down to room temperature. In the second step, the obtained black powder sample was dispersed in a ceramic disk and heated at the 250 °C for 90 min with a heating rate of 1 °C min^{-1} , and the $\text{Co}_3\text{O}_4@\text{C}$ and $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$ were fabricated. The resulted $\text{Co}_3\text{O}_4@\text{C}$ and $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$ was resuspended in the mixture of water and ethanol (v:v = 1:1), and stored at 4 °C for further use.

2.4. Preparation of the $\text{O}_2\cdot^-$ sensor

A glassy carbon electrode (GCE) was polished with 1.0, 0.3 and 0.05 μm alumina slurry to a mirror-like, respectively, followed by rinsing thoroughly with doubly distilled water. The electrode was successively sonicated in 1:1 nitric acid, acetone and doubly distilled water, and then allowed to dry at room temperature. Then 6 μL of $\text{Co}_3\text{O}_4@\text{C-MWCNTs}$ aqueous solution (1.0 $\text{mg}\cdot\text{mL}^{-1}$) was dropped on the surface of GCE and dried in air to obtain the final modified electrode.

2.5. Generation of superoxide anion

The chemical generation of $\text{O}_2\cdot^-$ was performed by dissolving KO_2 in dimethyl sulphoxide (DMSO) solution (containing 18-crown-6), and stored together with 4 Å molecular sieve. The solubility of KO_2 in DMSO can be increased by adding 18-crown-6. After sonicating the solution

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