

STRUCTURE AND MAGNETIC PROPERTIES OF SiO₂ COATED Fe₂O₃ NANOPARTICLES SYNTHESIZED BY CHEMICAL VAPOR CONDENSATION PROCESS

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Abstract. Magnetic nanoparticles for applications in separation and purification processes must satisfy several basic requirements. They should be superparamagnetic, i.e. possess low coercivity (H_c) and low retentivity (M_r), to enable re-dispersion after magnetic capture. In this study, the synthesis of SiO₂ coated γ -Fe₂O₃ nanocomposite particles has been attempted to achieve the above magnetic properties. The synthesis method is based on the decomposition and oxidation of two metalorganic precursor, iron (III) acetylacetonate and tetraethylorthosilicate (TEOS) by the chemical vapor condensation process. The synthesized SiO₂ coated γ -Fe₂O₃ nanoparticles consisted of large amount of amorphous SiO₂ phase shell enclosing the crystalline 20~30 nm γ -Fe₂O₃ nanoparticle core. The H_c and M_r values of SiO₂ coated γ -Fe₂O₃ nanoparticles were 34.5 Oe and 0.118 emu/g, respectively. These low H_c and M_r values were the results of very fine and spherical γ -Fe₂O₃ particles well dispersed in the SiO₂ matrix. Also, from FT-IR analysis it was shown that the surface properties of the coated nanoparticles were similar to those of conventional fumed silica. Finally, the feasibility of SiO₂ coated γ -Fe₂O₃ nanoparticle for magnetic separation media in various bio processes was discussed.

1. INTRODUCTION

In recent years, magnetic particles have been offering attractive properties for various biochemical applications. Especially, a study on iron oxide nanoparticles has been of interest in bio separation process [1]. Magnetic particle-based separation technique provides several advantages over conventional separation techniques because they are fast, gentle and compatible with complex and polluting biological chromatographic processes. In spite of an increasing popularity in biotechnological applications, only a few successful attempts have been made to scale up magnetic separations in biotechnology.

Magnetic nanoparticles such as γ -Fe₂O₃ are often used in bio processes in which the particle dispersion in aqueous solution plays a significant role in controlling the processes and the final properties. In case of uncoated γ -Fe₂O₃ nanoparticles, the dispersion is stable only in highly acidic or highly

basic media conditions. This indicates that surface modification of the nanoparticles is required to improve the dispersion property by increasing the stability of particles in aqueous media [2]. The silica coating on iron oxide particles can be mentioned as an example [3-5]. It was reported that silica-coated iron oxide particles are easily and homogeneously dispersed in aqueous solutions having a wide pH range [6]. Additionally, the silica shell provides the core particle with biocompatibility and different reaction sites which alter the particle conductivity and optical properties. In spite of the merits of this surface modification, the silica coating on iron oxide is mostly being processed by aqueous hydrolysis methods. Yet there have been nearly no attempt for coating silica on iron oxide by gas phase methods. From a practical point of view, co-synthesis of silica coated iron oxide composite particles by gas phase technique has a great potential to realize functional nanocomposites.

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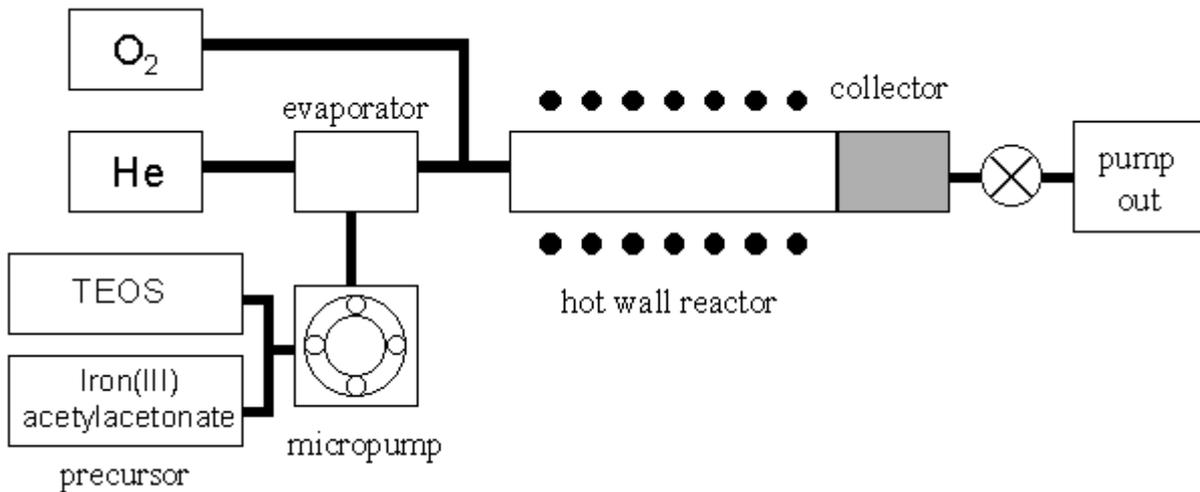


Fig. 1. Schematic diagram of CVC process.

In this study, the synthesis of silica coated γ -Fe₂O₃ nanocomposite particles by chemical vapor condensation (CVC) process [7-9] was investigated and the particle magnetic properties were measured to investigate the feasibility in applications as bio separation media.

2. EXPERIMENTAL PROCEDURE

Iron(III) acetylacetonate (SIGMA Co., 99.9%) and tetraethylorthosilicate (TEOS, SIGMA Co., 99.9%) were used as metalorganic precursors for the synthesis of γ -Fe₂O₃ and SiO₂, respectively. Both precursors were poured into the evaporator (held at 215 °C) by a micro pump at a flow rate of 0.3 ml/min. The precursor vapor was delivered into the reactor furnace by a carrier gas, namely helium at a flow

rate of 2 l/min (refer to Fig. 1). Simultaneously, the reaction gas (oxygen) was fed into the reactor at a flow rate of 3 l/min. The processing temperature was maintained at 1000 °C and the operating pressure was 40 mbar. For comparison, uncoated γ -Fe₂O₃ nanoparticles were also prepared as the reference sample under the same temperature and pressure conditions. The synthesized particles were sampled in the collecting chamber held at room temperature. The powder characteristics and the magnetic properties were investigated using X-ray diffractometry (XRD), transmission electron microscopy-energy dispersive spectrometry (TEM-EDS), vibrating sample magnetometry (VSM) and Fourier-transform infrared (FT-IR) spectrometry.

3. RESULTS AND DISCUSSION

Fig. 2 shows the X-ray diffraction patterns of uncoated iron oxide particles (Fig. 2a) and silica coated iron oxide particles (Fig. 2b) synthesized by the CVC process. It is found that the uncoated particle consists of the γ -Fe₂O₃ crystalline phase with a small amount of amorphous iron oxide phase while the XRD spectrum of the coated sample (Fig. 2b) reveals a large peak corresponding to the amorphous SiO₂ phase and a small peak due to γ -Fe₂O₃. Moreover, the XRD spectrum of the coated sample (Fig. 2b) does not give any proof of the presence of Fe₂O₃-SiO₂ solid solution phase. The average crystallite size of γ -Fe₂O₃ phase was calculated from X-ray diffraction peaks using Scherrer formula and it was found to be 25.4 nm for γ -Fe₂O₃-SiO₂ and 17.7 nm for the reference γ -Fe₂O₃, respectively [10]. The result of this calculation is consistent with the micro-

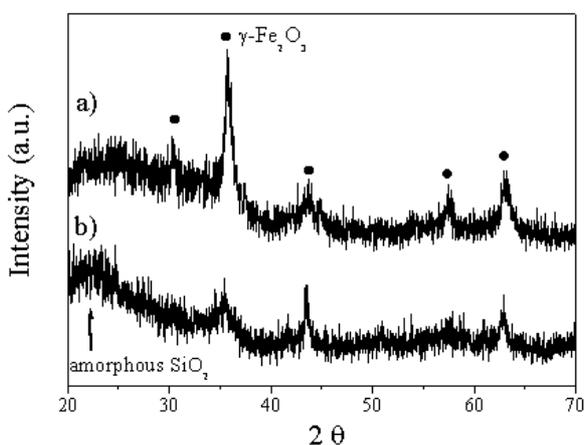


Fig. 2. X-ray diffraction patterns : (a) uncoated and (b) SiO₂ coated γ -Fe₂O₃ nanoparticles synthesized by CVC process.

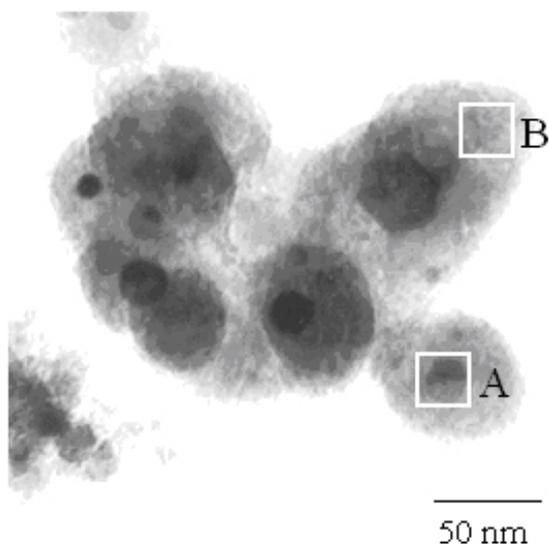


Fig. 3. TEM morphology of SiO₂ coated γ -Fe₂O₃ nanoparticles synthesized by CVC process.

structure observation. Namely, TEM micrograph of γ -Fe₂O₃-SiO₂ powder (Fig. 3) reveals that nearly spherical particles of 20–30 nm in diameter are located in the core of larger particle phase (≥ 50 nm). According to the EDS analysis for two positions on γ -Fe₂O₃-SiO₂ powder, as represented in Fig. 3, the composition ratio of Fe to Si in the core part (position A) was 80:20 in at. % whereas that in the shell part (position B) was 9:91. This analysis intuitively implies that the core part is mainly composed of iron compound while the shell part consists of silicon compound. By comparison with the result of X-ray diffraction pattern (Fig. 2), it is thought that the core phase is γ -Fe₂O₃ and the shell part is amorphous SiO₂. In particular, the core particle of around 20 nm in diameter (Fig. 3) is consistent with the crystallite size of γ -Fe₂O₃ (25.4 nm) in core-shell γ -Fe₂O₃-SiO₂ particle as obtained from the XRD analysis. Consequently, this indicates that the core phase is γ -Fe₂O₃.

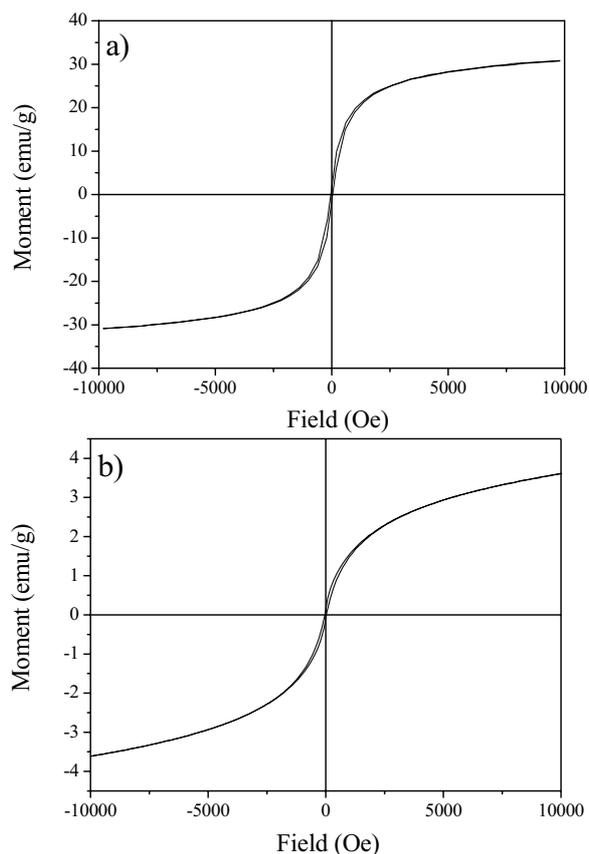


Fig. 4. Magnetic hysteresis loops : (a) uncoated and (b) SiO₂ coated γ -Fe₂O₃ nanoparticles synthesized by CVC process.

The magnetic properties for both samples measured by VSM are depicted in Fig. 4 and summarized in Table 1. The saturation magnetization (M_s) of the uncoated γ -Fe₂O₃ nanoparticles is 30.8 emu/g which is as low as half of the value of M_s for bulk γ -Fe₂O₃. Such a low saturation magnetization of γ -Fe₂O₃ nanoparticles can be attributed to the presence of amorphous phase and the surface anisotropy of γ -Fe₂O₃ nanoparticles [11]. This explanation might be supported by the fact that the uncoated γ -Fe₂O₃ nanoparticles in the present study (Fig. 2a) contain a small amount of amorphous iron oxide

Table 1. Magnetic properties of SiO₂ coated and uncoated γ -Fe₂O₃ nanoparticle synthesized by CVC process.

γ -Fe ₂ O ₃ nanoparticle	M_s (emu/g)	H_c (Oe)	M_r (emu/g)	Content of γ -Fe ₂ O ₃ (%)
SiO ₂ coated	3.6	34.6	0.118	8
uncoated	32.1	37.9	1.51	100

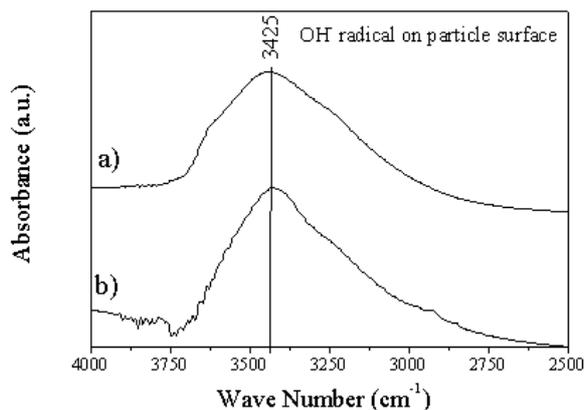


Fig. 5. FT-IR spectra: (a) SiO₂ coated γ -Fe₂O₃ nanoparticles synthesized by CVC process and (b) conventional fumed SiO₂ particles.

phase. On the other hand, the saturation magnetization of SiO₂ coated γ -Fe₂O₃ nanoparticle is much lower (3.6 emu/g), which is basically due to large volume of amorphous SiO₂ phase in the coated nanoparticle sample. This is favorably supported by the result of the EDS analysis for the coated nanoparticles. Indeed, the average composition ratio of γ -Fe₂O₃ to SiO₂ revealed to be 8:92 as calculated from 15 at.% Fe and 85 at.% Si, that is the values obtained from the EDS analysis. Therefore, the large amount of SiO₂ phase (10 times larger than that of the γ -Fe₂O₃ phase) decreased the saturation magnetization of the coated nanoparticle sample.

The coercivity (H_c) was measured to be consistently less than 40 Oe, which is remarkably small compared to that of bulk γ -Fe₂O₃ (250–350 Oe). This low coercivity was mainly due to the equiaxed γ -Fe₂O₃ nanoparticles prepared by the CVC process, as a result of the anisotropy of the particle shape, and the disorder of the crystallographic axis. Moreover, the low M_s and H_c indicated that the synthesized γ -Fe₂O₃ nanoparticles exhibited near superparamagnetism at room temperature, meaning that a large amount of ultrafine particles with sizes less than 20 nm was present in the sample, which is in agreement with the XRD and TEM results. The interest in magnetic properties of the coated nanoparticle sample is that the retentivity (M_r) is much smaller than that of γ -Fe₂O₃ nanoparticles, which is mainly responsible for high dispersion of the γ -Fe₂O₃ nanoparticles in the SiO₂ matrix. Therefore, these low values of M_s , M_r and H_c for the SiO₂ coated γ -Fe₂O₃ nanoparticles are favorable

for bio separation media as the particle is demagnetized and re-dispersed in aqueous solution after exposure to an external magnetic field.

Fig. 5 shows the FT-IR analysis of the SiO₂ coated γ -Fe₂O₃ nanoparticles compared with commercial SiO₂ particles used in conventional chromatographic process. For the coated sample, the band of the OH groups at the SiO₂ surface was detected at 3425 cm⁻¹ and exhibited the same shape and frequency as the corresponding band of the commercially used SiO₂ particles. Considering that the CVC process is performed at high temperature, the amount of OH⁻ groups at the surface of the coated nanoparticles is thought to be very large compared to that of the chemically synthesized SiO₂. This implies that the SiO₂ coated γ -Fe₂O₃ nanoparticles synthesized by the CVC process present high compatibility to various bio processes.

4. CONCLUSION

SiO₂ coated γ -Fe₂O₃ nanoparticles were successfully synthesized by CVC process using two metalorganic precursors (iron acetylacetonate and TEOS). The results of XRD and TEM analyses proved that 20–30 nm diameter γ -Fe₂O₃ nanoparticle core was covered with SiO₂ amorphous phase shell. The SiO₂ coated γ -Fe₂O₃ nanoparticles exhibited superparamagnetic behavior indicated by low M_s and H_c at room temperature. This is mainly due to the surface and shape anisotropy of very fine and spherical γ -Fe₂O₃ core particles. Especially, SiO₂ coated γ -Fe₂O₃ nanoparticles have a M_r retentivity 10 times smaller than that of γ -Fe₂O₃ due to the good dispersion of γ -Fe₂O₃ core particles in the SiO₂ matrix. From the FT-IR analysis, it appears that SiO₂ coated γ -Fe₂O₃ nanoparticles are compatible with bio processes and have higher potential for magnetic separation media in conventional separation and purification fields.

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