



How temperature determines formation of maghemite nanoparticles



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ARTICLE INFO

Article history:

Received 27 June 2014

Received in revised form

15 September 2014

Accepted 29 September 2014

Available online 1 October 2014

Keywords:

Iron Oxide Nanoparticles

Micromixer

SAXS

XANES

Carboxydextran

ABSTRACT

We report on the formation of polymer-stabilized superparamagnetic single-core and multi-core maghemite nanoparticles. The particle formation was carried out by coprecipitation of Fe(II) and Fe(III) sulfate in a continuous aqueous process using a micromixer system. Aggregates containing 50 primary particles with sizes of 2 nm were formed at a reaction temperature of 30 °C. These particles aggregated further with time and were not stable. In contrast, stable single-core particles with a diameter of 7 nm were formed at 80 °C as revealed by small-angle X-ray scattering (SAXS) coupled in-line with the micromixer for particle characterization. X-ray diffraction and TEM confirmed the SAXS results. X-ray absorption near-edge structure spectroscopy (XANES) identified the iron oxide phase as maghemite.

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1. Introduction

Magnetic colloids, also known as magnetic fluids or ferrofluids, consist of surface-coated magnetic nanoparticles dispersed in a liquid carrier. Magnetic fluids have a wide range of applications including heat and mass transfer applications such as liquid cooled loudspeakers and high power transformers [1,2], environmental applications like water cleaning [3] and biomedical applications. This last topic is probably one of the most appealing research areas. Applications on stem cell labeling [4], metastasis diagnostics [5], in vitro biodetection [6] and even in vivo cancer treatment [7] have been reported.

The crystal formation in solution is of key importance for generation of nanoparticles for these applications. Nucleation of small crystals from solution is classically described by the spontaneous formation of a nucleus that grows when it exceeds a critical size, which is determined by the surface energy to bulk energy ratio [8]. If several solid phases are possible, the formation of the thermodynamically stable phase can be preceded by metastable intermediates that stepwise transform to the final product. This is known as Ostwald's step rule, which states that phases more similar to the solution structure form more readily [9]. Further nucleation and growth often do not occur through the addition of atoms or molecules but may also involve aggregation and coalescence of small clusters. Such mechanisms have been termed as non-classical because they cannot be described within the classical nucleation and growth framework [10].

Here, we study the formation of iron oxide nanoparticles by coprecipitation of Fe(II) and Fe(III) sulfate at different temperatures in a micromixer. This is a continuous aqueous process which is monitored online by coupling with SAXS. To the best of our knowledge, using a micromixer and quick SAXS, is reported for the first time.

2. Materials and methods

2.1. Materials

Ammonium hydroxide, ferric sulfate hexahydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$) and ferrous sulfate tetrahydrate ($(\text{Fe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O})$) of analytical grade was purchased from Aldrich. Carboxydextran with a molar mass of $40 \times 10^3 \text{ g mol}^{-1}$ was purchased from Maito Sanyo, Japan.

2.2. Experimental setup

The experimental setup used for the synthesis of iron oxide nanoparticles is shown schematically in Fig. 1. It has two reservoirs: the first contains an aqueous solution of the iron salts and carboxydextran, the second contains ammonium hydroxide solution. Both reservoirs are connected via two HPLC pumps (Merck/Germany) with a reactor system composed of a micromixer and a microcapillary reactor. The micromixer is a caterpillar-type mixer (R600) made of polychlorotrifluoroethylene (PCTFE), purchased from the Institut für Mikrotechnik Mainz, Germany. The mixing principle of the micromixer was described in detail elsewhere [11].

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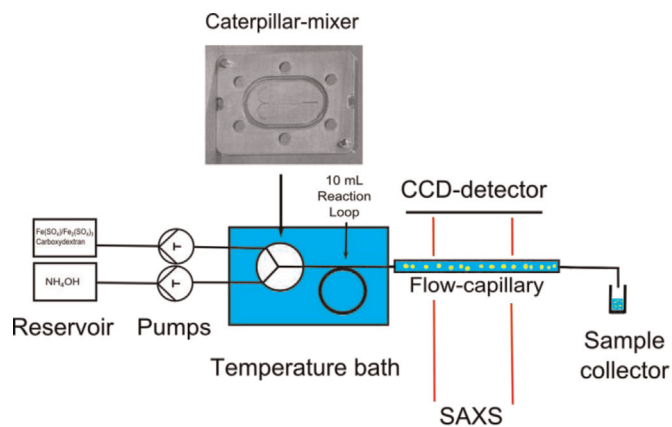


Fig. 1. Experimental setup for the continuous synthesis of polymer stabilized iron-oxide nanoparticles. The microreactor is directly connected to the SAXS device via PEEK tubing for particle characterization. The size of the microreactor is about $6.4 \text{ cm} \times 4.8 \text{ cm}$.

The microcapillary was made of stainless steel with a diameter of $750 \mu\text{m}$ and a total volume of 10 mL. The complete reaction system was placed in a temperature bath (Huber CC-318B, Germany) and interconnected with a quartz flow capillary (inner diameter 1 mm and wall thickness $10 \mu\text{m}$) embedded in the SAXS instrument. The inner volume of the complete system was 11.3 mL.

2.3. Nanoparticle preparation

The nanoparticles were synthesized using the method by Bee [12], which was adapted to the micromixer synthesis. Briefly, an aqueous solution of ferric and ferrous sulfate with a molar ratio of 2:1 Fe(III) to Fe(II) and a total iron concentration of $8.6 \times 10^{-3} \text{ mol L}^{-1}$ was prepared. Carboxydextran was added in a weight ratio of 3:1 with respect to the iron salts and then the solution was sparged with nitrogen for 30 minutes. This solution was mixed continuously inside the microreactor with a degassed solution of 25% ammonium hydroxide. The volume ratio of the stream of the iron salts solution to the stream of the ammonium hydroxide solution was 19:1. The experiment was conducted at two different temperatures of $30 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$ and three different flow rates of 8 mL min^{-1} , 4 mL min^{-1} and 2 mL min^{-1} . These flow rates represent reaction times of 84 s, 162 s and 326 s before SAXS measurements.

2.4. SAXS measurement

The experiment was performed at the BAMline at BESSY (Berlin, Germany) on a Kratky type camera SAXSess (Anton Paar, Austria). The exposure time was 30 s. The measured intensity was corrected by subtracting the intensity of a capillary filled with pure reagent solution. After background correction the data were de-convoluted (slit-length de-smearing). All data processing was performed with the SAXSquant 3.5 software (Anton Paar, Austria). The scattering vector is defined as $q = 4\pi/\lambda \sin(\theta/2)$ with the scattering angle θ and the wavelength $\lambda = 0.154 \text{ nm}$. The SAXS data evaluation was performed using the Guinier–Porod model [13], where the scattering intensity $I(q)$ is defined by a Guinier contribution at low and a Porod contribution at high q -values:

$$I(q) = \frac{G}{q^5} \exp\left(\frac{-q^2 R_g^2}{3-s}\right) \text{ for } q \leq q_1 \text{ and}$$

$$I(q) = \frac{D}{q^d} \text{ for } q \geq q_1$$

where R_g is the radius of gyration, s is the Guinier exponent, d is the Porod exponent, and G and D are Guinier and Porod scaling factors, respectively. The q -value of transition point q_1 is given by

$$q_1 = \frac{1}{R_g} \left(\frac{(d-s)(3-s)}{2} \right)^{\frac{1}{2}}$$

For data interpretation we used the IRENA program package [14] applied to the model above.

2.5. XRD measurement

The XRD measurement was performed at the μ -Spot beamline at BESSY II Berlin, Germany. The samples were dried on Kapton thin film and measured in transmission with a $100 \mu\text{m}$ wide beam at an energy of 15 keV. The crystallite size D_{311} was determined from the (311) reflection using a modified Debye–Scherrer-equation

$$D_{311} = \frac{2\pi I(q_{\max})}{\int I(q) dq},$$

where $I(q_{\max})$ is the scattering intensity at the peak maximum and the denominator is the integral peak width of the (311) reflection.

2.6. XANES measurement

X-ray absorption near-edge structure measurements were carried out at the BAMline beamline at BESSY II Berlin, Germany. The dried precipitates were measured in fluorescence mode with standard 45° geometry [15] at the K -edge of iron ($E_o = 7112 \text{ eV}$). The incident beam intensity was monitored using a 50 mm ionization chamber filled with air at ambient pressure. The energy was scanned using a Si(111) double crystal monochromator with a relative energy resolution of 2×10^{-4} . The XANES scans were carried out in the range from 7032 eV (80 eV below the edge) to 7182 eV (70 eV above the edge) with a step of 1 eV. The fluorescence signal of the characteristic radiation of iron was recorded using a silicon drift detector. The obtained XANES spectra underwent the standard data treatment procedure using Iffeffit 1.2.11c [16].

3. Results and discussion

3.1. SAXS Results

SAXS scattering curves of iron oxide nanoparticles were measured online at different times after mixing of the reagent solutions in the micromixer (see Fig. 1). Nanoparticles could be characterized with sizes in the range of $\pi/q_{\max} = 1 \text{ nm}$ to $\pi/q_{\min} = 45 \text{ nm}$. The figures in the top row of Fig. 2 display curves collected during particles formation at $30 \text{ }^\circ\text{C}$; the bottom row are corresponding curves of particle formed at $80 \text{ }^\circ\text{C}$. We found that the scattering intensities display a characteristic Power law decay of $q^{-1.87}$, $q^{-1.67}$ and $q^{-1.87}$ for reaction times of 84 s, 162 s and 326 s in the q -range between 0.07 nm^{-1} and 0.9 nm^{-1} (Fig. 2 a–c). We assume that these characteristic slopes result from mass fractal structures produced by aggregation of small primary particles.

The scattering intensity in the Porod region scales with $q^{-3.76}$, which is observed for reaction times of 84 s and 162 s at q -values larger than 0.9 nm^{-1} . This scaling is indicative for a rough surface of the primary particles since a q^{-4} -scaling must be expected for particles with a smooth surface. The radius of the primary particles was $(1.1 \pm 0.1) \text{ nm}$ for a reaction time up to 162 s after

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