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COMMUNICATION

Formation of Uniformly Sized Metal Oxide Nanocuboids in the Presence of Precursor Grains in an Apolar Medium

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Uniformly sized Mn_3O_4 nanocuboids were produced in the presence of tiny round grains ~3 nm in diameter covered with oleic acid in toluene. The formation of the rectangular nanocrystals surrounded with {100} and (001) faces is attributable to oriented attachment of the precursor grains in the apolar medium in which the metal and hydroxide ions are insoluble.

Since Penn and Banfield¹ reported oriented attachment of TiO_2 nanocrystals in an aqueous phase, the phenomena have attracted much attention as nonclassical crystallization. Various types of the oriented attachments have been studied for a wide variety of crystals.²⁻⁶ The previous works are classified into two categories: ordered arrangement of nanocrystals with molecular-mediated contact and crystallographic fusion of nanocrystals through direct contact. In the former, well-defined arrays, so-called mesocrystals or superlattices, are produced with faceted nanocrystals that are covered with organic molecules. 2D and 3D superlattices were formed via self-assembly of the nanocubes in the same crystallographic orientation.²⁻⁴ Diverse supercrystals having well-defined micrometric facets are constructed via the 3D-oriented assembly of nanocubes.^{2,7-11} In the latter, the crystallographic fusion of nanocrystals was investigated in detail by direct observation.^{5,6} Several well-defined morphologies, such as rods,¹² sheets,¹³ and multipods,¹⁴ were produced through the fusion of nanocrystals. However, formation of uniformly sized blocks has not been observed through the attachment of nanograins. Here, we demonstrate the formation of faceted ~20-nm cuboids from precursor particles (~3 nm in diameter) in an apolar medium.

Recently, size- and shape-controlled nanoparticles, including nanospheres, nanooctahedra, nanorods, and nanoplates, have been synthesized with various types of crystals.¹⁵⁻¹⁹ As mentioned above, well-defined and uniformly sized rectangular nanoblocks, such as

nanocubes and nanocuboids, are important for the fabrication of ordered superlattices. Nanocubes have been synthesized from several cubic crystals, including metals and metal oxides.^{2,7,20-23} On the other hand, the detailed formation process of the uniformly sized nanocubes and nanocuboids has not been established for various oxide materials. Monitoring the formation process is an important clue for production of novel faceted nanocrystals from diverse cubic and tetragonal systems.

In the previous work, we prepared monodisperse tetragonal Mn_3O_4 nanoblocks using a two-phase (water and toluene) solvothermal system.²⁴ A wide variety of ordered arrays were obtained through self-assembly of the well-defined cuboids. Fabrication of the ordered arrays of Mn_3O_4 nanocrystals has attracted much interest because of its potential applications, such as for an active catalyst,^{25,26} magnetic devices,²⁷ and electrode materials.²⁸⁻³² In the present study, the formation process of the rectangular 18-nm blocks surrounded with stable {100} and (001) faces was demonstrated by monitoring the time-dependent evolution of binary size-distribution through oriented attachment of the tiny precursor grains under the solvothermal condition. The metal and hydroxide ions are insoluble in the apolar medium. Thus, the epitaxial attachment of primary nanocrystals in the apolar organic phase is deduced to be essential for the formation of the well-defined crystalline blocks.

We prepared manganese oxide nanoblocks in a two-phase system composed of an upper toluene solution and a lower aqueous solution under a solvothermal condition. In a typical synthesis process, 0.60 mmol manganese(II) chloride tetrahydrate and 35 wt% hydrogen peroxide (4 cm³) were dissolved in 31 cm³ of water in a 100 cm³ Teflon container. Oleic acid (3.97 mmol) and *tert*-butylamine (2.31 mmol) were added into 30 cm³ toluene. The organic mixture was added to the Teflon container without stirring. At this time, oxygen gas was generated through decomposition of hydrogen peroxide. When the generation of oxygen gas roughly stopped, the Teflon container was put into a stainless steel autoclave. The autoclave was

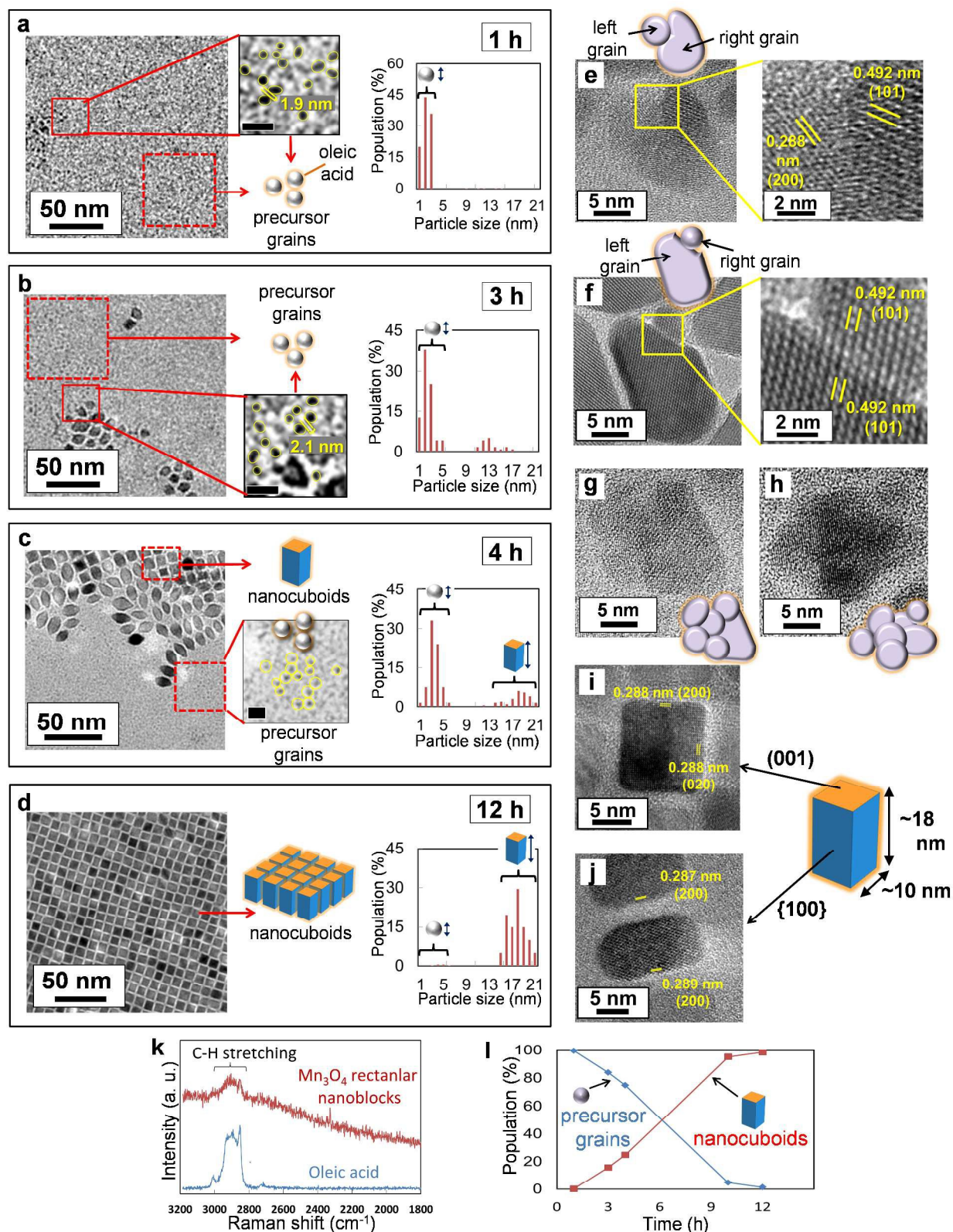
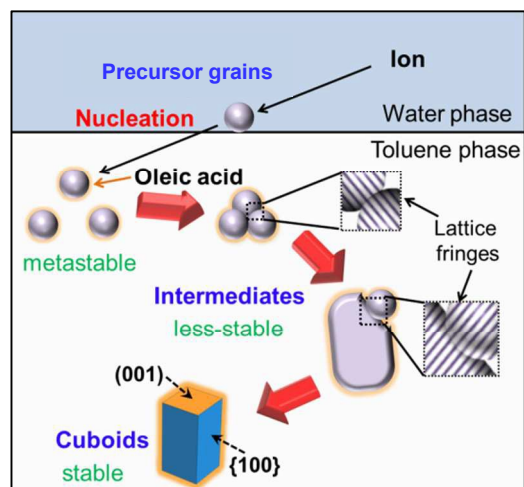


Fig. 1 TEM images with schematic illustrations and size-distribution histograms of Mn₃O₄ nanocrystals obtained by the solvothermal reaction for 1 h (a), 3 h (b), 4 h (c), and 12 h (d) (Scale bars of insets are 10 nm). HRTEM images and schematic illustrations of the large Mn₃O₄ nanocrystals consisting of small grains via oriented attachment (e–h) and the Mn₃O₄ rectangular nanoblocks (i, j). Raman spectra of the Mn₃O₄ rectangular nanoblocks and oleic acid (k). Time-dependent population of Mn₃O₄ nanoparticles (l).

heated at 115°C for 1–12 h. After the reaction, the resultant dark brown liquid (upper phase) was transferred into a glass vial. A copper grid covered with a collodion film was placed on a piece of filter paper. A drop of the resultant dispersion was placed on the grid. The excess medium of the dispersion was absorbed by the filter paper. The products deposited on the grid were characterized by the transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and fast Fourier transform (FFT) profiles using a FEI TECNAI-F20.

Fig. 1 shows the time evolution of the size, shape, and population of the Mn_3O_4 nanoparticles in the toluene phase under the solvothermal condition. Primary round particles ~ 3 nm in diameter (precursor grains) were mainly obtained in the initial stage of the reaction (1 h) (Fig. 1a). After the reaction for 3 h, the precursor grains and relatively large nanocrystals ~ 13 nm in length were observed (Fig. 1b). Interestingly, medium-sized grains in the range of 6–10 nm were hardly observed in the organic medium. The large particles were found to consist of several grains that are assigned to Mn_3O_4 ($a = 0.576$ nm and $c = 0.944$ nm, ICDD No. 01-080-0382) from the lattice fringes (Fig. 1e). The typical particle is divided into two domains due to difference of lattice fringes observed by HRTEM. Because the angle between $[200]$ in the left grain and $[101]$ in the right one (31°) is approximately corresponding to the theoretical value between these directions of a single-crystalline Mn_3O_4 (31.4°), these small grains are aligned in almost the same crystallographic direction in the large particle. The presence of the complex particles and the absence of the medium-sized grains suggest that the large-sized crystal was formed by oriented attachment of the primary nanograins in the apolar organic medium. After the reaction for 4 h, rectangular nanoblocks measuring ~ 18 nm (18-nm cuboids) were produced with the precursor round grains (Fig. 1c). We observed few medium-sized grains in the range of 6–12 nm even in this stage. Thus, the binary size-distribution is characteristic in this system. We found an incomplete rectangular nanoblock accompanied with a small Mn_3O_4 nanocrystal (Fig. 1f). The continuous lattice fringe at the interface strongly indicates that the oriented attachment of the large block and the small grain of the metal oxide crystal occurred in the apolar medium. Fig. 1g and h also show several intermediate states between the faceted nanocuboids and the precursor grains. The grain boundaries were blurred through fusion of the grains. The bottlenecks and pores are deduced to be quickly filled through removal of the surfactant. When the reaction time was prolonged to 10–12 h, the population of the 18-nm cuboids increased in contradiction to a decrease of the population of the precursor round grains (Fig. 1d and l). After the reaction for 12 h, most of the products were uniformly sized 18-nm cuboids having well-defined facets. The resultant cuboids exhibit truncated cuboids having four $\{100\}$ faces in the oblong shape and two $\{001\}$ faces in the square shape. The width and length of the nanocuboids synthesized under the typical reaction condition were ca. 10 nm and 18 nm, respectively (Fig. 1i and j). As shown in Fig. 1d, the well-defined cuboids formed superlattices in the square grid pattern. The formation of the highly ordered arrays indicates the uniformity of the cuboids. Because the interparticle distance of nanocuboids, ca. 3 nm, was nearly twice the length of the organic molecule (1.7 nm) (Fig. 1j), the cuboids were covered with oleic acid and were slightly tilted. We confirmed the presence of oleic acid that covered the nanocuboids by the presence of specific stretching vibration modes of C-H around 2900 cm^{-1} in the Raman scattering spectra using a Renishaw InVia (Fig. 1k). We estimated the amount of manganese ions in the toluene phase containing oleic acid after the solvothermal treatment by the inductively-coupled plasma atomic emission spectroscopy using a Shimadzu ICPE-9000. The



Scheme 1 Shape evolution from precursor grains to cuboids through oriented attachment in an apolar organic medium.

concentration of manganese ions in the toluene phase was 3.1×10^{-6} mol/dm³ that was less than a ten-thousandth of that in the water phase. Moreover, hydroxyl ions as a counterpart of the metal ions for ion-by-ion growth are hardly dissolved in the apolar medium. Thus, the ion-by-ion growth is not dominant for the formation of Mn_3O_4 cuboids in toluene.

The faceted nanocrystals of various metal oxides in organic media through two-phase routes were reported by previous works.³³ However, the quantitative characterization of the size-distribution was insufficient to clarify the formation mechanism. Scheme 1 shows the possible formation process of the cuboids through oriented attachment in the two-phase system. The pH value of the aqueous phase near the water–toluene interface is deduced to be locally increased through the hydrolysis of *tert*-butylamine contained in the organic phase. (The overall pH value of the water phase was increased from 7.31 to 8.10 by the solvothermal reaction.) The nuclei of manganese compounds are generated in the water phase near the interface or at the interface. The precursor grains coated by oleic acid moved into the toluene phase. The interparticle distance, ca. 2 nm, indicates the presence of oleic acid molecules that are ca. 1.7 nm in length around the particles (insets of Fig. 1a and b). Since the distance between the precursor grains was smaller than that of the faceted 18-nm cuboids, the density of oleic acid covering the precursor grains is inferred to be lower than that on the cuboids. As shown in Fig. 1, we mainly observed the precursor grains and the faceted 18-nm cuboids without the intermediate-sized particles. The population of the nanocuboids increased with consumption of the precursor grains (Fig. 1l). If the growth occurs through the regular ion-by-ion process, the mean size would increase gradually. Thus, the binary size-distribution indicates that the 18-nm cuboids were formed through the attachment of the precursor grains. Moreover, we found the epitaxial attachment of the small grains ~ 5 nm in length into the large Mn_3O_4 particles having almost continuous lattices like a single crystal (Fig. 1e and f). The low solubility of manganese and hydroxyl ions in the apolar medium supports that the oriented attachment is dominant of the formation of the cuboids. The evolution of the distribution indicates that the precursor round grains are metastable and the faceted 18-nm blocks are stable under the

reaction condition. The intermediate particles with undefined shapes would be less stable than the precursor spheres and the faceted 18-nm blocks. As shown in Fig. 1g and h, the grain boundaries in the intermediate states between the nanocuboids and the precursor grains were blurred through fusion of the grains. This suggests that the bottlenecks and pores are quickly filled through surface diffusion including removal of the surfactant. The surface diffusion would be a main pathway for the development of morphologies in the small region below 10 nm. As demonstrated in the TEM images, the crystal growth proceeded through fusion of the precursor grains.³⁴ Thus, various sizes of the intermediates are basically present in the present system. However, we observed a very small amount of the intermediates because of their low stability originating from undefined shapes. The intermediates have an excess surface energy in comparison with the spherical grains and the faceted nanocuboids. The shape evolution to the faceted cuboids is induced to reduce the surface energy. Finally, the nanocuboids with the stable facets are rapidly formed by the fusion of a few dozen of the precursor grains. Further attachment by facing {100} and (001) is inferred to be suppressed by a strong adsorption of oleic acid molecules to the faces.

As shown in Fig. S1, the morphologies of Mn₃O₄ nanocrystals depended on the amount of oleic acid. Polydisperse round nanoparticles were obtained at a concentration of oleic acid lower than the standard condition (Fig. S1a). A sufficient amount of oleic acid is needed to transfer a large number of the manganese oxide nanoparticles from the aqueous phase to the organic phase. The faceted rectangular nanoblocks are formed through oriented attachment of a plentiful amount of primary particles covered with oleic acid. On the other hand, spherical and octahedral nanoparticles were mainly obtained with a small amount of the cuboids at a higher concentration of oleic acid (Fig. S1b). An excess amount of oleic acid would suppress the oriented attachment of the precursor grains and inhibit the formation of regular rectangular nanoblocks. We obtained larger rectangular nanoblocks (The width and length of the nanoblocks were ca. 20 nm and 30 nm, respectively.) by the addition of twice the amount of manganese sources (1.20 mmol), oleic acid (7.94 mmol), and *tert*-butylamine (4.62 mmol) (Fig. S2). The size of the final product increases with an increase in the number of primary nanoparticles produced under the solvothermal condition. These results suggest that the molar ratio of manganese sources, oleic acid, and *tert*-butylamine is essential for the formation of uniformly sized Mn₃O₄ rectangular blocks.

Conclusions

We produced uniformly sized Mn₃O₄ nanocuboids in toluene under a solvothermal condition. The rectangular nanocrystals surrounded with {100} and (001) faces were produced in the presence of tiny round grains as a precursor in toluene. Because the metal and hydroxide ions are insoluble in the apolar medium, the formation of the metal oxide blocks is attributable to the attachment of the precursor grains. The non-classical growth process is regarded as an important route to uniformly sized nanocrystals.

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Notes and references

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- R. L. Penn and J. F. Banfield, *Science*, 1998, **281**, 969.
- A. Demortière, P. Launois, N. Goubet, P.-A. Albouy and C. Petit, *J. Phys. Chem. B*, 2008, **112**, 14583.
- K. X. Yao, X. M. Yin, T. H. Wang and H. C. Zeng, *J. Am. Chem. Soc.*, 2010, **132**, 6131.
- F. Dang, K. Kato, H. Imai, S. Wada, H. Haneda and M. Kuwabara, *Cryst. Growth Des.*, 2011, **11**, 4129.
- W. Lv, W. He, X. Wang, Y. Niu, H. Cao, J. H. Dickerson and Z. Wang, *Nanoscale*, 2014, **6**, 2531.
- H.-P. Zhou, Y.-W. Zhang, H.-X. Mai, X. Sun, Q. Liu, W.-G. Song and C.-H. Yan, *Chem. — Eur. J.*, 2008, **14**, 3380.
- J. Zhang, H. Yang, K. Yang, J. Fang, S. Zou, Z. Luo, H. Wang, I.-T. D. Bae and Y. Jung, *Adv. Funct. Mater.*, 2010, **20**, 3727.
- T. Wang, X. Wang, D. LaMontagne, Z. Wang, Z. Wang and Y. C. Cao, *J. Am. Chem. Soc.*, 2012, **134**, 18225.
- C.-J. Chen, R.-K. Chiang and Y.-R. Jeng, *J. Phys. Chem. C*, 2011, **115**, 18142.
- C.-W. Liao, Y.-S. Lin, K. Chanda, Y.-F. Song and M. H. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 2684.
- M. Agthe, E. Wetterskog, J. Mouzon, G. Salazar-Alvarez and L. Bergström, *CrystEngComm*, 2014, **16**, 1443.
- C. Pacholski, A. Kornowski, and H. Weller, *Angew. Chem. Int. Ed.* 2002, **41**, 1188.
- C. Schliehe, B. H. Juarez, M. Pelletier, S. Jander, D. Greshnykh, M. Nagel, A. Meyer, S. Foerster, A. Kornowski, C. Klinke and H. Weller, *Science*, 2012, **329**, 550.
- D. Zitoun, N. Pinna, F. Nathalie and C. Belin, *J. Am. Chem. Soc.* 2005, **127**, 15034.
- T. P. Bigioni, X.-M. Lin, T. T. Nguyen, E. I. Corwin, T. A. Witten and H. M. Jaeger, *Nat. Mater.*, 2006, **5**, 265.
- W. Lu, Q. Liu, Z. Sun, J. He, C. Ezeolu and J. Fang, *J. Am. Chem. Soc.*, 2008, **130**, 6983.
- A. Singh, R. D. Gunning, A. Sanyal and K. M. Ryan, *Chem. Commun.*, 2010, **46**, 7193.
- K. An, N. Lee, J. Park, S. C. Kim, Y. Hwang, J.-G. Park, J.-Y. Kim, J.-H. Park, M. J. Han, J. Yu and T. Hyeon, *J. Am. Chem. Soc.*, 2006, **128**, 9753.
- T. Yu, J. Moon, J. Park, Y. I. Park, H. B. Na, B. H. Kim, I. C. Song, W. K. Moon and T. Hyeon, *Chem. Mater.*, 2009, **21**, 2272.
- F. Dang, K. Kato, H. Imai, S. Wada, H. Haneda and M. Kuwabara, *Cryst. Growth Des.*, 2010, **10**, 4537.

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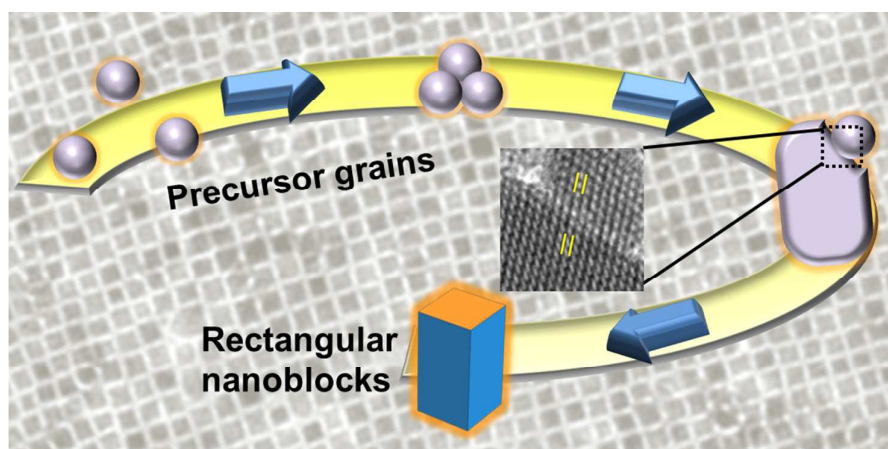
- 21 Z. Quan and J. Fang, *Nano Today*, 2010, **5**, 390.
- 22 S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
- 23 F. Dang, K. Mimura, K. Kato, H. Imai, S. Wada, H. Haneda and M. Kuwabara, *Nanoscale*, 2012, **4**, 1344.
- 24 Y. Nakagawa, H. Kageyama, Y. Oaki and H. Imai, *J. Am. Chem. Soc.*, 2014, **136**, 3716.
- 25 P. Zhang, Y. Zhan, B. Cai, C. Hao, J. Wang, C. Liu, Z. Meng, Z. Yin and Q. Chen, *Nano Res.*, 2010, **3**, 235.
- 26 M. Biswal, V. V. Dhas, V. R. Mate, A. Banerjee, P. Pachfule, K. L. Agrawal, S. B. Ogale and C. V. Rode, *J. Phys. Chem. C*, 2011, **115**, 15440.
- 27 W. S. Seo, H. H. Jo, K. Lee, B. Kim, S. J. Oh and J. T. Park, *Angew. Chem., Int. Ed.*, 2004, **43**, 1115.
- 28 J. Pan, Y. Sun, Z. Wang, P. Wan and M. J. Fan, *Alloys Compd.*, 2009, **470**, 75.
- 29 J. Wang, N. Du, H. Wu, H. Zhang, J. Yu and D. Yang, *J. Power Sources*, 2013, **222**, 32.
- 30 J. Gao, M. A. Lowe and H. D. Abruña, *Chem. Mater.*, 2011, **23**, 3223.
- 31 H. Wang, L.-F. Cui, Y. Yang, H. S. Casalongue, J. T. Robinson, Y. Liang, Y. Cui and H. Dai, *J. Am. Chem. Soc.*, 2010, **132**, 13978.
- 32 C. Wang, L. Yin, D. Xiang and Y. Qi, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1636.
- 33 T. Nguyen and T. Do, *J. Phys. Chem. C*, 2009, **113**, 11204.
- 34 M. H. Nielsen, D. Li, H. Zhang, S. Aloni, T. Y.-J. Han, C. Frandsen, J. Seto, J. F. Banfield, H. Cölfen and J. J. De Yoreo, *Microsc. Microanal.*, 2014, **20**, 425.

TOC

Formation of Uniformly Sized Metal Oxide Nanocuboids in the Presence of Precursor Grains in an Apolar Medium

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Oriented attachment of Mn_3O_4 primary particles covered with oleic acid was found to occur in an organic medium. Faceted nanocuboids were produced through the oriented attachment and subsequent crystallographic fusion.