

Synthesis of iron oxide nanoparticles of narrow size distribution on polysaccharide templates

M NIDHIN, R INDUMATHY, K J SREERAM* and BALACHANDRAN UNNI NAIR

Chemical Laboratory, Central Leather Research Institute, Chennai 600 020, India

MS received 20 July 2007

Abstract. We report here the preparation of nanoparticles of iron oxide in the presence of polysaccharide templates. Interaction between iron (II) sulfate and template has been carried out in aqueous phase, followed by the selective and controlled removal of the template to achieve narrow distribution of particle size. Particles of iron oxide obtained have been characterized for their stability in solvent media, size, size distribution and crystallinity and found that when the negative value of the zeta potential increases, particle size decreases. A narrow particle size distribution with $D_{100} = 275$ nm was obtained with chitosan and starch templates. SEM measurements further confirm the particle size measurement. Diffuse reflectance UV–vis spectra values show that the template is completely removed from the final iron oxide particles and powder XRD measurements show that the peaks of the diffractogram are in agreement with the theoretical data of hematite. The salient observations of our study shows that there occurs a direct correlation between zeta potential, polydispersity index, bandgap energy and particle size. The crystallite size of the particles was found to be 30–35 nm. A large negative zeta potential was found to be advantageous for achieving lower particle sizes, owing to the particles remaining discrete without agglomeration.

Keywords. Iron oxide nanoparticles; photon correlation spectroscopy; polysaccharides; Kubelka–Munk formula.

1. Introduction

The synthesis of nanomaterials with uniform particle size is a subject of intensive research in recent times because of their fundamental scientific interest as well as for the technological importance. These nanomaterials exhibit very interesting electrical, optical, magnetic and chemical properties, which could not be achieved by their bulk counterparts (Colvin *et al* 1994). Nanomaterials may also be used in various technological applications viz. refrigeration systems, medical imaging, drug targeting and other biological applications, and catalysis (Kesavan *et al* 1999). The synthesis of nanoparticles of magnetic metal and metal oxides have been reported in recent times by using different chemical methods viz. sonochemical, solvothermal, micro emulsion etc (Rao *et al* 2004). But the major drawbacks of these synthetic procedures are the low dispersion in solvents and wide particle size distribution. To overcome these drawbacks, research is focused on the colloidal chemistry route to synthesize surface modified nanoparticles with proper surface coating that drives the particles to solubilize in a specific solvent and also maintain a particular size (Guin *et al* 2006). The iron oxides and hydroxides are of special importance because of their wide applications in pigments, magnetic devices,

anticorrosive agents, and catalysts (Kesavan *et al* 1999). The fabrication of low valent iron nanoparticles is also very important for their potential applications in the waste water cleanup process (Suslick *et al* 1996; Sun *et al* 2004). Studies on the hematite (Fe_2O_3) nanoparticles have been performed extensively. However, the synthesis of nanosized Fe_2O_3 with uniform size is one of the important issues of the present research for understanding the fundamental properties of nanomaterials. Various chemical routes have thus been proposed to synthesize ultra fine nanoparticles of Fe_2O_3 , including hydrothermal reaction method, sol-gel process, chemical coprecipitation etc (Dormann *et al* 1988). These methods usually involve synthesizing a precursor gel of iron, followed by decomposing the gel or precursor into the designed crystalline iron oxide phase at an elevated temperature. However, the uniformity of the size of the particle of these nanomaterials was rather poor.

Nanooxide materials have found wide ranging applications particularly as catalysts and as starting materials for making advanced structural ceramics. During sintering and shaping of oxidic materials for practical applications, use of nanosized particles as starting materials can be of great advantage because of the availability of large surface areas of the nanoparticles. It may be noted that surface areas of particles for a given quantity of material scales as $1/\langle d \rangle$, where $\langle d \rangle$ is the average diameter (linear dimension) of the particles (Rao *et al* 2005). Nanostructured hematites such as shuttle-like, nanowire, nanorod

*Author for correspondence (kjsreeram@clri.info)

and nanotube (Liu *et al* 2005) have been developed for applications in pigments, catalysts, gas sensors and as raw materials for ferrites. Templating is commonly employed for the controlled production of materials with ordered structure having desired properties. In the past, templates like aluminium oxide, carbon nanotubes, surfactants, polymer fibres and egg shell membranes have been employed. In this work, we report the preparation of nanoparticles of iron oxides in the presence of polysaccharides templates. In the presence of template (chitosan, alginate and starch), the spatial separation of the particles, coupled with the careful removal of the template through selective conditions, enable the synthesis of highly crystalline, monodispersed particles of <100 nm. The crystallite size of the particles was found to be 30–35 nm. A large negative zeta potential was found to be advantageous for achieving lower particle sizes, owing to the particles remaining discrete without agglomeration.

Polysaccharides are macromolecules carrying a relatively large number of functional groups that are either charged or under suitable conditions, can be charged. The molecules may constitute either polycations or polyanions since the net charge of these macromolecules depends on the functional groups, which may be either positively or negatively charged, or both. Chitosan, alginate and starch are well known polysaccharides that can be used as thickening agents in the food industry and in drug release system in pharmaceutical applications. Chitosan is a linear polysaccharide composed of randomly distributed β -(1-4)-linked D-glucosamine(deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It has a number of commercial and possible biomedical uses. Starch is a complex carbohydrate which is insoluble in water; it is used by plants as a way to store excess glucose. Starch is composed of glucose polymers of amylase and amylopectin. Usually these are found in a ratio of 30 : 70 or 20 : 80, with amylopectin found in larger amounts than amylase. Alginate is a linear polysaccharide consisting of two active binding sites of β -D-mannuronic acid and α -L-guluronic acid. It forms a gum when extracted from the cell walls of brown algae, is used by the food industry to increase the viscosity and as emulsifier and functions as stabilizers of nanoparticles. It is used in the indigestion tablets and the preparation of dental impressions. It is also used in reactive dye printing.

2. Experimental

2.1 Preparation of starting material

In the case of chitosan template, 2.5 g of chitosan was dissolved in 2% acetic acid (100 ml) in the case of starch and alginate templates and 2.5 g of starch/alginate was dissolved in 100 ml of water. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to know volume of the template solutions such that the polysaccharide:Fe ratio varied from 1:1 to 1:4. The

resultant solution was stirred for 30 min. The template-iron mixed solution was treated at 800°C (heating rate of 5°C/min) and maintained at that temperature for 120 min, after which it was cooled to room temperature at a rate of 10°C/min.

2.2 Characterization of iron oxide

Measurement methods need to adequately take into account the agglomeration of the oxide nanoparticles in the dispersing fluid or the data should be correlated through different techniques of particle size measurement. The particle size and zeta potential were evaluated by a dynamic light scattering technique with a Zetasizer 3000HSA (Malvern Instruments, UK). Zeta potential determinations were based on electrophoretic mobility of the nanoparticles in diluted suspensions (5 mg in 25 mL). These measurements were performed atleast in triplicate with independent particle batches. The particle size was measured in *n*-propanol as in our earlier work (Sreeram *et al* 2006). The intensity average diameter was computed using the CONTIN program. The crystalline character and phase purity were estimated from powder XRD measurements, carried out on an XPERT PRO, PANalytical instrument using a $\text{CuK}\alpha$ radiation. The diffuse reflectance UV-vis spectra were recorded using a Perkin-Elmer lambda 35 UV-vis spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse reflectance accessory. Barium sulfate was used as a white standard. The principle of operation involved projection of light of a known spectral energy on the pellet of pigment kept at 90° to the light source and measurement of the intensity of the reflected light using photo detectors. The bandgap values were calculated using Kubelka-Munk function which is given by

$$K - M = (1 - R)^2 / 2R,$$

where *R* is the reflectance value. A plot between *K - M* and wavelength is drawn and the absorption edge is determined from the plot. The value of the wavelength is substituted in the formula

$$E \text{ (eV)} = 1236 / \text{wavelength (nm)}.$$

Polydispersity index is a parameter to define the particle size distribution of nanoparticles obtained from photon correlation spectroscopic analysis. It is a dimensionless number extrapolated from the autocorrelation function and ranges from a value of 0.01 for monodispersed particles and up to values of 0.5–0.7. Samples with very broad size distribution have polydispersity index values > 0.7.

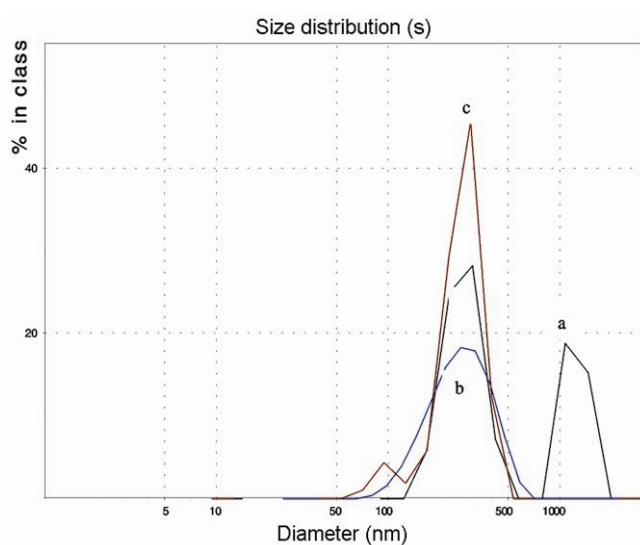
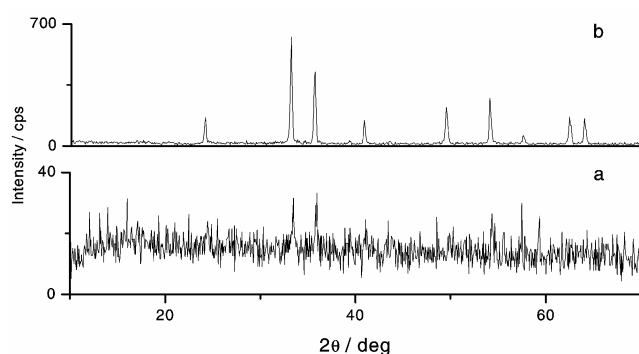
3. Results and discussion

3.1 Template assisted synthesis of iron oxide

The variation in zeta potential and intensity average diameter of the iron oxide particles are presented in table 1.

Table 1. Variation in zeta potential (in mV) and particle size of iron oxide with template.

Template polysaccharide : Fe	Zeta potential (mV)	Polydispersity index	Intensity average diameter (nm)
Without template	+21.6 ± 2.7	0.71	260 (40%), 400 (60%)
Alginate (1 : 1)	-4.0 ± 5.7	0.39	325 (56%), 2349 (44%)
Alginate (1 : 2)	-5.1 ± 8.1	0.46	298 (72%), 1719 (28%)
Alginate (1 : 3)	-5.6 ± 2.7	0.55	275 (84%), 1227 (16%)
Alginate (1 : 4)	-11.9 ± 6.6	0.31	279 (66%), 1247 (34%)
Chitosan (1 : 1)	1.3 ± 3.8	0.48	265 (85%), 1747 (15%)
Chitosan (1 : 2)	-10.9 ± 4.1	0.11	274 (100%)
Chitosan (1 : 3)	-12.0 ± 2.5	0.15	273 (100%)
Chitosan (1 : 4)	-14.2 ± 4.5	0.13	279 (100%)
Starch (1 : 1)	13.0 ± 3.5	0.27	598 (100%)
Starch (1 : 2)	16.6 ± 4.0	0.11	577 (100%)
Starch (1 : 3)	18.3 ± 2.4	0.12	380 (100%)
Starch (1 : 4)	-13.1 ± 6.7	0.28	279 (100%)

**Figure 1.** Particle size distribution plot for iron oxide prepared using a. alginate, b. chitosan and c. starch at polysaccharide : Fe ratio of 1 : 4 and at a temperature of 800°C and rate of heating of 5°C/min for a dwell time of 120 min.**Figure 2.** X-ray diffraction pattern of iron oxide generated a. without template and b. with starch template (starch : Fe 1 : 4) (temperature, 800°C, 5°C/min, 120 min dwell time).

In the case of iron oxide, proper choice of templates could prevent aggregation of particles. Some templates are known to stabilize the nanoparticles while some result in inhomogeneity. Choice of templates based on their ability to prevent aggregation results in stable homogeneous nanoparticles. It can be found that the zeta potential had a large negative value when the synthesis was carried out in the presence of a template, indicating the stability of the nanoparticles against agglomeration. The alginate and chitosan templates resulted in a large negative zeta potential value, while the same has been observed only at a polysaccharide : Fe ratio of 1 : 4 in the case of starch. The intensity average diameter calculated from the particle size distribution, however, showed a variation with respect to the template. The particle size distribution pattern for the iron oxide particles with template is presented in figure 1. In the case of alginate as a template, two distinct sets of particles, 66% of which had an intensity average diameter of 279 nm, have been observed. In the case of chitosan and starch the particles though distributed over a larger range had only one distinct set of particles, resulting in an intensity average diameter of 279 nm in both the cases. The polydispersity index values obtained in this study further corroborates the observations made, with lower values being observed for relatively monodisperse systems.

3.2 Characterization of iron oxide prepared by template assisted synthesis

The X-ray diffraction pattern for iron oxide particles synthesized in the absence/presence of starch is presented in figure 2. It can be seen that the iron oxide particles are not sufficiently crystalline in the absence of the template, while the same improves in the presence of the template, as suggested by the markedly sharpened, high intense peaks in the diffractogram. All peaks of the diffractogram

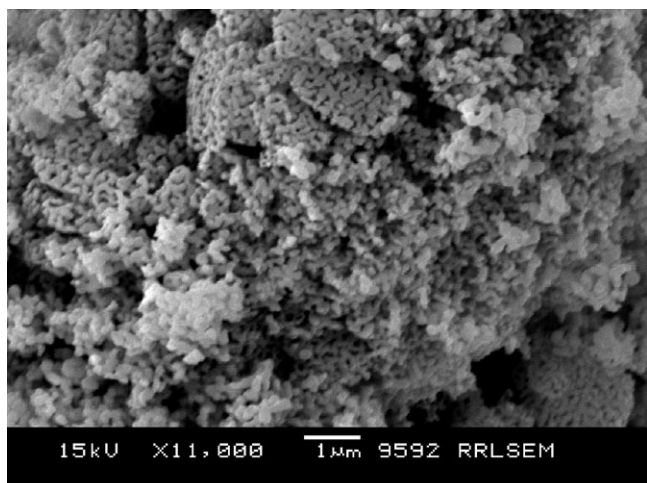


Figure 3. Scanning electron micrograph of iron oxide particles generated with chitosan template (chitosan : Fe 1 : 4).

are in agreement with the theoretical data of hematite (JCPDS card no. 33-0664). The scanning electron microscopic measurements of the iron oxide particles showed uniform particles of around 290 nm when a chitosan template was employed (figure 3).

The crystallite size was calculated using the Debye-Scherrer formula,

$$D = 0.9\lambda/\beta\cos\theta,$$

where D is the particle size, λ the wavelength of the X-ray used, β , θ are the half-width of X-ray diffraction lines and half diffraction angle of 2θ . The crystallite size was found to be between 32 and 35 nm in the presence of template. The bandgap energy observed followed the order starch (2.01 eV) < chitosan (2.09 eV) < alginate (2.21 eV). This observed trend was similar to that observed in particle size, where the intensity average diameter decreased as the bandgap energy decreased. α -Fe₂O₃ samples showed absorption maxima at 460 nm. The band can be assigned to charge transfer from oxygen to the metal centre. One can expect to see the ligand field transitions in these cases. However, since these transitions are Laporte forbidden, they have very low intensity. Hence, in the presence of intense charge transfer transitions one cannot detect them.

4. Conclusions

Polysaccharides can be used as templates for the synthesis of iron oxide nanoparticles. The particle size and zeta potential varied for different templates. There is a direct correlation existing between zeta potential, polydispersity index, bandgap energy and particle size. The salient observations of this study is that larger the negative zeta potential lower will be the particle size, polydispersity index decreases as the negative value of zeta potential increases and lower the particle size, lower will be the bandgap energy. The particle size distribution was uniform and particles were more or less monodisperse for chitosan and starch template assisted synthesis. The iron oxide synthesized was crystalline and matched with that of hematite.

Acknowledgement

The authors thank CSIR for the funding received under the CSIR Young Scientist Project.

References

- Colvin V L, Schlamp M C and Alivisatos A P 1994 *Nature* **370** 354
- Dormann J L, Bessais L and Fiorani D 1988 *J. Phys.* **C21** 2015
- Guin Debanjan, Manorama Sunkara V, Radha S and Nigam A K 2006 *Bull. Mater. Sci.* **29** 617
- Kesavan V, Sivanand S P, Chandrasekaran S, Kolytyn Y and Gedanken A 1999 *Angew. Chem. Int. Ed.* **38** 3521
- Liu X M, Fu S Y, Xiao H M and Huang C J 2005 *J. Solid State Chem.* **178** 2798
- Morup S and Tronc E 1994 *Phys. Rev. Lett.* **72** 3278
- Rao C N R, Muller A and Cheetam A K (eds) 2004 *The chemistry of nanomaterials: Synthesis, properties and applications* (Weinheim: Wiley)
- Rao K J, Mahesh Krishnamurthy and Kumar Sundeep 2005 *Bull. Mater. Sci.* **28** 19
- Sreeram K J, Indumathy R, Rajaram A, Nair B U and Ramasami T 2006 *Mater. Res. Bull.* **41** 1875
- Sun S, Murray C B, Weller D, Folks L and Moser A 2004 *Science* **287** 1989
- Suslick K S, Fang M and Hyeon T 1996 *J. Am. Chem. Soc.* **118** 11960