Micro-rings of Manganese Dioxide Nanocrystals on Mica

Sadaaki Yamamoto,* Osamu Matsuoka, and Shoko Sugiyama
Performance Materials R&D Center, Mitsui Chemicals Inc., 1190 Kasama-cho, Sakae-ku, Yokohama 247-8567

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Circularly ordered self-assembly (micro-ring) of manganese dioxide nanocrystals were formed simply by dewetting a manganese dioxide colloidal aqueous solution on mica. The balance between the repulsive force of the nanocrystals and the compressive force of shrinking droplets plays an important role in forming this peculiar nanosize assembly.

Formation of assemblies with higher hierarchy is of great interest for creating new functional materials. Current methods to achieve higher hierarchy from molecules involve, for example, Langmuir-Blodgett method[1] and self-assembling.[2,3] Recently, methods for producing ordered patterns of polymers have been reported in this journal. These methods involve highly complex yet technically simple processes. Karthaus etal. showed that ordered patterns of nanometer-sized poly(styrene) aggregates are achieved by pouring a dilute polymer solution over a flat mica surface.[4] They postulated that the mechanism for the aggregate formation is dewetting of the hydrophobic poly(styrene) from the hydrophilic mica. Also, Sano et al. reported that ordered nanometer-sized poly(ethylene) dots are formed by rubbing the thin polymer plate against the surface of a silicon wafer just below the melting point of the polymer.[5]

We developed a simple technique of architecture formation for substances with ordered structure on a solid substrate. We constructed an architecture of manganese dioxide nanocrystals, namely, circularly ordered assembly (micro-rings) of the nanocrystals, simply by dewetting a photochemically produced manganese dioxide colloidal solution on mica. Manganese oxides are of great interest for example, as electrode materials for a wide variety of primary and secondary lithium batteries,[6] as oxidizing agents and catalysts for oxidation[7] and hydration reaction of nitriles to amides.[8-11] Morphology plays an important role in the performance of manganese dioxide. For example, such morphology determines the performance of rechargeable lithium batteries.[12] Therefore, determining the factors that control the structure of manganese dioxides is critical. The micro-rings of manganese dioxide nanocrystals are potentially useful for investigating factors that control the morphology of manganese dioxides.

In developing the method, we used $KMnO_4$(Junsei Chemical GR grade) and KOH(Kokusan Kagaku GR grade) without further purification. A colloidal solution of manganese dioxide was prepared by photochemical reduction of $KMnO_4$ in an alkaline aqueous solution. A freshly prepared 1×10^{-4}M $KMnO_4$ aqueous solution (adjusted to pH10 by KOH) was photo-irradiated at room temperature in air using a high pressure Hg lamp (WACOM BMO500, 500W) with a water filter. The solution was photo-irradiated until the absorption of MnO_4^- ion in the wavelength region of 500 to 600 nm disappeared completely and the absorption peak intensities at around 340 and 215 nm for the colloids did not change any more. The UV-vis absorption spectrum agreed with that of the colloid produced by γ-irradiating alkaline aqueous solution of $KMnO_4$,[13] thus confirming that the photoroduct was manganese dioxide colloids. Sample for AFM imaging were prepared by dewetting the colloidal solution on mica. A drop of the colloidal solution was placed on freshly cleaved mica, which was then placed in a vacuum vessel. Excess water was removed by evacuation followed by drying at room temperature for more than 12 hrs. Samples for TEM imaging were prepared by applying a drop of the colloidal solution on a copper grid covered with a carbon film and then removing excess water by adsorption using filter paper and by evaporation using N_2-gas stream.

AFM imaging was done in ambient air using SPI-3600 (SII) in a contact mode. TEM images, electron energy loss spectra(EELS), and energy dispersed spectra(EDS) were taken by a JEOL-2010 high-resolution analytical electron microscope with an accelerating voltage of 200 kV. The UV-visible absorption spectra were recorded using a Shimadzu UV-2200 spectrophotometer.

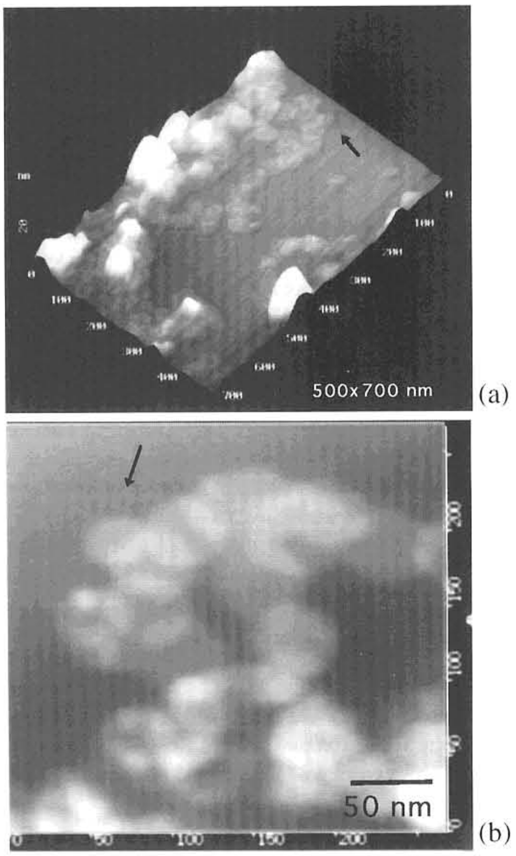

Figure 1. AFM images of manganese dioxide nanocrystals on mica for (a) a scan area of 700 x700 nm^2 and (b) a scan area of 250 x 250 nm^2, magnified image of the area indicated by arrow in (a).

Figure 1 shows a representative AFM image of the sample obtained by dewetting the colloidal solution on mica. A wide-scan three- dimensional image (Figure 1a) clearly shows a chain-like aggregate consisting of uniform, nearly circular structures with a mean diameter of 40 nm. A close-up image (Figure 1b) obtained by zooming in on a region of 250 x 250 nm^2 (arrow in Figure 1a) clearly shows that each circular structure in Figure 1a was actually a ring of small particles, each about 10 nm in

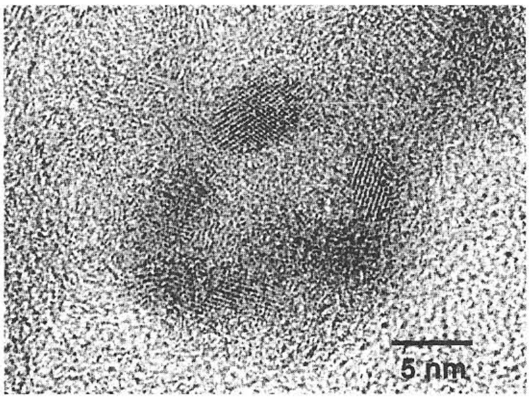

Figure 2. High-resolution TEM image of manganese dioxide nanocrytals.

diameter and about 3nm high. These ring aggregates were confirmed by high-resolution TEM imaging (Figure 2). The size of each particle in the ring aggregate was about 3-5 nm, which agrees well with the effective kinetic size of 4.2 nm calculated from kinetic data.[10] The larger size of the particles imaged by AFM (Figure 1b) than that imaged by TEM or estimated by the kinetic method is due to the convolution effect of AFM. Images showed lattices of 0.23, 0.25, and 0.33 nm, indicating that the particles were nanosize crystals (i.e., nanocrystals). EDS analysis indicates that each particles contained K, Mn and O at an atomic ratio of K:Mn=1:8 to 12. The Mn-M_{23} loss peak shape in EELS of the particles was similar to that of Mn^{4+} ,suggesting that the particles in the ring aggregates are manganese dioxides nanocrystals that contain K ions, namely KMn_8O_{16} with a hollandite-type structure.[14] However, we could not definitively assign the nanocrystals as KMn_8O_{16} because the lattice constant of 0.69 nm characteristic for KMn_8O_{16} was not observed.

The colloidal solution of manganese dioxide is extremely stable in a sealed condition. For several years after preparation, its absorption spectrum does not change. The stability against flocculation is due to negative charging of the nanocrystal surfaces in an alkaline condition caused by the reaction of surface hydroxyl groups with OH^- ions or OH^- adsorption at the surface.[13] This means that a repulsive force exists between the nanocrystals. During the dewetting process, each water droplet, which contains several nanocrystals, shrinks, thus drawing the nanocrystals together. However, the repulsive force prevents their aggregation. This force increases as the nanocrystals draw nearer to each other. When the diameter of the droplets shrinks to the size of the ring aggregate (about 40nm), the nanocrystrals maintain their separation because the repulsive force overcomes the compressive force of the droplet. The droplet continues to shrink and finally disappears from the mica surface, leaving the nanocrystals in the ordered circular form, or micro-ring.

Recently, we obtained KMn_8O_{16} needle–like crystals by heating the colloidal solution (pH =0.5). Based on this finding that the nanocrystals act as a precursor of KMn_8O_{16}, we are currently researching the factors that control the morphology of KMn_8O_{16} by investigating the progress of the micro-rings under various conditions, such as various pH, temperature or additives.

In conclusion, circular self-assembly (micro-ring) of manganese dioxide nanocrystals were formed simply by dewetting a manganese dioxide colloidal aqueous solution on mica. The balance between the repulsive force of the nanocrystals and the compressive force of shrinking droplets plays an important role in forming this peculiar nanosize assembly. This work demonstrates that the combination of charged nanocrystals and the simple dewetting on substrates is a potential architecture for generating substances having an ordered structure.

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