Synthesis and Characterization of 3-Aminopropyltriethoxysilane-Modified Superparamagnetic Magnetite Nanoparticles

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The aminosilane-modified magnetite nanoparticles were synthesized by the coprecipitation and surface modification with 3-aminopropyltriethoxysilane (APTTS). The superparamagnetic APTTS/Fe_3O_4 nanospheres with an average diameter of 10 nm were characterized significantly with functional group, well dispersion and stabilization in aqueous fluids, as well as a maximized saturation magnetization of 63.54 emu/g.

In recent years, magnetic nanomaterials such as magnetite nanoparticles (Fe_3O_4 NPs) have attracted a great deal of attention for their wide biomedical applications.[1–3] Applied in biomedicine, Fe_3O_4 NPs should have the properties of biocompatibility, paramagnetism, specific targeting, and stabilization in aqueous solution. However, for ultrafine Fe_3O_4 NPs, the large surface area-to-volume ratios and the magnetic dipole–dipole attractions between particles always result in agglomeration,[4] which is one of the critical obstacles to be overcome in producing stable magnetic fluids. The modification technique frequently employed makes use of the interaction between magnetic nanoparticles surface and functional groups of organic molecules.[5–11]

Here, the aminosilane agent of 3-aminopropyltriethoxysilane (APTTS) is considered as a candidate for modification on the surface of Fe_3O_4 NPs directly, for the advantages of the biocompatibility as well as high density of surface functional group of $-NH_2$, allowing for connecting to other targeting biomolecules.[5] In the paper, the APTTS/Fe_3O_4 NPs were prepared with simple operations, and display well dispersion and stability in aqueous solvents, while they still maintain their physical characteristics of superparamagnetism with high saturation magnetization.

The Fe_3O_4 NPs were prepared via improved chemical coprecipitation method. Typically, 0.3967 g of $FeCl_2{\cdot}4H_2O$ (2 mmol) and 0.5406 g of $FeCl_3{\cdot}6H_2O$ (2 mmol) were dissolved in 150 mL of deionized water, such that $Fe^{2+}/Fe^{3+} = 1$. The mixed solution was transferred into a 250-mL three-necked flask, and 8 mL of $NH_3{\cdot}H_2O$ (1.5 mol/L) was injected into the mixture rapidly, stirred under N_2 at 40 °C. Then, the additional $NH_3{\cdot}H_2O$ (1.5 mol/L) was added to adjust the pH value to 9–10, and the growth of Fe_3O_4 nanocrystalline was allowed to proceed for 30 min in the suspension at 60 °C. The Fe_3O_4 precipitates were collected by applying a magnet, and washed with 50-mL deionized water for three times, and then dissolved in 150-mL ethanol/water (volume ratio, 1:1) solution. A solution of APTTS was added into the Fe_3O_4 suspension, stirred under N_2 atmosphere at 40 °C for an hour. Then the solution was cooled to room temperature. The prepared APTTS-modified Fe_3O_4 NPs were collected with a magnet, and washed with 50 mL of ethanol, followed by deionized water for three times.

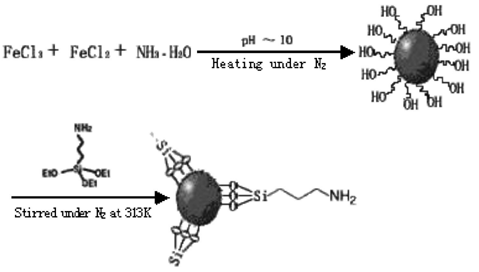

Figure 1. Chemical reaction schemes for surface modification of APTTS on the surface of Fe_3O_4 nanoparticles.

The scheme for the surface modification of APTTS on Fe_3O_4 NPs was illustrated in Figure 1. It was reported that Fe_3O_4 NPs prepared in the aqueous phase are covered with a number of hydroxy (–OH) groups.[3,5,8] Consequently, it was inferred that the APTTS could be immobilized directly on the surface of Fe_3O_4 NPs through silanization reaction with –OH groups. Fourier transform infrared (FT-IR) spectroscopy provided a valuable tool for studying the surface modification.[6,9,10] The FT-IR spectra of unmodified and APTTS-modified Fe_3O_4 NPs were determined with a Nicolet 5DXB FT-IR spectrometer. As shown in Figure 2, the Fe–O stretching vibration at 579 cm^{-1}, O–H stretching vibration about 3410 cm^{-1} and O–H deformed vibration at 1623 cm^{-1} were observed both in Figures 2a and 2b, suggesting that –OH groups coat on the surface of Fe_3O_4 NPs as reported.[3,5,8] The intensity band at 3423 cm^{-1} in Figure 2b probably contributed to free amino groups on the APTTS-modified Fe_3O_4 NPs, which can be overlapped by the O–H stretching vibration band. The outstanding features in going from (a) to (b) are the appearance of the peaks at 1105, 1385, and 2921 cm^{-1}. The Si–O stretching vibration observed at 1105 cm^{-1} significantly reveals that the covalent bonds of Fe–O–Si are formed after APTTS modification. The bands around 2921 and 1385 cm^{-1} were assigned to $-CH_2$ and C–N stretching vibration, respectively. The results provided the evidences that APTTS can be bonded on the Fe_3O_4 NPs surface through silanization reaction with –OH groups.

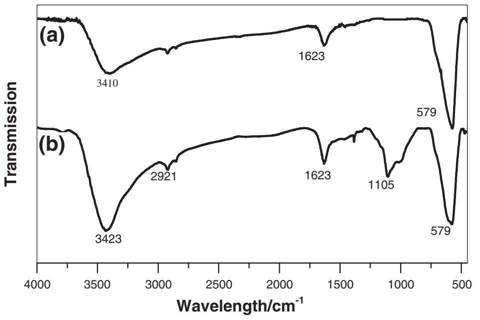

Figure 2. FT-IR spectra of (a) unmodified, (b) APTTS-modified Fe_3O_4 NPs.

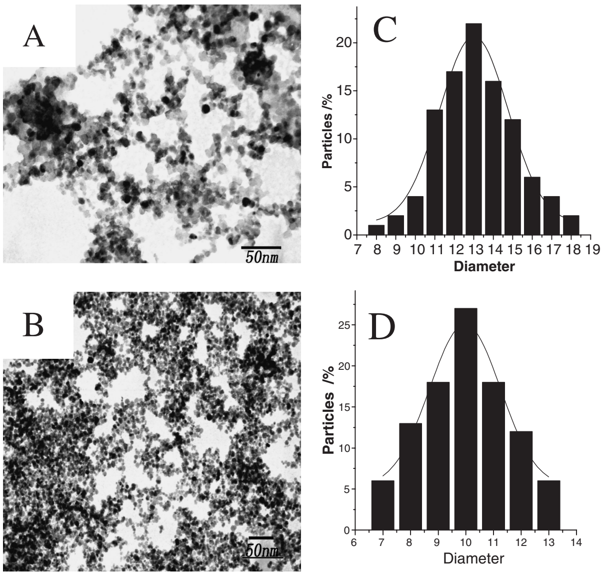

Figure 3. TEM images of (A) Fe_3O_4 NPs and (B) APTTS-modified Fe_3O_4 NPs together with the corresponding particle size histograms (panels C and D, respectively).

The typical transmission electron microscope (TEM) images indicated that the obvious agglomeration was observed with the unmodified Fe_3O_4 NPs (Figure 3A), and the diameters ranged from 8 to 18 nm (Figure 3C). In contrast, the ultrafine APTTS/Fe_3O_4 nanospheres showed relatively well dispersion (Figure 3B), with narrow size distribution of 10 ± 2 nm in diameter (Figure 3D). Accordingly, the electrostatic interaction between amino groups of APTTS coated on the surfaces prevents the aggregation of Fe_3O_4 NPs. Furthermore, the colloidal stability of Fe_3O_4 NPs dispersed in aqueous solution was evaluated by monitoring the ultraviolet–visible (UV–vis) absorbance at $\lambda = 400$ nm as a function of time.[8] For the unmodified Fe_3O_4 NPs, the colloidal stability time was about 1.5 h (Figure 4). In contrast, the maximum colloidal stability time for APTTS-modified Fe_3O_4 NPs was observed for up to 26 h with the molar ratio of APTTS/Fe_3O_4 reaching at 4:1, suggesting that the optimal surface modification was obtained at the molar ratio. These findings clearly demonstrated that APTTS-modified Fe_3O_4 NPs have relatively well dispersion and stability in aqueous fluids.

The magnetization curves of the dried Fe_3O_4 NPs were measured at room temperature with a vibrating sample magnetometry (VSM, LDJ-9600). As shown in Figure 5, no reduced remanence and coercivity were detected, indicating both unmodified and APTTS-modified Fe_3O_4 NPs are superparamagnetic. The least-squares fits showed that the magnetization curves obeyed Langevin function.[4]

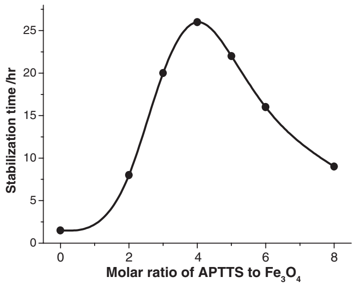

Figure 4. The curve shows the stability time of Fe_3O_4 colloidal suspensions as a function of molar ratios of APTTS to Fe_3O_4.

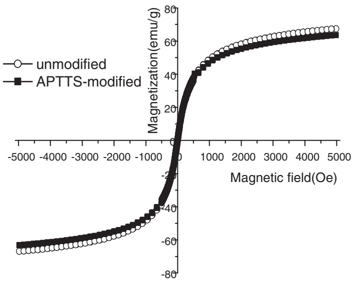

Figure 5. VSM magnetization curves of unmodified and APTTS-modified Fe_3O_4 NPs with the molar ratio of 4:1.

The mean sizes and size distributions for unmodified and APTTS-modified Fe_3O_4 nanospheres were calculated from magnetization data,[4,12] which were ≈13.4 ± 3.9 and 9.6 ± 2.1 nm, respectively. The values were in agreement with the TEM observations. The unmodified Fe_3O_4 NPs show a saturation magnetization (M_s) of 67.15 emu/g. By contrast, the M_s value of APTTS/Fe_3O_4 NPs decreased to 63.54 emu/g at the optimal modification with molar ratio of 4:1. The decrease in M_s comes from the detachment from dipole coupling due to the well distribution of the APTTS-modified Fe_3O_4 NPs. As reported earlier, the experimental M_s values for various modified Fe_3O_4 NPs ranged from 3 to 60 emu/g.[2,5,10,11] As a comparison, APTTS-modified Fe_3O_4 NPs displayed a maximized saturation magnetization of 63.54 emu/g, approaching the limit M_s value of 60–70 emu/g for Fe_3O_4 NPs with diameter distribution ranges less than 20 nm.[10]

In conclusion, we have reported an effective way to synthesize APTTS-modified Fe_3O_4 NPs with an average diameter of 10 nm. Characterized by TEM and UV–vis, the ultrafine APTTS/Fe_3O_4 nanospheres had well dispersion and stabilization in aqueous fluids, and the optimal surface modification molar ratio of APTTS to Fe_3O_4 was found to 4:1. Displaying functional group of $-NH_2$, high saturation magnetization, the superparamagnetic APTTS-modified Fe_3O_4 NPs are of significance for magnetic applications in biomedicine.

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