

Inorganic Nested Polyhedra

Gennady Dantsin

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Since the discovery of graphitic nanotubes in carbon soot there has been great interest in nested polyhedra.¹ The most commonly used method for preparing graphitic nanotubes is the arc-discharge route, which involves generating a plasma arc across two graphitic tubes with an applied potential in an inert environment.² Soot material is deposited on the cathode from the anode. This soot contains both carbon clusters (C_{60} , C_{70} , etc.) and graphitic nanotubes. These carbon based materials are generally characterized by surface techniques such as TEM, EELS, and electron diffraction. The ability of layered inorganic materials, which are analogous to graphite, to form nested polyhedra has been investigated.

A common theme among layered materials is that nanoparticles formed under high energy conditions minimize their surface energy, attributed to dangling bonds, by folding to form nested polyhedra (Figure 1).³ The closure of these sheets leads to an unreactive nested nanoparticle surface with different chemical properties than the bulk. Such a surface would be useful for solid state lubrication purposes.

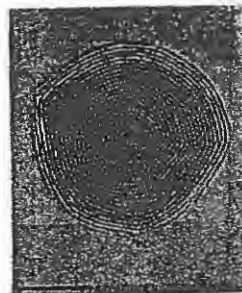


Figure. 1. Nested polyhedral particle of WS_2 . Scale bar is 10 nm.

The hollow cores of the nanotubes have been encapsulated with various materials.⁴ Metals, metal carbides, and oxides were encapsulated by arc-discharge and chemical routes. The arc method was achieved by loading the graphite anode with the metal precursor.^{5,6} The chemical insertion method was to oxidize the nanotube caps with nitric acid, then react the open nanotubes with the metal nitrate or halide to incorporate the desired metal oxide.⁷

The potential for nanotubes to function as templates has been explored. Encapsulation of V_2O_5 in graphitic nanotubes was investigated because of the proven ability of V_2O_5 to function as an oxidation catalyst, as well as, a ceramic material. The oxide preferentially coats the inside of the tube, as well as, the outside of the nanotube. It is believed to coat the outside of the nanotube by partial removal of the vanadyl oxygen closer to the graphitic sheet. This type of structure would have an oxygen deficient vanadium oxide stoichiometry which is confirmed by EELS.⁸

Nanotube growth of graphite-like layered materials, such as BN has also been investigated.^{9,10} The insulating nature of hexagonal boron nitride necessitates modification of the arc-discharge reactor used on the synthesis. TEM revealed long (100 nm) nanotubes that were capped with dense metal particles. This contrasts with the capping in graphitic nanotubes which form isolated pentagons in the hexagonal graphitic sheet. In the boron nitride isolated pentagons are unfavorable due to formation of B-B or N-N bonds which are not found in the bulk material.

Doping of the BN moiety into a graphitic nanotube is also of interest due to theoretically predicted semi-conducting properties of the composite.^{11,12} EELS shows evidence for a new composite material with a $B_xC_yN_z$ structure.^{13,14} Comparison of the core ionization fine structure for boron, nitrogen, and carbon in the composite shows changes in the σ^* regions from those of the boron nitride structure.

Sandwiching BN hexagonal sheets between graphitic layers was done with the arc-discharge method which utilized HfB_2 as the anode, and an N_2 atmosphere as the source of nitrogen.¹⁵ Two types of structures were seen, nested polyhedra with a dense metal particle in the center and nanotubular polyhedra. EELS profiling of the nanoparticles showed the BN layers sandwiched in between the graphitic ones. The boron and carbon K edge ionization region show an increase in the σ^* intensity as the tube is scanned from the edge to the center. This is a characteristic feature of graphitic nanotubes.¹⁶

Molybdenum and tungsten sulfide are similar to graphite in their layering scheme. Nested polyhedral structures of these materials are made by annealing tungsten and molybdenum films in air and then subsequently reducing them with forming gas, followed by sulfidation with H_2S .^{17,18} Treatment of MO_3 precursors with H_2/N_2 and H_2S yields similar results. Electron diffraction patterns are consistent with closed polyhedra in three dimensions. Models that take into account the closure of these sheets are proposed to initiate with metal vacancies that allow for incorporation of triangular (Figure 2) and rhombohedral shapes into these hexagonal sheets allowing the structures to close.¹⁹

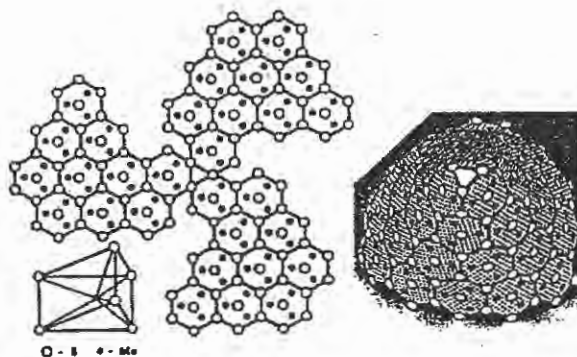


Figure 2. Closure model for MoS_2 nested polyhedra.

The proposed mechanism for the transformation of the MO_3 precursor to the nested polyhedra involves initial reduction followed by inward sulfidation of the outer layers.²⁰ Thus the size of the nanoparticle is determined by the size of the incipient oxide precursor.^{21,22} The elimination of the dangling bonds in these layered MS_2 ($M=Mo, W$) nanoparticles makes them useful as solid state lubricants. These hollow nested polyhedra show superior lubricating properties in tribological studies compared to their bulk layered counterparts.²³

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