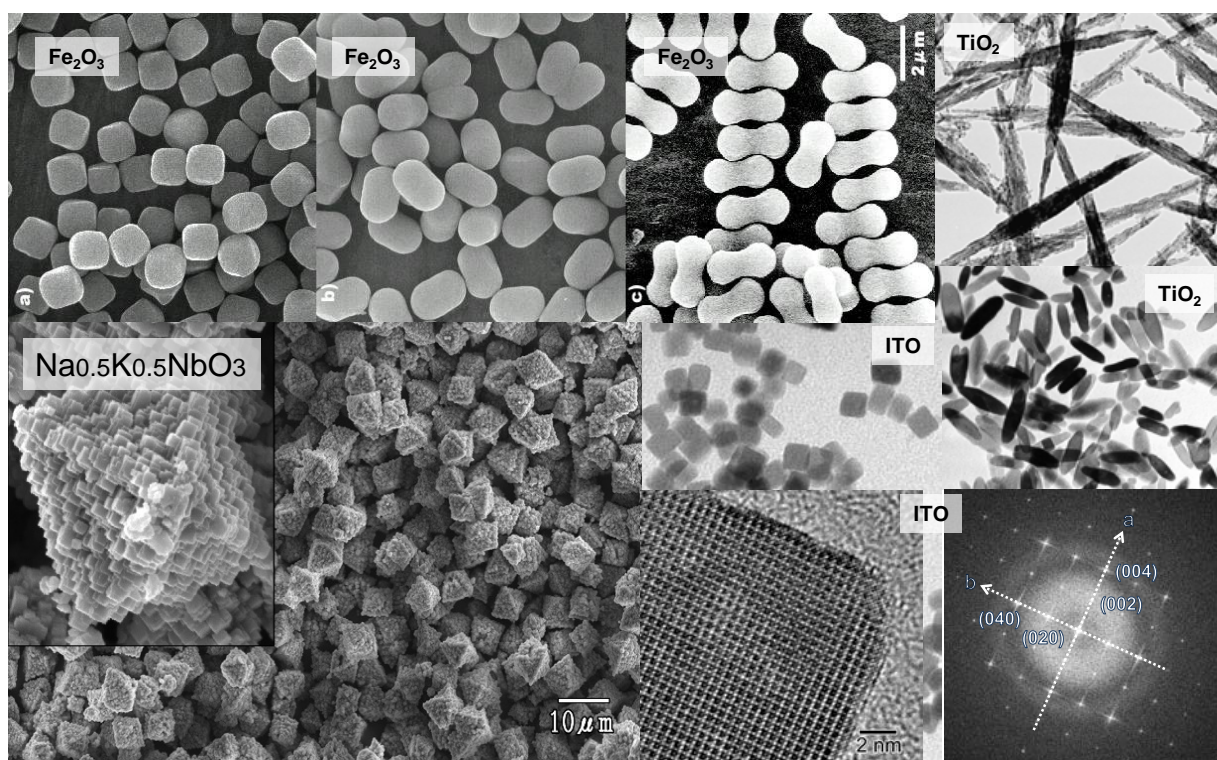


Concept and Procedure for the Synthesis of Uniform Nanoparticles in Liquid Phase with Large Quantity

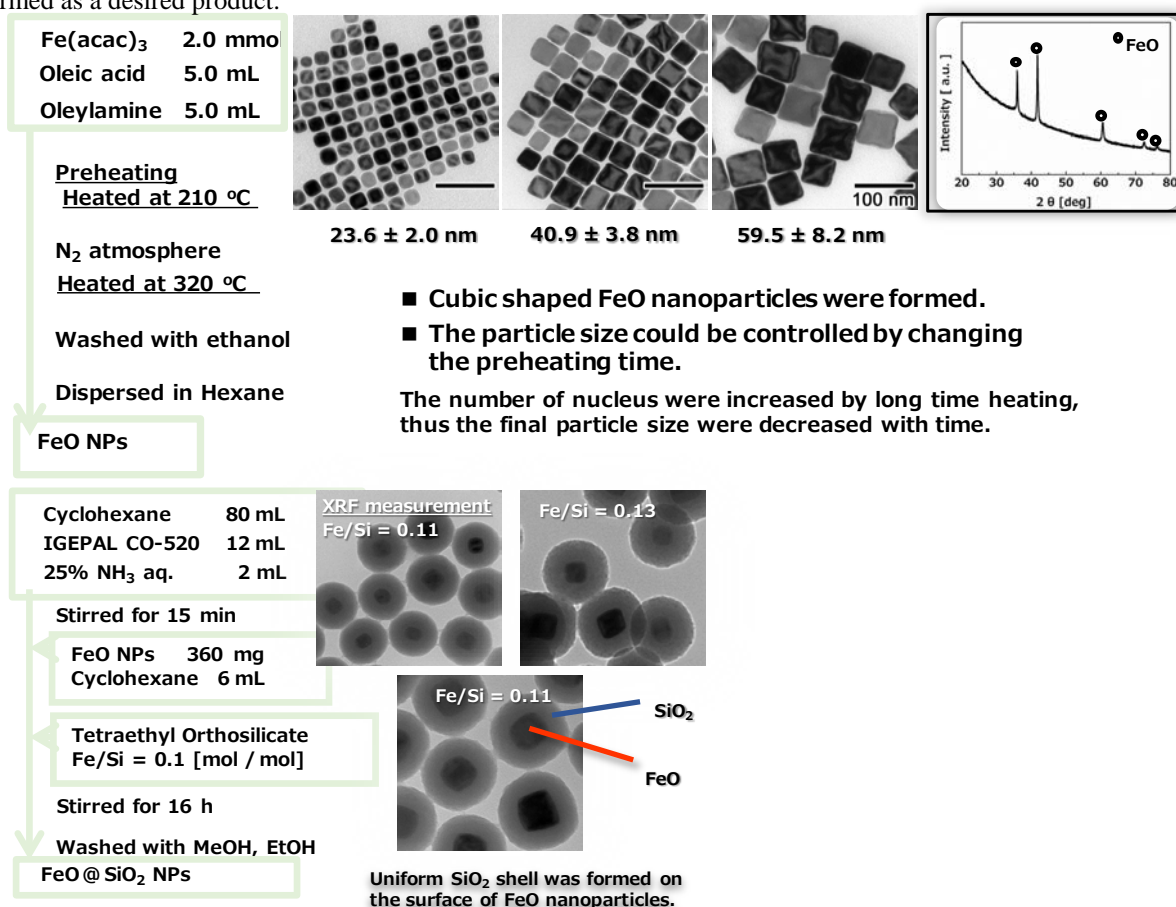
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Since monodispersed particles have excellent uniformity in size, shape, composition, and structure both of bulk and surface, they can be used as highly functional materials for industrial use due to unified characteristics under one standard based 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.



Reference

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