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Rapid Communication

Single-Crystalline Mesoporous Molybdenum Nitride Nanowires with Improved Electrochemical Properties

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We report single-crystalline mesoporous molybdenum nitride nanowires (meso-Mo_3N_2-NWs) prepared by topotactic reaction using single-crystalline molybdenum oxide nanowires. The single-crystalline nature of meso-Mo_3N_2-NWs was clearly observed by field-emission transmission electron microscopy. The meso-Mo_3N_2-NWs exhibited mesoporous structure with $\sim$45 m^2/g in specific surface area and $\sim$4.6 nm in average pore size confirmed by a nitrogen sorption measurement. Due to high specific surface area and mesoporous structure, meso-Mo_3N_2-NWs showed much higher specific capacitance and excellent charging–discharging performance as compared with Mo_3N_2 prepared using conventional nitridation process.

I. Introduction

Transition -metal oxides, carbides, sulfides, and nitrides are extensively technological interest with a variety of applications due to their particular electronic, magnetic, and catalytic properties.[1–4] Among the transition-metal compounds, transition-metal nitrides are regarded as promising materials for optical storage devices, high-speed integrated circuits, microscopic metal links, reforming catalyst, energy storage devices, and electrical applications.[5–7] In particular, the molybdenum nitrides constitute an important class of interstitial compounds with exceptional chemical stability, enhanced physical properties, and good electrical conductivity.[8–11]

Recently, the molybdenum nitrides can be used in electrodes for thin film capacitor due to electrical properties.[12,13] The thin film capacitors are new charge storage devices with a higher energy density than conventional dielectric capacitors and with a higher power density than batteries.[14] On the basis of electrode materials used and the charge storage mechanisms in a thin film capacitor, the electrochemical capacitors are classified as electrical double-layer (EDL) capacitors which employ carbon or other similar materials as blocking electrodes.[15] Typical electrodes except for carbon materials in a thin film capacitor have been fabricated using transition-metal complex materials.[16] However, the transition-metal complex materials are lower capacitance per weight in comparison with carbon materials due to very dense physical structure. Thus, there have been several ways to improve the capacitance of the transition-metal complex: increasing specific surface areas of electrode materials, doping secondary materials, and mixing transition-metal complex with carbon material.[17] Among them, the high specific surface area of the transition-metal complex electrodes can be important factor for the enhanced capacitance of the EDL capacitors.

In particular, it is expected that a mesoporous nanostructure synthesized by chemical or physical route can be a candidate of high specific surface area electrodes for EDL capacitor electrodes. The crucial advantages for mesoporous structures are electrochemical active surface areas and controlled pore sizes in the nanometer range. It has been reported that a variety of mesoporous materials have been typically synthesized using template such as zeolite, ordered mesoporous silica or carbon, and metal organic framework.[15] However, conventional template methods are not simple to manipulate mesoporous molybdenum nitride nanostructures with high surface area and uniform pore size distribution.

Herein, we prepared single-crystalline mesoporous molybdenum nitride nanostructure materials prepared using single-crystalline molybdenum oxide nanowires. The structural and electrochemical properties of the materials were characterized by field-emission transmission electron microscopy (FE-TEM), fast Fourier transformation (FFT), X-ray diffraction (XRD), and cyclic voltammograms (CVs). The surface area and pore size of the as-synthesized sample were analyzed by a nitrogen sorption measurement.

II. Experimental Procedure

(1) Synthesis of Mesoporous Molybdenum Nitride Nanowires

To prepare single-crystalline mesoporous molybdenum nitride nanowires, single-crystalline molybdenum oxide nanowires were prepared using a hydrothermal method. For single-crystalline molybdenum oxide nanowires, ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$ $4H_2O$, 99%, Sigma Aldrich, Steinheim, Germany was dissolved in 5 M HNO_3 (70%, Sigma Aldrich) with constant stirring at 25°C for 1 h and then kept at 160°C for 3 h. After the hydrothermal process, the resulting precipitate was cooled to room temperature, washed several times with ethanol and distilled water, and then filtered using a filtration. The molybdenum oxide nanowire powder was obtained after drying in 50°C oven. For single-crystalline mesoporous molybdenum nitride nanowires, the single-crystalline molybdenum oxide nanowire powder was loaded into on quartz boat, which was inserted into a vitreous quartz tube inside a cylindrical furnace, heated at 700°C for 1 h, and then maintained at 700°C for 3 h in the NH_3 flow of 100 mL/min. The samples were cooled down to room temperature in flowing NH_3, and passivated for 2 h in flowing 1% air to avoid drastic reoxidation to MoO_3 when they were exposed to air. Also, molybdenum trioxide (MoO_3, 99.5%, Sigma Aldrich) was used for nitride formation to compare with the present work.

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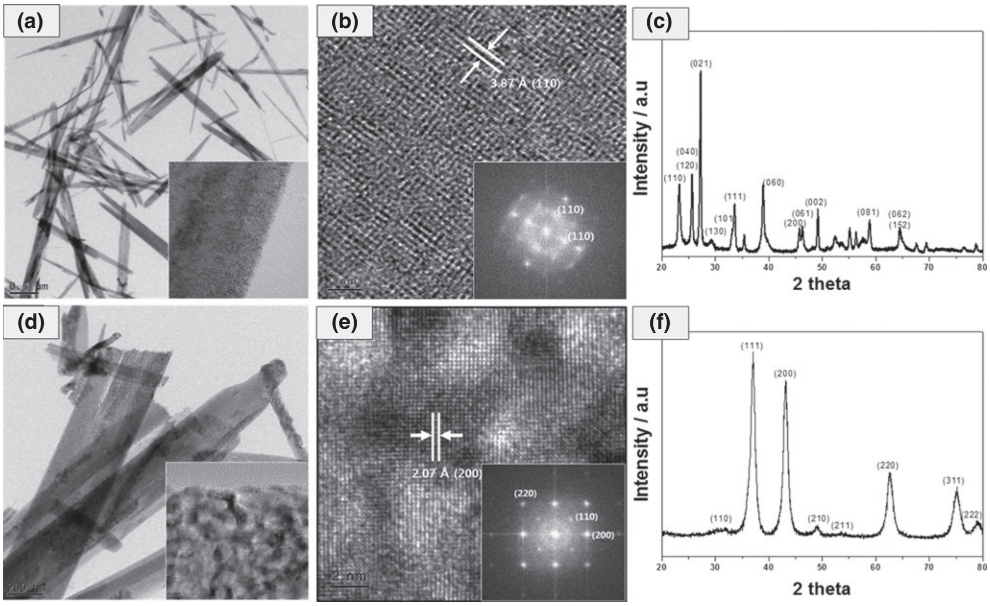

Fig. 1. (a) TEM image, (b) HR-TEM image and FFT pattern, and (c) XRD pattern of MoO_3-NWs. (d) TEM image, (e) HR-TEM image and FFT pattern, and (f) XRD pattern of mesoporous Mo_3N_2.

(2) Structural Analysis

The as-prepared samples were characterized by field-emission transmission electron microscopy (FE-TEM; Tecnai G2 F30, FEI company, Hillsboro, OR). The TEM samples were prepared by placing a drop of the nanoparticle suspension in ethanol on a carbon-coated copper grid. Structural analysis of the samples was carried out by an X-ray diffraction (XRD) method using a Rigaku diffractometer equipped with a Cu$K\alpha$ radiation source of $\lambda = 0.15\,418$ nm with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2θ between 20° and 80° was explored at a scan rate of $5°\mathrm{min}^{-1}$. The surface area and porosity of the synthesized samples were analyzed by a nitrogen sorption measurement (ASAP 2020 Physisorption Analyzer; Micromeritics, Norcross, GA).

(3) Electrochemical Analysis

Electrochemical properties of the electrodes were measured in a three-electrode cell at 25°C using a potentiostat (PGSTAT101, Metrohm Autolab B.V., Utrecht, Netherlands). A Pt wire and Hg/HgO (in saturated NaOH) were used as counter and reference electrode, respectively. The glassy carbon electrode as a working electrode was polished with 1, 0.3, and 0.05 μm Al_2O_3 paste and then washed in deionized water. The slurries for electrochemical analysis were prepared by homogeneously mixing the nitride powders and 25 g/L of poly(vinylidene fluoride) in N-methylpyrrolidinone solution. The electrodes were formed by dropping 0.7 μL of the slurry on the glassy carbon electrode and then dried at 50°C oven. To compare electrochemical properties of the electrodes, cyclic voltammetric curves were obtained in 1*M* KOH solution at 25°C.

III. Result and Discussion

Figure 1(a) reveals that the diameters of as-synthesized MoO_3 nanowires (MoO_3-NWs) range from 0.5 to 5 μm. Nanowire lengths vary in the range of a few hundred nanometers. Representative high-resolution TEM (HR-TEM) image and corresponding FFT pattern of a MoO_3-NW [Fig. 1(b)] confirm the single-crystalline nature of the nanowire and also demonstrate that the nanowire growth is along the [110] direction. Powder XRD pattern of the reaction product composes of randomly oriented MoO_3-NWs [Fig. 1(c)]. The unit cell parameters for MoO_3-NWs are determined to be 3.96, 13.86, and 3.7 Å, identical to those of the bulk orthorhombic MoO_3 material (JCPDS #35-0609). In contrast, as shown in TEM images [Figs. 1(d) and(e)], the as-prepared Mo_3N_2 sample shows mesoporous nanowires with a pore diameter of ~4.0 nm (meso-Mo_3N_2-NWs). The single-crystalline nature of the meso-Mo_3N_2-NWs is clearly observed in a lattice-resolved HR-TEM image and the corresponding FFT pattern of the image, indicating a wire growth in the [200] direction. The XRD pattern of the sample prepared using single-crystalline MoO_3-NWs consists of randomly oriented molybdenum nitrides (Mo_3N_2) [Fig. 1(f)]. The unit cell parameter for Mo_3N_2 is determined to be 4.165 Å, in agreement with that of the bulk cubic Mo_3N_2 material with space group of Pm-3m (221) (JCPDS #01-089-5025).

As indicated in isothermal characteristic curve and pore size distribution (Fig. 2), the meso-Mo_3N_2-NWs exhibit a type IV hysteresis loop indicating mesoporous structure with ~45 m^2/g of specific surface area and ~4.6 nm of mean pore size, which is in agreement with that observed by HR-TEM. On the other hand, the sample prepared at 700°C in NH_3 atmosphere using commercial MoO_3 powders (comm-Mo_3N_2) seems to be less porous and polycrystalline in TEM image. However, in the XRD pattern, the comm-Mo_3N_2 can be indexed to a cubic lattice with the cell parameter of

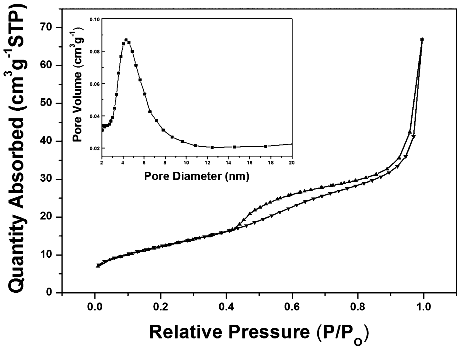

Fig. 2. Characteristic curve of nitrogen gas adsorption–desorption isotherm of Mo_3N_2-NWs. The inset indicates the pore size distribution of Mo_3N_2-NWs.

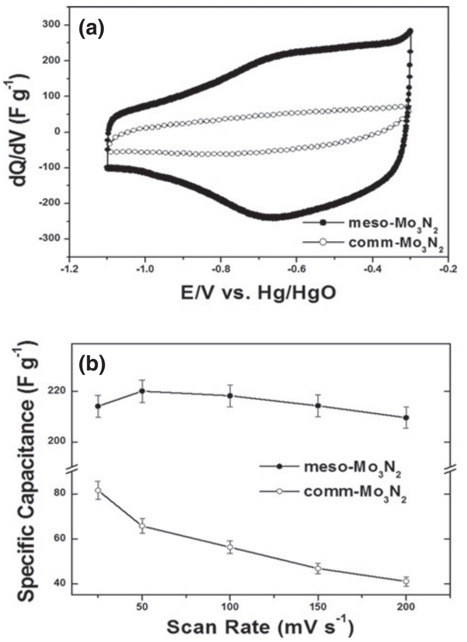

Fig. 3. (a) CVs of meso-Mo_3N_2-NWs and comm-Mo_3N_2 at 50 mV/s and (b) specific capacitance of the samples as a function of scan rate in 1*M* KOH at 25°C.

4.165 Å, identical to that of meso-Mo_3N_2-NWs. Volpe and Boudart[17] reported the synthesis of high-surface area molybdenum nitrides in the topotactic reaction using MoO_3 platelets in NH_3. The topotactic reaction is defined to occur when a solid product has well-defined crystallographical orientation relative to the starting (parent) material.[17] During the present nitridation process with the MoO_3-NWs, the increased oxygen vacancies in the molybdenum nitride might lead to the rearrangement of the oxide structure, giving rise to the formation of pores in the framework of the molybdenum nitride.

Figure 3(a) shows the CVs of meso-Mo_3N_2-NWs and comm-Mo_3N_2 in 1*M* KOH at 25°C. The charging–discharging cycling behaviors of the materials may lead to the double-layer mechanism with no significant oxidation-reduction peaks. The ideal CV curve of electrochemical capacitor materials should be rectangular current(*I*)–potential(*V*) response. The meso-Mo_3N_2-NWs exhibit a considerably rectangular *I*–*V* response and good supercapacitive performance from −1.1 to −0.3 V. The specific capacitance of meso-Mo_3N_2-NWs ($\sim$220 F/g) is much higher than that of comm-Mo_3N_2 ($\sim$66 F/g) at a scan rate of 50 mV/s. As the capacitance of EDL capacitor is proportional to the surface area of the electrode, meso-Mo_3N_2-NWs having high specific surface area can be favorable for such a high specific capacitance EDL capacitor. Figure 3(a) and (b) show the effect of CV scanning rate on the specific capacitance. Theoretically, specific capacitance of ideal EDL capacitor material is not affected by CV scanning rate. However, the actual EDL electrode at high scanning rate cannot completely react, resulting in decreasing specific capacitance with increasing scanning rate. When the scanning rate increases from 25 to 200 mV/s, the specific capacitance of comm-Mo_3N_2 reduces by $\sim$48.1%. In contrast, meso-Mo_3N_2-NWs with increasing scanning rate display a remarkably slight reduction of $\sim$4.5%, representing excellent charging–discharging properties. This implies that the electrolyte even at a high scan rate can easily penetrate in meso-Mo_3N_2-NWs with uniform mesopores. However, as such an electrochemical capacitance might be related to the formation of MoO_3 phase by surface oxidation, maintaining the conductive nitride core, modified mesoporous Mo_3N_2 structures should be further suggested and designed for more efficient and stable electrochemical reaction systems.

IV. Conclusions

We have prepared single-crystalline mesoporous Mo_3N_2 nanowires by means of topotactic reaction process with single-crystalline MoO_3 nanowires as a starting material. The topotactic reaction produces single-crystalline Mo_3N_2 nanowires with well-defined mesoporous structure. The mesoporous nitride structure is likely to be due to the rearrangement of the oxide structure into metal nitride, giving rise to the formation of pores in the framework of the molybdenum nitride. The high specific surface area and mesoporous structure of Mo_3N_2 nanowires result in higher specific capacitance and improved charging–discharging properties as compared with Mo_3N_2 prepared by typical nitridation process using commercial MoO_3.

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