Various-Shaped Uniform Mn_3O_4 Nanocrystals Synthesized at Low Temperature in Air Atmosphere

Taekyung Yu,[†] Jaewon Moon,[†] Jinkyung Park,[†] Yong Il Park,[†] Hyon Bin Na,[†]
Byung Hyo Kim,[†] In Chan Song,[‡] Woo Kyung Moon,[‡] and Taeghwan Hyeon*[,†]

National Creative Research Initiative Center for Oxide Nanocrystalline Materials and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea, and Department of Radiology, Seoul National University College of Medicine,
Seoul National University Hospital, Seoul 110-744, Korea

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We report a novel and facile method for the synthesis of manganese oxide (Mn_3O_4) nanocrystals with various sizes and shapes. Mn_3O_4 nanocrystals were synthesized via a reaction of manganese(II) acetate with water in xylene in the presence of surfactants at the temperature of as low as 90 °C in air atmosphere. Structural characterizations revealed that the synthesized nanocrystals were tetragonal Mn_3O_4 structure and that they were highly crystalline in spite of the low reaction temperature. The size and shape of the nanocrystals were readily controlled by varying the experimental conditions such as precursors, surfactants, and injection temperature of water. Nanoplates with a thickness of 5 nm and side dimensions of 9, 15, and 22 nm were synthesized using oleylamine as the surfactant. When carboxylic acid was used as the cosurfactant along with oleylamine, spherical nanocrystals were obtained with sizes of 5.5, 6.2, 7.2, 8.5, and 15 nm. Interesting anisotropic nanostructures including nanowires and nanokites were also prepared by changing the injection temperature of water. Mechanistic studies revealed that in situ generated manganese hydroxide ($Mn(OH)_2$) mainly contributes to the nucleation, whereas the manganese−oleylamine complex contributes to the shape-controlled growth process. The current procedure can be readily applicable to large-scale synthesis because of their facile and mild reaction conditions including low reaction temperature and air environment and the use of nontoxic and inexpensive reagents. For example, under optimized reaction conditions, we were able to synthesize as much as 4.5 g of 15 nm sized Mn_3O_4 nanoplates using a 1 L reactor. Water-dispersible 9 nm sized Mn_3O_4 nanoplates exhibited specific relaxivity (r_1) value of 0.13 mM^{-1} s^{-1}, demonstrating the potential application of the nanocrystals to T_1 contrast agent for magnetic resonance imaging (MRI).

Introduction

The early stage of nanocrystal research has been driven mainly by the scientific interest to study the size dependent properties in nanometer scale.[1] The quantum confinement effect observed for semiconductor nanocrystals, quantum dots (QDs), is the most renowned example.[2] Nowadays, the interest in nanocrystals has grown to a great extent because of their potential technological applications such as energy storage and conversion,[3] display devices,[4] bioimaging and related biomedical applications,[5] data storage media,[6] sensors and electronic devices,[7] and catalysis.[3,8c] For the practical use of nanocrystals in these technological applications, the development of the economical, large-scale synthetic process of uniform nanocrystals is highly required because the physical properties are directly dependent on their dimensions.[9] With respect to economic efficiency, there are two important points in the synthesis of uniform nanocrystals,

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* Corresponding author. E-mail: thyeon@snu.ac.kr.
[†] Seoul National University.
[‡] Seoul National University College of Medicine.

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that is, inexpensive starting materials and simple synthetic processes. In many cases, organometallic compounds, which are generally expensive and hard to handle, are required to synthesize highly uniform nanocrystals. Furthermore, the reported synthetic methods for high-quality nanocrystals are often hard to scale up as is described below. Consequently, simple synthetic procedures with mild and environmentally friendly synthetic conditions and using inexpensive and nontoxic precursors are highly desirable for the large-scale synthesis of uniform nanocrystals. There are many conventional synthetic methods for metal oxide materials such as sol−gel process[10] and ceramic processing methods.[11] However, these methods are not useful for the synthesis of uniform metal oxide nanocrystals due to the difficulties in controlling the size and shape uniformity in the nanometer scale. For the synthesis of uniform-sized metal oxide nanocrystals, the hot-injection method,[12] heat-up process,[13] and reverse-micelle method[14] are generally used. The hot-injection and the heat-up processes are generally carried out in hot surfactant solutions and have been widely used to synthesize uniform nanocrystals due to their advantages of high crystallinity, size uniformity, and good dispersibility in various organic solvents. Very recently, the Hyeon group reported the generalized synthetic method of monodisperse metal oxide nanocrystals using an inexpensive and nontoxic metal−oleate complex as the starting material.[15] In this method, a large quantity of monodisperse nanocrystals were synthesized via the thermal decomposition of metal−oleate complexes. The Hyeon group also synthesized uniform nanocrystals of various oxides through nonhydrolytic sol−gel reactions at high reaction temperature.[16] However, this still has some room for improvements including high reaction temperature (>300 °C) and inert atmospheric conditions. Reverse micelle processes, which are another popular synthetic method for nanocrystals, are generally carried out in ambient and mild reaction conditions and at low reaction temperature of <100 °C,[14,17] which offers several advantages for the large-scale synthesis. However, unfortunately, nanocrystals synthesized via this process are generally poorly crystalline because of low reaction temperature, and consequently postsynthetic heat treatment is necessary to get highly crystalline nanocrystals. Furthermore, the synthetic process is very inefficient because a large amount of solvent is used to synthesize a very small amount of nanocrystals. For example, 1 L of solvent was used to synthesize a subgram scale of nanocrystals. Therefore, for the industrial application, it is strongly required to develop a synthetic process producing monodisperse metal oxide nanocrystals of good crystallinity in high yield under mild and ambient reaction conditions.

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Manganese oxides have attracted considerable interest as a result of their potential applications to various fields including catalysis, secondary batteries, ion exchange, molecular adsorption, and supercapacitors.[18] Recently, uniform-sized manganese oxide nanocrystals with various compositions and shapes have been synthesized.[19] However, most of these nanocrystals have been synthesized by high temperature reactions in inert atmosphere. We herein report on the controlled synthesis of manganese oxide (Mn_3O_4) nanocrystals with various shapes from the reaction between manganese(II) acetate and water in xylene in the presence of surfactants. The synthesis was performed at the reaction temperature of as low as 90 °C and in air atmosphere. Nonetheless, the synthesized nanocrystals exhibit good size uniformity and high crystallinity. Furthermore, the size and shape of the nanocrystals can be easily controlled by varying the reaction conditions.

Experimental Section

Materials. The following chemicals were purchased from various vendors and used without further purifications: oleylamine (approximate C18-content 80−90%, Across), oleic acid (technical grade 90%, Aldrich), stearic acid (95%, Aldrich), 4-hydroxy benzoic acid (TCI), octanoic acid (98+%, Aldrich), octylamine (99%, Aldrich), xylene (98.5+%, Aldrich), manganese(II) acetate (98%, Aldrich), manganese(II) acetate tetrahydrate (99+%, Aldrich), and 1,2-distearoyl-*sn*-glycero-3-phospho ethanol amine-*N*-[methoxy-(polyethylene glycol)-2000] (mPEG-2000 PE) (Avanti Polar Lipids, Inc.).

Synthesis of Spherical Mn_3O_4 Nanocrystals. One millimole of manganese(II) acetate (0.17 g) and a mixture of carboxylic acid and oleylamine (OM) were dissolved in 15 mL of xylene in air atmosphere. After slowly heating to 90 °C, 1 mL of DI water was injected into the solution under a vigorous stirring, and the resulting solution was aged at 90 °C for 3 h. A total of 100 mL of ethanol was added to precipitate the nanocrystals, which was followed by centrifugation to retrieve the nanocrystals in powdery form. The nanocrystals synthesized were well dispersible in organic solvents such as *n*-hexane and chloroform. The size of the nanocrystals was controlled by varying the kind of carboxylic acid (oleic acid or stearic acid) and the oleic acid/oleylamine ratio. For the synthesis of 5.5 nm sized Mn_3O_4 nanospheres, 2 mmol of stearic acid (0.57 g) and 10 mmol of oleylamine (2.67 g) were used while keeping the other experimental conditions unchanged. When we used a mixture of 2 mmol of oleic acid (0.57 g) and 10 mmol of oleylamine (2.67 g), 6.2 nm sized Mn_3O_4 nanospheres were obtained. For the synthesis of 7.2 nm sized Mn_3O_4 nanospheres, 3 mmol of oleic acid (0.85 g) and 9 mmol of oleylamine (2.39 g) were needed. The 8.5 nm sized Mn_3O_4 nanospheres were produced by using a mixture of 4 mmol of oleic acid (1.13 g) and 8 mmol of oleylamine (2.13 g). In the case of 15 nm sized Mn_3O_4 nanorices, a mixture of 6 mmol of oleic acid (1.70 g) and 6 mmol of oleylamine (1.61 g) was used with keeping other reaction conditions the same as those for the synthesis of the 5.5 nm sized nanospheres.

Synthesis of Mn_3O_4 Nanoplates. To obtain the Mn_3O_4 nanoplates with side dimension of 9 nm, 1 mmol of manganese(II) acetate (0.17 g) and 12 mmol of oleylamine (3.3 g) were dissolved in 15 mL of xylene in air atmosphere. After slowly heating to 90 °C, 1 mL of DI water was injected into the solution under vigorous stirring, and the resulting solution was aged at 90 °C for 3 h. The size of the nanoplates was controlled by varying the metal precursors and the surfactant. When we used 1 mmol of manganese(II) acetate tetrahydrate (0.24 g) instead of manganese(II) acetate, Mn_3O_4 nanoplates with a side dimension of 15 nm were prepared. For the synthesis of 22 nm sized Mn_3O_4 nanoplates, the synthesis was conducted after mixing 1 mmol of manganese(II) acetate (0.17 g), 2 mmol of 4-hydroxy benzoic acid (0.27 g), and 10 mmol of oleylamine (2.67 g) in 15 mL of xylene, and other experimental conditions were the same as those for the 9 nm nanoplates.

Synthesis of Nanowires and Nanokites of Mn_3O_4. Mn_3O_4 nanowires with length of ~100 nm were synthesized as follows. One millimole of manganese(II) acetate (0.17 g), 2 mmol of oleic acid (0.56 g), and 10 mmol of oleylamine (2.67 g) were dissolved in 15 mL of xylene in air atmosphere. One milliliter of DI water was added to the solution under vigorous stirring, and the resulting solution was kept at room temperature for about 2 h. Then, the solution was slowly heated to 90 °C and aged at the same temperature for 3 h. For the synthesis of Mn_3O_4 nanowires with length of >400 nm, 0.5 mmol of manganese(II) acetate hydrate (0.12 g), 0.25 mmol of oleic acid (0.07 g), and 1.25 mmol of oleylamine (0.31 g) were used while keeping the other experimental conditions unchanged.

Water-Dispersible Mn_3O_4 Nanocrystals. Water-dispersible and biocompatible Mn_3O_4 nanocrystals were prepared by the previously reported method with some modifications.[21] Ten milligrams of Mn_3O_4 nanocrystals was dispersed in 1 mL of chloroform. To this dispersion, 20 mg of mPEG-2000 PE in 2 mL chloroform was added. After evaporating the solvent, the residue was incubated at 60 °C in vacuum for 1 h. Upon the addition of 10 mL of water, a clear and brown suspension was generated. After filtration (0.2 μm syringe filter, cellulose acetate), excess mPEG-2000 PE was removed by ultracentrifugation (40 000 rpm, 1 h, 2 times).

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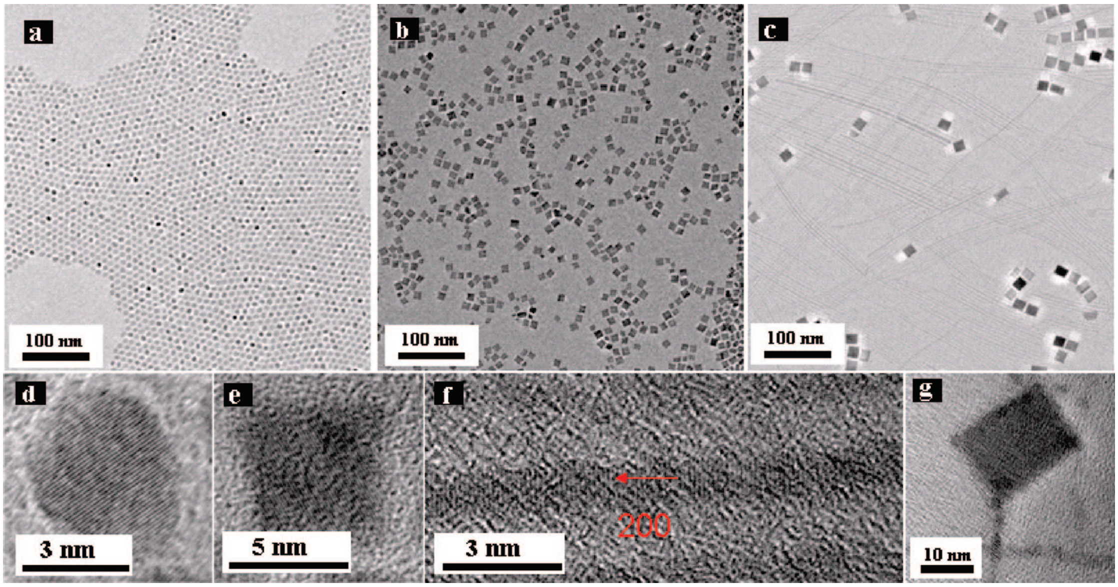

Figure 1. TEM images of Mn_3O_4 nanocrystals of (a) 6 nm nanospheres, (b) 9 nm nanoplates, and (c) a mixture of 15 nm nanoplates and 150 nm nanowires and HRTEM images of (d) 6 nm nanospheres, (e) 9 nm nanoplates, (f) 150 nm nanowires, and (g) nanokites.

Measurement of MRI Relaxation Properties of the Nanocrystals. The values of T_1 and T_2 relaxation times of the water-dispersed nanocrystals were measured with a 1.5 T clinical MRI scanner for various nanocrystal concentrations. An IR-FSE sequence with 30 multiple values of TIs (TR/TE/TI = 4400 ms/13 ms/24−4000 ms) for the T_1 measurement and a conventional CPMG sequence with 12 multiple TEs (TR/TE = 3300 ms/13, 26, 39, 52, 70, 140, 210, 280, 400, 800, 1200, 1600 ms) for the T_2 measurement were performed with a head coil on a 1.5 T MRI scanner. T_1 and T_2 relaxation times were calculated by fitting the signal intensities with increasing TEs or TIs with a monoexponential function or $|[1 - (1 - k)\exp(-TI/T_1)]M_0|$[22] using a nonlinear least-squares fit of the Levenberg−Marquardt algorithm.

Characterization Methods. The synthesized nanocrystals were characterized using transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). TEM images were obtained with a Jeol EM-2010 microscope. X-ray diffraction patterns were obtained with a Rigaku D/Max-3C diffractometer, equipped with a rotating anode and a Cu Kα radiation source ($\lambda = 0.15418$ nm). The magnetic properties of the nanocrystals were characterized using a superconducting quantum interference device (SQUID, MPMS 5XL Quantum Design SQUID magnetometer).

Results and Discussion

Synthesis and Characterization of Mn_3O_4 Nanocrystals. Uniform-sized Mn_3O_4 nanocrystals with sphere, plate, wire, and kite shapes were synthesized from the reaction of manganese(II) acetate with water in xylene at 90 °C in the presence of surfactant (oleylamine or a mixture of carboxylic acid and oleylamine) in air atmosphere. Although there are several reports on the synthesis of metal oxide nanocrystals from the reaction of metal salts in oleylamine,[16b] the reactions were carried out at very high temperature of >180 °C under inert atmosphere. In contrast, we were able to synthesize Mn_3O_4 nanocrystals using water as a reagent at the temperature of as low as 90 °C and in air atmosphere. XRD patterns of the nanocrystals with the four shapes were all assigned as tetragonal Mn_3O_4 (hausmannite) structure (Supporting Information, JCPDS 80-0382). TEM images shown in Figure 1 revealed that all of the nanocrystals with different shapes were highly crystalline and uniform in both size and shape. The zero-field cooling magnetization data in the SQUID measurements showed that the blocking temperatures of the 6 nm sized Mn_3O_4 nanospheres and 15 nm sized nanoplates were 34.3 and 41.3 K, respectively (Supporting Information), demonstrating the size dependent magnetization properties, which was consistent with the previous reports.[19g] The detailed synthetic procedures and characterizations of the Mn_3O_4 nanocrystals with four different shapes are described below.

We performed several experiments to understand the formation mechanism. When the synthesis was conducted in the presence of oleic acid only and without using oleylamine, clear transparent solution was generated and no nanoparticle was observed in the TEM image. To understand the role of oleylamine in the synthesis, we performed the synthesis in the absence of oleylamine under various pH values. When the synthesis was conducted under acidic conditions of pH < 6, no nanoparticle was produced. When the reaction was conducted at pH of 6.5 and in the absence of oleylamine, aggregates of small nanoparticles of ~2 nm were produced. On the basis of these results, we assume that the pH of the reaction mixtures is very important for the nucleation process. Furthermore oleylamine seems to act as a base to increase the pH of the reaction mixtures and consequently affects the nucleation process. We also postulated that manganese hydroxide ($Mn(OH)_2$) is an intermediate species for the formation of Mn_3O_4. When $Mn(OH)_2$, which was prepared using the reported method,[23] was reacted under very similar reaction conditions but in the absence of oleylamine, we were still able to synthesize Mn_3O_4 nanocrystals (Supporting Information). Consequently, we presumed that Mn_3O_4 nanocrystals were synthesized from

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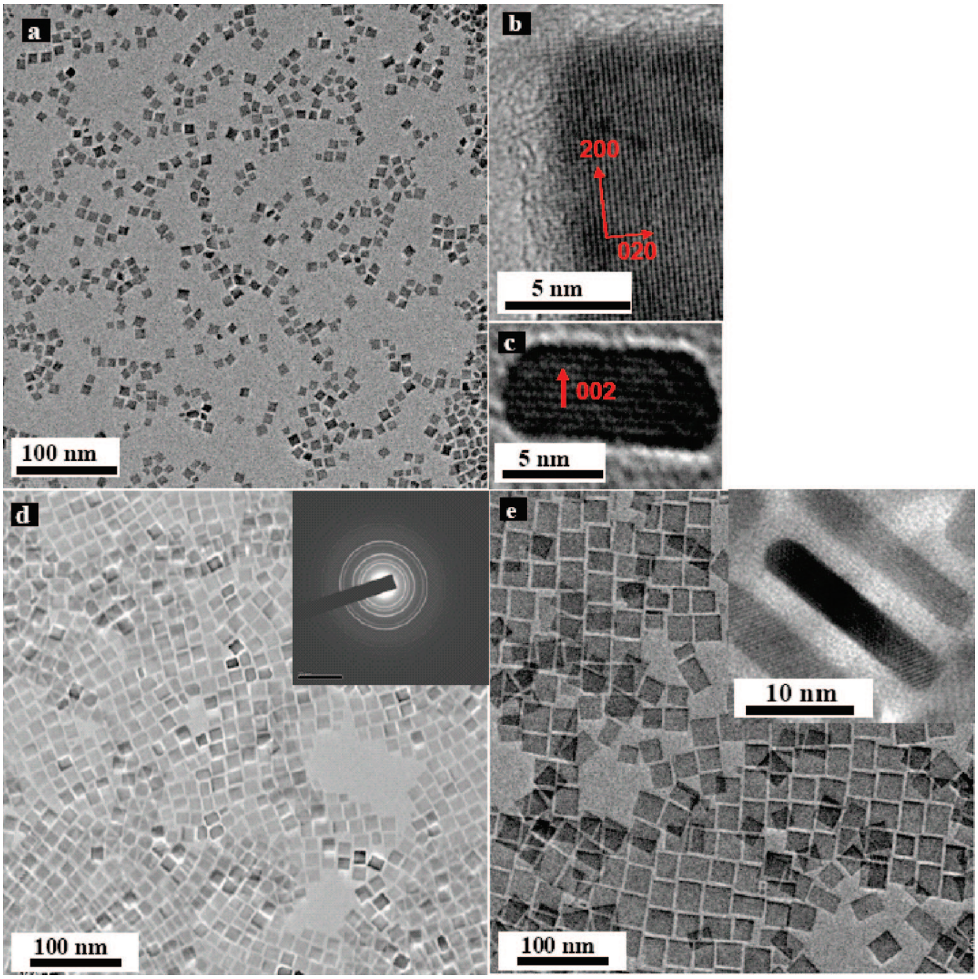

Figure 2. (a) TEM and (b) HRTEM images of 9 nm Mn_3O_4 nanoplates. The *d*-spacing value of the lattice planes parallel to the edge is 0.288 nm which is assigned as (200) plane. (c) HRTEM image of the edge of a nanoplate. The lattice plane parallel to the face is assigned as (002) whose *d*-spacing value is 0.47 nm. (d) TEM image and electron diffraction pattern (inset) of 15 nm Mn_3O_4 nanoplates and (e) TEM of 22 nm Mn_3O_4 nanoplates (inset: HRTEM image of a lateral face of the nanoplate).

$Mn(OH)_2$ which was generated from the reaction of manganese(II) acetate with water in the presence of oleylamine. Furthermore, we were able to synthesize the 15 nm sized nanocrystals in large quantities of 4.45 g from a single batch reaction using a 1 L reactor under optimized synthetic conditions (Supporting Information).

Mn_3O_4 Nanoplates. Mn_3O_4nanoplates with an average side dimension of 9 nm were synthesized by the reaction of manganese(II) acetate, oleylamine, and water in xylene at 90 °C in air atmosphere. The TEM images show that the nanoplates have a uniform side dimension and a thickness of 5 nm (Figure 2). A high-resolution TEM (HRTEM) image of faceted nanoplates resting on its face shows that the edges of the square-shape nanoplate are surrounded by (100) planes (Figure 2b). Also, a HRTEM image of a nanoplate standing perpendicular on the substrate reveals that the faces of the nanoplates are (001) planes (Figure 2c). To control the side dimension of the Mn_3O_4 nanoplates without changing the thickness, the experimental conditions including the precursors and the composition of the surfactants were varied. The nanoplates with a side dimension of 15 nm were prepared using manganese(II) acetate tetrahydrate as precursor instead of manganese(II) acetate, while keeping the other experimental conditions unchanged (Figure 2d). We were able to synthesize Mn_3O_4 nanoplates with side dimension of 22 nm by adding 4-hydroxy benzoic acid as a cosurfactant to oleylamine (Figure 2e).

There have been numerous publications on the shape controlled synthesis of nanocrystals.[24] The shape of colloidal nanocrystals generally relies upon several factors such as crystal structure and the selective adsorption of surfactant onto the specific crystal plane. Alivisatos and co-workers reported disk-shaped Co nanocrystals having wurzite hexagonal crystal structure.[25] They proposed that alkylamines adsorb on the (001) plane of Co nanocrystals and inhibit the growth of the (001) face. For our Mn_3O_4 nanocyrstals, plate shaped nanocrystals were synthesized using oleylamine, whereas spherical shaped nanocrystals were synthesized when carboxylic acid was added as cosurfactant in the presence of oleylamine. These experimental results suggested that selective attachment of oleylamine onto the (001) plane

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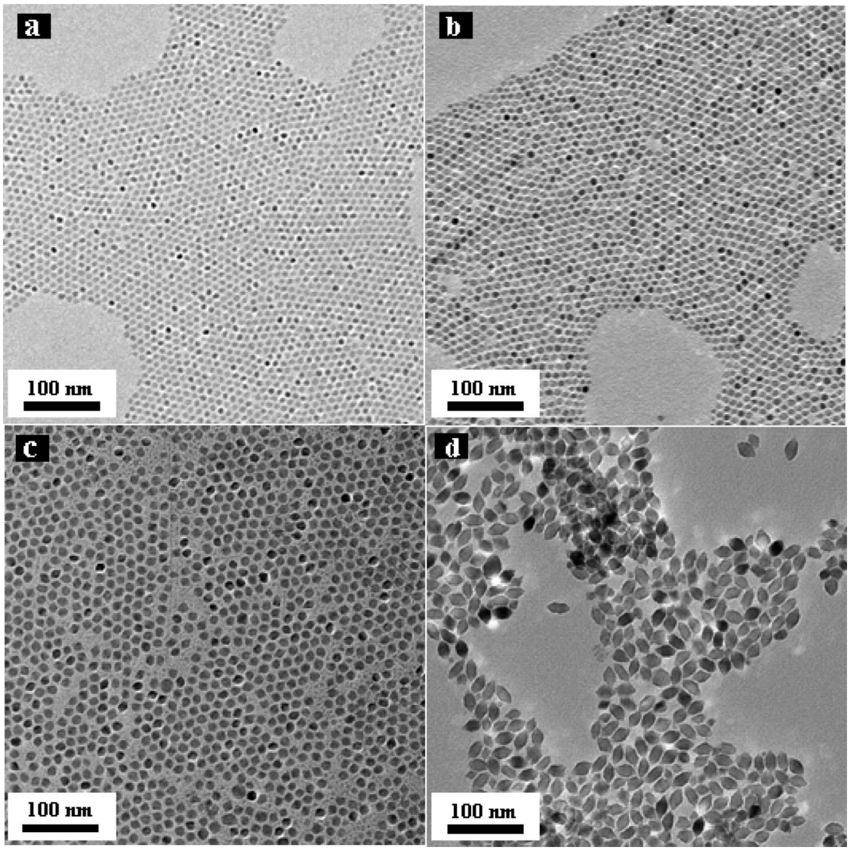

Figure 3. TEM images of spherical Mn_3O_4 nanocrystals with sizes of (a) 6.2 nm, (b) 7.2 nm, and (c) 8.5 nm and (d) TEM image of nanorices with length of 15 nm.

of Mn_3O_4 nanocrystals leads to a plate shaped nanocrystal. On the other hand, carboxylic acid, known as more strongly binding surfactant than oleylamine, could well stick to all planes of nanocrystals and form the spherical shaped nanocrystals. The Hyeon group reported the synthesis of monodisperse iron oxide nanoparticles with a continuous size spectrum of 6, 7, 8, 9, 10, 11, 12, and 13 nm.[26] In that report, we found that the precursor, iron pentacarbonyl, mainly contributes to nucleation, whereas the in situ generated iron−oleate complex contributes exclusively to the growth process. As described above, the nucleation seems to occur by the reaction of the in situ synthesized $Mn(OH)_2$, whereas the Mn−oleylamine complex seems to react on the nuclei to form Mn_3O_4 nanocrystals. When the synthesis was conducted using the manganese−oleate complex, only spherical shaped and polydispersed nanocrystals were synthesized (Supporting Information). When aqueous manganese(II) acetate solution was injected into the oleylamine−xylene solution at 90 °C to prevent the formation of the manganese−oleylamine complex, 8 nm sized spherical Mn_3O_4 nanocrystals were produced (Supporting Information). On the basis of these results, we propose that manganese hydroxide ($Mn(OH)_2$) mainly contributes to the nucleation, whereas the manganese−oleylamine complex contributes to the shape-controlled growth process.

Spherical Mn_3O_4 Nanocrystals. In the current synthetic method, carboxylic acid turned out to play an important role in the shape control of the Mn_3O_4 nanocrystals. We were able to synthesize spherical Mn_3O_4 nanocrystals with various sizes by using a mixture of oleylamine and carboxylic acid as surfactant (Figure 3). Smaller nanocrystals with an average diameter of 5.5 nm were prepared by using a mixture of stearic acid and oleylamine (Supporting Information). The size control of the nanocrystals was carried out by using various ratios of oleylamine and oleic acid with keeping other reaction conditions the same as those for the synthesis of the 9 nm sized nanoplates. When the ratio of oleylamine/oleic acid was reduced from 5 to 2, the size of the nanocrystals increased from 6.2 to 8.5 nm (Figure 3a,c); when the ratio was 1, larger 15 nm sized rice-shaped nanocrystals were generated (Figure 3d). When the ratio was decreased to less than 1, almost no nanocrystals were generated. It seems that as the amount of oleic acid in the reaction mixture increases, the nucleation of the nanocrystals is blocked, which results in the increase in the amount of the monomers for the growth of individual nuclei.

Mn_3O_4 Nanowires and Nanokites. The nanoplates and spherical nanocrystals of Mn_3O_4 presented so far were synthesized by injecting water into the reaction mixture composed of manganese precursor and surfactant at 90 °C, followed by aging at that temperature. Consequently, the overall synthetic process is similar to the hot-injection method, although the injection temperature is much lower than the conventional hot-injection method.[11,27] The Hyeon group and others employed the "heating-up" method, which involves slow heating-up of the reaction mixtures to high reaction temperature and subsequent aging, to synthesize

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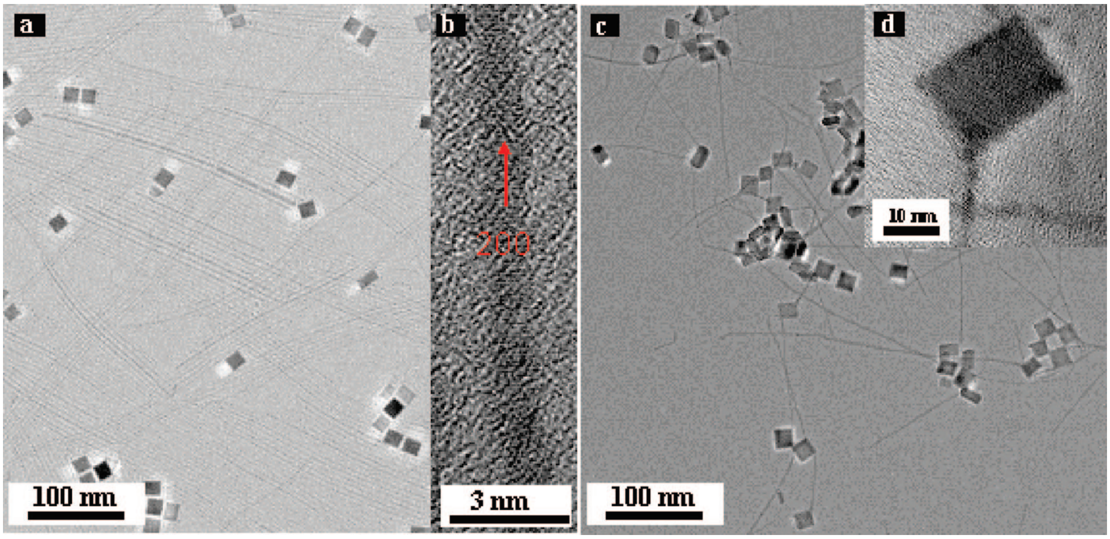

Figure 4. (a) TEM image of a mixture of 15 nm Mn_3O_4 nanoplates and 150 nm Mn_3O_4 nanowires, (b) HRTEM image of a 150 nm Mn_3O_4 nanowire, and (c) TEM and (d) HRTEM images of Mn_3O_4 nanokites.

uniform nanocrystals of various compositions and shapes.[12] We employed this "heating up" method to synthesize Mn_3O_4 nanowires. In this process, water was added to the reaction mixture composed of manganese(II) acetate (0.17 g, 1 mmol), oleic acid (0.56 g, 2 mmol), oleylamine (2.67 g, 10 mmol), and 15 mL of xylene at room temperature and in air atmosphere. The resulting solution was slowly heated to 90 °C and aged at that temperature for 3 h. The TEM image showed that the product was a mixture of Mn_3O_4 nanowires with a diameter of 2 nm and length of >150 nm (∼60%) and 15 nm nanoplates (∼40%) (Figure 4a). The HRTEM image shows that the nanowires grew along the [100] direction (Figure 4b). Careful investigation of the TEM images (Figure 4c) revealed that some nanowires attached to the nanoplates, building a "kite" structure (Figure 4d). The nanokites consist of a nanoplate head and a nanowire tail. To elucidate the formation process of the nanokites a series of sampling experiments were conducted by drawing aliquots from the reaction solution at various temperatures and aging times during the synthesis, and TEM images were taken for these aliquots (Supporting Information). Before the reaction temperature reached 90 °C, no nanocrystals were produced. After 3 min of aging at 90 °C, a small amount of nanowires was generated without any nanoplate formation. When the aging time reached 10 min, the nanoplates appeared in the solution. However, no nanokite was observed in the TEM image of the sample drawn from the solution at this point of time. Consequently, the nanokites seems to be formed via a two-step reaction in which the nanowires and the nanoplates were formed independently and the nanowires came into contact and attached with the nanoplates forming the nanokites during the aging process. By decreasing the amount of surfactants, we also were able to control the length of the nanowires. When we performed the reaction using 1.25 mmol of oleylamine and 0.25 mmol of oleic acid, Mn_3O_4 nanowires with diameter of 7 nm and lengths of more than 400 nm were produced (Figure 5).

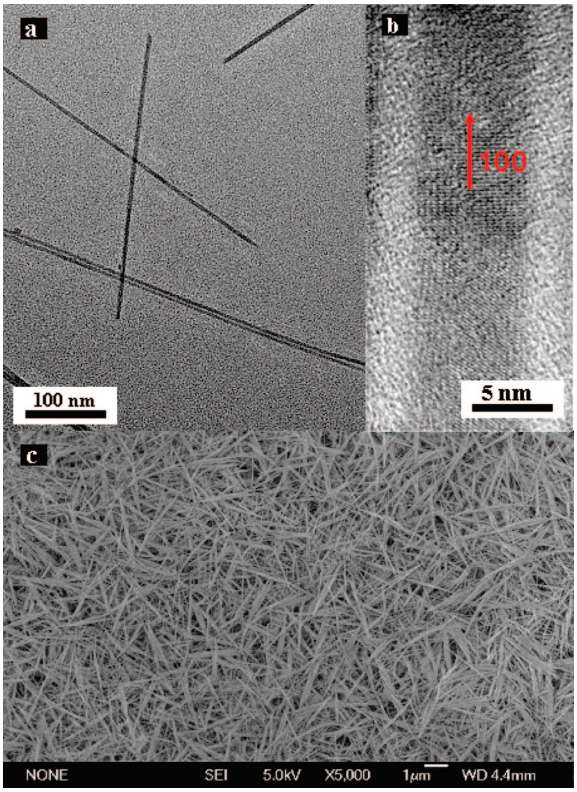

Figure 5. (a) TEM, (b) HRTEM, and (c) SEM images of long Mn_3O_4 nanowires of >400 nm.

MRI Contrast Effect of Mn_3O_4 Nanocrystals. Recently, the Hyeon group reported on the synthesis and application of MnO nanocrystals as a new T_1 MRI contrast agent.[20] Like MnO nanocrystals, Mn_3O_4 also has Mn^{2+} ions which have T_1 MRI contrast effect. To examine the possibility of using Mn_3O_4 nanocrystals as an MRI contrast agent, the 9 nm sized nanoplates dispersed in organic solvent were coated with a poly(ethylene glycol) (PEG)−phospholipid shell to make them water-dispersible and biocompatible (Supporting Information). The nanocrystals were stable in water dispersion without degradation or aggregation for several weeks. T_1 and T_2 relaxation times of Mn_3O_4 nanocrystals were measured

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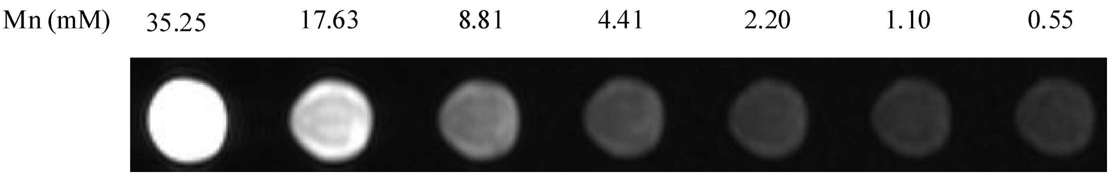

Figure 6. T_1-weighted MR images of the 9 nm Mn_3O_4 nanoplates.

with a 1.5 T clinical MRI scanner. Figure 6 showed T_1-weighted images and their relaxation times for various nanocrystal concentrations. To further investigate the MRI contrast effect, the specific relaxivities (r_1 and r_2) were also measured. The 9 nm sized Mn_3O_4 nanoplates had 0.13 mM^{-1} s^{-1} of r_1 and 0.55 mM^{-1} s^{-1} of r_2 (Supporting Information). These values are similar to those of the previously reported MnO nanocrystals.[20]

Conclusion

Uniform Mn_3O_4 nanocrystals with shapes of sphere, plate, wire, and kite were prepared via the mild reaction of manganese(II) acetate, oleylamine, and water in xylene in the presence of surfactants at the temperature of as low as 90 °C in air atmosphere. The size and shape of the nanocrystals were easily controlled by varying the synthetic parameters. Interestingly, in spite of the low reaction temperature of 90 °C, the Mn_3O_4 nanocrystals synthesized were highly crystalline. Mechanistic studies reveal that the nucleation occurs by the reaction of the in situ synthesized $Mn(OH)_2$, whereas the Mn−oleylamine complex reacts on the nuclei to form Mn_3O_4 nanocrystals. The current synthetic procedure is readily applicable to the large-scale synthesis for the industrial applications because of their simplicity and the mild reaction conditions, namely, the low reaction temperature, the air atmosphere, and the use of nontoxic and cheap reagents. For example, we were able to synthesize as much as 4.5 g of 15 nm sized Mn_3O_4 nanoplates using a 1 L reactor. In addition to their novel shape and size uniformity, Mn_3O_4 nanocrystals exhibited a good T_1 contrast effect, demonstrating their potential applications to the T_1 MRI contrast agent.

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Supporting Information Available: TEM results of sampling experiments of Mn_3O_4 nanokites. A TEM image of 9 nm sized water dispersible Mn_3O_4 nanoplates. MRI results of relaxation times of the Mn_3O_4 nanocrystal dispersion in water. A photograph of the powders of the 15 nm sized Mn_3O_4 nanoplates. This material is available free of charge via the Internet at http://pubs.acs.org.

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