The Preparation of Polyhedral $\alpha$-Fe$_2$O$_3$ Nanoparticles and their Sensing Properties

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ABSTRACT: $\alpha$-Fe$_2$O$_3$ nanoparticles with polyhedral morphology were synthesized by a hydrothermal method. Parallelepiped $\alpha$-Fe$_2$O$_3$ nanoparticles with a narrow size distribution were successfully synthesized by hydrothermal method. The structural and morphological properties of $\alpha$-Fe$_2$O$_3$ nanoparticles were characterized by X-ray diffract meter (XRD), Scanning electron microscope (SEM), and transmission electron micrograph (TEM). The sensing capability of the polyhedral $\alpha$-Fe$_2$O$_3$ nanoparticles was investigated, the results showed that The polyhedral nanoparticles possessed the linearly response current related to the concentration of H$_2$O$_2$ in wide range concentration.

1. INTRODUCTION

As the most stable iron oxide under ambient conditions, hematite($\alpha$-Fe$_2$O$_3$) were used in the field of pigments [1], catalysts [2], magnetic recording media [3], water splitting [4], anticorrosive agents and gas sensors [5], owning to its low cost and environmental friendliness. Many efforts were devoted to preparing $\alpha$-Fe$_2$O$_3$ nanocrystals with different geometries and exposed surfaces owing to their shape-related properties [6, 7]. Up to now, various $\alpha$-Fe$_2$O$_3$ nanocrystals with well-defined shapes have been synthesized, but most of these nanocrystals are enclosed by low-index {111}, {101} or {100} facets [8, 9]. There are just a few reports on the preparation of $\alpha$-Fe$_2$O$_3$ nanocrystals with high-index facets exposed. For example, Gao et al. synthesized uniform pseudocubic $\alpha$-Fe$_2$O$_3$ nanoparticles enclosed by {012} facets [10]. Yin and coworkers reported tetrakaidecahedral and oblique parallelepiped $\alpha$-Fe$_2$O$_3$ nanocrystals which was enclosed by high-index facets (such as {012}, {102} and {-210}) [11]. However, the octodecahedral $\alpha$-Fe$_2$O$_3$ nanocrystals with high-index facets were not reported yet.

In the present work, octodecahedral $\alpha$-Fe$_2$O$_3$ nanocrystals with dominant high-index {112} facets were prepared in the assistance of formamide via a facile wet-chemical method. Furthermore, the sensing capabilities of these $\alpha$-Fe$_2$O$_3$ nanocrystals targeting at H$_2$O$_2$ were investigated.

2. EXPERIMENTAL

In a typical experiment, 3.6 mmol of iron chloride (FeCl$_3$·6H$_2$O) and 10 mL of formamide were added into 60 mL of distilled water and stirred until totally dissolved. The solution was then transferred into a 100 mL stainless steel autoclave and kept at 220 °C for 24 h and then cooled naturally. The products were washed with distilled water and absolute ethanol for several times, and then dried at 60 °C for 4 h. The formamide-dependent experiments were similar except the amount of formamide was changed to 1.8 mL, 5 mL and 12 mL. X-ray powder diffraction (XRD) spectrum of the products was acquired by a Philips X’Pert PRO SUPER X-ray diffractometer. The morphology of the sample was examined by scanning electron microscope (SEM, X-650) and high-resolution transmission electron microscope (HRTEM, JEOL-2010). Electrochemical response was measured on an electrochemical workstation (CHI760A, USA) at room temperature. The preparation of the H$_2$O$_2$ sensor and measurement methods were similar to that described by Li and co-workers [12].

3. RESULTS AND DISCUSSION

The purity and crystallinity of the typically synthesized product was determined by XRD (Fig. 1a). All peaks in the pattern can be perfectly indexed.
to hematite (α-Fe₂O₃, JCPDS 33-0664). The morphology of the product was investigated by SEM. Fig. 1b, 1c and 1d show typical SEM images at different magnifications. The low magnification image (Fig. 1b) clearly reveals that the products are uniform polyhedron with sizes near 150 nm. As shown in the high-magnification SEM images (Fig. 1c, 1d), the particles are bound by six top planes and twelve side planes. The cross-section in the middle of the crystals is a regular hexagon and the crystals have a three-fold axis.

![Figure 1. XRD patterns (a) and SEM images (b-d) of synthesized α-Fe₂O₃ nanoparticles.](image)

To investigate the crystal structure of the polyhedral particles, TEM and HRTEM analysis was carried out. Fig. 2a shows the TEM image of a typical octodecahedron, and Fig. 2b-d are the HRTEM images of regions b, c and d in Fig. 2a. On the edges of particle (Fig. 2b and 2c), two kinds of lattice fringes which parallel to edges are identified, and their interplane distances are scaled to 0.273 and 0.238 nm, which match the (104) and (112) facets of α-Fe₂O₃, respectively. In Fig. 2d, two continuous lattice fringes can be resolved at the corner, and their interplane distances well agree with that shown in Fig. 2b and 2c. Similar results also could be obtained from its fast Fourier-transform (FFT) pattern (inset in Fig. 2d). Based on the above evidence and the highly symmetric structure of particles, it can be concluded that the octodecahedral α-Fe₂O₃ enclosed by six {104} and twelve {112} facets. The six equivalent top planes could be indexed to (104), (0-14), (-11-4), (01-4), (-10-4), (1-1-4), and the twelve equivalent side planes are (112), (2-12), (1-22), (-1-1-2), (-212), (-222), (11-2), (2-1-2), (1-2-2), (-1-1-2), (-21-2) and (-12-2), respectively. In Fig. 2e, geometrical model of the ideal octodecahedron enclosed by these facets has been presented.

The presence of formamide played a significant role in tailoring the morphology of octodecahedral α-Fe₂O₃ nanoparticles. Fig. 3 shows SEM images of the α-Fe₂O₃ obtained by adding different amount of formamide. With formamide increasing, the dominant facets of octodecahedral α-Fe₂O₃ have a sequential variation from {104} planes to {112} facets (Fig. 3a-c). The size of particles gradually changed from 200 nm to 100 nm, and the particles morphologies also changed continuously (Fig. 4d). The reason for {112} facets increased by decreasing {104} facets is speculated as the formamide selectively adsorption on {112} facets. The formamide mainly affect the growth process of α-Fe₂O₃ by the coordination between Fe³⁺ ions on the facets and lone pair electrons of N atom in formamide. Therefore, the adsorption of formamide on the facets would depend on their crystal structures. Seen from the crystal structures of {104} facets (Fig. 3d), the {104} facets are mainly terminated by oxide atoms, which can block the adsorption of formamide by steric hindrance effect. Comparing with {104} facets, some Fe³⁺ are exposed on the surface of {112} facets, which will facilitate the adsorption of formamide and restrain the growth process on {112} facets. With the mount of formamide increasing, the adsorption on {112} facets would accordingly increase. This would directly result in the slow growth of {112} facets, and thus the area of {112} facets would increase gradually and finally dominate the particle surface. Besides the coordination effect, the surface energy may be the other reason for the evolution of {112} facets. High surface can facilitate the adsorption of ions or molecules in the solution so as to decrease the surface energy. On the synthesized particles, {112} and {104} facets are the mainly exposed facets, and seen from Fig.3 the area increasing of {112} facets together with the decreasing of {104} facets. Therefore, the evolution process may depend on the surface energy of them. According to [13], the {104} facets possess lower surface energy than {112} facets, which lead to the α-Fe₂O₃ particle surface are dominated by {104} facets when the
concentration of formamide is low. With the increase of concentration, more and more formamide molecules would preferentially adsorb on \{112\} facets due to its high surface energy, and thus restrain its growth, and finally result in the area increase of \{112\} facets.

Figure 3. a) SEM images of octodecahedral $\alpha$-Fe$_2$O$_3$ particles obtain with addition of 1.8 mL (a), 5 mL (b) and 12 mL (c) of formamide. (d) Evolution process of \{112\} facets and side-view crystal structure of \{104\} and \{112\} facets.

As the most stable iron oxide, $\alpha$-Fe$_2$O$_3$ is potentially suitable for detecting hydrogen peroxide in a physiological system (pH 7.2) [14]. Because dominant \{112\} facets are high-index and high surface energy facet, the sensing properties of these $\alpha$-Fe$_2$O$_3$ particles might be enhanced. Fig. 4A shows the cyclic voltammograms of a bare GC electrode and the octodecahedral $\alpha$-Fe$_2$O$_3$ nanoparticles-modified electrode in the presence of 2.55 mM H$_2$O$_2$ at PBS solution (pH 7.2). For the bare GC electrode, there is only a small background current observed in buffer, whereas a big magnification can be observed while the electrode was modified by the octodecahedral $\alpha$-Fe$_2$O$_3$ nanoparticles. The reduction process starts from -0.2 V and has a peak at -0.5 V, suggesting that the $\alpha$-Fe$_2$O$_3$ is catalytic to the reduction of H$_2$O$_2$. Fig. 4B shows the typical amperometric response of the octodecahedral $\alpha$-Fe$_2$O$_3$ modified GC electrode to the successive addition of H$_2$O$_2$ at an applied potential of -0.5 V (vs. SCE) (inset: its corresponding calibration plot (right down) and high-resolution of partly plot(left up)).

4. CONCLUSIONS

In summary, octodecahedral $\alpha$-Fe$_2$O$_3$ nanoparticles with high-index facets exposed have been successfully synthesized in high yields under the assistance of formamide. The sensing capability of \{112\} dominant facets particles toward H$_2$O$_2$ was investigated, and the response current was enhanced and stable with a linear response in the concentration range of 10 µM-3.55 mM.

5. ACKNOWLEDGEMENTS

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