

Ultrathin inorganic molecular nanowires based on transition metal oxide

Nanowires are one-dimensional (1D) materials, whose diameters are on the order of nanometers or smaller and whose length can be increased without limitation. Different compounds, such as metallic compounds, semiconducting compounds, metal oxides, and organic polymers, can be grown to form nanowires, which have been attracting much attention owing to their large surface area, quantum mechanical effects, and other unique properties.

Molecular wires, as a type of nanowire, are grown in length by repeating a single molecular unit. The common types of molecular wires are organic, organometallic, and biological polymers, which have been widely applied to nanotechnology, semiconductors, electrochemistry, and cell biology. In the inorganic field, all-inorganic molecular wires are very rare, leaving a field full of challenges. The most common example of inorganic molecular wire is $[\text{Mo}_6\text{S}_{9-x}\text{I}_x]_n$ [1,2]. The material is assembled by growing the molecule unit $\text{Mo}_6\text{S}_{9-x}\text{I}_x$ along the *c*-axis to form a nanowire. The material shows excellent magnetic, electronic transport, biological, mechanical, and optical properties and has been applied to field emitters, composites, nonlinear optical limiters, chemisensors, biosensors, lubricants, Li batteries, and molecular-scale connectors for molecular electronics.

Transition metal oxide molecular wires have various advantages over organic molecular wires including their stable structure, tunable chemical composition, and tunable property. Metal oxides with a nano-architecture can be formed by the assembly

of metal oxygen octahedra. 0D nanomolecular clusters and 2D nanomolecular sheets are obtained by this approach. However, no molecular nanowire assembled using transition metal oxide octahedra has been reported so far.

Herein, we report the first crystalline transition metal oxides based on molecular wires, which were formed by repeating the hexagonal molecular unit $[\text{X}^{\text{IV}}\text{Mo}^{\text{VI}}_6\text{O}_{21}]^{2-}$ (*X* = Te or Se) along the length, denoted as Mo-Te oxide and Mo-Se oxide, respectively [3]. The molecular wires assemble in a hexagonal manner with water and ammonium cations between them to form crystals. Breakage of a crystal forms small nanowires, even single molecular wires, which can be observed by TEM and AFM.

The materials were synthesized by a hydrothermal method. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was used as a Mo source, and Se^{IV} (SeO_2) and Te^{IV} (formed by reduction of the $\text{Te}(\text{OH})_6$ with VOSO_4) were used as the Se and Te sources, respectively. After the reaction mixture was heated at 448 K for 24 h, the resulting solid was recovered from the solution by filtration.

Mo-Te oxide can grow into a large crystal that is suitable for single-crystal X-ray analysis. Single-crystal X-ray structural analysis performed at beamline **BL40XU** combined with elemental analysis and valence analysis showed that six Mo-O octahedra surrounded one Te or Se ion in the *a*-*b* plane, forming the molecular unit $[\text{X}^{\text{IV}}\text{Mo}^{\text{VI}}_6\text{O}_{21}]^{2-}$ (*X* = Se or Te) (Fig. 1(a,b)). Hexagonal $[\text{X}^{\text{IV}}\text{Mo}^{\text{VI}}_6\text{O}_{21}]^{2-}$ units were stacked along the *c*-axis to form prismatic clusters

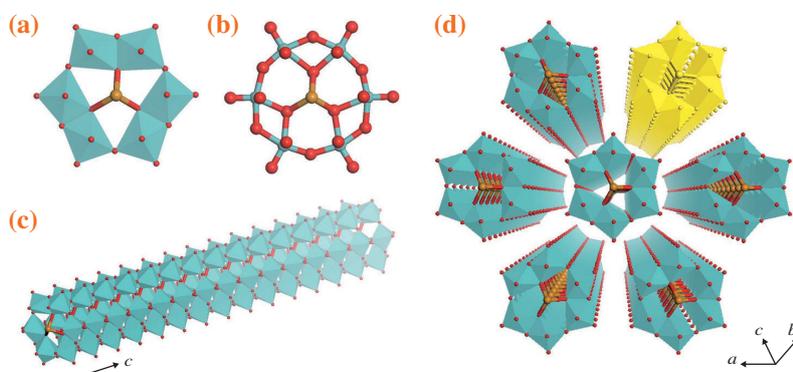


Fig. 1. Structural representations: (a) polyhedral representation of hexagonal unit $[\text{Te}^{\text{IV}}\text{Mo}^{\text{VI}}_6\text{O}_{21}]^{2-}$ or $[\text{Se}^{\text{IV}}\text{Mo}^{\text{VI}}_6\text{O}_{21}]^{2-}$, (b) ball-and-stick representation of hexagonal unit $[\text{Te}^{\text{IV}}\text{Mo}^{\text{VI}}_6\text{O}_{21}]^{2-}$ or $[\text{Se}^{\text{IV}}\text{Mo}^{\text{VI}}_6\text{O}_{21}]^{2-}$, (c) single molecular wire, and (d) assembly of single molecular wires into crystalline Mo-Te oxide (or Mo-Se oxide). A single molecular wire is highlighted in yellow; Mo, blue; Te (Se), yellow; O, red.

(Fig. 1(c)) as molecular wires. The anionic molecular wires were further packed parallel to each other in a hexagonal manner to form the material (Fig. 1(d)), and ammonium cations and water were between the molecular wires. The nanowires were *ca.* 1.2 nm in width and micrometer scale in length.

Single molecular wires can be isolated from the crystalline Mo-Te oxide based on molecular wires using a simple process (Fig. 2(a)). Proton exchange cracked the crystal of Mo-Te oxide. Breakage of crystals after proton exchange was more clearly shown by SEM. Mo-Te oxide maintained its rod shape after proton exchange, and some gaps could be observed on the crystal surface (Fig. 2(b)).

Mo-Te oxide after proton-exchange could be disassembled into smaller particles by dispersion in ethanol using ultrasound. Thin particles and even

single molecular wires can be observed. High-resolution TEM (HRTEM) revealed that the molecular wires were <5 nm in width and ~100 nm in length, and some isolated molecular wires were 1.5 nm in width (Fig. 2(c)). The isolated nanowires were further characterized by AFM, and the diameter of the nanowires was determined by line profile analysis. AFM images of Mo-Te oxide after isolation experiments show tubular particles. Figure 2(d) shows typical particles with diameters of *ca.* 1.2 nm (particle i), and the diameter of particle (i) was identical to that of a single molecular wire (Fig. 2(e)). The diameter of particle (ii) was *ca.* 4.8 nm, which is ascribed to a structure with four layers of molecular wires (Fig. 2(f)).

The separated nanowire shows acid catalytic activity for ester formation from alcohol, which indicated similarity in activity to homogeneous heteropoly acids.

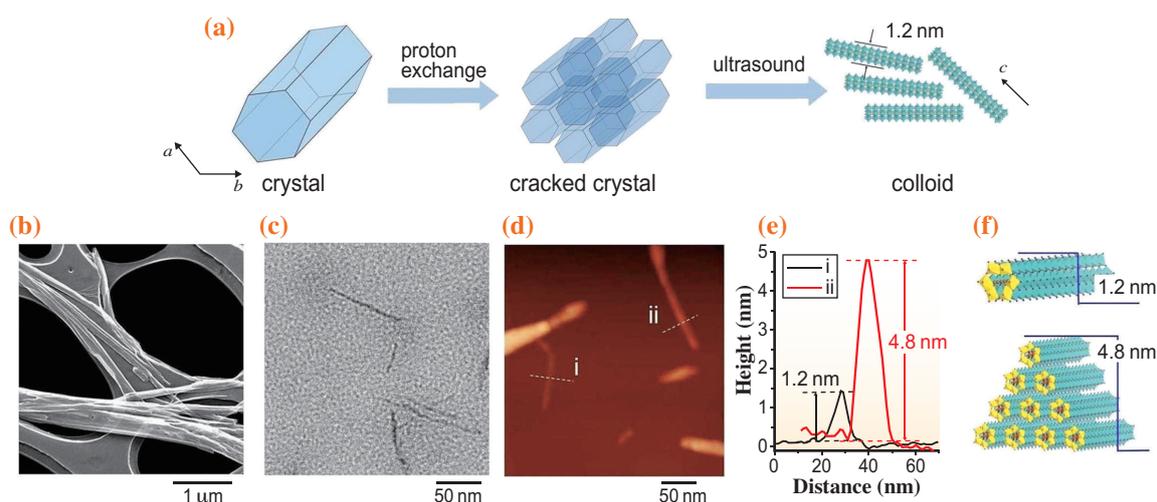


Fig. 2. Mo-Te oxide molecular wire: (a) isolation process for crystalline Mo-Te oxide to obtain nanowires, (b) SEM images of Mo-Te oxide after proton exchange, (c) HR-TEM images of Mo-Te oxide after ultrasound irradiation, (d) AFM images of Mo-Te oxide after ultrasound irradiation, (e) line profiles from AFM images, and (f) proposed structures from line profile analysis, with yellow highlighting the a-b plane of the materials.

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