

A novel Prussian blue-magnetite composite synthesized by self-template method and its application in reduction of hydrogen peroxide

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A novel Prussian blue (PB)-Fe₃O₄ composite has been prepared for the first time by self-template method using PB as the precursor. According to this method, Fe₃O₄ nanoparticles distributed uniformly on the surface of PB cube. The feed ratio of sodium acetate to PB has been proved to be a key factor for magnetic properties and electro-catalysis properties of the composite. Under the experimental conditions, the saturation magnetization value (*M_s*) of PB-Fe₃O₄-2 composite was 22 emu g⁻¹, while the *M_s* value of other samples reduced. The composites also showed a good peroxidase-like activity for the oxidation of substrate 3,3,5,5-tetramethylbenzidine (TMB) in the presence of H₂O₂. The catalytic reduction of hydrogen peroxide capacity was PB-Fe₃O₄-1 > PB-Fe₃O₄-2 > PB-Fe₃O₄-3 > PB-Fe₃O₄-0, which confirmed the Fe(II) centres in PB surface and Fe₃O₄ nanoparticles had synergistic effect on catalytic reduction of hydrogen peroxide.

KEYWORDS

composite materials, H₂O₂, magnetic Prussian blue, nanoparticles, self-template

1 | INTRODUCTION

Prussian blue (PB) is a class of cyano-bridge coordination polymers with the formula of Fe^{III}₄[Fe^{II}(CN)₆]₃. It can provide Fe(III) and Fe(II) as catalytic active sites, and plays a vital role in the applications of catalysis, sensors and drug delivery which has attracted more attention of many researchers.^[1] Besides, it was also reported that Fe₃O₄ nanoparticles exhibited peroxidase-like activity. But the applications of pure magnetic Fe₃O₄ were limited owing to agglomeration of the small particles for their large ratio of surface area to volume which led to a sharp decrease in catalytic activity.^[2]

Inspired by these unique properties, PB and Fe₃O₄ composites have been prepared by methods previously studied,

such as hydrothermal synthesis^[2] and layer-by-layer processes.^[3] But, these processes were always complicated. In addition, composites with different structures have been reported such as core@shell structured Fe₃O₄@PB by layer-by-layer method.^[4] And PB-Fe₃O₄ nanoparticles by one-pot hydrothermal route using ferric (III) chloride and potassium ferricyanide as precursors.^[2] However, the morphology of the composite was irregular. In this paper, a new synthetic method was used to synthesize Fe₃O₄ nanoparticles modified PB cube (simplified as PB-Fe₃O₄ composite), the Fe₃O₄ nanoparticles with average particle sizes of 100 nm were distributed uniformly on the surface of PB cube. In general, Fe³⁺ and Fe²⁺ centers were contained at the nodes of PB,^[5] and the presence of Fe³⁺ and Fe²⁺ provides the conditions for the synthesis of Fe₃O₄.^[6] Given that PB could

provide Fe^{3+} and Fe^{2+} , magnetic PB- Fe_3O_4 composite would be fabricated by self-template synthesis strategy. To the best of our knowledge, however, preparation of new structure PB- Fe_3O_4 composite by using PB through the self-template method has not been reported so far.

Herein, a self-template method that PB was used not only as the template but also as iron source for the formation of Fe_3O_4 to synthesize a novel composite material, which consists of micron-sized PB cube and nano-scale Fe_3O_4 spherical particles. Moreover, magnetic and electrochemical properties were investigated. Besides, the composites were applied in a promising catalyst for the reduction of hydrogen peroxide.

2 | EXPERIMENTS

PB cube was prepared following the procedure described earlier.^[7] In a typical experiment, 0.11 g $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ was dissolved in 50 ml of 0.1 M HCl solution under magnetic stirring. After a clear solution was obtained, the beaker was placed into an electric oven and heated at 80°C for 24 h. Blue products were collected by centrifugation and washed several times with distilled water and ethanol until the supernatant was clean, finally dried at 60°C for 12 hours.

Magnetic PB- Fe_3O_4 composite was fabricated as follows. Firstly, 0.01 g PB was dispersed in 20 ml ethylene glycol under ultrasonic condition. Afterward, sodium acetate (NaAc) was added into the homogeneous solution with vigorous stirring for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 ml capacity). The autoclave was heated at 200°C for 10 hours, and then cooled to room temperature. The final product was washed with distilled water and ethanol for several times. Moreover, by adjusting the concentration ratio of NaAc to PB on 0, 400, 700, 1000, the obtained products were then marked as PB- Fe_3O_4 -0, PB- Fe_3O_4 -1, PB- Fe_3O_4 -2, PB- Fe_3O_4 -3, respectively.

The morphology of composites was recorded on a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F). Phase analysis was characterized by X-ray diffraction (XRD, Rigaku D/max 2200/PC). The magnetic

measurements were performed by a Quantum Design MPMS-XL SQUID magnetometer. Cyclic voltammetry and chronoamperometry were conducted with electrochemical workstation (CV, Shanghai Chenhua Co., Ltd., Shanghai, China CHI821C).

To study the catalytic properties of the composite, the catalytic activity experiments were carried out by a method reported by Qin *et al.*^[8] In a typical process, 2 mg PB- Fe_3O_4 composite was dissolved in 10 ml sodium citrate buffer solution (50 mM, pH 4.0) followed by adding 1 ml H_2O_2 (100 mM) and 1 ml TMB (8 mM). Then the reaction was recorded by a UV-vis spectrophotometer (UV-6300, Mapada) at 652 nm. Besides, PB- Fe_3O_4 samples were immobilized onto the surface of platinum electrode in the presence of 0.4 mM H_2O_2 in pH 6.0 Phosphate buffer solutions (PBS, 0.1 mM)^[9] to study the influence of different PB- Fe_3O_4 samples on the electrochemical behavior.

3 | RESULTS AND DISCUSSION

The magnetic PB- Fe_3O_4 composite was prepared through a self-template method shown in Figure 1. Here, PB cube was obtained from iron ions and cyanide ions, and then the PB functioned as both a solid support and iron source for the Fe_3O_4 growth. Under the action of NaAc and ethylene glycol, the Fe^{2+} -CN- Fe^{3+} bond in the PB surface was broken, and Fe_3O_4 was generated through self-template method.^[10]

The crystal structure of the PB- Fe_3O_4 composites were studied by XRD in Figure 2. Three diffraction peaks around 17, 24° and 35° were assigned to PB, which could be assigned to the (200), (220) and (400) planes of PB cube.^[7] The peak type of PB- Fe_3O_4 -0 composite and PB was completely consistent indicating that PB had no change on the surface and that Fe_3O_4 nanoparticles were not obtained under the conditions of NaAc and ethylene glycol. After Fe_3O_4 nanoparticles were coated on PB surface, three new diffraction peaks were observed at 31, 36, and 63°, which further confirmed the existence of Fe_3O_4 nanoparticles in the composite.^[11] Compared to PB- Fe_3O_4 -1 and PB- Fe_3O_4 -3, the diffraction peaks

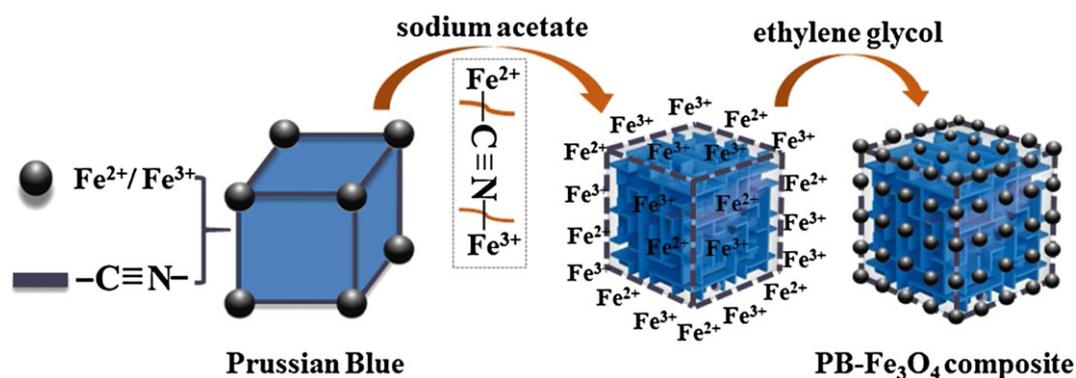


FIGURE 1 Schematic representation of the development process of PB- Fe_3O_4 composite

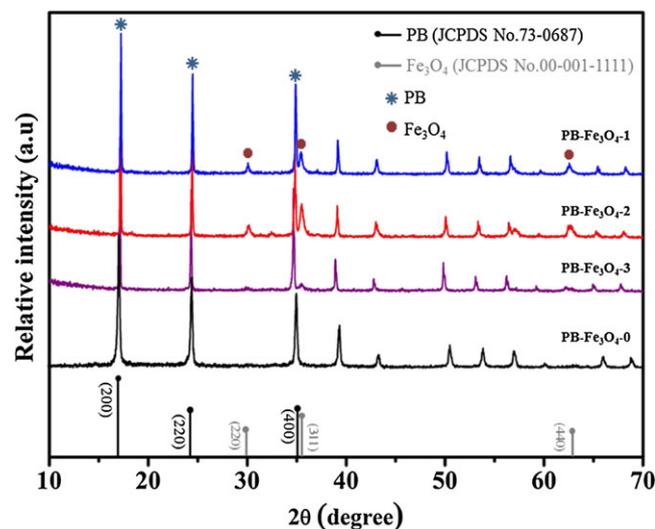


FIGURE 2 XRD patterns of magnetic PB-Fe₃O₄ composites

corresponding to Fe₃O₄ nanoparticles of PB-Fe₃O₄-2 became stronger, indicating it had the best crystal structure of Fe₃O₄ nanoparticles.

The morphology and distribution of Fe₃O₄ nanoparticles of the synthetic composite were demonstrated by SEM. As clearly observed from the Figure 3a, bare PB is a smooth surface cube with a size of 2 μm. Figure 3b showed the material surface morphology of PB-Fe₃O₄-0 was still relatively smooth without spherical particles, which confirmed that PB-Fe₃O₄-0 composite was PB. NaAc may play a decisive role in the synthesis of composite materials. In order to explore this problem, a series of control experiments were carried out. First, the same acetate concentration of KAc instead of NaAc was used for the experiment. Then, the NaOH and Na₂CO₃ solution with the same pH as the NaAc solution was prepared respectively. The experimental results showed that the KAc and NaOH trial did not precipitate. Although the Na₂CO₃ test was precipitated, it was not a PB-Fe₃O₄ composite (Figure 3c).

Under the action of NaAc, the Fe²⁺-CN-Fe³⁺ bond in the PB surface was broken, subsequently, Fe₃O₄ spherical particles was generated by self-assembly and the surface of the cube became rough. Furthermore, the concentration of NaAc for the formation of composite also had a significant impact. Herein, the uniform distribution and quantity of Fe₃O₄ can be tuned by changing the ratio of NaAc to PB. When the ratio of NaAc to PB increased from 400 to 700 as shown in Figure 2d-e, the number of spherical particles increased significantly, and their dispersion was more uniform. A possible explanation for this phenomenon was high concentration of NaAc resulting in more vacant Fe³⁺, which provided more opportunities to generate Fe₃O₄ nanoparticles. However, when the NaAc concentration increased to 1000, Fe₃O₄ nanoparticles easily aggregated into blocks, and the dispersibility was greatly reduced (Figure 3f).

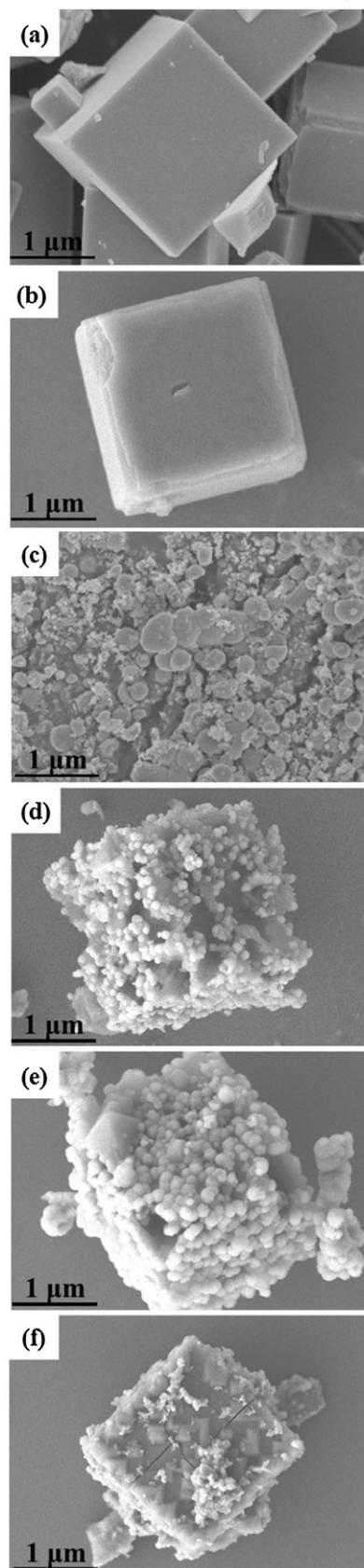


FIGURE 3 SEM images of (a) PB, (b) magnetic PB-Fe₃O₄-0 composite, (c) composite prepared with Na₂CO₃ instead of NaAc; SEM images of magnetic PB-Fe₃O₄-1 (d), PB-Fe₃O₄-2 (e), PB-Fe₃O₄-3 (f)

Figure 4 showed the magnetic properties of the magnetic PB-Fe₃O₄ composites with the different concentration ratio of NaAc to PB examined on a VSM. The saturation magnetization value (*M_s*) of the bare PB was almost zero. And, the *M_s* of PB-Fe₃O₄-1 and PB-Fe₃O₄-3 were roughly 10 emu g⁻¹ under an applied magnetic field of 5.0 × 10³ Oe. However, PB-Fe₃O₄-2 composite had the maximum *M_s* (22 emu g⁻¹) due to the Fe₃O₄ nanoparticles with good crystalline performance under this condition which can also be confirmed by the XRD (Figure 2). It was noteworthy that NaAc affected the formation of Fe₃O₄ and thus the magnetic properties of the materials.

Electrochemical behaviors of PB-Fe₃O₄-modified electrode showed that three samples showed a reduction peak near 0.28 V (Figure 5), it revealed that these samples had the ability to catalyze the hydrogen peroxide and had a consistent reaction mechanism. Also, it can be seen that these three samples with the potential negative shift, the current potential was getting smaller and smaller, indicating that the catalytic reduction of hydrogen peroxide capacity is PB-Fe₃O₄-1 > PB-Fe₃O₄-2 > PB-Fe₃O₄-3. It should be noted that the separate PB-Fe₃O₄-0 sample was not participated in cyclic voltammogram testing because PB have two typical pairs of redox waves showing the oxidation of Prussian Blue to Prussian Green as well as the reduction to Prussian White.^[12]

Furthermore, the catalytic activity of the composite was demonstrated by catalytic oxidation of the chromogenic substrate TMB which can be oxidized to a blue reaction product with maximum absorbance at 652 nm in the presence of H₂O₂.^[13] Figure 6 presented the time course curves of the different reaction systems catalyzed by PB-Fe₃O₄ samples and Fe₃O₄ within 120 minutes. It showed different catalytic activity towards TMB which was consistent with the previous conclusion.

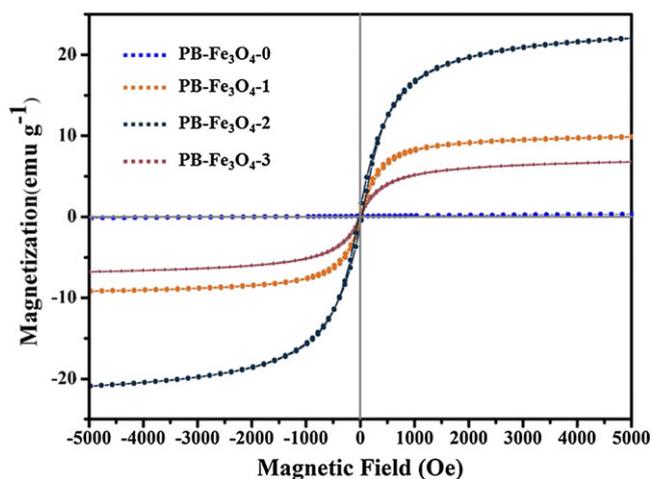


FIGURE 4 Magnetization curves of PB-Fe₃O₄-0, PB-Fe₃O₄-1, PB-Fe₃O₄-2, and PB-Fe₃O₄-3 samples measured at 300 K(B)

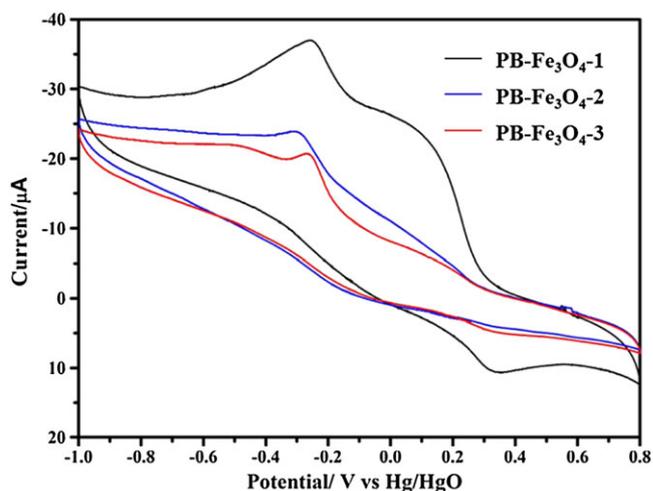


FIGURE 5 Cyclic voltammograms of PB-Fe₃O₄-1, PB-Fe₃O₄-2, PB-Fe₃O₄-3 composites electrode in the presence of 0.4 mmol/l H₂O₂ in pH 6.0 PBS, scan rate 100 mV/s

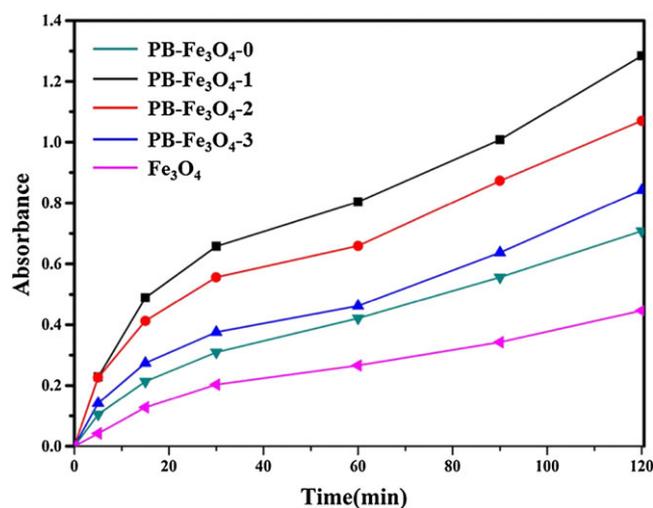


FIGURE 6 The absorbance-time course curves of PB-Fe₃O₄ samples and control group

From the above experimental results can be known, in the synthesis of PB-Fe₃O₄ composites, the most important mechanism was that NaAc disrupted the Fe²⁺-CN-Fe³⁺ bond in the PB surface, resulting in PB surface defected, making more Fe(II) sites exposed, which promoted the catalytic reaction. When the concentration of NaAc increased, the surface of PB was destroyed more seriously, the more Fe(II) sites were exposed, the better the catalytic activity was. The PB-Fe₃O₄-1, compared to the PB-Fe₃O₄-2, the exposed Fe(II) sites increased. From the experimental results of catalytic performance (Figure 5), the catalytic activity of PB-Fe₃O₄-1 was stronger than that of PB-Fe₃O₄-2, which showed that the Fe(II) sites in PB were contributed to the catalytic reaction.

But compared with PB-Fe₃O₄-1 composite, the catalytic activity of PB-Fe₃O₄-0 sample was significantly

reduced. Figure 2(b, d) showed that the Fe_3O_4 nanoparticles in PB- Fe_3O_4 -1 were more than PB- Fe_3O_4 -0, indicating that Fe_3O_4 nanoparticles themselves also played an important role. So, in PB- Fe_3O_4 composite, the Fe(II) centres of PB were responsible for catalytic reduction of hydrogen peroxide. Simultaneously, Fe_3O_4 nanoparticles themselves but not the Fe(II) ions were contributed to the catalytic reduction of hydrogen peroxide.^[14]

4 | CONCLUSIONS

In summary, magnetic PB- Fe_3O_4 composite was successfully synthesized by a facile method on the basis of self-template. PB not only served as the template but also provided iron source for the formation of Fe_3O_4 . The magnetic property of the composite can be tuned by the concentration of NaAc, and when the ratio was 700, it was the highest. In addition, PB- Fe_3O_4 composites exhibited good performance in electrocatalysis of hydrogen peroxide. Obviously, the PB- Fe_3O_4 composites film could be used as a promising platform for the development of biosensors related to hydrogen peroxide.

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REFERENCES

[1] J. Jang, D. S. Lee, *Ind. Eng. Chem. Res.* **2016**, *55*, 3852.

- [2] E. Y. Jomma, S. N. Ding, *Sensors* **2016**, *16*, 243.
- [3] P. Xue, J. N. Bao, L. Zhang, Z. G. Xu, C. J. Xu, Y. L. Zhang, Y. J. Kang, *J. Mater. Chem. B* **2016**, *4*, 4717.
- [4] F. X. Bu, L. Xu, W. Zhang, C. Y. Jin, R. J. Qi, R. Huang, J. S. Jiang, *Chem. Commun.* **2015**, *51*, 6198.
- [5] X. Q. Zhang, S. W. Y. Gong, Y. Zhang, T. Yang, C. Y. Wang, N. Gu, *J. Mater. Chem.* **2010**, *20*, 5110.
- [6] J. Liu, Z. K. Sun, Y. H. Deng, Y. Zou, C. Y. Li, X. H. Guo, L. Q. Xiong, Y. Gao, F. Y. Li, D. Y. Zhao, *Angew. Chem. Int. Ed.* **2009**, *48*, 5875.
- [7] L. Zhang, H. B. Wu, X. W. Lou, *J. Am. Chem. Soc.* **2013**, *135*, 10664.
- [8] F. X. Qin, S. Y. Jia, F. F. Wang, S. H. Wu, J. Song, Y. Liu, *Catal. Sci. Technol.* **2013**, *3*, 2761.
- [9] X. S. Chai, Q. X. Hou, Q. Luo, J. Y. Zhu, *Anal. Chim. Acta* **2004**, *507*, 281.
- [10] H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen, Y. D. Li, *Angew. Chem. Int. Ed.* **2005**, *44*, 2782.
- [11] X. F. Meng, Y. L. Xu, X. F. Sun, J. Wang, L. L. Xiong, X. F. Du, S. C. Mao, *J. Mater. Chem. A* **2015**, *3*, 12938.
- [12] G. Zhao, J. J. Feng, Q. L. Zhang, S. P. Li, H. Y. Chen, *Chem. Mater.* **2005**, *17*, 3154.
- [13] D. L. Li, S. H. Wu, F. F. Wang, S. Y. Jia, Y. Liu, X. Han, L. W. Zhang, S. L. Zhang, Y. M. Wu, *Mater. Lett.* **2016**, *178*, 48.
- [14] H. Wei, E. K. Wang, *Anal. Chem.* **2008**, *80*, 2250.

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