

One method fits many types: The oxidative precipitation of magnetic iron oxide nanoparticles from ferrous citrate

Tim Granath¹, and Karl Mandel¹

¹ Chair of Chemical Technology of Materials Synthesis, Julius-Maximilians-University Würzburg, Würzburg, Germany

The oxidative precipitation is a well described method yielding ferromagnetic iron oxide nanoparticles from iron(II) salts such as ferrous sulfate or ferrous chloride [1]. Nevertheless, the surface modification of these nanoparticles is a challenge. Due to their attractive magnetic forces they tend to form agglomerates more easily than nanoparticles in general and are therefore more difficult to modify in the form of individual particles when no sufficient repulsion is given. Such repulsion can, for example, be effected through electrostatic repulsion by a small ionic molecule such as citrate. On the one hand, this molecule adsorbs strongly on the surface and, on the other hand, it prevents particle agglomeration due to the remaining charge. Typically, this type of stabilization is a downstream process and therefore only conditionally suitable for subsequently dissolving the agglomeration that already occurs during particle synthesis. To solve this problem, the method of oxidative precipitation was adapted with the intention to obtain citrate-modified ferromagnetic iron oxide nanoparticles directly. For this purpose, ferrous citrate was used instead of ferrous sulfate. In addition, a high OH⁻ concentration was required to overcome the inhibiting effect of citrate on particle formation [2]. While under these conditions the use of ferrous sulfate yields the expected octahedral iron oxide nanoparticles with a relatively wide size distribution (Fig. 1a), ferrous citrate causes the formation of spherical nanoparticles. These particles are significantly larger, have a narrower size distribution and show bulk-like magnetic properties (Fig. 1b). A reduced OH⁻ concentration reveals a region in which several reaction pathways are likely to compete with each other yielding multiple iron oxide and hydroxide species (Fig. 1c). Further reduction of the OH⁻ concentration finally produces spherical nanoparticle clusters with reduced ferromagnetic properties (Fig. 1d). Remarkably, the use of O₂ instead of NO₃⁻ as oxidant leads to the direct formation of citrate-modified superparamagnetic iron oxide nanoparticles (Fig. 1e).

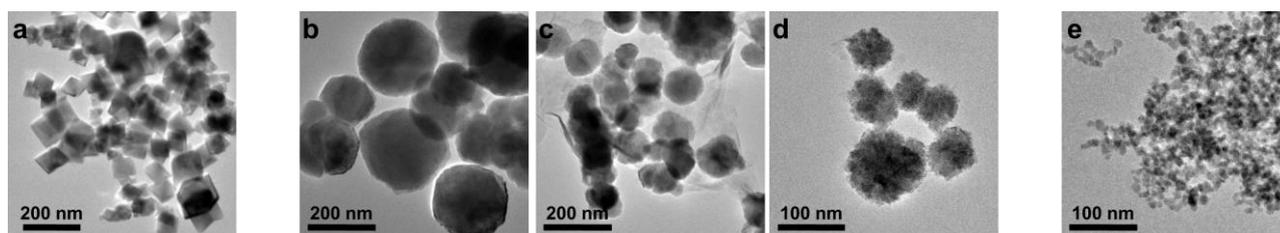


Figure 1. TEM images of iron oxide nanoparticle products obtained from ferrous sulfate (a) and ferrous citrate (b-e) by the method of oxidative precipitation under basic conditions. Images (b-d) show the products obtained at high (b), medium (c) and relatively low (d) OH⁻ concentrations. Image (e) shows the superparamagnetic product when O₂ is used as oxidizing agent instead of NO₃⁻.

[1] T Sugimoto, E Matijević, *J. Colloid Interface Sci.* **74** (1980), 227.

[2] J Jing et al., *J. Nanopart. Res.* **14** (2012), 827.

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