C. R. Chimie xxx (2017) 1–8

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Novel PEI–AuNPs–Mn^{III}PPIX nanocomposite with enhanced peroxidase-like catalytic activity in aqueous media

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ARTICLE INFO

Article history:
Received 4 September 2017
Accepted 30 November 2017
Available online xxxx

Keywords:
Peroxidase-like activity
Mn porphyrin
Gold nanoparticles
Polyethyleneimine
Activation of H_2O_2

ABSTRACT

Mn porphyrin provides a possibility to constitute the novel mimic catalyst with peroxidase-like activity. A simple method for preparing a novel catalyst PEI–AuNPs–Mn^{III} PPIX, used in aqueous media, was presented in this paper. The covalent anchoring of Mn^{III}PPIX and PEI were verified, meanwhile gold nanoparticles with the diameter less than 10 nm were dispersed uniformly and stably. The remarkable peroxidase-like catalytic activity of PEI–AuNPs–Mn^{III}PPIX was displayed in the oxidative degradation of azo dye acid orange 7 (AO7) as the model reaction in the presence of trace of H_2O_2. The synergistic effects of PEI–AuNPs and Mn^{III}PPIX on the enhancement of catalytic activity were observed at pH 2.0. Possible pathways involving in the formation of active radicals are proposed. The construction of PEI–AuNPs–Mn^{III}PPIX nanocomposite offers a new insight into the application of Mn porphyrin upon activation of H_2O_2, which have potential applications in many fields.

1. Introduction

Synthetic metalloporphyrins are regarded as an ideal platform for catalysis with peroxidase-like activity and draw much interest because of their versatile applications such as epoxidation of alkenes, oxidative degradation of xenobiotics, biosensors, and so on [1–6]. Among the biomimetic metalloporphyrins, iron (Fe) and manganese (Mn) stick out, due to their availability and importance of redox cofactors. In sharp contrast to Fe, analogous Mn porphyrin–catalyzed oxidations remained undeveloped. Mn reconstituting heme proteins such as horseradish peroxidase (Mn^{III} HRP) [7], microperoxidase-8 (Mn^{III}MP-8) [8], cytochrome *c* peroxidase (Mn^{III}CcP) [9], and myoglobin (Mn^{III}Mb) [10] have been prepared, but showed much lower reactivity toward hydrogen peroxide (H_2O_2).

Efforts were made to improve their activities by introducing amino acid residues with imidazole functional groups [11–13]. Similar works have been done for synthetic Mn porphyrins. The additives containing nitrogen such as imidazole and its derivatives [6,14,15] and pyridine derivatives [16] are most applied because of the axial ligand effect due to the formation of hydrogen bond between nitrogen and H_2O_2 coordinated at the Mn center. This effect is generally more pronounced in the reactions catalyzed by Mn^{III} porphyrins [17]. Other methods reported with higher catalytic activation of H_2O_2 include the choice of Mn porphyrin nanocomposite with the tail of carboxylic groups [6,14], the addition of a carboxylic acid [16], and the immobilization of Mn porphyrin to supports (amino-functionalized montmorillonite [17], chlorinated graphene oxide [18], modified multiwall carbon nanotube [19], and so on).

Because most synthetic models are designed to function in generally organic homogeneous solution rather than the environmentally benign aqueous media [5], water-soluble mimics come into notice. The

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https://doi.org/10.1016/j.crci.2017.11.010

biocompatible polymer with imidazole groups and carboxymethylated imidazolium groups was used to support Mn porphyrin in the preparation of the water-soluble mimics [20].

Murakami and Konishi [21] found the remarkable cocatalytic effect of gold nanoclusters on olefin oxidation catalyzed by the Mn porphyrin nanocomposite. Au nanoparticles (AuNPs) have enormous applications due to their unique physicochemical features such as biocompatibility, amphilicity, larger surface carrier capabilities, and gold electronic conductivity [22–24]. However, their tendency of agglomeration needs to be prevented for effective use. To synthesize well-dispersed AuNPs, various nanoreactor systems have been used; among them, polyethyleneimine (PEI) displays the reduction of $AuCl_4^-$ to AuNPs under mild conditions and steric stabilization for AuNPs [25–28]. In our previous study, PEI–AuNPs–hemin nanocomposite was proved to have a much-improved peroxidase-like catalysis for decomposing H_2O_2 [28], which indicated that the PEI–AuNPs can enhance the catalytic activity of metalloporphyrins.

In this study, we designed and synthesized a nanocomposite of Mn^{III} protoporphyrin IX chloride (Mn^{III}PPIX) associated with PEI–AuNPs, which is in a stable colloidal state in water. The oxidative degradation of azo dyes is often used to test the efficiency of peroxidase and its mimic system [29–36]. We herein used PEI–AuNP–Mn^{III} PPIX nanocomposite-catalyzed oxidative degradation of acid orange 7 (AO7), a kind of azo dye, as the model reaction and reported the notable peroxidase-like catalytic ability of this nanocomposite. The possible mechanisms are also proposed.

2. Experimental section

2.1. Materials and apparatus

All the reagents used here were of analytical grade. In particular, branched PEI (average molecular weight, M_W = 25 kDa) was purchased from J&K Scientific Ltd. (Shanghai, China). Hydrogen tetrachloroaurate(III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Sigma–Aldrich (St. Louis, MO) and Mn^{III}PPIX from Frontier Scientific Inc. AO7 (C.I. 15510) was purchased from Beijing Chemical Reagents Co.

UV–vis spectra were recorded using a UV-3600 UV–VIS–NIR spectrophotometer (Shimadzu, Japan). Fourier transform infrared (FTIR) spectrum analysis was performed using an FTIR-8400S spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM) image was obtained using a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 200 kV.

2.2. Preparation and characterization of PEI–AuNPs–Mn^{III}PPIX

PEI–AuNPs were synthesized as described in our previous report [28]. Then, the PEI–AuNPs were added into a 0.1 mM Mn^{III}PPIX solution (in 0.1 M phosphate-buffered saline [pH 9.0]) in a stoichiometric ratio of 1:0.12. The mixture was stirred at 25°C. After 1 h, the mixture was centrifuged at 14,000 rpm for 60 min, and then the precipitate was washed and centrifuged again in ultrapure water for three times. So prepared PEI-AuNPs-Mn^{III}PPIX was dispersed in water with a final concentration of 0.5 mg/mL and stored at 4°C in the dark for further use.

2.3. Catalytic experiments of PEI–AuNPs–Mn^{III}PPIX

AO7 stocking solution (1000 mg/L) was prepared by dissolving it in 0.1 M phosphate-buffered saline at various pHs between 1.0 and 9.0. The AO7 oxidative degradation was carried out at 25°C in the dark for 120 min as follows: certain amounts of the catalyst were added into the 24 mg/L AO7 solution and the reaction was initiated by adding precalculated amount of H_2O_2. The residual AO7 was quantified by spectrophotometric assay at 484 nm, the maximum peak of AO7. Control reactions in different systems were carried out.

3. Results and discussion

3.1. Preparation and characterization of the catalyst, PEI–AuNPs–Mn^{III}PPIX

Scheme 1 shows the preparation route for PEI–AuNPs–Mn^{III} PPIX. PEI was used as a reducing and protective agent to prepare the PEI–AuNPs by one-step thermal process synthesis [28]. Next, PEI–AuNPs–Mn^{III}PPIX was prepared by an amidation reaction between carboxyl groups of porphyrin and the amino groups of PEI–AuNPs. Thus, Mn^{III}PPIX is heterogenized and protected from forming dimer, which was supposed to be one of the most important deactivation reasons for metal porphyrin [18].

The prepared catalyst was in a stable colloidal state in water and was characterized using UV–vis spectroscopy and FTIR (Fig. 1).

The UV–vis spectrum of Mn^{III}PPIX shows three absorption peaks at 370, 464, and 554 nm, respectively. Compared to the spectra of PEI–AuNPs and Mn^{III}PPIX, all three peaks were red shifted, which suggests that the conjugation is formed in the PEI–AuNPs–Mn^{III}PPIX nanocomposite [37,38]. The calculated diameter of AuNPs was 9.6 nm according to Haiss's theory [39]. The FTIR spectrum of the PEI–AuNPs–Mn^{III}PPIX features several characteristic bands. The strong and broad band near 3450 cm^{-1} belongs to stretching vibration of NH from PEI. There are absorption peaks of stretching vibration of NH_2^+ at 2948, 2843, and 2300 cm^{-1}. The peak at 1632 cm^{-1} can mainly be assigned to a C=O stretching in carboxyl or amide groups. The peaks at 1469 and 1017 cm^{-1} are attributed to the NH deformation vibration and CN stretching vibration. The informative spectroscopic data confirmed the covalent anchoring of Mn^{III}PPIX and PEI.

The morphology of PEI–AuNPs–Mn^{III}PPIX was further characterized by TEM, and Fig. 2 presents its representative TEM image and the size distribution.

As shown in Fig. 2, the PEI–AuNPs–Mn^{III}PPIX had an approximately spherical morphology and dispersed uniformly with the average diameter of 9.4 nm (200 particles

Please cite this article in press as: H. Xie, et al., Novel PEI–AuNPs–Mn^{III}PPIX nanocomposite with enhanced peroxidase-like catalytic activity in aqueous media, Comptes Rendus Chimie (2017), https://doi.org/10.1016/j.crci.2017.11.010