Application of a Two-phase Liquid-Liquid System to the Synthesis of Iron-Containing Nanoparticles

Takuya Nakanishi, Hironori Iida, Harumi Takada, and Tetsuya Osaka

Department of Applied Chemistry, School of Science and Engineering, Waseda University
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Magnetic nanoparticles have received much attention because of their applications in various fields, and thus, a lot of methods for synthesis of magnetic nanoparticles have been developed and reported. As for the metal nanoparticles, methods through decomposition or chemical reduction of organometallic compounds at high temperature are investigated extensively. In the present study, we focus on a two-phase liquid-liquid system, which has been established for the synthesis of gold nanoparticles [1], as a novel approach to the synthesis of magnetic nanoparticles containing iron. Because the two-phase liquid-liquid system has been applied to the synthesis of gold-alloys including gold-platinum and gold-palladium [2], it is expected to be useful for its application to the magnetic iron-alloy nanoparticles if the synthesis of iron nanoparticles is conveniently achieved. In addition, the oxidation of iron nanoparticles has been reported to bring about the formation of monodisperse iron-oxide nanoparticles [3–5]. Thus, we are aiming at establishing the novel synthetic method for the iron-containing magnetic nanoparticles.

Most of the procedure for synthesis of nanoparticles was essentially the same as that described in the literature [1], except for the use of ferric chloride ($FeCl_3$) instead of hydrogen tetrachloroaurate ($HAuCl_4$): metal ions are extracted from solution to toluene using a phase-transfer reagent, tetraoctylammonium bromide ($[CH_3(CH_2)_7]_4N^+Br^-$; TOABr), and then reduced with reducing agent, sodium borohydride ($NaBH_4$).

First, an extraction of iron(III) species into toluene phase with TOABr (Step 1 in the Figure) was investigated. To accomplish the transfer as tetrachloroferrate ($FeCl_4^-$), ferric chloride was dissolved in HCl aqueous solution. With the addition of toluene solution of TOABr, a lemon yellow was transferred from the aqueous phase to the toluene phase. Here, the aqueous phase remains yellow after the vigorous stirring with the toluene phase containing TOABr when the aqueous solution does not contain HCl.

Subsequently, a reduction of transferred iron(III) species with the contact to the aqueous solution containing $NaBH_4$ (Step 2 in the Figure) was carried out, with and without the addition of dodecanethiol ($C_{12}H_{25}SH$) to the toluene phase. In the presence of thiol, toluene phase became violet with reduction by borohydride and further proceeding of reduction resulted in the formation of dark green/black precipitate staying at the toluene/water interface. On the other hand, in the absence of thiol, toluene phase became colorless immediately and black precipitate dispersed into aqueous phase, resulting in orange colloidal solution. Thus, the capping with thiol was suggested to be one of the keys for stabilizing nanoparticles.

Details of structure and properties of the products thus prepared and collected will be reported with the optimized condition of synthesis. Further application of this method to the synthesis of iron-oxide and/or iron-alloy nanoparticles will be also discussed.

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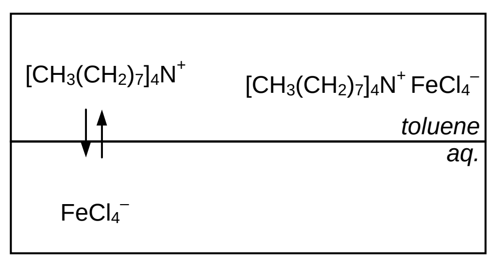
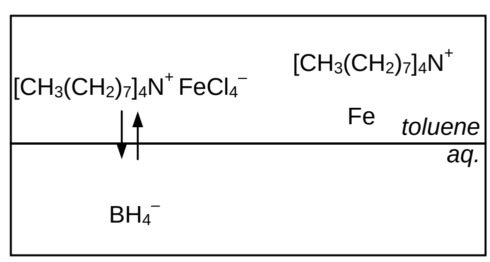


Step1: Extraction of tetrachloroferrate to toluene phase.



Step2: Reduction of tetrachloroferrate with borohydride.

Figure. Schematic representation of the synthesis of iron nanoparticles by using a two-phase liquid-liquid system.