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Orientation-selective alignments of nanoblocks in *a* and *c* directions of a tetragonal system through molecularly mediated manipulation†

Yoshitaka Nakagawa, Hiroyuki Kageyama, Yuya Oaki and Hiroaki Imai*

Tetragonal Mn_3O_4 nanocuboids were aligned in selective crystallographic directions by molecularly mediated manipulation. Alignment in the *a* direction was produced by *a* face-by-*a* face assembly of hydrophobic nanocuboids covered with oleic acid. Another 1D array in the *c* direction was obtained through *c* face-to-*c* face assembly with the replacement of the organic modifiers.

Based on recent developments in colloidal chemistry, diverse nanometric crystals with well-defined morphologies, such as spheres,[1] octahedra,[2] and plates,[3] have been successfully synthesized as uniform nanometric building blocks. Self-assembly of the inorganic nanocrystals into ordered architectures is a fascinating phenomenon as a bottom-up approach to achieve a wide range of novel functional materials. Well-aligned ensembles of the nanocrystals often exhibit interesting collective properties that are different from those displayed by individual nanocrystals and bulky large crystals.[4,5] 2D and 3D close-packed arrays of uniform spherical nanoparticles are built through self-assembly in liquid media.[1,6] However, dimension-controlled assembly of spherical particles for 1D, 2D, and 3D arrangements is fundamentally difficult because of their shape isotropy.

Recently, nanocrystals with anisotropic shapes have attracted much attention as useful building blocks for the fabrication of various ordered assemblies. 1D, 2D, and 3D arrangements consisting of nanorods have been achieved through dimension-controlled assembly by means of their shape anisotropy.[7–11] Moreover, two types of 1D arrays were obtained through side-by-side and end-to-end attachments of anisotropic nanoblocks, such as gold nanorods.[12–15] However, the crystallographic directions of the building units in these assemblies were not aligned like polycrystalline structures because strictly oriented attachment through face-to-face contact was not achieved by nanorods that are not surrounded by well-defined faces.

The next challenge is how to manipulate the alignment of nanometric building blocks with uniform crystallographic directions, which is very important for controlling chemical and physical properties, such as ion permeability, catalytic properties, and magnetic properties. Single-crystalline architectures would be obtained by the epitaxial attachments of nanocrystals that are oriented in the same direction.[16–18] This is an interesting approach to micrometric architectures with specifically designed shapes and crystallographic directions using nanometric blocks. One promising candidate for solving the problem is using rectangular nanoblocks, including nanocubes and nanocuboids that tend to assemble in the same crystallographic direction like a single crystal by facing well-defined facets. Nanocubes covered with amphiphilic molecules were synthesized from various cubic crystals of metals and metal oxides.[19–30] A wide variety of 2D and 3D single-crystal-like superlattices are formed *via* the oriented self-assembly of the building blocks.[22–25] Micrometer- and millimeter-scale assemblies consisting of the nanocubes have been fabricated on a substrate convective self-assembly using their dispersion.[31–34] However, the regulation of the direction and dimension of the oriented self-assembly of isotropic nanocubes is basically hard without any external fields or complicated surface modification.[35,36] On the other hand, the crystallographic orientations of 1D, 2D, and 3D ordered arrays consisting of manganese oxide nanocuboids have been sufficiently controlled for the fabrication of diversely shaped assemblies by means of shape anisotropy of building blocks.[37] Single-crystalline 1D chains and 2D panels were achieved through the epitaxial attachments of crystallographically aligned nanocrystals.[38] On the other hand, direction-selective 1D alignment of the anisotropic nanoblocks has not been achieved sufficiently by using systems composed of single building blocks and a single medium.

In the present work, 1D arrays elongated along the *a* and *c* axes were selectively fabricated using tetragonal Mn_3O_4 nanocuboids by means of crystallographic anisotropy of the building blocks through molecularly mediated manipulation. As shown in Fig. 1, surfaces of the building blocks were modified through selective molecular exchange by means of different degrees of

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan. E-mail: hiroaki@applc.keio.ac.jp

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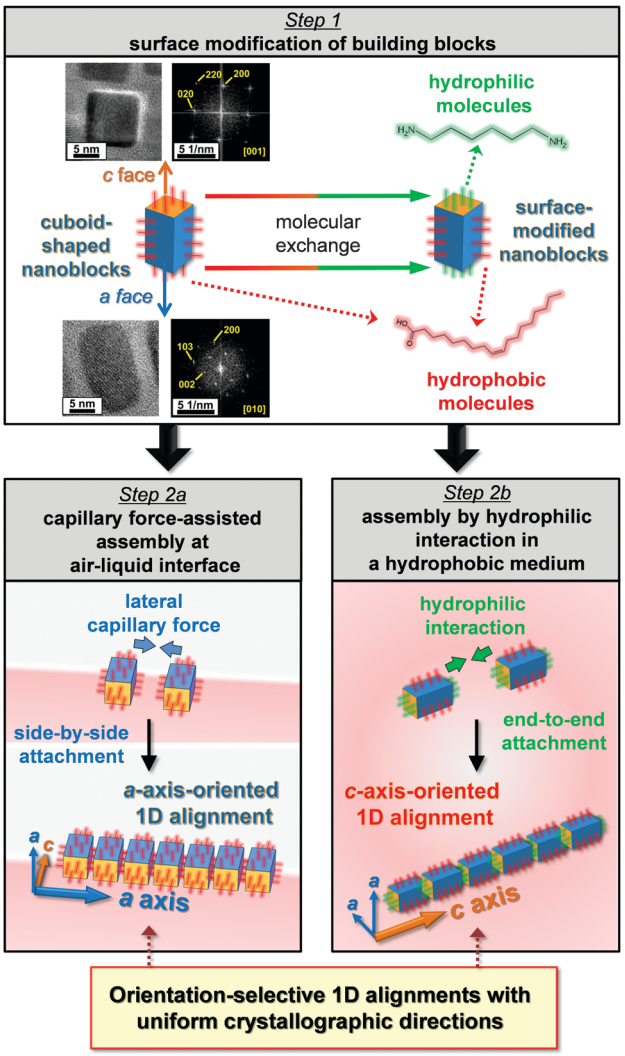

Fig. 1 Formation processes of 1D arrays elongated along *a* and *c* axes using tetragonal Mn_3O_4 nanocuboids by means of crystallographic anisotropy of the building blocks. Step 1: Anisotropic rectangular nanoblocks of tetragonal Mn_3O_4 covered with hydrophobic molecules were synthesized using a two-phase solvothermal method. The *c* faces of anisotropic nanoblocks were modified by the molecular exchange of hydrophilic and hydrophobic molecules. HRTEM images and the corresponding FFT patterns of Mn_3O_4 rectangular nanoblocks with a projection direction of [001] and [010]. Step 2a: The *a*-axis-oriented alignment of nanoblocks through side-by-side attachment at the air–liquid interface is assisted by lateral capillary forces. Step 2b: The *c*-axis-oriented alignment of nanoblocks through end-to-end attachment in a hydrophobic medium is formed by hydrophilic interaction of the surface-modified nanoblocks.

adsorption of organic molecules (Step 1). Anisotropic nanoblocks covered with hydrophobic molecules were well-dispersed in hydrophobic dispersion. A 1D array elongated along the *a* direction was obtained through side-by-side (*a* face-by-*a* face) assembly of the anisotropic blocks with evaporation of the dispersion medium (Step 2a). Surface-modified nanoblocks that exposed hydrophilic *c* faces were assembled in hydrophobic dispersion by facing the hydrophilic faces. Another 1D array elongated along the *c* axis was then obtained in the hydrophobic medium by end-to-end (*c* face-to-*c* face) attachment (Step 2b). We regulated the crystallographic orientation of the alignment of the nanocrystals using a single hydrophobic dispersion medium and single building blocks. The face-selective exchange of the molecules adsorbed on the nanocuboids is essential for nanometric manipulation based on the hydrophobic–hydrophilic interaction.

Anisotropic rectangular nanoblocks of tetragonal Mn_3O_4 were synthesized using a two-phase solvothermal method reported in our previous work.[37,39] As shown in Fig. 1, the fast Fourier transform (FFT) spots corresponding to the lattice fringes of tetragonal Mn_3O_4 (a = 0.576 nm and c = 0.944 nm) were observed by high-resolution transmission electron microscopy (HRTEM). The width and length of the nanocuboids that exhibited truncated cuboids with four {100} faces and two (001) faces were *ca.* 10 nm and *ca.* 20 nm, respectively. The presence of oleic acid covering the nanocuboids was confirmed by Raman spectroscopy.[39] The terminal COO^- of oleic acid is deduced to be attached to the surface of the Mn_3O_4 nanoblocks because the Mn_3O_4 nanoblocks were produced through oriented attachment of tiny nanoparticles of manganese compounds covered by dehydrogenated oleic acid in the aqueous phase.[39] The hydrophobic nanoblocks were well dispersed in a hydrophobic dispersion medium, such as a mixture of toluene and hexane.

After evaporation of the hydrophobic dispersion medium, we observed the 1D alignment of several Mn_3O_4 nanocuboids on a collodion film by transmission electron microscopy (TEM) (Fig. 2a). The average number of nanoblocks in the 1D chains was 5.6 ± 3.5. The inter-particle distance (3.0 ± 0.22 nm) is close to twice the molecular length of oleic acid (1.7 nm) (Fig. 2b and c). This suggests that the nanoblocks were covered with the organic molecules that were slightly tilted. Anisotropic Mn_3O_4 nanoblocks aligned along the *a* axis (*a*-axis-oriented 1D alignment) were confirmed by the FFT patterns of lattice fringes obtained from the four adjacent nanocuboids (Fig. 2c and d).

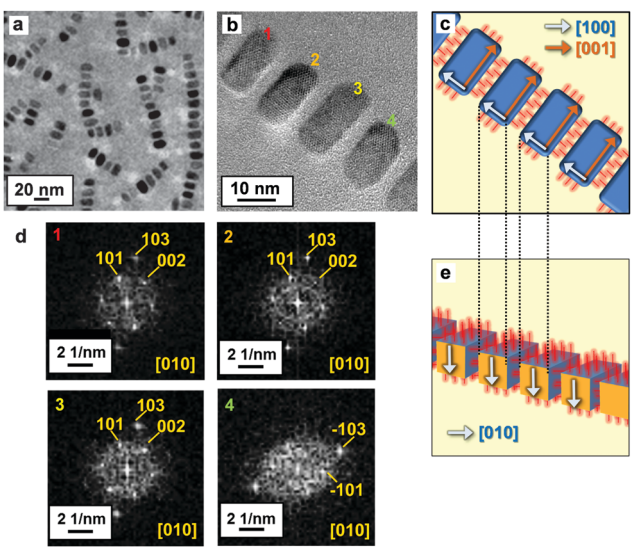

Fig. 2 TEM image (a), HRTEM image (b), and schematic illustrations (c and e) of 1D arrays consisting of aligned Mn_3O_4 rectangular nanoblocks along the *a* axis; FFT patterns corresponding to the lattice fringes of the aligned Mn_3O_4 nanoblocks (d).

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Moreover, the nanocrystals in the *a*-axis-oriented 1D arrays were shown to be highly aligned, like a single crystal, because the crystal zone axes of all nanoblocks corresponded to [010] (Fig. 2e). The deviation of crystallographic orientation was estimated to be $\sim 2^{\circ}$ from FFT patterns of adjacent nanoblocks. Mn_3O_4 cuboids tend to be aligned in the ⟨100⟩ direction with side-by-side attachment of rectangular {100} faces. The hydrophobic nature of the surface resulted in the stable dispersion of nanocuboids in a mixture of toluene and hexane. The *a*-axis-oriented 1D alignment was deduced to be formed through the side-by-side (*a* face-by-*a* face) attachment of lateral capillary forces at the air–liquid interface (Fig. 1, Step 2a). Because the surface areas of the rectangular faces are larger than those of the square faces, the rectangular side contacts more effectively decrease the total surface energy of the assemblies than the square side contacts.[37]

The direction of the alignment was controlled in the same medium by modifying the specific faces of the nanoblocks with organic molecules (Fig. 1, Step 1). The nanoblocks covered with hydrophobic molecules (oleic acid) were dispersed in an aqueous solution of hexamethylenediamine with a 30 min ultrasonication treatment. After the treatment, the end faces (*c* faces) of the anisotropic Mn_3O_4 blocks were hydrophilized by replacing oleic acid with hexamethylenediamine. When the resultant nanoblocks were redispersed in the toluene–hexane mixture, linear chains aligned along the *c* axis (*c*-axis-oriented 1D alignment) were formed in the liquid medium (Fig. 3a and b). The anisotropic Mn_3O_4 nanoblocks aligned in the *c* direction were confirmed by FFT patterns of lattice fringes obtained from the seven adjacent nanocuboids (Fig. 3c and d). Moreover, the nanocrystals in the *c*-axis-oriented 1D arrays were shown to be highly oriented alignments because the crystal zone axes of all the nanoblocks corresponded to [010] (Fig. 3e). The deviation of crystallographic orientation was estimated to be $\sim 5^{\circ}$ from FFT patterns of the adjacent nanoblocks. The average number of nanoblocks in the *c*-axis-oriented 1D chains was 3.6 ± 1.7. Because the nanocuboids were spatially separated (inter-particle distance: 1.1 ± 0.35 nm), their surfaces were covered by organic molecules. The thickness of the adsorbed molecular layers, which was smaller than that of the oleic acid molecule (molecular length: 1.7 nm), suggests that oleic acid adsorbed on the *c* faces was replaced by hexamethylenediamine (molecular length: 0.86 nm) (Fig. 3b). Oleic acid molecules adsorbed onto the surfaces of the nanoblocks are exchanged for hexamethylenediamine by ultrasonication because hydrophobic surfaces are unfavorable in an aqueous medium. Because the surface energy of the *a* faces is higher than that of the *c* faces, the detachment of oleic acid molecules from the *a* face is unfavorable.[40] Hydrophobic molecules covering the *c* faces are preferentially replaced by hexamethylenediamine molecules. Thus, surface-modified nanoblocks with hydrophobic *a* faces and hydrophilic *c* faces are obtained. The *c*-axis-oriented 1D alignment was produced by end-to-end attachment because attaching hydrophilic *c* faces is favorable in the hydrophobic medium (Fig. 1, Step 2b).

In summary, we fabricated direction-selective 1D architectures consisting of anisotropic nanoblocks through a 2-step process with molecularly mediated manipulation based on the interactions between adsorbed molecules on the block surfaces and a dispersion medium. Nanocuboids were selectively aligned in a hydrophobic medium by modifying the specific faces of the cuboids. Hydrophobic nanoblocks covered with oleic acid molecules are well dispersed in a hydrophobic medium. 1D arrays elongated in the *a* direction of the tetragonal crystal were produced through side-by-side (*a* face-by-*a* face) attachment of the highly dispersed nanocuboids at the air–liquid interface. Surface-modified nanoblocks with hydrophobic *a* faces and hydrophilic *c* faces were prepared through selective surface modification of the hydrophobic nanoblocks. Another 1D array aligned in the *c* direction of the tetragonal crystal was obtained by the end-to-end (*c* face-to-*c* face)

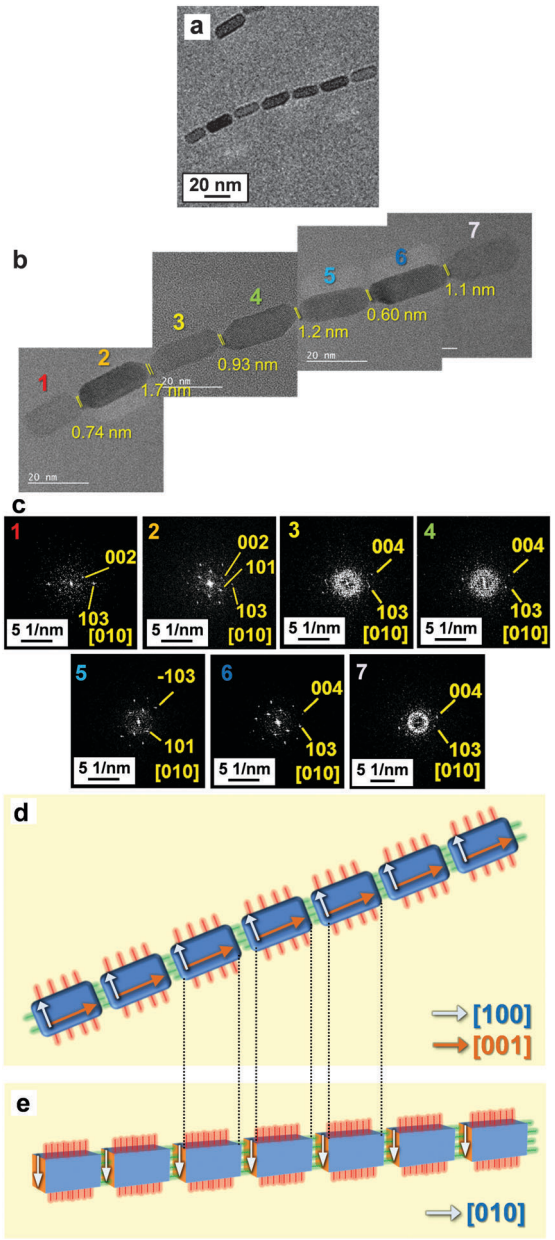

Fig. 3 TEM image (a), HRTEM images (b), and schematic illustrations (d and e) of aligned nanoblocks along the *c* axis; FFT patterns corresponding to the lattice fringes of the aligned Mn_3O_4 nanoblocks (c).

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attachment in a hydrophobic medium by attaching the hydrophilic *c* faces of the nanocuboids. Faceted cuboids with shape and crystallographic anisotropy are useful building blocks for the fabrication of various elaborate architectures with uniform crystallographic directions. Molecularly mediated manipulation of the building blocks is regarded as a novel direction-controlled accumulation technique for designing a wide variety of functional nanomaterials.

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