

Metal–organic frameworks-derived synthesis of porous FeP nanocubes: An effective peroxidase mimetic



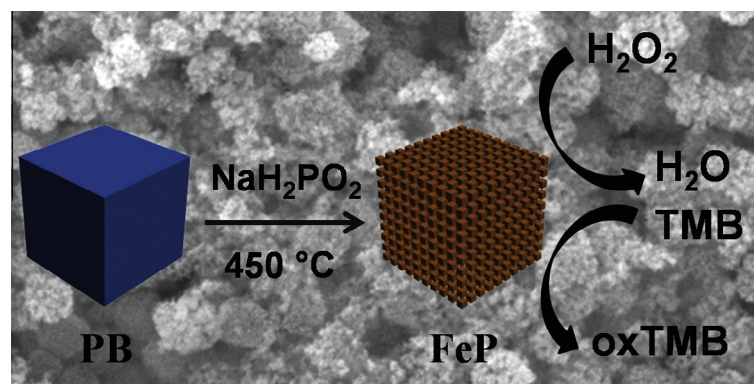
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GRAPHICAL ABSTRACT

A facile process was demonstrated toward the synthesis of porous FeP nanocubes through thermal phosphidation reaction, using Prussian blue as iron-based metal–organic frameworks precursors. Then, the FeP nanocubes were exploited as a peroxidase mimetic.



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ABSTRACT

Starting with metal–organic frameworks (MOFs), a facile process was demonstrated toward the synthesis of porous FeP nanocubes. Herein, Prussian blue nanocubes were used as iron-based MOFs precursors, and converted into FeP nanocubes through the thermal phosphidation reaction. Then, the FeP nanocubes were exploited as a peroxidase mimetic, which not only has the advantages of low cost, high stability, and easy preparation, but also follows Michaelis–Menten behaviors and shows strong affinity to substrates. On the basis of high catalytic activity of FeP nanocubes, a rapid, and convenient approach was developed for the colorimetric detection of H_2O_2 from $2\text{ }\mu\text{M}$ to $130\text{ }\mu\text{M}$ and with a detection limit of $0.62\text{ }\mu\text{M}$. The good catalytic activity and high stability make the porous FeP nanocubes a useful catalyst for a wide range of potential applications in catalysis and biotechnology.

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1. Introduction

Peroxidases are a large family of enzymes that typically catalyze the decomposition of peroxides to product hydroxyl radicals, which can oxidize many organic substrates to reduce their toxicity

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[1]. With good catalytic performance, peroxidases have been applied in many fields [2–4], such as waste water treatment and adhesives in manufacturing processes [5]. Among them, horseradish peroxidase (HRP) is commonly used in techniques such as ELISA and immunohistochemistry, due to they can catalyze the conversion of chromogenic substrates (e.g., 3,3',5,5'-tetramethyl benzidine (TMB)) into colored products [6,7]. However, natural enzymes, being protein-based macromolecules, bear some serious drawbacks in that they are unstable against denaturation or protease digestion, and their preparation and storage are expensive [8]. To overcome the stability and cost issues of biological catalyst, lots of efforts have been made to use stable enzyme mimetics as substitutes for natural enzymes. A variety of nanomaterials, such as noble metal [9,10], carbon materials [11,12], transition metal based alternatives [13–15], have been extensively developed as enzyme mimetics. Among these materials, some iron-based metal–organic frameworks (MOFs), like PCN-222 with porphyrinic Fe(III) centers [16], Fe(III)-based MIL-68 [17], MIL-100 [17] and Prussian blue [15], were recently found to be effective peroxidase mimics.

MOFs are well-ordered crystalline porous materials that consist of metal clusters coordinated to organic ligands. The crystalline structures of MOFs make them have unusual properties such as permanent nanoscale porosity, and high surface area. Thus, MOFs have been explored extensively in fields of gas storage, sensing, and catalysis [18,19]. Although the structure of MOFs is beneficial to their applications [20], unfortunately, most MOFs are unstable under alkaline conditions or ambient atmospheric environment [21,22]. Prussian blue (PB) is considered as the first synthetic MOF, which is a mixed-valence iron(III) hexacyanoferrate(II) compound. It is well known that PB would convert into $\text{Fe}(\text{OH})_3$ in an alkaline solution [21], which will limit their practical use in various catalysis reaction processes. Transition metal phosphides are a class of well-known catalysts and have recently attracted lots of research interest in catalysis because of their excellent catalytic performance over the wide pH range [23]. On the other hand, MOFs have been demonstrated as templates/precursors to construct carbon materials or metal oxides via thermolysis [24–26], and their pores are stable during elimination of the organic ligands. Inspired by these ideas, a phosphate reaction has been conducted using PB nanocubes as precursors, and porous FeP nanocubes were obtained. Interestingly, it has been found that the as-obtained FeP nanocubes possess excellent intrinsic peroxidase-like activity and can catalytically oxidize peroxide substrate 3,3',5,5'-tetramethylbenzidine (TMB) by H_2O_2 to produce a typical color reaction. The peroxidase-like catalytic property of FeP was further investigated through steady-state enzyme kinetics theory and methods with H_2O_2 and TMB as the substrates. Compared with PB precursor, FeP nanocubes have better stability under alkaline conditions. Finally, the FeP were successfully used as peroxidase mimetics for the colorimetric detection of H_2O_2 .

2. Experimental

2.1. Chemicals

3,3',5,5'-tetramethylbenzidine (TMB) and sodium hypophosphite (NaH_2PO_2) were obtained from Aladdin Industrial Inc. (Shanghai, China). Poly (*N*-vinyl-2-pyrrolidone) (PVP, relative molecular mass 30,000–40,000) and HRP was obtained from Shanghai Chemical Factory (Shanghai, China). Hydrogen peroxide (H_2O_2) and potassium hexacyanoferrate(II) trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) were purchased from Beijing Chemical Reagent Factory (Beijing, China). All the reagents were used as received without

further purification. All aqueous solutions were prepared with Milli-Q water ($>18.2 \text{ M}\Omega \text{ cm}$) from a Milli-Q Plus system (Millipore).

2.2. Apparatus

X-ray diffraction (XRD) spectra were obtained on a D8 ADVANCE (Germany) using $\text{Cu K}\alpha$ (0.15406 nm) radiation. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with $\text{Al K}\alpha$ X-ray radiation as the X-ray source for excitation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope (Holland) under an accelerating voltage of 200 kV, and a Hitachi H600 electron microscope (Japan) under an accelerating voltage of 100 kV. The sample for TEM characterization was prepared by placing a drop of prepared solution on a carbon coated copper grid and drying at room temperature. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) analysis were inspected on a Hitachi S-4800 microscope. Nitrogen adsorption and desorption isotherms were measured on an ASAP 2020 (Micromeritics, USA). Pore size distribution (PSD) curves were calculated by the Barrett–Joyner–Halenda (BJH) method from the absorption branch. UV–Vis detection was carried out on a PGENERAL T6 UV–Vis spectrophotometer (China).

2.3. Synthesis of porous FeP nanocubes

To synthesize FeP nanocubes, PB nanocubes were firstly prepared according to the literature [27]. In a typical procedure, PVP (3.00 g) and $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (0.132 g) were added to a HCl solution (0.1 M, 40 mL) under magnetic stirring. After the mixture was stirred for 30 min, the bottle was then placed into an electric oven and heated at 80 °C for 20 h. The obtained blue product was washed several times with deionized water and finally dried at room temperature for further use. Secondly, the obtained PB nanocubes were transferred into a tubular furnace for phosphidation under N_2 flow. 0.05 g PB and 0.5 g NaH_2PO_2 powder were put at two separate positions in a fused silica tube with NaH_2PO_2 at the upstream side of the tubular furnace. Then the PB was heated to 450 °C at a rate of 3 °C min^{-1} and maintained at this temperature for 2 h under protection of N_2 . Black FeP powder was obtained after cooled to ambient temperature under N_2 flow.

2.4. H_2O_2 detection using porous FeP nanocubes as peroxidase mimetics

To detect H_2O_2 , experiments were carried out using 20 μg FeP nanocubes in a reaction volume of 2 mL NaAc-HAc buffer (pH 4.0) with 250 μM TMB as the substrate. The concentration of H_2O_2 was 20 mM, unless otherwise stated. Reactions were monitored at 652 nm and recorded after 5 min at 40 °C.

2.5. The steady-state kinetic assays

The steady-state kinetic assays were carried out at room temperature in a 2 mL of TMB– H_2O_2 –FeP reaction system. The kinetic analysis of FeP nanocubes with TMB as the substrate was performed with TMB– H_2O_2 –FeP system with constant H_2O_2 concentration of 5 mM and 10 $\mu\text{g}/\text{mL}$ FeP nanocubes but varied TMB concentration (50–900 μM). The kinetic analysis with H_2O_2 as the substrate was performed with constant TMB concentration of 0.1 mM and 10 $\mu\text{g}/\text{mL}$ FeP nanocubes but varied H_2O_2 concentration (1–20 mM).

All the reactions were monitored in timescan mode at 652 nm using the UV–Vis spectrophotometer. A series of initial reaction

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