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The Formation of ReS_2 Inorganic Fullerene-like Structures Containing Re_4 Parallelogram Units and Metal−Metal Bonds

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Since the discovery of C_{60}, research into the field of carbon fullerene chemistry has developed rapidly.[1] A number of important breakthroughs have allowed for the preparation of other carbon-based nanostructures such as single- and multiwalled carbon nanotubes.[2a−c] More recently, so-called inorganic fullerene-like analogues (IFs) of these carbon-based materials have been discovered, and their properties have been studied.[3a−d] Initially, these materials were derived from layered metal chalcogens of the form $2H\text{-}MX_2$ with M = Mo, W and X = S, Se,[3e−i] although more recently IFs have been formed from layered metal halides such as $NiCl_2$, $CdCl_2$, and $TlCl_3$[4a−c] and oxides such as TiO_2 and V_2O_5.[5a,b] Additionally, IFs formed from chalcogens have been extended to include those based on Nb[6a] or Ta[6b] and also mixed-metal chalcogens such as W−Nb−S[6c] or W−Mo−S.[6d]

With the exception of the oxides, all of the above have in common a six-membered ring substructural motif (Figure 1a), which conveys smooth curvature within extended layers[7a] and which may then combine with triangular or rhombohedral defects[7b] resulting in three-dimensional closed or scroll-like nanostructures. We describe here a departure from this basic template in the formation of nanostructures derived from an ReS_2 framework in which the substructural motif consists of Re_4 parallelogram units[8a] which distort from the hexagonal motif (Figure 1b). With respect to the bulk structure, this distortion results in a reduction of symmetry from $P6_3/mmc$ (Figure 1a) to $P\text{-}1$ (Figure 1b). With regard to the bonding properties, the d^3 Re center which forms part of the t_{2g} band has two electrons strongly hybridized with the p orbitals of the sulfur with the remaining d electron residing in the delocalized $d_{x^2-y^2}$ and d_{xy} metal orbitals. It is the overlap of these orbitals with neighboring Re centers that form the Re_4 parallelogram units containing Re−Re metal bonds. This, in turn, results in a gap in the middle of the bonding and antibonding t_{2g} bands, thus giving rise to the semiconducting nature of ReS_2.[8b,c]

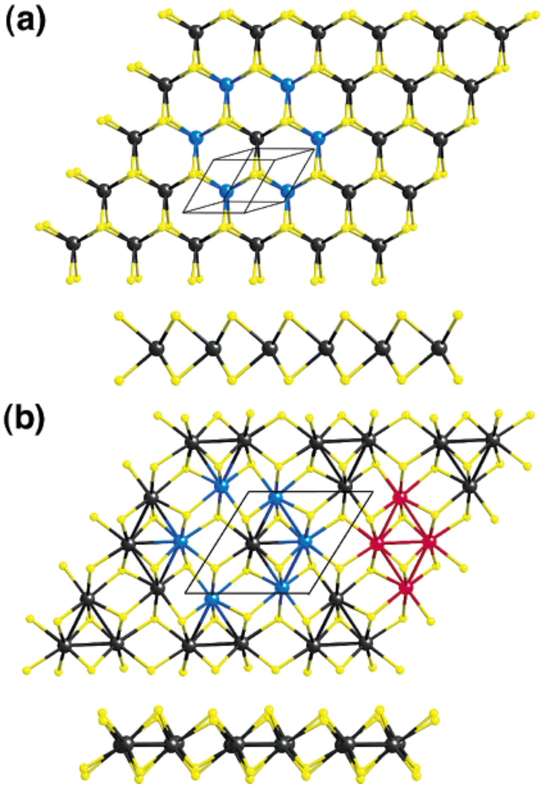

Figure 1. (a) Top-down and side-on depictions of a single layer of $P6_3/mmc$ WS_2 with a W hexagonal motif indicated in blue. (b) Top-down and side-on depiction of a single ReS_2 layer derived from the triclinic $P\text{-}1$ bulk form. An equivalent but distorted Re "hexagon" to that shown in (a) is indicated in blue, while a Re_4 parallelogram unit is indicated in red. Note Re−Re metal−metal bonds.

ReS_2 IF nanostructures were prepared by direct sulfidization of ReO_2, formed from the decomposition of ReO_3. The parent oxide was obtained from Aldrich (99.9%) and used without further purification. The oxide samples were ball-milled for 30 h prior to sulfidization to produce particles in the submicron range. The ReO_3 samples were decomposed to ReO_2 by heating to 700 °C under a flow of nitrogen prior to sulfidization. All sulfidizations were carried out in a standard flow reactor at 700 °C with a flow rate of H_2S of approximately 4 mL min^{-1}. All of the resulting products were characterized by high-resolution transmission electron microscopy (HRTEM) using a JEOL 3000F microscope fitted with an energy-dispersive X-ray analysis (EDX) system and by X-ray powder diffraction (XRD) using a Philips 1729 diffractometer equipped with Cu $K\alpha_1$ radiation operated at 40 kV and 30 mA.

In general, sulfidization of commercial ReO_3 produced no complete IF ReS_2 particles, although a high degree of curvature was observed in fragments imaged by HRTEM. Therefore, ReO_2 was prepared by disproportionation of ReO_3, resulting in the formation of both monoclinic and orthorhombic forms of the reduced oxide. These reduced forms[9] were found to be more susceptible to sulfidization. Sulfidization of ReO_2 formed complete ReS_2 IF-like cages encapsulating crystalline ReO_2 (Figure 2a) or amorphous ReO_x particles (Figure 2b) as confirmed by HRTEM imaging and EDX microanalysis (Figure 2c). Additionally, XRD

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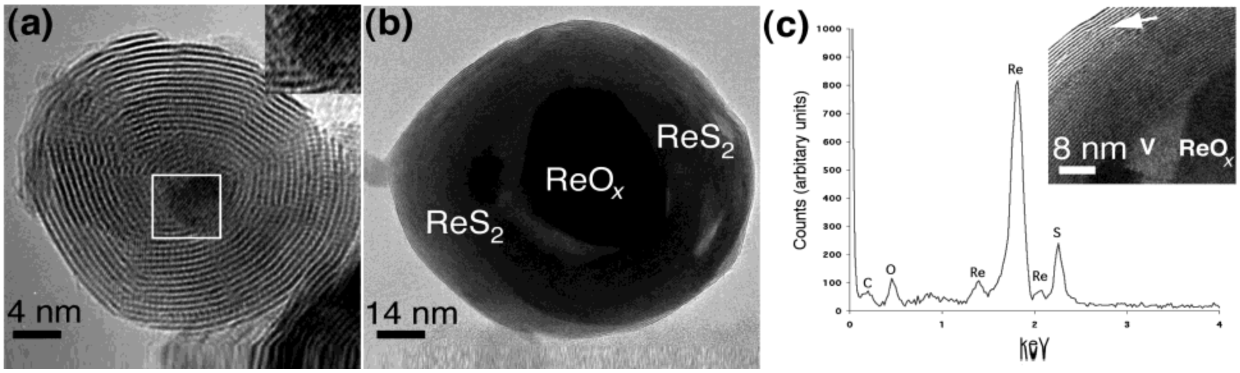

Figure 2. (a) HRTEM micrograph showing a small ReO_2 particle encapsulated by spheroidal ReS_2 layers. The 0.29 nm lattice fringes (inset) correspond to ReO_2 {111} planes. (b) HRTEM micrograph showing a large amorphous or polycrystalline ReO_x particle encapsulated by spheroidal ReS_2 layers. (c) EDX spectrum from (b). Inset: ReO_x−ReS_2 interface region. A small void is labeled (V), while the arrow depicts a layer dislocation.

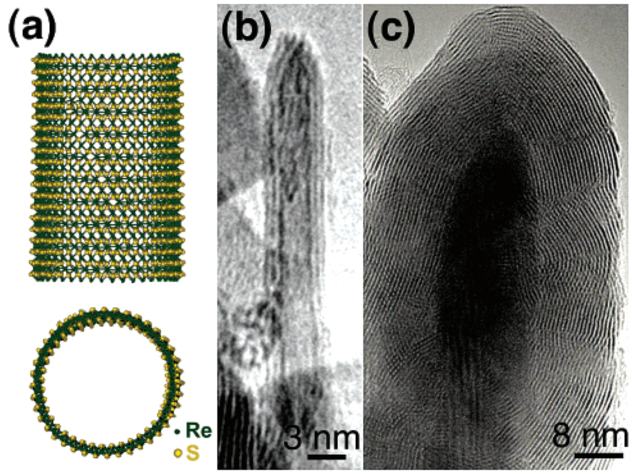

Figure 3. (a) Minimum energy calculation of a zigzag (20,0) ReS_2 nanotube exhibiting a 36 Å internal diameter (side and top view). (b) HRTEM micrographs showing a hollow ReS_2 IF tubule-like structure. (c) HRTEM micrographs showing an elongated ReS_2 nanoparticle formed around an ReO_x encapsulate of similar morphology.

powder patterns obtained from partially sulfidized ReO_2 particles confirmed that this sulfide material was derived from *P*-1 ReS_2 (see Supporting Information).

In the HRTEM, the obtained ReS_2 layers are visible as dark 0.61 nm lattice fringes corresponding to the (100) plane of ReS_2[9] and, in general, displayed extremely smooth curvature with few sharp disclinations, suggesting this originated from the bending of the ReS_2 layers rather than from the incorporation of defects which tend to produce much more angular curvature in IF-like nanoparticles.[7b] Increasing the time of the sulfidization step resulted in complete consumption of the oxide core and the formation of hollow ReS_2 IF cages.

The size and morphology of the obtained encapsulates were determined by the comparative size and morphologies of the precursor particles, and as the majority of the precursor particles exhibited spheroidal shapes, the IF nanoparticles tended to be spheroidal. Minimum energy calculations based on the minimization of a cohesive energy function parametrized for ReS_2 using a conjugate gradient indicate that ReS_2 nanotubes constitute feasible metastable states (Figure 3a), and a few nanotubule-like structures were observed (Figure 3b and c), although these were fewer than 5% of the total products. A similar approach has been used to generate the unit cells of MoS_2 and WS_2 nanotubes.[6a]

In conclusion, we have demonstrated the synthesis of the first ReS_2 inorganic fullerene structures. The ability of ReS_2 to form such structures has been attributed to the Re_4 parallelogram structural units, which represents the first example of a nonhexagonal-based layer structure forming inorganic fullerenes.

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Supporting Information Available: XRD powder patterns calculated for idealized *P*6_3/*mmc* and *P*-1 ReS_2 and observed experimental XRD powder pattern for partially sulfidized ReO_2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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