

Synthesis of Nanoporous Molybdenum Carbide Nanowires Based on Organic–Inorganic Hybrid Nanocomposites with Sub-Nanometer Periodic Structures

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Transition-metal carbides have attracted much attention as promising materials for their outstanding bulk and surface physicochemical properties originating from the unique metal–carbon chemical bonds and noble-metal-like d-state density around Fermi level, such as thermal stability, mechanical hardness, superconductivity and high catalytic performance in hydrocarbon conversion.¹ Traditionally, they were synthesized via the temperature-programmed reduction (TPRe) method which employs the gas–solid reactions between oxides and the mixture of hydrogen and carbon-containing gases including CH₄, C₂H₆, C₃H₈, and C₄H₁₀.² However, incomplete transformation is difficult to be avoided since the reactions take place only on the gas–solid interface. Meanwhile, the bulky products generated from such process are often covered by polymeric carbon species resulting from the pyrolysis of excessive carbon-containing gases,³ reducing the surface activity. Furthermore, the complex and strict synthetic conditions, such as precise control of temperature ramping rate (≤ 1 °C/min) and gas components and flow rate, have heavily limited the large-scale manufacture of

carbide materials. For Mo₂C, the mass of product synthesized in one TPRe process is normally less than 1.0 g for complete carburization in high space velocity (6000 h⁻¹).^{2,3} Obviously, employing a large amount of flammable gases at high temperature is very dangerous, which challenges the rigid manipulation in the experiment. Therefore, easy and safe strategies for the controllable preparation of nanostructured carbides and relevant materials through homogeneous reactions are highly desired, aiming at their large-scale manufacture and application.

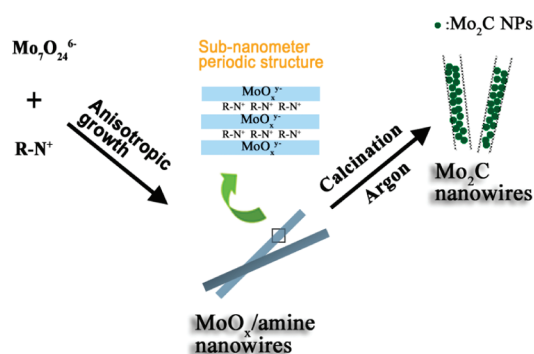
Recently, a series of novel organic–inorganic hybrid nanowires is reported,⁴ e.g., ZnS/n-butylamine, WO_{2.72}-(N₆C₁₂₃H₁₃₆O₂₂)_{0.04}, ZnSe(diethyl-enetriamine)_{0.5}, GeO_x/ethylenediamine, and PbS/L-cysteine, which is significant for the various functional properties and tunable sub-nanometer periodic structures. During our recent experiments, we have found that such hybrids can provide quasi-homogeneous reactions uniformly throughout the whole nanowire in secondary treatments, because of their sub-nanometer-contacting inorganic and organic components. This will successfully avoid the disadvantages of interface reactions in material preparations, such as TPRe process for carbide synthesis, and hence inspire us to exploit a new route for preparing functional nanomaterials. In this paper, this strategy is first introduced to synthesize carbides by employing organic–inorganic hybrid nanocomposites as precursors. Scheme 1 depicts the schematic illustration for the preparation of Mo₂C nanowires through easily calcining the preprepared subnanometer periodic MoO_x/amine nanowires under inert atmosphere. In this process, the intercalating amine molecules act as both reducing agent and carbon resource. The as-obtained Mo₂C nanowires composed of small nanoparticles possess uniform one-dimensional (1D) morphology, abundant nanoporosity, and large surface free from depositing carbon, suggesting good surface activity for electrochemistry and catalysis. A probe reaction of producing hydrogen from methanol decomposition was carried out in our work. Remarkably, this strategy is easily controlled and safe compared with the TPRe method for the absence of flammable hydrogen and carbon-containing gases, suggesting a possible approach to the large-scale preparation of carbides. Being tunable and universal for various carbides and relevant nanostructures, our strategy opens up opportunities for developing functional materials in many fields.

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Scheme 1. Schematic Illustration for the Synthetic Strategy of Mo₂C Nanowires on the Basis of Organic-Inorganic Hybrid Nanowires



As one of the organic–inorganic hybrid precursors used here, Mo₃O₁₀(C₆H₈N)₂·2H₂O nanowires were first prepared through the reaction between ammonium heptamolybdate and aniline at 50 °C. The crystalline structure is validated by X-ray diffraction (XRD) characterization (Figure S1 in the Supporting Information). Their 1D morphology of several micrometers in length and 80–120 nm in width is well-observed by scanning electron microscope (SEM, Figure 1a). The uniform subnanometer periodic lattice (~1.37 nm) of (101) is clearly identified by a transmission electron microscope (TEM), and the selected-area electron diffraction (SAED) pattern obtained on the single nanowire can be well-indexed (Figure 1b). Furthermore, the presence of the organic species is demonstrated by the CHN elemental analysis result (N, 4.31 wt %; C, 22.22 wt %; H, 3.00 wt %). The hybrid components of aniline and molybdate in the nanowires have also been confirmed by infrared spectrum and thermogravimetric analysis (Figures S2 and S3 in the Supporting Information).

The subnanometer periodic hybrid structure of Mo₃O₁₀(C₆H₈N)₂·2H₂O nanowires significantly facilitates the preparation of Mo₂C through the reactions between organic and inorganic components at high temperature. After the calcination of the organic–inorganic hybrid nanowires at 725 °C in argon flow, Mo₂C nanowires are successfully obtained (Figure 2a), which are confirmed as hexagonal phase (JCPDS: 35–0787) by XRD pattern (Figure 2b). Although some of the nanowires seem to be stacked to bundles in the SEM image of Figure 2a, the TEM observation with higher magnification shows that they are still essentially individual nanowires (Figure S4 in the Supporting Information). Only Mo and C signals are detected by the energy dispersive spectroscopy attached on TEM (Figure S5 in the Supporting Information), and the carbon content determined by CHN elemental analysis is 5.90 wt %, quite consistent with the theoretical value in Mo₂C. Figure 2c further displays that such nanowires are composed of nanoparticles (10–15 nm), and the SAED pattern in the inset is well-indexed as Mo₂C. The sintering at the junctions of neighboring nanoparticles is observable in the high-resolution TEM (HRTEM) image (Figure S4c in the Supporting Information), which benefits maintaining nanowire

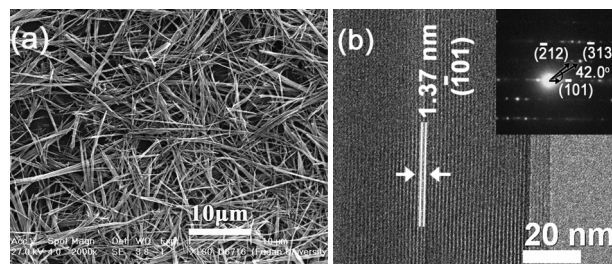


Figure 1. (a) SEM and (b) TEM images of the as-synthesized Mo₃O₁₀-(C₆H₇N)₂·2H₂O nanowires. Inset of b is the SAED pattern obtained on the single nanowire in b.

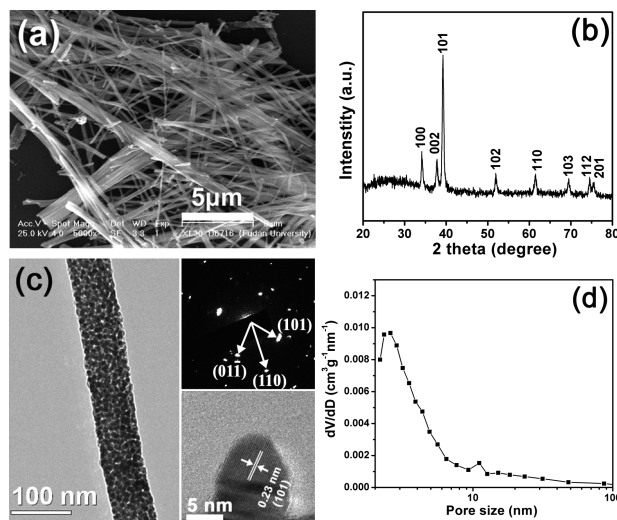


Figure 2. (a) SEM image, (b) XRD pattern, (c) TEM image, inset of c HRTEM image, and (d) pore size distribution of Mo₂C nanowires. The SAED pattern in inset of c is obtained on the Mo₂C nanowire.

morphology. Notably, compared with the bulky Mo₂C partially covered by depositing carbon from traditional TPRE process (Figure S6 in the Supporting Information), there is rarely carbon layer observed on the surface of Mo₂C nanoparticles in nanowires by HRTEM (inset of Figure 2c). The absence of residual carbon in Mo₂C nanowires is also confirmed by Raman spectrum (Figure S7 in the Supporting Information). Meanwhile, a larger BET surface area of 51.3 m²/g is revealed by the N₂ sorption isotherms vs. that of bulky Mo₂C synthesized via TPRE process (22.4 m²/g) (Figure S8 in the Supporting Information). The pore-size distribution indicates abundant nanoporosity presenting in mesoscale (Figure 2d), which may result from the aggregation of Mo₂C nanoparticles inside the nanowires (TEM image in Figure 2c). Because of their novel 1D nanostructure with large surface and enriched nanoporosity, the Mo₂C nanowires are expected to possess high surface activity as easy-manipulated building blocks in catalysis and electrochemistry.

Importantly, this new synthetic strategy is tunable and universal for various molybdenum carbides and relevant nanostructures. For example, MoO₂-doped MoC nanowires and Mo-doped Mo₂C nanowires can be achieved by changing calcination temperature (Figures S9 and S10 in the Supporting Information). Because of the diverse catalytic or conductive properties of MoO₂ and Mo, the

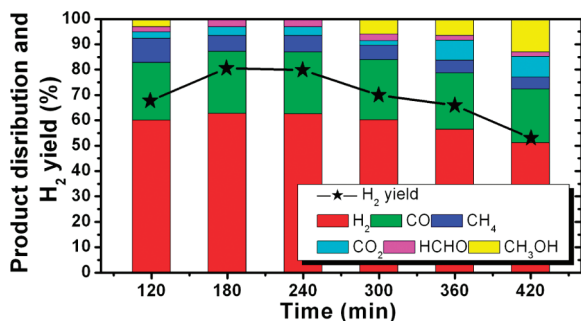


Figure 3. Decomposition of methanol at 450 °C over Mo₂C nanowires prepared from Mo₃O₁₀(C₆H₇N)₂·2H₂O nanowires as a function of time on stream.

doping agents might improve their performances for some application.⁵ Furthermore, other novel nanostructured Mo₂C can also be realized by varying the organic components in the hybrid nanowires. The nanoporous Mo₂C nanowires of cubic phase (JCPDS: 15–0457) and MoO₂-doped cubic phase Mo₂C nanowires have been successfully fabricated by employing MoO_x/1,6-hexanediamine and MoO_x/imidazole nanowires as precursors, respectively (Figures S11 and S12 in the Supporting Information). The tunability of this strategy will exploit its potential in designing novel nanostructures through simple and safe treatments of subnanometer periodic organic–inorganic hybrid materials.

To test the catalytic properties of nanoporous Mo₂C nanowires, we have carried out the production of hydrogen from methanol decomposition as a probe reaction, which is believed to be a promising approach for providing clean and efficient hydrogen fuel on-site in application because of the high hydrogen content in methanol.⁶ Several materials, mainly noble metals, have been used to attempt to catalyze methanol decomposition,⁷ and Mo₂C catalysts with platinum-like catalytic properties are considered an effective and cheap substitute for the high-cost noble metal.⁸ Herein, the Mo₂C nanowires with

large surface and abundant nanoporosity exhibit good performance in this reaction, as displayed in Figure 3. Hydrogen is the dominant product, whose distribution in the tail stream from reactor is about 60%. The hydrogen yield is as high as 80% after the reaction time of 180 min, and even after 360 min it keep over 65%, better than that of bulky counterpart obtained by TPre method (Figure S13 in the Supporting Information). This could be attributed to the better coke tolerance for the large surface of Mo₂C nanowires.⁹ Furthermore, these Mo₂C nanowires provide ideal nanostructure and surface for their further modification toward practical application. For example, through facile potassium modification the Mo₂C nanowires exhibit a H₂ yield of 90% even after 600 min in methanol decomposition (Figure S14 in the Supporting Information).

In conclusion, nanoporous Mo₂C nanowires have been successfully synthesized through facilely calcining the organic–inorganic hybrid nanowires with subnanometer periodic structures. The subnanometer contact between molybdenum oxides and amine molecules in the hybrid nanowires remarkably facilitates the achievement of Mo₂C nanowires with large surface and enriched nanoporosity, which benefits the high performance in the production of hydrogen from methanol catalytic decomposition. Because of the safety, easy control, low cost, and unique product structure, the current synthetic strategy makes it possible to scale up the manufacture and application of Mo₂C materials. Furthermore, with the discovery of more and more organic–inorganic hybrid nanocomposites, this synthetic strategy will pave the way for designing novel nanostructures of carbides and relevant materials in many fields.

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Supporting Information Available: Experimental section, physical characterization, and additional figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) The coke formation extents over Mo₂C catalysts during methanol decomposition have been compared in a tubular reactor under ~15% CH₃OH/Ar flow at 450 °C. After reaction for 240 min, the amount of coke deposits over Mo₂C nanowires and bulky Mo₂C determined by CHN elemental analysis is 40.1 and 34.0 mg C/g_{cat} (corresponding to 0.78 and 1.57 mg C/m²_{cat}), respectively. Combining their textural property, the good performance of the Mo₂C nanowires may be attributed to its better coke tolerance on larger surface.