Synthesis of Iron Oxide Nanoparticles with Control over Shape Using Imidazolium-Based Ionic Liquids

Chang-Moon Lee, Hwan-Jeong Jeong, Seok Tae Lim, Myung-Hee Sohn, and Dong Wook Kim*

Department of Nuclear Medicine, Cyclotron Research Center, Research Institute of Clinical Medicine, Chonbuk National University Medical School, Jeonju, Jeonbuk 561-712, Korea

ABSTRACT Ionic liquid (IL)-coated iron oxide nanoparticles (IONs) were synthesized by the thermal decomposition of $Fe(CO)_5$ in an IL/DMF solvent system in the absence of stabilizing surfactants at 90 °C for 1 h. The IL, [omim][BF_4], could regulate the shape and allow the preparation of anisotropic IONs, such as barlike and wirelike nanoparticles. The barlike IONs prepared using this method showed good superparamagnetic behavior in a magnetic field and a MR contrast enhancement effect in a MR scanner.

KEYWORDS: iron oxide • nanoparticle • crystal growth • shape regulation • ionic liquids

1. INTRODUCTION

The synthesis and applications of functional inorganic nanoparticles are of great interest in science and technology (1). In particular, iron oxide nanoparticles (IONs) are quite attractive nanoscale materials for a wide range of biomedical applications, including molecular imaging using magnetic resonance imaging (MRI) because IONs have many desirable characteristics, such as paramagnetism, uniform size, ease of surface modification and functionalization, and relatively low toxicity (2).

Several methods, such as micelle synthesis, sonochemical synthesis, coprecipitation, and thermal decomposition techniques, have been used to prepare IONs (3, 4). Among these methods, the thermal decomposition of metal-complex precursors in high-boiling organic solvents containing fatty acids or amines as stabilizing surfactants is the most popular method for synthesizing high-quality IONs (5). However, although this method provides size-controllable and monodisperse nanocrystals with a regular and good crystallite morphology compared to other methods, it requires a high reaction temperature to induce nucleation and subsequent nanoparticle growth (3, 5). Moreover, this method cannot control the shape of IONs to produce one-dimensional nanometer-sized IONs, such as nanobars (6) and nanowires. These anisotropic nanomaterials have received considerable attention in the nanotechnology research area because of their unique shape-dependent properties and resulting applications (7).

Over the past decade, 3-dialkylimidazolium salts as representative, tailor-made ionic liquids (Figure 1) have been studied extensively investigated for a variety of applications in chemistry (8), and have been used as eco-friendly alternative reaction media instead of conventional volatile solvents for reaction acceleration (9), separation (10), and electrochemistry (11). In particular, imidazolium-based ILs are benign media for the synthesis of nanostructured materials on account of their high ionic conductivity, high thermal and electrochemical stability, supramolecular network, low toxicity, wide liquid range, etc. (12). The synthesis of IONs by the thermal decomposition of $Fe(CO)_5$ with stabilizers in IL [bmim][Tf_2N] was also reported (13, 14). ILs can act not only as a stabilizing surfactants because they provide electrostatic protection for the synthesis of metal nanoparticles (12, 15) but also as shape-regulating surfactants in the media for the synthesis of anisotropic metal nanoparticles (16), such as rodlike CdS, ZnSe (16), CoPt (17), and gold nanoparticles (18), Te nanowires (19), metal fluoride nanobars (20, 21), etc.

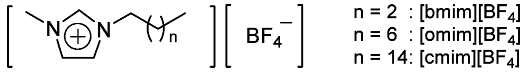

FIGURE 1. Imidazolium-based ionic liquids. bmim = 1-*n*-butyl-3-methylimidazolium cation; omim = 1-*n*-octyl-3-methylimidazolium cation; cmim = 1-*n*-cetyl-3-methylimidazolium cation.

Scheme 1. Synthesis of Ionic-Liquid-Coated Iron Oxide Nanoparticles Fe_2O_3@[omim][BF_4]

$$Fe(CO)_5 \xrightarrow[\text{[omim][BF}_4\text{] / DMF}]{90\ ^\circ C\text{, 1h}} Fe_2O_3@\text{[omim][BF}_4\text{]}$$

Herein, we present that IONs can be synthesized by the thermal decomposition of $Fe(CO)_5$ using 3-dialkylimidazolium-based ILs as reaction media in the absence of stabilizing surfactants under mild reaction conditions. Moreover, the use of the ILs can regulate the shape of IONs and allow the preparation of anisotropic IONs.

2. RESULTS AND DISCUSSION

IL-coated IONs were prepared using the procedure shown in Scheme 1. Commercially available IL [omim][BF_4] and $Fe(CO)_5$ were used as the reaction medium and metal precursor, respectively. Dimethyl formamide (DMF) was also

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* Corresponding author. Telephone: +82-63-250-2396. FAX: +82-63-255-1172. E-mail: kimdw@chonbuk.ac.kr.

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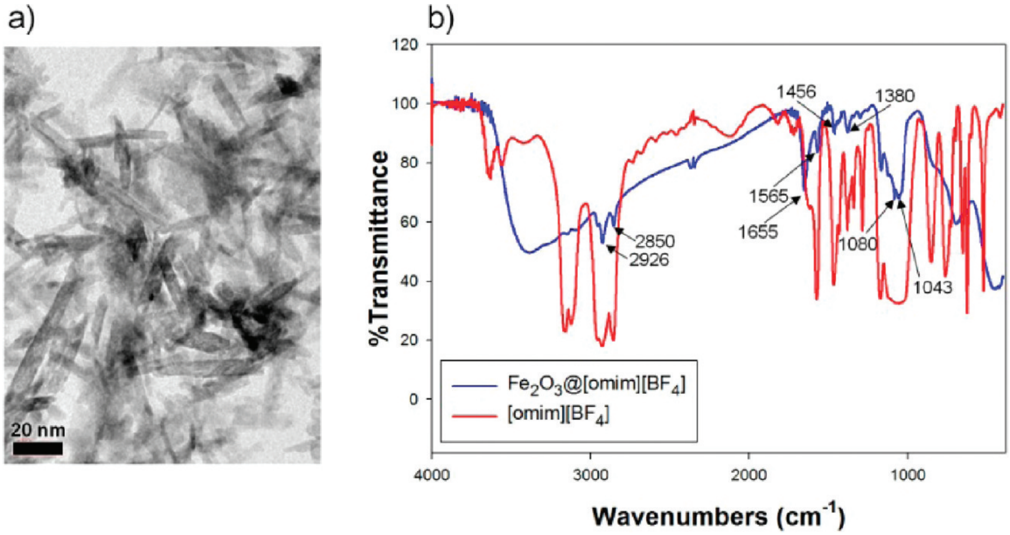

FIGURE 2. (a) TEM bright-field image of Fe_2O_3@[omim][BF_4] nanobars prepared in [omim][BF_4]/DMF (v/v = 1:1.5). (b) Comparison of the infrared spectra of Fe_2O_3@[omim][BF_4] nanobars and free [omim][BF_4].

used as a cosolvent to increase the solubility of $Fe(CO)_5$ in the reaction media. After adding $Fe(CO)_5$ at 60 °C, the reaction solution of $Fe(CO)_5$ in [omim][BF_4] and DMF (v/v = 1:1.5) was heated to 90 °C for 1 h, and the color of the reaction solution changed immediately from bright-orange to dark-black. This indicates that the decomposition reaction of $Fe(CO)_5$ to nanoparticles was performed in the absence of a surfactant at relatively lower temperatures. The nanoparticles could be separated and isolated easily from the crude reaction solution through an external magnetic field using a rare-earth magnet.

The nanoparticles obtained from the decomposition of $Fe(CO)_5$ in [omin][BF_4]/DMF (1:1.5) were characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and infrared (IR) spectroscopy. The XP spectra of the IONs showed peaks at 711.73 (Fe_2p1) and 725.28 (Fe_2p3) eV, which were assigned to γ-Fe_2O_3 (see Supporting Information). Interestingly, TEM observations of these IONs showed the presence of anisotropic, bar-shaped nanoparticles (Figure 1a). Furthermore, electron diffraction pattern analysis (Figure 4a, inset) of the IONs shows that all major diffractions could be assigned to the crystal planes of Fe_2O_3 phase ({220}, {311}, {400}, and {422}, space group $P4_1$ 32, JCPDS card 39−1346) (18). The average length and width of the bar-shaped nanoparticles was 30 ± 9.7 and 5.7 ± 1.8 nm, respectively. As shown in Figure 2b, a comparison of the IR spectrum of these iron oxide nanobars and free [omim][BF_4] indicated the existence of [omim][BF_4] on the surface. The C−N stretching band at 1565 cm^{-1} for the imidazolium group of IL and the C−H stretching band at 2850 and 2928 cm^{-1} from the alkyl groups of IL were observed. The asymmetric and symmetric carbonyl stretching vibration of $Fe(CO)_5$ near 2000 cm^{-1} was not seen because of the interaction between the carbonyl groups of $Fe(CO)_5$ and the [omin] cation. Consequently, IL [omim][BF_4] coated iron oxide, Fe_2O_3@[omim][BF_4], nanobars could be obtained from the above-mentioned reaction, indicating the possibility of ILs as a stabilizer for the synthesis of IONs.

Figure 3 shows the behavior of the Fe_2O_3@[omim][BF_4] nanobars in a magnetic field. These nanobars could be collected by a magnet within a few minutes (Figure 3a). The paramagnetic properties of Fe_2O_3@[omim][BF_4] nanobars were examined using superconducting quantum interference device (SQUID) magnetometry. The nanobars exhibited superparamagnetic behavior, showing a high M_s of 58 emu/g Fe at room temperature (Figure 3b). As shown in Figure 3c, the signal contrast-enhancement effect of Fe_2O_3@[omim][BF_4] nanobars was observed by the T_2-weighted spin echo MRI at 1.5 T.

The effect of the IL concentration ([omim][BF_4]) in the reaction media on the formation of IONs was examined by carrying out a decomposition reaction of $Fe(CO)_5$ to Fe_2O_3@[omim][BF_4] nanoparticles in the [omim][BF_4]/DMF solvent of different ratios (v/v = 1:0, 1:1.5, 1:3, or 0:1), and the formation of the magnetite products was observed by TEM imaging. No magnetite nanoparticles were formed when only [omim][BF_4] or DMF was used as the solvent in this decomposition reaction. On the other hand, the use of a [omim][BF_4]/DMF mixture solvent system allowed the formation of magnetite-products. TEM showed that significantly different nanostructured magnetite was formed depending on the IL concentration in the reaction media. Fe_2O_3@[omim][BF_4] nanobars were produced by the reaction in the [omim][BF_4]/DMF solvent (1:1.5, Figure 4a), whereas anisotropic wirelike nanoparticles were produced in [omim][BF_4]/DMF (1:3, Figure 4b). This shows that ILs can act as efficient shape-regulating cosolvents by controlling their concentration in the reaction media for the synthesis of anisotropic IONs. The decomposition reactions in [cmin][BF_4] (cmim = 1-*n*-octyl-3-methylimidazolium)/DMF (1:1.5) and [bmin][BF_4] (bmim = 1-*n*-butyl-3-methylimidazolium)/DMF (1:1.5) were next examined to determine the influence of the carbon chain length of imidazolium of ILs on the synthesis of IONs. Although they had a broad size distribution, TEM showed that significantly different shaped-IONs, spherical IONs, were obtained from the reaction using both [cmin][BF_4] and [bmin][BF_4] compared to that using [omim]-

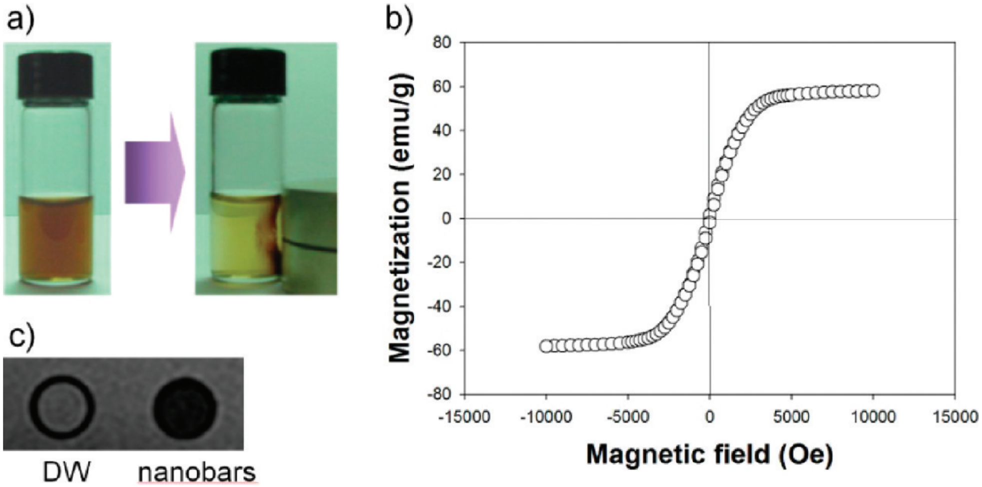

FIGURE 3. Superparamagnetic behavior of Fe_2O_3@[omim][BF_4] nanobars: (a) Photograph of the nanobars collected toward a magnet. (b) Magnetization curves of the nanobars at room temperature. (c) Phantom images of water and the nanobars in water (1.0 mg/mL) acquired from T_2-weighted MRI.

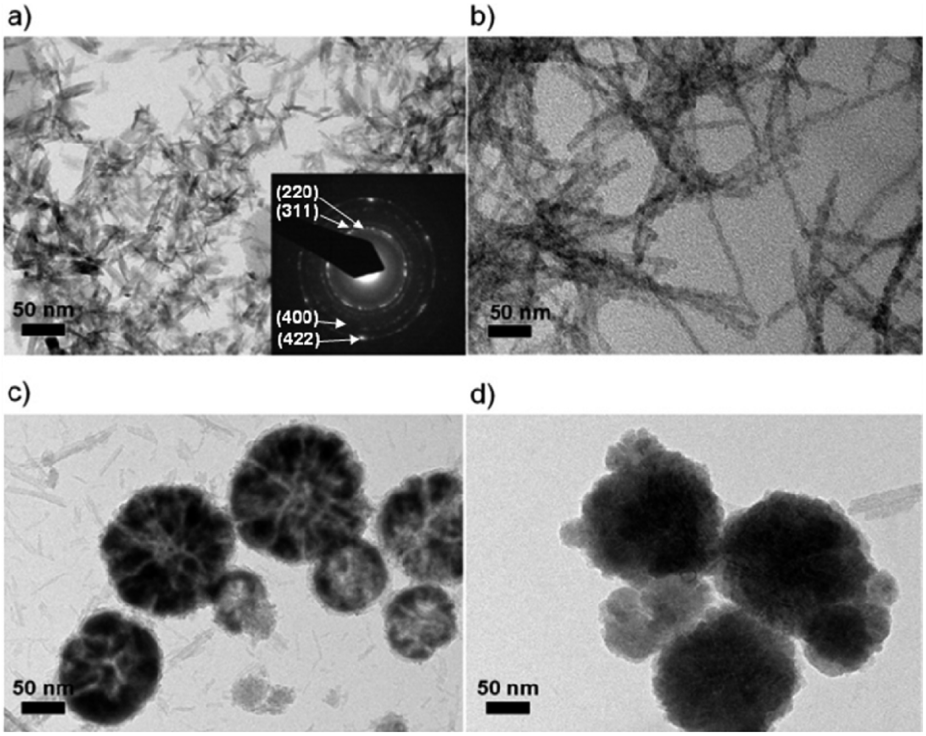

FIGURE 4. (a) TEM image and electron-diffraction pattern of the Fe_2O_3 nanobars prepared in [omim][BF_4]/DMF (1:1.5). (b) TEM image of Fe_2O_3 nanowires prepared in [omim][BF_4]/DMF (1:3). (c) TEM image of the IONs prepared in [cmim][BF_4]/DMF (1:1.5). (d) TEM image of the IONs prepared in [bmim][BF_4]/DMF (1:1.5).

[BF_4]. This suggests the possibility of a shape-regulating solvent design by structural modification of the ILs (Figure 4c,d, respectively).

3. CONCLUSION

In summary, IL-coated IONs with a controlled shape were synthesized by the thermal decomposition of $Fe(CO)_5$ in an IL/DMF mixture solvent system. The IL, [omim][BF_4], plays a key role in stabilizing and regulating the shape as well as enhancing the reactivity of decomposition for the formation of these anisotropic IONs, such as barlike and wirelike IONs. Furthermore, the one-dimensional bar-like Fe_2O_3@[omim][BF_4] nanoparticles prepared by this method showed good superparamagnetic behavior in a magnetic field and a MR contrast enhancement effect in a MR scanner. Because they are expected to have the shape-dependent physical and biological properties, these barlike or wirelike Fe_2O_3@[omim][BF_4] nanoparticles will provide new opportunities for biomedical applications, particularly molecular imaging using MRI. Further studies on the development of more efficient tailor-made ILs through structural modifications, IL-based synthetic protocols for higher-quality anisotropic IONs, and the application of these unusual IONs to MRI-based molecular imaging probes are currently underway.

4. EXPERIMENTAL SECTION

General. Unless otherwise noted, all reagent and solvents were commercially available. To characterize the shape of the nanoparticles, transmission electron microscopy was carried out at 200 kV. To prepare the samples for the TEM observations, small droplets were placed on carbon-coated copper TEM grids. X-ray photoelectron spectroscopy (XPS) was performed using a VG Multilab 2000. The saturation magnetization (Ms) value was measured using a superconducting quantum interference device (SQUID) at 300 K in a magnetic field from 10 000 Oe to −10 000 Oe. To confirm the signal enhancement effect of the IONs, the IONs (1.0 mg/mL) were suspended in water and MR phantom imaging was performed using a clinical 1.5 T MR scanner.

Typical Procedure for the Synthesis of Fe_2O_3@[omim]-[BF_4] Nanobars. The IONs were synthesized using a slight modification of the method described elsewhere (1). 1.0 mL of [omim][BF_4] and 1.0 mL were added to a vial. The mixture solution of [omim][BF_4] and DMF was maintained by stirring at 60 °C for 30 min; 0.1 mL of $Fe(CO)_5$ in 0.9 mL of DMF was added to the mixture solution at 60 °C. The reaction mixture was stirred at 90 °C for 1 h. The color of the reaction solution changed from bright-orange to dark-black. A magnet was applied to the reaction mixture solution to collect the nanoparticles. The supernatant was discarded with fresh ethanol and distilled water. The crude nanoparticles were washed with ethanol and water three times, and the isolated IONs were obtained as a dark black solid.

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Supporting Information Available: Procedure and XPS data of nanoparticles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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