



Surface hydrophobization of magnetite nanoparticles with polyhexylsilsesquioxane in diethylamine as reaction solvent



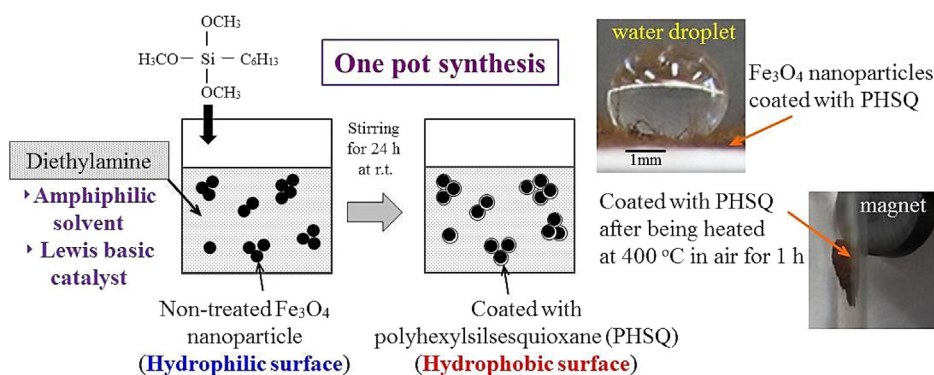
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HIGHLIGHTS

- A facile method for surface hydrophobization of magnetite nanoparticles was proposed.
- The nanoparticles were spontaneously coated with polyhexylsilsesquioxane (PHSQ).
- Diethylamine worked as both the reaction solvent and the Lewis basic catalyst.
- The PHSQ coating contributed to the surface hydrophobicity of the nanoparticles.
- The PHSQ coating enhanced the chemical durability of the core magnetite.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile method for surface hydrophobization of magnetite (Fe_3O_4) nanoparticles with polyhexylsilsesquioxane was proposed. The surface-hydrophobizing coating formed of polyhexylsilsesquioxane on the surface of the magnetite nanoparticles was spontaneously generated from hexylated silanol moiety dissolved in diethylamine. Due to the Lewis basicity, diethylamine worked as the catalyst for the polycondensation of the hexylated silanol. At the same time, the relatively low polarity of diethylamine was found favorable for maintaining the dispersibility of the polyhexylsilsesquioxane-coated magnetite nanoparticles. Moreover, the presence of the surface-hydrophobizing coating was effective for suppressing the transition of the magnetite phase to hematite ($\alpha\text{-Fe}_2\text{O}_3$) even under highly oxidative condition since the polyhexylsilsesquioxane coating blocked oxygen molecules from the access to the surface of the magnetite nanoparticles as evidenced by the absence of micropores in the polyhexylsilsesquioxane coating layer.

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1. Introduction

Metal oxide nanoparticles need to be uniformly dispersed in such nonpolar media as toluene or alkanes in various practical sit-

uations. Since the surface of metal oxides is generally hydrophilic due to the presence of hydroxyl groups, it needs to be modified to hydrophobic surface with nonpolar functional groups. The surface hydrophobization is also effective for fabricating composite materials formed of metal oxide and nonpolar polymer since they need to be uniformly incorporated with each other [1–7].

An auxiliary benefit of the surface modification is the protective effect due to the presence of the surface-modifying layer for the hydrophobization. For example, coating the surface of magnetite

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(Fe_3O_4) with nanometer-thick shell hinders the elimination of the ferromagnetic due to the further oxidation of the magnetite to hematite [8,9].

In the present study, a facile method was proposed to form a nanometer-thick hydrophobic layer formed of partially alkylated siliceous polymer (alkyl- $\text{SiO}_{3/2}$) on the surface of magnetite nanoparticles. Since the surface of the magnetite nanoparticles has hydroxyl groups, silanol formed by the hydrolysis of the alkoxy-silane can be anchored on to it. Further polycondensation of the silanol is expected to give rise to the formation of the nanometer-thick shell of alkylated polysilsesquioxane.

There have been a number of studies of methods for surface hydrophobization with organic polysilsesquioxane derived from organosilane [8–20]. Li et al. used aminopropyltrimethoxysilane (APTMS) as the source of organic polysilsesquioxane [9]. They achieved both immobilization of amino groups on the surface of magnetite nanoparticles and the suppression of the transition of magnetite to hematite. Sasaki et al. hydrophobized the surface of magnetite nanoparticles with polyphenylsilsesquioxane derived from phenyltriethoxysilane (PTES) [10]. The surface-modified magnetite nanoparticles were uniformly dispersed in chloroform. Iijima et al. coated barium titanate (BaTiO_3) with poly(3-glycidoxypropyl)silsesquioxane [11]. They examined the effect of the species of the reaction solvent since they needed to find the optimum preparation condition where they could obtain the most uniform composite formed of the BaTiO_3 nanoparticles and epoxy resin. In their study, the nanoscopic structure of the coating layer was revealed significantly influenced by the solvent species. They found that the choice of the reaction solvent is important in controlling the properties of the coated nanoparticles.

In the present work, we sought for a simple method to fabricate magnetite nanoparticles which can be easily and stably dispersed in such highly nonpolar media as alkanes or toluene. During the formation of the hydrophobic thin coating on the surface of the core magnetite nanoparticles, they aggregate to a visible size or precipitate due to the increasing surface hydrophobicity in polar solvent. In order to avoid the aggregation, we need to lower the permittivity of the reaction solvent. Here, the results obtained using diethylamine as the reaction solvent for the formation of polyhexylsilsesquioxane (PHSQ) coating are reported focusing on the dispersibility in toluene, a highly nonpolar solvent. Besides the relatively nonpolar properties of diethylamine, its Lewis-basic property is expected to catalyze the condensation of silanol groups. In fact, a solution of silanol moiety derived from tetraethylorthosilicate on adding diethylamine shows that the condensation of silanol was markedly catalyzed by the presence of diethylamine with the Lewis basicity. Moreover, the effect of the formation of the PHSQ coating for hindering the transition of magnetite (Fe_3O_4) to hematite ($\alpha\text{-Fe}_2\text{O}_3$) was examined.

2. Experimental

2.1. Materials

Iron (III) chloride (FeCl_3), diethylamine, ethanol, methylisobutylketone and toluene were purchased from Wako Pure Chemical Industries (Japan). Iron (II) chloride (FeCl_2) was obtained from Kojundo Chemical Laboratory (Japan). 1 M ammonia aqueous solution was obtained from Kanto Chemical Industries (Japan). Hexyltrimethoxysilane ($\text{CH}_3(\text{CH}_2)_5\text{Si}(\text{OCH}_3)_3$) was obtained from Shin-Etsu Chemical (Japan). These reagents were used as provided without further purification. Water used for the sample preparation was purified by distillation.

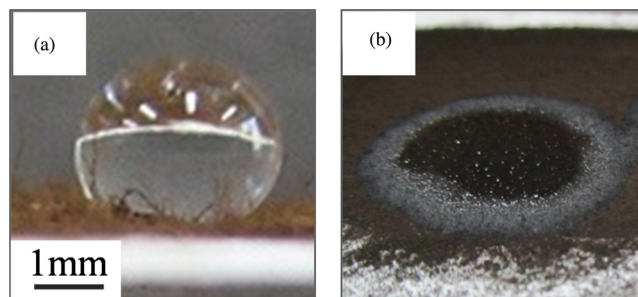


Fig. 1. (a) Sideways view of a water droplet on the layer of densely smeared magnetite nanoparticle coated with polyhexylsilsesquioxane derived from hexyltrimethoxysilane. (b) immediate permeation of water droplet into the layer of densely smeared bare magnetite nanoparticles.

2.2. Preparation of magnetite nanoparticles

Magnetite nanoparticles were prepared by co-precipitation of divalent and trivalent Fe ions at the stoichiometric molar ratio (1:2). FeCl_2 (2.52 g) and FeCl_3 (6.48 g) were dissolved in 200 ml of distilled water. Then, 160 ml of 1 M aqueous ammonia was added into the solution followed by immediate formation of precipitate of magnetite (Fe_3O_4). After stirring, the precipitate was collected with a magnetic piece attached to the bottom of the reaction bottle and rinsed with distilled water three times to remove the residual ammonium chloride.

2.3. Surface modification of magnetite nanoparticles with polyhexylsilsesquioxane

The aqueous slurry (6 g) of the prepared magnetite (mass fraction: 20%) was dispersed in diethylamine (150 g) by ultrasonication for 15 min. Hexyltrimethoxysilane (3 g) was added into the above dispersion and the ultrasonication was continued for 30 min for complete dissolution of hexyltrimethoxysilane. The obtained dispersion of magnetite was stirred for 24 h at room temperature. The sample magnetite nanoparticles were obtained after removing the supernatant liquid by centrifuge. The obtained sample was rinsed with methylisobutylketone and ethanol to remove the unreacted hexyltrimethoxysilane.

2.4. Characterization

Scanning transmission electron microscope (TEM, Hitachi HD-2700 (200 kV)) was used for the observation of the nanoparticulate samples. The particle size in dispersion was measured using dynamic light scattering (DLS, ELSZ-2000ZS (Otsuka Electronics, $\lambda = 628 \text{ nm}$)). The X-ray diffraction was measured using Shimadzu XRD-6000 ($\text{CuK}\alpha$, $\lambda = 1.504 \text{ \AA}$). Nitrogen adsorption measurement was carried out at 77 K using Belsorp-mini II (Bell Japan). The specific surface area was estimated by the Brunauer–Emmett–Teller method.

3. Results and discussion

3.1. Surface hydrophobization of magnetite nanoparticles

Fig. 1(a) shows the sideways view of a water droplet placed on densely smeared magnetite nanoparticles which were surface-modified with polyhexylsilsesquioxane (PHSQ) derived from hexyltrimethoxysilane. The apparent contact angle which is much larger than 90° shows that PHSQ layer is formed on the surface of the magnetite nanoparticles. In contrast to the surface-treated magnetite, the layer of smeared bare magnetite instantly

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