



High oxidase-mimic activity of Fe nanoparticles embedded in an N-rich porous carbon and their application for sensing of dopamine

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ABSTRACT

The N-doped porous carbon (NC) has been regarded as one of the promising support materials for nanoparticles (NPs) catalyst due to its inherent virtues such as porosity, large surface areas, and heteroatom incorporation. In this work, Fe/NC-800 hybrid was facilely prepared by uniform dispersion of in situ formed FeNPs onto NC-800 from carbonization of ZIF-8 at 800 °C for the first time. The optimized Fe/NC-800 catalyst was characterized by TEM, XPS and XRD. Compared with sole FeNPs and NC-800, the Fe/NC-800 catalyst exhibited an enhanced oxidase-like activity that could oxidize the colorless 3,3',5,5'-tetramethylbenzidine (TMB) to the heavy blue without extra oxidants such as H₂O₂. The possible reason for the enhanced oxidase-like activity of the Fe/NC-800 was discussed on the basis of the experiments of radical scavengers, indicating the importance of superoxide (O₂^{•-}) and singlet (¹O₂) in colorimetric reaction between TMB and Fe/NC-800 hybrid. Furthermore, the oxidase-like activity of Fe/NC-800 was significantly inhibited by dopamine (DA), leading to blue color fading. On this basis, a sensitive and selective colorimetric sensor was fabricated for the quantitative analysis of DA with a linear range of 0.01–40 μM and a low detection limit of 10 nM. The proposed colorimetric method was successfully applied to determine DA in human serum and injection samples, suggesting a promising application in biological analysis.

1. Introduction

Dopamine (DA), as a kind of imperative excitatory neurotransmitter, plays a key role in the central and peripheral nervous systems [1]. The abnormal level of DA would induce neurological diseases, including Parkinson's disease [2], Alzheimer's disease [3] and so on. Therefore, the quantitative determination of DA in biological fluids is of great importance, which has received widespread attention. Up to now, a variety of approaches have been employed for detecting DA, including chromatography [4], chemiluminescence [5], electrochemical [6–9], fluorescence [10–12] and colorimetric methods [13–17]. Among these methods, colorimetric method has aroused great attention due to the advantages of simplicity, cost-effective, facile and visual detection.

To establish a colorimetric analysis system, enzyme catalytic chromogenic substrate is a good choice. However, easy denaturation, sensitivity of catalytic activity to environmental change, high cost and rigorous storage condition make it difficult to realize the wide applications of natural enzymes. In recent years, various nanozymes, the nanomaterials with the ability to imitate the functions of natural

enzymes, have attracted considerable attentions due to their advantages such as high stability, good tunability in catalytic activities and low cost in preparation compared to the natural enzymes. These include metal nanoparticles (NPs) [18,19], metal alloy [20], metallic oxide [21,22], metal organic frameworks [23,24], carbon materials [25] and so on. Among these nanozymes, metal NPs-based nanozymes are attractive because of their abundant redox sites and high catalytic activity. Unfortunately, the application of metal NPs is limited due to their inherent shortcomings (e.g., agglomeration, storage difficulty and heterogeneous distribution). To address the agglomeration issue, most of the metal NPs were usually modified by some chemical agents. However, the agents covering on the surface will occupy partial reactive sites, leading to a relative lower catalytic activity [18,26]. Recent study demonstrates the success of encapsulating of nanoparticles into specific matrix to prevent their aggregation and remain high activity. In particular, various carbon materials, including mesoporous carbon [27], single-shell carbon [28], and graphene [29], were found to be effective to anchor active metal catalysts. Compared with common carbon materials, N-doped porous carbon (NC) derived from metal organic framework (MOF) integrated many advantages like large surface area, porosity,

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heterogeneous atom doping and good thermal stability. Thus, MOF-derived carbonaceous materials have been explored as matrix to support catalysts for application in energy and environment fields [30,31]. However, there is rare investigation on its use for in situ encapsulating of active metal nanoparticles for biosensing application, like DA detection based on enzyme mimicking property.

Here, for the first time, the potential of Fe/NC-800 hybrids as oxidase mimetic for the detection of DA was evaluated. To this end, first, the NC-800 was synthesized via a direct pyrolysis of ZIF-8 precursor (at 800 °C) and was used for loading of in situ formed FeNPs by sodium borohydride reduction of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as iron precursor to form Fe/NC-800 hybrids. The obtained Fe/NC-800 hybrids were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectrum, and X-ray photoelectron spectra (XPS). Second, the oxidase-like activity of the as-prepared materials was evaluated by using 3,3',5,5'-tetramethylbenzidine (TMB) as the substrate. Third, the effect of DA on the oxidase-like activity of Fe/NC-800 hybrids was explored and optimized. Finally, a colorimetric biosensor was developed for quantification of trace levels of DA in various samples, including human serum and dopamine hydrochloride injection. To our knowledge, this is the first report on DA detection based on the oxidase-like activity of Fe/NC-800 hybrids obtained by capsulation of in situ generated FeNPs into the MOF-derived N-doped porous carbon.

2. Experimental section

2.1. Chemicals and reagents

All chemicals were of analytical reagent grade and used as received without any further treatment. Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and polyvinylpyrrolidone (PVP, K30) were purchased from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). Methanol was supplied by Chongqing Taixin Chemical Co. Ltd. (Chongqing, China). 2-Methylimidazole (MIM), dopamine hydrochloride, *p*-benzoquinone and sodium borohydride (NaBH_4) were obtained from Aladdin (Shanghai, China). Iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), acetic acid (HAc), sodium acetate (NaAc), and ethanol were obtained from Chongqing Chemical Reagents Company (Chongqing, China). TMB and superoxide dismutase (SOD) were purchased from Sigma-Aldrich (Shanghai, China). H_2O_2 and HCl were purchased from Chongqing Chuandong Chemical Co., Ltd. (Chongqing, China). Glucose and lactose were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Glycine was purchased from Chengdu Chemical Reagents Company (Sichuan, China).

2.2. Instrumentation

The scanning electron microscope (SEM) images were taken on Hitachi model S-4800 field emission electron microscope (Hitachi, Japan) with an accelerating voltage of 20 kV. The X-ray diffraction (XRD) patterns of the as-prepared products were recorded with a TD-3500 X-ray diffractometer (Dandong, China) under the conditions of nickel filtered Cu K α radiation ($\lambda = 0.15406$ nm). Thermogravimetric (TG) data were collected using a TA-SDT Q600 (Texas Instruments, Inc., New Castle, DE) in the temperature range from 40 °C to 800 °C at a heating rate of 20 °C/min. The transmission electron microscopy (TEM, Tecnai G2 F20) equipped with energy dispersed X-ray detector (EDX) was applied for the detailed microstructure and composition information for the prepared samples. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Thermo ESCALAB 250XI with an excitation source of Al K α (1486.6 eV). Raman spectra were obtained on a Renishaw Raman microscope (Renishaw inVia Raman microscope, UK). The specific surface area was determined with the Brunauer-Emmett-Teller (BET) method based on the N_2 adsorption-desorption isotherm data measured on an ASAP 2020 Micromeritics instrument (Maize, USA) at 77 K. Absorbance measurements were performed on a

UV-2450 spectrophotometer (Shimadzu, Suzhou).

2.3. Preparation of ZIF-8 and Fe/NC

ZIF-8 was synthesized according to previous literature [32] with slight modification. Briefly, a methanol solution (40 mL) of zinc nitrate (0.805 g) was added dropwise into a methanol solution (40 mL) containing mixture of MIM (0.526 g) and PVP (2 g) under stirring. After being stirred at room temperature for 5 min, the mixture was aged for 24 h at room temperature. After completion of the reaction, the mixture was centrifugated, and the ZIF-8 white powders were collected and washed several times with fresh methanol before drying at 60 °C for 12 h.

To synthesize FeNPs/NC, first, a one-step pyrolysis of ZIF-8 solid was carried out in a temperature-programmed tube furnace under a steam of N_2 (50 mL/min) to get the N-doped porous carbon materials. In detail, 0.3 g ZIF-8 was placed in a ceramic boat and the tube furnace was heated to 600–1000 °C with a heating rate of 5 °C/min, and kept for 2 h at the temperature. After cooling to room temperature, the obtained black samples were washed thoroughly using HCl to remove the residual Zn species, then rinsed with deionized water and ethanol in turn, and dried at 60 °C for 12 h. The resultant black materials obtained at carbonization temperature of 600, 700, 800, 900 and 1000 °C were denoted as NC-600, NC-700, NC-800, NC-900, and NC-1000, respectively. Second, in order to synthesize FeNPs/NC hybrids, 20 mg of NC powder was dispersed in 10 mL deionized water, then 30 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added. The resulting mixture was under ultrasonic treatment for 30 min and kept stirring for 3 h at room temperature. Then 3 mL of 40 mg/mL NaBH_4 was added dropwise under vigorous stirring and the mixture was stirred for another 30 min. Next, the FeNPs/NC catalysts were retrieved by an external magnet, rinsed with deionized water and ethanol for several times, and then dried under vacuum at 50 °C for 5 h. The vacuum drying Fe/NC-800 powder was used to prepare Fe/NC-800 suspension. To this end, 2 mg of the dried Fe/NC-800 powder was dispersed in 5 mL of deionized water.

2.4. Oxidase mimic activity and kinetic studies of Fe/NC-800

The oxidase mimic activity of Fe/NC-800 was evaluated by its catalytic oxidation of TMB (a typical colorimetric substrate) by dissolved oxygen to produce a blue solution with the characteristic absorbance at 652 nm. To this end, 0.25 mL of Fe/NC-800 (400 mg/L) and 0.25 mL of TMB (2 mM) were added into 4.5 mL of NaAc buffer (0.2 M, pH 3.5) in sequence. The absorbance of ultimate solution was monitored at 652 nm after incubation for 25 min at 30 °C.

To evaluate the kinetic of Fe/NC-800, 0.25 mL of different concentrations of TMB was added into a mixture containing 0.25 mL of Fe/NC-800 (400 mg/L) and 4.5 mL of acetate buffer (0.2 M, pH 3.5), then the solution was incubated at 30 °C, and the absorbance of the mixture at 652 nm was recorded at an interval of 30 s. The kinetic parameters, such as V_{max} and K_m , were calculated by Lineweaver-Burk equation: $\nu = V_{\text{max}} \times [S]/(K_m + [S])$, in which V_{max} and K_m represented the maximal reaction velocity and Michaelis constant represented the affinity of enzyme for substrate, respectively.

2.5. Colorimetric DA assay

The sensing system containing Fe/NC-800 (0.25 mL, 400 mg/L), 0.25 mL DA with varied concentration from 0 to 2 mM, and TMB (0.25 mL, 2 mM), NaAc buffer (4.25 mL, 0.2 M, pH 3.5) was monitored by UV-Vis spectrophotometer after 25 min reaction at 30 °C. The absorption spectra of the system were recorded from 500 to 800 nm after the addition of different levels of DA. The net absorbance at 652 nm ($\Delta A = A_0 - A$) versus DA concentration were used for the calibration, where A_0 is the absorbance of the blank solution, and A is the absorbance of DA sample solution. For dopamine determination in serum

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