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Review

Magnetic nanocrystals for biomedical applications

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1. Introduction

Nanocrystals are a special class of nanoparticles with improved crystallinity. Often besides the desired properties of nanoparticles related with quantum effects and high specific surface, other important properties suffer a very important damage. This is the case of the magnetic properties. Magnetic nanocrystals (>10 nm) combine the nanometric dimension and therefore the superparamagnetic behavior with magnetic properties such as saturation magnetization close to the bulk value. In this review we will describe the preparation of magnetic nanocrystals and their performance in selected biomedical applications that are expected to be strongly dependent on the nanoparticle magnetic response.

2. Preparation of magnetic nanocrystals

High-quality magnetite nanocrystals up to 20 nm can be obtained by thermal decomposition of organic iron precursors in the presence of a surfactant [1–3]. These materials need a complex

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processing process for changing the organic solvent used for the synthesis to water without much damage of the colloid. An alternative aqueous route described by Sugimoto [4] that can enable the growth of magnetic iron oxide nanocrystals up to 100 nm but has attained less attention in spite of their advantageous use of water as solvent and no surfactants. Most of the Fe_3O_4 nanocrystals used in this work were synthesized by an adaptation of the Sugimoto's process that we call oxidative precipitation [5]. Briefly, the $Fe(OH)_2 \cdot Fe(OH)_3$ (green rust) obtained by alkalinizing an iron (II) sulfate ($FeSO_4$) solution in presence of sodium nitrate was aged at 90 °C for 24 h giving time to the green rust to dissolve in favor of magnetite nucleus growth [6]. The experiment was carried out in a system consisting of a three-necked round bottom flask placed in an oil bath with mechanical stirring. Before salt precipitation, nitrogen was flowed during 2 h in two different solutions, one was 20 ml of 0.01 M H_2SO_4 were the appropriate amount of $FeSO_4 \cdot 7H_2O$ was dissolved and the other was 180 ml of water were the appropriate amount of sodium hydroxide and sodium nitrate were dissolved. The acid $FeSO_4$ solution was quickly added to the basic mild oxidant solution under stirring in the presence of nitrogen and the system was heated to 90 °C. After 10 min the nitrogen was interrupted and also the agitation. The system was left undisturbed during 24 h permitting the growing of monodispersed nanocrystals. At the end of the process the system was cooled down and the magnetic nanocrystals were separated by magnetic decantation followed by five washings with distilled water.

X-ray diffractograms and transmission electron microscopy show that magnetite was the only phase obtained. The particle size obtained depends neatly on the excess of NaOH (computed by subtraction from the nominal NaOH concentration after mixing the OH^- consumption by the formation of $Fe(OH)_2$ and the neutralization of H_2SO_4). The sodium nitrate concentration (in excess) varies among 0.1 M–0.2 M depending on the iron concentration. Particle sizes obtained ranged between 180 and 22 nm being the smallest at an excess of 0.02 M NaOH. The iron sulfate concentration in the range 0.02–0.2 M has a secondary influence on particle size at a constant NaOH excess, being favorable for smaller sizes with larger iron concentrations. In a typical experiment the nominal concentrations after mixing were $[FeSO_4] = 0.1$ M, $[NaOH] = 0.21$ M and $[KNO_3] = 0.1$ M, the solvent employed was alternatively water and ethanol/water 50% vol. The reaction yielded for a 200 mL of total volume, 3 g of magnetite nanocrystals of 76 and 45 nm respectively (Fig. 1).

The method can be adapted to the production of magnetic core–shell nanocrystals by substituting part of the iron by bismuth. Bismuth oxide concentrates in the outermost shell in amounts up to 20% (at) with a reduction of the particle size down to 8 nm [7].

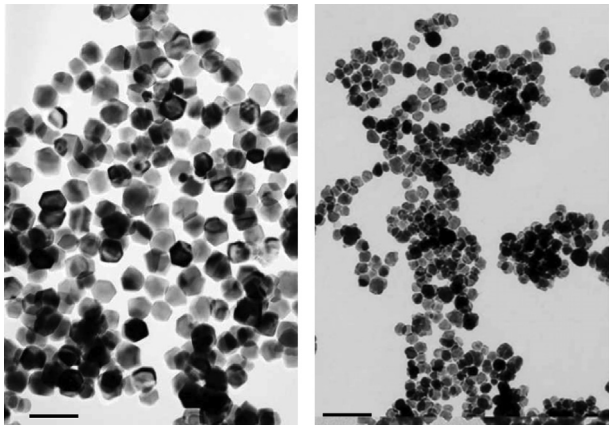

Fig. 1. Nanocrystals of Fe_3O_4 obtained by oxidative precipitation in water (left) and ethanol 50% vol. (right) under the conditions described in the text. The scale bar represents 200 nm.