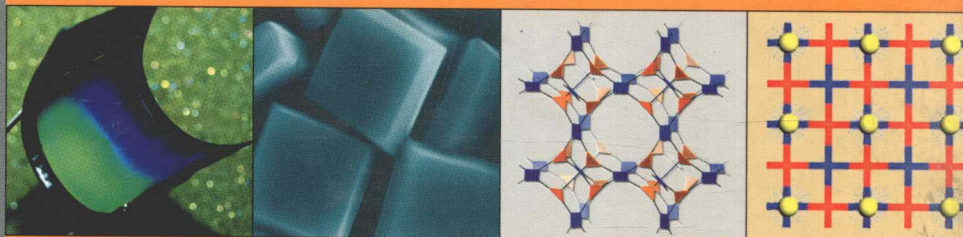


Volume **II**

The Chemistry of



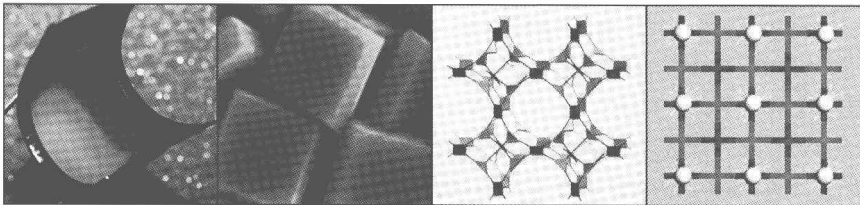
Nanostructured Materials

Peidong Yang editor

 World Scientific

Volume **II**

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Editor

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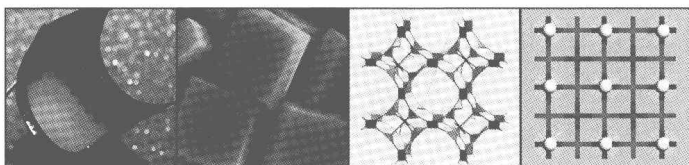
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PREFACE

Nanostructures have attracted steadily growing interest due to their fascinating properties, as well as their unique applications relative to their bulk counterparts. The ability to generate such structures is now central to the advance of many areas in modern science and technology. In the past decades, significant progress has already been made in the field of low-dimensional nanostructures. With these nanostructures as the functional components, a variety of nanoscale devices have been fabricated as prototypes by many research groups around the world, with notable examples including nanoscopic lasers and transistors, logic and memory units, light-emitting diodes, as well as energy generation and storage devices.

Among many of the potential applications for nanomaterials, energy generation and storage become increasingly important. For the next few decades, the annual global consumption of energy is estimated to rise significantly. Assuming current policies and practices remain in place, most of the increased energy production is expected to come from the combustion of liquid fuels, such as oil, natural gas, and coal. A commensurate increase in CO₂ (a prominent greenhouse gas) emissions is anticipated, much of which is due to burning coal – the fastest growing source of energy globally. In order to moderate global reliance on exhaustible natural resources and their environmentally hazardous combustion, more scientific efforts should be directed towards reducing the cost of energy production from renewable sources.

There exist many potential renewable energy technologies in the form of solid state devices, such as, for example, solar cells, which convert solar energy in the form of light to the more practical form of an electricity. In addition, a large collection of condensed matter phenomena involve the conversion of energy from one form to another, and some

proceed with efficiency near unity. Consequently, the study of energy conversion in nanomaterials is a field full of opportunities for practical and socially significant applications.

This book, as a sequel to the 2003 book “Chemistry of Nanostructured Materials”, focuses on the energy applications of nanomaterials. The individual chapters, written by experts within the field, will review ways in which nanostructured materials can enable advanced solid state energy conversion and storage devices. More importantly, all of these studies reflect beautifully the central theme of the nanomaterials research — *rational synthesis with a purpose*.

I would like to thank all the authors for their time and efforts to put together these comprehensive review articles, Dr. Frank Tsung for assistance in editing and formatting final version of the individual chapters. I personally hope that researchers at different levels will find this book useful and interesting. Enjoy reading and see you at sequel III.

Peidong Yang @ Berkeley
Spring 2010

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CHAPTER 1

MAGNETICALLY TUNABLE COLLOIDAL PHOTONIC CRYSTALS

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Nanostructured superparamagnetic particles can be self-assembled to form colloidal photonic crystals whose photonic properties can be tuned widely, rapidly, and reversibly in the visible spectrum. The successful assembly is achieved by establishing a balance between interparticle repulsive and attractive forces. While the attractive force can be induced through the application of external magnetic fields, the repulsive forces need to be created by engineering the particle surface in accordance to the polarity of the solvents. The dynamic photonic structures can be rapidly fixed in a polymer matrix through instant assembly of superparamagnetic colloidal particles in UV curable resin followed by an immediate UV curing process. Combining with an emulsification procedure, the fixation process can be used to produce magnetochromatic microspheres that can change their colors through the manipulation of their relative orientation using external magnetic fields. By using hygroscopic salt solutions as inks, we also demonstrate the use of the polymerized photonic structures in applications such as rewritable photonic papers.

1. Introduction

Colloidal photonic crystals form a class of photonic band gap materials that can be fabricated under ambient conditions of pressure and temperature.¹⁻³ The periodic modulation of refractive indices in such dielectric materials creates a forbidden gap in the photonic band structure

that excludes the existence of optical modes within a specific range of frequencies. Colloidal photonic crystals are therefore attractive optical materials for controlling and manipulating the flow of light: they can be used as low and high reflection coatings on lenses and mirrors, color changing paints and inks, waveguides for directing the propagation of light along a specific channel, laser cavities, and active components in optical computers.⁴⁻⁸ It has been especially difficult to produce photonic crystals with band gaps located in the visible regime by using conventional lithographic techniques as this requires feature sizes of just a few hundred nanometers.⁹⁻¹⁶ The fabrication challenges have provided a major driving force for study of alternative approaches to photonic crystal preparation, such as the self-assembly of monodisperse colloidal particles.¹⁷ In this case, the periodic modulation of dielectric constant is realized by self-assembling monodisperse colloidal objects into ordered arrays. The resulting photonic properties are determined by the symmetry and lattice constant of the crystals, and the refractive index contrast between the colloids and the surrounding medium. Colloid size is typically in the range of several hundreds of nanometers so that a band gap in the visible regime may be achieved.

It is highly desirable that a photonic crystal possesses a tunable band gap which can be conveniently controlled by external stimuli. For example, field addressable photonic crystals may be used as optical switches which allow full automation and a high degree of integration of the optical circuits. Military vehicles covered with such materials may be able to dynamically change their colors and patterns to match their surroundings. The photonic effect can be used as a mechanism for developing chemical and bio-sensors that can detect target analytes by outputting optical signals. They may also be used as photonic "ink" in a flexible display media that can be reused many times.

In principle, the stimuli can be any means that effectively induces changes in the refractive indices of the colloids or the surrounding matrix, and the lattice constants or spatial symmetry of the colloidal arrays. For example, oxide materials such as WO_3 , VO_2 and BaTiO_3 have been used as matrix materials for producing tunable photonic crystals because the refractive indices of these materials are sensitive to electric fields or temperature changes.¹⁸⁻²⁰ Colloidal arrays infiltrated with liquid crystals

also show tunable photonic properties upon the application of an external electric field or a change in temperature.²¹⁻²³ The majority of approaches to tunable photonic crystals, however, are focused on controlling the lattice constants or spatial symmetry of the crystals through the application of chemical stimuli, temperature variation, mechanical forces, electrical or magnetic fields, or light.²⁴⁻³² A notable example is a hydrogel/colloidal array composite in which the lattice spacing can be tuned by the swelling and deswelling of the hydrogel.³³ However, wide use of these systems in practical applications is hampered by limited tunability of the band gap (with peak position changes typically in the range of tens of nanometers), a slow response to the external stimuli (typically several minutes to a few hours), and difficulty of integration into existing photonic systems. The small tuning range is mainly due to the limited changes in the crystal structure that the external stimuli can induce. The slow response is usually the result of retarded physical/chemical changes that the external stimuli can cause.

Incorporation of superparamagnetic components into colloidal building blocks allows for effective control over photonic properties of the assembled structures by using externally applied magnetic fields. The choice of magnetic fields as the external stimuli may offer improved spectral tunability, response rate, and facility of integration into existing photonic systems.³⁴⁻³⁶ The main effect of the magnetic fields is the creation of attractive forces between neighboring particles along the field direction, to assist the ordering of the particles, and to tune the photonic property by changing the interparticle spacing. Previous studies along this direction have met with limited success largely due to the difficulties in obtaining magnetic colloidal building blocks with controllable size, morphology, stability, surface structure and magnetic property. The pioneer work by Asher *et al.* focused on polymer colloids embedded with superparamagnetic nanoparticles of iron oxide.³⁷⁻³⁹ Although a field-responsive photonic property was realized, the volume fraction of the magnetically active materials was so low that the application of magnetic field cannot initiate the ordering of particles. Colloidal crystals have to be pre-constructed by using a separate self-assembly process, and the magnetic fields could only induce small changes in the particle separation of the preformed structures. As a result, the tuning range of

the diffraction was still very limited. It has also been shown that emulsion droplets containing iron oxide nanoparticles can organize into ordered structures in the presence of an external magnetic field.^{40,41} Since emulsions are not thermodynamically stable systems, the long-term stability of the oil droplets against dissociation or aggregation is questionable.

In this chapter, we discuss our recent efforts in the self-assembly of nanostructured superparamagnetic particles for building colloidal photonic crystals whose photonic bandgap properties can be tuned widely, rapidly, and reversibly. We start with the introduction of a solution phase synthesis for producing superparamagnetic magnetite building blocks that possess the physical and surface properties required for optimal assembly. Then we discuss the assembly of the superparamagnetic particles in colloidal solution under the balanced interaction of attractive and repulsive forces. As the attractive forces can be induced through the application of external magnetic fields, we focus our discussion on the creation of various types of repulsive forces by modifying the surface properties of particles in accordance to the polarity of solvents. We show that by establishing the proper force balance, photonic structures can be conveniently assembled in various solvents including water, alcohol, and nonpolar systems. Finally, we will demonstrate the fixation of the color of the photonic structures by embedding the particle assemblies in a curable polymer matrix. By combining with an emulsification procedure, the fixation process can be used to produce magnetochromatic microspheres that can change their colors when their relative orientation is manipulated using external magnetic fields. By using hygroscopic salt solutions as inks, we also show the use of the polymerized photonic structures in applications such as rewritable photonic papers.

2. Superparamagnetic Building Blocks

To be used in magnetically responsive photonic crystals, an idea building block is supposed to meet the following requirements: (1) The colloids are expected to possess a uniform shape, a controllable size and a narrow size distribution so that the lattice constant can be precisely

tuned and crystal defects can be eliminated as much as possible; (2) Materials with high refractive index contrast to the surrounding medium are needed in order to obtain strong diffraction intensity; (3) Superparamagnetic property is essential for achieving reversible optical response because significant magnetic interactions need to be initiated only through the application of external magnetic fields; (4) Colloidal particles made of pure magnetic materials with a high saturated magnetic moment are preferred, as it will favor a faster response to the external magnetic field and a lower responsive threshold of field strength; (5) These magnetic particles are also expected to have appropriate surface property which not only renders the particles high solubility in the dispersion medium but also produces sufficient repulsion to balance the magnetically induced attraction during the self-assembly process.

The synthesis of building blocks with all the required properties has been difficult. A particular challenge is the transition from superparamagnetism to ferromagnetism that seems to be inevitable when the particle size falls into the range of 100-200 nm. Recently, we have developed a one-pot high-temperature polyol process for the synthesis of polyelectrolyte-capped superparamagnetic “colloidal nanocrystal clusters” (CNCs) of magnetite (Fe_3O_4), which happens to be the ideal building blocks for the fabrication of magnetically tunable photonic crystal structures. Briefly, Fe_3O_4 CNCs are prepared by hydrolyzing FeCl_3 with NaOH at around 220°C in a diethylene glycol solution with polyacrylic acid (PAA) as a surfactant.⁴² Under the reductive atmosphere provided by DEG at high temperature, Fe^{3+} partially transforms into Fe^{2+} and finally forms Fe_3O_4 particles. The particle size can be tuned from 30 to 180 nm with a relatively narrow distribution. In addition, magnetite has a high refractive index (2.42) that is close to that of rutile (2.60), making it a more appropriate material than commonly used silica or polystyrene for photonic crystal applications.

As shown in the transmission electron microscopy (TEM) image in Fig. 1, these magnetite CNCs have a unique cluster-like structure. Each cluster is composed of many interconnected primary nanocrystals with size of ~ 10 nm. The crystallographic alignment of the primary crystals to the adjacent ones are observed in the high resolution TEM analysis, suggesting the possible formation mechanism of CNCs through

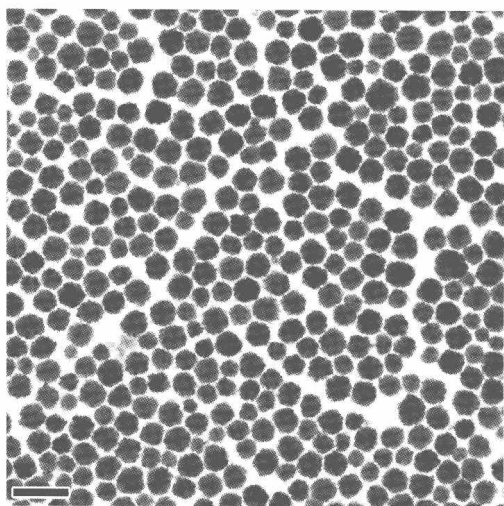


Figure 1. A typical TEM image of Fe_3O_4 CNCs. Scale bar is 200 nm.

oriented attachment and subsequent high-temperature sintering during synthesis.⁴²⁻⁴⁴ Although the overall size of the Fe_3O_4 CNCs can reach 180 nm in diameter, the size of the primary nanocrystals is not significantly affected by the attachment and sintering. X-ray diffraction measurements also show that 53-, 93- and 174-nm Fe_3O_4 CNCs possess grain sizes that are comparable to that of 8-nm Fe_3O_4 single crystal nanodots. The unique and complex structure allows Fe_3O_4 CNCs to retain the superparamagnetic behavior at room temperature even though their overall size exceeds the critical size distinguishing ferromagnetic and superparamagnetic magnetite (30 nm). As shown in Fig. 2, the magnetization hysteresis loops of CNCs with various sizes show typical superparamagnetic characteristics with immeasurable remanence or coercivity at 300 K.

The cluster-like structure also renders the Fe_3O_4 CNC a much higher saturated magnetization and thereby a stronger magnetic response to external fields than the individual nanoparticles. The saturated magnetization (σ_s) was measured by sweeping the field between -20 kOe and 20 kOe, and determined to be 63.5, 56.7, 30.9, and 21.2 emu/g for 174-, 93-, and 53-nm CNCs and 8-nm particles respectively. The decrease of σ_s for small particles may be attributed to an increasing

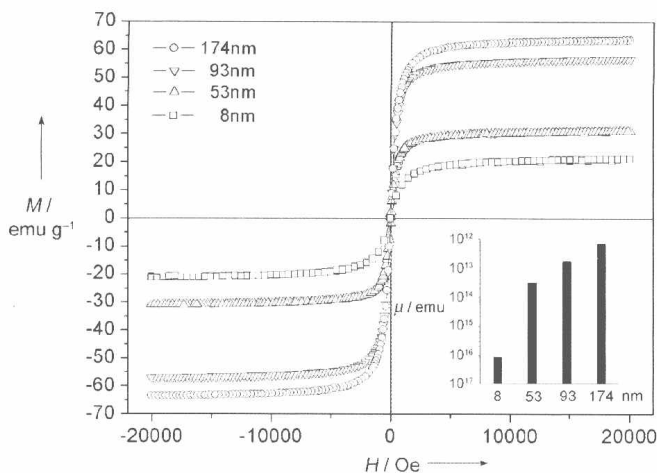


Figure 2. Mass magnetization (M) as a function of applied external field (H) measured for 53-nm, 93-nm, 174-nm CNCs and a reference sample of 8-nm single crystalline nanoparticles of Fe_3O_4 . Insert shows the magnetic moment (μ) per cluster (or particle) plotted in a logarithmic graph. Adapted with permission from Ref. 42 © 2007 Wiley.

weight percentage of PAA in the products. By fitting the hysteresis loops to the Langevin paramagnetic function, the magnetic moments for a 8-nm particle, and 53-nm, 93-nm, 174-nm individual clusters are calculated to be 8.45×10^{-17} , 3.23×10^{-14} , 1.79×10^{-13} , 7.13×10^{-13} emu respectively, clearly suggesting much stronger magnetic response of CNCs than that of individual nanoparticles (Fig. 2).⁴² As will be discussed in detail later, the strong magnetic response makes it possible to instantly assemble the particles into ordered structures (less than 1 s) and rapidly tune the photonic property by using a relatively weak magnetic field (100-400 Oe). The as-prepared Fe_3O_4 CNCs are covered with a layer of highly charged polyelectrolyte surfactant, therefore displaying a superior dispersibility in aqueous solution. Particle powders after purification and several-month storage can still be dispersed instantly in water without detectable aggregation. The good water solubility can be attributed to the surface structure of clusters: the PAA molecules bind to the particle surface through the strong coordination of carboxylate groups with iron cations while the uncoordinated carboxylate groups on the polymer chains extend into aqueous solution, rendering the

particle surface negative charges and preventing aggregations. Due to the chemical nature of polyacrylate ligands, the Fe_3O_4 CNCs disperse well in neutral and basic solution but precipitate in acidic environment. After removing the excess electrolytes, a strong electrostatic repulsion builds up among neighboring CNCs, thus further enhancing the stability of the dispersion.

3. Colloidal Self-Assembly and Photonic Property Tuning

3.1. Aqueous System

Integrated with features such as superparamagnetic property, large and uniform sizes, and highly charged surfaces, the as synthesized Fe_3O_4 CNCs can readily assemble in aqueous solution into photonic crystal structures whose optical signals can be instantly tuned by using external magnetic fields.⁴⁵ With white light illumination, the colloidal photonic crystals in the solution show brilliant colors from red to blue when the strength of applied magnetic field is increased (Fig. 3). This visual effect, observable in direction parallel to the magnetic field, results from the Bragg diffraction of incident light by the periodically ordered structures assembled from Fe_3O_4 CNCs. Such optical response to the external magnetic field is instant and fully reversible, and the required field strength for realizing the ordering of CNCs and color tuning is merely above 100 G. In this section, the mechanism of magnetic assembly and manipulation of photonic stop band will be discussed.

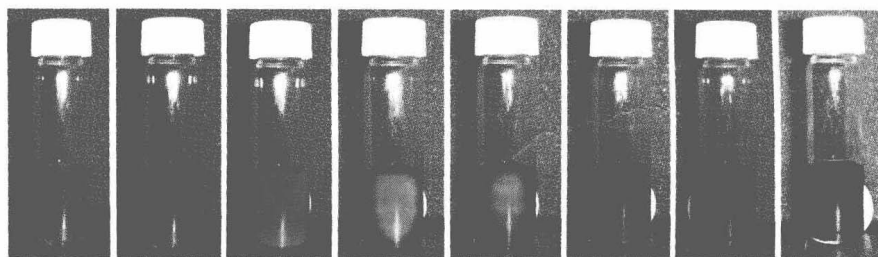


Figure 3. Photographs of aqueous solution of Fe_3O_4 CNCs in response to the changing magnetic field. The sample-magnet distance decreases gradually from left to right.

The self-assembly behavior of the CNCs in response to external magnetic fields has been studied *in situ* through optical microscopy (Fig. 4).⁴⁶ A thin film of CNC solution is formed by sandwiching a CNC droplet between two cover glasses, and a vertically movable magnet is placed underneath the horizontal glasses, so that the sample-magnet distance (also the field strength) can be conveniently controlled. In the absence of magnetic field, the colloids are well dispersed in water due to Brownian motion (Fig. 4a). When a magnetic field is vertically applied, the colloids line up along the field and appear as isolated bright spots in the optical dark field (Fig. 4b). These bright spots show short-range hexagonal order when viewed from the top. As shown in Fig. 4c, a slight tilt ($\sim 15^\circ$) of the magnet from the vertical orientation confirms that each spot is actually a chain of particles. The chains appear even longer when the magnetic field is tilted further away from vertical orientation. The strong optical diffraction is therefore believed to result from the periodical arrangement inside each chain with interparticle distances

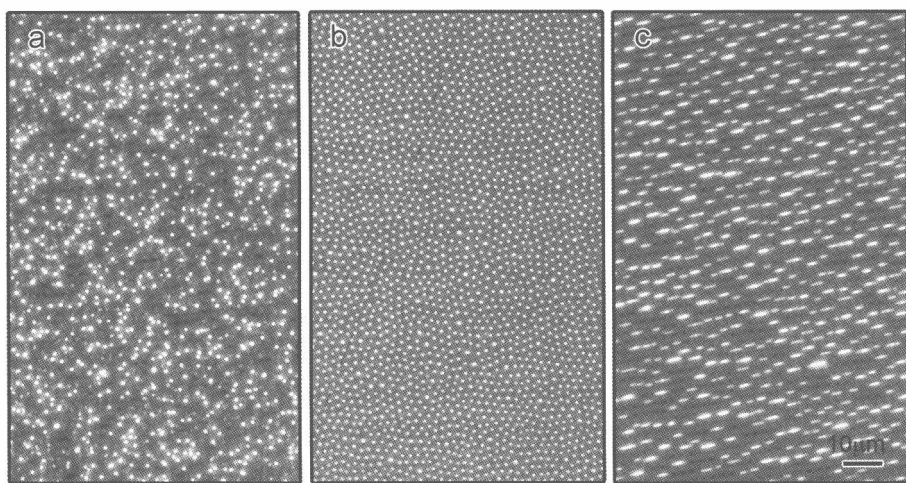


Figure 4. (a, b) Dark-field optical microscopy images showing the assembly of Fe_3O_4 CNCs dispersed in an aqueous film encapsulated between two glass slides in a magnetic field parallel to the viewing angle. The field strength increases from (a) to (b). (c) Dark-field optical microscopy image illustrating the assembly of CNCs into chainlike structures by slightly tilting the magnetic field ($\sim 15^\circ$ from the view angle). Adapted with permission from Ref. 46 © 2008 American Chemical Society.