A facile preparation of MSS@FePt nanocomposites and their application for H_2O_2 detection

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Abstract. In this report, Platinum iron nanoparticles (FePt NPs) were attached onto Mesoporous silicon spheres (MSS) by a facile polyol process. Based on the prepared nanoparticles, a novel colorimetric sensor for fast and sensitive determination of H_2O_2 was established. The established colorimetric sensing platform exhibited perfect peroxidase-like activities confirmed by oxidating 4, 4'-Bi-2, 6-xylidine (TMB) with H_2O_2. After optimizing the reaction conditions, the linearity of H_2O_2 determination ranged from 40 to 300 \( \mu \)M and the limit of detection (LOD) of 18.27 \( \mu \)M.

1. Introduction

Hydrogen peroxide (H_2O_2) has the pivotal positions in amounts of domains, for instance mineral industrial, agricultural and agrions, bioanalysis and clinical diagnosis [1-4]. Recently, series of analysis technics have been established to sensitive and rapid detect H_2O_2, for instance, electrochemical, fluorescence, chemiluminescence and colorimetric [5-7]. Among these established analysis technics, high attentions have been paid to colorimetric, due to its advantages of cost-effective, high-efficiency, high convenience, high-sensitivity and other superiority.

As a series of well-attended nanomaterials, nano-enzymes are utilized to imitate and substitute the traditional enzymes. In spite of the high-efficiency, the application of traditional enzymes are limited by their inherent defects, for instance instability, high manufacturing cost and harsh conditions of the application. To overcome these mentioned drawbacks, nano-enzymes are paid a lot of attentions. Up to now, amounts of nanomaterials were synthesized and applied in series of fields, for example Fe_3O_4 NPs [7], Co_3O_4 NPs [8], CeO_2 NPs [9], MnO_2 nanosheets [10], CuO NPs [11], V_2O_5 nanoparticles [12] and noble metals (Au, Pt) [13]. In order to further improve the peroxidase-like ability of platinum-based nanomaterials, more than two kinds of metallic elements or noble metals were brought into the horizon of researchers. Until now, few studies have been report to study the peroxidase-like activity of FePt NPs.

In this study, we obtained a peroxidase-like nano-enzyme MSS@FePt NPs by in-situ reduction Fe (acac)_3 and Pt (acac)_2 on the surface of mesoporous silicon spheres. Furthermore, the obtained nanoparticles were utilized as a colorimetric sensor for H_2O_2 determination.
2. Materials and methods

2.1. Materials and Characterization

4, 4’-Bi-2,6-xylidine (TMB), hydrogen peroxide (H₂O₂), Iron(III) acetylacetonate (Fe(acac)₃) and Acetylacetone Platinum(II) (Pt(acac)₂) were got from Aladdin. These TEM images were provided by the transmission electron microscopy (JEOL, JEM-2100, and Japan). These UV-vis spectras were performed on a Cary 4600 spectrometer (USA).

2.2. Preparation of MSS@FePt NPs

Mesoporous silicon spheres (MSS) were prepared according to the reported literature [15]. MSS@FePt NPs were prepared by a modified polyol process [16]. 0.1g MSS, 0.2 mmol Pt (acac)₂ and 0.4 mmol Fe (acac)₃ were introduced into three-neck flask. Then, the mixture were heating to a certain temperature under N₂ atmosphere and refluxed with constant stirring for 1 h. After cooled to room temperature, the obtained NPs were centrifuged at 10000 rpm for 10 min and washed with ethanol for three times.

2.3. Colorimetric Detection of H₂O₂

In the typical operation, 200 μL TMB (1mM), 200 μL MSS@FePt HNPs (30 μg/mL) and 200 μL H₂O₂ (0.2 M) were sequentially added into 1400 μL Citric acid buffer (pH 4.2). When the reaction solutions were incubated for 3 min, the absorption of the solution was performed on the UV-vis spectrometer.

3. Results and Discussion

3.1. Synthesis and Characterization of MSS@FePt NPs

In this study, MSS@FePt NPs were easily prepared by a facile polyol process. Firstly, MSS were simply synthesized by a hydrolysis method under alkaline conditions. The hybrid nanoparticles were uniformly well-formed spheres with an average diameter of 200 nm, shown in Figure 1A. The (110) plane of FePt NPs with a lattice spacing of 0.224 nm was also observed in Figure 1B.
Figure 1. The TEM image of MSS@FePt NPs (A), the HRTEM of MSS@FePt NPs (B), and the inset is the adjacent fringe spacing of FePt NPs.

To study the peroxidase-like properties of MSS@FePt NPs, these colorimetric reactions were carried out with TMB as chromogenic substrate. As shown in Figure 2A, the strongest absorbance at 652 nm was obtained in system a (TMB+MSS@FePt+H2O2, line a), compared to the other systems. This result indicated that, in the presence of H2O2, MSS@FePt NPs can catalyze the decomposition of H2O2 inducing the oxidation of TMB rapidly. However, without H2O2, MSS@FePt NPs can barely catalyze the oxidation of TMB, producing none color change in system b (TMB+MSS@FePt), shown in the inset of Figure 1(A). Similarly, the control experiments (system c and d) without MSS@FePt NPs or H2O2 show negligible color variation. These results clearly demonstrate that MSS@FePt NPs possess peroxidase-like activity. In addition, the UV absorbance changes at 652 nm of MSS@FePt NPs were further investigated.

Figure 2. (A) The UV-vis spectra of these obtained nano-enzymes. (B) Experiments to investigate the peroxidase-like activity.
Figure 3. The dose-response curve for H$_2$O$_2$ determination.

Based on the excellent peroxidase-like activity of MSS@FePt NPs, a colorimetric method was established for H$_2$O$_2$ detection. With increasing H$_2$O$_2$ from 1 µM to 1000 µM, displayed in Figure 3, the absorbance of the colorimetric system at 652 nm raised gradually. The typical H$_2$O$_2$ concentration-response curve was shown in Figure 3, as depicted in Figure 3, the linear range of the H$_2$O$_2$ determination was found to be 40 to 300 µM and the limit of detection (LOD) of 18.27 µM.

4. Conclusion

In summary, MSS@FePt NPs were synthesized in a facile way and applied as peroxidase-like enzyme to establish a sensitive and fast sensing platform for colorimetric determination of H$_2$O$_2$. Verified by series of experiments, MSS@FePt NPs exhibit excellent peroxidase-like activity. Under optimized conditions, the linearity of H$_2$O$_2$ detection ranged from 40 to 300 µM and the LOD was 18.27 µM. Compared to other methods, MSS@FePt NPs-based colorimetric sensor for detection H$_2$O$_2$ is a sensitive, simple and cheap assay.

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