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Impact of cadmium and phosphate ions on the hematite nanorings formation

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ABSTRACT

It has been suggested that the addition of divalent metal cations during the hydrothermal synthesis of hematite (α -Fe₂O₃) in the presence of phosphate ions has a strong impact on the hematite morphology, crystal growth and dissolution (Gotić et al., J. Mol. Struct. 993 (2011) 167). In this work, the same system was modified with divalent cadmium ions and the impacts of cadmium and phosphate ions on the hematite nanorings formation have been studied. It has been found that formed hematite and akaganeite (β -FeOOH) precipitates did not contain any trace of cadmium impurities. On the contrary, the modification with divalent cadmium cations changes the PO₄³⁻/Fe³⁺ molar ratio in the system. Upon the addition of cadmium ions the PO₄³⁻/Fe³⁺ molar ratio changes from 0.036 in a pure system to 0.051 in the cadmium modified system. The relative increase of phosphate concentration at early stage of precipitation induced the change of spindle to spherical morphology and formation of the poorly crystallised akaganeite-like phase. The appearance of akaganeite-like phase directly correlated with the delay in the crystallisation of hematite. Besides, the relative increase of phosphate concentration has the prevailing effect for the change of spindle to pseudosphere and nanotube to nanoring particle morphologies.

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1. Introduction

Hematite (α -Fe₂O₃) nanoparticles have been widely used as (photo)catalysts, pigments and sensors. Besides, the morphology of hematite nanoparticles (HNPs) has a high influence on their physicochemical properties. For instance, Zhang et al. [1] reported the superior optical and magnetic properties of spindle shaped HNPs in comparison to ellipsoid, like-spherical and quasi-cubic HNPs. Zhou et al. [2] have found that the morphology of HNPs plays an important role in photocatalytic degradation of rhodamine B organic dye in water under visible light. The nanorods (1D) exhibited the greatest photoreactivity in comparison to nanoplates (2D) and nanocubes (3D), because the exposed facets essentially dictate the photocatalytic activity among well-defined hematite morphologies. Thus, the control of HNPs morphology is very important for possible applications. The nanotube and nanoring morphologies are especially attractive due their unique magnetical and optical properties. The magnetic nanoring possesses the vortex

state characterized by a magnetic moment circulating around the ring [3,4]. In such a state magnetization turns out of the plane at the very centre of the vortex structure. A magnetic vortex can store two bits of information by switching the vortex core polarization [5]. α -Fe₂O₃ particles could be converted to ferrimagnetic Fe₃O₄ or γ -Fe₂O₃ particles under the hydrogen flow or in static hydrogen conditions at temperatures about 350 °C [6]. The morphology of α -Fe₂O₃ nanorings is perfectly preserved upon their conversion to Fe₃O₄ or γ -Fe₂O₃ [3,4].

A convenient and reproducible one-pot procedure for a large-scale synthesis of iron oxide nanotubes has recently been developed by Jia et al. [3]. These authors have shown that phosphate anions can induce the preferential dissolution of the hematite spindle precursor to form single-crystalline iron oxide nanotubes. What is important in this so many times used hydrothermal route is a temperature threshold of about 200 °C, which should be exceeded in order to obtain hematite nanotubes (HNTs). In addition to that, a long reaction time is required (48 h). These are very likely reasons why the hematite NTs were not discovered earlier. The same authors [7] have extended the hydrothermal synthesis of hematite nanotubes in the presence of phosphate to the synthesis of

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hematite nanorings by introducing sulphate into the system. Fan et al. [8] have shown that the size and shape could be controlled from nanotube to nanorings by simple adjustment of the reactants concentration and molar ratio. In order to synthesize hematite nanorings Hu et al. [9] modified Jia's procedure [3] by introducing microwave radiation into the hydrothermal process. Li et al. [10] were one of the first who synthesized novel ring-like α -Fe₂O₃ nanoparticles by a hydrothermal route. They used a redox reaction of Fe²⁺ and S₂O₈²⁻ in the presence of polyethylene glycol [10]. Hexagonal and circular nanorings have been obtained [11] using hydrothermal synthesis in the presence of SO₄²⁻ and VO₄³⁻ anions and by adjusting the pH of reaction solutions. The cooperative action of the SO₄²⁻ and VO₄³⁻ anions was the crucial factor in the formation of a hematite ring-like structure. The crystallization, Ostwald ripening and oriented dissolution mechanism was proposed to explain the formation process of the ring-like structures [11].

Contrary to the approach of introducing additional anions for better control of hematite nanotube/nanoring morphology, Gotić et al. [12] have exploited the benefits of introducing the divalent metal cations M²⁺ (M = Mn, Cu, Zn, Ni) into the system. It has been suggested that the addition of divalent metal cations during the hydrothermal synthesis of hematite in the presence of phosphate ions has a strong impact on the hematite morphology, crystal growth and dissolution [12]. However, the morphology and phase composition of formed iron oxides in an early stage of hydrothermal precipitation have not been studied. Moreover, the addition of divalent metal cations into the system changes the PO₄³⁻/Fe³⁺ molar ratio in the system. Thus, the aim of this work is to study the morphology and phase composition of iron oxides formed in an early stage of hydrothermal precipitation and to distinguish the impact of cadmium and phosphate ions on the hematite nanorings formation.

2. Experimental

2.1. Chemicals

All chemicals were of analytical purity and used as obtained. M-Q water (resistance 18 MΩ) and absolute ethanol (*Kemika*) were also used. The chemicals NH₄H₂PO₄, FeCl₃·6H₂O and CdCl₂·4H₂O were supplied by *Kemika*, Zagreb.

2.2. Synthesis

Samples were synthesized by hydrothermal treatment of a mixture of FeCl₃ and NH₄H₂PO₄ at 231 °C [3,12]. The experimental procedure was as follows: 3.2 mL of aqueous 0.5 mol dm⁻³ FeCl₃ solution and 2.9 mL of aqueous 0.02 mol dm⁻³ NH₄H₂PO₄ solution were mixed by stirring in a glass flask with a magnetic glass stirrer. Double distilled water was then added to the final volume of 80 mL. The mixture was stirred for 15 min, then transferred to two 50-mL Teflon-lined stainless steel autoclaves for hydrothermal treatment at 231 °C for 15, 30, 60 min, 2 h and 48 h. The autoclaves were cooled down to room temperature, the precipitates were separated by centrifugation, rinsed with double distilled water and absolute ethanol, and dried overnight at 60 °C. In order to study the influence of divalent metal cations, aqueous solution of CdCl₂ were prepared and added to aqueous solution of FeCl₃ so that molar ratio was [Fe³⁺]/[Cd²⁺] + [Cd²⁺] = 0.3. The mixture was stirred for 15 min, then transferred to 50-mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 231 °C for 15, 30, 60 min, 2 h and 48 h. The experimental conditions for the synthesis of all samples are given in Table 1.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded at 20 °C using the APD 2000 X-ray powder diffractometer, with CuKα (λ = 1.54059 Å) radiation (40 kV and 30 mA conditions), graphite monochromator, NaI-Tl detector) manufactured by *ItalStructures*, Riva Del Garda, Italy. The XRD patterns were recorded over the 10–100° 2θ range with a 2θ step of 0.03° and a counting time per step of 9–13 s. The samples were put on XRD zero-quartz holder in the form of a thin layer.

The thermal field emission scanning electron microscope (FE-SEM), model JSM-7000F, manufactured by *Jeol Ltd.*, was connected to the EDS/INCA 350 (energy dispersive X-ray spectroscopy) manufactured by *Oxford Instruments Ltd.*

The ⁵⁷Fe Mössbauer spectra were recorded in the transmission mode using a standard instrumental configuration by *WissEl GmbH* (Starnberg, Germany). ⁵⁷Co in the rhodium matrix was used as a Mössbauer source. The spectrometer was calibrated at 20 °C using the standard α-Fe foil spectrum. The velocity scale and all the data refer to the metallic α-Fe absorber at 20 °C. The experimentally observed Mössbauer spectra were fitted using the *MossWinn* program.

The Fourier transform infrared (FT-IR) spectra were recorded at 20 °C using a *Perkin-Elmer* spectrometer model 2000. The specimens were pressed into small discs using a spectroscopically pure KBr matrix. The spectra were recorded using a KBr beam splitter in the mid IR region (4000–400 cm⁻¹).

The atomic resolution microscopy (ARM) was performed on a 200 kV cold field-emission gun (FEG) Cs-probe corrected transmission electron microscope (Jeol ARM 200 CF), coupled with a Gatan Quantum ER electron energy-loss spectroscopy (EELS) system and energy-dispersive X-ray spectrometry (Jeol Centurio 100). Samples were dispersed in ethanol and placed on a holey carbon coated copper grid. The specimens were additionally coated with carbon to prevent excessive charging of the samples under the electron beam.

3. Results and discussion

Fig. 1 shows SEM images of samples F15 and F30. The both samples consist of spindle-shaped nanoparticles; the more regular spindles with sharper tips are found in sample F30.

Fig. 2 shows SEM images of Cd-modified samples. An evolution of nanoparticle morphology from amorphous-like (a) to nanorings (e) are visible. SEM images show the samples CD15 (a); CD30 (b); CD60 (c); CD2h (d) and CD48h (e). The comparison of samples F15 and F30 (Fig. 1) with the equivalent samples CD15 and CD30 (Fig. 2a and b) one can see a significant change in the morphology of the particles.

Fig. 3 shows TEM and SEM images of sample F60. Fig. 3a shows TEM image of spindle-like particles at low magnification with corresponding particle length and width distributions (insets); Fig. 3b shows the TEM image of spindle tip at high magnification and Fig. 3c show TEM image at atomic resolution. Fig. 3d shows SEM image of sample F60 with corresponding spindle width (e) and length (f) distributions. The mean particle length and width distributions was calculated using the normal function. D_{mean} stands for the mean particle length or width and σ stands for standard deviation. The spindle length ($D_{\text{mean}} = 379.8 \pm 58$ nm) and spindle width distributions ($D_{\text{mean}} = 64.2 \pm 8$ nm) calculated from TEM image are in very good agreement with spindle length ($D_{\text{mean}} = 369.8 \pm 67$ nm) and spindle width distributions ($D_{\text{mean}} = 70.7 \pm 8$ nm) calculated from SEM image. The particle aspect ratio (length/width) calculated from SEM is 5.2 and calculated from TEM is 5.9.

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