Supporting Information

Soft-chemical exfoliation of $Na_{0.9}Mo_2O_4$: Preparation and electrical conductivity characterization of a molybdenum oxide nanosheet

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Experimental procedure

Synthesis of MoO$_2$ nanosheet. MoO$_2$ nanosheets were synthesized 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 (Kojundo Chemical Lab., 99.9%) and Mo (Wako, 99.9%). Na_2MoO_4 was obtained by thermal dehydration of $Na_2MoO_4 \cdot 2H_2O$ (Wako, 99.0%) at 180 ^{o}C in air. The starting materials in the mole ratio of 2.55:1:0.85 Na_2MoO_4:MoO_2:Mo were ground for 30 min in a mortar, which was pre-heated at 180 ^{o}C. 1 g of this mixture was sealed in a Au tube (4.7 mm ID $\times$ 5 mm OD $\times$ 50 mm length), which was further enclosed in an evacuated ($< 10^{-2}$ Pa) and sealed fused silica tube. This setup was heated at 750 ^{o}C for 36 h. The product of this reaction was washed in Milli-Q water (> 18 MΩ cm) in order to remove water-soluble un-reacted starting component Na_2MoO_4 as much as possible.

Second, the product was reacted with 1 M HCl solution for 1 day at 60 ^{o}C twice in order to exchange interlayer Na^+ with H^+. The acid treated product was washed in the Milli-Q water and dried in air at room temperature. After this acid-exchange procedure, the minor impurity phases (Na_2MoO_4, $Na_2MoO_4 \cdot 2H_2O$) were removed. These processes to protonate

the interlayer cation were necessary in order to activate the bulk precursors for the following exfoliation process based on an acid-base reaction.

Finally, 0.4 g of the protonated sample was reacted with 100 mL of 1.46×10^{-3} M tetrabutylammonium hydroxide (TBAOH) aqueous solution. 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. The mixture was vigorously shaken for 1 week in order to promote the exfoliation of the protonated layered bulk precursor into MoO_2 nanosheets. The exfoliation was complete without noticeable sediments.

Film Fabrication for characterizations. Si, Pyrex and fused silica substrates were cleaned by dipping in HCl/CH_3OH (1:1 in volume) solution and then in concentrated H_2SO_4 for 30 min each. These substrates were immersed in an aqueous solution of polyethylenimine (pH 9.2, 2.5 g dm^{-3}) for 20 min in order to turn the surface positively charged, washed in Milli-Q water, immersed in a colloidal suspension of negatively charged MoO_2 nanosheets (pH 5.2, 0.129 g dm^{-3}), and then washed in the Milli-Q water. The immersion time in the nanosheet suspension was 5 min for AFM observation and 40 min for in-plane X-ray diffraction (XRD), UV-Vis absorption and resistivity measurement samples. The deposition process was repeated to fabricate the multilayer-film samples.

Characterizations. Powder XRD profiles of the bulk precursors were acquired using Cu Kα radiation on a Rigaku RINT2000 diffractometer. The diffraction peaks were indexed, and the lattice parameters were refined using APPLEMAN software.[1] The in-plane XRD pattern of a monolayer film of MoO_2 nanosheets was obtained using the synchrotron radiation ($\lambda = 0.11979(3)$ nm) of the Photon Factory BL-6C at High Energy Accelerator Research Organization (KEK). The lattice parameters were refined using CellRef software. The morphology analysis of the nanosheets on a Si substrate was performed by AFM using a Seiko Instruments SPA-400 AFM system with a Si tip cantilever (20 N m^{-1}) in the DFM mode. UV-Vis absorption spectra of the multilayer-film samples on a fused silica substrate were measured on a Hitachi U-4100 spectrophotometer in a transmission mode. Na and Mo contents in the protonated bulk precursor were determined by ICP-AES (inductively coupled plasma atomic emission spectroscopy) on a Seiko Instruments

SPS1700HVR spectrophotometer. Approximately 50 mg of the sample was dissolved in HNO_3 for this analysis.

In-plane X-ray diffraction

Figure S1 shows the in-plane XRD profile of the MoO_2 nanosheets deposited on a Si substrate. All the observed peaks can be indexed as *kl* reflections of a 2D rectangular cell, and the refined lattice parameters are *b* = 0.2902(4) and *c* = 0.5018(5) nm. These parameters correspond well with the in-layer lattice parameters of its bulk precursors suggesting that the exfoliated MoO_2 nanosheet topotactically retains the structural feature of its bulk precursor.
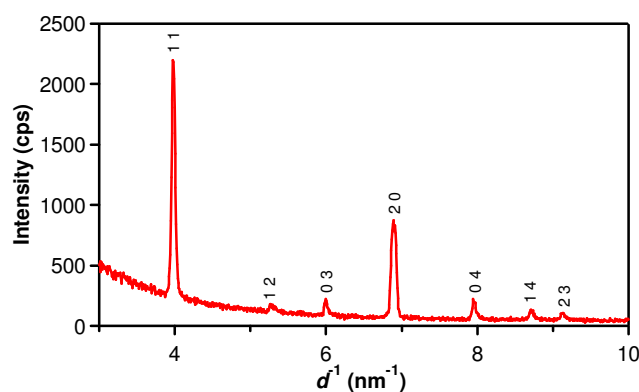

Figure S1. In-plane XRD patterns of MoO_2 nanosheets.

Resistivity characterization

The sheet resistance of 10-layer films of the MoO_2 nanosheets on a Pyrex substrate was measured by 2-probe method. As mentioned above, the multilayer-film sample of MoO_2 nanosheet was fabricated by repeated layer-by-layer deposition. In order to make sure that well packed nanosheet films were prepared at each deposition cycle, UV-Vis absorption spectra of the multilayer-film samples on a fused silica substrate were measured after each deposition cycle as shown in Figure S2. The linear increase in the absorption was observed as the number of depositions (layers) increases. This indicates the consistent coverage of the substrate by the nanosheet film at each deposition cycle.
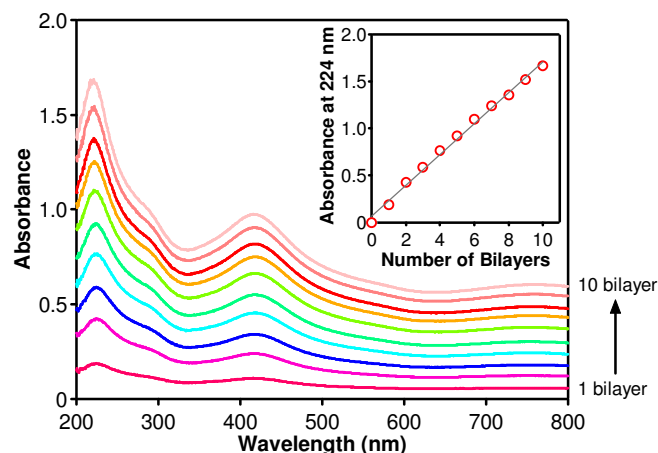
Figure S2. UV-Vis absorption spectra of MoO_2 multilayer films deposited on a fused silica substrate. The inset shows absorbance at 224 nm as a function of the number of bilayers.

3 mm × 3 mm Au electrodes with their intervals of 0.3, 0.5 and 1 mm were deposited on the 10-layer film sample by spattering as shown in Figure S3.
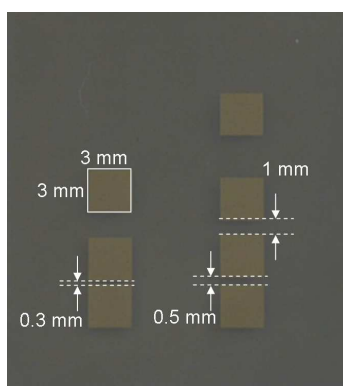

Figure S3. Photograph of 10-layer MoO_2 nanosheet film sample with Au electrodes.

Sheet resistance was calculated using the following equation:

$$R = \rho L/Wt = R_s L/W$$

where, R is resistance, ρ is resistivity, L is distance between electrodes, W is electrode (sample) width, t is sample thickness and R_s is sheet resistance.

REFERENCES

(1)   Appleman, D. E.; Evans, H. T. J., Indexing and least-squares refinement of powder diffraction data (Job 9214); U.S. Geological Survey Computer Contribution No. 20, PB National Technical Information: Springfield, VA: **1973**; p 60.