

# NEW SYNTHETIC APPROACH TO VARIABLE-SIZED MAGNETITE NANOCRYSTALS CAPABLE OF FORMING STABLE COLLOIDAL SOLUTIONS

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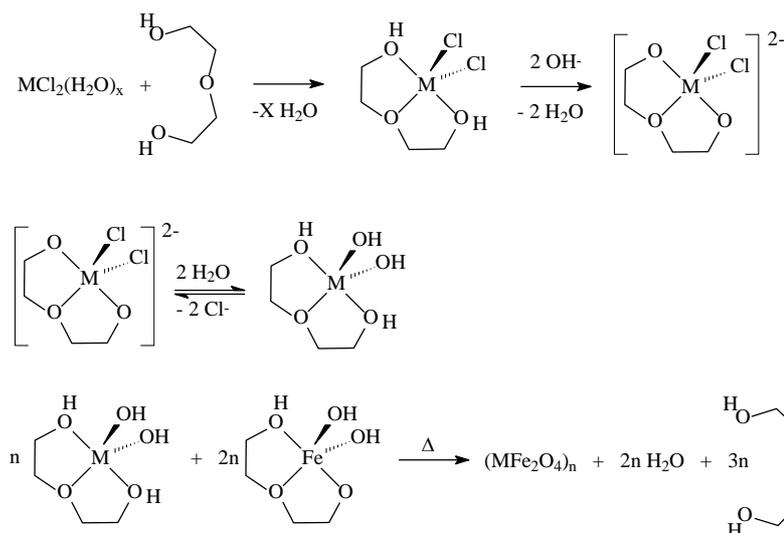
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Nanocrystalline magnetite has recently come under increasing scrutiny, because of its high chemical stability, biocompatibility and original magnetic properties, making it attractive for high performance biological and medical applications. Advanced manipulation of this material requires highly stable colloidal dispersions of monodisperse nanoparticles with a tunable size, regular shape, smooth surface which can be further functionalized with biomolecules via chemical modification of their surfaces. However, despite the progress achieved in designing new synthetic strategies, large scale synthesis of high quality magnetite nanocrystals with a rigorous control of the crystal growth during the chemical process is still a challenge in nanotechnology [1-3]. We report here on a new chemical approach to prepare nanocrystalline Fe<sub>3</sub>O<sub>4</sub> particles capable of forming highly stable colloidal dispersions. The obtained nanocrystals possess chemically active surface that is available for further derivatization which enables them to be used as building blocks for biomedical applications. Additionally, this method provides high product yield and is easily scalable.

The new synthetic route is based on hydrolysis of chelated alkoxide complexes of Fe<sup>2+</sup> and Fe<sup>3+</sup> at elevated temperatures in solutions of the highly polar non-aqueous solvent diethylene glycol (Scheme 1) [4].

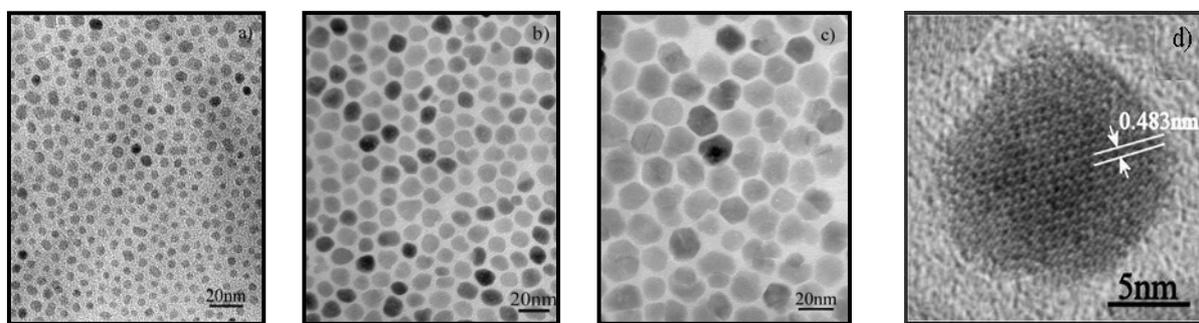


**Scheme 1.** Formation of chelated metal alkoxide complexes and their decomposition yielding colloidal transition metal ferrites

Changing the temperature and the concentration of reactants, allowed us control over the rate of reaction and crystallization. The size of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles was controlled by changing the

complexing strength of the reaction medium. This was accomplished by adding a second solvent, N-methyl diethanol amine, with relatively similar values for dielectric constant and boiling point as compared with diethylene glycol., but different donor properties. The result was a better control over the rate of hydrolysis of metal chelates, a better stability of the colloidal solutions, and therefore larger nanocrystals than those obtained from diethylene glycol solutions[5].

The obtained Fe<sub>3</sub>O<sub>4</sub> nanocrystals were highly soluble in polar protic solvents (water, methanol). Their chemically active surfaces allowed us perform post-synthesis reactions with different capping agents, such as long-chain carboxylic acids, yielding hydrocarbon-soluble nanocrystalline products. The crystal structure and morphology of the obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles were investigated by X-ray diffractometry (XRD) and transmission electron microscopy (TEM, HRTEM, SAED). The X-ray diffraction patterns of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with various sizes were found to match well with that of cubic crystalline bulk magnetite (JCPDS file No.19-629) with no other secondary iron oxide phases. The crystallite size estimated from the six most intense peaks of each diffraction pattern appeared in good agreement with size determined from TEM measurements (Figs.1a, b, and c). This is an indication that most of the nanoparticles are single-crystalline. The HRTEM micrograph (Fig.1d) reveals lattice fringes with a fringe separation of 4.83Å, which corresponds to {111} lattice planes. This value agrees well with that of 4.85Å determined from the analysis of the XRD pattern.



**Figure 1.** TEM micrographs Fe<sub>3</sub>O<sub>4</sub> nanocrystals with average sizes of 5.7nm (a), 12.7nm (b), 16.8nm (c); HRTEM image of a typical 12.8nm-sized Fe<sub>3</sub>O<sub>4</sub> nanoparticle(d)

The composition of the nanocrystal surface was determined from nuclear magnetic resonance (NMR) and infrared (IR) measurements. Thermogravimetric analysis (TGA) was also performed.

In conclusion, we were successful in designing a new synthetic strategy enabling preparation of highly stable monodisperse magnetite colloids. The extent to which the experimental conditions influence the size of the synthesized nanoparticles has been established. This experimental concept is currently pursued for the synthesis of other nanostructured transition metal oxides of technological interest.

## References

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