

## Inorganic Nanotubes and Fullerene-like Nanoparticles from Layered Compounds

by R. Tenne

The landmark discovery of carbon fullerenes<sup>1</sup> and carbon nanotubes<sup>2</sup> has led to a surge of research into the chemistry and physics of inorganic nanostructures. This discovery established a new paradigm, *i.e.*, that polyhedral structures are the thermodynamically stable form of carbon with the sole constraint that the size of the nanoparticle is not allowed to grow beyond a given size. The driving force for the formation of these closed cage nanostructures has been linked to the instability of the planar graphite sheet, when its dimensions shrink below a few ten nm.

Soon after, it was hypothesized that this virtue should not be limited to carbon only, and is likely to be a generic feature of all compounds having a layered structure. Layered structured materials, like MoS<sub>2</sub>, are characterized by their anisotropic (2-D) structure. Here molecular slabs made of molybdenum atoms sandwiched between two sulfur planes with strong Mo-S covalent bonds are stacked together through weak van der Waals forces. The propensity of such layered materials to form hollow closed structures stems from the excess energy of the dangling bonds in the rim atoms, which

become abundant when the size of the particles shrinks below 0.1 micron.<sup>3,4</sup> Thus, while the bulk molybdenum atom is bonded to six sulfur atoms, it is only fourfold bonded at the

rim. Likewise, sulfur atoms in the periphery of the layer are bonded to only two molybdenum atoms instead of being linked to three Mo atoms in the bulk. These rim atoms induce instability in the planar MoS<sub>2</sub> structure, which is remedied by folding the layer and healing the unsaturated bonds. These new nanophases were termed inorganic fullerene-like structures (IF). In analogy to carbon fullerenes, these structures include single and multilayer polyhedra (onions) as well as nanotubes. Figure 1 shows a transmission electron microscope (TEM) image of a part of a perfectly crystalline multi-wall WS<sub>2</sub> nanotube. Such long and almost flawless nanostructures can be obtained by a variety of methods in large amounts.

Nanotubes of BN were among the first to be synthesized,<sup>5</sup> followed by the synthesis of IF from most other layered metal dichalcogenides, various oxides, and metal dihalides. (For a recent review consider Ref. 6.) Moreover, nan-

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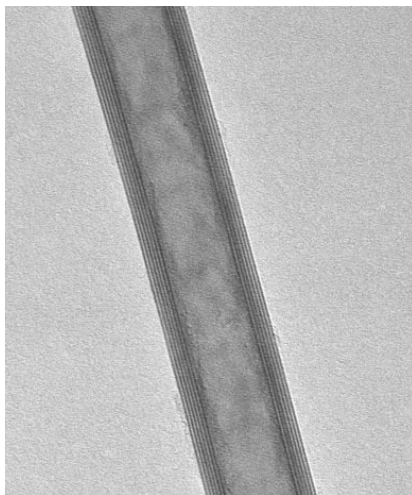


FIG. 1. Part of a WS<sub>2</sub> nanotube imaged by TEM. Note that the distance between each of the two atomic layers (fringes) is 0.62 nm.

otubes and fullerene-like nanoparticles of various other layered compounds with metallic and semiconducting character have been studied via first principle calculations.<sup>7</sup>

More recently, nanotubular structures from 3-D compounds, like GaN<sup>8</sup> or In<sub>2</sub>O<sub>3</sub><sup>9</sup> were reported. Because folding of slabs of 3-D compounds in an even fashion is energetically unfavorable, a new mechanism must be invoked to explain the growth of such nanostructures. It is likely that such nanotubes grow along an easy growth axis, like the (0001) plane, and consequently they are expected to be faceted. The atomic structure of the joints between each two such facets is yet to be determined.

Extensive mathematical research has been devoted to polyhedra made of a single layer, which occur in graphite or in BN. Surprisingly however, mathematical analysis of polyhedra and nanotubular structures made of two and more interconnected layers has started only very recently; see for example Ref. 7. Indeed, most of the inorganic layered materials comprise more than one atomic layer, with strong chemical bonds interconnecting between the atoms of the different layers. Therefore a mathematical analysis of multilayer polyhedra is called for.

In sharp contrast with carbon fullerenes and nanotubes, a synthetic procedure for IF polyhedra with accurate size and shape control is still lacking, to the exception of perhaps BN polyhedra. Such control is required if one wishes to elucidate the properties of such polyhedra on an atomistic basis and determine the structure-properties relationships, accurately. This discrepancy does not seem to be a fundamental obstacle, however, but rather a practical misgiving, which will be overcome in the foreseeable future.

The trigonal prismatic structure of MoS<sub>2</sub> suggests that stable triangles or rhombi can be formed and inserted into the hexagonal (trigonal) framework, rather than pentagons.<sup>10</sup> Indeed MoS<sub>2</sub> tetrahedra and octahedra, having four triangles and six rhombi in their corners, respectively, were found. Such nanoclusters could be considered as the analogues of C<sub>60</sub> in MoS<sub>2</sub> and in various other layered compounds.<sup>11</sup> They can be reproduced from the soot of laser ablated MoS<sub>2</sub> targets as shown in Fig. 2, but their detailed structure is not yet fully understood. Unfortunately, these octahedra cannot be produced in sufficient quantities so far, which would permit a detailed study of their structure and properties and allow for an exquisite comparison with theoretical models.

Unlike their carbon counterparts, the physical properties of IF have not been thoroughly investigated, so far. While MoS<sub>2</sub> nanotubes were found to be semiconductors, their NbS<sub>2</sub> and NbSe<sub>2</sub> analogues were observed to exhibit metallic and even superconducting behavior at low temperatures. In contrast to carbon nanotubes and semiconductor quantum dots, the bandgap of IF-WS<sub>2</sub> was found to decrease with the shrinking diameter of the nanoparticles.<sup>7</sup> This unexpected behavior was attributed, on the one hand, to the small quantum-size effect of the exciton in the <001> direction (perpendicular to the layers), and to the large elastic energy implicated in the folding of the nanostructure.

While the Young's modulus of WS<sub>2</sub> nanotubes was found to be only fifth (~200 GPa) of that of carbon nanotubes, they were nonetheless found to be much more resistant to shockwave impact.<sup>12</sup> The quasi-spherical shape of fullerene-like WS<sub>2</sub> (MoS<sub>2</sub>) nanoparticles; their mechanical stability, and their low

surface energy suggests that they could offer substantial benefits for tribological contacts, especially under extreme loads, where fluid lubricants are squeezed out of the contact area and fail to prevent high friction and wear. The advantageous behavior of these novel solid lubricants has been confirmed through numerous measurements and tests.<sup>13</sup> The commercial application of these nanomaterials in various technologies is further pursued by NanoMaterials, Ltd.

The richness of the chemical apparatus that can be employed for the synthesis and chemical modifications of such nanotubes offers numerous interesting observations and applications for such nanostructures. Thus, MoS<sub>2</sub> nanotubes were found to be a very efficient and selective catalyst for CO methanation.<sup>14</sup> Application of various kinds of nanotubes, like those made of V<sub>2</sub>O<sub>4.5</sub>-alkyl amine, as cathode materials in lithium intercalation batteries,<sup>15</sup> or hydrogen insertion of TiS<sub>2</sub> nanotubes<sup>16</sup> has been studied.

Further work is needed to ameliorate the synthetic apparatus of IF nanoparticles in order to gain accurate size and shape control. Once realized, self-assembled crystals consisting of such nanoparticles are expected to reveal new physical behavior, remotely related, if at all, to the bulk 2-D materials. ■

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### References

1. H. W. Kroto, J. R. Heath, S. C. O'Brein, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
2. S. Iijima, *Nature*, **354**, 56 (1991).
3. A. R. Tenne, L. Margulis, M. Genut, and G. Hodes, *Nature*, **360**, 444 (1992).
4. Y. Feldman, E. Wasserman, D. J. Srolovitz and R. Tenne, *Science*, **267**, 222 (1995).
5. N. G. Chopra, J. Luyken, K. Cherry, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, *Science*, **269**, 966 (1995).
6. M. Nat and C. N. R. Rao, *Dalton Trans.*, **1**, 1-25 (2003).
7. G. Seifert, H. Terrones, M. Terrones, G. Jungnickel, and T. Frauenheim, *Phys. Rev. Lett.*, **85**, 146 (2000).
8. J. Goldberger, R. He, Y. Zhang, S. Lee, H. Yan, H.-J. Choi, and P. Yang, *Nature*, **422**, 599 (2003).
9. Y. Li, Y. Bando, and D. Golberg, *Adv. Mater.*, **15**, 581 (2003).
10. Margulis, G. Salitra, R. Tenne, and M. Talianker, *Nature*, **365**, 113 (1993).
11. P. A. Parilla, A. C. Dillon, K. M. Jones, G. Riker, D. L. Schulz, D. S. Ginley, and M. J. Heben, *Nature*, **397**, 114 (1999).
12. Y. Q. Zhu, T. Sekine, K. S. Brigatti, S. Firth, R. Tenne, R. Rosentsveig, H. W. Kroto, and D. R. M. Walton, *J. Am. Chem. Soc.*, **125**, 1329 (2003).
13. L. Rapoport, N. Fleischer, and R. Tenne, *Adv. Mater.*, **15**, 651 (2003).
14. J. Chen, S.-L. Li, Q. Xu, and K. Tanaka, *Chem. Comm.*, 1722 (2002).
15. M. E. Spahr, P. Stoschitzki-Bitterli, R. Nesper, O. Haas, and P. Novak, *J. Electrochem. Soc.*, **146**, 2780 (1999).
16. J. Chen, S.-L. Li, Z.-L. Tao, Yu-T. Shen, and C.-X. Cui, *J. Am. Chem. Soc.*, **125**, 5284 (2003).

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