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# Single-crystalline mesoporous $Mo_2N$ nanobelts with an enhanced electrocatalytic activity for oxygen reduction reaction

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ABSTRACT

We demonstrate mesoporous molybdenum nitride nanobelts as a cathode catalyst synthesized by a topotactic reaction process. The molybdenum nitride nanobelts exhibit a single-crystalline face-centered cubic $Mo_2N$. Moreover, the molybdenum nitride nanobelts exhibit a mesoporous structure with ~4.3 nm as an average pore size and ~41.9 $m^2\,g^{-1}$ as a specific surface area. The improved electrocatalytic activity of mesoporous molybdenum nitride nanobelts toward oxygen reduction reaction in alkaline solution might be mainly attributed to high specific surface area and mesoporous structure.

## 1. Introduction

Oxygen-reduction reaction (ORR) is an important reaction in the field of electrochemical energy conversion systems such as fuel cells [1] and metal air batteries [2]. Despite a large thermodynamic driving force of ORR, the ORR has been well known to be kinetically sluggish even in the presence of metallic electrocatalysts [3]. Currently, although electrocatalysts based on Pt-based precious metals are of great technological significance, the cost and scarcity of the precious metals can hinder the large-scale utilization of these materials. Thus, since it is of great importance to develop and synthesize ORR catalysts based on non-precious metals, many materials have been tested for the ORR, including various transition-metal complexes [4], metal oxides, carbon nanomaterials doped with nonmetallic elements or polymers [5].

For the past decade, significant progress has been achieved in the catalytic activity and durability of non-precious group catalysts prepared from transition metals such as Fe and Co, nitrogen and carbon [6]. In particular, transition metal nitrides (TMNs) are also known as class of interstitial compounds with various physical or chemical properties such as high strength, high hardness, good electrical conductivity, and corrosion resistance. These properties are desired attributes of catalytic materials that require resistance against attrition and sintering under reaction conditions. Among them, molybdenum nitrides including face centered cubic $\gamma$-$Mo_2N$, tetragonal $\beta$-MoN, and hexagonal $\delta$-MoN have various properties such as hydrotreating catalysts, electrochemical capacitor, and oxygen reduction reaction catalyst. The structures of metal nitrides influence their catalytic activities toward the ORR [7]. Sun et al. compared two carbon-supported molybdenum nitrides, MoN/C and $Mo_2N$/C, prepared under different experimental conditions in an $NH_3$ atmosphere [8]. From the density functional theory calculations, it was found that both the MoN and the $Mo_2N$ facilitate the dissociation of oxygen molecules, and the suitable geometric structure of the nitride catalysts toward the ORR. Furthermore, Zhang et al. have reported that $Mo_2N$/C showed the improved electrochemical activity in oxygen reduction reaction, because the molybdenum nitride can act as an active adsorption site of oxygen due to the formation of 4-fold-type vacancies in the electron distribution in molybdenum by the addition of nitrogen [9].

Herein, we prepared single-crystalline mesoporous molybdenum nitride nanobelts using molybdenum oxide as a template. The structural and chemical properties of the samples were characterized by field-emission scanning electron microscopy (FE-SEM) and field-emission transmission electron microscopy (FE-TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The surface area and pore size of the as-synthesized samples were analyzed by a nitrogen sorption measurement. The electrochemical properties of the samples were characterized by cyclic voltammetry and rotating ring disk electrode (RRDE) analysis.

## 2. Experimental

For single-crystalline molybdenum oxide nanobelts as a precursor, ammonium molybdate tetrahydrate was dissolved in 5 M

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$HNO_3$ with constant stirring at 25 °C for 1 h and then reacted in autoclave at 160 °C for 3 h. The resulting precipitate was washed several times with ethanol and dried in oven at 50 °C. The molybdenum oxide powder was heated at 700 °C for 3 h under the $NH_3$ flow of 100 mL $min^{-1}$. The sample was cooled down to 25 °C in flowing $NH_3$, followed by passivation for 2 h in 1% air.

The as-prepared samples were characterized by FE-SEM and FE-TEM using a Tecnai G2 F30 system operating at 200 kV. 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 the XRD method using a Bruker AXS D2 Phaser equipped with a Cu $K_\alpha$ radiation source of $\lambda = 0.15418$ nm with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The surface area and porosity of the synthesized samples were analyzed by a nitrogen sorption measurement (Micromeritics ASAP 2020 adsorption analyzer). XPS (Thermo Scientific, K-Alpha) analysis was carried out with the Al $K_\alpha$ X-ray source of 1486.8 eV at the pressure below $1 \times 10^{-8}$ Torr and 200 W beam power.

Electrochemical properties of the electrodes were measured in a three-electrode cell at 25 °C using a potentiostat (CHI 700C, CH Instrument). Pt wire and Hg/HgO (in saturated 1 M KOH) 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 2.5 g $L^{-1}$ 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 in oven at 50 °C. Cyclic voltammograms (CVs) of the samples were obtained in Ar- or $O_2$-saturated 1 M KOH solution with a scan rate of 50 mV $s^{-1}$ at 25 °C. The oxygen reduction current–potential curves of the samples were obtained by sweeping the potential from −0.9 to 0.0 V at a scan rate of 5 mV $s^{-1}$ and rotation disk speed of 1600 rpm using an RRDE analysis. The ring potential was maintained at 0.15 V.

## 3. Results and discussion

Fig. 1(a) shows that FE-SEM image of $MoO_3$ nanobelts as a precursor. FE-SEM and TEM images of the porous $Mo_2N$ prepared using $MoO_3$ nanobelts are indicated in Fig. 1(b), (c). In the powder XRD pattern of the as-synthesized sample, the diffraction peaks of

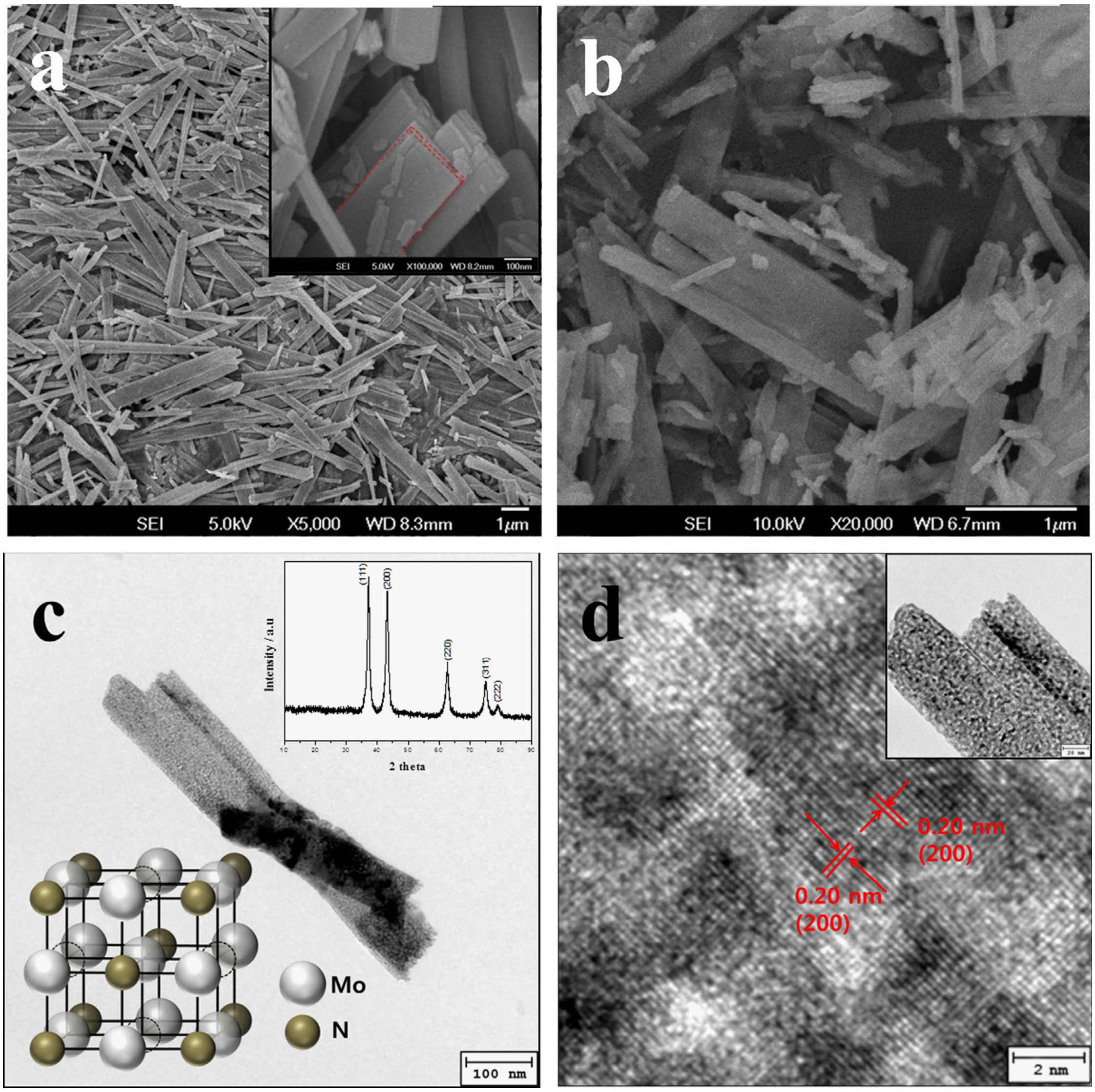

**Fig. 1.** (a) FE-SEM image of $MoO_3$ nanobelts. (b) FE-SEM image of the mesoporous $Mo_2N$. (c) HR-TEM image of the mesoporous $Mo_2N$. The insets indicate the XRD pattern and crystal structure of the mesoporous $Mo_2N$. (d) HR-TEM image of the mesoporous $Mo_2N$.