

Functionalization of magnetic nanocrystals by oligo (ethylene oxide) chains carrying diazonium and iniferter end groups

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ABSTRACT

The water stability of iron oxide nanoparticles (NPs) is a major issue for biomedical and biological applications. This paper presents a versatile approach for preparing water-soluble iron oxide nanoparticles coated by bifunctional oligo(ethylene oxide) (OEO) chains, carrying on the one side a diazonium end group for covalent grafting at the NP surface and on the other side an iniferter group (diethyl dithiocarbamate) for initiating the growing of poly(methacrylic acid). The nanoparticles were synthesized by coprecipitation in basic media and functionalized *in situ* by adding the diazonium salt directly in the synthesis medium. Oligo(ethylene oxide) with various chain lengths (from one to three monomer units) was grafted at the NP surface using this approach. The length of the OEO spacer between the NP surface and the iniferter end group was found to be a critical parameter for controlling the colloidal stability of the hybrid NPs. The polymerization time was also shown to strongly influence their colloidal stability, emphasizing the interest to control the interfacial properties of the hybrids for obtaining stable dispersions in water.

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1. Introduction

Iron oxide nanoparticles have been extensively used for various applications in biotechnology [1–4] such as ferrofluids [5], hyperthermia [6,7], magnetic resonance imaging (MRI) [8,9], and releasing of therapeutic agents [10–13], due to their high biocompatibility, their non-toxicity, and their unique superparamagnetic behavior. For a wide range of applications such as the design of stable fluids, gels, contrast agents or drug delivery, the size, charge, and surface chemistry of the magnetic particles are particularly important [14–16].

However, the synthesis of ultra-small superparamagnetic iron oxide (USPIO) particles with controlled size, shape, and colloidal stability in various solvents is a hard task. Indeed, it is well known that NPs have a large surface-to-volume ratio and tend to aggregate so as to minimize their surface energies. In order to prevent the particles from aggregation, the use of surfactants, polymers, biomolecules, or inorganic layers (such as silica, metal or non-metal elementary substances) is often required. Other methods to engineer stable nanoparticles rely on the use of functional groups

such as phosphonate [17], catechol [18], dopamine [19], or carboxylic groups [20] to modify the nanoparticle surface.

Although these anchoring groups are strongly effective in several non-aqueous environments, they often fail on metal oxide surfaces in aqueous or protic media because of the hydrolytic instability of the surface attachment and/or the dynamic nature of the interaction. Therefore, developing efficient and reproducible functionalization strategies for obtaining strong and stable linkages between the iron oxide nanoparticle surface and the organic coating still remains challenging. Diazonium salt chemistry has been successfully applied to the modification of carbon-based [21–25] and metallic planar or nanoparticle surfaces [26–29], affording strong carbon or metal–carbon linkages. The covalent bonds that are formed by reduction of diazonium compounds to the corresponding radical are stronger than those obtained by self-assembly methods. Therefore, the diazonium salt chemistry has been employed for the modification of a wide range of electrode surfaces and more recently for the functionalization of a large variety of nanoparticles [30].

Concerning oxide particles, the grafting of aryl groups derived from diazonium salts was successfully performed by taking advantage of the transformation of the diazonium species to diazoates in basic media [31]. This original strategy afforded a monolayer of functional aryl groups covalently grafted to iron oxide NPs and was expanded to graft polymerization initiators for the growth of polymers [32–34] from the NP surface. It was also used for fluores-

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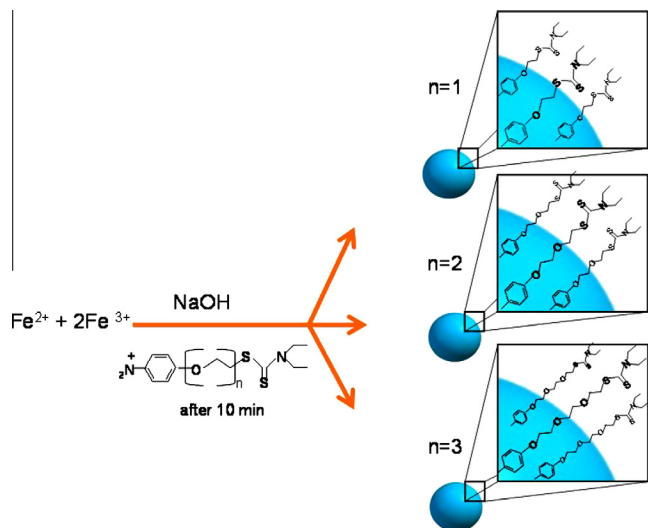


Fig. 1. General method for the synthesis and *in situ* functionalization of iron oxide NPs by bifunctional oligo(ethylene oxide) chains of various lengths, terminated by a diazonium moiety and an iniferter end group. The diazonium salt was introduced *in situ* in the synthesis medium of the NPs, after 10 min of reaction.

cence labeling [35] or for the dense covalent attachment of magnetic iron oxide nanoparticles onto larger silica particles [36].

In the present study, we focus on optimizing the colloidal stability of polymer-coated USPIO NPs in water by introducing oligo(ethylene oxide) spacers of various sizes between the aryl anchoring moiety and the polymerization initiator. The effect of the oligo(ethylene oxide) chain length on the nanoparticle size and colloidal stability was first studied. Then, iniferter photo-polymerization of methacrylic acid was achieved leading to hybrid nanomaterials composed of a magnetic core and a pH sensitive polymer shell. Corresponding reaction pathway to fabricate the water-soluble iron oxide nanoparticles is depicted in Fig. 1.

2. Experimental

2.1. Materials

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH (Aldrich) were used for the synthesis of iron oxide (magnetite) nanoparticles. Diethyldithiocarbamate (DEDTC), ethylene glycol, diethylene glycol, triethylene

glycol, 4-Nitrophenol, triethylamine methylsulfonyl chloride, sodium nitrite (NaNO_2), hydrochloric acid (HCl), and potassium carbonate (Aldrich) were used for the synthesis of the diazonium salts. All the solvents and methacrylic acid were obtained from Acros and used as received.

2.2. Characterization

FT-IR spectra were obtained by transmission on an Equinox 55 spectrometer on pressed KBr pellets in the range $400\text{--}4000\text{ cm}^{-1}$ with a 4 cm^{-1} resolution. Electron microscopy and diffraction studies were conducted on a JEOL-100 CX II microscope. Samples for TEM were prepared by drying one droplet of 0.5 vol.% of particles onto a carbon-coated (300 mesh) grid. Powder X-ray diffraction data were collected on a Siemens D5000 Kevex diffractometer (30 min) using Cu K α radiation ($\lambda = 1.5405\text{ \AA}$). Differential thermal and thermogravimetric analyses were carried out on a Setaram TG 92-12 thermal analyzer in the temperature range $20\text{--}800\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a flow of air at 80 ml/min in an alumina crucible.

2.3. Preparation of the materials. Synthesis of the diazonium salts

The synthetic strategy followed was similar for the three salts and is described in details in supporting information. A summary of the procedure is proposed in the form of a scheme in Fig. 2. Briefly, diazonium salts were synthesized by the diazotization of aniline derivatives. These salts were prepared by suspending aniline derivatives in a 50/50 by volume hydrochloric acid and distilled water. The mixture was cooled to $3\text{ }^\circ\text{C}$ in an ice bath, and then, 1 equivalent of sodium nitrite was slowly added. The mixture was stirred for 15 min.

2.4. Fe_2O_3 nanoparticle preparation and functionalization

USPIO nanoparticles were prepared by co-precipitating ferrous and ferric ions in aqueous solution. Briefly, 24 mmol of FeCl_3 and 12 mmol of FeSO_4 were dissolved in 50 mL of distilled water. The solution was purged with nitrogen, and the inert atmosphere was maintained for the duration of the synthesis. Then, 25 mL of water containing NaOH ($c = 1\text{ M}$) was rapidly added under vigorous stirring. The color of the solution changed immediately from yellow to brown, indicating the formation of Fe_2O_3 nanoparticles.

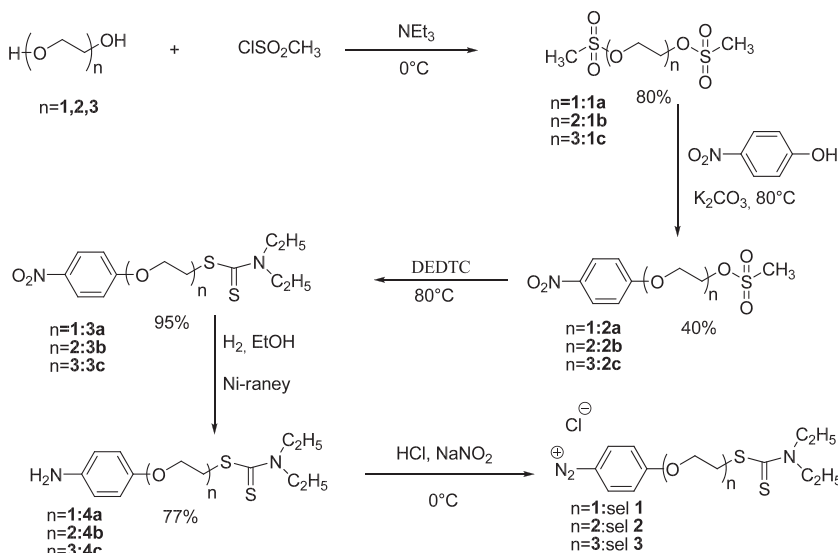


Fig. 2. Strategy used for the synthesis of diazonium salts carrying on one side a DEDTC function and on the other side an oligo(ethylene oxide) chain.

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