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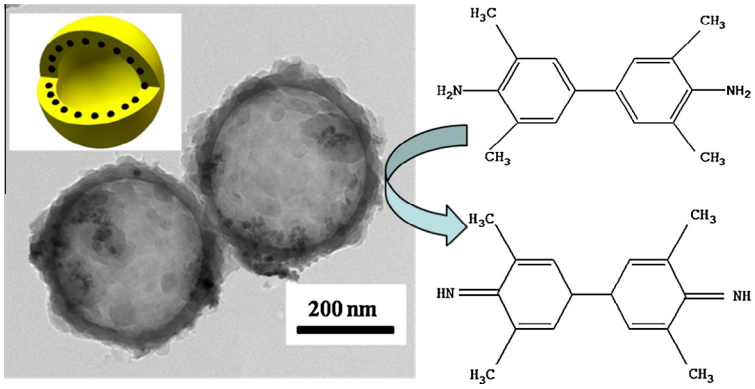
Magnetically separable and recyclable Fe_3O_4–polydopamine hybrid hollow microsphere for highly efficient peroxidase mimetic catalysts

Shujun Liu, Jianwei Fu *, Minghuan Wang, Ya Yan, Qianqian Xin, Lu Cai, Qun Xu *

School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, PR China

GRAPHICAL ABSTRACT

Magnetically separable and reusable Fe_3O_4–polydopamine hybrid hollow microspheres based on template-induced covalent assembly method exhibit highly efficient peroxidase mimetic catalytic activity and stability.



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ABSTRACT

Magnetic Fe_3O_4–polydopamine (PDA) hybrid hollow microspheres, in which Fe_3O_4 nanoparticles were firmly incorporated in the cross-linked PDA shell, have been prepared through the formation of core/shell PS/Fe_3O_4–PDA composites based on template-induced covalent assembly method, followed by core removal in a tetrahydrofuran solution. The morphology, composition, thermal property and magnetic property of the magnetic hybrid hollow microspheres were characterized by SEM, TEM, FT-IR, XRD, TGA, and vibrating sample magnetometer, respectively. Results revealed that the magnetic hybrid hollow microspheres had about 380 nm of inner diameter and about 30 nm of shell thickness, and 13.6 emu g^{-1} of magnetization saturation. More importantly, the Fe_3O_4–PDA hybrid hollow microspheres exhibited intrinsic peroxidase-like activity, as they could quickly catalyze the oxidation of typical substrates 3,3′, 5,5′-tetramethylbenzidine (TMB) in the presence of hydrogen peroxide. Compared with PDA/Fe_3O_4 composites where Fe_3O_4 nanoparticles were loaded on the surface of PDA microspheres, the stability of Fe_3O_4–PDA hybrid hollow microspheres was greatly improved. As-prepared magnetic hollow microspheres might open up a new application field in biodetection, biocatalysis, and environmental monitoring.

* Corresponding authors at: School of Materials Science and Engineering, Zhengzhou University, 75 Daxue Road, Zhengzhou 450052, PR China.
E-mail addresses: jwfu@zzu.edu.cn (J. Fu), qunxu@zzu.edu.cn (Q. Xu).

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1. Introduction

Currently, there is growing interest in the use of nanoparticles for a wide range of biomedical and technological applications. Among well-known nanoparticles, magnetic Fe_3O_4 nanoparticles are of special interest because of their potential in biological imaging or separation techniques. For instance, Fe_3O_4 nanoparticles have been widely used experimentally for numerous applications such as separation of biomolecules [1–3], drug and gene targeting [4,5], tissue engineering [6], magnetic resonance imaging [7–9], magnetic biosensors [10], biocatalysts [11], wastewater treatment [12–17] and as mediators of heat for cancer therapy [18,19]. More recently, Fe_3O_4 nanoparticles have been found surprisingly to possess intrinsic peroxidase-like activity [20–26]. Peroxidase catalysis owns a wide range of practical applications. For instance, the ability to catalyze the oxidation of organic substrates to produce a color change or reduce their toxicity is frequently employed as a detection tool or in wastewater treatment. However, naked nanoparticles generally incline to aggregate to form larger particles because of Van der Waals forces, resulting in a significant deterioration of their original activity [27–29]. To solve this problem, many support materials for anchoring Fe_3O_4 nanoparticles have

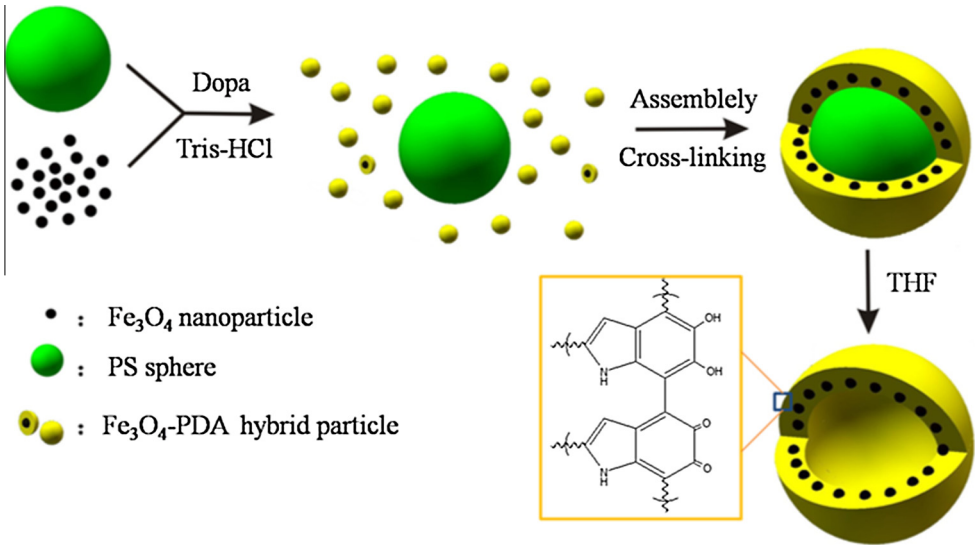

Fig. 1. Schematic illustration of the preparation procedure of magnetic Fe_3O_4–PDA hybrid hollow microspheres.

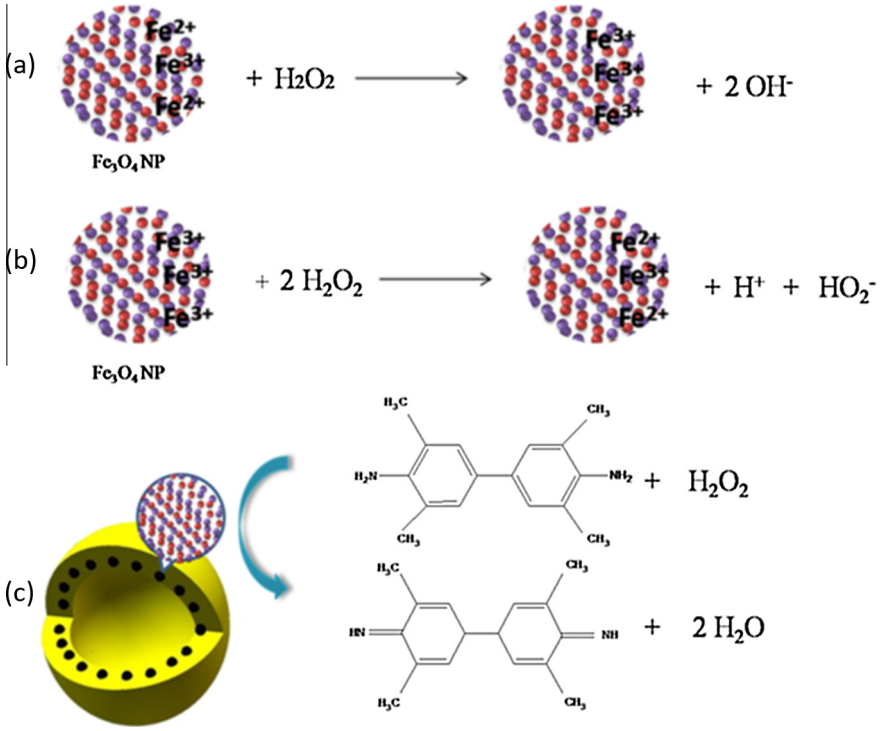

Fig. 2. Schematics of (a) oxidation and (b) reduction processes on Fe_3O_4 nanoparticles in the presence of H_2O_2, and (c) the peroxidase mimetic reaction of the TMB substrate by Fe_3O_4–PDA hybrid hollow microsphere catalyst. (Fe_3O_4: black sphere, Fe: light purple sphere, O: red sphere). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)