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Magnetic iron oxide nanoclusters with tunable optical response

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Abstract

We have developed a modified synthetic protocol for the growth of monodispersed, superparamagnetic, flower-like colloidal nanoclusters (CNCs), which are consisted of smaller iron oxide nanocrystals with adjustable size. We show that their optical properties can be tuned by applying an external magnetic field. The latter controls the subtle balance of the CNCs' mutual interactions (magnetic versus electrostatic) and drives their assembly in aqueous media. Spectrophotometric measurements reveal that a diffuse reflectance maximum, in the visible range, is related to the CNCs organization. As the strength of the external magnetic field increases, in the range 160–600 G, the spectral weight of this feature shifts towards the blue region of the spectrum. The induced photonic crystal-like response entails a remarkable magneto-optical behavior, closely associated with the size-dependent characteristics of the CNCs ensemble. Such materials pave the way for promising technological implementations in photonics.

Keywords: Magnetic nanoclusters; Photonic crystals; Iron oxide nanocrystals; Secondary structures

1. Introduction

Monodispersed colloidal microspheres of silica or polystyrene, ranging from tens of nanometers to several microns have been used as building blocks to form photonic crystals because of their capability to assemble in ordered structures [1]. The parameters that may play a role in shaping the optical properties of such photonic crystals are the structure type, the lattice spacing, the contrast between the areas of high and low dielectric constant, as well as, the shape and the size of the building blocks. Therefore the research for identifying alternative pathways for the rational design of related systems, with tunable characteristics, is highly required. Along these lines the synthesis of monodispersed magnetic oxide nanocrystals with various wet chemistry approaches has received much attention in the recent years due to their modular nature and consequent diverse application capabilities, ranging from magnetic storage materials to medical diagnostics [2,3]. A major challenge in such nanoscale materials, which determines their versatile properties (structural, magnetic, optical, etc.) is to afford a well defined shape and size. In that respect, magnetic nanoparticles in the range of a few nanometers exhibit radically different properties than their bulk counterparts. For example, when the size of a ferro- or ferrimagnetic particles decreases below a

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critical value, characteristic for each material, the particles' state changes from that of a motif with multiple magnetic domains to one with a single domain. Such small particles do not have permanent magnetic moments in the absence of an external field but can respond to an external magnetic field. These particles are referred to as superparamagnetic and have important applications [2,4].

Superparamagnetism in nanomaterials has motivated recent research efforts to explore nanocrystals' organization over large length scales by the application of external stimuli, such as a magnetic field. Among various examples of assembly in colloidal matter, an interesting nanostructured system which has received much attention entails the self-assembly of highly charged polystyrene particles containing iron oxide nanocrystals. In this case the hybrid material has been synthesized by emulsion polymerization [5,6]. Introducing magnetic components in nanoscale colloidal building blocks can help tuning the collective properties of the secondary structure [7,8]. Asher and co-workers have demonstrated that Bragg diffraction of visible light from such materials can be controlled by applying an external magnetic field, which can both alter the lattice constant as well as increase the strain of the fcc crystal lattice [5].

Progress in this direction has been recently made by Yin et al. who succeeded in using pure magnetic materials with strong response to an external magnetic field as building blocks for constructing colloidal photonic crystals. He has developed a wet chemistry approach to synthesize secondary structures, i.e. clusters of Fe_3O_4 colloidal nanocrystals (CNCs) [9]. These secondary structures (30–180 nm) retain superparamagnetism at room temperature and enhanced saturation magnetization as they are composed of a number of iron-oxide nanocrystals, with less than 10 nm size. It is interesting to note that in these samples the grain size, as calculated from X-ray powder diffraction (XRD) patterns, remains the same for all the different diameter CNCs [10]. Consequently, their magnetic and optical properties are only dependent on the CNC size itself. Very interestingly, these CNCs respond efficiently upon the application of an external magnetic field and assemble into ordered arrays within an aqueous medium. The assembly of the structures allows for the tuning of the diffraction wavelength in the visible spectral range. The CNCs with averaged dimensions of 60–100 nm form chain-like structures only when the magnetic field is sufficiently strong. Light is diffracted from the red to blue with increasing field strength, between 67.8 and 352 G.

In this work, a modified synthesis protocol of iron-oxide nanoclusters has been developed to afford CNCs with not only overall diameter modification but also importantly a tunable primary nanocrystal dimension. We discuss two examples of CNCs with different diameter, namely of 40 and 120 nm, each incorporating a variable size primary iron-oxide nanoparticles. We study the CNCs physical behavior and highlight the influence of the grain size on their magnetic and optical response.

2. Experimental details

In a typical synthesis, 0.8 mmol $FeCl_3$ (anhydrous, 98%), 8 mmol poly(acrylic) acid ($M_w = 1800$) were dissolved in diethylene glycol (DEG) under magnetic stirring at room temperature. The yellowish solution was heated at 220 °C under Ar flow for 1 h until a quantity of DEG–NaOH hot solution was injected in this mixture (Table 1). The color of the solution turned black in a few minutes. After reaction for 1 h, the solution was cooled to room temperature. The iron oxide CNCs were washed three times with a mixture of deionized water and ethanol and redispersed in water [10]. The purification process was followed by repeating cycles of magnetic separation and dispersion again in water. The second solution, which was added at 220 °C in the above mixture of reagents, was prepared from 50 mmol of NaOH in 20 ml of DEG after heating at 120 °C for 1 h. The solution was cooled at 70 °C and kept at this temperature. All the synthetic parameters are presented in Table 1.

The incorporation of NaOH produces water molecules and increases the alkalinity of the solution as it gives hydroxylate anions, accelerates the hydrolysis of the $FeCl_3$ in magnetite nanocrystals and produces clusters with increased size [10]. The DEG plays a dual role in the reaction, namely, as a reducing agent and as solvent. Also, it determines the water level in the reaction and affects the size of the grains [8–10]. A slow addition of the reducing agent also helps the growth of larger primary particles but leads in smaller cluster dimensions.

A JEM 100C JEOL transmission electron microscope (TEM; operating at an acceleration voltage of 100 kV) and a JEOL 2011 high-resolution electron microscope (HRTEM; operating at an acceleration

Table 1
Synthetic parameters.

CNC size (nm)	Grain size (nm)	DEG volume (ml)	NaOH volume (ml)	Addition of NaOH
40	12.2	34	3.6	Slow
120	7.7	40	3.8	Fast