Synthesis of Polycrystalline Mo/MoO$_x$ Nanoflakes and Their Transformation to MoO$_3$ and MoS$_2$ Nanoparticles

Ji Chan Park and Hyunjoon Song*

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

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Mo-based materials continue to be of great research interest because of their intrinsic mechanical and catalytic properties. For instance, pristine molybdenum oxide and supported composites have been employed as a major component of hydrogen sensing, electrochromic coloration, and selective oxidation of hydrocarbons.[1] Further, molybdenum disulfide is used in the most effective industrial catalysts for hydrodesulfurization (HDS) reaction and in an excellent high-temperature lubricant.[2] For these applications, molybdenum disulfide nanoparticles have been prepared by several routes, such as sono(electro)chemical,[3] solvothermal,[4] and chemical vapor deposition methods.[5] However, the products were commonly obtained as irregularly agglomerated powders in which the domains identified by transmission electron microscopy (TEM) were at least 10−30 nm in size. So far, to the best of our knowledge, there have been no general synthetic schemes reported describing the synthesis of uniform molybdenum oxide and sulfide nanoparticles with sub-10 nm diameters. It is anticipated that colloidal forms of molybdenum-based materials with very small diameters would exhibit superior catalytic performance due to their large surface area and high density of coordinatively unsaturated surface atoms. Herein, we report the preparation and size control of polycrystalline Mo/MoO$_x$ nanoflakes via the thermal decomposition of molybdenum carbonyl in the presence of stabilizing surfactants, and the subsequent transformation to single-crystalline MoO$_3$ and MoS$_2$ nanoparticles within 2 nm diameters by in situ addition of oxygen and sulfur into the colloidal solution.

Briefly, a slurry of Mo(CO)$_6$ powder in phenyl ether in the presence of oleic acid was slowly heated up to 310 °C and allowed to stir at the same temperature for 35 min to ensure complete decomposition of the metal precursor. The reaction temperature should be increased at a low ramping rate because of the severe sublimation of molybdenum carbonyl at high temperature >150 °C. During the reaction, the initial white slurry was gradually dissolved in the solvent with the concomitant color change to bright brown and the solution finally turned to black after aging. The resulting particles were separated from the reaction mixture by centrifugation, and dispersed in hexane. The low-resolution TEM image (see Figure S1a in the Supporting Information) shows that the particles form a two-dimensional array. They are uniform in size, but irregular in shape. The TEM image with a higher magnification (Figure 1a) represents a flake-type morphology of the particles, and the average particle size is estimated as 9.6 ± 1.0 nm by counting more than 200 nanoparticles. Selected area electron diffraction (SAED) ring patterns (Figure 1a, inset) originated from Mo(110) and (200) planes. High-resolution TEM (HRTEM) image (Figure 1b) exhibits a polycrystalline nanoflake structure in which single-crystalline domains are observed. The average distance between adjacent lattice fringes is 0.22 nm, consistent with the value of Mo(110) plane. X-ray diffraction (XRD) data (see Figure S2a in the Supporting Information) also represent a broad signal at 40.6° corresponding to cubic Mo (JCPDS card 42-1120). But X-ray photoelectron spectroscopy (XPS; see Figure S2b in the Supporting Information) reveals collapsed peaks in the range of Mo 3d$_{3/2}$ and 3d$_{5/2}$ orbital signals, which can be deconvoluted into three sets of the peaks from Mo, MoO$_2$, and MoO$_3$, respectively.[6] This indicates that the final particles were partially oxidized Mo/MoO$_x$ nanoflakes due to rapid particle oxidation in air during the separation and sampling processes for analysis; the formation of pure molybdenum particles might be obtained during the reaction, however.[7]

The different-sized nanoflakes were successfully synthesized by increasing the molar ratio of oleic acid/Mo from 1.0 to 1.4 and 1.6. Figure 1c shows smaller Mo/MoO$_x$ nanoflakes with an average diameter of 6.0 ± 0.5 nm when 1.4 equiv. of oleic acid was used. The particles were readily aligned as a two-dimensional array (see Figure S1b in the Supporting Information). The polycrystalline lattice fringe image of a particle can be observed in the inset of Figure 1c. The addition of 1.6 equiv. of oleic acid in the reaction mixture generated very small particulates (Figure 1d), and the shapes were difficult to define because of their small size. The average diameter is estimated to be 2.5 ± 0.2 nm. XRD peaks of the different-sized particles (see Figure S2a in the Supporting Information) are similar to those of the large Mo/MoO$_x$ flakes.

Polycrystalline Mo/MoO$_x$ nanoflakes are basically created through a heterogeneous reaction. Instead of using Mo(CO)$_6$ powder, Mo(CO)$_3$(NCMe)$_3$ was chosen as a homogeneous molybdenum precursor because of its good solubility in

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* Corresponding author. E-mail: hsong@kaist.ac.kr.

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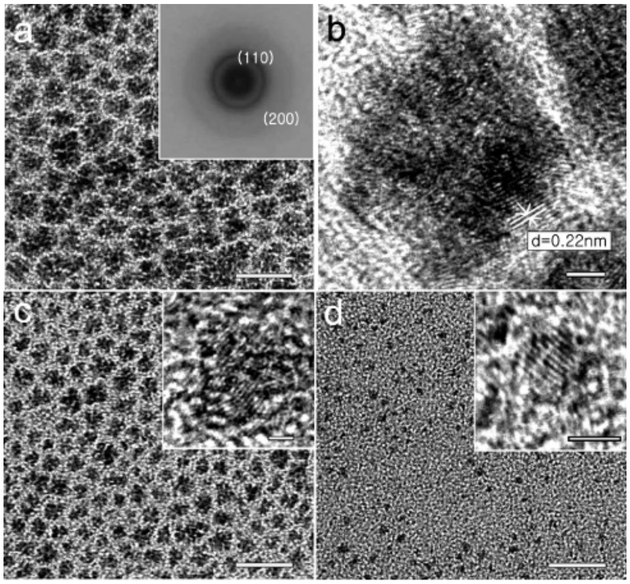


Figure 1. (a) TEM image and SAED pattern (inset), and (b) HRTEM image of 9.6 nm Mo/MoO$_x$ nanoflakes. (c) TEM and HRTEM (inset) images of 6.0 nm Mo/MoO$_x$ nanoflakes. (d) TEM and HRTEM (inset) images of 2.5 nm Mo/MoO$_x$ naoparticles. The white bars represent 20 nm (a, c, d) and 2 nm (b, insets of c and d).

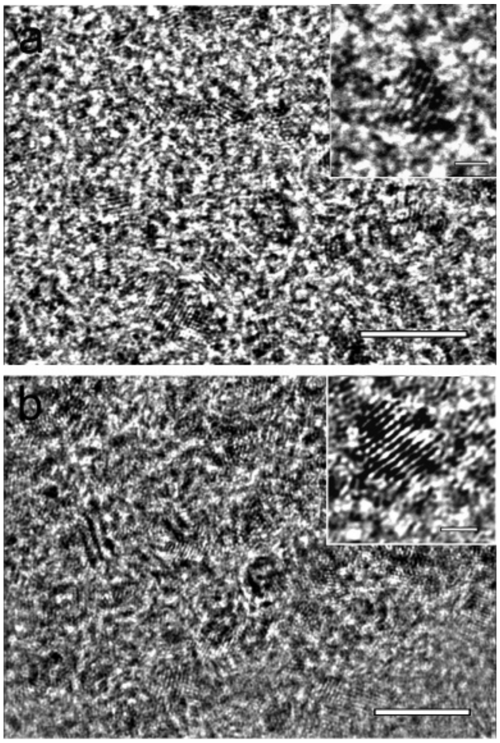
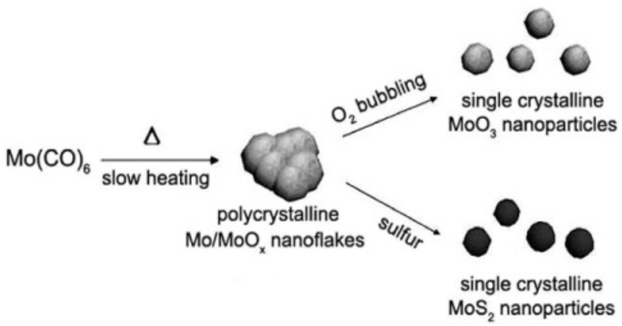


Figure 2. HRTEM images of (a) MoO$_3$ and (b) MoS$_2$ nanoparticles. The white bars represent 5 nm (a, b) and 1 nm (insets).

Scheme 1. Synthesis of Single-Crystalline MoO$_3$ and MoS$_2$ Nanoparticles from the Polycrystalline Mo/MoO$_x$ Nanoflakes



phenyl ether. This tris-acetonitrile derivative was expected to promote homogeneous decomposition of the precursor via the formation of Mo-oleic acid intermediates at relatively low temperature,[8] but the final product contained irregular nanoparticles with wide size distributions around 5 nm (see Figure S3 in the Supporting Information). It is suggested that the Mo(CO)$_3$(NCMe)$_3$ precursor formed a number of different intermediates with oleic acid and that the decomposition rates were rapid enough to make high seed concentration, resulting in small and irregular particulates. In contrast, the slow decomposition of Mo(CO)$_6$ powders in a slurry led to the steady and continuous supply of unstable Mo sources. The initial seed concentration was also limited because of the low decomposition rate under a heterogeneous environment. Consequently, the particles were grown gradually to afford uniform Mo/MoO$_x$ colloids.

The Mo/MoO$_x$ nanoflakes are very stable under an inert atmosphere. They retain their flake-type structure even after sonication for 30 min, indicating that the structure is not an aggregate of smaller nanoparticles. However, when the nanoflakes were stored in air for several days, the colloids fragmented into particles less than 5 nm in diameter (see Figure S4 in the Supporting Information), comparable to the single-crystalline domain size of the original nanoflake structure. This fragmentation reveals that air oxidation of the polycrystalline nanoflakes readily occurs in the grain boundaries and defects because of the high reactivity of these domains.[9] This fragility was exploited for the synthesis of single-crystalline MoO$_3$ and MoS$_2$ nanoparticles (Scheme 1).

To afford MoO$_3$ nanoparticles, oxygen was bubbled into the hot Mo/MoO$_x$ colloidal solution for 30 min at 310 °C. The resulting particles were too small to be viewed by low-resolution TEM, and could be identified only by lattice fringes in the HRTEM image (Figure 2a). The inset of Figure 2a shows a single-crystalline molybdenum oxide particle with the distance between adjacent lattice fringes of 0.31 nm, which matches that distance of the MoO$_3$(021) plane. The average particle size is estimated to be 1.3 ± 0.2 nm. XPS spectrum in Figure 3a exhibits two bands of the binding energies at 232.8 (Mo 3d$_{5/2}$) and 235.9 eV (Mo 3d$_{3/2}$), assignable to the characteristic signals of the Mo(VI) phase.[10] The XRD pattern in Figure 3b has two broad peaks, also corresponding to the spectrum of orthorhombic MoO$_3$ (JCPDS card 76-1003). Several researchers have reported the spontaneous spread of MoO$_3$ on various oxide surfaces and their catalytic activity for oxidation reaction.[11] But most of the catalysts were composed of irregular particles and

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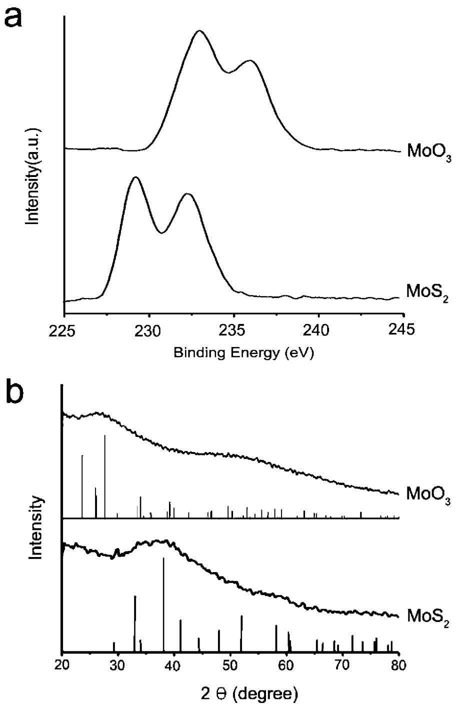

Figure 3. (a) XPS and (b) XRD spectra of MoO_3 and MoS_2 nanoparticles.

aggregates greater than 100 nm in size. Song et al. have successfully generated small MoO_3 particles on Au substrates with the branch width of 2−6 nm by chemical vapor deposition, but the particles were transformed to two-dimensional islands.[12] In comparison, our MoO_3 particles are tiny but uniform and stable in solution, having many advantages for use in catalysis.

MoS_2 nanoparticles were prepared by the addition of 2.5 equiv. of elemental sulfur into the hot Mo/MoO_x colloidal solution at the same temperature. The particles are spherical with the average size of 1.9 ± 0.2 nm, and HRTEM image shows the lattice fringes of a single-crystalline particle (Figure 2b). The distance between neighboring fringes is 0.24 nm, corresponding to the MoS_2(104) plane distance. Energy dispersive X-ray (EDX) analysis of the sample gives an atomic ratio of 1.97 for the ratio of sulfur/molybdenum, essentially identical to the defect-free MoS_2 phase. Two bands appear at 229.3 (Mo $3d_{5/2}$) and 232.4 eV (Mo $3d_{3/2}$) in the XPS spectrum, also consistent with the bands for MoS_2 materials (Figure 3a). The XRD data in Figure 3b exhibit a broad peak at 38.4°, which is very close to the highest peak at 38.2° of the rhombohedral MoS_2 (JCPDS card 74-0932). All analyses reveal the formation of single-crystalline MoS_2 nanoparticles. Our synthetic protocol is rather similar to the conventional solid-state reaction of stoichiometrically mixed molybdenum and sulfur powders in terms of the compositions.[13] Duphil et al. have synthesized MoS_2 nanoparticles in an organic solvent by the reaction of $Mo(CO)_6$ and sulfur, but the final product was obtained as big amorphous aggregates.[7] It is suggested that the presence of oleic acid and relatively high-temperature condition could provide tiny but regular single-crystalline MoS_2 nanoparticles in our experiment. The particles were effectively stabilized by the coordination of oleic acid on the surface, which prevents the severe aggregation.

In conclusion, in an effort to explore how to conveniently prepare new nanoscale materials for catalysis and other possible industrial uses, we have synthesized polycrystalline Mo/MoO_x nanoflakes through the thermal decomposition of molybdenum carbonyl in the presence of stabilizing surfactants. The particle sizes were controlled by using different molar ratio of surfactants/Mo. The Mo/MoO_x nanoflakes were readily transformed into single-crystalline MoO_3 and MoS_2 nanoparticles with very small sizes <2 nm by the subsequent addition of oxygen and sulfur, respectively. These tiny molybdenum-based nanoparticles are expected to be excellent heterogeneous catalysts for various reactions such as epoxidation and hydrodesulfurization because of their high surface-to-volume ratio and active edge atoms. The synthesis of molybdenum-based bifunctional catalysts and their reaction studies are in progress.

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Supporting Information Available: Details of experimental procedures, TEM images, XRD, and XPS spectra of Mo/MoO_x nanostructures. This material is available free of charge via the Internet at http://pubs.acs.org.

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