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Direct Synthesis of Molybdenum Carbide Nanosheets via A Pseudo-Topotactic Solid-State Reaction of Exfoliated Molybdate Nanosheets

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1 Introduction

In the last decade, primitive structural conversion of exfoliated nanosheets has demonstrated significant potential in the design of 2D materials; for instance, the structural conversion of chalcogenide nanosheets such as MoS_2 produces several polymorphs with different properties. In contrast to these structural conversions, reduction of graphite oxide nanosheets into graphene without disruption of the sheet-structure can be depicted as a simplification of the composition from a C-O binary system to a C mono-component system. Thus, structural conversions using the exfoliated nanosheets are known to be mainly attained in the same composition system or a simpler composition system. Should the exfoliated nanosheets topotactically react with foreign species in a solid-state reaction, various derivative nanosheets would be created depending on the ingredient used.

In this study, we propose a direct synthetic route for Mo_2C nanosheets based on a pseudo-topotactic reaction of electrostatic self-assembled monolayer pairs consisting of MoO_2 nanosheets and organic polymers [1].

2 Experiment

Layered molybdates, $Na_{0.9}Mo_2O_4$, were soft-chemically delaminated into a mass of dispersed elemental host layers, i.e. MoO_2 nanosheet suspension [2]. Immersing Si substrate pre-coated with cationic polymers used as a binder into the obtained suspension yields sub-monolayer films in which a pair of the anionic nanosheets and polymer monolayers lay flat to the substrate. Multilayer films of the nanosheets/polymers pairs were then fabricated by repeating the aforementioned process up to ten times. And heat-treatments of these films were performed by increasing the temperature from that of the surrounding environment at a rate of 10˚C min^{-1} to set temperatures of 200, 300, 400, 500, 600 and 700˚C under H_2 gas-flow-controlled conditions. After heating at the selected temperature for 1 hour, the samples were left to cool in a quartz tube furnace.

3 Results and Discussion

Topographical and structural changes occurring within MoO_2 nanosheets deposited on the substrate before and after heat-treatment under the H_2 gas atmosphere were examined by AFM and in-plane XRD analyses. As shown in Fig. 1A, the as-deposited nanosheets are visualized as lamellar objects below 2 nm in thickness and sub-micrometer in lateral size in this study. Most of the MoO_2 nanosheets were adsorbed onto the substrate as monolayers despite the inevitability of some overlap and gaps between the nanosheets under the present fabrication process. The in-plane XRD pattern of MoO_2 nanosheets (Fig. 1a) is indexable to a 2D rectangular unit cell of b = 0.290(1) and c = 0.502(5) nm [2]. The XRD patterns and morphology remained nearly unchanged until the MoO_2 nanosheets were heated to 300˚C, indicating the structural robustness of the MoO_2 nanosheets. However, heating at 400˚C triggered peak-boarding and a change in the intensity ratios of reflections *11* and *20*, and at 500˚C the 2D rectangular unit cell seemed to transform into a 2D hexagonal one (d = 0.2887(2) nm) due to the loss of reflections *12* and *03*. This symmetry improvement may originate from the reduction of the MoO_2 nanosheets induced by heating under the reduction atmosphere. After heating above 600˚C, these XRD peaks distinctively shift to smaller d^{-1} values, yielding a larger 2D hexagonal unit cell of d = 0.3000(3) nm. This shift cannot simply be attributed to deoxygenation as is often the case with several exfoliated nanosheets. Considering the d-value of ~ 0.3 nm in the heated film, the most likely phase is β-Mo_2C (JCPDS No. 075-6678). Interestingly, lamellar objects are still observed in the sample heated to 600˚C (see Fig. 1B). The average thickness of the generated Mo_2C sheets (~ 2 nm), acquired from the AFM image, seems to be similar to those of conventional oxide-type nanosheets including its precursor nanosheet, which indicates the formation of the Mo_2C monolayer [1].

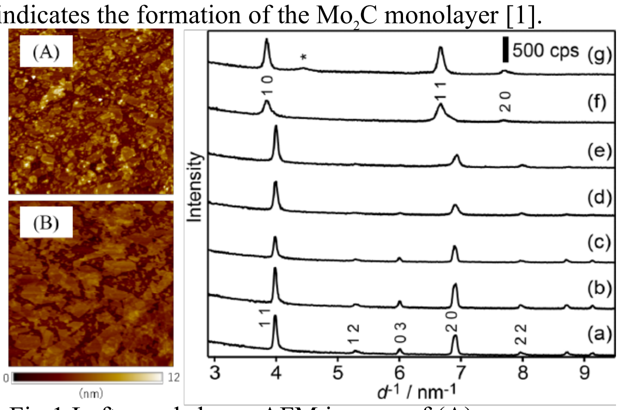

Fig.1 Left panel shows AFM images of (A) as-grown film of the MoO_2 nanosheet, and (B) its annealed samples at 600˚C for 1h under H_2 flow. Right panel shows in-plane XRD patterns for (a) as-grown film, and its heated films at (b) 200, (c) 300, (d) 400, (e) 500, (f) 600, and (g) 700˚C for 1h under H_2 flow. The asterisk refers to *110* of bcc-Mo.

References
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