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Template synthesis of highly crystalline and monodisperse iron oxide pigments of nanosize

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Abstract

Synthesis of highly crystalline and monodisperse iron oxide nanoparticles is reported. The separation of Fe centers through site-specific binding to a polysaccharide–alginate matrix enables the generation of particles with a monodisperse or narrow size distribution character, resulting in transparent pigments. Site-specific interactions coupled with gel like character of alginate is proposed as the mechanism behind generation of lower particle sizes. Alginate-Fe complexes developed were subjected to heat treatment to provide for crystalline character and development of hematite (α-Fe_2O_3). Conditions most ideal for achieving monodispersity and lower sizes have been optimized and confirmed through microscopic and photon correlation spectroscopic measurements.

Keywords: A. Nanostructures; A. Oxides; B. Chemical synthesis; C. Electron microscopy; C. X-ray diffraction

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1. Introduction

Several advanced materials for magnetic, catalytic and pigment applications require precursor inorganic oxides which are monodisperse and typically in the size range of a few nanometers to sub-micrometers [1]. Below a critical size, Fe_2O_3 nanoparticles can be used for niche applications like transparent iron oxide pigments, due to their durability, shade, UV absorption and added value [2]. Careful control of the preparation process of transparent iron oxide pigments results in the formation of pigments with very small primary particle sizes. When fully dispersed, they do not scatter light and are hence completely transparent. The very small primary particle size results in powders with high surface areas and relatively high oil absorption figures.

There are several reports on the preparation of narrow size iron oxide particles for biomedical applications. The processes include careful choice of pH, concentration of the reactants, temperature, method of mixing, and rate of oxidation [3]. The sensitivity of the preparative method complicates both the reproducibility and scale up of the

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process. In the case of pigments, the methodology adopted to achieve monodispersity and lower sizes has to be cost effective as well. One method adopted is the micropulversation of the conventionally produced iron oxides. Micropulverization does not produce easier-to-disperse transparent iron oxide pigments, as the aggregates tend to become compacted and are thus more difficult to wet out and disperse.

Recently, several colloidal chemical synthetic procedures have been developed to produce monodisperse nanoparticles of various materials. This includes the classical LaMer mechanism, wherein a short burst of nucleation from a supersaturated solution is followed by the slow growth of particles without any significant additional nucleation, thereby achieving a complete separation of nucleation and growth [4]. Synthetic procedure that combines slow, continuous nucleation and fast, autocatalytic surface growth have also been reported [5]. Further, in several preparative methodologies, agglomeration of the nano-oxide generated takes place on exposure to air. This is prevented by employing surfactants or by capping with oleic acid [6].

Precipitation of inorganic particles in a cross-linked polymer matrix or network of gel often prevents coagulation of particles, giving rise to monodisperse particles. However, the particles obtained exhibit large particle sizes, possibly due to generation of iron hydroxide aggregates.

In this work, we report the template synthesis of monodisperse iron oxide in the below 200 nm regime by using a polysaccharide template. Alginic acid, a naturally occurring polysaccharide that forms rigid cross-linked gels in the presence of di- and trivalent cations has been employed. Conditions ideal for achieving monodispersity coupled with narrow sizes have also been developed.

2. Experimental section

2.1. Materials

All reagents used in this study were of AnalaR grade and locally procured. Sodium alginate $[C_6H_7O_6Na]_n$ obtained from *Macrocystis pyrifera* of medium viscosity was used in this study. The molecular weight of the alginate was taken from our previous work [7].

2.2. Experimental procedure

To a solution of the alginate, ferrous sulfate was added drop wise such that the mole ratio of Fe:Alg was 250:1 to 3500:1. Ferrous sulphate is the preferred salt, as it is readily available, a byproduct, from the manufacture of titanium dioxide pigment or from the steel pickling industry. After the addition was complete, the solution was kept stirring for about 10 min and then transferred to alumina boats and heated in a muffle furnace at known temperature for a defined period of time. Unless specified, the heating rate was maintained at 5 °C/min. The study was carried out at constant pH of 4.0 so that the carboxyl groups in the alginate can bind to the metal ion effectively. After the heating period, the samples were cooled to room temperature at 10 °C/min.

2.3. Analysis and characterization

Light scattering measurements were carried out at 90° on a photon correlation spectrometer (PCS) from Malvern Instruments—Zetasizer 3000 HSA equipped with a digital autocorrelator. The CONTIN method was used for data processing [8,9]. The concentration of iron oxide nanoparticles was set to 0.2 mg iron oxide/ml for all measurements. Electrophoretic mobility measurements were performed using the same setting equipped with a platinum electrode. The electrode was cleaned for 10 min in an ultrasonic bath prior to each measurement and pre-equilibrated for 2 min in an aliquot of the sample. For zeta potential measurements, the samples were diluted in various solvents of known viscosity, refractive index and dielectric constant. The dispersion was prepared by sonicating in an ultrasound cleaner of 30 ± 5 kHz for 10 min. Dispersion, which gave maximum zeta potential values, is expected to be stable against aggregation processes.

For scanning electron microscopic measurements (Jeol JSM5600LV), the powder samples were sprinkled on a carbon tape, which was fixed on a brass stub. Then, the sample surface was coated with gold in a sputtering unit. The X-ray diffraction (XRD, XPERT PRO, PANalytical) patterns of the particles were recorded using Cu Kα radiation.