Synthesis and characterization of magnetic nanocomposites with Fe$_3$O$_4$ core

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Abstract. To improve the infrared absorbing performance of the ferrite magnetic material which has good electromagnetic wave absorbing performance, the core-shell structured multilayer coating is introduced to achieve multiple wavelength range absorbing. Nanocomposites Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$ and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ have been prepared using a series of chemical methods. The results of TEM and XRD analysis show that multilayer coated structures exit in both Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$ and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ and that the core-double shell particles are all in nano-scale. The saturation magnetization and the coercivity of Fe$_3$O$_4$ at room temperature are 72 A⋅m$^2$/kg and 3.82 kA/m, respectively. Further coating of SiO$_2$ and Al$_2$O$_3$ or TiO$_2$ decreases the saturation magnetization and the coercivity while all nanocomposites remain ferromagnetic. There is no obvious improvement of the infrared absorbing ability of Fe$_3$O$_4$ nanoparticles in coating of SiO$_2$ while further coating of Al$_2$O$_3$ or TiO$_2$ reduces the infrared emissivity from 0.97 of Fe$_3$O$_4$ nanoparticles to about 0.83 of the core-double shell nanocomposites.

1. Introduction

Fe$_3$O$_4$ has recently been developed as an excellent electromagnetic and microwave absorbing material [1-3]. However, the infrared absorbing performance of iron oxide magnetic materials is poor [4] and there leaves an open question how to improve the infrared absorbing performance for their use, for example, in aircrafts.

Surface coating is one of the methods which have often been used for modifying or improving material performances [5]. There are several promising techniques for coating particles, most of them are chemical processes, such as the precipitation method, the sol-gel method and the electrochemistry method. However, it is difficult to control the thickness and composition of the coating layer on the particle surface using most of these techniques, which limits their application. The heterogeneous nucleation method is usually used in surface coating because of its simple procedure, low cost and, especially, easy controlling of the thickness and composition of the coating layer [6]. The proper shell thickness is favorable to keep the coated particles stable physically and magnetically. Meanwhile with this method it is convenient for surface modification of the core/shell nanoparticles.

The infrared absorbing performance of aluminium and alumina has been studied for many years [7,8] and it is believed that aluminium and alumina show excellent infrared absorbing ability at wavelength range of 2–15μm. On the other hand, TiO$_2$ shows excellent transparency and stability [9]. Coating of Al$_2$O$_3$ and TiO$_2$ is expected to be used to improve the infrared absorbing performance while not affect the microwave absorbing performance of the Fe$_3$O$_4$ magnetic material. However, Al$_2$O$_3$ and...
TiO$_2$ layer is difficult to be coated onto Fe$_3$O$_4$ nanoparticles by chemical processes directly and a middle layer is sometimes necessary to be introduced. Ulman [10] found that, among materials employed as protection layers, SiO$_2$ is one of the most ideal materials for protecting Fe$_3$O$_4$ nanoparticles due to its reliable chemical stability, biocompatibility, and reactivity with various coupling agents. In this work, SiO$_2$ have been used as a middle layer and the Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) nanocomposites have been synthesized using a variety of chemical methods. The structure, magnetic properties and the infrared absorbing performance have also been investigated.

2. Experimental methods
Fe$_3$O$_4$ magnetic nanoparticles were synthesized by using the titration hydrolysis method [11]. The Fe$_3$O$_4$/SiO$_2$ core-shell nanocomposites were then prepared by the hydrolysis process [12]. The Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$ and the Fe$_3$O$_4$/SiO$_2$/TiO$_2$ core-double shell nanocomposites were finally prepared by the heterogeneous nucleation process [13] and the sol-gel process, respectively.

TEM was performed on a Tecnai-G2 20 Transmission Electron Microscope. TEM specimens were prepared by redispersing the nanocomposites in ethanol and then applied drop-wise onto carbon coated copper grids. Dried samples were submitted to Bruker D8 Advance XRD (Cu-K$_\alpha$, $\lambda$=0.15405 nm) for structure analysis. For FTIR, nanoparticles and nanocomposites were mixed with KBr and pressed to the shape of tablets and the spectra were collected on a NEXUS 670 Fourier Transform Infrared Spectrometer. Magnetization curves were measured at room temperature by using a Vibrating Sample Magnetometer. Emissivity was measured at wavelength range of 1-22$\mu$m by using a Dual Wave Band Emission instrument.

3. Results and discussion

![Figure 1](image)

Figure 1. TEM bright field images of: (a) Fe$_3$O$_4$; (b) Fe$_3$O$_4$/SiO$_2$; (c) Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$ and (d) Fe$_3$O$_4$/SiO$_2$/TiO$_2$.

TEM was first used to study Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$/SiO$_2$ core-shell nanocomposites and Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) core-double shell nanocomposites. Figure 1(a) shows the dispersed Fe$_3$O$_4$ particles with a diameter of 10–15 nm, which are spherical with a smooth surface. In Figure 1(b), Fe$_3$O$_4$/SiO$_2$ core-shell composites are also spherical with a diameter of 15–20 nm. TEM images of
Fe₃O₄/SiO₂/Al₂O₃(TiO₂) core-double shell nanocomposites are shown in Figure 1(c) and 1(d). The shape of the enlarged Fe₃O₄/SiO₂/Al₂O₃(TiO₂) core-double shell nanocomposites becomes irregular. The core-double shell nanocomposites in Figure 1(c) and 1(d) have aggregated, which disagrees with the fact that the magnetic force should become weaker from Fe₃O₄ nanoparticles in Figure 1(a) to double-shell coated nanocomposites in Figure 1(c) and 1(d). It might result from the fact that the surface energy of the Al₂O₃ and TiO₂ is larger than that of Fe₃O₄ or SiO₂. The size of all particles obtained from TEM bright field images is listed in Table 1. The increased size of the nanocomposites proves the successful coating of subsequent shell layers.

| Material            | Emissivity | σₛ(A m²/kg) | Hₐ(kA/m) | Particles size (nm) |
|---------------------|-------------|-------------|----------|---------------------|
| Fe₃O₄               | 0.97        | 72          | 3.82     | 10~15               |
| Fe₃O₄/SiO₂          | 0.96        | 35          | 3.02     | 15~20               |
| Fe₃O₄/SiO₂/Al₂O₃    | 0.82        | 29          | 2.87     | 20~25               |
| Fe₃O₄/SiO₂/TiO₂     | 0.85        | 25          | 2.31     | ~30                 |

**Figure 2.** XRD patterns of (a) Fe₃O₄, (b) Fe₃O₄/SiO₂, (c) Fe₃O₄/SiO₂/Al₂O₃, (d) Fe₃O₄/SiO₂/TiO₂ and (e) Baked Fe₃O₄/SiO₂/TiO₂.

XRD was used to characterize the crystal structure of nanoparticles and nanocomposites. In Figure 2(a), the crystal structure of Fe₃O₄ nanoparticles is well indexed to the inverse cubic spinel phase. A series of characteristic peaks at 2θ = 31°, 36°, 43°, 53°, 57°, 63° and 74° agree with the standard Fe₃O₄ XRD spectrum. The average particle size calculated from the full width at half-maximum of the peak at 2θ = 36° using Sherrer formula is about 12 nm in good agreement with that obtained from TEM image in Figure 1(a). An additional peak is observed at 2θ = 33°, corresponding to γ-Fe₂O₃ arising from oxidation of Fe₃O₄ in air. In Figure 2(b), at 2θ = 20°~25° no obvious peak of crystalline SiO₂ is found. It might result from the fact that the silica shell coating onto the Fe₃O₄ core is amorphous. In
Figure 2(c), peaks at $2\theta = 32^\circ, 33^\circ, 45^\circ, 47^\circ$ and $66^\circ$ agree with the standard $\gamma$-Al$_2$O$_3$ XRD spectrum. Fe$_3$O$_4$ characteristic peaks have been weakened because of the surface coating of shell layers. As shown in Figure 2(d), in the XRD pattern of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposites there appear no clear peaks corresponding to TiO$_2$ and the characteristic peaks of Fe$_3$O$_4$ core has also weakened as observed in Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$ nanocomposites. In order to confirm the existence of TiO$_2$ shell the prepared Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposites has been baked in vacuum at 400 $^\circ$C for 15 minutes. The XRD spectrum of the baked Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposites is shown in Figure 2(e). Peaks at $2\theta =25^\circ$, $38^\circ, 48^\circ$ and $55^\circ$ match the characteristic peaks of (101), (004), (200) and (211) planes of the anatase phase of TiO$_2$ well. Unlike that in Figure 2(c), the main phase in Figure 2(c) is no longer Fe$_3$O$_4$, but TiO$_2$ and the characteristic peaks of Fe$_3$O$_4$ are very weak, almost hardly to see, which indicates that the TiO$_2$ shell is thicker than the $\gamma$-Al$_2$O$_3$ shell and agrees well with the TEM observation. The weakened intensity of characteristic peaks of Fe$_3$O$_4$ core has also confirmed the cover-up of subsequent layers.

FTIR spectra were also used to prove the core-double shell structure, which are shown in Figure 3. In all curves in Figure 3, the bands at 1626 and 3412 cm$^{-1}$ can be assigned to the H–O–H stretching modes and bending vibration of the free or adsorbed water, respectively. In the (a) curve, three main absorptions centered around 585, 1400 and 3140 cm$^{-1}$ are observed, each corresponding to Fe–O, O–H bending vibrations and O–H stretching vibration, respectively. In the (b) curve, the Fe$_3$O$_4$ high-intensity bands at 1400 and 3140 cm$^{-1}$ have disappeared, and also the Fe$_3$O$_4$ high-intensity band at 585cm$^{-1}$ has been weakened. The broad high-intensity band at 1091 cm$^{-1}$ is due to the asymmetric stretching bonds of Si–O–Si in SiO$_2$ associated with the motion of oxygen in Si–O–Si antisymmetric stretch. The band at 799 cm$^{-1}$ is assigned to the Si–O–Si symmetric stretch, while the sharp band at 470 cm$^{-1}$ corresponds to the Si–O–Si or O–Si–O bending modes. The band at 953 cm$^{-1}$ is assigned to the Si–O–Si symmetric stretch. The band at 567 cm$^{-1}$ is an indication of the presence of Si–O–Fe. In the (c) and (d) curves, the Fe$_3$O$_4$ high-intensity band at 585cm$^{-1}$ and the SiO$_2$ high-intensity band at 1091 cm$^{-1}$ have all been weakened. In curve (e) the high-intensity band at 580 cm$^{-1}$ is Al-O stretching vibration of Al$_2$O$_3$. In general, the coordination number of the aluminum species forming Si–O–Al bond is four or six. The six-coordinated aluminum species shift the position of Si–O symmetric stretch band (around 1091 cm$^{-1}$) of pure silica to lower frequency and cause the ring structure band at 799 cm$^{-1}$ to disappear [14]. In curve (d), the band at 1070 cm$^{-1}$ is related to the stretching vibration band of Ti-O-Si. The broad absorption bands of the stretching vibration band of Ti-O-Si and Ti-O-Ti in the region 450–755 cm$^{-1}$ are observed. From the above information, one can see that Fe$_3$O$_4$ core has been covered by SiO$_2$ and Al$_2$O$_3$(TiO$_2$) shells successfully.

Magnetization curves were recorded at room temperature and all the core nanoparticles, core-shell and core-double shell nanocomposites were proved to be ferromagnetic. The room temperature saturation magnetization ($\sigma_S$) and coercivity ($H_c$) of Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) nanocomposites have been obtained from magnetization curves and data are listed in Table 1. The saturation magnetization of Fe$_3$O$_4$ nanoparticles is only about 20% lower than that of bulk Fe$_3$O$_4$ magnetite ($\sigma_{\text{bulk}} = 92$ A·m$^2$/kg [15]). The decrease of the saturation magnetization from Fe$_3$O$_4$ nanoparticles to Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) nanocomposites is believed to result from the nonmagnetic shell layer coating. The coercivity decreases from Fe$_3$O$_4$ nanoparticles to Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) nanocomposites. This is also believed to result from the nonmagnetic shell layer coating. Canted spin configurations may exist near the boundary between the core and the shell, resulting in a decrease of the magnetic anisotropy [16]. The presence of the amorphous shell may also affect the magnetic anisotropy. Finally there may exist exchange coupling between nearby Fe$_3$O$_4$ nanoparticles, which decreases due to SiO$_2$ and Al$_2$O$_3$(TiO$_2$) shell coating.
Figure 3. FTIR spectra of (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$/SiO$_2$, (c) Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$ and (d) Fe$_3$O$_4$/SiO$_2$/TiO$_2$.

The infrared absorbing performance of Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) nanocomposites has been investigated. The infrared emissivity absorption data are listed in Table 1. The infrared emissivity of the Fe$_3$O$_4$/SiO$_2$ core-shell nanocomposites is almost the same as that of Fe$_3$O$_4$ nanoparticles at wavelength range of 1~22μm while further coating of Al$_2$O$_3$(TiO$_2$) decreases the infrared emissivity from 0.97 to about 0.83 at wavelength range of 1~22μm, which indicates that the coating of Al$_2$O$_3$ or TiO$_2$ has improved the infrared absorbing performance of the Fe$_3$O$_4$ nanoparticles.

4. Conclusion
In summary, the Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) core-double shell nanocomposites were successfully synthesized using a series of chemical methods. The shape of most Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) nanocomposites is spherical. The Fe$_3$O$_4$/SiO$_2$/Al$_2$O$_3$(TiO$_2$) nanocomposites remain ferromagnetic with a saturation magnetization of 25-35 A·m$^2$/kg and a coercivity of 2.2-2.9 kA/m. Coating of Al$_2$O$_3$ and TiO$_2$ shell layers improves the infrared absorbing performance of the Fe$_3$O$_4$ nanoparticles. The results show that core-multishell structured nanocomposites have the potential for multiple wavelength range absorbing, and they are expected to become a new series of absorbing materials in the future. This work also provides a promising route to improve and modify magnetic materials with high stability, proper magnetic properties and, especially, good absorbing performance.

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