Effect of Solvents on the Preparation of Silica-Coated Magnetic Particles

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The influence of solvents on magnetic particles aggregation during silica coating by the Stober method has been studied, and a simple method has been developed to produce well-dispersed silica-coated magnetic particles using methanol.

Magnetic nanoparticles offer attractive properties for various applications. Stable colloidal sols, for instance, can be used for the magnetic separation of cells.[1,2] However, due to their fine particle size, surface modifications are required to engineer magnetic particles of greater stability against coagulation and protection of the iron oxide substrate particles from leaching in an acidic environment. Philipse et al. have used a two-step process to prepare a silica coating on magnetic particles, but this method is quite complicated.[3]

During the coating process, to avoid agglomeration of the cores, the important objective is to obtain well-dispersed core particles. Many research studies showed that ethanol and 1-propanol were usually used as solvents for preparing silica coating, and TEOS (tetraethyl orthosilicate) was allowed to hydrolyze in it.[4–6] However, magnetic particles easily agglomerate in ethanol and 1-propanol, which makes it difficult to obtain silica-coated particles with a good dispersion. In our study, the silica-coated magnetic particles were prepared using simple method, and the influence of several alcohols on the dispersion of the magnetic particles was studied.

The aqueous magnetic ferrofluid was prepared according to Massart's method.[7] A 1mol/L $FeCl_3$ solution in water was mixed with a solution of 2 mol/L $FeCl_2$ in 2 mol/L HCl. The chloride mixture was quickly added to 250 mL of 0.7 mol/L ammonia in an open vessel under vigorous mechanical stirring. After 30 min of stirring, the precipitate was collected on the vessel wall by a permanent magnet and the clear supernatant was decanted. The precipitate was dispersed in distilled water and the appropriate amount tetramethylammonium hydroxide (TMA, 25%, Aldrich Co.) to get a homogeneous ferrofluid without any visible aggregates. Here, in this report, this ferrofluid was called MF solution.

A 0.5 mL aliquot of MF solution in 30 mL of various solvents was used to detect the electrophoretic mobility and zeta potential.

Table 1 shows that different alcohol media lead to quite different surface charges on the magnetic particles. It can be seen that as the carbon chain of the alcohol becomes longer, the electrophoretic mobility of the magnetic particle decreases, and the zeta potential approaches to zero. This means that the surface charge of the magnetic particles in 1-butanol was almost near to zero, which easily results in agglomerates if the surface is hydrophilic. Sediment experiments also showed that after adding MF solution to 1-butanol, even after mechanical vibration, a homogenous solution still could not be obtained, and the magnetic particles quickly sediment. When a small amount of MF solu-

Table 1. The electrophoretic mobility and zeta potential of magnetic particles in different solvents

Alcohol	Electrophoretic mobility $/\times 10^{-9} m^2 V^{-1} S^{-1}$	Zeta potential[a] /mV
Methanol	–38.4	–12.6
Ethanol	–6.9	–3.3
1-Propanol	–2.8	–2.1
1-Butanol	–1.3	–1.1

[a]Zeta potential was calculated using the Helmholta–Smoluchowski equation.[8] Viscosity and dielectric constant of the different alcohols were obtained from a reference.[9]

tion is added to ethanol or 1-propanol, a homogeneous suspension could be obtained with vibration, but the magnetic particles would settle after several minutes without stirring. By adding MF solution to methanol, a brown clear solution can be obtained, and this state can be maintained for at least 24 h. Therefore, it can be concluded that methanol is a suitable media to disperse the magnetic particles. The different charges of magnetic particle in different solvents can be due to the polarity of the solvents.

Stober's early research suggested that when using different alcoholic solvents to prepare SiO_2, the final particles sizes obtained under comparable conditions were the smallest in methanol and the biggest in 1-butanol, and there was a tendency toward a wide size distributions with the higher alcohols.[10] Therefore, to obtain a uniformly coated magnetic particles, methanol also seemed to be a good selection for the process of coating the magnetic particles.

One mL of MF solution was put in 100mL of methanol (or 1-butanol) in a closed reaction flask (concentration of particle is about 0.07 g/L), and then ultrasonically vibrated for 10 min. This reaction flask was carried in a 20 °C water bath. After the temperature became constant, 4 mL of ammonia and 0.08 mL of TEOS was injected into flask, and left for 12 hours. A centrifuge was used to remove some of the coated magnetic particles, which were washed and dispersed in water to measure their zeta potential. Some particles were dried to get the FTIR spectra. A TEM was used to observe the particles.

Figure 1 shows TEM photograph of the coated magnetic particles. Figure1a is the particles produced in methanol, and it can be seen that the magnetic particles are coated by the silica layer and its thickness is about 5 nm. Magnetic particles aggregate little and have relatively uniform dispersion. However, the particles produced in 1-butanol (Figure1b) are heavily agglomerated, and the SiO_2 coating was thick.

Figure 2 shows the relationship between the zeta potential and the pH value in aqueous solution. Some authors have reported that the isoelectric point for magnetic is at pH 7,[3] and for SiO_2 (prepared by Stober method) is at about 3.[5] Both silica-coated magnetic particles from methanol and 1-butanol solutions have isoelectric points around pH 4, which is close to that of the SiO_2 particles.
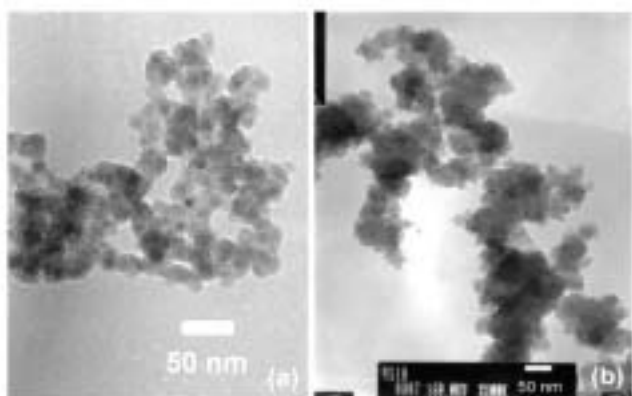
Figure 1. TEM pictures of silica-coated magnetic particles (a) using methanol as solvent in coating process (b) using 1-butanol as solvent in coating process.
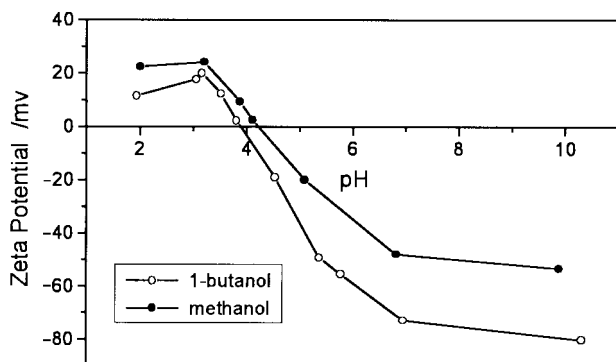
Figure 2. Zeta potential of coated magnetic particles in aqueous solution
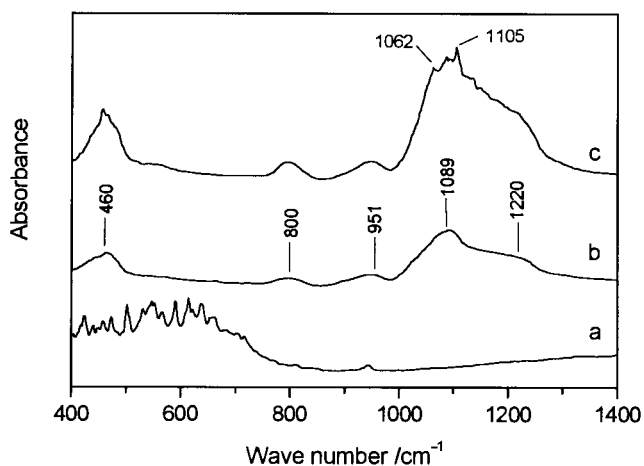
Figure 3. FTIR spectra of magnetic particle (a), SiO_2 (b) and coated magnetic particle (c).

Figure 3 is the FTIR spectrum of the dried magnetic particle (a), SiO_2 (b) and coated particle (c) (FTIR spectra of the particles produced in methanol and 1-butanol are the same). We focus the spectral analysis on the region from 400 to 1400 cm^{-1}. The spectrum of the unmodified magnetic particle shows the main maxima related to the Fe–O vibrations between 400 and 700 cm^{-1}, and the peaks of SiO_2, are located at 460, 800, 951, 1089, and 1220 cm^{-1}, which is in agreement with the data in reference 11. The coating of the magnetic particles with silica induces the presence of new absorption bands at 456, 795, 951, 1086, and 1220 cm^{-1}, which can be related to the formation of the silica layer. Possibly due to a weak intensity, almost no absorption bands of magnetic particle can be seen in the spectrum of the coated particles. Several absorption band such as 1065, and 1105 cm^{-1} can be observed in the spectrum of the coated magnetic particles. These bands cannot be assigned to iron or silicon single oxides. On the basis of data by other researchers who studied ferrisilicate zeolites,[12,13] these bands may be attributed to the vibration of the Fe–O–Si bond.

In summary, the influence of several solvents on magnetic particles have been studied, and well-dispersed magnetic particles could be produced in methanol. The zeta potential and FTIR results show that silica-coated magnetic particles can be prepared by a simple method.

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