

Preparation of uniform nanoparticles through novel thermal treatment process

* Yuanzhe Piao¹⁾

¹⁾ *Graduate School of Convergence Science and Technology, Seoul National University, Seoul, 151-742, Republic of Korea*

parkat9@snu.ac.kr

ABSTRACT

In this work, the preparation of various uniform nanoparticles through novel thermal treatment processes is introduced. (I) A general method, termed as a “wrap/bake/peel process”, is developed for nanostructural transformation. (II) Self-assembled uniform-sized ferrite nanocrystals embedded carbon nanosheets are synthesized simultaneously through a single heating procedure using metal-oleate complex as the precursor for both ferrite and carbon. (III) A transformation of hydrophobic iron oxide nanoparticles to hydrophilic and biocompatible maghemite nanocrystals by controlled thermal treatment followed by dextran coating is reported. (IV) Uniform carbon nanocapsules with mesoporous shells are synthesized by coating their outer shells with silica to prevent aggregation during their high-temperature annealing.

1. INTRODUCTION

Monodisperse nanoparticles have attracted increased attention because of their many unique properties. Many kinds of uniform nanoparticles with a controlled particle size and shape have been prepared to tailor novel functionalities for numerous applications. The present proceeding paper highlights our recent progress in the preparation of various uniform nanoparticles through novel thermal treatment processes. Several examples of applications of these uniform nanoparticles are also given. (I) A general “wrap/bake/peel process”, is developed for nanostructural and chemical transformation [1]. Depending on the thermal treatment conditions, hollow nanocapsules of either hematite or magnetite were able to be produced. (II) Through a single heating procedure using metal-oleate complex, self-assembled uniform-sized ferrite nanocrystals embedded carbon nanosheets are synthesized simultaneously [2]. As a demonstration of the ferrite/carbon nanocomposite as anode material for Lithium-ion battery, electrochemical experiments were carried out in a coin type cell assembly. The nanocomposite electrodes exhibited large power capability with good cycling stability. (III) A simple and versatile strategy to transform hydrophobic iron oxide nanoparticles to hydrophilic and biocompatible maghemite nanocrystals by thermal treatment followed by dextran coating is reported [3]. Through the process, highly crystalline bare maghemite nanoparticles with high magnetization were produced. Polyanionic CM-dextran coated iron oxide nanoparticles are stable under various conditions. In vivo MR imaging using these nanoparticles successfully showed

significant signal enhancement. (IV) Monodisperse hollow carbon nanocapsules with mesoporous shells are synthesized by coating their outer shells with silica to prevent aggregation during high-temperature thermal treatment [4]. The as-prepared carbon nanocapsules exhibited a high surface area and formed stable dispersions in aqueous solution after the pegylation process. The drug-loading and drug-release properties of the nanocapsules were also investigated.

2. EXPERIMENTAL

2.1 Thermal treatment of iron oxide nanoparticles in air

Salt and iron oxide nanoparticles were dispersed in non-polar organic solvent. The mixture was mixed by stirring and organic solvent was evaporated. The resulting mixture was heated in air. After annealing, the salt was dissolved in water and iron oxide nanoparticles were collected by centrifugation. The salt washing was repeated three times. The resulting nanoparticles were dispersed in distilled water.

2.2 Dextran coated iron oxide nanocrystals

1 g of dextran derivative was dissolved in water (pH 6–7). The annealed mixture of iron oxide nanoparticles and salt was added slowly to the dextran derivative solution under stirring. Dextran coated iron oxide nanoparticles were collected by centrifugation. Removal of salt and the dextran coating using a dextran derivative solution were repeated three times. The resulting nanoparticles were dispersed in distilled water.

2.3 Synthesis of the hollow carbon nanocapsules

Uniform silica nanoparticles were dispersed with a mixture solution of ethanol and water. A mixture of ammonium hydroxide, TEOS, and C18TMS was added to the mixture and the solution was stirred for 24 h at RT. Then, a second portion of TEOS was added to the mixture and the solution was stirred for a further 24 h. Thereafter, core/inner-shell/outer-shell nanostructures were obtained. The nanoparticles were collected by centrifugation and treated with H_2O_2 at RT for 15 h; the nanoparticles were collected by centrifugation again and re-dispersed in a mixture of water and H_2SO_4 . The resulting solution was heated to obtain the SiO_2 @carbon@ SiO_2 composite. Finally, the composite was dispersed in NaOH solution to remove the core and outer shell of the silica. The carbon materials were collected by centrifugation and washed with deionized water and ethanol.

3. RESULTS AND DISCUSSION

3.1 Nanostructural transformation

The overall process is composed of (1) the wrapping of nanoparticles with a silica coating, (2) heat treatment and (3) the etching of the silica layer. A thin silica shell is coated on each nanoparticle. The nanostructure is calcined in air to form a hollow nanostructure coated with a silica shell. To prepare the magnetite nanocapsules, the air-calcined sample is further heat treated under a H_2 flow. Finally, the silica shell is etched away by sonicating the sample in NaOH solution. The iron oxide nanocapsules are isolated by centrifugation and washing several times with deionized water.

Thermogravimetric analysis and differential thermal analysis were carried out to understand the formation mechanism of hollow iron oxide nanocapsules. The current

process is quite general and can be used for the nanostructural transformation of various kinds of material to produce many useful nanostructured materials.

3.2 Self-assembled uniform-sized ferrite nanocrystals embedded carbon nanosheets

In the direct synthesis of the ferrite/carbon hybrid nanosheets, two strategies were adopted. First, the surface of thermally stable salt particles was used as the template for the 2-D nanostructure. Second, metal-oleate complex was used as the precursor of both ferrite and carbon. Upon heating under inert atmosphere, the coating layer on the surface of the salt particles was converted to a carbon sheet of uniform thickness. In the synthesis, an aqueous solution of metal chloride and sodium oleate were mixed together, whereupon salt was added and then ground mechanically until it became a fine powder. This mixture was heated under inert atmosphere to form 2-D ferrite/carbon hybrid nanosheet structures. Finally, the hybrid nanosheets were separated by dissolving salt particles in deionized (DI) water.

The morphology of the hybrid nanosheets was analyzed by electron microscopy. Well-ordered uniform iron oxide nanocubes were embedded in a carbon sheet. When these ferrite/carbon nanosheets were employed as lithium ion battery anodes, the electrochemical performances showed outstanding enhancement of durability and rate performance as compared to the 3-D agglomerated nanocomposites. These synthetic procedures are not only easily scalable for mass production but also extensible to various 2-D inorganic-nanoparticle/carbon nanocomposites that can potentially be applied to practical energy storage and conversion devices.

3.3 A transformation of hydrophobic iron oxide nanoparticles to hydrophilic and biocompatible maghemite nanocrystals

Uniform sized iron oxide nanoparticles were prepared by thermal decomposition of iron-oleate complex. The nanoparticles and salt were mixed in organic solvent and the solvent was evaporated under mild heating. After heated at high temperature for 5 h under an air atmosphere and subsequent removal of the salt by dissolution with water, well dispersed nanoparticles were obtained. The crystal structure of the nanoparticles after the thermal treatment was characterized by using X-ray diffraction to track phase changes induced by thermal treatment. To characterize the magnetic properties of the iron oxide nanoparticles, vibrating sample magnetometer measurements were also conducted. After removing the salt, the iron oxide nanoparticles, which are bare nanoparticles without surfactant stabilization, could be dispersed in water owing to the presence of hydroxyl group on the particle surface. As the pH was varied, surface charge of the nanoparticles changed, which subsequently affected the hydrodynamic diameters. The bare nanoparticles tend to aggregate and precipitate at pH 7. To impart stability in aqueous media as well as biocompatibility to the nanoparticles, dextran was used as a stabilizer. Salt removal process and dextran coating were conducted simultaneously to minimize particle aggregation.

CM-dextran coated iron oxide nanoparticles were applied for in vivo MR imaging. CM-dextran coated nanoparticles were chosen instead of DS coated ones because of their better colloidal stability and high relaxivity. Nanoparticles were injected into a mouse through its tail vein. The MR images taken before and after injection showed that the nanocrystals accumulated in the liver and spleen within 2 h, which is similar to those using commercial MRI contrast agents. The MR signal enhancement was clearly

observed in these organs, demonstrating that CM-dextran coated nanoparticles could be potentially useful for T2 MRI contrast agent.

3.4 Monodisperse hollow carbon nanocapsules with mesoporous shells

Uniform silica nanoparticles were coated with an organosilicon compound to produce a $\text{SiO}_2@\text{C18TMS}$ core-shell nanostructure. Then, TEOS was added as an in situ media to coat the outer silica layer. The organic moieties in the core/inner-shell/outershell nanostructures were polymerized by using sulfuric acid and were carbonized under a nitrogen atmosphere. Finally, the core, inner shell, and outer shell of the silica were removed to obtain the monodisperse hollow carbon nanocapsules. The nitrogen-adsorption isotherms of the silica nanoparticles and the hollow carbon nanocapsules were also analysed. The hollow carbon nanocapsules exhibit a type-IV isotherm with a H_2 hysteresis loop, which suggests that the hollow carbon nanocapsules have a mesoporous structure with “ink-bottlelike” pores.

To disperse the material in aqueous solution, the hollow carbon nanocapsules were PEGylated according to a literature procedure. The resulting PEGylated nanocapsule samples were observed for over three months and they were found to retain excellent stability in physiological solutions at room temperature. To study the drug-storage and drug-release properties of these nanocapsules as a candidate for drug-delivery applications, ibuprofen was selected as a model drug, because it is a well-known anti-inflammatory pharmaceutical agent. The ibuprofen-storage capacity and drug-release rates of the nanocapsules were characterized and monitored. These hollow carbon nanocapsules were demonstrated good drug-loading and drug-release properties with low cytotoxicity. According to these results, these hollow carbon nanocapsules have potentials as drug delivery vessels for therapeutic applications.

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