Dispersion Characteristics of α -Fe₂O₃ Nanopowders Coated with Titanium Dioxide by Atomic Layer Deposition

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ABSTRACT

A TiO₂ nanofilm was deposited on α -Fe₂O₃ nanopowders using the atomic layer deposition method. The TiO₂ film was prepared at 300°C using Ti(N(CH₃)₂)₄ and H₂O as the precursor and reactant gas, respectively. The thickness and composition of the TiO₂ surface were characterized by TEM and EDS measurements. The TEM results showed that the growth rate of the film was about 0.12 Å/cycle. The EDS and SAED analyses showed the presence of titanium oxide on the surface of the α -Fe₂O₃ nanopowders, confirming the deposition of the TiO₂ nanofilm. The Zeta potential and sedimentation test results showed that the dispersibility of the coated nanopowders was higher than that of the uncoated nanopowders. This is attributed to the electrostatic repulsion between the TiO₂-coated layers on the surface of the α -Fe₂O₃ nanopowders. The results revealed that the TiO₂-coated layers modified the surface characteristics of the α -Fe₂O₃ nanopowders and improved their dispersibility.

Key words : α -Fe₂O₃, Nanopowders, Atomic layer deposition, TiO₂, Dispersibility

1. Introduction

Magnetic nanopowders play a key role in drug delivery, magnetic resonance imaging and new generation of high-density magnetic recording media.¹⁻³⁾ Hence, iron oxide-based magnetic nanopowders such as Fe₃O₄ and Fe₂O₃ (α -Fe₂O₃, γ -Fe₂O₃) are being studied extensively.⁴⁻⁷⁾ Iron oxide nanopowders have gained immense attention in the fields of biotechnology and medicine owing to super-paramagnetic characteristics. However, to be used in these fields, iron oxide nanopowders should satisfy the following requirements: uniform shape and size, resistance to aggregation, chemical stability and super-paramagnetism.^{8,9)} Various studies are being conducted to meet these requirements and to solve the aggregation problem of iron oxide nanopowders. Research to reduce agglomeration of iron oxide nanopowder used as MRI contrast enhancement.¹⁰⁾ A previous study has reported that the dispersion and magnetic properties of iron oxide nanoparticles can be controlled by controlling their average particle size.¹¹⁾ Another study has reported that the dispersibility of spherical iron oxide nanoparticles can be improved by coating silica on their surface.¹²⁾ There have been reports on the fabrication of polymers with uniformly distributed magnetic iron oxide nanoparticles.¹³⁾

In this study, we improved the dispersibility of α -Fe₂O₃ nanopowders by coating chemically stable TiO₂ on their surface via atomic layer deposition (ALD). The thickness of the TiO₂ thin film-coated α -Fe₂O₃ nanoparticles was measured

and their diffraction pattern was obtained. We also investigated the effect of the thickness of the TiO₂ thin film on the dispersion characteristics of α -Fe₂O₃ nanoparticles.

2. Experimental Procedure

The α -Fe₂O₃ nanopowders used in this study were 99.5% pure and had an average particle size of 30 nm (Hefei Quantum Quelle Nano Science & Technology). The TiO₂ thin films were fabricated by ALD. Ti(N(CH₃)₂)₄(TDMAT) was used as the Ti source and H₂O was used as the reaction gas. Inert Ar gas (6N) was purged into the system. In addition, a vertical flow-type reactor was used in our previous work¹⁻⁴⁾ to efficiently deposit TiO₂ on the α -Fe₂O₃ nanopowders. The precursor of Ti(N(CH₃)₂)₄(TDMAT) was delivered from a stainless steel container with the carrier of Ar at 70°C. The delivery lines were maintained at 70°C to prevent condensation of TDMAT inside the lines. The reactor temperature and the working pressure in the reactor were approximately 300°C and 1 torr, respectively. H₂O was used as a reactant gas and Ar was used as a carrier and purge gas. The opening and closing sequences of the air valves were controlled by using a computer. The ALD process consisted of a given number of identical cycles. The TiO₂ film thickness was controlled by varying the number of ALD cycles.

The surface of the α -Fe₂O₃ nanopowders was characterized by transmission electron microscopy (TEM, JEM-2100/JEOL). In order to confirm the presence of Ti, the resulting film was analyzed by energy dispersive spectroscopy (EDS, Oxford-INCA). Selected area electron diffraction (SAED) pattern analysis was carried out to determine the exact composition

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of the coated film. In addition, a zeta potential and particle size analyzer (Zeta-PSA, ELSZ/Photal) was used to evaluate the dispersibility of the coated α -Fe₂O₃ nanopowders. 0.006 g of α -Fe₂O₃ nanopowders was diluted in ethanol and then their sedimentation was monitored.

3. Results and Discussion

3.1. Changes in the surface of α -Fe₂O₃ with the number of ALD cycles

The thickness of the TiO₂ layer deposited on the α -Fe₂O₃ nanopowders was determined from the TEM results. It was observed that the thickness of the coated layer increased with an increase in the number of ALD cycles. The TEM images are shown in Fig. 1. Fig. 1(a) shows the TEM image of the uncoated α -Fe₂O₃ nanoparticles, while Fig. 1(b) shows the TEM image of the TiO₂-coated α -Fe₂O₃ nanoparticles when the deposition was carried out for 200 cycles. In Fig. 1(a), the brighter part corresponds to the carbon film of the TEM grid used for preparing the TEM samples and the darker part corresponds to the α -Fe₂O₃ nanoparticles. In Fig. 1(b), the edge of the α -Fe₂O₃ nanoparticles (the interface between bright and dark portions) is the TiO₂ thin film deposited by the ALD method.

Figure 2 shows the graph of the thickness of the deposited film (as measured from the TEM image) as function of the number of cycles. From this graph, the deposition rate was found to be ~ 0.12 Å/cycle.

The results of the EDS analysis of the thin films produced using different number of ALD cycles (0, 50, 100, 150, and 200 cycles) are given in the Table 1 from the EDS results, it was found that the uncoated α -Fe₂O₃ (0 cycles) nanopowders did not show any Ti peak. However, all the coated samples (50, 100, 150, and 200 cycles) showed Ti peaks. With an increase in the number of ALD cycles, the amount of Ti (in at%) coated on the surface of the α -Fe₂O₃ nanopowders

Fig. 2. Growth rate as a function of the number of ALD cycles.

Table 1. EDS Data of Uncoated and TiO₂-Coated α -Fe₂O₃ Nanopowders

	EDS analysis (at%)		
	Fe	Ti	O
Uncoated	19.23	-	80.77
50 cycles	41.67	0.21	58.12
100 cycles	10.51	0.24	89.26
150 cycles	31.71	0.69	67.60
200 cycles	56.39	1.81	41.80

increased.

Figure 3 shows the SAED pattern of the uncoated α -Fe₂O₃ nanopowders (Fig. 3(a)) and TiO₂-coated α -Fe₂O₃ nanoparticles obtained after 100 ALD cycles (Fig. 3(b)). From Fig. 3(a), the d values were measured to be 2.6952, 2.2937, and 1.8373 Å and corresponded to the (121), (222), and (220) planes of rhombohedral α -Fe₂O₃, respectively (JCPDS card No. 85-0599). From Fig. 3(b), the d values of 2.6543, 1.9384, and 1.5182 Å corresponding to the (110)/(130), (222)/(230), and (132)/(151) planes of α -Fe₂O₃/orthorhombic TiO₂ respec-

Fig. 1. TEM images of (a) uncoated α -Fe₂O₃ nanopowders, (b) TiO₂-coated α -Fe₂O₃ nanopowders obtained after 200 ALD cycles.

Fig. 3. SAED patterns (a) uncoated α -Fe₂O₃ and (b) TiO₂-coated α -Fe₂O₃ obtained after 100 ALD cycles.

tively (JCPDS card No. 82-1123). Thus, it was confirmed that TiO₂ with orthorhombic structure was deposited on the surface of α -Fe₂O₃ nanopowders.

3.2. Zeta potential as a function of the number of ALD cycles

The zeta potential of the TiO₂-coated α -Fe₂O₃ nanopowders obtained after 50 - 200 ALD cycles is shown in Fig. 4. The zeta potential was dependent on the number of ALD cycles and was found to be ranging from -10.51 (for 50 cycles) to -27.48 mV (for 200 cycles). The absolute value of the zeta potential of TiO₂-coated α -Fe₂O₃ was 12.03 - 18.12 mV greater than that of uncoated α -Fe₂O₃. Therefore, it was confirmed that the charge on the α -Fe₂O₃ nanopowders increased with an increase in the number of ALD cycles. This means that the dispersion stability of α -Fe₂O₃ improved with an increase in the electrostatic repulsion between the α -Fe₂O₃ particles due to the increase in the charge of coated α -Fe₂O₃.^{14,15)}

3.3. Sedimentation change with the number of ALD cycles

The variation in the sedimentation characteristics of the

Fig. 4. Zeta potential of the uncoated α -Fe₂O₃ nanopowders and TiO₂-coated α -Fe₂O₃ nanopowders obtained after various ALD cycles.

TiO₂-coated α -Fe₂O₃ nanopowders with the number of ALD cycles was analyzed. For the sedimentation test, 0.006 g of α -Fe₂O₃ nanopowders was diluted in ethanol and dispersed by ultrasonic waves. Fig. 5 shows the sedimentation characteristics of the TiO₂-coated α -Fe₂O₃ nanopowders at different time intervals (1 h, 6 h, 16 h, and 3 days). It was found that the dispersion characteristics of the uncoated α -Fe₂O₃ sample and the coated sample obtained after 50 cycles deteriorated gradually as the sedimentation duration was increased beyond 6 h. As a result, the dispersion properties of these samples were lost after 3 days. This caused the precipitation and aggregation of the particles. The coated samples obtained after 100 - 200 ALD cycles showed good dispersion characteristics. In addition, it was found that the coated samples obtained after 100, 150, and 200 ALD cycles maintained their dispersion characteristics even after a sed-

Fig. 5. Sedimentation behavior of (a) uncoated sample and TiO₂-coated samples obtained after (b) 50, (c) 100, (d) 150, and (e) 200 ALD cycles.

imentation time of 16 h. However, after 3 days, the coated sample obtained after 150 ALD cycles showed precipitation. On the other hand, the coated sample obtained after 200 ALD cycles showed a high dispersion stability. From these results, it is clear that the TiO_2 coating prevented the aggregation of the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles and improved their dispersibility.

4. Conclusions

In order to prevent the agglomeration of $\alpha\text{-Fe}_2\text{O}_3$ nanopowder particles, a TiO_2 thin film was coated on their surface by ALD. The TiO_2 coating produced an electrostatic repulsive force between the $\alpha\text{-Fe}_2\text{O}_3$ nanopowder particles and improved their dispersion stability. The dispersion stability of the coated samples increased with an increase in the thickness of the TiO_2 coating. Hence, the TiO_2 coating prevented the aggregation of the $\alpha\text{-Fe}_2\text{O}_3$ nanopowder particles and improved their dispersibility.

Acknowledgments

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