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Cu (II)-based metal-organic xerogels as a novel nanozyme for colorimetric detection of dopamine

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ABSTRACT

Cu (II)-based metal-organic gels (Cu-MOGs), which are formed by 4-[2,2′:6′,2″-terpyridine]-4′-ylbenzoic acid (Hcptpy) and Cu (II) through ionic interactions, π-π stacking, van der Waals and hydrogen bonding, have been simply synthesized and used for the preparation of Cu (II)-based metal-organic xerogels (Cu-MOXs). Owing to the metal active sites in Cu-MOXs, Cu-MOXs were successfully applied to chromogenic experiment. The peroxidase substrate 3,3′,5,5′-tetramethylbenzidine (TMB), which could be catalyzed by Cu-MOXs from TMB to the oxidation state of TMB (oxTMB) and the color of TMB could be changed from colorless to blue with maximum absorbance at 657 nm, was selected as chromogenic agent. Thus, the Cu-MOXs-TMB-H_2O_2 system based on MOXs was established. Due to the inhibitory effect of dopamine (DA) on oxidation process of TMB, the characteristic absorption peak intensity of oxTMB decreased when the DA was added into the mixed solution. Subsequently, the Cu-MOXs-TMB- H_2O_2 system was used for DA detection. The linear range for DA was 0.5 μM–20 μM and the detection limit was 85.76 nM. Our work has helped to develop the promising application of Cu-MOGs material in the field of nanozymes property.

1. Introduction

Nanozymes, which have nanostructures and enzyme mimicking activities, have attracted plenty of attention due to their unique features such as multifunctions, tunable activities, mass production, robustness, low cost and recyclability [1–3]. Compared with nature enzymes and classic artificial enzymes, nanozymes have been widely used in ebola virus detection [4], peroxidase mimic [5], cancer diagnosis [6], monitoring of heparin activity [7], tissue engineering [8], ameliorate neurodegeneration [9] and so on. Up to now, a variety of materials including iron oxide [10], CuS NPs [11], C_{60}-C_3 [12], CeO_2 [13], AuNPs [14], nanoflower [15–19] and metal-organic frameworks (MOFs) [20,21] have been used as nanozymes. Nevertheless, the synthesis methods of these nanozymes are time-consuming and difficult. According to literature reports, metal-organic gels (MOGs), which constituted by the self-assembly of organic small molecule ligand and metal ions through various noncovalent interactions [22,23], could rapidly synthesize under mild conditions and have been used as nanozymes only for organocatalysis [24–26] and chemiluminescence [27]. Hence, the other properties of MOGs as nanozymes remain to be further studied.

As an essential neurotransmitter, dopamine (DA) is involved in brain information transmission and influences the emotions and perceptions of humans [28,29]. Lower or higher levels of DA in the brain can cause various diseases [30,31]. Consequently, it is necessary to examine the content of DA for the diagnosis of all kinds of diseases. Until now, a series of strategies such as electrochemistry [32], enzymatic methods [33], chromatography [34], fluorescence methods [35] and capillary electrophoresis [36] has been used for examining the content of DA. Nevertheless, the methods above require costly instruments and complicated procedures and restrain the DA detection in practical applications. It is known that colorimetry is a simple, low-cost, stable and rapid method [37] applied to DA detection in actual samples [38]. Thus, the feasible detection method, which was based on the color fading of oxidized peroxidase substrate [39], was developed. According to literature reports, the materials, which are applied to DA detection, incorporate carbon dots [40], graphene [41], hybrid nanotubes [42,43], metal-organic frameworks (MOFs) [35] AgNPs/MIL-101 (Fe) [44] and so on. However, there is no report of MOGs as nanozymes used for the detection of DA through colorimetry as yet. Longer synthesis time and harsh synthetic conditions may cause obstruction for experiments compared with MOGs which could rapidly synthesis under mild conditions. Hence, it is possible to develop a simple, fast and mild method used to detect DA based on the enzyme property of MOGs.

On account of the metal active sites in Cu-MOXs which act as nanozymes for chromogenic experiment, Cu-MOXs were rapidly synthesized under mild conditions and used for selectively monitor DA. Just as shown in Scheme 1, Cu-MOXs could catalyze the peroxidase substrate 3,3′,5,5′-tetramethylbenzidine (TMB) to the oxidation state of TMB (oxTMB) by ·OH radicals produced from H_2O_2 and the solution

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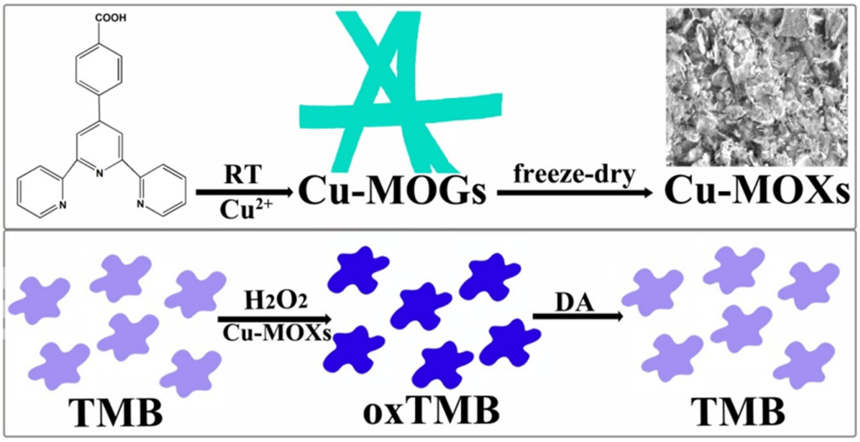

Scheme 1. Schematic illusion process for the Cu-MOXs and the schematic diagram of detection of DA.

will turn blue. Then, the oxidation process of TMB will be confined and the characteristic absorption peak intensity of oxTMB also decreases when the DA was added into the mixed solution. On account of the inhibitory effect of DA on oxidation process of TMB, the colorimetry based on Cu-MOXs-TMB-H_2O_2 system for DA detection was established.

2. Experimental

2.1. Materials and Reagents

4-[2, 2′: 6′, 2″-Terpyridine]-4′-ylbenzoic acid (Hcptpy, 97%) was obtained from Shanghai UCHEN Inc. 3,3′,5,5′-tetramethylbenzidine (TMB), dopamine hydrochloride (DA), glucose (Glc), urea, ascorbic acid (AA) and uric acid (UA) were purchased from Sigma-Aldrich (St. Louis, MO). Histidine (His), isoleucine (Ile), threonine (Thr), serine (Ser), tryptophan (Trp), proline (Pro), leucine (Leu), lysine (Lys), arginine (Arg) and alanine (Ala) were obtained from Beijing Dingguo Changshen Biotech Co Ltd. $CuCl_2$, $CuSO_4$, $Cu(NO_3)_2$, NH_4Cl, NaCl, $MgCl_2$, KCl, $CaCl_2$ and NaOH were obtained from Aladdin, All reagents were analytical grade and used without further purification. Urine samples were obtained from two healthy volunteers of the Southwest University and the use of human urine was approved by the University of Southwest Institutional Review Board. An individual written consent agreement was obtained from the participants before beginning the work on this study, and the research didn't involve our country's residence. Ultra-pure water (18.2 MΩ/cm) was used throughout the experiment.

2.2. Apparatus

The morphology of Cu-MOGs was characterized by an S-4800 scanning electron microscope (SEM) (Hitachi, Japan). Transmission electron microscopic (TEM) characterization was performed on JEOL JEM-1200EX TEM instrument (JEOL, Japan). X-ray diffraction (XRD) patterns was collected on a X-Pert3 Powder with a Cu sealed tube ($\lambda = 1.5406$ Å). N_2 adsorption-desorption isotherms, which was used for measure the Brunauer-Emmett-Teller (BET) surface area, was obtained at 77 K on ASAP 2020, USA. Thermo gravimetric analysis (TGA) were measured with a METTLER TGA/DSC 1 SF/1382 (NETZSCH, Germany). Fourier-transform infrared (FTIR) spectra were recorded on a FITI-8400 (Shimadzu, Japan) in the range of 4000–500 cm^{-1} using the KBr disk method at RT. A constant-temperature water-base boiler (Jiangsu, China) was used to control the reaction temperature. All the UV–vis absorption spectra were recorded with a U-3010 spectrophotometer (Hitachi Co., Tokyo, Japan).

2.3. Synthesis of Cu-MOXs

In preparation of Cu-MOXs, 7 mg of Hcptpy was dispersed in 0.5 mL H_2O with 25 μL of 2 M NaOH, and then 0.5 mL $CuCl_2 \cdot H_2O$ solution (272.8 mg $CuCl_2 \cdot H_2O$ dissolved in 10 mL H_2O) was rapidly injected into ligand solution. Subsequently, let the mixture set for a minute and Cu-MOGs, which evaluated based on the tube inversion test, were obtained. Finally, Cu-MOXs is prepared by freeze-drying and stored for further use.

2.4. Detection of DA

Detection of DA was carried out as follows: 50 μL of 10 mM TMB, 20 μL of 10 mM H_2O_2, 200 μL of 0.2 M HAc-NaAc buffer (pH 4.4), 22.5 mg of Cu-MOXs and a certain concentration of DA solution (200 μL) was added into 2 mL EP vial. Then, the mixture was diluted to 1 mL with ultra-pure water (18.2 MΩ·cm). Finally, The mixture was incubated at 55 °C for 20 min and then used for DA measurement by monitoring the absorbance change at 657 nm on a U-3010 spectrophotometer.

3. Results and Discussion

3.1. The Formation and Characterization of Cu-MOXs

The molecule 4-[2, 2′: 6′, 2″-terpyridine]-4′-ylbenzoic acid (Hcptpy) was chosen as the ligand to form Cu-MOXs in that (1) the terpyridine group in Hcptpy endows it with coordination ability and facilitates the formation of π-π stacking, which plays a crucial role in the formation of gel [23]. (2) The carboxyl in Hcptpy may lead to aggregation of molecules through hydrogen bonding interactions and subsequently promotes the gel self-assembly process.

The formation of Cu-MOXs highly depended on molar ratio of metal: ligand (M/L) and cationic source. Firstly, we investigated the synthesis conditions of M/L from 1:2 to 6:1. Just as shown in Fig. S1, the M/L = 4:1 was the best synthesis ratio. While the M/L was lower, it may cause fewer ionic interactions and cannot form a stable gel. While the M/L was higher, it could also form Cu-MOXs but the peroxidase mimic activity was dissatisfactory. Then, the cationic source was explored including $CuCl_2$, $CuSO_4$ and $Cu(NO_3)_2$ (Fig. S2). Results showed that the peroxidase mimic activity of Cu-MOXs was optimal while the metal salt was $CuCl_2$. The reason for the $CuCl_2$ as the optimal cationic source might be that the halide bridging of metal centers plays a significant role in the formation of Cu-MOXs [45]. Thus, the M/L = 4:1 and $CuCl_2$ were selected as the synthesis conditions for Cu-MOXs.

Cu-MOXs, which were obtained by vacuum freeze-drying from Cu-MOGs, was composed of nanosheet and interconnected to form a