



One-step synthesis and functionalization of hydroxyl-decorated magnetite nanoparticles

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Abstract

Magnetite nanoparticles covered by a layer of ω -hydroxycarboxylic acid were synthesized in one step by high-temperature decomposition of iron(III) ω -hydroxycarboxylates in tri- and tetra-ethylene glycol. The nanoparticles were characterized by TEM, XRD, IR, XPS and NMR techniques in order to show that they comprise a crystalline magnetite core and actually bear on the outer surface terminal hydroxy groups. The latter ones are convenient “handles” for further functionalization as opposed to the chemically-inert aliphatic chains which cover conventionally synthesized nanoparticles. This was shown by several examples in which the hydroxy groups on the nanoparticle surface were easily transformed in other functional groups or reacted with other molecules. For instance, the hydroxyl-decorated nanoparticles were made water soluble by esterification with a PEGylated acetic acid. The reactive behavior of the surfactant monolayer was monitored by degrading the nanoparticles with aqueous acid and isolating the surfactant for NMR characterization. In general, the reactivity of the terminal hydroxyl groups on the nanoparticle surface parallels that observed in the free surfactants. The reported hydroxyl-decorated magnetite nanoparticles can be thus considered as pro-functional nanoparticles, i.e., a convenient starting material to functionalized magnetic nanoparticles.

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1. Introduction

Magnetic nanoparticles (NPs) are useful in several fields, particularly in the biomedical field [1–4], where they find application in the separation of bacteria and bio-molecules [5] and in diagnostics and therapeutics [6–8]. Most interest in the use of magnetic nanoparticles in the bio-medical field has focused on the magnetic iron oxides Fe_3O_4 (magnetite) and $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) because of their chemical stability and biological compatibility. Methods have been developed to synthesize both magnetite [9–12] and maghemite [13] nanoparticles with high crystallinity and narrow diameter distribution by thermal de-

composition of an iron precursor in presence of a long-chain alkyl surfactant. However, as-synthesized iron oxide NPs are not directly suited to most applications since the magnetic core is covered with a chemically-inert shell comprising hydrophobic long-chain alkyl surfactants [14]. On one hand, it is far from easy to covalently attach a bio-active moiety to the alkyl tails that constitutes the NP surface because of the low reactivity and poor selectivity typical of aliphatic chains. It should be however noted that the most wide-spread surfactant for iron oxide NPs, i.e. oleic acid, bears a double bond that can be exploited to change the surface properties of the NPs. Indeed, Lee and Harris obtained magnetic NPs soluble in water and alcohol by ozonolysis of oleic-acid capped magnetic NPs [15]. On the other end, the one-step synthesis of magnetic NPs bearing (bio)chemical functionality appears difficult because of the

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high temperature ($>200\text{ }^{\circ}\text{C}$) needed for solvothermal synthesis. So, to introduce a (bio)chemical functionality at the surface of magnetic NPs, one usually has to resort to ligand exchange procedures [5] that are often time- and reagent-consuming and difficult to control.

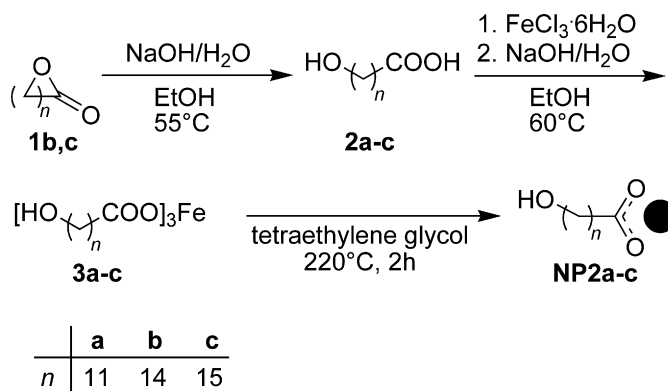
Therefore, we focused on the surfactant protective layer rather than on the magnetic nanocrystal and aimed to introduce a convenient chemical “handle” on the NP surface. We managed to synthesize hydroxyl-decorated magnetite NPs in one step by high-temperature decomposition of iron(III) ω -hydroxycarboxylates. These NPs bear on their outer surface terminal hydroxy groups that can be easily transformed into a variety of chemical groups and bound to other molecules, as is herein illustrated by a few examples. For instance, the NPs were endowed with water solubility by reaction with an appropriate PEGylated molecule. Therefore, these hydroxyl-decorated magnetic NPs can be considered as *pro-functional* NPs, i.e., a convenient starting material to prepare truly functional magnetic NPs. The use of these *pro-functional* NPs will afford shorter preparative procedures without hampering synthetic flexibility.

In designing the synthesis of iron oxide NPs covered by a layer of ω -substituted carboxylic acid, one has to consider (i) the synthetic utility of the terminal group and (ii) the undesired reactions that such group might undergo during the synthesis. Cost and toxicity of reactants and solvent and synthetic scalability should also be considered. We conceived that the thermal decomposition of iron(III) ω -hydroxycarboxylates could satisfy most of these requirements. The thermal decomposition of metal oleates has already been shown to be an effective method to synthesize metal oxide NPs [10–12,16,17] and to be scalable up to decagram level [10]. The hydroxyl group is stable at high temperature in the presence of iron and offers synthetic flexibility for subsequent functionalization. Of course, polymerization of the hydroxyacid easily occurs in the anhydrous high-temperature conditions typical of NP synthesis. It can be avoided by (i) blocking the carboxylic group as iron carboxylate before decomposition and (ii) scavenging the ω -hydroxyacid freed by the decomposition of the carboxylate precursor by using an oligoethylene glycol as solvent. Reactants and solvent are cheap and have low toxicity [18–20].

Another crucial issue in the synthesis and functionalization of NPs is the accurate determination of the actual surfactant bound to the inorganic core. We believe that spectroscopic techniques applied to the NPs as such [21] could be not always sufficient to ascertain the identity of the surfactant. Therefore, after synthesis and after each functionalization stage the NPs were degraded and the surfactant bound to the NPs was spectroscopically identified by comparison with a sample of independently synthesized surfactant.

2. Experimental

The 15-hydroxypentadecanoic **2b** and 16-hydroxyhexadecanoic **2c** acids were obtained by alkaline hydrolysis of the corresponding lactones **1b**, **1c** (Scheme 1) [22], whereas 12-hydroxydodecanoic acid **2a** is commercially available. Iron(III) ω -hydroxycarboxylates **3** were synthesized from $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$



Scheme 1. Synthesis of hydroxyl-decorated magnetite nanoparticles. The black circle symbolizes the magnetite nanoparticle covered by a monolayer of the juxtaposed molecule. Note that **2a** is commercially available, therefore it is not present in the first step of this scheme.

and $\text{HO}-(\text{CH}_2)_n-\text{COOH}$ (**3a**: $n = 11$, **3b**: 14, **3c**: 15) by a modified literature prescription [10,11], which consisted in dissolving the corresponding hydroxyacid **2** (9.19 mmol) and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (3.21 mmol) in ethanol (15 ml). Then, a solution of NaOH (9.19 mmol) in water (15 ml) was slowly added dropwise under magnetic stirring, further 20 ml of water were added and the reaction mixture was heated at $60\text{ }^{\circ}\text{C}$ for 3 h. The product precipitated as a salmon-pink solid, which was filtered and washed several times with water and acetone. Iron(III) ω -hydroxycarboxylates **3** were characterized by IR and NMR spectroscopy (see the supplementary material).

In a typical synthesis of hydroxyl-decorated magnetite NPs, a suspension of iron ω -hydroxycarboxylate salt **3** (1.00 mmol) in tetraethylene glycol (17 ml) was heated under argon to $220\text{ }^{\circ}\text{C}$ with a constant heating rate of $3.3\text{ }^{\circ}\text{C min}^{-1}$. After aging at $220\text{ }^{\circ}\text{C}$ for 2 h, the reaction crude was cooled to room temperature. The NPs were precipitated from the crude by adding toluene or acetone, separated by centrifugation, washed twice with acetone/toluene 1:1 v/v and were finally re-dispersed in ethanol.

The magnetite NPs were characterized by TEM, IR, XRD. TEM images were obtained by a Zeiss EFTEM LEO 912AB (120 kV) microscope. IR spectra were recorded with a BioRad FTS-40 spectrometer. XRD spectra have been collected using $\text{CuK}\alpha$ radiation on a Philips PW 1820 with scintillation counter or on a Bruker D8, Lynx-Eye multichannel energy discriminating solid state detector; Rietveld analysis was performed using the TOPAS package. XPS measurements were performed by an M-Probe Instrument (SSI) equipped with a monochromatic $\text{AlK}\alpha$ source (1486.6 eV).

To identify the surfactant actually bound to the NPs, the latter were degraded with 4 M aqueous H_2SO_4 (4 ml) and the freed surfactant was extracted with diethyl ether ($3 \times 10\text{ ml}$). The organic phase was washed with water and brine, dried over sodium sulfate, and the solvent evaporated under reduced pressure. The ^1H NMR spectra (CDCl_3 or $\text{DMSO}-d_6$) of both reference samples and compounds obtained from NP degradation were recorded with a Bruker Avance 400 MHz spectrometer.

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