

## Non-aqueous synthesis of water-dispersible $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$ core-shell nanoparticles

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2011 Nanotechnology 22 055701

(<http://iopscience.iop.org/0957-4484/22/5/055701>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 163.152.21.57

The article was downloaded on 23/12/2010 at 01:34

Please note that [terms and conditions apply](#).

# Non-aqueous synthesis of water-dispersible $\text{Fe}_3\text{O}_4\text{--Ca}_3(\text{PO}_4)_2$ core-shell nanoparticles

HongLing Liu<sup>1</sup>, JunHua Wu<sup>2</sup>, Ji Hyun Min<sup>3</sup>, Peng Hou<sup>1</sup>, Ah-Young Song<sup>3</sup> and Young Keun Kim<sup>2,3</sup>

<sup>1</sup> Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, People's Republic of China

<sup>2</sup> Pioneer Research Center for Biomedical Nanocrystals, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Korea

<sup>3</sup> Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Korea

E-mail: [feitianshenhu@yahoo.com](mailto:feitianshenhu@yahoo.com) and [ykim97@korea.ac.kr](mailto:ykim97@korea.ac.kr)

Received 6 October 2010, in final form 17 November 2010

Published 22 December 2010

Online at [stacks.iop.org/Nano/22/055701](http://stacks.iop.org/Nano/22/055701)

## Abstract

The  $\text{Fe}_3\text{O}_4\text{--Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles were prepared by one-pot non-aqueous nanoemulsion with the assistance of a biocompatible triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO-PPO-PEO), integrating the magnetic properties of  $\text{Fe}_3\text{O}_4$  and the bioactive functions of  $\text{Ca}_3(\text{PO}_4)_2$  into single entities. The  $\text{Fe}_3\text{O}_4$  nanoparticles were pre-formed first by thermal reduction of  $\text{Fe}(\text{acac})_3$  and then the  $\text{Ca}_3(\text{PO}_4)_2$  layer was coated by simultaneous deposition of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$ . The characterization shows that the combination of the two materials into a core-shell nanostructure retains the magnetic properties and the  $\text{Ca}_3(\text{PO}_4)_2$  shell forms an hcp phase ( $a = 7.490 \text{ \AA}$ ,  $c = 9.534 \text{ \AA}$ ) on the  $\text{Fe}_3\text{O}_4$  surface. The magnetic hysteresis curves of the nanoparticles were further elucidated by the Langevin equation, giving an estimation of the effective magnetic dimension of the nanoparticles and reflecting the enhanced susceptibility response as a result of the surface covering. Fourier transform infrared (FTIR) analysis provides the characteristic vibrations of  $\text{Ca}_3(\text{PO}_4)_2$  and the presence of the polymer surfactant on the nanoparticle surface. Moreover, the nanoparticles could be directly transferred to water and the aqueous dispersion-collection process of the nanoparticles was demonstrated for application readiness of such core-shell nanostructures in an aqueous medium. Thus, the construction of  $\text{Fe}_3\text{O}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  in the core-shell nanostructure has conspicuously led to enhanced performance and multi-functionalities, offering various possible applications of the nanoparticles.

## 1. Introduction

Magnetic nanoparticles are of interest for uses in biomedical applications, to manipulate or transport carriers to a specific site by applying an external magnetic field [1–3]. In particular, magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles hold a unique position. This magnetic material exhibits many fascinating phenomena such as charge ordering, mixed valency, and a metal-insulator transition known as the Verwey transition [4]. For its exceptional biocompatibility,  $\text{Fe}_3\text{O}_4$  including other forms of iron oxide nanoparticles has been marked out for its biomedical

relevance [5–7]. In the meantime, calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) and related compounds, as important bioactive materials, have found a variety of applications [7–11]. For instance,  $\text{Ca}_3(\text{PO}_4)_2$  is favored as a DNA transfection vehicle owing to its immediate take-up during preparation in the presence of DNA molecules [7, 8, 12, 13]. Nevertheless, the transfection efficiency is usually not in a competitive position to commercially available transfection agents based on polymers and liposomes. Nano-engineering the two materials in the configuration of the magnetic nanoparticles covered with a thin  $\text{Ca}_3(\text{PO}_4)_2$  shell, the ensuing core-shell nanostructure

would exercise both magnetic and bioactive functions in concert, providing the desired multi-functionality [7, 14, 15]. Such a structural nano-assembly can have the extra advantages of protecting the core nanoparticles from oxidation, dodging direct contact between biological tissues and the core nanoparticle material, offering enhanced performance, and affording an easy, effective chemical process.

In addition, a biofriendly, hydrophilic, and functionalizable surface is actively sought for biomedical uses and is usually achieved through a second step of surface modification [16, 17]. In our research, high-quality nanoparticles could be obtained by nanoemulsion methods, in particular using biocompatible, hydrophilic polymer surfactants such as poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO-PPO-PEO) and poly(vinylpyrrolidone) (PVP) [14, 15, 18, 19]. In this work we aim to combine the magnetic properties of  $\text{Fe}_3\text{O}_4$  and the functions of  $\text{Ca}_3(\text{PO}_4)_2$  into a single entity for potential applications and we report the synthesis and characterization of water-dispersible  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles by one-pot non-aqueous nanoemulsion assisted by PEO-PPO-PEO [15, 18–20]. The analysis shows the combination of the two materials into a core-shell nanostructure retaining the magnetic properties, and the  $\text{Ca}_3(\text{PO}_4)_2$  shell forms an hcp phase on the surface of the seeding  $\text{Fe}_3\text{O}_4$  nanoparticles. The magnetic hysteresis curves of the nanoparticles were further fitted by the Langevin equation, obtaining the effective magnetic dimensions of the nanoparticles which reveal the enhanced susceptibility as a consequence of the surface covering. The FTIR analysis shows the fingerprint vibrations of  $\text{Ca}_3(\text{PO}_4)_2$  and the presence of the polymer surfactant on the nanoparticle surface. Furthermore, the nanoparticles could be directly transferred to water and an aqueous dispersion-collection process of the nanoparticles was demonstrated for application readiness of such core-shell nanostructures in aqueous medium.

## 2. Experimental details

### 2.1. Materials

The precursors used for the one-pot non-aqueous nanoemulsion synthesis of water-dispersible  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles assisted by PEO-PPO-PEO include iron (III) acetylacetonate ( $\text{Fe}(\text{acac})_3$ , 99.9%), calcium acetate hydrate ( $\text{Ca}(\text{ac})_2$  or  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ , 99.99%), the PEO-PPO-PEO triblock copolymer (Pluronic P-123,  $M_n = 5800$ ) as the surfactant, and 1,2-hexadecanediol ( $\text{C}_{14}\text{H}_{29}\text{CH}(\text{OH})\text{CH}_2(\text{OH})$ , 90%) as the reducing agent, all of which were purchased from Aldrich (Steinheim, Germany). Phosphoric acid (85%) and ammonium hydroxide (28–30%) were procured from Baker (Ward Hill, MA, USA) for production of ammonium phosphate ( $(\text{NH}_4)_3\text{PO}_4$ ). Additional chemicals comprise octyl ether ( $\text{C}_8\text{H}_{17}\text{OC}_8\text{H}_{17}$ , 99%, Alfa) and solvents such as hexane and ethanol. All other materials were purchased from Aldrich (Phillipsburg, NJ, USA) and were used as-received.

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$ core-shell nanoparticles

The  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles were prepared by controlled sequential synthesis in which a  $\text{Ca}_3(\text{PO}_4)_2$  shell was deposited onto the surface of the  $\text{Fe}_3\text{O}_4$  seeds (cores) in a one-pot process [14, 15]. First, the  $\text{Fe}_3\text{O}_4$  seeding nanoparticles were produced through the thermal reduction of  $\text{Fe}(\text{acac})_3$  (0.5 mmol) dissolved in dioctyl ether (10–20 ml) by 1,2-hexadecanediol (0.6468 g) at 300 °C in the presence of PEO-PPO-PEO (0.7512 g) [15]. Some of the colloidal solution containing the synthesized magnetite nanoparticles was taken out for analysis and the rest, without separation, was mixed with calcium acetate hydrate (3 mmol, 474.5 mg) and ammonium phosphate (2 mmol, 292.1 mg). Magnetic stirring was continued overnight, then the solution was homogenized at 80 °C for 30 min and heated to a high temperature (300 °C) to promote the formation of the  $\text{Ca}_3(\text{PO}_4)_2$  crystalline shell on the magnetite core. After the reaction, the resultant  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles were precipitated by the addition of anhydrous ethanol from the dioctyl ether, separated from the supernatant by centrifugation, and redispersed in ethanol or hexane. The process was typically repeated twice or more to remove the solvent molecules and other residuals from the nanoparticles.

### 2.3. Characterization of the $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$ core-shell nanoparticles

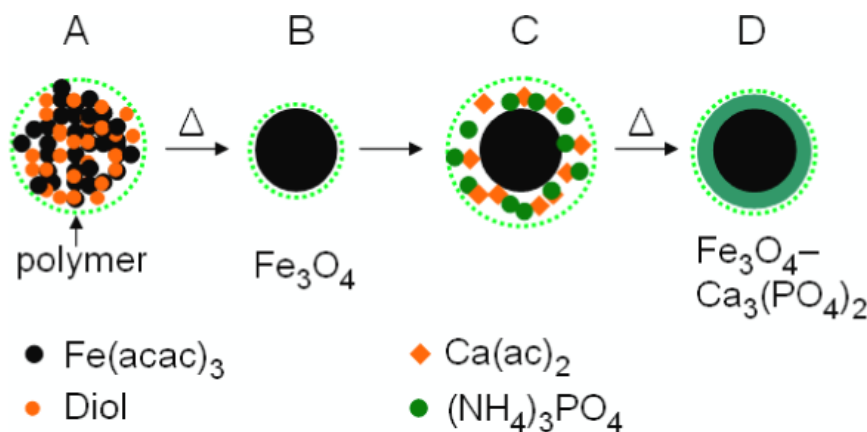
The  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles were examined by FTIR. The washed nanoparticles and the pure PEO-PPO-PEO polymer were crushed with a pestle in an agate mortar, separately. The individually crushed material was then mixed with KBr (IR spectroscopy grade, Merck, Germany) in the proportion of  $\sim 1:100$ . Subsequently, the mixture was compressed into a 2 mm semi-transparent disc for FTIR measurements using an Avatar 360 FTIR spectrometer (Nicolet Company, USA). The morphology and particle size of both seeding and core-shell nanoparticles were analyzed by transmission electron microscopy (TEM, JEM-100II and JEOL 2010F), whereas the crystal structure of the nanoparticles was studied by x-ray diffractometry (XRD, Bruker M18XCE or X'Pert Pro,  $\lambda = 1.54056 \text{ \AA}$ ) and high-resolution TEM/selected-area electron diffraction (HRTEM/SAED, JEOL 2010F). In addition, magnetic characterization was performed on the dried samples to evaluate the magnetic properties of the nanoparticles at room temperature by a vibrating sample magnetometer (VSM, Lakeshore 7300).

### 2.4. Magnetic analysis on the hysteresis curves of the $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$ core-shell nanoparticles

The Langevin equation was employed to analyze the hysteresis curves of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles, in comparison to the seeding  $\text{Fe}_3\text{O}_4$  nanoparticles.

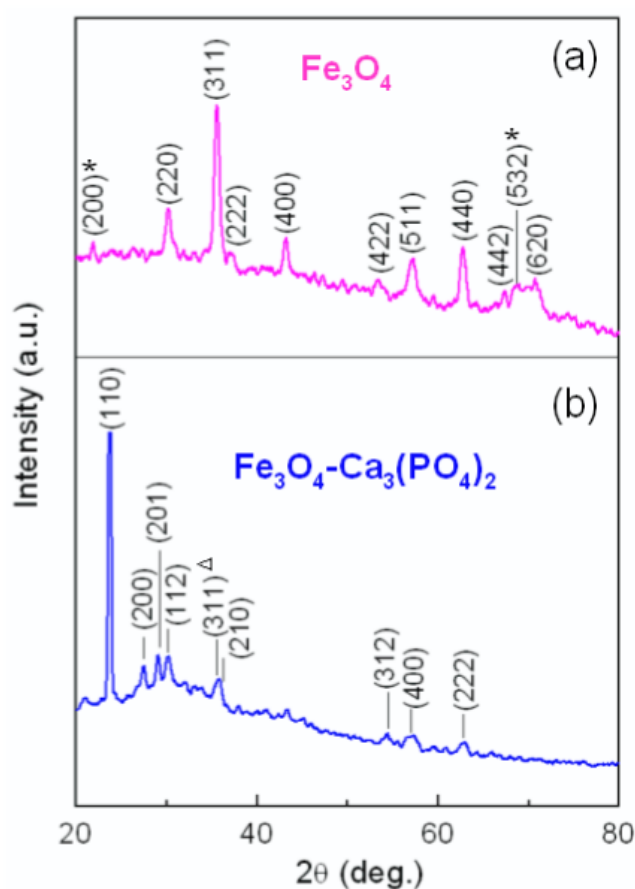
## 3. Results and discussion

As illustrated in scheme 1, the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles were prepared by the controlled sequential



**Scheme 1.** Schematic route for the growth of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles in the nano-micelles formed by the PEO-PPO-PEO macromolecules.

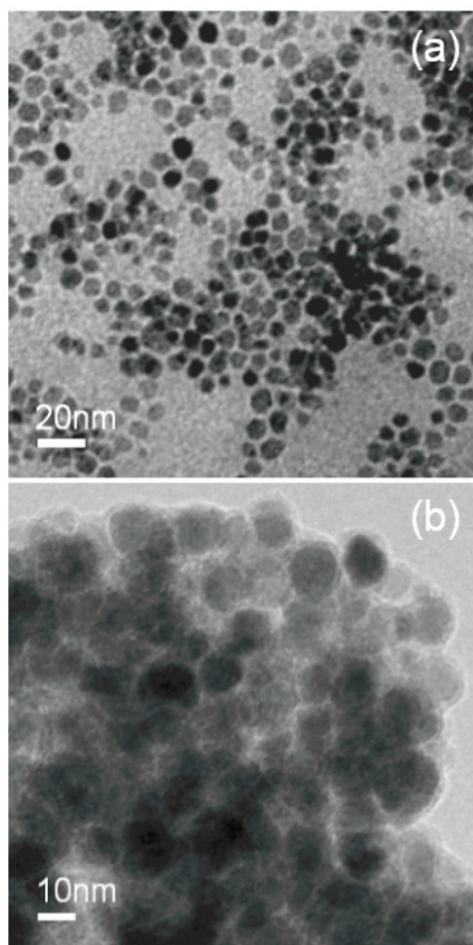
synthesis of depositing a  $\text{Ca}_3(\text{PO}_4)_2$  shell onto the surface of the pre-formed  $\text{Fe}_3\text{O}_4$  seeds (cores) [15]. First, the iron precursor and 1,2-hexadecanediol under magnetic stirring and steady heating from room temperature to 125 °C were mixed with the polymer surfactant molecules in the solvent of octyl ether to form the nano-micelles, as described in stage A. Then, the temperature was rapidly raised to 300 °C to generate the  $\text{Fe}_3\text{O}_4$  seeding nanoparticles through the thermal reduction of  $\text{Fe}(\text{acac})_3$ , as indicated in stage B. Subsequently, calcium acetate and ammonium phosphate were added to the solution and homogenized overnight under magnetic stirring, allowing diffusion of the  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$  and  $(\text{NH}_4)_3\text{PO}_4$  molecules into the nano-micelles for coprecipitation, as depicted in stage C. Further homogenization was performed at 80 °C for a short time. Afterward, the temperature was elevated quickly to 300 °C to guarantee the robust formation of the  $\text{Ca}_3(\text{PO}_4)_2$  crystalline shell on the  $\text{Fe}_3\text{O}_4$  surface, as shown in stage D. After the reaction, the resultant  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles were separated from the supernatant and purified for further analysis. The microstructure and grain size of both  $\text{Fe}_3\text{O}_4$  seeds and  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  nanoparticles were acquired by XRD and TEM. Figure 1(a) represents the diffraction pattern obtained from the cubic inverse spinel structure of the synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles as the seeds, with the major peaks matching to the standard diffraction peaks of the corresponding bulk material (JCPDS no. 88-0315). The minor peaks, (200) and (532) as labeled by the stars, are anomalous scatterings due to the nanosizing effect which could lead to an incomplete extinction of the forbidden diffractions in the perfect lattices, particularly as a consequence of the limited dimension, ensuing defects, and nano-faceting [21]. In figure 1(b), the coating of the  $\text{Ca}_3(\text{PO}_4)_2$  layer by the simultaneous precipitation of  $\text{Ca}^{+2}$  and  $\text{PO}_4^{3-}$  onto the  $\text{Fe}_3\text{O}_4$  core nanoparticles yields diffraction peaks arising from  $\text{Ca}_3(\text{PO}_4)_2$ . The diffraction pattern can be properly indexed to a hexagonal phase (hcp) of  $\text{Ca}_3(\text{PO}_4)_2$  with the crystallographical parameters of  $a = 7.490 \text{ \AA}$  and  $c = 9.534 \text{ \AA}$ . Obviously, the distinct peaks show that the  $\text{Ca}_3(\text{PO}_4)_2$  layer deposited on the magnetite core is in a highly crystalline state. In contrast, the diffractions reflecting the  $\text{Fe}_3\text{O}_4$  core are much diminished but barely recognizable at



**Figure 1.** XRD analysis of  $\text{Fe}_3\text{O}_4$  seeds and  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles. (a) The pattern for  $\text{Fe}_3\text{O}_4$ . Anomalous reflections are marked by the stars. (b) The pattern for  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$ . The concomitant (311)  $\text{Fe}_3\text{O}_4$  reflection is labeled by the triangle.

the position of the (311) diffraction, the strongest peak in the bulk magnetite. This result is due to the shielding effect from the formation of the  $\text{Ca}_3(\text{PO}_4)_2$  layer on the  $\text{Fe}_3\text{O}_4$  surface and indicates a core-shell nanostructure [15]. We remark that the peak at the position of 30.18° was assigned to (112) hcp- $\text{Ca}_3(\text{PO}_4)_2$ , rather than (220)  $\text{Fe}_3\text{O}_4$ , since hcp- $\text{Ca}_3(\text{PO}_4)_2$

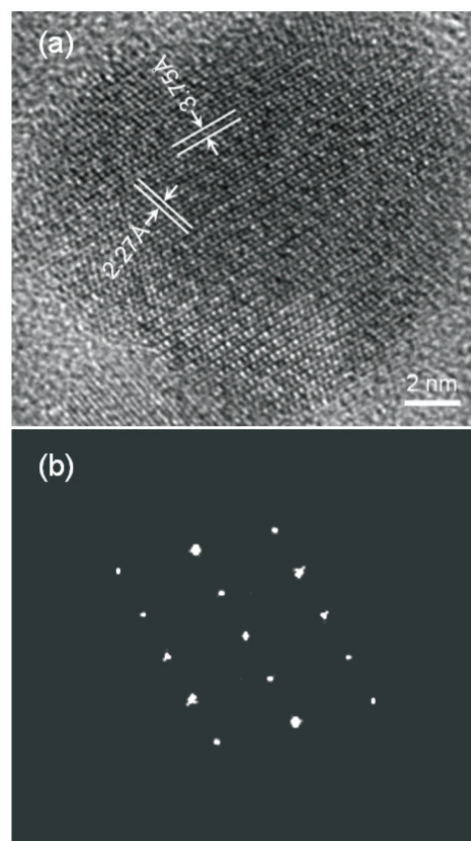




**Figure 2.** Bright-field TEM image analysis of the nanoparticles. (a)  $\text{Fe}_3\text{O}_4$  seeding nanoparticles. (b)  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles.

overall is a dominant phase in the diffraction pattern and, with reference to the weak presence of the strongest (311) peak from  $\text{Fe}_3\text{O}_4$ , the contribution of the peak (220) from  $\text{Fe}_3\text{O}_4$  is relatively minimal (compare figures 1(a) and (b)). In addition, comparing the positions of the  $\text{Fe}_3\text{O}_4$  peaks from the pristine and core-shell nanoparticles in the diffraction patterns shows no evidence of peak shifting, suggestive of diminutive impact on the magnetic core structure from the  $\text{Ca}_3(\text{PO}_4)_2$  coating on the  $\text{Fe}_3\text{O}_4$  surface. Based on the full width at half maximum (FWHM) of the (110) peak of  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles by the Scherrer equation, moreover, the average particle size of the nanoparticles is estimated to be  $\sim 13.5$  nm, supposing that the broadening of the peaks in the XRD pattern is predominantly due to the finite size of the nanoparticles [22]. The evaluation is reasonably consistent with the TEM observation discussed below.

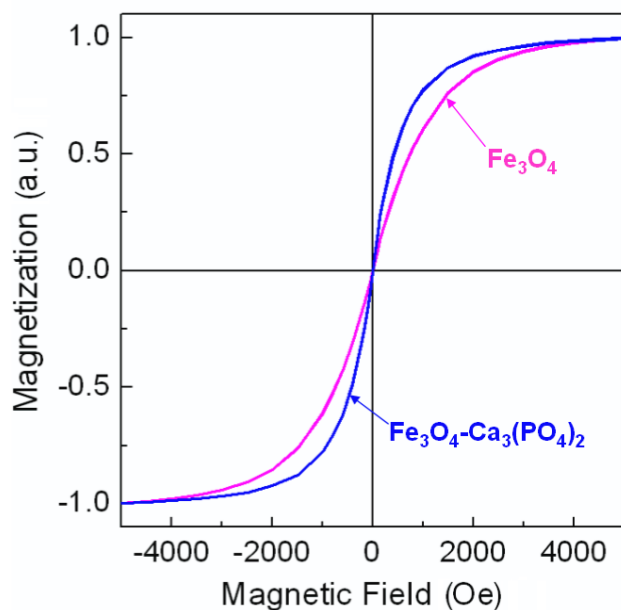
The TEM microimages show that the spherical shape of the  $\text{Fe}_3\text{O}_4$  seeds (figure 2(a)) is retained by the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles (figure 2(b)). It is found that the core  $\text{Fe}_3\text{O}_4$  nanoparticles have an average diameter of  $\sim 8.5$  nm, with a narrow particle size distribution (figure 2(a)), while the particle size of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles increases and yields a nanoshell of  $\sim 3$  nm in



**Figure 3.** High-resolution TEM image and its Fourier transform of an individual  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticle.

thickness on the average, signifying the formation of a shell in the core-shell nanoparticles (figure 2(b)). Indeed, the core-shell nanostructure is clearly demonstrated in figure 2(b).

Figure 3(a) shows the high-resolution TEM image of a single  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticle coated by PEO-PPO-PEO. Evidently, the distinct fringe lattices run almost uniformly over the entire nanoparticle, indicative of the single-crystallinity of the nanoparticle. As labeled, the spacing of  $3.75$  Å corresponds to the (110) reflection of the  $\text{Ca}_3(\text{PO}_4)_2$  hexagonal phase, whereas the lattices of the  $2.27$  Å spacing are assigned to the (203) reflection of the same phase. Interestingly, the (220) lattices are discernible in the image. The related fast Fourier transform (FFT) of the lattice image, as shown in figure 3(b), corroborates once more the single-crystallinity of the individual nanoparticle. Nonetheless, the lattices showing the core material of  $\text{Fe}_3\text{O}_4$  are not apparent in the high-resolution imaging, which is consistent with the XRD outcome discussed above and attributed to the preferential scattering of the shell material rather than the core material. Similar phenomena have been observed in other core-shell nanostructures [15]. As the aperture is large to encompass more than one nanoparticle, in addition, the selected-area electron diffraction (SAED) produces a powder pattern, illustrating the superposition of diffractions of the disoriented  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticle. We note that valuable information of nano-diffraction will be acquirable in future work from a single nanoparticle to



**Figure 4.** Hysteresis curves of the  $\text{Fe}_3\text{O}_4$  seeds and  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles.

(This figure is in colour only in the electronic version)

assist direct clarification of the nano-architecture of such nanoparticles.

As shown in figure 4, the magnetic properties of the  $\text{Fe}_3\text{O}_4$  and core-shelled  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  nanoparticles were comparatively recorded in the individual hysteresis curves at room temperature obtained by VSM. It is clear from the curves that both nanoparticles behave superparamagnetically at room temperature. Moreover, it is found that the  $\text{Fe}_3\text{O}_4$  sample is hard to saturate, in comparison with the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  one. Nonetheless, the susceptibility of the core-shelled  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  nanosystem is considerably enhanced after the nanoshell coating, a phenomenon as observed in other core-shelled magnetic nanoparticles [15]. This outcome has a direct impact on applications in such areas as biomedicine, where higher susceptibility of magnetic specimens boosts the performance of operation [5, 6]. We emphasize that magnetic nanoparticles behaving superparamagnetically hold great promise in biological and medical fields for they can be simply and reversibly manipulated by an external magnetic field, as demonstrated below.

Different from the corresponding bulk ferromagnetic materials that are able to easily form multiple crystal and magnetic domains, the magnetic nanoparticles obtained from the nanoemulsion synthesis can assume single-crystalline and thereby magnetic monodomains and have zero coercivity given that the thermal energy is higher than the anisotropy energy of one of the nanoparticles as a result of dimension shrinkage. Alternatively, the nanoparticles in the form of magnetic monodomains act like single giant spins. Therefore, the corresponding superparamagnetic magnetization is describable by a Brillouin function or Langevin function on assemblies of magnetic nanoparticles with freely rotating magnetic

moments [18, 23],

$$\frac{M}{M_s} = \coth(\alpha) - \frac{1}{\alpha} \quad (1)$$

where

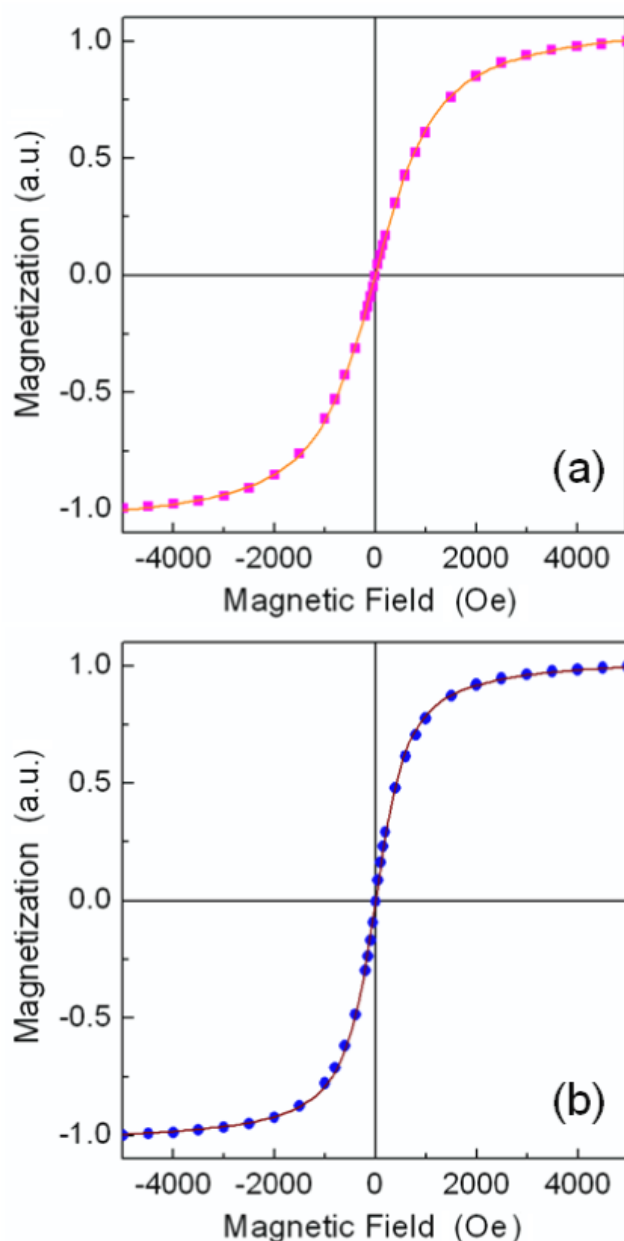
$$\alpha = \frac{\mu H}{k_B T} \quad (2)$$

and  $M/M_s$  is the magnetization normalized to the saturation magnetization,  $H$  the external applied magnetic field,  $T$  the temperature, and  $k_B$  the Boltzmann constant. The magnetic moment  $\mu$  of the individual particles concerned can be obtained from fitting of the Langevin function to the experimental data. Of significance, it is possible to estimate the effective dimension of magnetic nanoparticles and to distinguish superparamagnetic behavior through the fitting of the Langevin function to the magnetization curves. For the former, the diameter of a nanoparticle,  $d$ , is related to the corresponding magnetic moment  $\mu$  by

$$\mu = M_s \frac{\pi}{6} d^3. \quad (3)$$

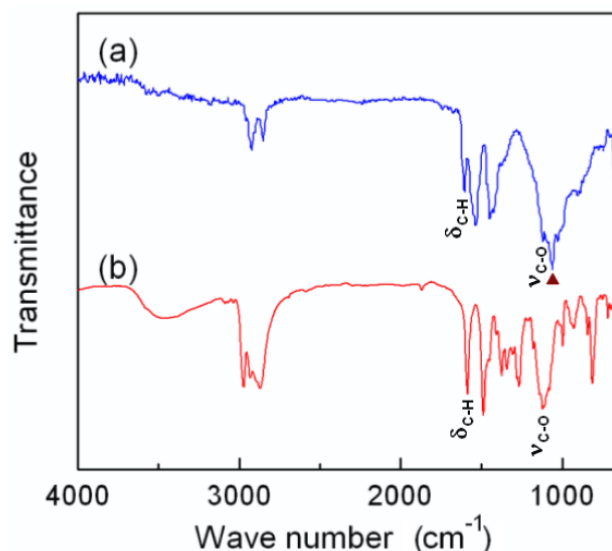
For the latter, deviation from the Langevin function indicates the nature of magnetic coupling among the nanoparticles when a monosized system or a single magnetic phase is considered. As shown in figure 5, the hysteresis curves of both  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  nanoparticles are well fitted to equation (1). In the figure, the fittings are represented by the curves and the experimental data are given in dots, separately. In terms of the fit, the parameter  $\beta = k_B T / \mu$  is estimated to be  $465.5 \pm 3.6$  Oe for the  $\text{Fe}_3\text{O}_4$  nanoparticles and  $244.1 \pm 3.3$  Oe for the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles, respectively. Using the bulk value of the saturation magnetization of  $M_s = 6000$  G at  $20^\circ\text{C}$  for the magnetic moment of  $\text{Fe}_3\text{O}_4$  in the nanoparticles [24] and applying equation (3), an effective nanoparticle diameter is estimated to be 7.0 nm for the  $\text{Fe}_3\text{O}_4$  nanoparticles and 8.7 nm for the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles, correspondingly. Clearly, the effective magnetic volume is increased from the  $\text{Fe}_3\text{O}_4$  nanoparticles to the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles after the  $\text{Ca}_3(\text{PO}_4)_2$  coating. The effective magnetic diameter of the  $\text{Fe}_3\text{O}_4$  nanoparticles is reduced but still comparable to their physical dimension from the TEM counting, whereas the effective magnetic diameter of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles is almost equivalent to the corresponding physical dimension of the core material in the bulk state, indicating the great enhancement in magnetic response. In addition, the nearly perfect fit proves the well-defined superparamagnetic behavior of both  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles at room temperature and strongly suggests the probable existence of a single magnetic phase.

The  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles were further examined by FTIR, as shown in figure 6(a). In the figure, the strong absorption at  $\sim 1060.0 \text{ cm}^{-1}$  as indicated by the solid triangle clearly reveals the vibration of the phosphate [25]. The other two characteristic peaks at  $\sim 1600.0$  and  $\sim 1110.0 \text{ cm}^{-1}$  may be assigned to the C-H bending vibration and the C-O-C stretching vibration

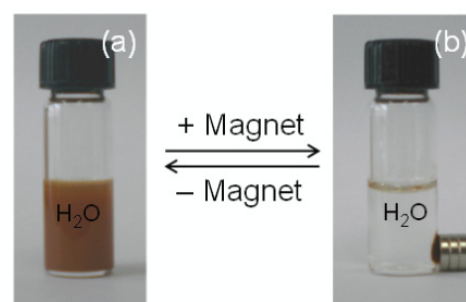


**Figure 5.** Analysis of the hysteresis curves for the  $\text{Fe}_3\text{O}_4$  seeds (a) and  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles (b). Experimental data are shown by dots and the fitting results by curves.

of the ether bonding from the polymer molecules on the nanoparticles, but red-shifted for the former and blue-shifted for the latter relative to the corresponding positions of  $\sim 1587.2$  and  $\sim 1120.5\text{ cm}^{-1}$  in the pure polymer (figure 6(b)), which could be attributed to changes in the elastic constants of the bonds of the macromolecules sitting on the nanoparticle surface of high curvature owing to the small nanoparticle size and interactions between the macromolecules and the nanoparticle surface [18, 20]. As the redundant PEO-PPO-PEO molecules were removed by the purification procedure, the phenomena indicate the covering of the PEO-PPO-PEO macromolecules on the surface of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles [18]. Owing to the PEO-PPO-PEO



**Figure 6.** FTIR spectra of (a) the PEO-PPO-PEO-coated  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles and (b) the pure PEO-PPO-PEO molecules. The triangle indicates the vibration position of  $\text{PO}_4^{3-}$ , together with the  $\nu_{\text{C-O}}$  and  $\delta_{\text{C-H}}$  bands from the polymer.



**Figure 7.** Photoimages of aqueous dispersion and magnetic manipulation of the polymer-coated  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles. (a) Yellowish brown, homogeneous dispersion of the nanoparticles in double-distilled (DD) water. (b) The clear, transparent solution of the nanoparticles after magnetic separation.

capping, therefore, the surfaces of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles are hydrophilic, which enables an easy transfer of the nanoparticles to an aqueous medium without additional surface decoration, as proof of the concept see figure 7.

We come to illustrate functioning of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles as potential nano-actuators and nano-transporters. The superparamagnetic attribute of the  $\text{Fe}_3\text{O}_4$  core in the core-shell nanoparticles (figure 4) enables rapid efficient separation and vector transportation. As mentioned above, the polymer-coated  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles could be readily transferred to an aqueous medium without more surface modification, as shown in figure 7(a). Under the influence of an external magnetic field, the nanoparticles change from a yellowish brown, homogeneous dispersion in double-distilled (DD) water (figure 7(a)) to a clear, transparent solution, with



all nanoparticles collected by a magnet (figure 7(b)). The collected nanoparticles can be simply and reversibly dispersed by agitation after removal of the magnetic field [18].

#### 4. Conclusions

In summary, we have synthesized the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles by the one-pot non-aqueous nanoemulsion process, integrating the magnetic properties of  $\text{Fe}_3\text{O}_4$  and the bioactive functions of  $\text{Ca}_3(\text{PO}_4)_2$  into single entities. The  $\text{Fe}_3\text{O}_4$  nanoparticles were pre-formed first by thermal reduction of  $\text{Fe}(\text{acac})_3$  and then the  $\text{Ca}_3(\text{PO}_4)_2$  nanolayer was coated by simultaneous deposition of  $\text{Ca}^{+2}$  and  $\text{PO}_4^{-3}$ . The combination of the two materials into a core-shell nanostructure retains the magnetic properties, and the  $\text{Ca}_3(\text{PO}_4)_2$  shell forms an hcp phase ( $a = 7.490 \text{ \AA}$ ,  $c = 9.534 \text{ \AA}$ ) on the  $\text{Fe}_3\text{O}_4$  surface. The magnetic hysteresis curves of the nanoparticles were further analyzed by the Langevin equation, showing significantly enhanced effective magnetic dimensions of the  $\text{Fe}_3\text{O}_4\text{-Ca}_3(\text{PO}_4)_2$  core-shell nanoparticles as a result of the surface covering. The FTIR analysis gives the characteristic vibrations of  $\text{Ca}_3(\text{PO}_4)_2$  and the presence of the polymer surfactant on the nanoparticle surface. Moreover, the nanoparticles could be directly transferred to water and the aqueous dispersion-collection process of the nanoparticles was demonstrated for application readiness of such core-shell nanostructures in an aqueous medium. Thus, the construction of  $\text{Fe}_3\text{O}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  in the core-shell nanostructure has led to enhanced performance and multi-functionalities, offering various possible applications of the nanoparticles.

#### Acknowledgments

This work was supported in part by the Scientific and Technological Development Projects, Science and Technology Department of Henan Province, China (Nos 092102210004 and 092300410031), the Natural Science Research Foundation Grants, Education Department of Henan Province, China (Nos 2009A150004 and 2009A150005), the Pioneer Research Center Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology, Korea (No. 2010-0002190), the Industrial Core Technology Development Program funded by the Ministry of Knowledge Economy, Korea (No. 10033183) and the Seoul R&BD Program (No. 10920), Korea.

#### References

- [1] Pankhurst Q A, Thanh N K T, Jones S K and Dobson J 2009 *J. Phys. D: Appl. Phys.* **42** 224001
- [2] Gao J, Gu H and Xu B 2009 *Acc. Chem. Res.* **42** 1097–107
- [3] Duguet E, Vasseur S, Mornet S and Devoisselle J-M 2006 *Nanomedicine* **1** 157–68
- [4] Walz F 2002 *J. Phys.: Condens. Matter* **14** R285–340
- [5] Gupta A K and Gupta M 2005 *Biomaterials* **26** 3995–4021
- [6] Huber D L 2005 *Small* **1** 482–501
- [7] Gil P R, Huhn D, del Mercato L L, Sasse D and Parak W J 2010 *Pharmacol. Res.* **62** 115–25
- [8] Welzel T, Radtke I, Meyer-Zaika W, Heumann R and Epple M 2004 *J. Mater. Chem.* **14** 2213–7
- [9] Dorozhkin S V 2010 *Acta Biomater.* **6** 715–34
- [10] Al-Qasas N S and Rohani S 2005 *Sep. Sci. Technol.* **40** 3187–224
- [11] Kollmann T, Simon P, Carrillo-Cabrera W, Braunbarth C, Poth T, Rosseeva E V and Kniep R 2010 *Chem. Mater.* **22** 5137–53
- [12] Zhang M and Kataoka K 2009 *Nano Today* **4** 508–17
- [13] Kakizawa Y, Miyata K, Furukawa S and Kataoka K 2004 *Adv. Mater.* **16** 699–702
- [14] Liu H L, Hou P, Zhang W X and Wu J H 2010 *Colloids Surf. A* **356** 21–7
- [15] Liu H L, Wu J H, Min J H, Lee J H and Kim Y K 2009 *J. Nanosci. Nanotechnol.* **9** 754–8
- [16] Salgueirino-Maceira V, Liz-Marzan L M and Farle M 2004 *Langmuir* **20** 6946–50
- [17] Hong R, Fischer N O, Emrick T and Rotello V M 2005 *Chem. Mater.* **17** 4617–21
- [18] Liu H L, Hou P, Zhang W X, Kim Y K and Wu J H 2010 *Nanotechnology* **21** 335602
- [19] Liu H L, Sonn C H, Wu J H, Lee K M and Kim Y K 2008 *Biomaterials* **29** 4003–11
- [20] Plank C, Schillinger U, Scherer F, Bergemann C, Remy J-S, Krotz F, Anton M, Lausier J and Rosenecker J 2003 *Biol. Chem.* **384** 737–47
- [21] Liu H L, Ko S P, Wu J H, Jung M-H, Min J H, Lee J H, An B H and Kim Y K 2007 *J. Magn. Magn. Mater.* **310** e815–7
- [22] Cullity B D and Stock S R 2001 *Elements of X-ray Diffraction* (Englewood Cliffs, NJ: Prentice-Hall) pp 167–71
- [23] O'Handley R C 2000 *Modern Magnetic Materials: Principles and Applications* (New York: Wiley) p 91
- [24] Smit J and Wijn H P J 1965 *Ferrites (Physical Properties of Ferrimagnetic Oxides in Relation to Their Technical Applications)* (Eindhoven: Philips's Technical Library) (Tokyo: The Netherlands and Tokyo Electrical Engineering College Press) p 157
- [25] Rehman I and Bonfield W 1997 *J. Mater. Sci., Mater. Med.* **8** 1–4