



Original Research Paper

High-purity core-shell α'' -Fe₁₆N₂/Al₂O₃ nanoparticles synthesized from α -hematite for rare-earth-free magnet applicationsTakashi Ogi^a, Qing Li^a, Shinji Horie^b, Akito Tameka^a, Toru Iwaki^a, Kikuo Okuyama^{a,*}^a Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan^b Technical Strategy Department, Research and Development Division TODA Kogyo Corporation, Otake, Hiroshima 739-0652, Japan

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ABSTRACT

α'' -Fe₁₆N₂ nanoparticles (NPs) have been identified as one of the most promising rare-earth-free magnetic materials and synthesized with high purity in laboratory investigation recently. This study reports characteristics and magnetic performance of spindle shaped core-shell α'' -Fe₁₆N₂/Al₂O₃ NPs successfully synthesized from hematite NPs. A two-step reaction process, i.e., hydrogen reduction and ammonia nitridation treatments, was employed to produce the α'' -Fe₁₆N₂ phase (making up to ~99 wt.% of the core content). The high-purity NPs exhibited saturation magnetization and coercivity of 186 emu/g and 2.2 kOe, respectively, at 300 K. The obtained α'' -Fe₁₆N₂/Al₂O₃ NPs possessed a spindle shape with an internal pore structure. Their porosity increased from ~10% to 50–60% during the two-step synthesis process, however, at the expense of crystallite size. The combined use of the present synthesis method and hematite NP enables reduction in the synthesis reaction time, as well as the fabrication of NPs with excellent magnetic performance. Furthermore, the present results suggest the potential of rare-earth-free magnetic core-shell α'' -Fe₁₆N₂/Al₂O₃ NPs in industrial applications.

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1. Introduction

Magnetic materials composed of rare-earth elements are essential components of modern technology such as in electric vehicles, wind turbines, and medical equipment. However, the availability of rare-earth elements is limited by supply conditions, natural abundance, and rapid demand growth for future application requirements [1,2]. Accordingly, in recent years, these concerns have driven the development of rare-earth-free magnetic materials with excellent magnetic properties [3,4].

α'' -Fe₁₆N₂ has been considered as one of the most promising candidates as a future rare-earth-free magnetic material since it was first reported in 1972 to exhibit superior magnetization in a film, which was prepared by reactive vapor deposition [5]. Subsequently, several methods have been employed to prepare magnetic film materials containing α'' -Fe₁₆N₂ phase such as molecular beam epitaxy [6,7], sputtering [8–10], and ion implantation [11,12] on different substrates. However, such developments on thin films cannot be translated to highly magnetic bulk materials [13].

Additionally, α'' -Fe₁₆N₂ is a metastable phase that can partially decompose to α -Fe and γ' -Fe₄N [14–17], further complicating the

synthesis of magnetic materials in bulk form. Accordingly, nanoparticles containing α'' -Fe₁₆N₂ phase have been synthesized for the purpose of fabricating bulk magnetic materials [18–20] and other direct applications such as magnetic recording media [21] and magnetic nanocomposite fibers and films [22,23].

Synthesis methods for preparing α'' -Fe₁₆N₂ NPs have been extensively investigated to increase the volume fraction of the α'' -Fe₁₆N₂ phase in the final material over the past decade [18,20,24–26]. Low-temperature nitridation processes have been developed to produce ferromagnetic α'' -Fe₁₆N₂ NPs by ammonia nitridation of fine α -Fe powder, which was reduced from vapor-grown γ -Fe₂O₃ [18,20,24,26,27]. The content of the α'' -Fe₁₆N₂ phase could also be improved from ~60–81 wt.% to ~91–99 wt.% by decreasing the humidity and prolonging the treatment time [15,20,26–28], as well as including an oxidation step before the reduction step [29]. Besides the nitridation conditions applied during synthesis, the NP size is known to influence the formation of the α'' -Fe₁₆N₂ phase [28,30]. As reported, NPs with a large diameter have a reduced tendency to react with core α -Fe under nitridation conditions [28,29]. Recently, the successful synthesis of single-phase α'' -Fe₁₆N₂ NPs in gram amounts was achieved under well-controlled conditions [24,25,31]. Pursuits in the preparation of the high-purity α'' -Fe₁₆N₂ are rationalized by the fact that the magnetic coercivity of the resulting NPs is significantly correlated to

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the content of the α' -Fe₁₆N₂ phase, according to Pearson's correlation analysis with the coefficient of determination $r^2 = 0.98$ and significance level $p < 0.01$ [27], as illustrated in Fig. S1.

However, the synthesis of such high-purity α' -Fe₁₆N₂ compounds is generally accompanied with reduced stability and sintering of the final material [24,25,29,31–33]. To address these issues, the magnetic NPs have been prepared to feature a shell structure to protect the core component (α' -Fe₁₆N₂) against oxidation, corrosion, magnetic lateral interaction among the particles, and particle agglomeration [24,34,35]. Furthermore, the shell component is expected to have attractive advantages in other applications such as in catalysis, sensors, and the biomedical field [36].

Though considerable efforts have been directed toward improving the purity of the α' -Fe₁₆N₂ phase and addressing the aforementioned issues, current synthesis methods are generally complex and time-consuming, and typically involve the use of expensive γ -Fe₂O₃ NPs. These factors accordingly limit the mass production of high-quality α' -Fe₁₆N₂ NPs, thereby restricting their synthesis to the laboratory scale only. Thus, developing an alternative synthesis method is desirable for the industrial applications of α' -Fe₁₆N₂ NPs.

In the present study, we report the synthesis of core-shell α' -Fe₁₆N₂/Al₂O₃ NPs from hematite NPs, as well as characterization of their magnetic performance. The effect of the pore (contained in the goethite NPs) on the formation of the α' -Fe₁₆N₂ phase and its magnetic property are briefly discussed. An analysis on the application of the current method in the industrial production of rare-earth-free magnetic NPs in relation to the advantages and disadvantages of the method is also presented.

2. Experimental

2.1. Preparation of core-shell α -Fe₂O₃/Al₂O₃ NPs

Fig. 1 shows a simplified illustration of the preparation process of the core-shell α' -Fe₁₆N₂/Al₂O₃ NPs. The preparation process mainly includes two steps, i.e., preparation and nitridation of core-shell α -Fe₂O₃/Al₂O₃ NPs. The preparation process of α -Fe₂O₃/Al₂O₃ NPs comprises a three-step reaction sequence described as follows. (1) Spindle shaped goethite NPs of different sizes were synthesized by mixing an aqueous solution of ferrous sulfate and sodium carbonate under aeration, as described elsewhere in detail [37]. The goethite particle size was controlled by varying the precursor concentration (Na₂CO₃ and FeSO₄) in the range of 10–100 mmol/L.

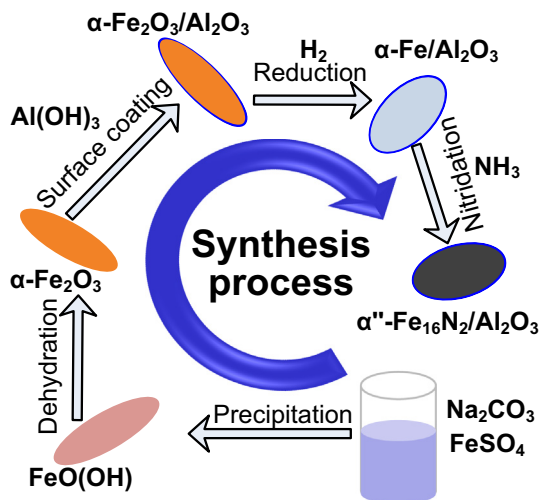


Fig. 1. Schematic of the synthesis of spindle shaped core-shell α' -Fe₁₆N₂/Al₂O₃ NPs.

(2) α -Hematite NPs were produced by dehydrating the goethite NPs in air at 500 °C in a rotating furnace, also described elsewhere in detail [38]. Pores were generated in the α -hematite NPs during the heating process owing to the removal of water molecules from the goethite NPs. The morphological characteristics of the α -hematite NPs were influenced by the calcination conditions employed [38]. (3) The obtained α -hematite NPs were then dispersed in water to which aluminum hydroxide was added for surface coating of the core. Alumina-coated α -hematite (core-shell α -Fe₂O₃/Al₂O₃) NPs were finally obtained following washing with pure water and subsequent drying in air [28].

The average particle size, density, and porosity of the three core-shell α -Fe₂O₃/Al₂O₃ NP samples (named as Hematite13, Hematite41, and Hematite110 with the number as their length) are listed in Table 1.

2.2. Synthesis of α' -Fe₁₆N₂/Al₂O₃ NPs

The core-shell α' -Fe₁₆N₂/Al₂O₃ NPs were synthesized via a two-step reaction sequence i.e., hydrogen reduction and ammonia nitridation. The synthesis method is detailed in our previous studies [22,24,28,34]. Briefly, reduction and nitridation were conducted using hydrogen and ammonia flows, respectively. Table 2 lists the temperature and treatment time applied during the synthesis processes. Since smaller size NPs are easier to be agglomerated and nitridated than larger size NPs. The optimal nitridation temperature for the three width samples of 8 nm, 22 nm, and 18 nm are 145 °C, 155 °C, and 150 °C, respectively. A decrease in NP diameter can reduce the optimal nitridation temperature and time. The prepared samples were immersed in pure toluene and then stored in a glove box for subsequent use.

2.3. Characterization

The morphology of the prepared NPs was analyzed using a scanning electron microscopy (SEM; S-5000, Hitachi), a transmission electron microscopy (TEM; JEM-2100F, Jeol), and a bright-field scanning transmission electron microscopy (STEM; JEM-ARM200F, Jeol) coupled with a high-angle annular dark-field (HAADF) imaging. The elemental composition of the α' -Fe₁₆N₂/Al₂O₃ NPs was determined using STEM coupled with an electron energy loss spectroscopy (STEM-EELS; HD-2700, Hitachi); the characterization instrument was equipped with an elemental analyzer (776-type ENFINA 1000, Gatan). The crystal size and chemical composition of the prepared NPs were examined by X-ray diffraction (XRD; RINT2000, Rigaku Denki Co. Ltd., Japan), using Cu K α irradiation and a 2θ scanning range of 20–80°, and energy-dispersive X-ray spectroscopy. The yield of α' -Fe₁₆N₂ phase was estimated from the obtained XRD diffraction intensity of α -Fe {110}, α' -Fe₁₆N₂ {220}, and α' -Fe₁₆N₂ {202} peaks, previously described in detail [29]. The elemental composition of samples was analyzed by inductively coupled plasma atomic emission spectrometry (SPS-4000, Seiko Co. Ltd., Japan). The magnetic performance of the prepared NPs was assessed using a superconducting quantum interference device (Quantum Design, Japan), operating at 5 K and 300 K. Additionally, the apparent density (ρ_{App}) of the core-shell α -Fe₂O₃/Al₂O₃ NPs was measured using a gas pycnometer (Accupyc II 1340, Shimadzu). Subsequently, using the theoretical densities of α -Fe₂O₃ (5.24 g/cm³) and Al₂O₃ (3.97 g/cm³), the true density of the core-shell α -Fe₂O₃/Al₂O₃ NPs was calculated as follows: $\rho_{\text{True}} = 3.97 \times \eta_{\text{Al}_2\text{O}_3} + 5.24 \times (1 - \eta_{\text{Al}_2\text{O}_3})$, where $\eta_{\text{Al}_2\text{O}_3}$ is the weight ratio of Al₂O₃. The porosity of the α -Fe₂O₃/Al₂O₃ NPs was calculated as follows: $1 - \rho_{\text{App}}/\rho_{\text{True}}$. The density and porosity of the synthesized core-shell α' -Fe₁₆N₂/Al₂O₃ NPs were also obtained using the same method.

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