

Preparation and Surface Modification of Monodisperse Fe₃O₄ Nano Particles

Zhong-Liang HU^{1,*}, Shi-Lin QIN², Zhao-Hui LI², Liu-Jiang XI¹ and Wei-Jian LIU¹

¹College of Metallurgic Engineering, Hunan University of Technology, Zhuzhou, 412007, China

²College of Chemistry, Xiangtan University, Xiangtan, 411105, China

Email: david10103@sina.com

*Corresponding author

Keywords: Fe₃O₄, Surface modification, Solvothermal method, Preparation

Abstract. Monodisperse Fe₃O₄ Nano particles have been successfully synthesized by solvothermal method using water and ethylene glycol as solvents, and their sizes could be controlled by changing the ratio of water to ethylene glycol. Subsequent surface modification of Fe₃O₄ had been carried out using tetraethyl orthosilicate and 3-Aminopropyl triethoxysilane as modification agents. The magnetic materials have been characterized by scanning electron microscopy, X-ray diffraction and Fourier-transform infrared spectroscopy. It was verified that SiO₂ layers have been coated on the surface of Fe₃O₄ and NH₂- groups have been grafted on the spherical surface of magnetic materials.

Introduction

Over the past decades, there is increasing interest in the preparation of nanosized magnetic materials because they have many versatile applications in the fields such as environment, gas sensors, lithium ion battery, pigment, biomedicine and magnetic separation [1-6]. Of the magnetic materials, Fe₃O₄ particles are the most frequently investigated ones due to their good magnetization and high surface area. Up to now, many different methods have been developed to prepare Fe₃O₄ nano particles (NPs), including co-deposition, sol-gel techniques, microwave plasma synthesis and solvothermal methods [7-10]. Among these methods, solvothermal process has the advantages of mild synthetic condition, simple manipulation and large scale-up production. More importantly, the morphology and size of the prepared Fe₃O₄ NPs could be adjusted in a solvothermal approach, so their properties could be controlled to some extent by this approach due to size and shape effects [11, 12].

However, nanosized Fe₃O₄ NPs tends to aggregate and oxidize during their application process, thus surface modification has become a common method to increase their stability. For example, Deng et al decorated SiO₂ on the surface of Fe₃O₄ to form a shell/core structure, and the prepared composites display good stability and have promising applications in biomedical fields [13]. Li et al coated Fe₃O₄ with a thin layer of TiO₂, and the materials show very high adsorption for phosphopeptides [14]. Recently, to graft functional groups on the surface of Fe₃O₄ NPs becomes a popular modification way because it could extend their applications and increase their performances. Huang et al prepared chitosan-Fe₃O₄ composites using epichlorohydrin as the crosslinking agent and found the composites have a high adsorption capacity for heavy metal [15]. Dupont et al coated Fe₃O₄ with EDTA-silane and found the composites could adsorb rare-earth ions selectively due to the introduction of the functional groups, thus providing a novel methodology for design of magnetic composites [6].

In this paper we used solvothermal approach to prepare Fe₃O₄ NPs, and the size of the magnetic NPs could be adjusted by changing the ratio of water to organic solvent. To improve the stability of Fe₃O₄ NPs and extend their applications, we firstly coated SiO₂ on the surface of Fe₃O₄ NPs to form Fe₃O₄@SiO₂ NPs, and subsequently introduced NH₂- groups on their surface, resulting in the NH₂-grafted Fe₃O₄@SiO₂ NPs. The prepared NH₂-grafted Fe₃O₄@SiO₂ NPs keep stable and are of good dispersion in solution. They could be not only used for adsorbents for heavy metals, biomaterials, but also served as an intermediate to produce functional magnetic composites.

Experimental

Synthesis of Fe₃O₄ NPs

A typical solvothermal synthesis of Fe₃O₄ NPs was carried out according to the following procedures. Firstly, 1.0 g of poly ethylene glycol (PEG) (M_w=4000) was added into a beak containing 40 ml of ethylene glycol, and the solution had been heated in a oil bath for 30 min under magnetic stirring, making PEG dissolve completely. Then 3.6 g of NaAc·3H₂O was added into the above solution under stirring, meanwhile x ml of distilled water was introduced into the mixture solution, and stirring had continued for 30 min to dissolve NaAc completely. The solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave had been kept at 200 °C for 8 h before being cooled in air naturally. Finally the products were centrifuged, washed with distilled water for several times, and dried at 60 °C for 6 h. The resulting Fe₃O₄ samples were signified as Fe₃O₄-1, Fe₃O₄-2, Fe₃O₄-3 when x is equal to 10, 5, 0 ml, respectively.

Synthesis of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-NH₂ NPs

To synthesize Si coated Fe₃O₄ NPs, 1.4 g of the prepared Fe₃O₄-2 NPs were added to a flask containing 5 ml of ammonia water (28 wt.%), the flask was put into a water bath, and had been mechanically stirred at 60 °C for 15 min. Then 4 ml of tetraethyl orthosilicate (TEOS) was added to the solution dropwise, and the reaction had continued for 8 h under stirring. The products were obtained by magnetic separation, washed with distilled water and anhydrous alcohol for several times, and finally dried at 60 °C for 6 h. The resulting sample was denoted as Fe₃O₄@SiO₂ for the Si layer was verified to be SiO₂ thereafter.

To synthesize NH₂-grafted Fe₃O₄@SiO₂ NPs, 1.0 g of Fe₃O₄@SiO₂ NPs were added to a flask containing a mixture solution of 40 ml of distilled water, 100 ml of isopropanol and 2 ml of 3-Aminopropyl triethoxysilane (APTES). The flask was then transferred into a water bath at 70 °C, making nitrogen continuously flow into it, and the reaction had lasted for 6 h under mild mechanical stirring. The resulting products were obtained by magnetic separation, washed with distilled water and anhydrous alcohol for several times, and finally dried at 60 °C for 6 h. The obtained sample was expressed as Fe₃O₄@SiO₂-NH₂.

Materials Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a powder diffractometer (D8 Advanced Diffractometer System, Bruker, Germany) using Cu K α radiation ($\lambda=0.1514\text{nm}$) in the 2 θ range of 20–80°. The operating tube voltage and current were 40 kV and 40 mA, respectively. Data were collected at a scanning speed of 0.02° min⁻¹ and a sampling angle interval of 0.02°.

The morphologies of the samples were observed by a scanning electron microscope (SEM; JSM-6360LV, JEOL, Japan).

Fourier-transform infrared (FTIR) spectra of the samples were recorded using an FTIR spectrometer (Spectrum One, PerkinElmer, US) with a resolution of 2 cm⁻¹ in the wavenumber range of 400 or 600–4000 cm⁻¹.

Results and Discussion

Fig.1 shows the SEM images of Fe₃O₄-1, Fe₃O₄-2 and Fe₃O₄-3. All the samples are well dispersed and do not aggregate. The sizes of the prepared Fe₃O₄ NPs range from one to several hundred nm. For Sample Fe₃O₄-1, its shape is generally cubic, and its size is less than 150 nm. The other two samples are spherical and the diameters of Sample Fe₃O₄-2 and Fe₃O₄-3 are about 200, 500 nm, respectively. The preparation of Fe₃O₄ samples were carried out at the same conditions except different water quantity. In this synthesis system, ethylene glycol acts as a reductant, and increasing water quantity reduces the concentration of ethylene glycol, thus the reductant reaction of Fe³⁺ to Fe²⁺ is slowed down, resulting less size of the Fe₃O₄ NPs. On the hand, NaAc was added for electrostatic

stabilization to prevent particle agglomeration, and PEG acts as stabilizers adsorbed on the Fe_3O_4 crystal facets, its concentration could affect the shape of Fe_3O_4 to some extent [16, 17].

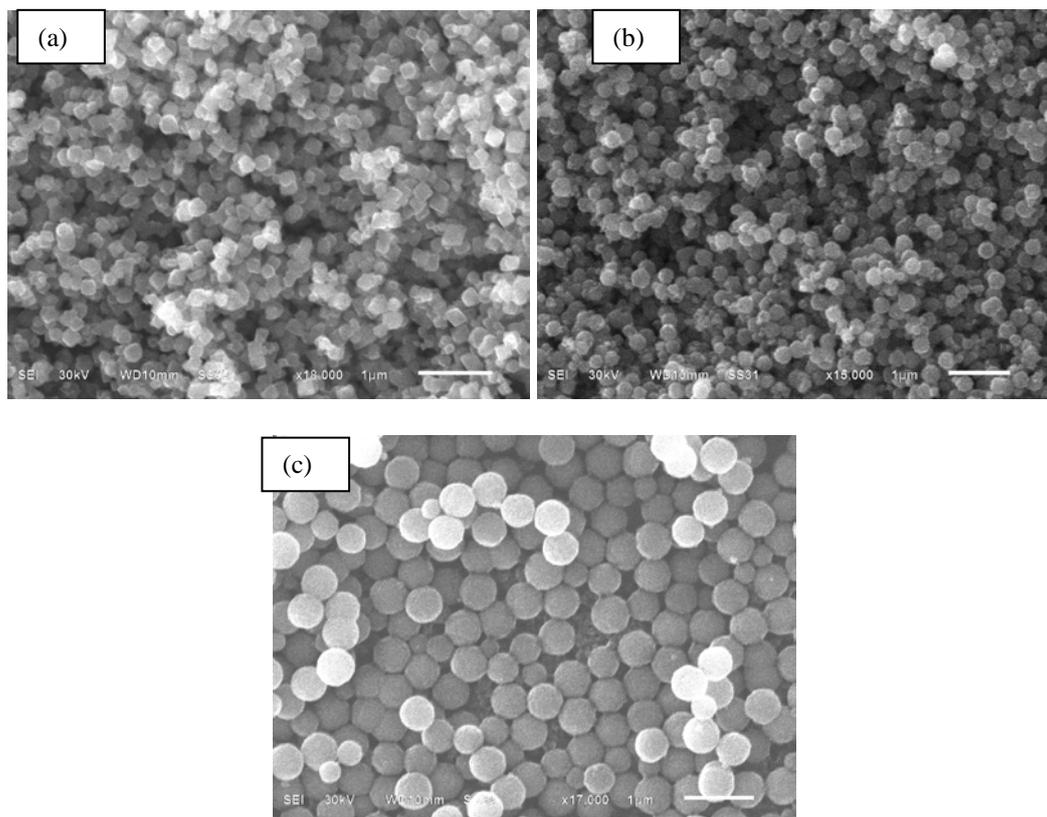


Fig. 1 SEM images of (a) Fe_3O_4 -1, (b) Fe_3O_4 -2 and (c) Fe_3O_4 -3.

Fig. 2 shows the SEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$. Compared with Fe_3O_4 -2 NPs, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs display some obvious changes. Firstly, the diameter of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ becomes markedly bigger, indicating that a layer of Si has been coated on the surface of Fe_3O_4 . Secondly, there are lots of villous fibers on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs, which could be due to the deposited coating. Compared with Fe_3O_4 -2 NPs, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ NPs have much bigger diameters, and show similar morphologies to $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs. However, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs exist as a single particle, while some $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ NPs seem to be connected each other, suggesting that the amine groups have successfully been grafted on the Si surface of NPs and connect the separated NPs.

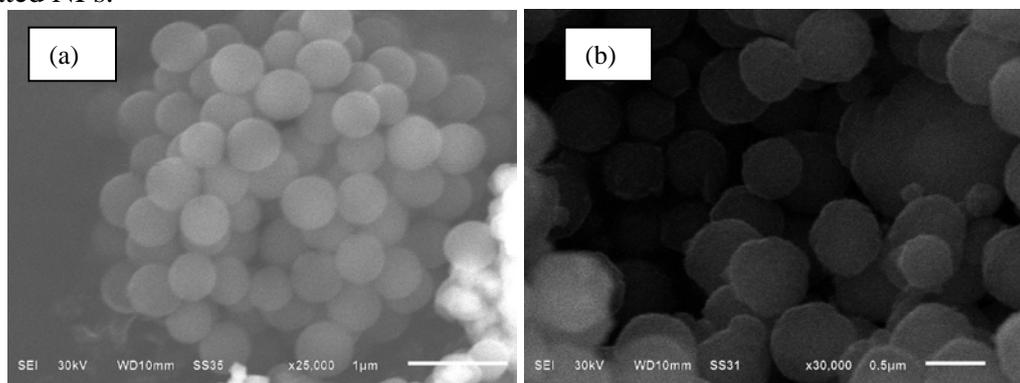


Fig. 2 SEM images of (a) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$.

Fig. 3 displays the XRD patterns of the prepared Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ NPs, which could identify crystallographic phase of the samples. All samples have typical XRD

patterns of magnetite (JCPDS No. 19-0629) and no other characteristic peaks of impurities could be detected, indicating that Fe_3O_4 NPs have been successfully produced. However, for the different Fe_3O_4 NPs, the XRD patterns of the samples differ largely from each other in the intensity and broadness of the peaks. Fe_3O_4 -1 displays broad peaks with low intensity, while Samples Fe_3O_4 -2 and Fe_3O_4 -3 shows much narrower and more intensive peaks, indicating their sizes are bigger than Fe_3O_4 -1's. Nevertheless, Samples Fe_3O_4 -2, $\text{Fe}_3\text{O}_4@SiO_2$, $\text{Fe}_3\text{O}_4@SiO_2-NH_2$ have almost identical XRD patterns, and it could be attributed to the fact that they all originated from the same parent of Fe_3O_4 -2. Based on the calculations with the Scherrer formula for the strongest (311) diffraction peak, the sizes of the prepared Fe_3O_4 NPs range from 100 to 500 nm, which are in good agreement with SEM's results.

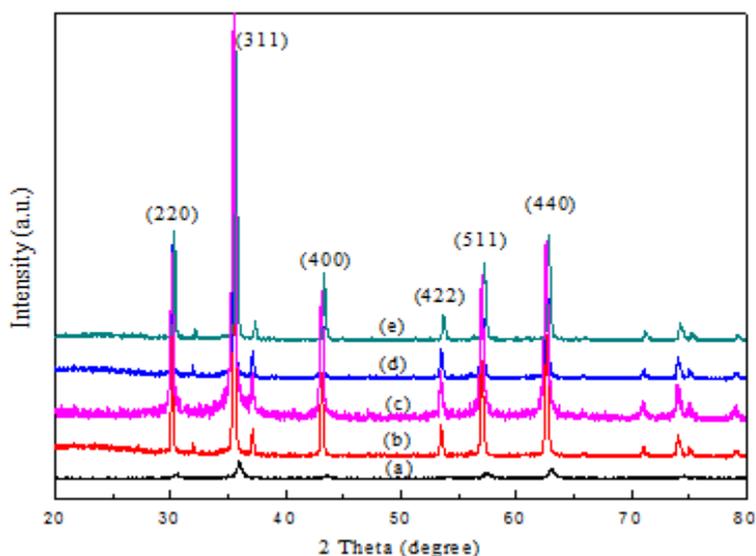


Fig. 3 XRD patterns of (a) Fe_3O_4 -1, (b) Fe_3O_4 -2, (c) Fe_3O_4 -3, (d) $\text{Fe}_3\text{O}_4@SiO_2$ and (e) $\text{Fe}_3\text{O}_4@SiO_2-NH_2$.

The spectra of FTIR of the Fe_3O_4 -2, $\text{Fe}_3\text{O}_4@SiO_2$ and $\text{Fe}_3\text{O}_4@SiO_2-NH_2$ samples are displayed in Fig. 4. For Fe_3O_4 NPs, only an obvious peak at 590 cm^{-1} is attributed to the stretching vibration of Fe-O bonds in the crystalline lattice of Fe_3O_4 [4, 18]. After coating SiO_2 layer, two peaks appear, one at 803 cm^{-1} is due to the bending vibration of Si-O-Si, the other at 1050 cm^{-1} shows a much strong intensity, and it corresponds to asymmetric stretching vibration of Si-O-Si. The FTIR analysis verifies again that SiO_2 layers have been successfully deposited on the surface of Fe_3O_4 . The FTIR spectra of $\text{Fe}_3\text{O}_4@SiO_2-NH_2$ reveal significant differences from that of $\text{Fe}_3\text{O}_4@SiO_2$. Due to the introduction of APTES, some new peaks emerge. The peak at 879 cm^{-1} comes from Si-O-Si symmetric stretching vibration. The absorption peak at 3310 cm^{-1} is due to the N-H stretching vibration of $-NH_2$ group, the peaks around 1380 cm^{-1} could respond to the bending vibration of N-H bonding, the stretching vibration of C-N bonding, and the bending vibration of C-H bonding. The peaks at 2920 cm^{-1} and 2850 cm^{-1} are ascribed to the C-H ($-CH_2$, $-CH_3$) stretching vibration. These absorption peaks could correspond to the matching groups in APTES molecules, indicating that APTES react with $\text{Fe}_3\text{O}_4@SiO_2$ and $-NH_2$ groups have been successfully grafted on the surface of $\text{Fe}_3\text{O}_4@SiO_2$ NPs.

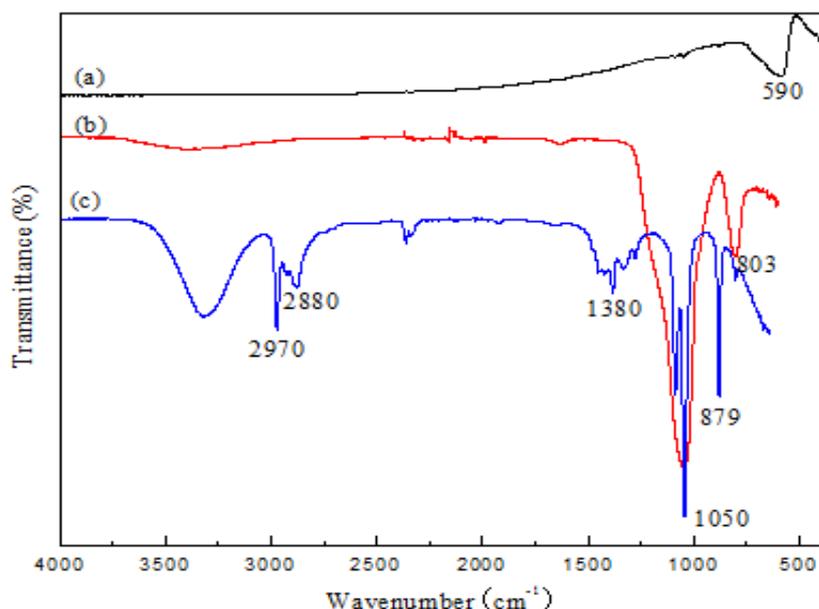


Fig. 4 FTIR spectra of (a) Fe_3O_4 -2, (b) $\text{Fe}_3\text{O}_4@SiO_2$ and (c) $\text{Fe}_3\text{O}_4@SiO_2-NH_2$.

Conclusions

- (1) Cubic Fe_3O_4 NPs with ~ 150 nm size and spherical Fe_3O_4 NPs with ~ 200 nm and 500 nm size have been prepared by solvothermal method using water and EG as solvents.
- (2) The sizes of Fe_3O_4 could be controlled by changing the ratio of water to ethylene glycol and EG acts a reductant to reduce Fe^{3+} to Fe^{2+} to form Fe_3O_4 .
- (3) A layer of SiO_2 have been coated on the surface of Fe_3O_4 NPs using TEOS as a modification agent, and consequent $-NH_2$ groups have been grafted on the surface of the resulting magnetic NPs using APTES as a modification agent.
- (4) The modified Fe_3O_4 NPs maintain good dispersity, and they could act as intermediates to prepare magnetic composites. The NH_2 -grafted Fe_3O_4 NPs could be used as absorbents for heavy metal and biomaterials due to their good magnetic and rich $-NH_2$ groups.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21376069, 21576075) and Key Project in Hunan Science and Technology Pillar Program (No. 2015WK3020).

References

- [1] G. Giakisikli, A. Anthemidis, Magnetic materials as sorbents for metal/metalloid preconcentration and/or separation. A review, *Anal. Chim. Acta.* 789 (2013) 1-16.
- [2] L.Z. Gao, J.M. Wu, S. Lyle, et al, Magnetite nanoparticle-linked immunosorbent assay, *J. Phys. Chem. C* 112 (2008) 17357-17361.
- [3] J. Xie, K. Chen, H.Y. Lee, et al, Ultrasmall c(RGDyK)-coated Fe_3O_4 nanoparticles and their specific targeting to integrin $\alpha v \beta 3$ -Rich tumor cells, *J. Am. Chem. Soc.* 130 (2008) 7542-7543.
- [4] X.H. Chen, X. Lai, J.H. Hu, et al, An easy and novel approach to prepare Fe_3O_4 -reduced graphene oxide composite and its application for high-performance lithium-ion batteries, *RSC Adv.* 5 (2015) 62913-62920.

- [5] C.J. Xu, S.H. Sun, New forms of superparamagnetic nanoparticles for biomedical applications, *Adv. Drug Deliver. Rev.* 65 (2013) 732-743.
- [6] D. Dupont, W. Brullot, M. Bloemen, et al, Selective uptake of rare earths from aqueous solutions by EDTA-functionalized magnetic and nonmagnetic nanoparticles, *ACS Appl. Mater. Inter.* 6 (2014) 4980-4988.
- [7] C. C. Lin, J.M. Ho, Structural analysis and catalytic activity of Fe₃O₄ nanoparticles prepared by a facile co-precipitation method in a rotating packed bed, *Ceram. Int.* 40 (2014) 10275-10282.
- [8] N.J. Tang, W. Zhong, H.Y. Jiang, et al, Nanostructured magnetite (Fe₃O₄) thin films prepared by sol-gel method, *J. Magn. Mater.* 282 (2004) 92-95.
- [9] P. Hojati-Talemi, J. Azadmanjiri, G.P. Simon, A simple microwave-based method for preparation of Fe₃O₄/carbon composite nanoparticles, *Mater. Lett.* 64 (2010) 1684-1687.
- [10] S. Saha, Hydrothermal synthesis of Fe₃O₄/RGO composites and investigation of electrochemical performances for energy storage applications, *RSC adv.* 4 (2014) 44777-44785.
- [11] W. Mechan-Mechan, A.V. Saveliev, A.M. Taylor, High rate flame synthesis of highly crystalline iron oxide nanorods, *Nanotechnology* 19 (2008) 125605.
- [12] Y. Xiong, J. Ye, X.Y. Gu, et al, Synthesis and assembly of magnetite nanocubes into flux-closure rings, *J. Phys. Chem. C* 111(2007), 6998-7003.
- [13] Y.H. Deng, W.L. Yang, C.C. Wang, et al. A novel approach for preparation of thermoresponsive polymer magnetic microspheres with core-shell structure, *Adv. Mater.* 15 (2003) 1729-1732.
- [14] Y. Li, J. Wu, D. Qi, et al, Novel approach for the synthesis of Fe₃O₄@TiO₂ core-shell microspheres and their application to the highly specific capture of phosphopeptides for MALDI-TOF MS Analysis, *Chem. Commun.* 20 (2008) 564-566.
- [15] G.L. Huang, H.Y. Zhang, X.S. Jeffrey, et al., Adsorption of chromium(VI) from aqueous solutions using cross-linked magnetic chitosan beads. *Ind. Eng. Chem. Res.*, 48 (2009), 2646-2651.
- [16] H. Deng, X. Li, Q. Peng, et al, Monodisperse magnetic single-crystal ferrite microspheres, *Angew. Chem. Int. Ed.* 44 (2005) 2782-2785.
- [17] C. Yang, J.J. Wu, Y.L. Hou, Fe₃O₄ nanostructures: synthesis, growth mechanism, properties and applications, *Chem. Commun.* 47 (2011) 5130-5141.
- [18] K. Yang, H.B. Peng, Y.H. Wen, et al, Re-examination of characteristic FTIR spectrum of secondary layer in bilayer oleic acid-coated Fe₃O₄ nanoparticles, *Appl. Surf. Sci.* 256 (2010) 3093-3097.