

Synthesis of Spinel Ferrite Particle/Organic Hybrid from Metal-Organics

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ABSTRACT

Nanocrystalline spinel particle/organic hybrid was successfully synthesized from iron(III) 3-allylacetylacetonate (IAA) and nickel acetylacetonate (NA) or nickel diammine 3-propenylacetylacetonate (NPA) by *in situ* hydrolysis. Spinel ferrite particle/organic hybrid was synthesized by hydrolysis of the IAA-NA by addition of methylhydrazine. Crystalline particles of below 10 nm in size were found to be dispersed in an organic matrix. Nanocrystalline particles were identified to be NiFe_2O_4 by X-ray diffraction analysis, electron diffraction and energy dispersive X-ray analysis. The saturation magnetization of the hybrid was dependent upon hydrolysis conditions. Nickel ferrite particles in the hybrid from IAA-NPA had a higher crystallinity and saturation magnetization than those from IAA-NA. Nanometer-sized nickel ferrite particle/organic hybrid showed a typical superparamagnetic behavior.

Keywords: spinel ferrite, metal-organics, hydrolysis, magnetic properties, hybrid

1 INTRODUCTION

Inorganic/organic hybrid materials attract great attention as newly emerging composite materials. Inorganic/organic hybrid material consists of a composite structure at nanometer level between the inorganic phase and organic phase, such as molecules, particles, layers and networks [1]. Nanocrystalline magnetic particles show unique phenomena of superparamagnetism [2] and quantum size effect [3]. The magnetic properties of the fine particles depend upon the crystalline phases, crystallinity and particle sizes. Magnetic particle/organic hybrid has various potential applications in magnetic and medical uses, such as magnetic recording [4], magnetic fluid [2], magnetic ink, magnetic resonance imaging [5] and thermomagnetic surgery [6]. Magnetic particle/organic composites have been synthesized using various methods, such as mixing of magnetic particles and organic phases [7], ion-exchange gels from ferrofluid materials [8] and particle formation in a polymer matrix [9]. Blending of small particles into organics is difficult because of aggregation due to van der Waals force. Especially, magnetic moment results in the aggregation of magnetic particles. Therefore, *in situ* formation of magnetic particles in an organic matrix is one

of the most favorable methods for the synthesis of such composites.

Iron allylacetylacetonate (IAA) has carbon-carbon double bonds for polymerization and chelated Fe-O bonds. The chelated Fe-O bond was reported to be hydrolyzed with ammonia water affording oxide particles [10]. The authors synthesized superparamagnetic $\alpha\text{-Fe}_2\text{O}_3$ /oligomer hybrid from the controlled hydrolysis of iron (III) allylacetylacetonate (IAA) and IAA oligomer [11]. Magnetic particle/oligomer hybrid was synthesized from the IAA oligomer in the presence of hydrazine [12]. Transparent magnetic particle/organic film was successfully synthesized from IAA under controlled polymerization and hydrolysis conditions, and revealed the quantum confinement effect [13].

This paper describes the synthesis of spinel oxide particles/oligomer hybrid material from metal acetylacetonates. IAA, nickel acetylacetonate (NA) and nickel (II) diammine 3-propenylacetylacetonate (NPA) were used as starting metal-organics. The reaction conditions for the formation of NiFe_2O_4 were investigated. Magnetic properties of spinel ferrite particle/organic hybrid were also evaluated. Nanocrystalline spinel ferrite particle/organic hybrid was successfully synthesized from IAA-NA or IAA-NPA under controlled hydrolysis conditions

2 EXPERIMENTAL

2.1 Synthesis of Spinel Particle/Organic Hybrid

Iron (III) tris(3-allylacetylacetonate) (IAA) and nickel (II) diammine 3-propenylacetylacetonate (NPA) were prepared by the method described in the literature [14]. Ethanol was dried over magnesium ethoxide and then distilled before use. Commercial methylhydrazine (CH_3NHNH_2) was used as received. Commercial nickel (II) acetylacetonate dihydrate was used after drying at 130°C and 10 Pa for 2h.

The experimental procedure is shown in Fig. 1. IAA and nickel acetylacetonate ($\text{Ni}(\text{acac})_2$, NA) were weighed with a molar ratio of 2, and dissolved in ethanol yielding a homogeneous solution. The solution was hydrolyzed with a mixture solution of methylhydrazine and water. The reaction mixture was then heated below 80°C from 0.5 to 24h. The solid product was obtained after removal of

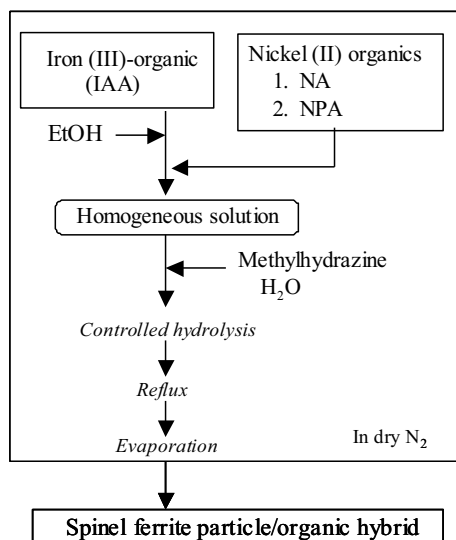


Fig.1 Experimental procedure for synthesis of spinel ferrite particle/organic hybrid

solvent followed by drying under vacuum at room temperature.

2.2 Characterization

The amount of organics of the hydrolysis products was analyzed by DTA-TG (Rigaku, TAS-100). The infrared absorptions of starting compounds and product were measured with FT-IR spectroscopy (Nicolet, Nexus-470). The phase of the product was identified by X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation with a monochromator (Rigaku, RINT-2500). The hybrid powder was analyzed by XPS (Jeol, JPS-9000MC). The magnetic particles in an organic matrix were observed by transmission electron microscopy (TEM, Hitachi, H-800) with an energy dispersive X-ray (EDX) analyzer. The magnetic properties were measured at room temperature using a vibrating sample magnetometer (VSM, Toei Industry, VSM-5).

3 RESULTS AND DISCUSSION

3.1 Synthesis of Spinel Particle/Organic Hybrid from IAA-NA by *in situ* Hydrolysis

In order to synthesize a homogeneous precursor solutions, $\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ was dehydrated at 130°C and 10 Pa for 2h. After the treatment, DTA-TG analysis revealed no weight loss due to removal of water at around 130°C . Thus, anhydrous $\text{Ni}(\text{acac})_2$ (NA) was obtained under the conditions. IAA and NA was mixed with a molar ratio of 2 yielding a brown solution.

The solution was hydrolyzed under various conditions. First, the solution was hydrolyzed ammonia water at 80°C

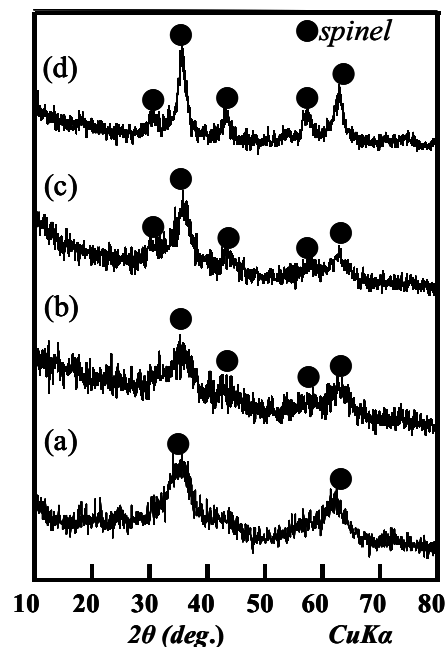


Fig.2 XRD of hybrid, (a) ammonia water, (b) metal/ methylhydrazine/ H_2O = 1/6/10 (molar ratio), (c) 1/6/20, (d) 1/6/40.

for 24h. The XRD of the product revealed two broad diffractions shown in Fig. 2(a). Then, the starting solution was hydrolyzed with methylhydrazine. Methylhydrazine (MH) was selected based upon the previous results by the authors [12,13]. The XRD patterns of the products are shown from Fig. 2(b) to 2(d). When the solution was hydrolyzed with (IAA-NA)/methylhydrazine(MH)/ H_2O = 1/6/10, several broad diffractions are observed as shown in Fig. 2(b). The pattern was almost similar to that obtained with ammonia. With increasing water in amount from 20 to 40, the diffractions increased in intensity as shown in Fig. 2(c) and 2(d). The diffraction pattern shown in Fig. 2(d) is in good agreement with that of spinel. Water promotes hydrolysis of metal-organics and crystallization of spinel particles.

Both NiFe_2O_4 and Fe_3O_4 have a cubic symmetry of crystal structure, and have a quite similar lattice constant to each other. Therefore, XRD analysis is not sufficient for phase identification. The hybrid shown in Fig. 2(d) was analyzed by XPS. The XPS spectrum exhibited not only Fe $2p_{3/2}$ peak at 711 eV but also Ni $2p_{3/2}$ peak at 855 eV. The ratio of peak area of Ni to Fe was 1/2.

Microstructures of spinel particle/organic hybrid was observed by TEM. The hybrid synthesized at (IAA-NA)/MH/ H_2O = 1/6/10 at 80°C for 24h consisted of black particles below 10 nm and an organic matrix. The selected area diffraction (SAD) pattern of the particles revealed spots on the rings, which supported the particles to be crystalline. The d values of the SAD pattern are in good agreement with those of nickel ferrite. The EDX analysis revealed that nickel and iron existed at a 1/2 ratio.

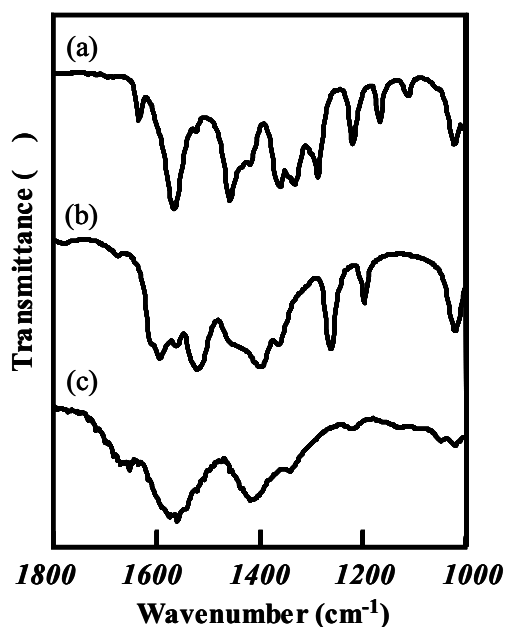


Fig. 3 FT-IR spectra of (a) IAA, (b) NA (c) NiFe₂O₄ particle/organic hybrid.

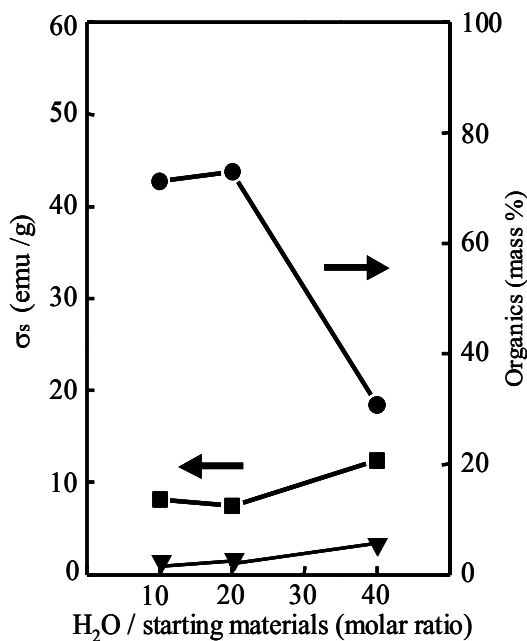


Fig. 4 Changes of saturation magnetization and organics of hybrids with amount of hydrolysis water, ▲ hybrid, ■ corrected σ_s value.

Figure 3 shows IR spectra of starting IAA, NA and hydrolyzed product. The spectrum of IAA shown in Fig. 3(a) include a C=C absorption band at 1640 cm⁻¹ and chelated carbonyl absorptions at 1570 and 1460 cm⁻¹. Similarly, the absorptions of chelated carbonyl groups are

observed at 1590 and 1520 cm⁻¹ in the spectrum of NA (Fig. 3(b)). After the reaction of (IAA-NA) with methylhydrazine and water at (IAA-NA)/MH/H₂O=1/6/10, the C=C absorption of IAA at 1640 cm⁻¹ disappears as shown in Fig. 3(c). The disappearance of C=C suggests the polymerization of allylacetylacetonate ligand during heating at 80°C for 24h. The absorptions of chelated carbonyl groups at 1565 and 1415 cm⁻¹ increase in bandwidth. The broadening of absorption indicates the coordination of the chelated ligand to nano particles.

The changes in saturation magnetization and amount of organics in the hybrids with water amount are summarized in Fig. 4. The hybrid was synthesized at (IAA-NA)/MH=1/6 at 80°C for 24h. The corrected values based upon the amount of NiFe₂O₄ and organics are also shown in Fig. 4. The amount of organics was measured by DTA-TG analysis. The saturation magnetization increases with increasing amount of added water for hydrolysis. The increase of saturation magnetization is attributable to the increase in size and crystalline regularity of spinel particles precipitated out in the organic matrix. The corrected saturation magnetization of the hybrid is about 20 emu/g, when the precursor was hydrolyzed at (IAA+NA)/MH/H₂O=1/6/40. The value was about 36 % of bulk NiFe₂O₄ (56 emu/g).

3.2 Synthesis of Spinel Particle/Organic Hybrid from IAA-NPA by *in situ* Hydrolysis

A precursor consisting of IAA and nickel (II) diammine 3-propenylacetylacetonate (NPA) was treated with a mixture solution of methylhydrazine and water. Figure 5 shows the XRD profiles of spinel particle/organic hybrid from IAA-NA and IAA-NPA with (Fe+Ni)/MH/H₂O=1/6/10 at 80°C for 24h. Spinel particles

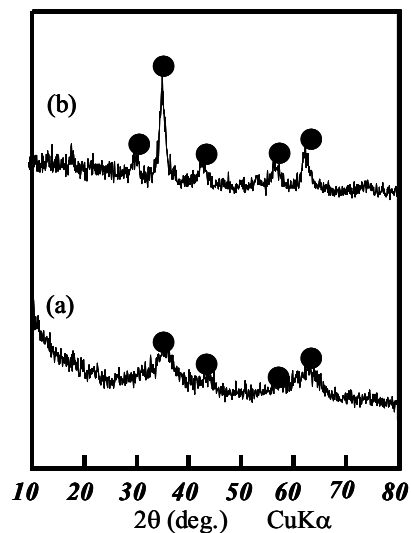


Fig. 5 XRD of NiFe₂O₄ particle/organic hybrid from (a) IAA-NA, (b) IAA-NPA at metal/MH/H₂O=1/6/10.

were also synthesized from IAA-NPA as shown in Fig. 5(b). The diffractions of NiFe_2O_4 particles in the organic matrix (Fig. 5(b)) is much more distinct than that from IAA-NA. The higher crystallinity of NiFe_2O_4 of the former than that of the latter is considered to derive from the reactivity of metal-organic bond of precursors. The reactivity of nickel-organic bond of IAA-NPA is more susceptible to hydrolysis and crystallization than that of IAA-NA.

Figure 6 shows the room-temperature magnetizations versus applied fields for specimens shown in Fig. 5. The magnetic induction increases with increasing applied field, although no hysteresis is observed. The magnetizations shown in Fig. 6(a) saturates rapidly at a low magnetic field. The curve shows neither residual magnetization nor coercive field. These results imply the formation of superparamagnetic particles. The corrected saturation magnetization of the hybrid shown in Fig. 6(a) was 43.5 emu/g, which was 78 % that of bulk NiFe_2O_4 . The curve shown in Fig 6(b) exhibits a similar behavior. Even at the high applied field of 10 kOe, the hybrid show no decrease in magnetic induction as shown in Fig. 6(a). This is considered to result from the high dispersion of magnetic particles in the organic matrix through chemical bonding.

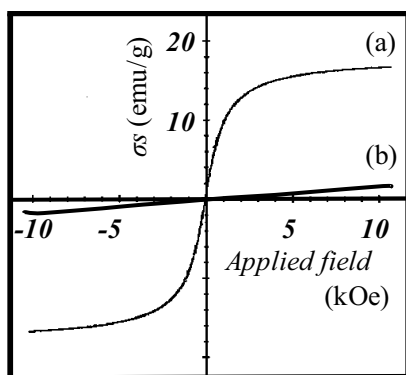


Fig. 6 BH curves of hybrids synthesized from (a) IAA-NPA, (b) IAA-NA at metal/MH/ H_2O =1/6/10.

4 CONCLUSIONS

Nanocrystalline spinel ferrite particle/organic hybrids were successfully synthesized through controlled hydrolysis of iron- and nickel-organics below 100°C . The results were summarized as follows:

1. The hybrid consisted of uniformly dispersed nano-sized NiFe_2O_4 particle and organic matrix.
2. The crystallinity of NiFe_2O_4 particles was dependent upon the amount of hydrolysis water in iron (III) tris(3-allylacetylacetonate) (IAA) and nickel (II) acetylacetonate system (NA).

3. NiFe_2O_4 particles from IAA-nickel (II) diammine 3-propenylacetylacetonate (NPA) had higher crystallinity than those from IAA-NA.
4. The hybrid revealed superparamagnetic behavior. The saturation magnetization of the hybrid was 43.5 emu/g at room temperature.

REFERENCES

- [1] "Organic/inorganic Hybrid Materials-2002", edited by C.Sanchez, R.M.Laine, S.Yang and C.J.Brinker, Mater. Res. Soc. Symp. Proc., 726, Mater. Res. Soc., Warrendale, 2002.
- [2] S.W.Charles and J.Popplewell, "Ferromagnetic Materials", Vol. 2, 509, edited by E.P.Wohlfarth, North-Holland, Amsterdam, 1980.
- [3] L.Zhang, G.C.Papaefthymiou and J.Y.Ying, *J. Appl. Phys.*, **81**, 6892, 1997.
- [4] L.Gunther, *Physics World* **3**, 28, 1990.
- [5] M.B.E.Olsson, B.R.B.Persson, L.G.Salford, U.Schröder, *Mag. Reson. Imaging*, **4**, 437, 1986.
- [6] R.W.Rand, H.D.Snow, D.G.Elliott and M.Snyder, *Appl. Biochem. Biotech.*, **6**, 265, 1981.
- [7] L.Nixon, C.A.Koval, D.A.Noble and G.S.Staff, *Chem. Mater.*, **4**, 117, 1992.
- [8] J.Ugelstad, A.Berge, T.Ellingsen, O.Aune, L.Kilass, T.N.Nilsen, R.Schmidt, P.Stenstad, S.Funderud, G.Kvalheim, K.Nustd, T. Lea, F. Vartdal and H.Danielsen, *Makromol. Chem. Macromol. Symp.*, **17**, 177, 1988.
- [9] R.F.Ziolo, E.P.Giannelis, B.A.Weinstein, M.P. O'Horo, B.N.Ganguly, V.Mehrotra, M.W.Russell and D.R.Huffman, *Science*, **257**, 219, 1992.
- [10] K.Higuchi, S.Naka and S.Hirano, *Adv. Ceram. Mater.*, **1**, 104, 1986.
- [11] T.Yogo, T.Nakamura, K.Kikuta, W.Sakamoto and S.Hirano, *J. Mater. Res.*, **11**, 475, 1996.
- [12] T.Yogo, T.Nakamura, W.Sakamoto and S.Hirano, *J. Mater. Res.*, **14**, 2855, 1999.
- [13] T.Yogo, T.Nakamura, W.Sakamoto and S.Hirano, *J. Mater. Res.*, **15**, 2114, 2000.
- [14] H.A.Tayim and M.Sabri, *Inorg. Nucl. Chem. Lett.*, **9**, 753, 1973.