Surface Modification of Magnetic Nanoparticles: Characterization and Colloidal Stability in Polar Solvents

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ABSTRACT

The surface of monodisperse maghemite (γ-Fe_2O_3) nanoparticles capped by oleic acid was modified to increase the stability of the suspension in polar solvents. The lyophobic surface coating of maghemite particles in ethanol was made to be more lyophilic by ozonolysis. The ozone oxidatively cleaved the double bond of oleic acid to form carbonyl and carboxyl groups on the surface of the nanoparticles which increased the stability of the maghemite particles in ethanol. Additionally, interfacial ligand exchange of the capping molecules was also done to make the particle surface more hydrophilic. The maghemite particles showed enhanced miscibility and short-term stability in water after interfacial ligand exchange. The structure changes of the capping molecules on the nanoparticle surfaces were investigated using Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). From these spectroscopy studies, the cleavage of the oleic acid and the formations of the carboxyl and carbonyl groups on the particle surface were confirmed. The shape and the magnetic properties of the maghemite particles were maintained after the surface modification. Ozonolysis is an effective method in modifying the lyophobic surface of the maghemite nanoparticles.

INTRODUCTION

Stable suspensions of magnetic nanoparticles in various polar solvents are needed in many technological fields such as hybrid material synthesis [1-3], medical application [4,5], and magnetic thin film fabrication [6,7]. In these research fields, the preparation of a stable and monodisperse suspension is the key issue. To enhance the suspension stability of nanoparticles, the control of surface functional groups on the suspending particles is required. Ferric oxide particles are widely studied iron-based magnetic particles. Several researchers have synthesized ferric oxide particles and their composites [12-20]. Maghemite (γ-Fe_2O_3) particles are one of the commonly used ferric oxide particles for their simple synthesis procedures and chemical stability. Recently, surfactant-based synthesis routes were developed in order to prepare monodisperse maghemite nanoparticles [12-17], which resulting in monodisperse maghemite nanoparticles capped with fatty acids. The hydrophobic alkyl chains on the surface of the synthesized maghemite particles produced stable suspensions only in apolar organic solvents such as toluene.

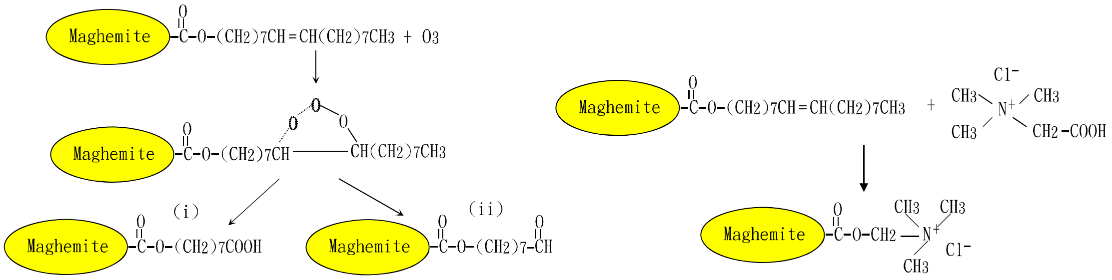
In order to prepare a stable magnetic particle suspension in alcohol which needed in many material processing and biological conjugation, the modification of these hydrophobic nanoparticles is required. The post modification of the hydrophobic surface of the synthesized monodisperse magnetic particles will be a promising method satisfying the requirements of monodispersity of the particles and colloidal stability in polar media.

Reaction of the ozone with the alkene group in oleic acid can convert the lyophobic surface groups to lyophilic ones. Ozone is a strong oxidant that reacts with hydrocarbons. In the previous studies on the ozonolysis of oleic acid, the alkene structure in oleic acid molecules were oxidatively cleaved to form carboxyl and carbonyl end groups [21,22]. We hypothesized that the resulting carboxyl and carbonyl groups with a short carbon chain will enhance the stability of the magnetic nanoparticles in a polar solvent such as ethanol. It is also deserved to investigate the applicability of the interfacial ligand exchange method to the oleic acid covered magnetic nanoparticles for the preparation of the magnetic hydrosols. In this work, the magnetic nanoparticles capped by the oleic acids were modified via ozonolysis and interfacial ligand exchange method in order to change the lyophobic surface to be lyophilic. After the surface modification by both methods, the changes of the functional groups on the particle surface were characterized.

EXPERIMENTS

Magnetic nanoparticle synthesis: The monodisperse magnetic nanoparticles were synthesized by the thermal decomposition of an iron oleate complex. Details of the procedure are given in the reference [14]. After the reaction, the nanoparticles capped by oleic acid formed a stable suspension in toluene. The hydrophobic magnetic suspension in toluene was precipitated by addition of excessive ethanol and then kept in ethanol for the surface modification.

Surface modification of the synthesized magnetic particles: The chemical reaction schemes for both surface modifications are presented in the figure 1. The ozone reacts with the alkene chain in the oleic acid and to form the primary ozonide [22]. The unstable primary ozonide is cleaved to form azelaic acid (figure 1a(i)) and 1-nonanal (figure 1a(ii)), which results in shortened carbon chains with carboxyl and carbonyl groups. The ligand exchange reaction between the oleate unit of the oleic acid and carboxylate unit of modifier is taken place on the magnetic particle surface (figure 1b). Here the betaine·HCl was used as a modifier which gives hydrophilicity after the interfacial ligand exchange.



(a) (b)

Figure 1. Reaction scheme of the surface modification on maghemite nanoparticle; (a)ozone oxidation of oleic acid – (i)azelaic acid formation (ii)1-nonanal formation., (b)ligand exchange with betaine·HCl.

Analysis and characterization: The chemical structure changes of the oleic acid on the magnetic nanoparticle surface were investigated using Fourier transform infrared (FT-IR) spectrometry and X-ray photoelectron spectroscopy (XPS) survey. The colloidal stability of the magnetic suspensions was investigated by monitoring changes of the beam absorbance with time, which is correspondent to monitor the turbidity of magnetic sol. A UV-visible spectrophotometer was used in monitoring the change of the beam absorbance, at a wavelength of 400 nm. The particle morphologies were observed using transmission electron microscopy. The magnetic property of the modified nanoparticles was investigated using the Physical Property Measurement System (PPMS) at 300K.

RESULTS AND DISCUSSION

The shapes of the magnetic nanoparticles were observed using TEM. In figure 2, TEM images of synthesized magnetic particles show high uniformity in a spherical shape with the average diameter of 11nm. After surface modification, the particles maintained their original spherical shapes without any deformation or growth. The XRD pattern of magnetic nanoparticles agreed with previous report on typical maghemite particles whose synthesis procedure was followed [14]. The particle diameter calculated by Scherrer's equation from the XRD result was 12nm, which agreed with the TEM observation.

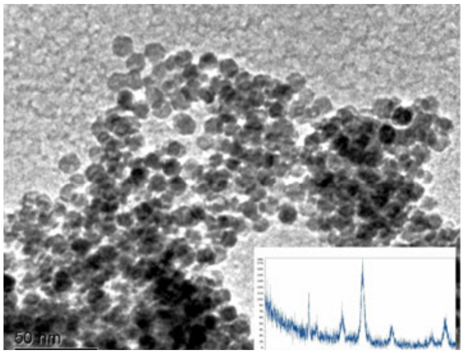


Figure 2. TEM images of magnetic particles before modification (inlet: XRD spectrum)

The structure changes of the capping molecule on the magnetic particles were investigated using FT-IR spectrometry and XPS survey. The FT-IR spectra of modified and unmodified magnetic particles are given in figure 3. The magnetic particles covered with oleic acids showed strong CH_2 peaks at 2921(ν_a C-H), 2850(ν_s C-H), and 1467 (δ_s C-H) cm^{-1} before modification (spectrum a). These peaks are known to be the characteristic peaks of CH_2 chains that are present in oleic acid [16,23]. After the reaction of ozone with magnetic particles, the characteristic CH_2 peak at 2921 and 2850 cm^{-1} were noticeably decreased (spectrum b). In addition, some peaks observed after the ozonolysis indicates the formation of carboxylic acid: (i) Broadened C=O peak at 1710cm^{-1} suggested the increase of carboxyl (or carbonyl) groups. (ii) Two characteristic peaks of azelaic acid were observed at 1460 and 1420cm^{-1}. The FT-IR spectrum of the ligand exchanged magnetic particle is presented in spectrum c. After the interfacial ligand exchange reaction, the CH_2 peaks at 2921 and 2850cm^{-1} were greatly reduced; however, some carbon chains of oleic acid still remained as is indicated by the existence of characteristic CH_2 peaks. A characteristic C-N peak was observed at 1190cm^{-1}, which indicates the reaction of betaine$\cdot$HCl with oleic acid. The FT-IR spectra agreed with XPS survey which showed the decrease of hydrophobic tail after the surface modification.

The colloidal stability of the magnetic suspension was quantified by monitoring the changes of the effective beam absorbance. The evolution of the normalized beam intensity with time is shown in figure 4 where the absorbance, A, was normalized by dividing with the initial absorbance, A_0. Notable decreases of absorbance were observed during the early stages. The lyophobic unmodified magnetic particle suspension in ethanol settled down rapidly at the early stage. A completely different behavior was observed for the magnetic particles treated with ozone. The ozonized magnetic particle suspensions showed little changes of the absorbance after eight days, which was thought to be a stable dispersion. The particles remained stable in ethanol even after more than four months. The ligand exchanged magnetic particles showed miscibility and short-term stability in the aqueous solution. The relative intensity of ligand exchange particles continuously decreased and reached 36% of the initial value after two weeks. The particles continued to settle and all of the ligand exchanged magnetic particles settled to the bottom of the container after three months. The ligand exchanged particles were not as stable as the reported magnetic particles prepared with caprylic acids.

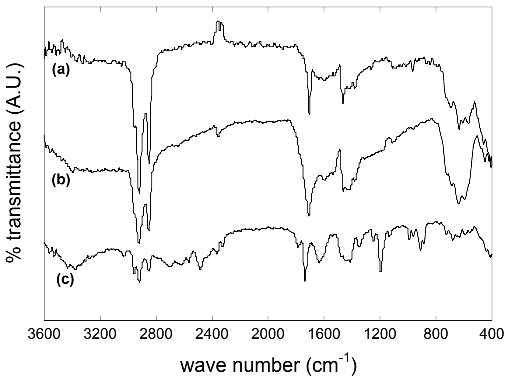


Figure 3. FT-IR spectra of the magnetic particles (a) before modification, (b) ozonized particles, (c) ligand exchanged particles.

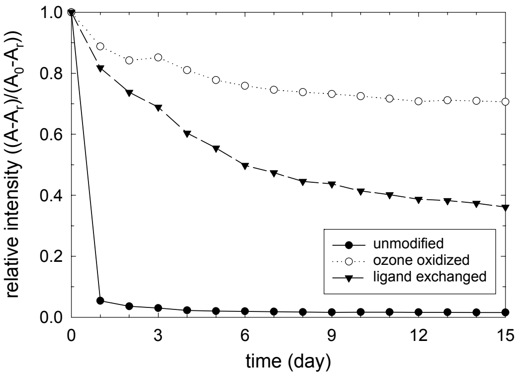


Figure 4. Beam intensity changes with time

CONCLUSION

The surface of the magnetic nanoparticles capped by oleic acid was modified via ozonolysis and the interfacial ligand exchange method. The reaction of ozone with oleic acid was effective in preparing the stable magnetic suspension in ethanol. The ozone oxidatively cleaved the alkene chain in the oleic acid to form shortened alkyl chains with carboxyl or carbonyl groups at the end. The shortened alkyl chain with polar groups increased the miscibility in ethanol resulting in stable nanoparticle suspension. The interfacial ligand exchange enhanced the stability in the water by changing the hydrophobic surface to a hydrophilic surface. The ligand exchange was effective in making magnetic particles with improved stability in aqueous media.

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