Dot-Like Formation of Metal Nanocrystals from Exfoliated Ruthenate Nanosheets*

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We studied the metallization behavior of molecularly thin $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets obtained from complete delamination of a layered ruthenate, $\text{K}_{0.2}\text{RuO}_{2.1}$. Heating at 200°C under a mixture of N_2 and H_2 transformed multilayers of the nanosheets into *hcp*-Ru metals. These metals have unique morphology reflecting the multilayer structure of the precursors. Interestingly, a monolayer state of the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets triggered a dot-like formation of Ru metal nanocrystals about 0.6 nm thick and several tens of nanometers wide, which represent a new family of 2D anisotropic metal nanomaterials. [DOI: 10.1380/ejsnt.2014.97]

Keywords: Ru; Metallic films; Nano structure chemistry

I. INTRODUCTION

Atomically controlled metal nanomaterials such as nanoparticles, nanorods, and nanowires have been widely studied. As they display intriguing physical and chemical properties associated with their surface state and shape at the nanometer scale, it is of importance to investigate their unique structures and dimensions for applications including electronics, optics, and magnetic devices, as well as catalysis [1].

Exfoliation of layered compounds such as clays [2, 3], oxides [4, 5], and graphite oxides [6, 7] into elemental host layers, called “exfoliated nanosheets”, is a cutting-edge technology that promises to allow two-dimensional (2D) control of nanomaterials. The nanosheets are a few nanometers thick and several micrometers wide. Thanks to their polyelectrolytic nature, they can be used as inorganic building blocks for electrostatic self-assembly based on oppositely charged ions, polymers, and molecules. Such artificial nano-architectures, *i.e.*, atomically controlled reactants, cannot be easily attained by conventional solid-state reaction, and often give rise to unpredictable thermodynamic reactivity. For instance, heating monolayer films of lepidocrocite-related $\text{Ti}_{0.91}\text{O}_2^{0.36-}$ nanosheets yielded anatase nanocrystals with a *c*-axis orientation [8]. The high dependency of this crystallization behavior on the number of deposited nanosheet layers indicates that both nucleation and growth of the anatase from the nanosheet film require extensive thermal activation of atomic diffusion. In the last decade, the chemical reduction of exfoliated graphite oxide nanosheets [7] has been shown to give distinct graphitic structures such as single- or multi-layered graphene, which can be regarded as a series of atomically controlled carbon nanomaterials.

Thus, secondary conversions of exfoliated nanosheets could pave the way to the creation of novel anisotropic nanomaterials.

More recently, we demonstrated that heating at up to 200°C under a mixture of inert gas and hydrogen caused topotactic conversion of a monolayer film of 2D hexagonal-type $\text{RuO}_2^{0.2-}$ nanosheets [9] obtained via exfoliation of NaRuO_2 into Ru metal nanosheets [10]. This unusual metallization can be understood as a low-temperature activation sufficient to release O atoms from the oxide nanosheets without extensive thermal diffusion of the constituent Ru atoms. The structural similarity between the 2D hexagonal precursor nanosheets with $a = 0.29$ nm and the resultant metal nanosheets with $a = 0.27$ nm seems to play an important role in the metallization, and motivated us to investigate the effect of initial structure on the metallization behavior. Here, we report that reduction of 2D oblique-type $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets obtained from the delamination of $\text{K}_{0.2}\text{RuO}_{2.1}$ [11, 12] triggered the dot-like formation of 2D anisotropic Ru metal nanocrystals.

II. EXPERIMENTAL

A. Material Synthesis

A dark-brown suspension of exfoliated ruthenate nanosheets was prepared as reported [12]. In brief, a pelleted mixture of K_2CO_3 and RuO_2 rutile (molar ratio of 5:8) was heated at 850°C for 12 h under Ar flow. The obtained sample was ground in an agate mortar and washed with ultrapure water ($> 18\text{M}\Omega$), yielding a layered potassium ruthenate, $\text{K}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ ($n = 0-1$). Ion-exchange of the interlayer potassium was conducted with 1 mol dm^{-3} HCl for 3 days at 60°C , resulting in layered protonic ruthenate, $\text{H}_{0.2}\text{RuO}_{2.1} \cdot n\text{H}_2\text{O}$ ($n = 0-0.9$) [12]. Then 0.4 g of this layered protonic ruthenate was added to 100 cm^3 of tetrabutylammonium hydroxide (TBA-OH) aqueous solution. The molar ratio of TBA ions to the exchangeable protons in the ruthenate precursor was 10:1. The mixture was vigorously shaken

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for more than 10 days to exfoliate the layered ruthenate into elemental host layers. Non-exfoliated ruthenate was removed by subsequent centrifugation at 2000 rpm for 30 min. The resultant suspension of unilamellar nanosheets with a chemical composition of $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ was used for monolayer film fabrication.

B. Monolayer Film fabrication

The ruthenate nanosheets were closely adsorbed on flat substrates via electrostatic self-assembly [13]. First, Si wafer with a native oxide and SiO_2 glass substrates were washed with a mixture of 12 mol dm^{-3} HCl and CH_3OH (1:1 by volume), followed by 18 mol dm^{-3} H_2SO_4 and finally ultrapure water. The substrates were then immersed for 10 min in an aqueous solution of 1 mass% cationic diblock copolymer composed of $\sim 14\%$ polyvinylamine and $\sim 86\%$ polyvinylalcohol to form a positively charged surface, and then reacted with the suspension containing anionic $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets (0.08 g dm^{-3}) for 20 min. After dipping, the film sample was carefully drawn out and washed with ultrapure water to remove physically adsorbed species. Heat-treatments of these films were performed by increasing the temperature from ambient temperature at a rate of 5°C min^{-1} to a preset temperature (200, 300, 400, 500°C) under gas-flow-controlled condition (10% H_2 and 90% N_2 , 250 ml min^{-1}). After keeping the samples at that temperature for 1 hour, they were cooled naturally in a tube furnace.

C. Measurements and analysis

Powder x-ray diffraction (XRD) patterns were collected by means of a Bragg-Brentano-type diffractometer (Rigaku Rint 2000) with Cu $K\alpha$ radiation ($\lambda = 0.15405$ nm). Mass loss up to 500°C under a mixture of 10% H_2 and 90% N_2 was measured by thermogravimetry (TG) (Rigaku Thermo Plus TG 8120). The microscopic structure of the layered ruthenate and the restacked film of nanosheets after the reduction treatment under 10% $\text{H}_2 + 90\%$ N_2 at 200°C was characterized by low-voltage scanning electron microscope (LV-SEM; Omicron NanoTechnology NanoSAM Lab with UHV-Gemini) [14]. All specimens were observed without a conductive coating under a primary electron beam of 700 eV to reveal the true surface morphology. A frequency modulation atomic force microscope (FM-AFM; JEOL JSPM-5400) with a 7-nm-diameter Si-tip cantilever (42 N m^{-1}) was used to obtain a high-resolution image of the morphological features of the nanosheets on the Si substrate. In-plane diffraction data for the as-grown nanosheet film and its heated derivatives were acquired by four-axis diffractometer equipped with a NaI scintillation counter in BL6C of the Photon Factory at the High Energy Accelerator Research Organization, Tsukuba, Japan.

III. RESULTS AND DISCUSSION

First, we considered the reduction of bulk-layered ruthenate, $\text{H}_{0.2}\text{RuO}_{2.1}\cdot 0.7\text{H}_2\text{O}$, consisting of regularly

FIG. 1: XRD patterns for metallized products obtained from (a) a powder of the protonic layered precursor and (b) a restacked film of the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets. Insets show surface-sensitive LV-SEM images.

FIG. 2: A TG curve of layered ruthenate, $\text{H}_{0.2}\text{RuO}_{2.1}\cdot 0.7\text{H}_2\text{O}$, used as a precursor for the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets, under a flow of 90% N_2 and 10% H_2 .

stacked slabs of RuO_6 octahedra, interlayer protons, and water [12]. Heating this material under a flow of 10% H_2 and 90% N_2 at 200°C yielded a powder sample with a metallic luster. The peaks in the powder XRD pattern after the heating were attributable to a single phase of bulk Ru metal, suggesting that the layered ruthenate was reduced (Fig. 1(a)). LV-SEM observation of the Ru metal powder revealed layered morphology in which the individual layers have many defects (inset). Mass loss of the protonated precursor up to 500°C revealed that metallization began at 110°C (Fig. 2). Mass loss of rutile-type RuO_2 nanoparticles occurred at a comparably low temperature [15]. The mass loss of approximately 31% matches well with the 31.5% mass difference between

FIG. 3: In-plane XRD patterns for (a) as-grown monolayer film, and film heated at (b) 200, (c) 300, (d) 400, and (e) 500°C.

$\text{H}_{0.2}\text{RuO}_{2.1}\cdot 0.7\text{H}_2\text{O}$ and Ru metal, indicating complete metallization.

Next, to investigate metallization behavior in the multi-layer state, we obtained a thin film composed of restacked $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets by drying a droplet of the exfoliated nanosheet suspension on the SiO_2 substrate. XRD analysis of the film (not shown) showed a series of strong diffraction peaks typical of lamellar ordering with $d = 1.68 \text{ nm}$ [11, 12]. This value can be explained by a layered structure in which the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets interleaved with TBA ions. After treatment under 10% $\text{H}_2 + 90\% \text{N}_2$ at 200°C, a metallic film exhibiting only one diffraction peak assignable to 002 of Ru metal in a halo pattern derived from the substrate was formed (Fig. 1(b)). This peak indicates that the Ru film has a strong c -axis orientation perpendicular to the substrate, despite the use of the amorphous surface. An LV-SEM image (inset) of a cross-section of the Ru metal physically peeled from the substrate shows that the lamellar morphology of the bulk case is roughly preserved.

The above two cases suggest the transformation of the ruthenate system into layered Ru metals with preferential orientation. In other words, the 2D anisotropy of the RuO_6 slab in the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheet should affect the nucleation and growth of the Ru metal. The defects observed in these morphological changes should account for the difference in Ru atom density between the precursor nanosheet and the produced Ru metal.

To identify the transition in an extremely thin $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheet in a monolayer state, we used a monolayer film in which the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets lay flat to the SiO_2 glass substrate. An in-plane XRD pattern of the as-deposited monolayer film showed a lot of diffraction peaks indexed by a 2D oblique cell with

FIG. 4: AFM images of the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets in a 2D oblique lattice (a) before and (b, c) after metallization. Broken circle in (c) indicates dot-like formation of Ru metal nanocrystals. Inset in (c) is a height profile along the line X–Y.

$a = 0.561(1) \text{ nm}$, $b = 512(1) \text{ nm}$, and $\gamma = 109.4(2)^\circ$ (Fig. 3(a)) [12]. After reduction at 200°C, only two XRD peaks were observed (Fig. 3(b)). As judged from the metallization behavior of the bulk systems mentioned earlier, they can be indexed as 100 and 110 of $hcp\text{-Ru}$. A lack of indexes associated with the $00l$ direction in the in-plane direction can be explained by the formation of Ru metal with a c -axis orientation perpendicular to the substrate. This preferential growth is consistent with the case of the multilayer state. As the reduction temperature was increased, a small peak at 4.7 nm^{-1} appeared (Figs. 3(c)–(e)). This peak is assignable to 101 of Ru metal, which is the strongest reflection in the polycrystalline Ru metal. Heat treatment above 300°C induces a rearrangement of the Ru atoms via thermal diffusion, consequently leading to a collapse of the c -axis orientation.

We used a true noncontact FM-AFM to examine morphological changes before and after the metallization of the monolayer film on a flat Si substrate. The as-deposited $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets appear as lamellar objects with an average thickness of $1.3 \pm 0.1 \text{ nm}$ and a width ranging from sub-micrometer to micrometer size (Fig. 4(a)). Their crystallographic thickness cannot be

defined accurately at present, as the precise crystal structure of the parent layered potassium ruthenate has still not been resolved. However, combined with the d -spacing of 0.456 nm revealed by XRD analysis of the anhydrous layered protonic ruthenate [12], the observed thickness of the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets in the AFM image is strong evidence of a single layer of RuO_6 octahedra, as is the case with the $\text{RuO}_2^{0.2-}$ nanosheets obtained from NaRuO_2 . The same AFM technique revealed that the $\text{RuO}_2^{0.2-}$ nanosheets, being composed of a single layer of edge-shared RuO_6 octahedra ($\sim 0.4\text{--}0.5$ nm thickness), had an average thickness of about 1.3 nm [9]. This apparently larger thickness measured by AFM than the crystallographic thickness can be explained by the presence of adsorbed species, possibly water molecules and charge-compensating protons, on the surface of the anionic nanosheets [16]. A majority of the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets were adsorbed as a monolayer on the substrate, although some gaps and overlaps between the nanosheets were inevitable under the fabrication recipe used. After the metallization, spotty objects were observed (Fig. 4(b)). High-resolution imagery revealed a dot-like formation of Ru metal nanocrystals from the oxide nanosheets (Fig. 4(c)). Interestingly, their average height of ~ 0.6 nm is much smaller than those of the precursor oxide nanosheets and conventional metal nanoparticles. Given the diameter of the tip used in this measurement, the nanocrystals seem to have a lateral size of several tens of nanometers. A coverage analysis based on height histograms of Figs. 4(a) and 4(b) (not shown) shows a decrement in the coverage from approximately 95% to less than 85% as a result of the gathering of the Ru ions to produce the Ru metal nanocrystals. Such shrinkage in both thickness and width likely stems from a large difference between the precursor nanosheets and the nanocrystals in the density of the Ru atoms in the in-plane direction.

Unlike the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets, the $\text{RuO}_2^{0.2-}$ nanosheets [9] gave rise to a topotactic metallization, *i.e.* transformation from “nanosheet” to “nanosheet”, despite the same reduction conditions. The resultant Ru metal nanosheets consist of Ru atoms in a 2D hexagonal package [10]. Shrinkage of their sheet size as estimated from AFM analyses agrees fairly well with a decrement of the in-plane lattice from 0.29 nm to 0.27 nm, about 7%. This is due to a similar atomic arrangement of the Ru atoms in these materials with the 2D hexagonal periodic structure. In practice, the Ru metal nanosheets produced early in the heating process ($< 200^\circ\text{C}$) have a slightly larger a -axis than that of bulk Ru metal. This fact may be evidence that the oxide nanosheets work as an embryo. Further heating at $> 300^\circ\text{C}$ caused a structural

relaxation: the a -axis of the Ru metal nanosheets became nearly the same as that of bulk Ru metal. Also, the growth of polycrystalline Ru metals was promoted until the polycrystalline component became dominant. On the other hand, the peak position of 100 and 110 of the Ru metal nanocrystals obtained here remained unchanged up to 500°C . The polycrystalline phase is still a minor component in the monolayer film heated at 500°C . Once the Ru metal nanocrystals are generated owing to the thermal diffusion of the constituent Ru atoms in the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheet, their isolated environment needs more intense thermal diffusion to grow as well. Thus, the dot-like Ru metal nanocrystals formed from the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheet should arise from the atomic-scale mismatch that requires a local gathering of the Ru atoms for nucleation. Nevertheless, the Ru metal nanocrystals have a similar thickness to that of the Ru metal nanosheets obtained via the topotactic conversion. A single layer of Ru crystals with various lateral sizes would be produced. Our findings demonstrate the great potential of atomic-scale reactants composed of exfoliated nanosheets as a solution-based nanotechnology for controlling the 2D anisotropy of metal nanocrystals.

IV. CONCLUSIONS

Our results show that reduction of the $\text{Ru}_{0.95}\text{O}_2^{0.2-}$ nanosheets led to the formation of thin metal nanocrystals presumably because of the large mismatch in the lateral arrangement of the Ru atoms. As the initial in-plane structure of the precursor nanosheets governs the resulting metal morphology, this would be of significant interest not only for fundamental metal sciences, but also for applications for the synthesis of conductive or catalytic materials. The unique metallization dependent on nanostructured reactants may pave the way for creating a diversity of anisotropic metal nanomaterials, including nanosheets and nanodots.

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