

MANUFACTURING OF SIZE CONTROLLED MAGNETITE NANOPARTICLES POTENTIALLY SUITABLE FOR THE PREPARATION OF AQUEOUS MAGNETIC FLUIDS

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Abstract. The effect of a biocompatible, water-soluble functionalised biopolysaccharide, carboxymethyl-cellulose (CMC) on the particle size and morphology of magnetite nanoparticles ($d \leq 8$ nm) synthesised in aqueous solutions has been systematically studied. Addition of the polysaccharide to the system resulted in significant decrease in the particle diameter (down to *ca.* 2.8 nm). The average particle size is independent of the degree of functionalisation and the molar weight of the polymer, but decreases systematically with the increasing concentration of CMC. Thus tailor made magnetite nanoparticles with $2.8 \text{ nm} \leq d \leq 7.5 \text{ nm}$ is possible to synthesize with addition of controlled amount of CMC to the reaction mixture.

Key words: carboxy-methyl cellulose, magnetite nanoparticles, size control, biocompatible magnetic liquids, aqueous ferrofluids.

INTRODUCTION

The recent development of biocompatible, functionalised ferrofluids and ferromagnetic particles has led to a range of novel biomedical and diagnostic applications [1]. New studies utilizing these nanoparticles and ferrofluids are continually appearing in the scientific literature and there are now several companies, which produce these products both for research and clinical applications.

Recently a special attention has been paid to the size selective synthesis of magnetite nanoparticles [2-4]. Furthermore, magnetite nanoparticles may form stable suspensions in the presence of various organic compounds, such as organic polymers. If the polymeric material is biocompatible, the resulting magnetic liquid is of potential use in a variety of *in vivo* applications [5]. Polymeric materials are also known to significantly decrease the particle size of magnetite when it is synthesised in the presence of them. It is, however, not well understood, which

property of the polymer controls the size and size distribution of the nanoparticles. In the present study, magnetite nanoparticles were synthesised in the presence of a water-soluble polysaccharide, carboxy-methyl cellulose (CMC). The effect of the molar mass, the degree of functionalisation (*i.e.*, the average number of carboxy-methyl groups per glucose unit within the polymer chain, DF) and polymer concentration have been systematically studied to identify the parameters that primarily determine the nanostructure of the magnetite formed.

EXPERIMENTAL

Magnetite nanoparticles were synthesised as described in the literature [5], by coprecipitation of equimolar Fe(III) and Fe(II) in the presence of NH_4OH , in the presence and absence of the polysaccharide. During the synthesis, a mixture of Fe(III) and Fe(II) (0.5 M: 0.5 M) was prepared from a FeCl_3 solution (made of solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and an FeCl_2 solution (made of dissolution of metallic iron in dilute HCl under N_2 stream). An equal volume of the a solution containing 0-10 %(w/w) CMC was then mixed with the iron mixture solution, and kept at constant temperature of 60°C for 15 min. An approximately equal volume of 1 M aqueous ammonia solution was then added to the system dropwise, until the solution reached the pH of 11.5. The mixture was heated for a further 15 min, with vigorous stirring. The suspension was dialysed (cut off 12400 D) against distilled water, until the conductivity dropped to $4.5 \mu\text{S}$ (three time as much as the conductivity of MilliQ water under identical conditions). In the absence of the polymer, an easily sedimenting suspension was obtained, while in the presence of CMC only a small fraction of the magnetite sedimented. The supernatant was then collected for further analysis, a fraction of which was freeze-dried. Powder X-ray diffraction analysis was used for the identification of the phases in the system and was found to be magnetite. The supernatants were characterized by transmission electron microscopy (FEI CM10, operating at 100 kV). Particle size and size distribution was obtained from the histograms of the samples, constructed from the measurement of at least 300 individual particles.

RESULTS AND DISCUSSION

The results of the TEM analyses are shown in Table 1. Reference sample was prepared in duplicate, with using manual stirring in one case (sample no. 2) magnetic stirring in the other (sample no. 3). The data are well comparable with those of ref. 5, and the magnetic stirring appeared to have no effect at all on the structure of the magnetite.

Table 1

The average size ($d \pm \text{STD}$) of magnetite nanoparticles synthesised in the presence and absence of CMC with varying degree of functionalisation (DF), M_w and concentration (^a data from [5])

No.	DF	CMC		d (nm)	STD (nm)
		M_w ($\times 10^3$ D)	c_{CMC} (%w/w)		
0	-	-	0	7.32 ^a	2.28
1	-	-	0	7.46	2.54
2	-	-	0	7.37	2.53
3	0.7	90	5.0	2.86	1.02
4	0.7	90	2.5	4.10	1.09
5	0.7	90	1.25	4.78	2.12
6	0.7	250	1.25	4.66	2.21
7	0.9	250	1.25	6.38	2.82
8	1.2	250	1.25	3.92	1.53

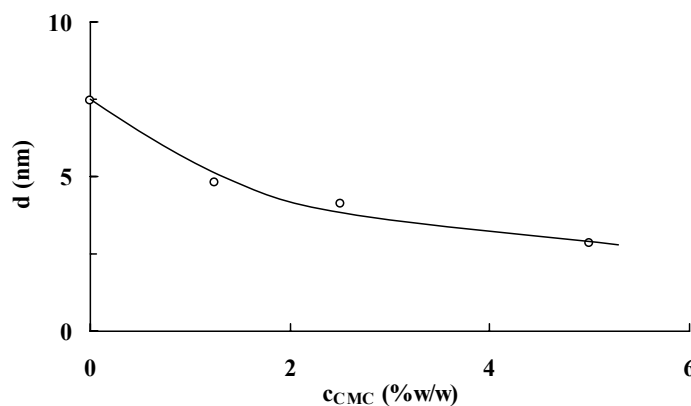


Fig. 1 – Dependence of the average magnetite particle size (d) on the concentration of CMC added to the reaction mixture.

Our results clearly demonstrate, that addition of CMC results in significant decrease in the particle size of the magnetite nanocrystals. The average particle diameter seems to be independent of the M_w of the polymer (compare samples 5 and 6), and the DF is of minor importance too (compare samples 6, 7 and 8). The particle size, however, appear to depend in a systematic way on the concentration of the polymer (see also Fig. 1) and addition of 5% (w/w) causes *ca.* 60% decrease in the particle size (Fig. 2). The polydispersity also decreases with the increasing CMC concentration. In conclusion, addition of known amount of CMC to the reaction mixture is a suitable tool for tailoring the diameter of the magnetite particles formed.

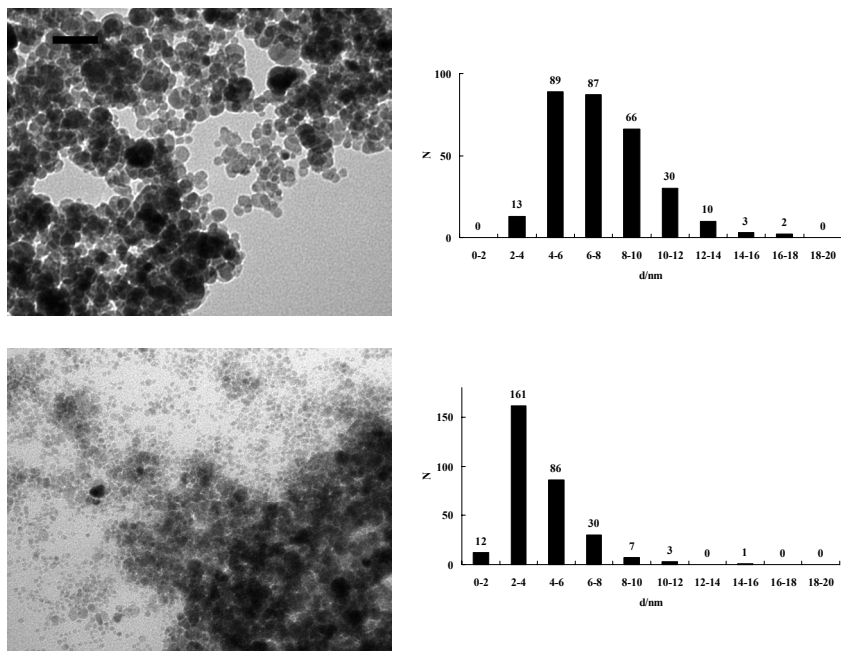


Fig. 2 – TEM images and histograms of magnetite nanoparticles synthesised in the absence (upper figures) and presence (lower figures) of CMC ($c_{CMC} = 5\%w/w$, $DF = 0.7$, $M_w = 70000\text{ D}$). Bar length 25 nm.

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