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Soft-Chemical Exfoliation of $Na_{0.9}Mo_2O_4$: Preparation and Electrical Conductivity Characterization of a Molybdenum Oxide Nanosheet

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S *Supporting Information*

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Recent discovery of graphene has generated intense interest because of its atomic scale sheetlike morphology with conductive property.[1] Regardless of its attractive feature, graphene lacks in thermal stability in air. On the other hand, oxide nanosheets, whose morphology also consist of less than a few nm thickness and μm-order lateral size, are thermally robust in air and possess a wide range of useful properties including high-*k* dielectric, photocatalytic, photochromic, photoluminescent and ferromagnetic properties, originating from their diverse crystal structures and chemical compositions.[2−6] Thus, oxide nanosheets are quite attractive members of nanomaterials in both practical and scientific aspects. Densely packed monolayer films of such oxide nanosheets can easily be fabricated by methods such as the Langmuir−Blodgett (LB) technique and layer-by-layer deposition utilizing polyions such as polyethylenimine (PEI) as electrostatic glue, and nanosheet-film-based devices can be developed by various combination of those films.[7] As a component of such nanoarchitectonics, an oxide nanosheet with metallic conductivity would be quite attractive and important. However, to the best of our knowledge, such conductivity has been observed only in RuO_2 nanosheets.[8] Thus, it is interesting and important to investigate a new oxide nanosheet with electrical conductivity.

We here report the first Mo-based oxide nanosheet MoO_2 prepared by soft-chemical exfoliation of layered molybdenum oxide $Na_{0.9}Mo_2O_4$. We chose $Na_{0.9}Mo_2O_4$ as the precursor of a possible conductive nanosheet because Mo in this phase is 3+/4+ mixed valent and extending Mo−Mo bonding interaction exists,[9] and properties of a layered oxide precursor are, in general, retained in the exfoliated nanosheets.

MoO_2 nanosheets were prepared in three-step reactions. First, the bulk precursor $Na_{0.9}Mo_2O_4$ was prepared by solid state reaction of Na_2MoO_4, MoO_2, and Mo at 750 °C in a Au tube that was enclosed in an evacuated fused silica tube. Second, the product of this reaction was washed in water and then reacted with 1 M HCl solution for 1 day at 60 °C. This process was repeated one more time in order to ensure the complete protonation. Finally, the protonated bulk precursor was reacted with a tetrabutylammonium hydroxide (TBAOH) aqueous solution for 1 week. The concentration of TBAOH was adjusted so that TBA^+ in the solution was equal to H^+ in the protonated bulk precursor assuming the chemical composition as HMo_2O_4. This concentration of TBAOH was used because $H_xMo_2O_4$ is amphoteric, and its dissolution was observed when the reacting TBAOH concentration was three-hold in excess or higher.

The pristine bulk precursor product $Na_{0.9}Mo_2O_4$ consists of aggregates of 10−50 μm-order platelet crystals. The platelet morphology reflects the structure of $Na_{0.9}Mo_2O_4$, which consists of layers of edge-shared MoO_6 octahedra parallel to $b-c$ plane interspersed with Na^+.[9] Powder X-ray diffraction (XRD) pattern of $Na_{0.9}Mo_2O_4$ is shown in Figure 1a. The majority of the reflections can be indexed based on the previously reported monoclinic structure of $Na_xMo_2O_4$,[9] except for low intensity peaks originating from a trace amount of $Na_2MoO_4 \cdot 2H_2O$ (PDF 34−0076). The color of this product is dark gray. The refined lattice parameters of $Na_{0.9}Mo_2O_4$ are $a = 1.2454(1)$, $b = 0.28877(6)$, $c = 0.49347(5)$ nm, and $\beta = 103.98(1)°$, and they agreed well with those reported previously.[9,10]

The color of the bulk precursor turned into black after the protonation. XRD pattern of the protonated bulk precursor is shown in Figure 1b. All the reflections can be indexed to a monoclinic structure. No reflection due to $Na_2MoO_4 \cdot 2H_2O$ was observed, and we believe that it was dissolved during the acid treatment. The refined lattice parameters are $a = 1.2936(8)$, $b = 0.2907(3)$, $c = 0.4898(4)$ nm, and $\beta = 96.96(7)°$. The lattice parameters b and c are close to the in-layer lattice parameters of $Na_{0.9}Mo_2O_4$. This suggests that the protonation reaction is topotactic and the protonated bulk precursor retains the layered structural feature of $Na_{0.9}Mo_2O_4$. On the other hand, lattice parameters a and β of this protonated bulk precursor are larger

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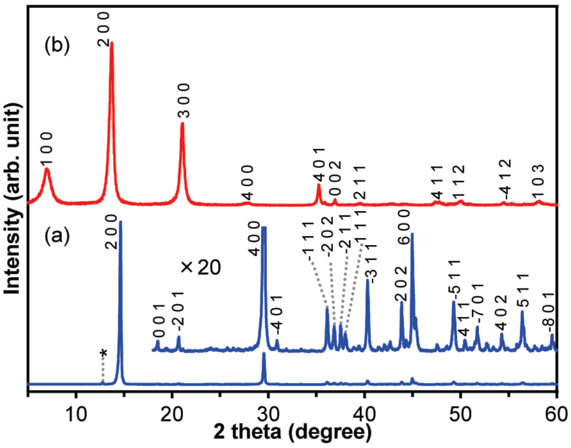

Figure 1. Powder XRD patterns of (a) $Na_{0.9}Mo_2O_4$ and (b) its protonated form. The diffraction peak position of $Na_2MoO_4 \cdot 2H_2O$ is indicated with *.

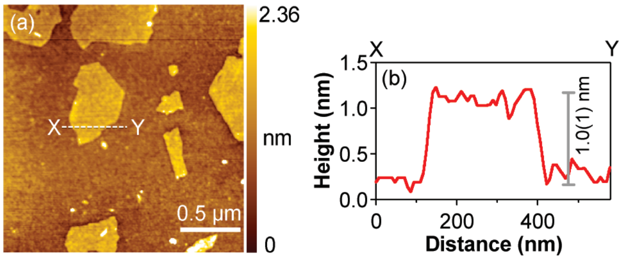

Figure 2. (a) AFM image and (b) cross-sectional profile of MoO_2 nanosheets deposited on a Si substrate.

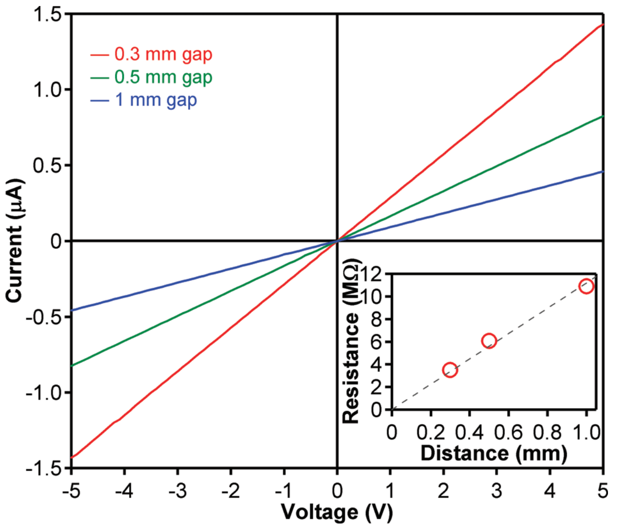

Figure 3. $I-V$ characteristic of 10-layer MoO_2 nanosheet film sample measured with the electrode distances of 0.3, 0.5, and 1 mm. The inset shows the resistance of 10-layer MoO_2 nanosheet film sample as a function of the electrode distances.

and smaller than those in the pristine precursor, respectively. The expansion of the lattice parameter a, which is related to the interlayer spacing, after protonation is attributed to the interlayer hydration. In addition, the relative shift of adjacent layers might also be causing the change in β. Furthermore, the protonated bulk precursor exhibits unusual intensity distribution where the intensity of 1 0 0 reflection is much lower than that of 2 0 0 reflection. This must be originated from extraordinary structural feature of the protonated bulk precursor. For example, protonation might be associated with hydration at every other interlayer just like the staging observed in the alkali-metal intercalated graphite.[11]

In case of $Na_xMo_2O_4$, interlayer Na^+ contents vary in the range of $0.55 < x < 1.9$.[10] Similarly, the interlayer H^+ content could vary depending on protonation conditions. However, we believe that the H^+ content in the protonated precursor in this study is close to that of Na^+ in the pristine precursor, assuming that there was no significant tendency to oxidize or reduce Mo during the protonation reaction. In addition, chemical analysis results indicate that the ion-exchange reaction is nearly complete and the remnant Na^+ in the protonated bulk precursor is below 0.2 wt %.

The reaction of the protonated bulk precursor with a TBAOH solution yielded a colloidal suspension of dark-green MoO_2 nanosheets. The exfoliation was complete without noticeable sediments. The morphology of MoO_2 nanosheets was observed by AFM (Figure 2). Their average height was 1.0(1) nm, and their lateral sizes range from several hundred nanometers to a few micrometers. This height of the nanosheet is larger than the thickness (0.55 nm) of a single MoO_2 layer in its precursor $Na_{0.9}Mo_2O_4$, estimated from its crystal structure, and the difference is attributed to the species, such as H_2O and TBA^+, existing between the nanosheets and the substrate. Thus, the uniform-thickness of the MoO_2 nanosheets prepared in this study is an indication of their homogeneously unilamellar nature.[4,5,12]

The electrical conductivity of the MoO_2 nanosheet has been examined on densely packed 10-layer films of the MoO_2 nanosheet fabricated by repeated layer-by-layer deposition on a Pyrex substrate using PEI as electrostatic glue. The coverage of the film was confirmed to be over 90% by AFM. Resistivity of this sample was measured by a two-probe method. The current flow between electrodes on the nanosheet film was measured under the applied voltage ranging from −5 to 5 V, and exhibited ohmic behavior (Figure 3). The inverses of the slopes of these $I-V$ responses are the resistance between those electrodes. The resistance as a function of the electrode distances is plotted in the inset of Figure 3. The sheet resistance of the MoO_2 nanosheet film sample was estimated to be 35 MΩ sq^{-1} (see the Supporting Information).[13] This is much higher than that of similar multilayer films of RuO_2 nanosheet (less than 1 kΩ sq^{-1}).[8] However, unlike most of the other d^0-transition metal based oxide nanosheets, such as $Ti_{0.91}O_2$ and $Ca_2Nb_3O_{10}$ which are insulators and whose resistivity is too high to be measured or not ohmic,[14] the multilayer films of MoO_2 nanosheets exhibited ohmic $I-V$ response. In this sense, the MoO_2 nanosheet is rather conductive. The existence of d-electrons due to the low valent Mo^{3+}/Mo^{4+} in the nanosheet must be an important factor for this conductivity. In addition, McCarley et al. reported that extended Mo−Mo bonds exist in the Mo−O layers of the precursor $Na_xMo_2O_4$.[9] Because the exfoliation into the MoO_2 nanosheets is topotactic (see the Supporting Information for the results from in-plane XRD), such Mo−Mo bonding interaction may exist in the MoO_2 nanosheets, providing a conduction path in the nanosheet structure.

In conclusion, we have synthesized the first Mo-based oxide nanosheet MoO_2, and found that it was electrically conductive. Even though the resistivity of this nanosheet is rather high, further work is underway in order to improve the conductive property of this MoO_2 nanosheet through surface modification to optimize charge carrier concentration and mobility.

ASSOCIATED CONTENT

Supporting Information. Details of experimental procedure, in-plane X-ray diffraction and resistivity characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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