



Short communication

## Facile synthesis of monodispersed silica-coated magnetic nanoparticles



Won-Yeop Rho<sup>a</sup>, Hyung-Mo Kim<sup>a</sup>, San Kyeong<sup>b</sup>, Yoo-Lee Kang<sup>a</sup>, Dong-Hyuk Kim<sup>a</sup>, Homan Kang<sup>c</sup>, Cheolwan Jeong<sup>b</sup>, Dong-Eun Kim<sup>a</sup>, Yoon-Sik Lee<sup>b,c</sup>, Bong-Hyun Jun<sup>a,\*</sup>

<sup>a</sup> Department of Bioscience and Biotechnology, Konkuk University, Seoul 143-701, Republic of Korea

<sup>b</sup> School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea

<sup>c</sup> Nano Systems Institute and Interdisciplinary Program in Nano-Science and Technology, Seoul National University, Seoul 151-742, Republic of Korea

## ARTICLE INFO

## Article history:

Received 14 November 2013

Accepted 4 December 2013

Available online 12 December 2013

## Keywords:

Silica-coated magnetic nanoparticles

Stöber method

Oleate-MNPs

Ligand exchange

## ABSTRACT

Silica-coated magnetic nanoparticles (MNPs) have great potential for use in field of biotechnology owing to their unique properties, which can be manipulated by an external magnetic field gradient. Herein, we describe a method for facile synthesis of monodispersed silica-coated MNPs (MNP@SiO<sub>2</sub> NPs). Commercially available oleate-MNPs were successfully converted to polyvinylpyrrolidone-MNPs (PVP-MNPs), and then coated with silica by the modified Stöber method. More than 95% of MNPs were individually coated with a silica shell; non-magnetic core silica nanoparticles (NPs) were not detected. Notably, the MNP@SiO<sub>2</sub> NPs are highly monodispersed in size (size distribution < 2.5%) and synthesis at the scale of grams was easily obtained by a simple scale up process. Moreover, aggregation was not detected upon storage of over three months.

© 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

### 1. Introduction

Because the magnetic nanoparticles (MNPs) have unique properties, which can be manipulated by an external magnetic field gradient, they have great potential for applicability in various applications such as micro fluid chips, for catalysis, and biosensing [1,2]. Synthesis of large quantities of monodispersed particles is very important, especially for biomedical applications [3,4]. One of the most promising methods for preparing monodispersed MNPs on a large scale is Hyeon's method, which is based on thermal decomposition of an iron source in the presence of surfactants and a mild oxidant [5–7]. However, the as-prepared MNPs exhibit hydrophobicity due to the surfactants, and therefore, proper surface modification of the MNPs is required for biomedical applications.

Silica has been widely incorporated in various nanoparticles (NPs), because it is nontoxic, biocompatible, optically transparent, chemically inert, thermally stable, and has a well-known surface chemistry [8–16]. Thus, coating MNPs with a silica layer can be a good strategy for bio-applications. Silica coating of oleate-stabilized MNPs can be performed by simple microemulsion-based methods that allowed for monodispersed ones [14,16,17]. However, there are some disadvantages of these methods, such as aggregation of the produced MNPs upon long-term storage, non-

reproducibility, and formation of particles without a core (non-core particle) formation.

The Stöber method is a widely used method for coating silica because of its advantages such as relatively mild reaction conditions, low cost, and a broad range of achievable particle size (tens to hundreds of nanometers) [18]. Thus far, hydrophilic MNPs (mostly non-uniform in size) have been coated with silica using this method [19,20]. However, the Stöber method cannot be directly applied for the synthesis of hydrophobic oleate-MNPs which can be prepared in uniform size because of their hydrophobicity [21,22].

In this paper, we report large-scale synthesis of monodispersed silica coated MNPs (MNP@SiO<sub>2</sub> NPs) generated by applying the Stöber method. They were prepared from commercially available oleate-MNPs after ligand exchange with polyvinylpyrrolidone (PVP) followed by silica coating. To the best of our knowledge, our method can provide the most highly monodispersed (104.2 ± 2.4 nm) silica-coated MNPs on the scale of grams. This was possible by applying the ligand exchange method and a well-ordered preparation step.

### 2. Experimental

#### 2.1. Materials

A dispersion of MNPs (18 nm in average diameter, oleate-stabilized in toluene) was purchased from Ocean Nanotech, Korea. Tetraethyl orthosilicate (TEOS), polyvinylpyrrolidone (PVP-10) and

\* Corresponding author. Tel.: +82 2 450 0521.

E-mail address: [BJUN@konkuk.ac.kr](mailto:BJUN@konkuk.ac.kr) (B.-H. Jun).

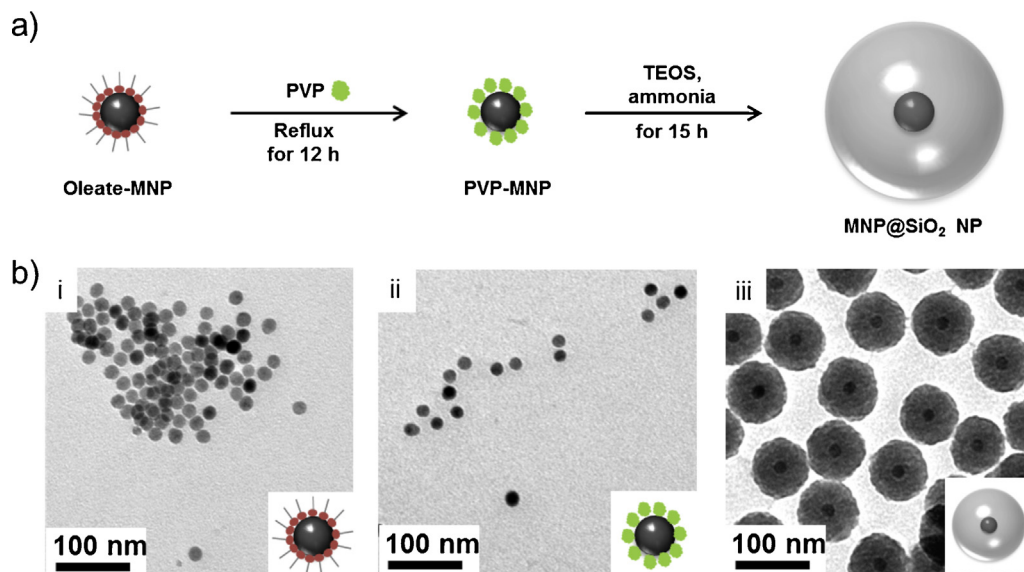


Fig. 1. (a) Illustration of the synthesis of silica-coated MNPs and (b) TEM images of MNPs at each step: (i) oleate-MNPs, (ii) PVP-MNPs, (iii) MNP@SiO<sub>2</sub> NPs.

dichloromethane (DCM) were purchased from Sigma–Aldrich. Diethyl ether (anhydrous), dimethylformamide (DMF), ethanol (EtOH), toluene, iron oxide, cyclohexane, and ammonium hydroxide (30 wt% in water) were sourced from Daejung Pharm. All chemicals were used as received without any further purification.

### 2.2. Ligand exchange of oleate-stabilized MNP with PVP

A dispersion of oleate-stabilized MNPs in toluene (0.2 mL) was transferred into a 15 mL vial and diluted with 5 mL of DMF–DCM (1:1, v/v). To this, 60 mg of PVP was added and refluxed at 100 °C for 12 h or overnight. The reaction mixture was then added dropwise into diethyl ether (10 mL) to precipitate the polymer-stabilized nanoparticles. The precipitate was washed once with diethyl ether and centrifuged at 4500 rpm for 5 min. The precipitate was transferred to 6.5 mL of EtOH to yield a stable dispersion of the PVP-stabilized MNPs. The precipitate could also be dispersed in several other solvents such as water, chloroform, dichloromethane, DMF, and DMSO to yield optically transparent dispersions.

### 2.3. Silica coating on PVP-stabilized MNP

EtOH dispersion of phase-transferred NPs (6.5 mL) was transferred into a 15 mL vial, and 0.28 mL of ammonium hydroxide (30 wt% in water) was added, followed by addition of 0.065 mL of TEOS in EtOH solution (10 vol%). The vial was stirred for 15 h at room temperature. The silica-coated nanoparticles were then isolated by centrifugation at 9000 rpm for 1 h and washed with EtOH. The collected silica-coated NPs were dispersed in distilled water. Then, 4 mL of TEOS in EtOH solution (3 vol%) was added by means of a syringe pump at a rate of 0.4 mL/h. After stirring for one day at room temperature, the resulting silica-coated MNPs were then centrifuged at 8500 rpm for 5 min and the silica-coated MNPs were dispersed in EtOH.

## 3. Results and discussion

Fig. 1a shows the fabrication process flow for the preparation of monodispersed silica-coated magnetic NPs (MNP@SiO<sub>2</sub> NPs). The MNP@SiO<sub>2</sub> NPs have a core–shell structure, with a magnetic core (18 nm in diameter) and a silica shell with a thickness of ca 43 nm. The MNP@SiO<sub>2</sub> NPs were prepared through a ligand exchange and

a sol–gel process based on the modified Stöber method. Each preparation step of MNP@SiO<sub>2</sub> NPs was visualized as in Fig. 1a and analyzed using transmission electron microscopy (TEM) images shown in Fig. 1b. The preparation steps are described in detail as follows.

We used commercially available MNP NPs (18 nm). As the preparation of MNP NPs is based on the thermal decomposition of iron–oleate complexes, MNP NPs were stabilized by oleates and thus exhibit hydrophobicity [23–25]. The hydrophobic surfaces of MNPs were modified to exhibit hydrophilicity by adding an excess amount of amphiphilic PVP to the oleate-MNPs, so that the oleate ligand on MNPs could be exchanged with PVP, and the surface of the MNPs could be silicated *via* the Stöber method.

Oleate-stabilized MNPs in chloroform were mixed with PVP dissolved in a mixture of DCM and DMF to form a clear dispersion. This mixture was kept at 100 °C overnight to enable the exchange of the oleates with excess PVP [26]. The ligand exchange process did not affect the size and shape of the MNPs, as is shown in Fig. 1b(ii). Moreover, any aggregation of the MNPs was not detected after ligand exchange. Additionally, the MNPs were able to be redispersed in hydrophilic solvents such as EtOH. This property change indicates that the oleate ligands on MNPs were successfully replaced by PVP. This ligand exchange method has been applied to other types of NPs, but, to the best of our knowledge, we are the first to apply this to MNPs.

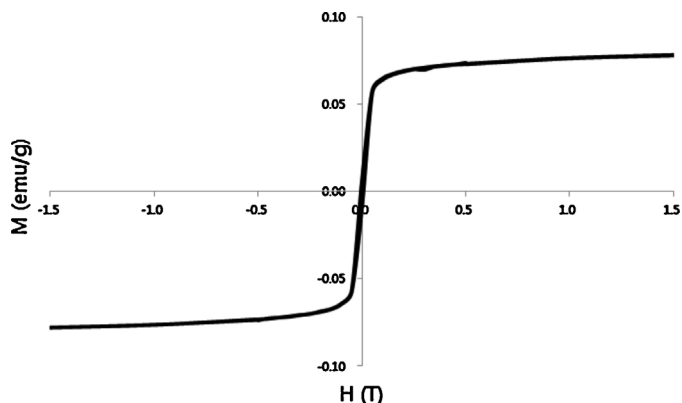


Fig. 2. Field-dependent magnetization of silica-coated MNP NPs at 300 K.

Download English Version:

<https://daneshyari.com/en/article/227314>

Download Persian Version:

<https://daneshyari.com/article/227314>

[Daneshyari.com](https://daneshyari.com)