

Magnetic field effects on crystallization by LLIP method

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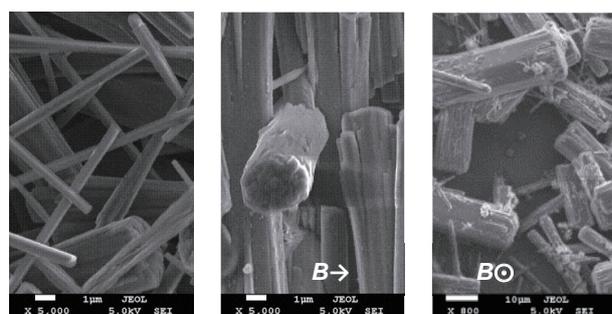
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Application of magnetic fields to crystallization have been studied in order to make a high quality and large crystal.¹⁻³⁾ Liquid-liquid interfacial precipitation (LLIP) method is one of technique of crystallization from solution. Two kinds of solvent are stacked to make their interface. One is a poor solvent for desired material, and the other is a good solvent saturated with the material. In general, right solvent is stacked on heavy one to prevent the convection owing to gravity. The seed crystal is born and grown at around the two-dimensional interface because the supersaturated layer is generated due to mutual diffusion of the two liquid. The sedimentation speed is low for small crystal and accelerated with increasing size of crystal according to Stoke's law. When the grown crystal is leaved from the interface and sunk to the bottom then the growth reaction is completed. Magnetic field and its gradient are thought to be influenced the crystallization processes as follows. The generation of seed crystal and the growth rate are controlled by the magnetic field because the degree of the super-saturation depended on the diffusion of solution is controlled by Lorentz force under the influence of magnetic field. The growth direction is also controllable magnetically because the posture of crystal is controllable against the two-dimensional interface if the crystal has anisotropic magnetic susceptibility. In addition, the crystal size is controllable because the staying period at around the super-saturated layer, which corresponds the reaction period, is controllable according to apply of magnetic force parallel or antiparallel to gravity.

In the experiments, some kinds of crystal were crystallized and the magnetic field effects of the size, morphology, magnetic orientation, and quality of crystal were estimated for C60-fullerene nano-rod (FNR), NaCl salt, ice, glycine, taurine, lysozyme, thaumatin, etc. as listed in Table 1.⁴⁾ For example, the long axis of FNR was oriented perpendicular to the magnetic flux as shown in Fig. 1(b). The volume of FNR was enlarged by 10 times in the homogeneous horizontal magnetic field of 13 T. Under the influence of the gradient vertical magnetic field, the volume was enlarged 100 times in the reduced gravity environment as shown in Fig. 2. The size effects were also recognized for other crystals as listed in Table 1. Moreover, changes of crystal habit and morphology were found as a magnetic field effect.

The magnetic field effect on size must be applicable to crystallization of protein for drug discovery, since crystallization for many unknown proteins is hard to make a good large crystal. If huge crystal is precipitated then the protein is analyzed easily by XRD structure analysis. A hen egg white lysozyme was crystallized by the LLIP method under the influence of magnetic field of up to 13 T. Ten times huge protein crystal was observed and its XRD structure analysis showed that the crystal kept high quality with the maximum resolution of 1.22 Å and R-merge of 4.6% (Fig. 3). The high mosaicity was



(a) $B = 0$ T (b) Horizontal $B = 9.6$ T (c) Vertical $B = 7.2$ T

Fig. 1 SEM images of FNRs crystallized in (a) zero magnetic fields, (b) horizontal homogeneous field of 9.6 T, and (c) vertical field of $B = 7.2$ T with gradient of $dB/dz = -58$ T/m. The directions of magnetic flux were shown as allow in images (b) and (c). The scale bars indicated 1 μm for (a) and (b), and 10 μm for (c).

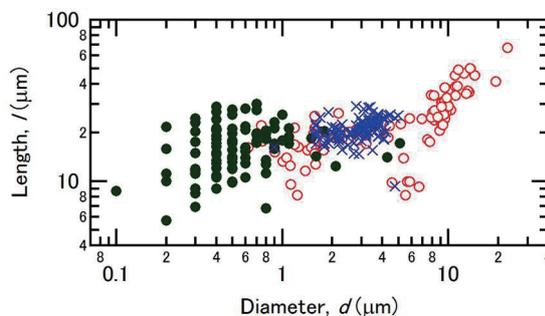


Fig. 2 Scatter plot for fullerene nano rod crystallized under the influence of magnetic fields. The symbols ●, ×, and ○, corresponded to the size for Fig. 1(a), (b) and (c), respectively.

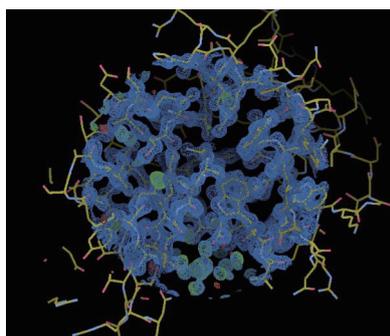


Fig. 3. The structure of lysozyme crystal precipitated under magnetic field with $BdB/dz = -587 \text{ T}^2/\text{m}$.



Fig. 4 Side view of the vertical interface under horizontal gradient magnetic field. the interface was indicated as broken line.

expected because the crystal aligned perfectly to magnetic flux.

In addition, a new one-dimensional reaction field was developed among a paramagnetic liquid and two kinds of diamagnetic liquid under the influence of horizontal gradient magnetic field as shown in Fig. 4. The paramagnetic liquid was forced toward the magnetic center (the left-hand direction in Fig. 4) due to horizontal magnetic force. The horizontal two-dimensional interface was changed vertical by the high magnetic field and the coexistent line among three liquids was appeared. We expect the new reaction field is available to make new low dimensional products.

Table 1. Typical experimental condition of LLIP method and the magnetic field effect

Raw material / Good solvent	Poor solvent (precipitant)	Diameter of reactor, d / mm	Reaction duration	Magnetic field effect	Remarks
C60 fullerene / Toluene	2-propanol	14.5	48 hr	Size x100, Orientation	rod crystal
Ice (water) / 1-BuOH	Toluene	5.0	3 hr	Root position, Orientation, Growth rate x6	$\sim 20 \text{ }^\circ\text{C}$
Glycine / Water	EtOH	14	2 hr	Polymorph, Orientation	$0 \text{ }^\circ\text{C}$
Taurine / Water	EtOH	14	2 hr	Crystal habit, Orientation	
Thaumatococin / Acid	(Rochelle salt)	6.8	20 day	Orientation	pH = 5.0
Lysozyme / TAE	PEG4000, (CoCl ₂ , etc.)	6.8	5 day ~ 2 month	Size x10, Orientation	negative g

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Numerical simulation on structure formation of magnetic particles under magnetic fields

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This study gives an attention to structure formation of magnetic particles by dipole-dipole interaction under magnetic fields in materials processing. When magnetic field is applied to medium containing magnetic particles, the direction of magnetic moment of magnetic particles align in the same direction as the magnetic field, and magnetic particles make chain clusters by the dipole interaction among particles¹. So, the magnetic field is useful tool on development of anisotropic materials.

In this time, we performed numerical simulations of the structure formation of magnetic particles whose size is on the order of micrometers in material processing, and studied the unsteady process of the formation and its feature. Figure 1 shows the schematic model of numerical simulation. The cube of simulation region is a part of the inside of the container and the periodic boundary condition for a 3D system is used. Magnetic particles are randomly dispersed in the container at the initial condition. The translational motion and the rotational motion of particles are governed by Newton and Euler equation, respectively. Here, we used DEM including the magnetic effect. About the simulation research of magnetic particles, A. Satoh has already published many studies². He deals with magnetic particles in magnetic fluids, and particle size is on the order of tens of nanometers. Therefore, he calculates using Brownian dynamics method in which particles do not collide directly with each other. He also discusses mainly the rheology of magnetic fluid due to the structure of magnetic particle, and not structure formation in unsteady process.

One example of numerical simulation results is shown in Fig. 2. Particles aligned in the direction of the magnetic field and made the structure formation of chain cluster. We discuss the structure formed by the magnetic particles and the formation process when the concentration and particle size of the particles in dispersion medium are changed.

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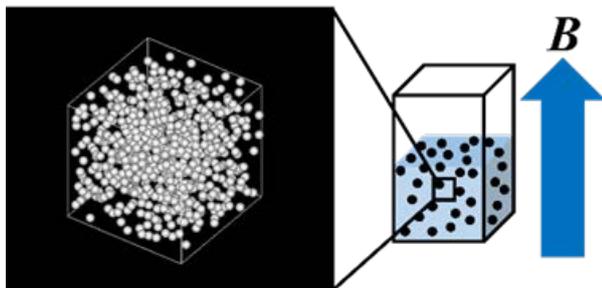
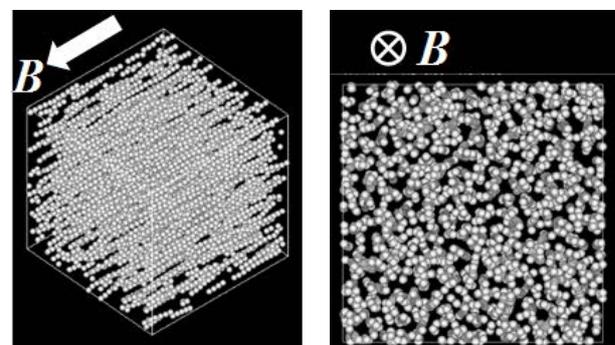


Fig. 1 Model of numerical simulation



(a) Isometric view

(b) Perpendicular section to the direction of magnetic field

Fig. 2 Result of numerical simulation

Liquid Crystal Magneto-Electropolymerization

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1. Alignment of Liquid Crystal Conjugated Polymers

Magnetic field [1] or shear stress [2] affords to produce uniaxial alignment of liquid crystals. Orientation of liquid crystal conjugated polymer has been achieved under magnetic field. The aligned polymer thus obtained in the magnetic field shows main-chain orientation accompanied by orientation of liquid crystal substituents.

2. Liquid crystal electropolymerization

Electrochemical polymerization in liquid crystals has been carried out. The polymer obtained in liquid crystal matrix shows liquid crystal like morphology observable with optical microscopy [3] and scanning electron microscopy. Although the polymer shows liquid crystal like optical texture, the polymer shows no fluidity (polymer solid film). This is due to the fact that molecular collective form imprinting from liquid crystal matrix to resultant polymer in the polymerization process was occurred.

3. Liquid crystal chiral electropolymerization

Chiral conjugated polymers were prepared by electrochemical polymerization of achiral monomers in a chiral liquid crystal (CLC) electrolyte solution [1,2]. The polymer films prepared in chiral liquid crystal shows "Electro-driven change in optical rotation". The optical rotation degree is comparable to that of Faraday rotators. The optical rotation degree can be precisely controlled by the external voltage less than 1 V. This can be a new physical effect in optical rotators. The ellipticity of this polymer is also found to exhibit hysteresis.

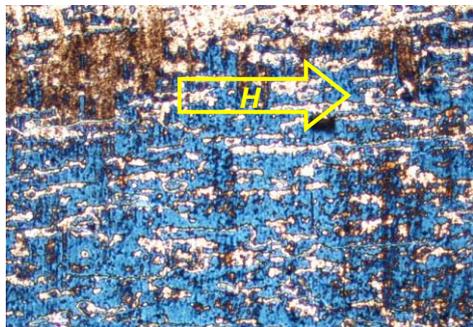


Figure 3. A polymer prepared in liquid crystal under magnetic field.

4. Liquid Crystal Magneto-Electrochemical Polymerization

We carried out electrochemical synthesis of conducting polymers in magnetic field of 12 T. The polymer thus obtained in the oriented liquid crystal show uniaxial form. Polarized absorption spectra of the polymers confirmed anisotropy and "linear polarized electrochromism" [2]. The uniaxial optical function is controlled by application of external voltage.

5. Liquid crystal magnetic orientation in solvent evaporation process

We developed a new method of magnetic orientation in solvent evaporation process via LC state to obtain aligned polymer. Uniaxial alignment of conjugated polymer in liquid crystal was achieved under magnetic field. A growth of the liquid crystal domains and magnetic orientation occur simultaneously in this process to form thin solid films with align liquid crystal order.

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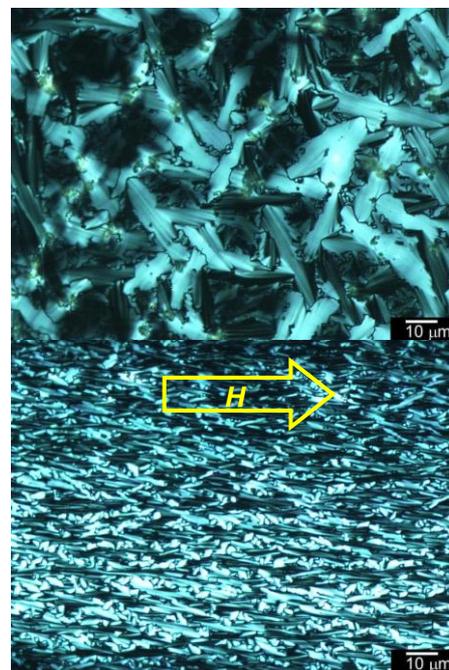


Figure 1. Polarizing optical microscopy images of unoriented polymer (top) and oriented polymer with magnetic field (bottom).

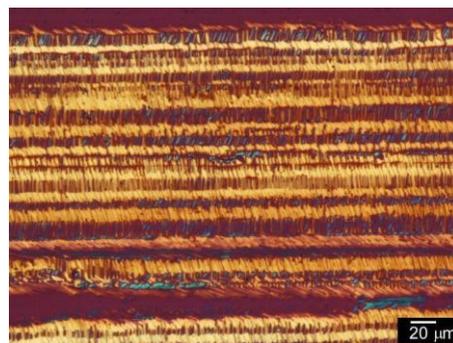


Figure 2. Alignment of a liquid crystal conjugated polymer with shear stress.

Composite Coatings Utilizing Magnetically Fixed Particles

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Composite coating is one of the methods to form films of composite materials utilizing electrodeposition. The electrodeposited film with co-deposited particles is augmented with additional functions which cannot be possessed by the matrix metal film alone. In general, composite coatings are formed by electrodepositing the matrix metal films co-deposited with particles from their suspended solutions. Homogeneity and amount of particles in the films, and the stability of suspended solutions depend on the characteristics of the particles and the matrix metals, so it is not easy to find the optimum condition to control these properties simultaneously. To overcome this problem, we have investigated a new method to form similar composite structures without using suspended solutions; the particles mixed with magnetic particles are fixed on the electrode by the attractive force from the magnets placed on its back side, and then, their gaps are filled with electrodeposited metal. Here, we call this method as composite coatings utilizing magnetically fixed particles (CCMFP). In this paper, we investigate alumina co-deposited nickel composite coatings as a model case of CCMFP, and show some necessity conditions to realize the formation of composite coatings by this method.

As a preliminary test, we tried to find the suitable condition for filling the gaps between nickel particles magnetically fixed on a copper working electrode with electrodeposited nickel without using alumina particles. Conventional Watts bath, which is one of the simplest nickel plating solution, was used as the electrolyte solution. The magnets for fixing the nickel particles were two types of neodymium magnets, we call them magnet A and B; the magnet A has the magnetic flux density of 360 mT with the size of $15 \times 10 \times 5 \text{ cm}^3$ and the magnet B is a bundle of small magnets having the magnetic flux density of 213 mT with the size of $1 \times 1 \times 5 \text{ cm}^3$ (total size: $16 \times 14 \times 5 \text{ cm}^3$). (Fig. 1) Electrodeposition using magnet A, however, did not result in the formation of a uniform film. One reason was that nickel was electrodeposited mainly on the nickel particles not on the copper electrode due to the conductivity of nickel particles. This problem was overcome by increasing the contact resistivity between each particle with thermally-formed nickel oxide. Another reason was non-uniform distribution of the magnetic field, and that was evaded using the magnet B with a bundle structure. After improving these two issues, bottom-up growth of electrodeposited nickel was achieved, but even so, the roughness of the film did not improve. We thought this was because the bottom-up filling of nickel slowed down during the electrodeposition process due to the recovery of conductivity between nickel particles by the dissolution of nickel oxide. To investigate the stability of the oxide, we performed electrodeposition using solutions with different pH values; then electrochemical measurements and thermodynamic estimations revealed that the nickel oxide was easily reduced at low pH, and moderately high pH without forming precipitates of nickel hydroxide in the solution was suitable for continuing uniform bottom-up filling. Nickel-alumina composite coating was conducted under the optimized condition written above, and it was successfully formed. (Fig. 2) Although the surface roughness of the composite film and uniformity of dispersion of alumina particles need further improvement, the results demonstrate the possibility of CCMFP as a potent method for the formation of composite coatings.

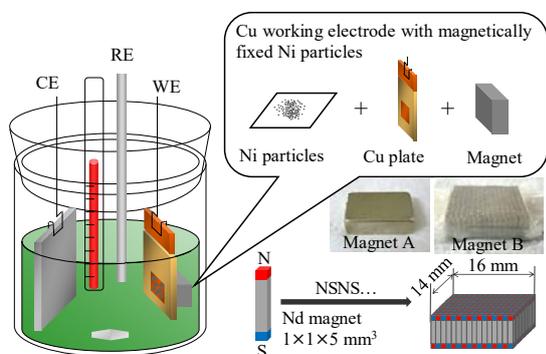


Fig. 1 Experimental setup of the three-electrode electrochemical cell for CCMFP with a Cu plate working electrode with magnetically fixed Ni particles, a Ni wire quasi reference and a Ni counter electrode. Photos of the magnet A and B, and the schematic structure of the magnet B are also presented.

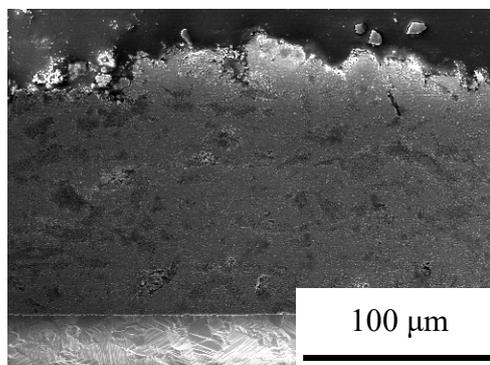


Fig. 2 Cross-sectional SEM image of Al_2O_3 -Ni composite film formed by CCMFP; darker gray parts are included Al_2O_3 particles.

High magnetic field effect on copper electrodeposition and anodic dissolution

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Magneto-electrochemistry is the electrochemistry in magnetic field, which is characterized by a macroscopic solution flow called magnetohydrodynamic (MHD) flow induced by Lorentz force resulting from electrolytic current and magnetic field. Mass transport in magnetic field is strongly affected by MHD flow, so that in electrodeposition and anodic dissolution, surface morphology of electrode can be controlled by magnetic field.

Numerous microscopic flows called micro MHD flow spontaneously occur in MHD flow. In a vertical magnetic field, a macroscopic tornado-like vortex called vertical MHD flow emerges over an electrode called vertical MHD electrode (VMHDE). In electrodeposition and anodic dissolution, lots of vortexes of micro MHD flows create screw dislocations having chirality depending on the direction of magnetic field. According to this process, copper electrodes with high chiral catalytic activities have been fabricated and applied to enantiomeric reactions [1]. However, in general, because of viscosity, about 1 μm vortexes mentioned above are impossible to rotate. For such a high performance of catalysis, something to drastically decrease the viscosity is required. One question therefore arises; what is it?

Answer is ionic vacancy created as a byproduct in electrode reaction; a polarized spherical free space of the order of 0.1 nm surrounded by oppositely charged ionic cloud, which is produced by the conservations of linear momentum and electric charge during electron transfer [2]. The average lifetime is about 1 sec [3], which is extraordinarily long comparing with a collision period of 10^{-10} sec of solution particle. The most important point is its migration without entropy production, which implies that it does not interplay with other solution particles, providing inviscid flow without viscosity. In copper anodic dissolution on a copper VMHDE, microbubbles originated from ionic vacancies has been observed (Fig. 1) [4]. Furthermore, the micro MHD flows make ionic vacancies distributed in mosaic, so that on the patterned vacancy layer, drilling effect of micro MHD vortexes leads to characteristic pit formation with high aspect ratio on a copper electrode surface (Magneto-drill effect) (Fig. 2).

Electrodeposition is also strongly affected by magnetic field. Unrelated with hydrogen evolution, copper dendrites develop in high magnetic fields (Magneto-dendrite effect) (Fig. 3) [5], where in place of hydrogen molecules, nanobubbles from ionic vacancies adsorb on 3D copper nuclei, inducing remarkable dendritic growth.

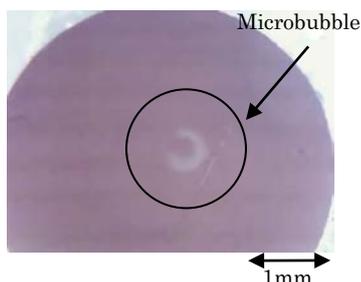


Fig 1. Microbubble globules on copper surface during copper dissolution at 8 T.

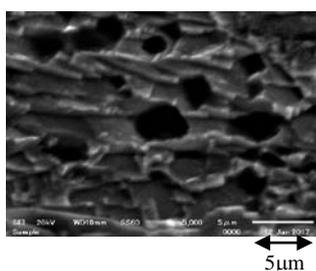


Fig. 2 Magneto-drill effect on a copper rod electrode at 10T.

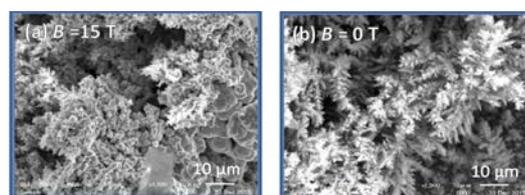


Fig. 3 Magneto-dendrite effect in copper deposition.

(a) $B = 15$ T without hydrogen gas evolution.

(b) $B = 0$ T with hydrogen gas evolution.

Reference

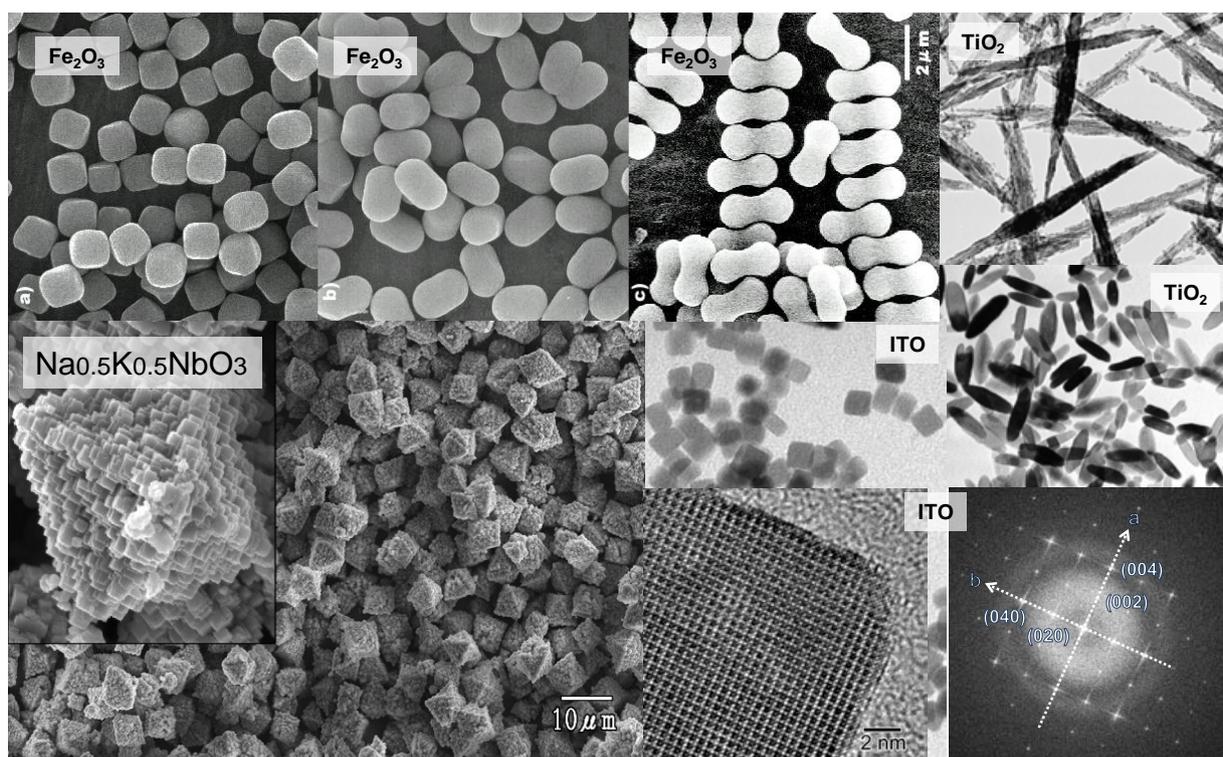
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Concept and Procedure for the Synthesis of Uniform Nanoparticles in Liquid Phase with Large Quantity

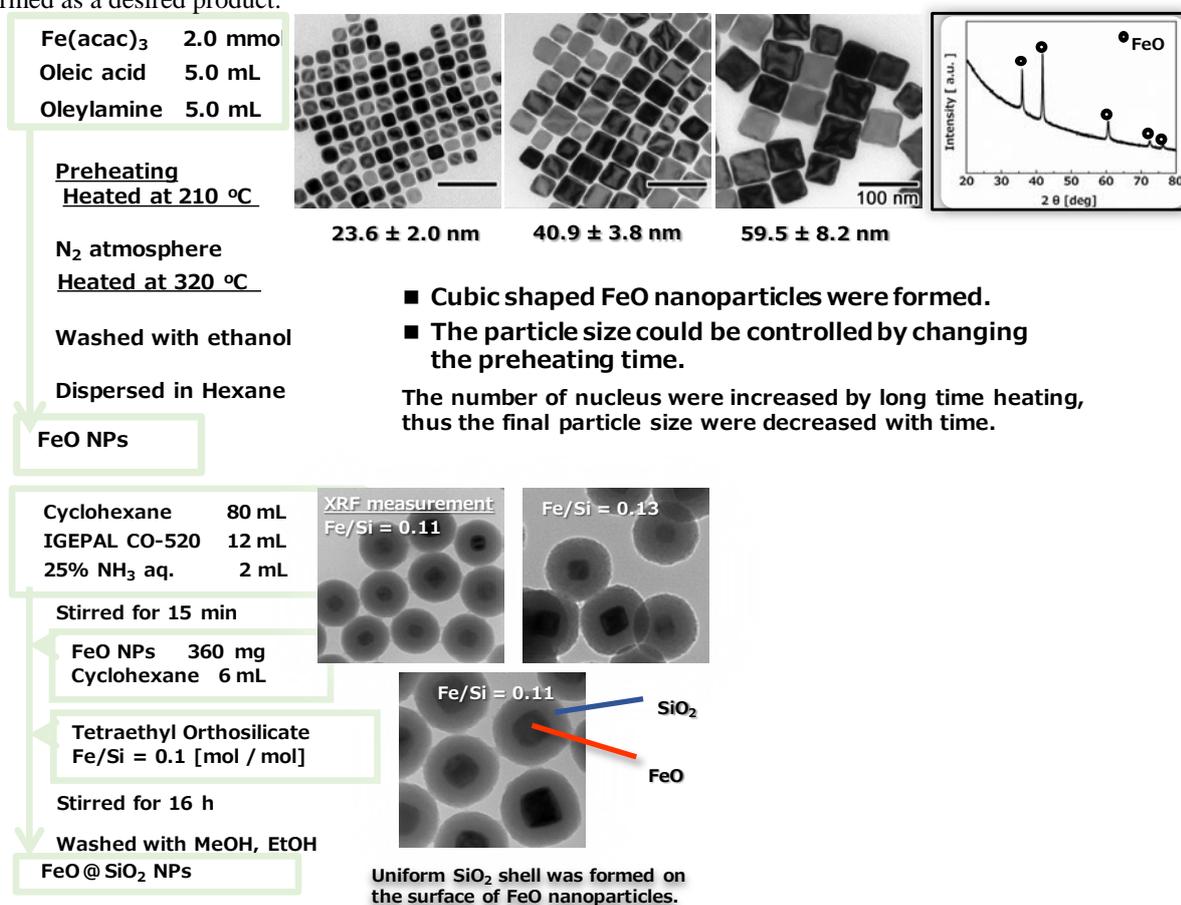
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Since monodispersed particles have excellent uniformity in size, shape, composition, and structure both of bulk and surface, they can be used as highly functional materials for industrial use due to unified characteristics under one standard based on their monodispersity. Among so many synthesis method of nanomaterials, Gel-Sol Method¹⁾ is unique in the production scheme from the dissolution of initially formed gel to the re-precipitation of monodispersed particles in solution phase, where the composition of ions and/or complexes are kept constant in the solution phase. For this method, particles are formed through nucleation and growth by a direct deposition of monomers onto growing particles, obeying LaMer model²⁾. Namely, the growth mechanism of particles is not via aggregation of primary particles. For hydrothermal processes, including Gel-Sol Method, the most important technique is to avoid tremendous coagulation between growing particles. As you know, DLVO theory³⁾ predicts adequate conditions of particle synthesis that we usually choose dilute solution system, where electrolyte concentration is too low to lead to the rapid aggregation. In contrast, Gel-Sol system shows the concentrated solution, including initially formed gel. For this method, growing particles are strongly immobilized in very viscous gel network to completely reduce Brownian motion, a trigger for the aggregation, in which a particle collides with another one. Namely, the particle formation rate is preponderantly higher than the coagulation one of growing particles in order to prevent aggregation. In this manner, Gel-Sol method can be applied in non-aqueous solution in place of aqueous one so as to establish the combination of solvothermal synthesis with Gel-Sol method. For hydrothermal procedure, we have been experienced that materials, which is predicted stoichiometrically to form in any condition, sometimes cannot be prepared. For example, α - Al_2O_3 cannot be formed by the hydrothermal synthesis method, where AlOOH , intermediate compound between initially formed $\text{Al}(\text{OH})_3$ and α - Al_2O_3 as a final product, is too stable to dissolve in aqueous solution in order to convert into α - Al_2O_3 . For the other example, ITO, indium tin oxide, is the same case: ITO is often used as Transparent Conductive Film on various devices, such as LCD, SmartPhone, etc. Although ITO is expected to form stoichiometrically via a hydrothermal method, ITO does not be obtained in the actual synthesis process. For these cases, we choose organic solvent such as alcohol etc., in



place of water, since there is too much oxygen sources, that is, water. Namely, the synthesis of magnetic nanoparticles is exemplified⁴⁾. It is very difficult to obtain single-phase ϵ -Fe₂O₃ nanoparticles, because ϵ -Fe₂O₃ phase is an intermediate phase on the transformation from γ -Fe₂O₃ phase to α -Fe₂O₃ phase. To prepare ϵ -Fe₂O₃ phase selectively, focusing on the formation energy of ϵ -Fe₂O₃ phase is important. The actual preparation method is shown as follows. First, FeO nanoparticles with the size of 24, 40 and 60 nm were synthesized by our previous method⁴⁾. As-obtained nanoparticles were coated with SiO₂ shell to prevent their tremendous aggregation during heat treatment. The resulting SiO₂ coated FeO nanoparticles were treated at 1000 - 1200 °C in the air. When 40 nm FeO nanoparticles with ca. 15 nm SiO₂ shell were treated, significant aggregation and increase in particle size were observed at every treatment temperatures. As-prepared nanoparticles were found the mixture of γ -Fe₂O₃, ϵ -Fe₂O₃ and α -Fe₂O₃ phases. When 40 nm FeO nanoparticles were treated to cover with ca. 40 nm SiO₂ shell, the particle aggregation was completely inhibited. The crystal structure was found to transform from γ -Fe₂O₃ phase to α -Fe₂O₃ phase via ϵ -Fe₂O₃ phase as the treatment temperature increased. The ϵ -Fe₂O₃ nanoparticles formed at 1100 °C showed large coercivity of 20.8 kOe at 300 K. As a result, the control in change in the crystal structure with temperature, under the complete inhibition against aggregation nor the growth in size, is the most important so that ϵ -Fe₂O₃ is selectively formed as a desired product.



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