



## Deposition and characterization of large-scale FePt nanoparticle monolayers on SiO<sub>2</sub>/Si surface

Hanbin Wang<sup>a</sup>, Hao Wang<sup>a,\*</sup>, Fujun Yang<sup>a</sup>, Jun Zhang<sup>a</sup>, Quan Li<sup>b</sup>, Minjie Zhou<sup>b</sup>, Yong Jiang<sup>c</sup>

<sup>a</sup> Faculty of Physics and Electronic Technology, Hubei University, Wuhan 430062, China

<sup>b</sup> Department of Physics, The Chinese University of Hong Kong, Hong Kong, China

<sup>c</sup> School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

### ARTICLE INFO

#### Article history:

Received 23 June 2009

Accepted in revised form 29 September 2009

Available online 5 October 2009

#### Keywords:

FePt nanoparticles

Spin-coating

SiO<sub>2</sub> surface

Monolayer

Particle density

### ABSTRACT

The deposition of uniform monolayers of FePt nanoparticles on macro-scaled SiO<sub>2</sub>/Si substrate was demonstrated by employing a simple spin-coating method. The surface morphology and particle density of the monolayers was studied with high resolution scanning electron microscope. FePt nanoparticle monolayers with different morphology were obtained on SiO<sub>2</sub> surface at length scales of 1.5 cm. The effects of surfactants, colloid concentration, solvents as well as the shape of the nanoparticles on the uniformity of the particle film were investigated. A primary high temperature annealing on the FePt monolayer films resulted in phase transition from the super-paramagnetic phase into the ferromagnetic one, while the monolayer exhibited limited particle-sintering.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Recent advances in solution synthesis allowed the preparation of nanoparticles (NPs) with monodispersed size, well defined shape, ordered assembly as well as size-dependent properties. These nanoparticles have been proposed as building blocks for nanodevice fabrication and processing. The bottom-up assembly of the building blocks into two-dimensional (2D) or 3D architectures has attracted intensive interest in the applications of super-lattice in sensors, biomedicine, magnetic storage media, nano-optoelectronics, and nanoelectronics [1,2]. Methods for the formation of 2D nanostructures include Langmuir–Blodgett (LB) technique [3–6], dip-coating [7–9] and spin-coating method [10,11], all of which involve the self-assembly behavior of the nanoparticles and their adsorption on the solid surface.

Two-dimensional magnetic nanoparticle monolayers are recently regarded as suitable structures for future ultra-high-density magnetic recording [12,13]. L1<sub>0</sub> FePt nanoparticles are favorable choices for the recording bits due to their high magnetization and large uniaxial anisotropy ( $K_u > 5 \times 10^7 \text{ erg/cm}^3$ ) [14]. Though this area is widely studied, most of the attention is devoted to the preparation of the FePt nanostructures and their transition from the magnetic-soft phase into the magnetic-hard one [15–18]. Delivering and assembling them onto a wafer scale substrate still remains a challenge towards real applications.

Several different routes to FePt nanoparticle monolayers have been described in the literatures. For instance, Sun et al. [13] adopted a polymer-mediated dip-coating method by using polyethylenimine to form FePt particle layer on silicon substrate. Though this process enables the deposition of FePt one monolayer at a time over large areas, the monolayer coverage is limited and self-assembly process of the FePt NPs is inhibited by the strong interaction between the nanoparticles and coupling layer. LB technique was also used to fabricate monolayer of 4 nm FePt NPs on glass substrate [19]. However, the homogeneity of the monolayer is not directly observed. Recently, Shukal et al. [20] studied the self-assembled monolayer of 3–4 nm FePt NPs on fluorinated carbon thin film substrate by the spin-coating method. While homogeneous nanoparticle monolayer was found at the length of several millimeters, the function of the fluorinated carbon remains unclear and the enhanced surface roughness bring by the fluorinated carbon layer cannot be neglected [8].

In the present work, we report our effort for the fabrication of FePt nanoparticle monolayers on a large bare SiO<sub>2</sub>/Si substrate (1.5 cm × 1.5 cm) by a controlled spin-coating method. The surface of SiO<sub>2</sub> and the as-synthesized FePt NPs were used without any chemical modification as we try to understand some of the intrinsic limitation of the monolayer formation on certain substrates. In the experiments, both ~6 nm spherical and cubical FePt nanoparticles were synthesized. We have investigated several parameters (surfactants, colloid concentration, solvents, and shape of the nanoparticles) that have effect on the surface morphology and particle density of the nanoparticle monolayers. It is found that the surfactants affect the adsorption behavior of FePt nanoparticles on SiO<sub>2</sub> surface remarkably and are the most important factor in the uniformity and particle density of the particle film. By

\* Corresponding author. Tel.: +86 27 88662550; fax: +86 27 88663390.

E-mail address: [nanoguy@126.com](mailto:nanoguy@126.com) (H. Wang).

optimizing the preparing condition, homogenous FePt nanoparticle monolayers were obtained on SiO<sub>2</sub>/Si substrate at length scales of 1.5 cm. A primary high temperature annealing process was performed on the monolayer film. The resulting FePt monolayers were transformed from the super-paramagnetic phase into the ferromagnetic one with limited nanoparticle-sintering.

## 2. Experimental

The 6 nm spherical FePt nanoparticles were synthesized following the synthesis procedure reported by Liu [15]. In the study, 0.5 mmol platinum acetylacetonate (Pt(acac)<sub>3</sub>) was added to a flask and mixed with 20 ml diocyl ether under a nitrogen atmosphere. After the solution was stirred for 15 min at room temperature, the flask was heated up to 100 °C and then 2 mmol oleic acid, 2 mmol oleylamine and 1.1 mmol Fe(CO)<sub>5</sub> were added. The heat rate was keeping at 5 °C per minute during the synthesis. The solution was heated to reflux temperature for 30 min before cooling to room temperature. The FePt nanocubes were synthesized by modifying the method reported by Sun [21]. In this synthesis, a solution of Pt(acac)<sub>3</sub>, 4 mmol oleic acid, 4 mmol oleylamine and 2 mmol Fe(CO)<sub>5</sub> in benylether were heated to 200 °C for 2 h under the nitrogen protection. The heating rate was also kept at 5 °C per minute before reaching 200 °C.

The chemical washing of FePt nanospheres and nanocubes is similar. After the prepared black solution was cooled to the room temperature, 20 ml ethanol was added into the solution, and the black products were then precipitated by mild centrifugation (3000 rpm). The yellow-brown supernatant was discarded. The precipitate were redispersed in 10 ml hexane and precipitated again with 10 ml ethanol by centrifugation. Further purification of the product was performed by dispersing the product into hexane, precipitating it out with ethanol, and centrifuging. Finally, the purified nanoparticles were dispersed in mixture of 5 mL hexane and 5 mL octane.

A 100 nm thick SiO<sub>2</sub> substrate was made by thermally growing the Si (100) substrate at 900 °C in oxygen environment. To fabricate FePt nanoparticle monolayers on SiO<sub>2</sub>, different concentrations of the FePt colloids were used in the spin-coating process. A drop of FePt colloid was deposited on a clean SiO<sub>2</sub> substrate with size of 1.5 cm × 1.5 cm. After 10 s the spin-coater was accelerated to 2000 rpm in 5 s. Rotation was maintained at this speed for 100 s. Thermal annealing of the particle films was performed in a vacuum chamber with a pressure of 10<sup>-5</sup> Pa. The annealing temperature was kept at 650 °C, with 1 h duration.

The size, shape and composition of nanoparticles were analyzed by transmission electron microscope (TEM, FEI CM120) at an accelerating voltage of 120 kV. The crystallinity of the FePt nanoparticle powder was characterized by X-ray diffraction (XRD, Bruker D5) with CuK<sub>α</sub> radiation. The morphology of the FePt nanoparticle monolayers was analyzed by scanning electron microscope (SEM, FEI Quanta 400 FEG). The magnetic properties of the FePt nanoparticle film were measured by a physical properties measurement system (PPMS).

## 3. Results and discussion

Fig. 1(a) and (b) are the TEM images of the as-synthesized spherical and cubical FePt NPs, respectively. The TEM images reveal that both the spherical and cubical nanoparticles are monodisperse and deposit on the carbon-coated copper grid with fairly uniform area density. The compositions of the FePt particles were determined by energy-dispersive X-ray (EDX). The average composition of the nanospheres and nanocubes are found to be Fe<sub>53</sub>Pt<sub>47</sub> and Fe<sub>50</sub>Pt<sub>50</sub>, respectively. Fig. 1(c) shows the size distribution of as-synthesized FePt NPs that is estimated from randomly selected ~300 NPs from the TEM image. The mean diameter was estimated to be 5.8 nm for the spherical particles and 6.1 nm for the cubical ones. Standard deviation of their size distribution is 8% and 11%. XRD spectra of the as-synthesized FePt nanoparticles are given in Fig. 1(d). The

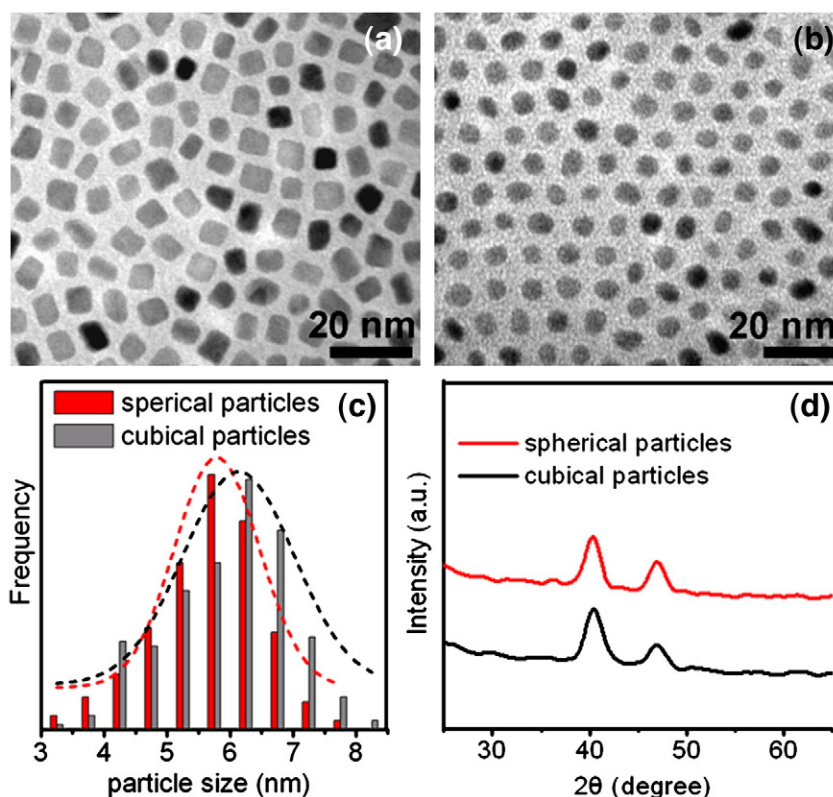
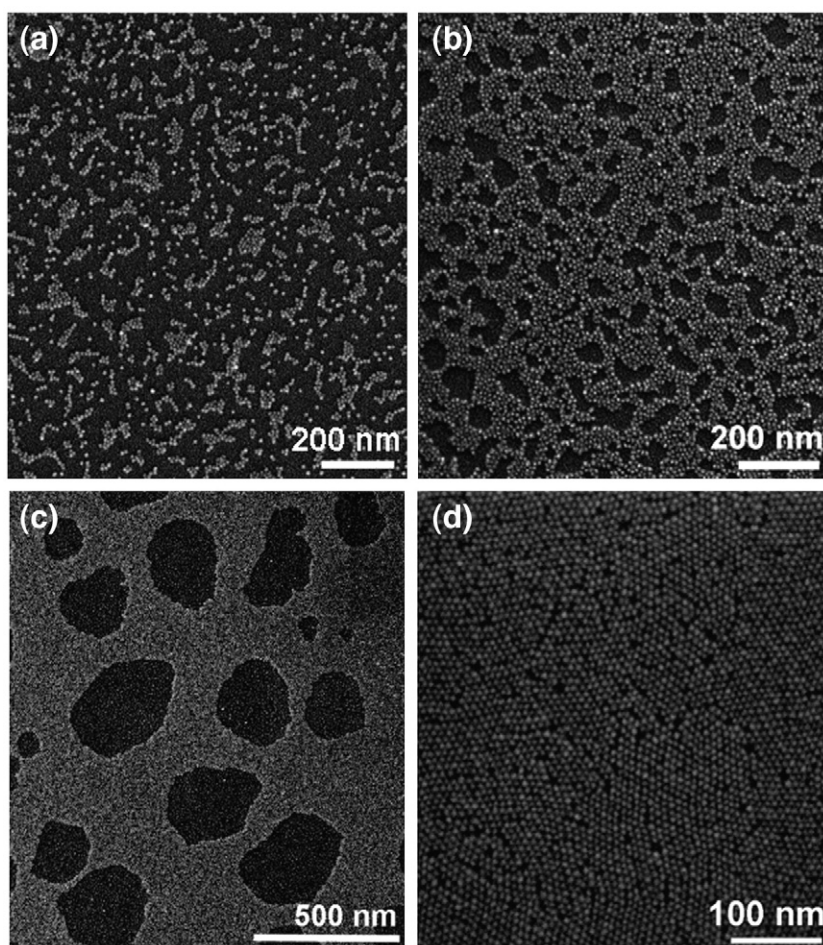


Fig. 1. TEM image of the as-synthesized (a) cubical and (b) spherical FePt nanoparticles assembled on the carbon-coated copper grid. (c) Size distribution of as-synthesized fcc-FePt NPs. (d) XRD spectra of the FePt NPs.



**Fig. 2.** Plan-view HRSEM images of the FePt nanocube monolayers assembled on SiO<sub>2</sub> surface with colloid concentration of (a) 0.5 mg/mL and (b) 2 mg/mL, respectively. (c) A typical SEM image of the spherical FePt particle monolayer assembled on SiO<sub>2</sub> surface. The white region is the compact FePt nanoparticle monolayer and the black region is the SiO<sub>2</sub> substrate. (d) A magnified view of self-assembly of spherical FePt NPs in the compact region of figure (c).

diffraction peaks are clearly broadened due to the reduced particle size in Fig. 1(a) and (b). The peaks can be indexed to (111) and (002) planes of a cubic unit cell, which corresponds to that of fcc structure. The crystal size determined by the Debye–Scherrer equation with XRD data is ~6 nm for both of the two type FePt particles, which is close to the particle sizes observed from TEM images.

The morphology and particle coverage of the FePt monolayers were investigated by high resolution scanning electron microscope (HRSEM). The particle coverage is defined as the ratio of the number of adsorbed particles on the substrate to the theoretical maximum number of close-packed particles on the substrate [7]. Fig. 2 shows the typical SEM images of the self-assembled FePt nanoparticles on SiO<sub>2</sub> substrates with different conditions. Fig. 2(a) is the SEM image of a diluted monolayer film of the FePt nanocubes. As revealed by the image, the nanocubes are well separated on the substrate. The particle coverage is found to be less than 20%. In order to obtain monolayer with higher particle density, FePt nanocube colloids with higher concentration were used in spin-coating while the other conditions were kept unchanged. Fig. 2(b) is the morphology of the FePt nanocube monolayer on SiO<sub>2</sub> with starting colloids concentration equal to ~2 mg/mL. As similar with the diluted one, the FePt nanocubes form a homogenous monolayer on the substrate with enhanced particle coverage. Systematically SEM observation revealed that the morphology is uniform over the whole substrate though ordered assembly is absent in the particle monolayer. The nearest inter-particle distance is found to be less than 3 nm, corresponding to the surfactant layer chemically-adsorbed on the particles [22]. This

indicates that in the self-assembly of FePt nanoparticles on SiO<sub>2</sub>, the thickness of the surfactant layer on particles is the key parameter governing the distance of the particles.

Fig. 2(c) and (d) are HRSEM images of the monolayers of spherical FePt NPs assembled on SiO<sub>2</sub> substrate. Different from those of nanocube monolayers, the films compose some dense areas in which the nanoparticles assembled compactly. However, between the dense areas there always exist some large particle-free gaps at range scale of several hundreds of nanometer. Although a magnified view of the compact area exhibits local ordered assembly of the spherical particles, as shown in Fig. 2(d), such morphology indicates the non-homogenous deposition of the FePt nanoparticles. The existence of the gaps seems common to the monolayer formation on various substrates by dip-coating [8,13] and LB technique [3]. Here, we suggest that the formation of the gaps is related to the weak interaction between the oleic acid/oleylamine passivated particles and the SiO<sub>2</sub> interface. When a droplet of the FePt colloid is cast onto the SiO<sub>2</sub> surface, the wetting properties cause it to diffuse onto the whole substrate. As the solvent evaporates to a liquid thin layer, the Van der Waals attraction and magnetic dipolar–dipolar attraction between the particles make the thin layer shrink on the substrate. This will give rise to the non-homogeneity of the particle monolayer or multilayer on the substrate. Furthermore, under the rotation of the substrate in the spin-coating, the multilayer structure is not stable due to the mobility of the particles and thus the monolayer morphology preserves. Increasing the colloidal concentration could reduce the area of gaps and thus ordered assembly regions could continue over

1  $\mu\text{m} \times 1 \mu\text{m}$ . However, full monolayer coverage is difficult to obtain whatever the colloidal concentration is.

To further investigate the influence of the concentration of surfactants on the formation of the particle monolayer, different amounts of surfactants (oleic acid and oleylamine with molar ratio 1:1) were added to the chemically washed FePt colloid for spin-coating. Fig. 3 is the HRSEM image of the nanoparticle film prepared by adding 0.01 M surfactant to the FePt colloid. Multilayers of the particles are found on the substrate with the particle-free gaps around them. In the multilayer, the particles pile up with some small clusters. If more surfactant is added into the colloid, obvious conglomeration is found on SiO<sub>2</sub> substrate during the spin-coating process. These phenomena indicate that the surfactants strongly influence the deposition of FePt nanoparticles on the SiO<sub>2</sub> surface. The mechanism could be explained as the following: the surfactant oleic acid and oleylamine in the particle colloid exist at two ways [22], 1) chemically-adsorbed on the particle surface; and 2) un-adsorbed molecules dissolved into solvent. The former surfactant stabilizes the nanoparticles in the non-polar solvent and facilitates proper mobility of FePt nanoparticles on the SiO<sub>2</sub> surface. The latter could adsorb onto the substrate and hence prohibit the adsorption of particles on the SiO<sub>2</sub> surface. Therefore, the mobility of the nanoparticles is greatly enhanced due to the reduced interaction energy between the particles and substrate. Under the drive of mechanical rotation, the FePt NPs in the presence of un-adsorbed surfactants are not stable on SiO<sub>2</sub> surface, they conglomerate with each other and form non-homogeneous multilayers on the substrate when the solvent evaporates.

The solvents are also found to be important in the uniformity and morphology of the particle film. Generally, the non-polar solvent hexane can evaporate quickly at room temperature and octane evaporates more slowly than hexane. We found that the use of hexane as the solvent would lead to the discontinuous morphology of the monolayer while the use of octane is unsuitable due to its slow evaporating rate on SiO<sub>2</sub>. In the spin-coating process, we choose the mixture of 1:1 hexane and octane as the solvent. This mixture could evaporate at a suitable rate, allowing more time for the diffuse of the FePt nanoparticles on the substrate surface to form a uniform monolayer.

It's known that the formation of uniform self-assembled films requires that the substrate can be wetted by the solvent [8,23]. The wetting properties of SiO<sub>2</sub> were studied by Truong and Wayner [24]. They noted that the wetting properties are determined by the capillary and van der Waals' force, and experimentally observed that the octane solution wets both Si and SiO<sub>2</sub>. Kim et al. [7] investigated the adsorption behavior of colloidal  $\gamma\text{-Fe}_2\text{O}_3$  NPs in octane solution on three different substrates (Si, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>) by a simple dip-coating method. It was found the morphology of these particle monolayers on the three substrates is similar. These match our results that SiO<sub>2</sub> can

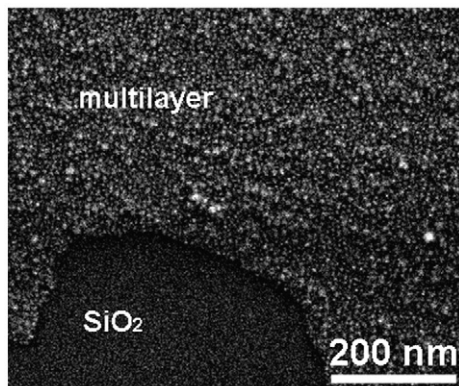


Fig. 3. HRSEM image of the FePt nanoparticle multilayer on SiO<sub>2</sub> substrate formed by adding 0.01 M surfactants in colloid.

be wetted by the mixture of hexane and octane. The different morphology of the cubical and spherical nanoparticle monolayers reflects their adsorption behaviors on SiO<sub>2</sub>. Fig. 4(a) shows a simple scheme of the adsorption of FePt nanoparticles onto SiO<sub>2</sub> surface with different particle shape. If we assume both of the NPs have the same surfactant thickness (1 nm), the adsorption area of a single cubical nanoparticle on the substrate is estimated to be 3 times larger than that of a spherical one. Therefore, the FePt nanocubes seem more stable once deposited on the SiO<sub>2</sub> surface. The enhanced interaction energy between the particles and the substrate ensures the uniformity of the particle film in the spin-coating. Shown in Fig. 4(b) is the relation between the colloid concentration and the estimated particle coverage of the two type monolayers on SiO<sub>2</sub> substrate. The particle coverage increases with the colloid concentration and saturates at certain range. The maximum particle coverage is about 0.67 for the spherical NPs and 0.59 for the cubical ones. Above the saturate range, increasing colloidal concentration does not yield higher particle coverage on the substrate. Some multilayer domains are observed in the nanocube monolayer while the monolayer morphology of the spherical NPs remains.

Before the FePt nanoparticles are used in the ultra-high density magnetic recording, the fcc NPs should be converted into the magnetic-hard fct phase [25]. An annealing temperature of 650 °C is desired to ensure the fcc–fct phase transition, while particle aggregation will happen in the conventional FePt nanoparticle system. It appears that the sintering of FePt NPs depends on sintering conditions. For example, Colak and Hadjipanayis [26] observed that FePt NPs with inter-particle distance of 4 nm on a TEM grid did not sinter when annealed at 800 °C for up to 120 min. Therefore, it is expected that if homogenous monolayer of FePt NPs is formed with proper inter-particle distance, the undesirable sintering of the nanoparticles could be controlled in the high temperature annealing. We found that particle-sintering of the close-packed nanoparticle monolayer is more serious than that of the diluted monolayer under the same annealing conditions. Fig. 5(a) and (b) show plan-view TEM images of the FePt nanocube monolayer on SiO<sub>2</sub> substrate before and after annealed at 650 °C for 1 h in vacuum. Very limited particle-

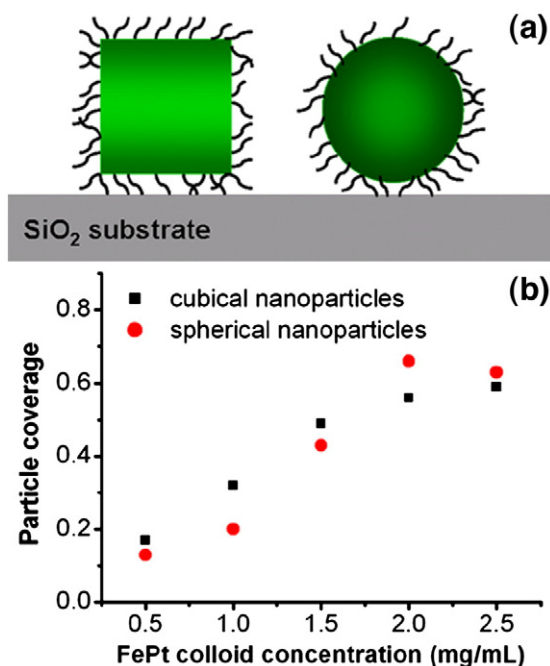
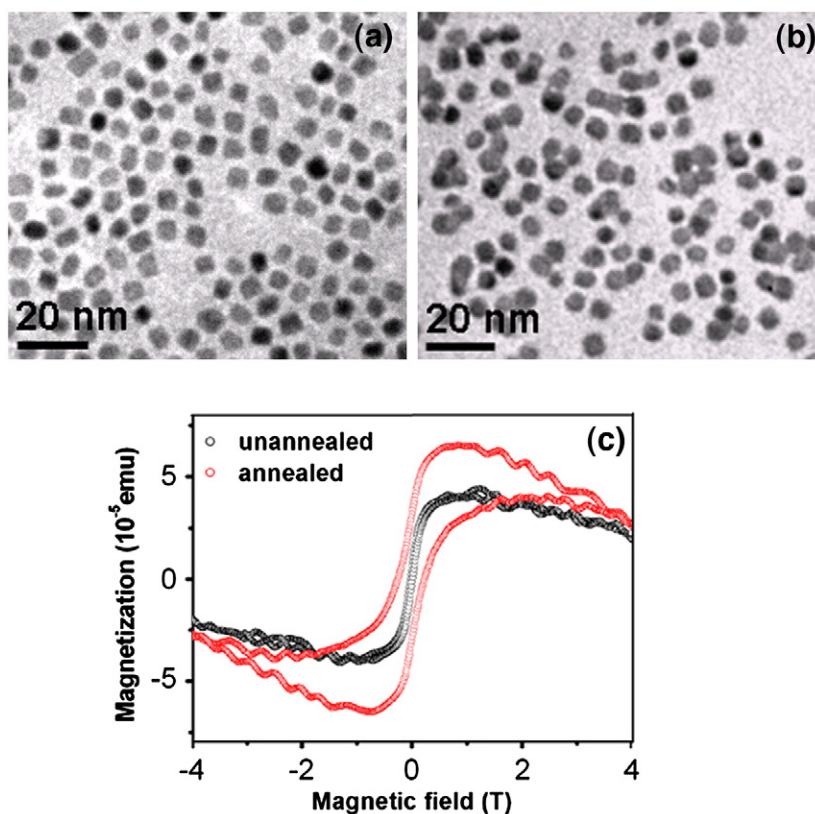


Fig. 4. (a) Schematic illustration of adsorption of FePt nanoparticles onto SiO<sub>2</sub> surface with different particle shapes. (b) Surface coverage of the cubical and spherical NPs as a function of colloid concentration, respectively.



**Fig. 5.** Plan-view TEM images of the FePt nanocube monolayer (a) before annealing and (b) after annealing at 650 °C for 60 min in vacuum. (c) Room-temperature hysteresis loops of the corresponding FePt monolayer before annealing and after annealing.

sintering is observed in the monolayer. Room-temperature magnetic hysteresis loops of the same film are plotted in Fig. 5(c). It indicates that the particle film is transformed from the super-paramagnetic phase into the ferromagnetic one while the monolayer morphology remains.

#### 4. Summary

In conclusion, we have investigated the adsorption behavior of colloidal FePt nanoparticles onto the surface of SiO<sub>2</sub> substrate by a simple spin-coating method. Uniform nanoparticle monolayer could be obtained at a macro-scale SiO<sub>2</sub> substrate by optimizing the experiment parameter. The morphology of the FePt nanoparticle monolayer onto SiO<sub>2</sub> surface is strongly dependent on the surfactants, colloid concentration, solvent as well as the shape of the nanoparticles. Compact assembly with long range order can be found in the spherical nanoparticle monolayer although there exist some particle-free areas. Homogeneous monolayer of the cubical FePt nanoparticles on SiO<sub>2</sub> substrate can be obtained on the whole substrate. It is believed that the simple method could be readily extended to the preparation of monolayers containing other surfactant capped nanoparticles with controlled size and properties for various nanodevice developments.

#### Acknowledgements

This work is supported in part by the National Nature Science Foundation of China under Grant No. 50371056, 50772032, 50801022 and 50801023, Research Fund for the Doctoral Program of China Education Ministry (20060512004), MOST of China (No. 2007CB936202), and the Natural Science Foundation Creative Team Project of Hubei Province (2007ABC005).

#### References

- [1] J.F. Wang, M.S. Gudiksen, X.F. Duan, Y. Cui, C.M. Lieber, *Science* 293 (2001) 1455.
- [2] J. Hu, L. Li, W. Yang, L. Manna, L. Wang, A.P. Alivisatos, *Science* 292 (2001) 2060.
- [3] S.J. Huang, G. Tsutsui, H. Sakaue, S. Shingubara, T. Takahagi, *J. Vac. Sci. Technol.*, B. 19 (2001) 2045.
- [4] V. Aleksandrovic, D. Greshnykh, I. Randjelovic, A. Fromsdorf, A. Kornowski, S.V. Roth, C. Klinke, H. Weller, *ACS Nano* 2 (2008) 1123.
- [5] D.K. Lee, Y.H. Kim, C.W. Kim, H.G. Cha, Y.S. Kang, *J. Phys. Chem.*, B. 111 (2007) 9288.
- [6] Q.J. Guo, X.W. Teng, S. Rahman, H. Yang, *J. Am. Chem. Soc.* 105 (2003) 630.
- [7] T.S. Yoon, J. Oh, S.H. Park, V. Kim, B.G. Jung, S.H. Min, J. Park, T. Hyeon, K.B. Kim, *Adv. Funct. Mater.* 14 (2004) 1062.
- [8] R.D. Tilley, S. Saito, *Langmuir* 19 (2003) 5115.
- [9] J.X. Huang, R. Fan, S. Connor, P.D. Yang, *Angew. Chem., Int. Ed.* 46 (2007) 2414.
- [10] Y.K. Hong, H. Kim, G. Lee, W. Kim, J. Park, J. Cheon, J.Y. Koo, *Appl. Phys. Lett.* 80 (2002) 844.
- [11] L. Meli, P.F. Green, *ACS Nano* 2 (2008) 1305.
- [12] V.F. Puentes, P. Gorostiza, D.M. Aruguete, N.G. Bastus, A.P. Alivisatos, *Nat. Mater.* 3 (2004) 263.
- [13] S.H. Sun, S. Anders, H.F. Hamann, J.U. Thiele, J.E.E. Baglin, T. Thomson, E.E. Fullerton, C.B. Murray, B.D. Terris, *J. Am. Chem. Soc.* 124 (2002) 2884.
- [14] D. Weller, A. Moser, L. Folks, M.E. Best, W. Lee, M.F. Toney, M. Schwickert, J.U. Thiele, M.F. Doerner, *IEEE Trans. Magn.* 36 (2000) 10.
- [15] V. Nandwana, K.E. Elkins, N. Poudyal, G.S. Chaubey, K. Yano, J.P. Liu, *J. Phys. Chem.*, C. 111 (2007) 4185.
- [16] S. Yamamoto, Y. Morimoto, Y. Tamada, Y.K. Takahashi, K. Hono, T. Ono, M. Takano, *Chem. Mater.* 18 (2006) 5385.
- [17] S. Kang, J.W. Harrell, D.E. Nikles, *Nano Lett.* 2 (2002) 1033.
- [18] M. Delalande, P.R. Maroux, P. Reiss, Y. Samson, *J. Mater. Chem.* 17 (2007) 1579.
- [19] Y. Wang, B.J. Ding, H. Li, X.Y. Zhang, B.C. Cai, Y.F. Zhang, *J. Magn. Magn. Mater.* 308 (2007) 108.
- [20] N. Shukla, E.B. Svedberg, J. Ell, *Surf. Coat. Tech.* 201 (2006) 3810.
- [21] M. Chen, J. Kim, J.P. Liu, H.Y. Fan, S.H. Sun, *J. Am. Chem. Soc.* 128 (2006) 7132.
- [22] M. Klokkenburg, J. Hilhorst, B.H. Erne, *Vib. Spectrosc.* 43 (2007) 243.
- [23] N. Shukla, J. Ahner, D. Weller, *J. Magn. Magn. Mater.* 272–276 (2004) e1349.
- [24] J.G. Truong, P.C. Wayner, *J. Chem. Phys.* 87 (1987) 4180.
- [25] Z.R. Dai, S.H. Sun, Z.L. Wang, *Nano Lett.* 1 (2001) 443.
- [26] L. Colak, G.C. Hadjipanayis, *Nanotechnology* 19 (2008) 235703.