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Tunable photonic crystals from emulsion containing magnetic nanoparticles

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ABSTRACT

We report a simple approach to synthesize emulsion of oleic acid (OA) containing Fe_3O_4-OA nanoparticles as magnetic building block of photonic crystals by combined chemical co-precipitation and emulsification technology. The emulsion droplets exhibit dominant size distribution of 80–110 nm and superparamagnetic behavior. A high loading fraction of magnetic compounds Fe_3O_4 in emulsion of 72% was achieved by the approach. Upon application of a magnetic field, the emulsion droplets in water facilely self-assemble into photonic crystals, and the stop bands could be tuned in ranging visible spectrum by moving position of magnet. The method to synthesize emulsion with high magnetic loading fraction should facilitate preparation of tunable photonic crystals and expand their application.

1. Introduction

Colloidal photonic crystals have attracted much attention because of their promise in optoelectronic applications that require the manipulation of photons, such as photonic components in telecommunication devices, lasers, and sensors [1–7]. The self-assembly of colloidal spheres is one of the most effective approaches for producing functional photonic crystals [8–11]. It is highly desirable for the envisioned applications that a photonic crystal possesses a tunable stop band, including the lattice constants or spatial symmetry, that can be conveniently controlled by external stimuli. Recently Yin et al. developed the high-temperature hydrolysis method to synthesize highly charged superparamagnetic Fe_3O_4 colloidal nanocrystal clusters as building block, and realized a magnetically tunable photonic crystal system by assembling the magnetic building block in aqueous solutions [12–14]. Stabilized by the balance of attractively magnetic and repulsively electrostatic forces, the nanocrystal clusters form ordered structures along the direction of the external magnetic field with a regular interparticle spacing on the order of hundreds of nanometers. As a result, the solutions strongly diffract visible light. In our previous research, it obtained robust and band-gap-controllable photonic crystals consisting of the superparamagnetic Fe_3O_4 nanocrystal clusters in a solidified polymer matrix by photopolymerization, while we found that utilizing high-temperature hydrolysis method to prepare magnetic colloidal nanocrystal clusters need to carefully control reaction conditions [15]. Therefore, a new simple method for producing magnetic building block will be desired and important, through which the synthetic conditions can be easily controlled and products can be conveniently obtained.

Herein we report the synthesis of water dispersible oleic acid (OA) emulsion droplets containing magnetite (Fe_3O_4)-OA colloidal nanoparticles with size of approximately 100 nm as building block to self-assemble magnetic controlled photonic crystals. The emulsions droplets show superparamagnetic behavior and high magnetic loading fraction, and can be directly employed for constructing colloidal photonic crystals with tunable stop bands that can be moved in the visible spectral region.

2. Experimental section

The magnetic emulsion of OA containing Fe_3O_4-OA (Fe_3O_4-OA@OA) was synthesized in aqueous phase. Firstly superparamagnetic Fe_3O_4 core nanoparticles were prepared by using chemical co-precipitation reaction [16]. $FeCl_3 \cdot 6H_2O$ (2.70 g) and $FeCl_2 \cdot 4H_2O$ (1.00 g) were dissolved by deionized water (100 ml) under N_2 gas protection. Ammonia aqueous solution (25%, 3.5 ml) was quickly charged into the solution with vigorous stirring, and the solution was stirred for an additional 3 h at room temperature. The resultant black powder, collected by a ferromagnet and washed three times with deionized water, is desired for Fe_3O_4 core nanoparticles. The Fe_3O_4-OA@OA emulsion was synthesized by using OA and Fe_3O_4 core nanoparticles. The Fe_3O_4 core nanoparticles were mixed with deionized water (100 ml) in a flask, into which surfactant OA (0.61 g) was drop-wise added. The mixture was stirred for 3 h at 80 °C under N_2 gas protection resulting in Fe_3O_4-OA nanoparticles. Then the nanoparticles and remanent OA in water were ultrasonically irradiated for 8 min on an ultrasonic cleaner (100 W, 42 kHz), giving rise to Fe_3O_4-OA@OA emulsion. A magnet with surface magnetic field of 2500 Oe, thickness of 2 cm and diameter of 3 cm was used to close the beaker of emulsion for photonic crystals with

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various structure colors by varying the distance between magnet and beaker.

The products were characterized with a powder X-ray diffractometer (XRD) (Bruker, D8 Focus) using a Cu Kα radiation ($\lambda = 1.5406$ Å), and transmission electron microscope (TEM) (Hitachi H-8100) with an accelerating voltage of 200 kV. The size distribution of emulsion was performed by a dynamic light scattering method using an NICOMP 380 ZLS (Particle Sizing System Co.). Magnetic characterization was conducted on a vibrating sample magnetometer (VSM) (LDJ, 9600-1) at 300 K. The reflection spectra of photonic crystals were recorded by UV-3100 spectrophotometer (Shimadzu Co.)

3. Results and discussion

The Fe_3O_4 core nanoparticles were synthesized by using chemical co-precipitation reaction. OA was selected as surfactant agent to synthesize Fe_3O_4-OA, because of the strong coordination of carboxylate groups with iron cations on the magnetite surface, and meanwhile an oil in water emulsion droplets with OA as shell was prepared. For forming emulsion of OA and its esters the ultrasonic treatment as an efficient method have been proved [17], and ultrasonic treatment also can prepare emulsion Fe_3O_4-OA@OA because the surface properties of Fe_3O_4-OA nanoparticles is similar to OA.

The TEM images of the Fe_3O_4 core and Fe_3O_4-OA nanoparticles, and Fe_3O_4-OA@OA emulsion are shown in Fig. 1. In these images the Fe_3O_4 particles could be clearly observed with nearly same average particle size, although not homogeneous, around 10 nm. Unlike Fe_3O_4 core and Fe_3O_4-OA nanoparticles the nanoparticles in Fe_3O_4-OA@OA emulsion are coated by OA layer, which is semitransparent in TEM image (Fig. 1c). From the TEM image of emulsion a dendrimer-shaped emulsion was observed, and the separate droplets could not be observed. But a size distribution of emulsion dispersed in water shows a dominant size at 80–110 nm, and a minor size at 4000–5000 nm (Fig. 1d). We suggest that the dendrimer-shaped emulsion in TEM is from flocculation or aggregation of droplet during the preparation of the TEM sample.

XRD curves (Fig. 2) of core, OA modified and emulsion particles exhibit strong same reflection peaks in the 2θ region of 10°–80°. The identical peaks could be assigned to originate from reflections by (220), (311), (400), (422), (511), (440) and (553) planes of Fe_3O_4 crystals, matching well with its standard cubic inverse spinel structure [18]. These results confirm that the particles are indeed in the crystalline status of Fe_3O_4. In other words, Fe_3O_4-OA@OA emulsion has been obtained through the above technical sequence.

The magnetic properties of the Fe_3O_4, Fe_3O_4-OA nanoparticles, and Fe_3O_4-OA@OA emulsion were investigated with a VSM at 300 K. Their hysteresis loops were illustrated in Fig. 3. The remanence (0.17–0.29 emu/g) and the coercivity (3.1 Oe) were negligible for three products (inset in Fig. 3), indicating that the emulsification does not affect superparamagnetic properties of the nanoparticles. The saturation magnetization was determined to be 66.1, 59.8, and 48.1 emu/g for Fe_3O_4, Fe_3O_4-OA nanoparticles, and Fe_3O_4-OA@OA emulsion, respectively. From the saturation magnetization values a magnetic mass loading fraction in emulsion droplet of 72% could be calculated.

Under external magnetic field the Fe_3O_4-OA nanoparticles as magnetic active component to drive micromachine have been demonstrated [19–23]. For single droplet of emulsion the magnetic moment μ can be determined by the Langevin paramagnetic function: $M(x) = N\mu[\coth x - (1/x)]$, where $x = mH/k_BT$, N is the number of particles, H the applied field, k_B the Boltzmann constant, and T the absolute temperature. According to the previous calculation μ dramatically increases in the aggregation form of particles, indicating that emulsion droplets would have much stronger response to external field than a single nanoparticle [14].

After the Fe_3O_4-OA@OA emulsion was obtained in deionized water, the emulsion droplets in the beaker readily self-assemble into colloidal

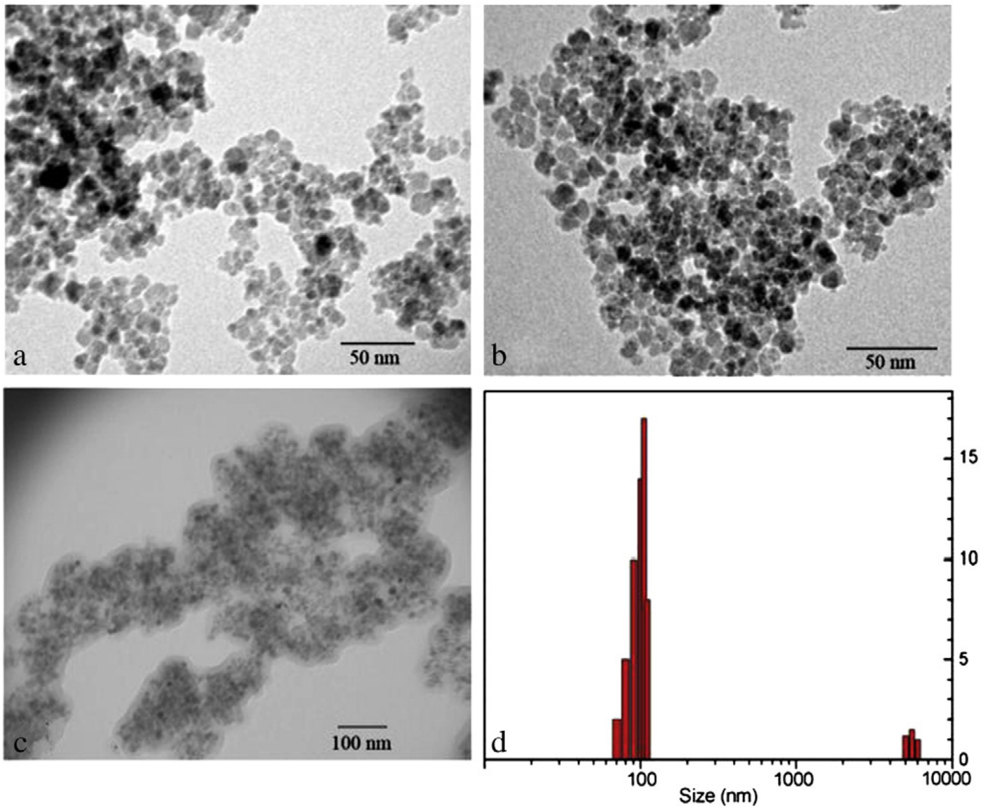

Fig. 1. Characteristics of synthesized products: (a) TEM image of Fe_3O_4 core nanoparticles, (b) TEM image of Fe_3O_4-OA nanoparticles, (c) TEM image of Fe_3O_4-OA@OA emulsion and (d) size distribution of Fe_3O_4-OA@OA emulsion.