一种新型纺锤状 $\alpha\text{-Fe}_2\text{O}_3$ 纳米晶的合成、表征及其表面性能

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摘要: 合成了一种新型的具有单晶结构的 $\alpha\text{-Fe}_2\text{O}_3$ 纳米晶(NFO-1). 在我们的合成方法中, 样品的形貌和结构在低反应浓度体系中运用无机盐和有机模板进行双重调控, 同时用溶剂挥发诱导自组装(EISA)来加速反应和在不改变形貌结构的前提下获得高产率样品. 所得 $\alpha\text{-Fe}_2\text{O}_3$ 纳米晶的形貌和结构对其表面修饰功能有明显的影响, NFO-1 因其特殊的纺锤状形貌而与表面功能试剂(多巴胺)之间的化学作用有明显的增强. 并且, 本文所描述的合成方法同样适用于其他过渡金属氧化物纳米单晶的合成. 我们预期, 这种方法可为新型纳米材料的合成提供新的途径.

关键词: $\alpha\text{-Fe}_2\text{O}_3$ 纳米晶; 模板导向; 溶剂挥发诱导自组装; 表面功能化

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Synthesis, Characterization and Surface Functionalization of Novel Spindle-Like $\alpha\text{-Fe}_2\text{O}_3$ Nanocrystals

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Abstract: We synthesized novel $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals (NFO-1) with single crystalline structure. In our synthetic strategy, the morphology and structure can be controlled simultaneously by the choice of inorganic salt (IS) and organic template (OT) in the extremely low precursor concentration reaction system. The evaporation-induced self-assembly (EISA) method was used to accelerate the reaction and to recover the synthesized $\alpha\text{-Fe}_2\text{O}_3$ with high yields while preserving its favorable shape and structure. The morphologies and structures of the obtained $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals greatly influence their surface functionalization capability. The chemical interaction between NFO-1 and the surface functionalization agent (dopamine) was obviously enhanced because of its special spindle-like morphology. The synthesis method described in this paper is suitable for the synthesis of other transition metal oxide single nanocrystals as well and we expect that this new route will be useful for the synthesis of novel nanomaterials.

Key Words: $\alpha\text{-Fe}_2\text{O}_3$ nanocrystal; Template-direction; Evaporation-induced self-assembly; Surface functionalization

Transition metal oxides have attracted significant attention in a variety of fields because of their unique structures and properties^[1-4]. In particular, the performance can be significantly enhanced by downsizing to nanometer scale according to recent research^[5-7]. Ferric oxides, the focus of this research, have a broad range of applications^[8-17], especially in the cancer tumor detec-

tion^[16], and selective separation and detection of bimolecular due to the apparent simplicity of postsynthesis surface functionalization^[17]. Stability of the chemical interaction between functional molecules and support is crucial for most medical applications because the support is the key to tracking or targeting treatments that the functional molecule is to perform^[18]. As a result, it is im-

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portant to shape-controlled synthesize ferric oxide nanostructures for the enhancement the interaction between functional molecules and ferric oxide nanostructures.

In recent years, a number of methods have been developed to produce ferric oxide nanocrystals possessing enigmatic morphogenesis^[19–26]. However, in both cases, the shape effects on their applications in surface functionalization have rarely been explored. Herein we report a new approach to the synthesis of novel spindle-like α -Fe₂O₃ nanocrystals. In our synthetic strategy, the morphology and structure can be jointly controlled by tuning the fraction of inorganic salt and organic template (IS-OT) in the extremely low precursor concentration reaction system, and the evaporation-induced self-assembly (EISA) method has been employed to accelerate the reaction and recover the synthesized α -Fe₂O₃ with high yields while preserving favorable shape and structure. The spindle-like morphology of the α -Fe₂O₃ nanocrystals synthesized by IS-OT double control self-assembly exhibits much enhanced the chemical interaction between α -Fe₂O₃ nanocrystals and the surface functionalization agent: dopamine (DA). Moreover, this strategy can be extended to synthesizing other transition metal oxide materials and complex oxides with special nanostructures.

In the soft template methods, surfactants have been used to organize silica into different forms^[27–31]. However, the transition metal oxide nanomaterials are more difficult to synthesize than silica nanomaterials because the transition metal oxide precursors are more reactive to hydrolysis and condensation compared to the precursors of silica, leading to the formation of undesirable non-uniform structures. Thus, the hydrolytic rate of the precursors is a very important factor to form the transition metal oxide nanomaterials. In this study, the rate of hydrolysis of the ferric oxide precursor can be strictly controlled by adjusting two more important affecting factors. Firstly, from the viewpoint of chemical reaction kinetics, the rate of chemical reaction is directly proportional to the reactant concentration, so the hydrolytic rate of the ferric oxide precursor is controllable by varying the precursor concentration (in this study, the molar ratio of ferric nitrate to H₂O is 1.2:11103.4). Secondly, appropriate precipitant is also essentially needed for the control of the hydrolytic rate of the ferric oxide precursor. In this case, urea is superior to other conventional precipitants such as sodium hydroxide and aqueous ammonia. The additions of sodium hydroxide and aqueous ammonia in the reaction system only cause the formation of disordered structures. The slowly strengthened alkalinescence generated by the hydrolysis of urea rendered the perfect adjustment of hydrolytic rate of ferric nitrate.

The nucleation has been regulated by inorganic salt and organic template double control self-assembly. Recently, Jia *et al.*^[24,26] found that the shape of nanomaterials can be influenced by the presence of phosphate and sulphate in the hydrothermal method. In our approach, magnesium nitrate has been used to regulate the structure of the synthesized hematite. Besides direct influence, we think that the structures of hematite can be indi-

rectly influenced by magnesium nitrate through regulating the structure of cetyltrimethyl-ammonium bromide (CTAB) micelles. Obviously, the template micellar structure is one of the main factors influencing the shape of synthesized materials in the soft template methods. On the other hand, the micellar aggregation parameters of cationic quaternary ammonium surfactants, such as translational diffusion coefficient of micelle, hydrodynamic radius, ionization fraction, and aggregation number, are greatly influenced by ionic strength^[32]. So the presence of magnesium nitrate can influence the structure of CTAB micelles and ultimately influence the structure of the synthesized hematite.

It is worth pointing out that the reaction is very difficult to be carried out in such low ferric nitrate concentration, and conventional techniques (such as centrifugation or filtration) are ineffective at recovering the sample synthesized by such low concentration reaction system. EISA is an efficient pathway to the preparation of nanometer-scale materials^[33–40]. We had used a modified EISA method in a previous study for synthesizing novel macroporous silica cages with tailoring pore architecture, and found that EISA method can accelerate the reaction and allow successful recovery of materials with high yields while preserving favorable shape and structure^[41]. So the EISA method was used to promote the reaction and recover the synthesized products in this study. It is remarkable that two types of ferric oxide single-nanocrystals with different morphologies are synthesized in this study (Scheme 1). The synthesized samples are designated as NFO-1 (with magnesium nitrate in the reaction system) and NFO-2 (without magnesium nitrate in the reaction system).

1 Experimental

1.1 Chemicals

The following chemicals were purchased and used as received without further purification. Cetyltrimethylammonium bromide (AR), ferric nitrate (Fe(NO₃)₃·9H₂O, AR), urea (AR), magnesium nitrate (AR), and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all experiments.

1.2 Synthesis

The α -Fe₂O₃ nanocrystals (NFO-1) were synthesized as follows: 0.4815 g Fe(NO₃)₃·9H₂O and 0.1486 g Mg(NO₃)₂ were dissolved in deionized water (200 mL) before adding CTAB (1.0983 g) and urea (CO(NH₂)₂, 1.1926 g) under stirring for 10 min to form a clear solution. The reaction mixture was kept static reaction for 24 h at room temperature (23 °C). The overall mixture composition (molar ratio) was 1.2 Fe(NO₃)₃:1.0 Mg(NO₃)₂:3.0 CTAB:20.0 CO(NH₂)₂:11103.4 H₂O. The mixture was then allowed to age in the airproofed Teflon flask at 85 °C under static condition for 24 h. After aged, the mixture was transferred into a beaker and concentrated at 60 °C (EISA). When little liquid was remained, the resulted red solid was washed with ethanol (100 mL×2) to remove the surfactants and collected through centrifugation and dried at room temperature. The remainder surfactants were removed by calcinations at 650 °C for 1 h. NFO-2 was

Scheme 1 Schematic illustration of the IS-OT double control self-assembly process of ferric oxide single-nanocrystals

To employ ferric nitrate as the source of the ferric oxide, the hydrolysis of ferric nitrate with the extremely low concentration was initiated through the hydrolysis of urea. The condensations of nuclei were controlled by the presence of the inorganic salt (magnesium nitrate) and organic template (CTAB). After aging with static condition, the products were recovered *via* evaporation-induced self-assembly (EISA) method. The resulting synthesis red solid was washed with ethanol to remove the surfactants and collected through centrifugation and dried at room temperature. The materials were then heat treated at high temperatures to promote crystallization.

synthesized using the NFO-1 synthesis system, except no addition of magnesium nitrate.

1.3 Characterization

XRD patterns were obtained with a Bruker D8-advance diffractometer by using Cu K α radiation (40 kV, 40 mA) with a step width of 0.01° (2 θ) and an acquisition time of 4 s per step. X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI5500ESCA analyzer. The main parameters were as follows: Mg K α , 200 W, vacuum $\sim 10^{-7}$ Pa. For Raman measurements, a confocal microprobe Raman instrument (RamLab-010, Jobin Yvon Horiba, France) was used. A 632.8 nm He-Ne laser excitation (0.1 mW) and a 50 $\times$ long working-distance objective (8 mm) were used in this work. The width of the slit and the size of the pinhole were set as 100 and 1000 μ m, respectively. Scanning electron microscopy (SEM) images were obtained on JEOL JSM-6700F electron microscope at 5 kV. The samples were first dispersed in ethanol and then were collected using copper grids covered with carbon films for analysis with gold coating. High-resolution transmission electron microscopy (HRTEM) experiments were performed on a JEOL JEM-3010F electron microscope with an acceleration voltage of 300 kV.

1.4 Electrochemical experiments

Electrochemical experiments were performed on a CHI 660C electrochemical analyzer (CH Instruments, Shanghai Chenhua Instrument Corporation, China) with a conventional three-electrode cell. The working electrode used was glassy carbon electrode (Aida Technology Limited Corp in Tianjin, 3 mm in diameter). A platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. Prior to each voltammetric experiment, the dissolved oxygen in solution was removed with purified nitrogen.

2 Results and discussion

It is necessary to confirm the chemical composition of NFO-1 considering that magnesium nitrate is added in the reaction system. The energy-dispersive X-ray (EDX) analysis (Fig.1b) confirms the presence of oxygen and ferric elements and the ab-

sence of magnesium element. X-ray photoelectron spectroscopy (XPS) also shows the presence of Fe and O components in the NFO-1 (Fig.1a). The results of Fe 2p_{1/2}, Fe 2p_{3/2}, and O 1s electron binding energies are 729.7, 716.2, and 535.1 eV, which are very similar to the values recorded in the literature^[42–43]. During the hydrolysis of urea, a pH favorable for the formation of α -Fe₂O₃ single-crystal structure can be achieved, while magnesium nitrate can not be hydrolyzed in such pH condition. So the magnesium nitrate can be removed during the further treatment. Raman spectroscopy is the important technique that could be effectively used to characterize different types of iron oxides. As shown in Fig.1c, which exhibits five strong resonant peaks at about 222, 287, 408, 494, and 608 cm⁻¹ in the range of 200–700 cm⁻¹, the positions of the peaks are in good agreement with the typical frequencies observed from α -Fe₂O₃^[44]. The wide-angle powder X-ray diffraction (XRD) is another effective method for confirming the structure of NFO-1. As shown in Fig.1d, several well-resolved diffraction peaks are clearly observed in the range of 20°–70°, which can be indexed as (012), (104), (110), (113), (024), (116), (214), and (300) reflections of α -phase of Fe₂O₃^[45–47]. The analysis results reveal that NFO-1 possesses the crystalline α -phase of Fe₂O₃.

We have further investigated the morphological structure of NFO-1 by SEM, TEM, and the selected area electron diffraction (SAED). As shown in Fig.2(a, b), NFO-1 possesses not only a very unique spindle-like morphology but also very uniform distribution in size. The average dimensions of these nanoparticles are 439 nm in long axis and 299 nm in short axis, and long/short axis ratios is 1.5 (see Supporting Information (available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>), Table S1). The information about the crystal can be derived from the high-resolution TEM (HRTEM) images. Fig.2(c–e) shows HRTEM images taken from the areas labeled c–e in a high-magnification TEM image of a separate NFO-1 particle (Fig.2b, the upper left inset, see Supporting Information, Fig.S1); they respectively show the lattice structures at the junction between different protuberances, the tip of the protuberance and the particle. They all clearly show lattice fringes that indicate crystallinity of the entire

Fig.1 XPS (a), EDX (b), Raman (c) spectra, and XRD pattern (d) of NFO-1 after calcination at 650 °C

particle.

The ideal spindle-like shape of NFO-1 was extremely sensitive to the synthetic conditions, especially the age time and the presence of $\text{Mg}(\text{NO}_3)_2$. In order to understand the formation process of NFO-1, the samples of NFO-11 and NFO-12 were synthesized by varying the crystallization time in the NFO-1 synthesis system (Fig.3). With the prolongation of the crystallization time, the nanoprotuberances in the centre of particles grow up to be horn-like outlines, while the highly ordered crystalline walls can be kept (see Supporting Information, Figs.S2 and S3).

Besides the influence of the crystallization time, the morphology and structure of NFO-1 can also be greatly affected by the presence of magnesium nitrate. In order to investigate the effect of magnesium nitrate on the morphology and structure of NFO-1, NFO-2 was synthesized based on the same prescription as NFO-1 except the addition of magnesium nitrate (Fig.4). As shown in Fig.4(a, b), NFO-2 contains spherical or ellipsoidal shape with uniform size (about 35 nm, see Supporting Information, Table S2). Comparing Fig.4 to Fig.1, it is clearly showed that the morphology of the synthesized NFO-2 is different from NFO-1. To obtain the crystal information of NFO-2, 5 nanoparticles are randomly chosen from Fig.4b and characterized using HRTEM, and HRTEM images confirm the single-crystallinity of NFO-2 (Fig.4(c–g), and see Supporting Information, Fig.S4), and the XRD pattern reveals that NFO-2 also possesses the crystalline α -phase of Fe_2O_3 (Fig.4h). The observation suggests that the morphology and structure of the synthesized samples have been clearly influenced by magnesium nitrate and the mechanism for the formation of NFO-1 may involve the participation of magnesium nitrate.

Under the magnesium nitrate and CTAB double control, there

are two possible routes to form NFO-1 nanocrystals (Fig.5). Route I: during the nucleation of Fe_2O_3 species, two types of Fe_2O_3 nuclei had been formed. The small nuclei were adsorbed on the surface of the large nuclei, and the protuberances were formed by the small nucleus. Route II: the protuberances directly grown in the centre of particles. Because of the absence of protuberances on the surface of the tip, Route II may be more possible than Route I.

The method described herein is not limited to the synthesis of single α - Fe_2O_3 nanocrystals, other novel transition metal oxide nanocrystals and complex oxides, such as Mn_3O_4 ^[48], Co_3O_4 , CuO , and $\text{SiO}_2/\text{Fe}_2\text{O}_3$, are also applicable in the NFO-2 synthesis system (see Supporting Information, Fig.S5, Fig.S6, and Fig.S7). The results reveal that the self-assembling actions of precursors are controllable in the extremely low precursor concentration re-

Fig.2 SEM and TEM images of NFO-1

(a) SEM image; (b) low-magnification TEM image, The inset shows the high-magnification TEM image of a separate NFO-1 particle, scale bar is 100 nm; (c–e) HRTEM images recorded in different regions in the upper inset of b showing the well-defined single nanocrystalline nature

Fig.3 SEM images of (a) NFO-1, (b) NFO-11, (c) NFO-12
crystallization time: (a) 24 h, (b) 48 h, (c) 72 h

action system and this method could be extended to synthesize other novel nanomaterials.

Interestingly, the obtained α -Fe₂O₃ nanocrystals with different morphologies and structures exhibited obviously different surface activities. We choose dopamine (DA) as the surface functional molecule to investigate the chemical interaction between α -Fe₂O₃ nanocrystals and the surface functionalization agent because DA is the important anchor molecule to immobilize the functional molecules on the iron oxide^[49]. Fig.6a shows the electrochemical responses of DA at the bare and the single α -Fe₂O₃ nanocrystals modified glassy carbon (GC) electrode in phosphate buffer solution at pH 7.0. As shown in Fig.6a, curve GC shows a cyclic voltammogram of the bare glassy carbon electrode at a scan rate of 20 mV·s⁻¹. A weak oxidation peak at 404.3 mV and a weak reduction peak at 18.6 mV can be observed (ΔE_{p-Bare} =385.7 mV), which reveals that there is an electrochemical response of dopamine at the bare GC electrode. But in curve NFO-2, at the

NFO-2 modified glassy carbon electrode with the anodic peak potential shifting negatively to 478.6 mV, the corresponding cathodic peak potential is -12.9 mV and $\Delta E_{p-NFO-2}$ =491.4 mV. It indicates that the electrochemical redox reaction of dopamine at the NFO-2 modified glassy carbon electrode is more difficult to carry out than that at the bare glassy carbon electrode. However, the cyclic voltammogram of NFO-1 modified glassy carbon electrode (Fig.6a, curve NFO-1) shows a different electrochemical response towards DA from that of the NFO-2 modified glassy carbon electrode. Comparing with the bare and NFO-2 modified glassy carbon electrodes, the remarkable enhancement in the peak currents shows promotional effects of NFO-1. An oxidation peak at 282.9 mV and a reduction peak at 87.1 mV ($\Delta E_{p-NFO-1}$ =195.7 mV) are clearly observed. These results reveal that the electron transfer velocity on the surface of NFO-1 is faster than that on the surface of NFO-2 and the better reversibility of the electrode reaction on the surface of NFO-1 than the latter, and a firmer attachment of DA was achieved in the surface of NFO-1. Commonly, the surface effects of nanomaterials will be strengthened with the decrease of particle size. But in this study, NFO-2 with smaller particle size exhibited weaker surface effects than NFO-1. We presume that the special spindle-like morphology of NFO-1 may lead to this result. Because of the presence of nanoprotuberances in the mid section of particles, the appropriate active sites may be available for DA sorption, benefiting to the enhanced chemical interaction between substrate and DA. This hypothesis can be confirmed by the CV experiments of NFO-11 and NFO-12. The CV experiments were carried out under similar experimental conditions, and the results were both almost similar to NFO-2. With the prolongation of the age time, the nanoprotuberances of NFO-11 and NFO-12 grew up to be horn-like outlines, and NFO-11 and NFO-12

Fig.4 (a) Low-magnification SEM image, showing the large-scale synthesis of NFO-2, (b) low-magnification TEM image of NFO-2, (c–g) HRTEM images recorded in different regions in (b), showing the single crystalline structure, (h) wide-angle powder XRD pattern of NFO-2

Scale bars in Fig.4(c–g) are 2 nm.

Fig.5 Possible formation and growth process of NFO-1

Insets are TEM images from Fig.3.

Fig.6 (a) Cyclic voltammograms obtained for DA on GC electrode, NFO-1 and NFO-2 modified GC electrodes; (b) continuous cyclic voltammograms obtained for DA at NFO-1 modified GC electrode

One mg NFO (NFO-1 or NFO-2) was ultrasound dispersed in ethanol (2 mL) for 10 min. Then 10 μ L of this suspension was coated on GC and dried. The electrochemical responses of DA at the bare and the NFO-1 mesoporous single nanocrystals modified GC were tested in pH 7.0 phosphate buffer solution (1.0×10^{-4} mol DA was added).

could not keep the special spindle-like morphology. So the samples could not provide appropriate active sites for DA sorption.

The types of interaction between NFO-1 and dopamine have been confirmed by a continuous CV experiment of NFO-1 modified glassy carbon electrode (Fig.6b). Seen from continuous cyclic voltammograms, it is found that the oxidation peak current of the first cycle is higher than that of the second cycle and after the third cycle the peak currents tend to be stable, which reveals that the adsorption process of oxidation state of dopamine controls the process of electrode reaction. While the reduction peak current is almost unchanged after several cycles, this indicates that the diffusion process of reduction state of dopamine controls the process of electrode reaction.

3 Conclusions

In conclusion, the novel α - Fe_2O_3 nanocrystals (NFO-1) with crystalline structures have been synthesized by IS-OT double control self-assembly method in the extremely low concentration system. The obtained α - Fe_2O_3 nanocrystals with different shapes exhibited obviously different surface activities. The capa-

bility of surface functionalization of NFO-1 is obviously enhanced because of its special spindle-like morphology. In addition, the synthesis method described herein is also suitable for the synthesis of other transition metal oxide single nanocrystals (such as Mn_3O_4 , Co_3O_4 , and CuO) and complex oxides ($\text{Fe}_2\text{O}_3/\text{SiO}_2$). The action mechanism, in which magnesium nitrate or other inorganic salts influence the morphology and structure of transition metal oxide single nanocrystals in the soft template synthesis process, will be an interesting research worth pursuing.

Supporting Information Available: free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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