

Oxidation of ferrous hydroxides with nitrate: A versatile method for the preparation of magnetic colloidal particles

F. Vereda*, J. de Vicente, R. Hidalgo-Alvarez

Grupo de Física de Fluidos y Biocoloides, Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada, Granada E-18071, Spain

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ABSTRACT

Slightly over 30 years ago, Sugimoto and Matijević published an article in this journal on the synthesis of uniform magnetite particles by the partial oxidation of ferrous hydroxide gels. The article has become a widely-used reference for the preparation of magnetite particles in aqueous media. A reason for this was the thoroughness of their study and the versatility of the process: the authors described conditions under which cubic nanometric (30–100 nm) crystals, or larger (0.4–1.1 μm) spherical particles, the latter having either a smooth or a rough surface, could be obtained. Further work by Matijević and other authors has shown that small modifications of the process, such as the addition of divalent cations other than Fe²⁺ to the system or the superposition of a magnetic field, can be used for the preparation of ferrite particles or rod-like particles, respectively. In this article we present a short description of the synthesis process and a brief overview of subsequent work carried out by other researchers that illustrates the versatility and the potential of this method.

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1. Introduction

In recent years, magnetic iron oxide particles have received a great deal of attention for the development of biomedical applications, such as immunoassays, targeted drug delivery, contrast agents for magnetic resonance imaging and magnetic hyperthermia. Among the iron oxides, magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) are the ones that exhibit the strongest magnetism. Both are ferrimagnetic, with room temperature saturation magnetizations of 92 emu/g for magnetite, and ca. 70 emu/g for maghemite [1]. The interest of magnetic particles for these applications arises from the fact that external magnetic fields can be used for their manipulation. Field gradients can be used for dragging the samples in a given direction or for localizing them in a region of interest, which for instance would allow the localized release of drugs. Alternating fields can be used to heat the particles, which can then act as localized heat sources and induce irreversible damage to tumor cells (magnetic hyperthermia), or can trigger the release of drugs if they are covered in a thermosensitive polymer, for example. Magnetic iron oxides are especially suited for these applications because they exhibit a low toxicity and large stability against oxidation (especially in the case of γ-Fe₂O₃) when compared to more highly magnetic materials like Fe, Co or Ni.

There are other factors that are important for biomedical applications: in general, particles should be stable in neutral pH and at

physiological salinity; they should be suitable to be functionalized and/or coated with biocompatible polymers that avoid degradation in the biological system and provide stability; furthermore, narrow size distributions and sizes below 100 nm are desirable to improve tissular diffusion, minimize sedimentation and reduce the dipolar interaction between particles [2].

Specific applications, whether they are biomedical or not, require magnetic particles with specific attributes. For the preparation of magnetorheological (MR) fluids, for instance, particles with a typical size of 1 μm are needed since in this case the magnitude of the magnetostatic interactions between the particles must be much larger than their thermal energy [3]. For magnetic hyperthermia particles in the vicinity of the single-domain/multi-domain critical size are desirable. For this reason, many synthesis routes [2,4–6] have been explored for the fabrication of particles that will ensure an adequate performance: proper size and size distribution, morphology, crystallinity and magnetic properties.

Liquid phase methods are normally inexpensive and offer better yields. For biomedical applications, the synthesis of magnetite in aqueous solutions has an additional advantage, since particles grown in organic media need further surface modification to make them hydrophilic. There are two main methods for the preparation of magnetite in aqueous media. One entails the co-precipitation of stoichiometric mixtures of ferric and ferrous hydroxides and their reaction in alkali media [7]. Particles between 2 and 17 nm are obtained with this method [6]. The second method [8] relies on the precipitation of a ferrous hydroxide and on its partial oxidation with a mild oxidant, such as nitrate. This is the procedure that

* Corresponding author. Fax: +34 958243214.

E-mail address: fvereda@ugr.es (F. Vereda).

Sugimoto and Matijević studied. It can be used for the fabrication of magnetite particles of two very different typical sizes: nanometric particles with sizes between 30 nm and 100 nm, and micrometric particles with a typical size around 1 μm . Because of its versatility and because of the current interest in magnetic iron oxide particles, this synthesis protocol is the subject of this article.

From a historical point of view, in the 1920s, Baudisch and Welo [9] set the basis for the fabrication of magnetite by partial oxidation of Fe^{2+} with nitrate. In 1956 David and Welch [10] reported a widely used procedure [11–14] that also relies on the reaction of nitrate with Fe^{2+} ions.

In 1980, following a series of reports by Matijević on the preparation of monodispersed metal oxide particles [15–17], Sugimoto and Matijević [8] published an article that has been a reference for the synthesis of magnetite in aqueous media for over three decades. By the partial oxidation of ferrous hydroxide with nitrate in sulfate media at 90 °C, the authors obtained uniform spherical magnetite particles with different sizes. Furthermore, they thoroughly studied the effects of several parameters on particle size and morphology, and provided a well founded model that explained their observations in terms of different mechanisms of growth. According to the authors, the different mechanisms were determined by the pH of the system in relation with the isoelectric point of magnetite.

It should be mentioned that around that time other authors were also working on the partial oxidation of ferrous hydroxide as a method for the preparation of magnetite (or, more generally, spinel ferrites). In 1981, for instance, Regazzoni et al. [18] studied six routes for the synthesis of magnetite. Three of those routes involved the formation of a $\text{Fe}(\text{OH})_2$ and its subsequent partial oxidation. Domingo and coworkers [19,20] also studied this system. These authors used FeCl_2 as the source of ferrous ion, and reported different sizes and morphologies (hexagonal platelets, octahedral and isometric crystal) depending on the $[\text{Fe}^{2+}]/[\text{OH}^-]$ ratio. More recently, Li et al. [21] published an extensive study on the preparation of magnetic iron oxide particles using the $\text{FeCl}_2\text{--NaNO}_3\text{--NaOH}$ system.

Our group has been using this process (the partial oxidation of ferrous hydroxide with nitrate) for the last few years, mainly for the synthesis of micrometric magnetic particles that could then be used in the preparation of magnetorheological (MR) fluids. In this article we present an account of the method described by Sugimoto and Matijević, and include a brief summary of the main results obtained later by other researchers that followed or introduced small modifications to that method. With this summary we hope to illustrate the versatility of the process. By adjusting the ionic composition of the reactant mixture, this process allows for the fabrication of magnetite nanoparticles, microparticles with either smooth or rough surfaces, or the incorporation of other divalent metallic cations, such as Ni^{2+} , Co^{2+} or Zn^{2+} to form ferrites. Furthermore, if the particle growth takes place at a pH close to the isoelectric point (IEP) of magnetite, which occurs when there is an excess of Fe^{2+} in the system, the growing particles can be assembled into permanent micron-sized linear aggregates by the superposition of a uniaxial external magnetic field. Other schemes introduced to control particle size will also be presented. The current interest in the process described by Sugimoto and Matijević is another reason to discuss it in this article. See in Fig. 1 the increase since 2005 in citations received by their article, probably due to the numerous potential applications of magnetite nanoparticles in the growing field of biotechnology.

2. Synthesis process

The process is an example of a phase transformation. It consists, basically, of the formation of a ferrous hydroxide precipitate and of

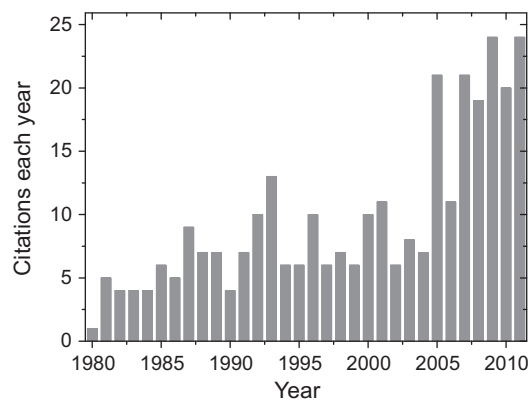


Fig. 1. Number of citations received each year by Sugimoto and Matijević's article [8]. (Source: Web of Science®)

its subsequent partial oxidation (aging) with a mild oxidant (NO_3^-) at 90 °C. In practice, two oxygen-free solutions are prepared: one containing NO_3^- and the base (such as KOH , NaOH or NH_3) and another one containing an Fe^{2+} salt. The green ferrous hydroxide precursor forms upon the mixing of the two solutions, and the system is then sealed and left undisturbed at 90 °C for several hours. During this time, the ferrous hydroxide is transformed into magnetite by means of a dissolution–oxidation–precipitation mechanism.

In their study [8], Sugimoto and Matijević used KOH as the base, KNO_3 to introduce the nitrate ion in the solution and, after testing several Fe^{2+} salts, reported that the best results were obtained with FeSO_4 . They stressed the importance of the sulfate anion, which is known to complex strongly with the ferric ion, in the growth process. Because the system is very sensitive to the presence of oxidants other than nitrate, dissolved oxygen was removed by bubbling nitrogen through the water used for the preparation of the solutions, through the solutions once they were prepared, and through the mixture of the two solutions until 5 min after the beginning of the aging. In other cases, the Fe^{2+} solution was prepared in acidic media [22–24]. This provides further stability against premature oxidation of this ion, and it is our experience that it helps with the reproducibility of the synthesis process. Regarding reproducibility, the use of a relatively new $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ salt is also important. We have observed that solutions prepared with freshly purchased $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were always clear, whereas after some storage time the salts may yield cloudy solutions. The cloudiness is the result of suspended particulates. Some authors filtered the Fe^{2+} solutions to remove these particulates [24].

3. Control of pH: preparation of nano- and micrometric particles with rough or smooth surfaces

Sugimoto and Matijević showed that the size and morphology of the resulting particles was strongly dependant on the initial pH of the reactant mixture, which was in turn determined by the relative concentrations of Fe^{2+} and OH^- ions. As these two ions combined in a 1–2 ratio to form the $\text{Fe}(\text{OH})_2$ precursor, an excess of Fe^{2+} can be achieved if the $[\text{FeSO}_4]$ is larger than $[\text{KOH}]/2$.

The excess of $[\text{Fe}^{2+}]$ is given by:

$$[\text{Fe}^{2+}]_{\text{Exc}} = [\text{FeSO}_4] - [\text{KOH}]/2$$

Similarly, the excess of $[\text{OH}^-]$ is:

$$[\text{OH}^-]_{\text{Exc}} = [\text{KOH}] - 2[\text{FeSO}_4]$$

Sugimoto and Matijević prepared particles in excesses of Fe^{2+} up to 0.3 M, and excesses of OH^- up to 0.2 M. An excess of Fe^{2+} resulted in the formation of relatively large spherical particles,

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