מכון ויצמן למדע
WEIZMANN INSTITUTE OF SCIENCE

# Inorganic nanotubes and fullerene-like particles from 2D layered compounds: state of the art


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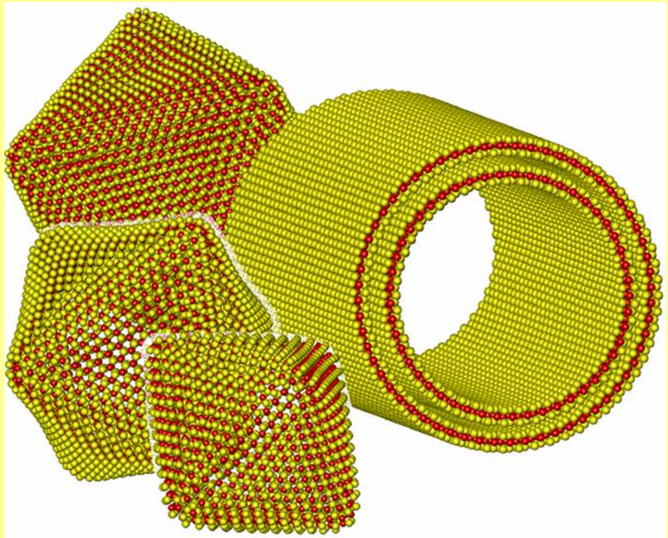
**Adams Seminar, Jerusalem 20.5.12**




**Minerva and Krupp Foundations, GIF, BSF, ISF, IMol&T, IMoST**
**“NanoMaterials, Ltd.”, H. Perlman, Waltcher, Gurwin and Horowitz Foundations, ERC, EU (“AddNano”),**


**Courtesy of Prof. G. Seifert, Dr. A. Enyashin, TU Dresden**

# The historical roots of nanotechnology: Metal nanoparticles in the old art and in modern therapy

- **Strong indications exist that already the Egyptian ancestors mastered some techniques to produce pigments; paints and cosmetics from various nanoparticles. A few more recent examples are due. The Lycurgus cup from the Roman period was produced by gold-silver nanoparticles impregnated into the glass by direct reduction/annealing process**

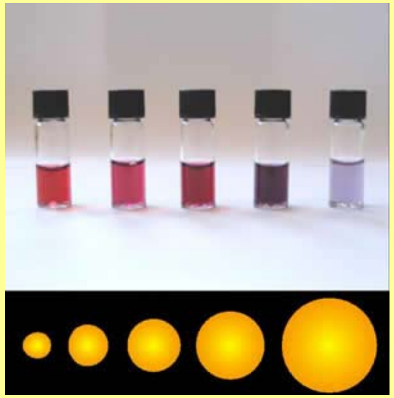
**Reflected light transmitted light**

**Lycurgus Cup**

**(4th century AD) British Museum**


**Industrial production: Ruby-glass baroque period**

**Suspensions of gold nanoparticles**



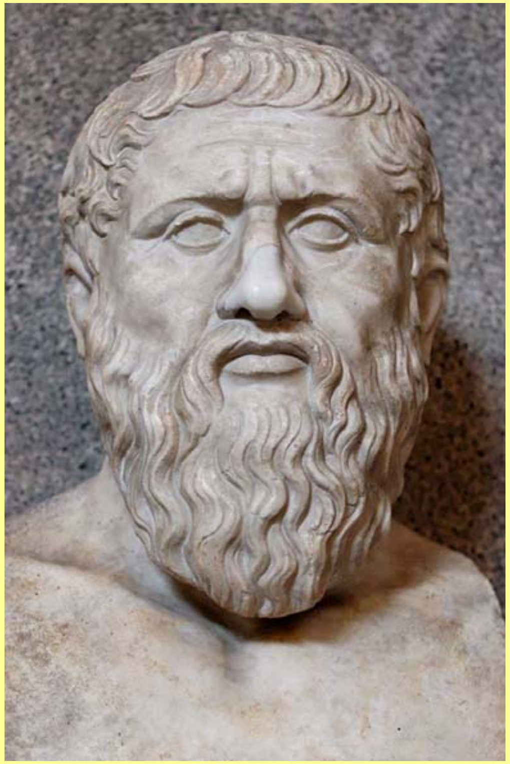
**Gold nanoparticles 2-7 nm**

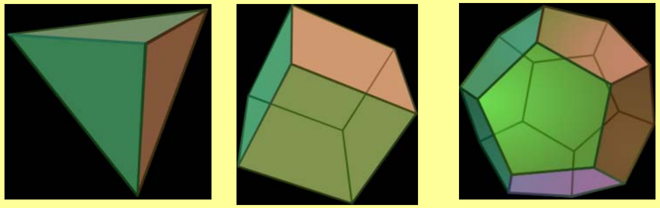
# רקע היסטורי: תקופת יון העתיקה

## Historical roots of fullerenes and nanotubes

(Other names: Pythagoras, Euclid, Theaetetus)

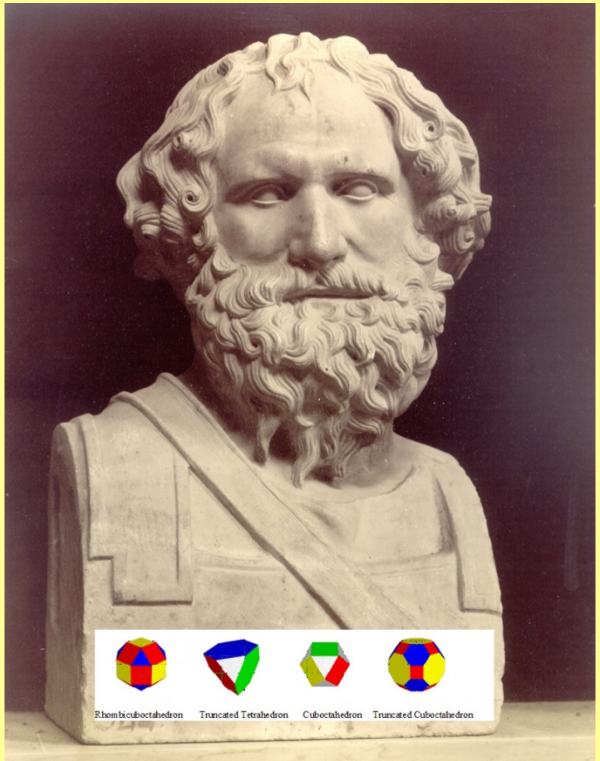
Plato (428-347 BC)





Regular polyhedra

Archimedes (287-211 BC)

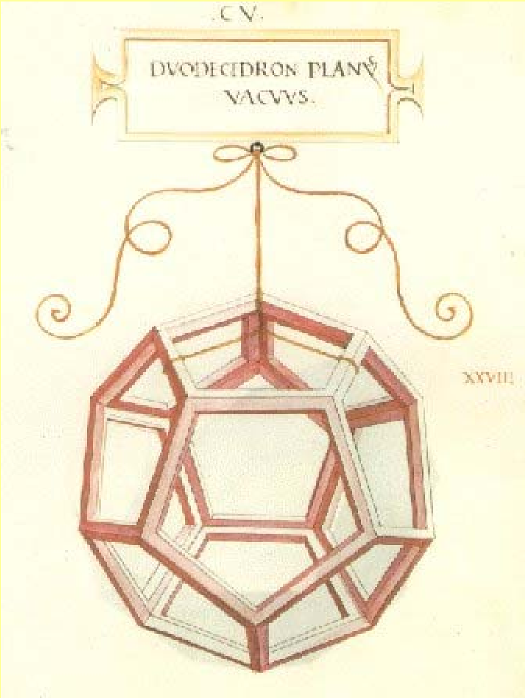



Semiregular polyhedra

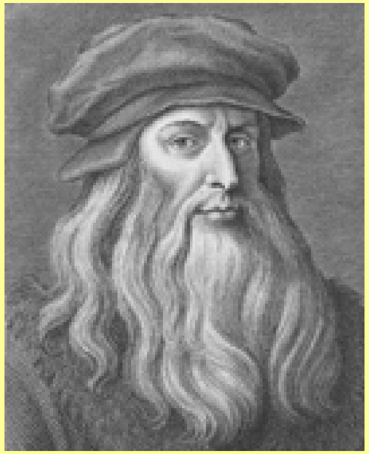
# תקופת הרנסאנס

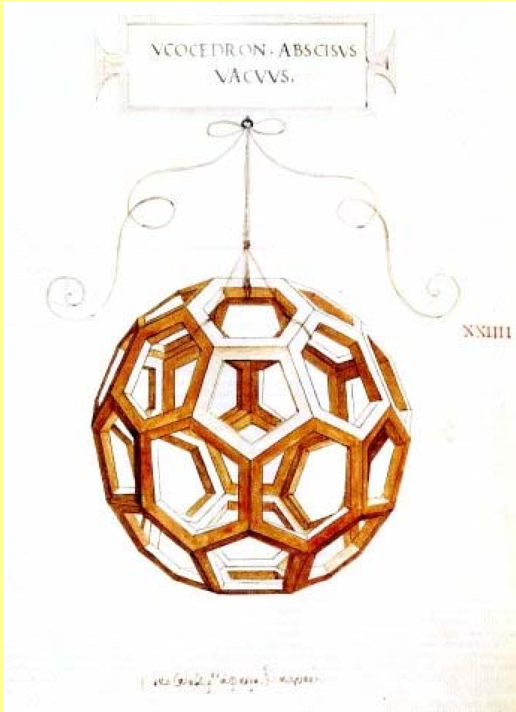
## Polyhedra: used during the Renaissance period by Leonardo de Vinci for decoration

(other names: Kepler-Poinsot, Pierro de-la Francesca, Pacioli, Dürer)




Platonian dodecahedron





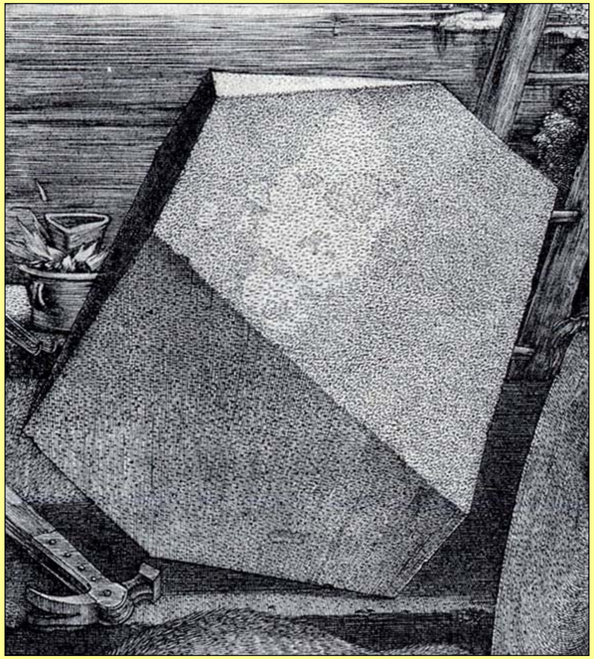

Archimedian: icosaheron

floor of Basilica of St Mark Vencice
Keplerian stellated dodecahedron

# תקופת הרנסאנס

Albrecht Dürer (1471-1528), the Father of Polyhedral Nets


**Melancholia I**



**truncated rhomboid**

# המאה ה-18

## Leonard Euler
## 1707-1783

(Other names: René Descartes, Adrien-Marie Legendre, Augustin Louis Cauchy)

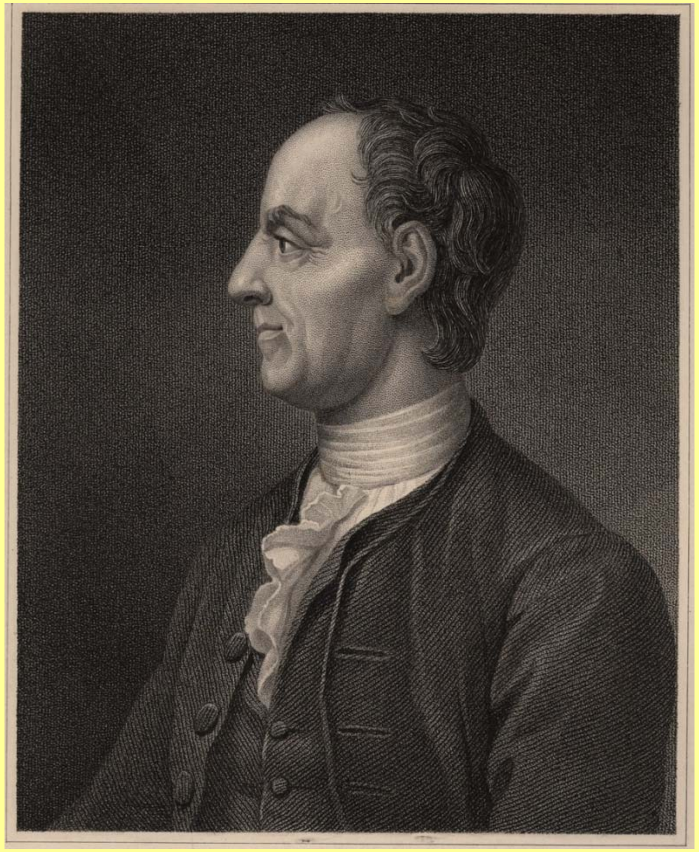
Euler Rule for Archemedians

N+V=E+2
N=P+H

N=polygons
V=vertices
E=edges

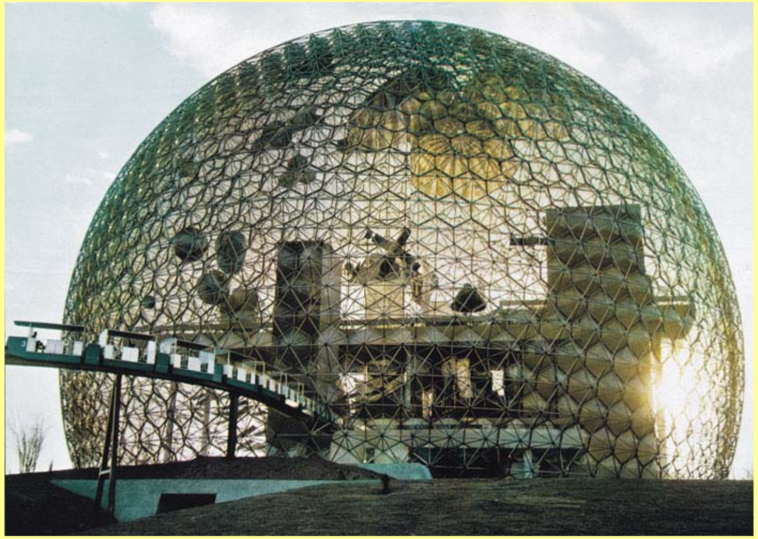
P-pentagons
H-hexagons

12 20

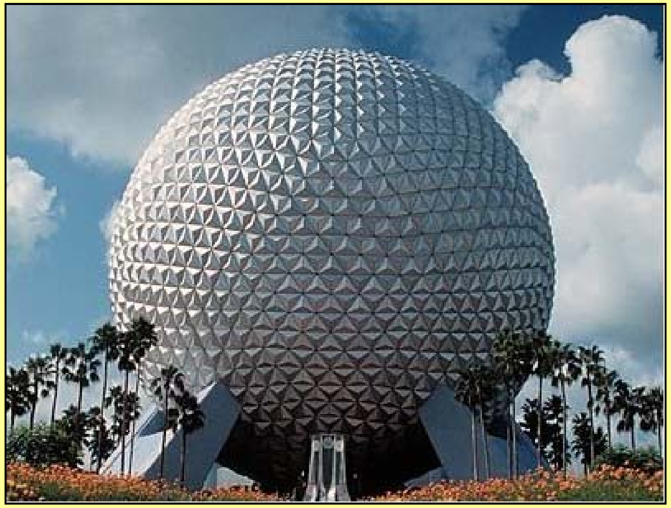


# המאה ה-20
## Geodesic domes

Richard Buckminster Fuller (1895-1983)
(Other names: Schwarzite and MacKay polyhedra)



Expo 67, Montreal



Epcot, Disney World

# המאמר הראשון המרמז על מנגנון ליצירת ננוצינוריות

## (תחילת שינוי הפרדיגמה הישנה- "חללים ריקים אינם אפשריים בחומר")



### *THE STRUCTURE OF THE CHLORITES*

BY LINUS PAULING

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated July 9, 1930

The close approximation of the values of *a* and *b* to those for the micas indicates that these crystals, too, are composed of tetrahedral and octahedral layers. The composition requires that in unit length along *c* there be two tetrahedral layers and two complete octahedral layers such as in brucite. Now we expect that as a rule the two faces of a constituent layer of a layer crystal will be equivalent, for if they were not equivalent there would be a tendency for the layer to curve, one face becoming concave and one convex, and this tendency would in general not be overcome by the relatively weak forces operative between adjacent layers. This symmetry is possessed by the layers of nearly all known layer structures—the micas, brittle micas, etc., brucite, hydrargillite, cadmium chloride, molybdenite and the A-modification of the sesquioxides. It is probable that

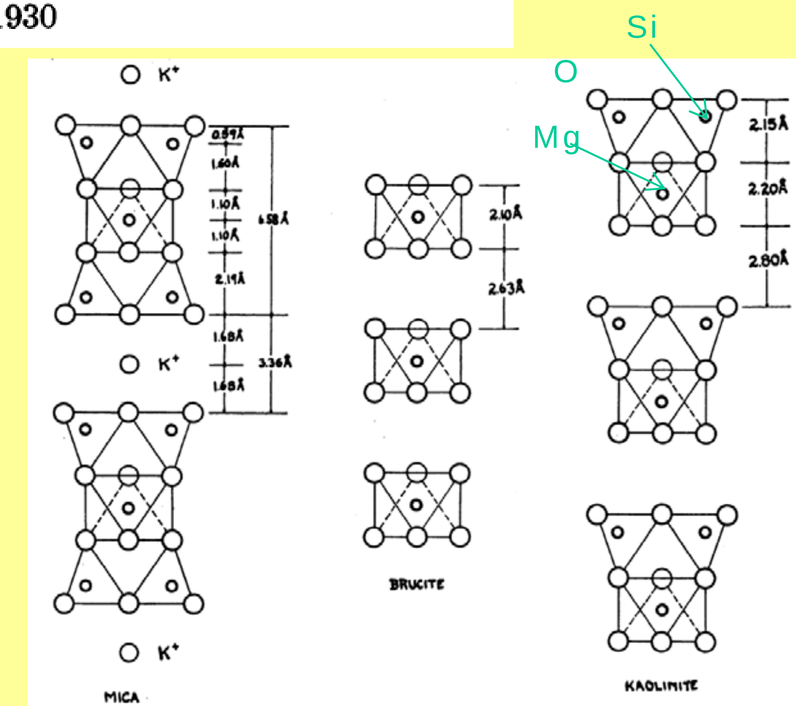



FIGURE 1

# מאמר ראשון על ננוצינוריות מטיפוס chrysotile (asbestos)



## Technical Papers

### Tubular Crystals of Chrysotile Asbestos

**Thomas F. Bates, Leonard B. Sand, and John F. Mink**

***The Pennsylvania State College, State College, Pennsylvania***

Electron micrographs taken at The Pennsylvania State College and at the National Bureau of Standards show features which indicate that both natural and synthetic chrysotile crystallizes in the form of hollow cylindrical tubes. These bear a striking resemblance to similar crystals of the clay mineral endellite described in 1949 (*2*) by the senior author together with F. A. Hildebrand and Ada Swineford. Fig. 1 is an electron micrograph of halloysite (dehydrated endellite) from Leaky, Real County, Texas. Figs. 2, 3, and 4 are micrographs of


Fig. 1.

chrysotile synthesized by Bowen and Tuttle (*3*) and first studied at high magnification by H. F. McMurdie and M. Swerdlow at the National Bureau of Standards for the Geophysical Laboratory.

Fig. 1 shows (at A) an oblique view of an end section of a tube, (at B) a tube which upon dehydration has split longitudinally and partly unrolled at one end, and (at C) so-called multiple tubes where one cylinder

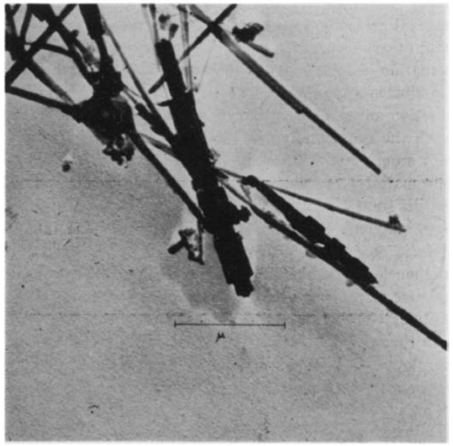



Fig. 2.

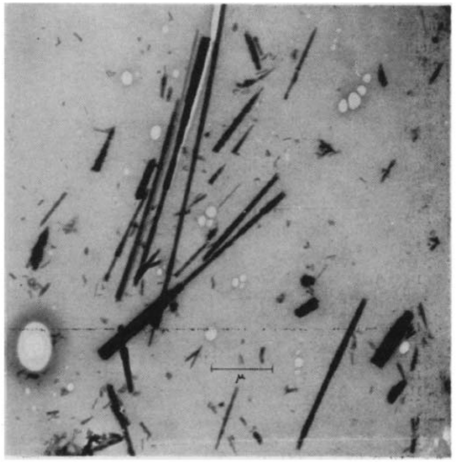
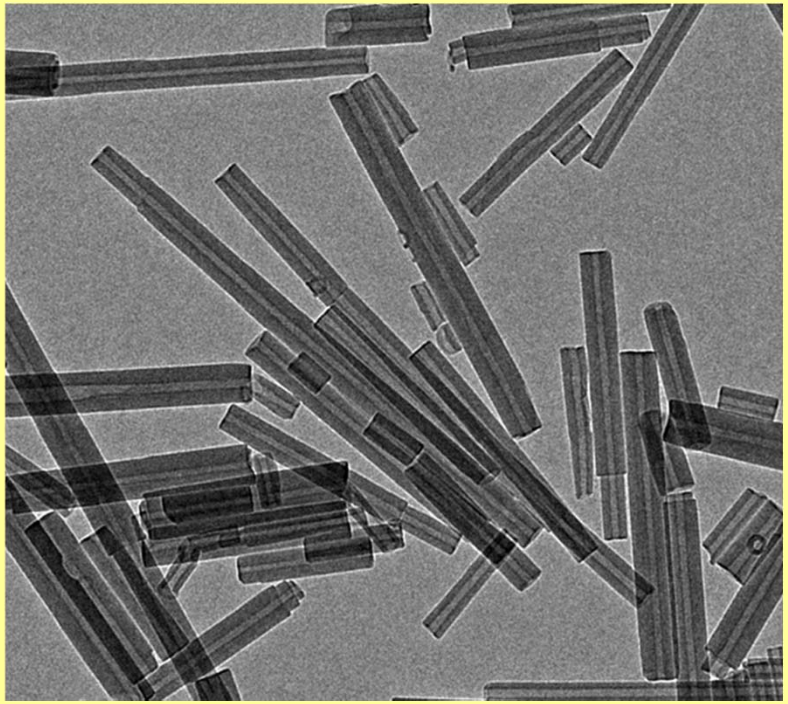
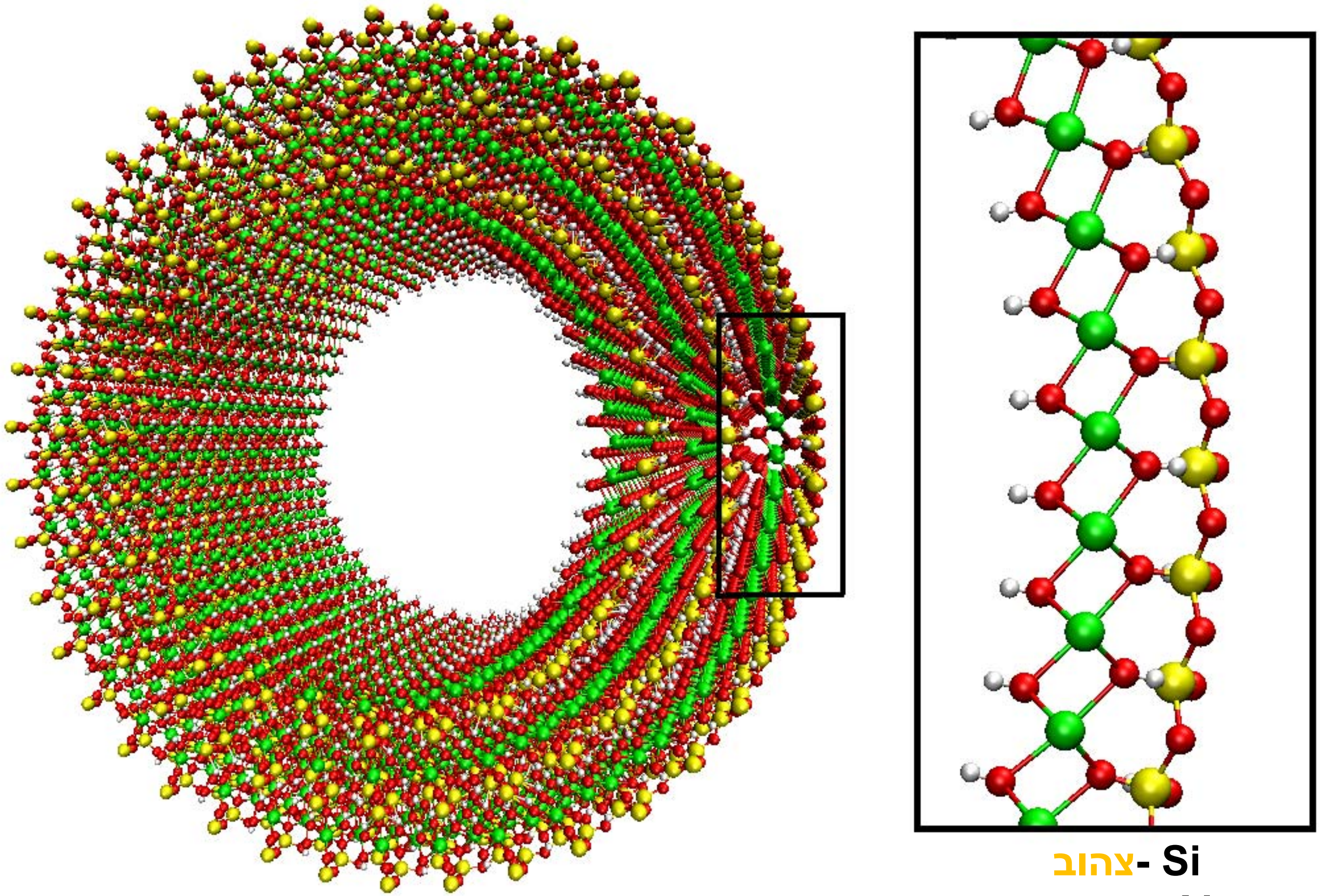



Fig. 3.



תמונת מיקרוסקופ של ננוצינוריות מטיפוס chrysotile

# האסימטריה בסריג הגבישי גורמת ליצירת ננוצינוריות



צהוב- Si
ירוק - Al
אדום - O

Chrysotile

Courtesy of Dr. A. Enyashin, RAS, Ekaterinburg

# המאמר הראשון על ננוצינוריות של פחמן

L.V. Raduskevich and V.M. Lukyanovich, *Journal of Physical Chemistry* (in Russian), Vol. 26, pp. 88-95 (1952)

1952 ЖУРНАЛ ФИЗИЧЕСКОЙ ХИМИИ т. XXVI, вып. 1

## О СТРУКТУРЕ УГЛЕРОДА, ОБРАЗУЮЩЕГОСЯ ПРИ ТЕРМИЧЕСКОМ РАЗЛОЖЕНИИ ОКИСИ УГЛЕРОДА НА ЖЕЛЕЗНОМ КОНТАКТЕ

*Л. В. Радушкевич и В. М. Лукьянович*

Данная работа возникла в связи с электронно-микроскопическим изучением структуры различных адсорбентов, главным образом активных углей, графита и т. п. При исследовании препаратов углерода мы обратили внимание на сажу, получающуюся при разложении окиси углерода на железном контакте при температуре около 600° С. Так как сажа из окиси углерода изучалась адсорбционными методами и для нее была определена удельная поверхность по изотерме адсорбции, то представлялось интересным проверить эти результаты путем непосредственного измерения размеров частиц. Но уже первые наблюдения, сделанные нами [1], показали, что образующийся из СО углерод имеет весьма своеобразную структуру, до настоящего времени никем не описанную, и поэтому, естественно, наше внимание было перенесено на систематическое изучение этой структуры, а также на условия ее образования.

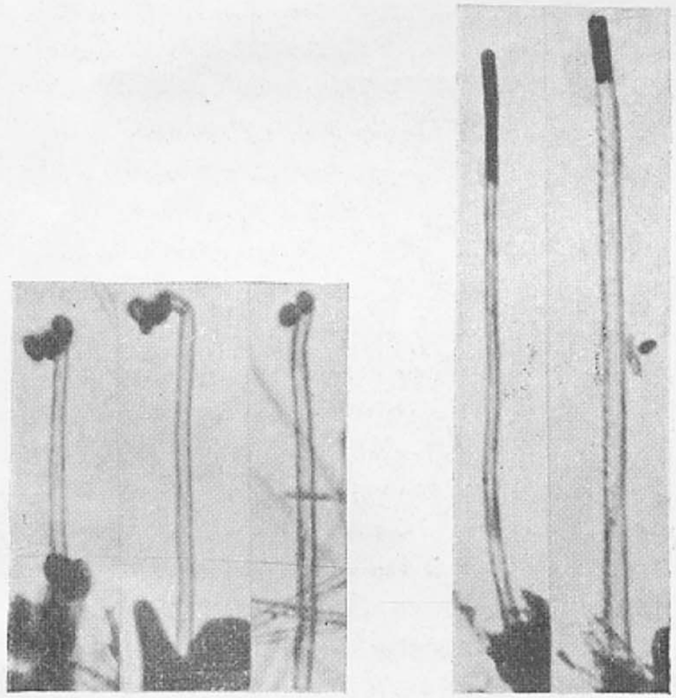


Рис. 7
× 20.000

# שני המאמרים החשובים ביותר בננו-פחמן

(the discovery of carbon fullerenes and carbon nanotubes)

162 LETTERS TO NATURE NATURE VOL. 318 14 NOVEMBER 1985

## $C_{60}$: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

**During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The $C_{60}$ molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.**

**Fig. 1** A football (in the United States, a soccerball) on Texas grass. The $C_{60}$ molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

graphite fused six-membered ring structure. We believe that the distribution in Fig. 3*c* is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise

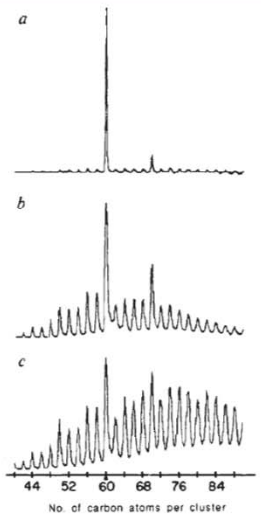



**Fig. 3** Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an



## Helical microtubules of graphitic carbon

**Sumio Iijima**

NEC Corporation, Fundamental Research Laboratories, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

**The synthesis of molecular carbon structures in the form of $C_{60}$ and other fullerenes[1] has stimulated intense interest in the structures accessible to graphitic carbon sheets. Here I report the preparation of a new type of finite carbon structure consisting of needle-like tubes. Produced using an arc-discharge evaporation method similar to that used for fullerene synthesis, the needles grow at the negative end of the electrode used for the arc discharge. Electron microscopy reveals that each needle comprises coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50. On each tube the carbon-atom hexagons are arranged in a helical fashion about the needle axis. The helical pitch varies from needle to needle and from tube to tube within a single needle. It appears that this helical structure may aid the growth process. The formation of these needles, ranging from a few to a few tens of nanometres in diameter, suggests that engineering of carbon structures should be possible on scales considerably greater than those relevant to the fullerenes.**

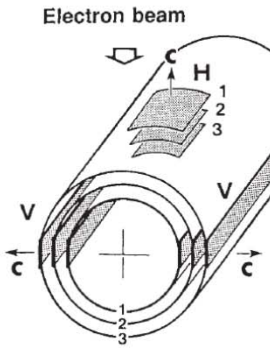



FIG. 2 Clinographic view of a possible structural model for a graphitic tubule. Each cylinder represents a coaxial closed layer of carbon hexagons. The meaning of the labels V and H is explained in the text.

graphite filaments[5]. The apparatus is very similar to that used for mass production of $C_{60}$ (ref. 9). The needles seem to grow plentifully on only certain regions of the electrode. The electrode

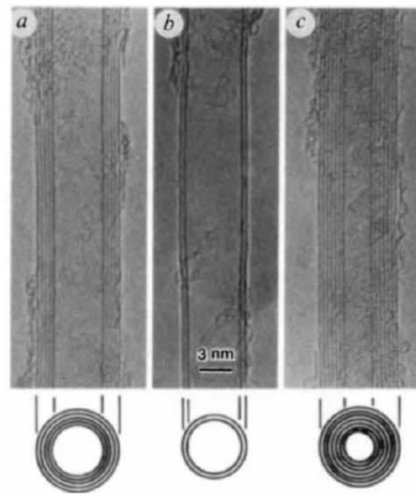
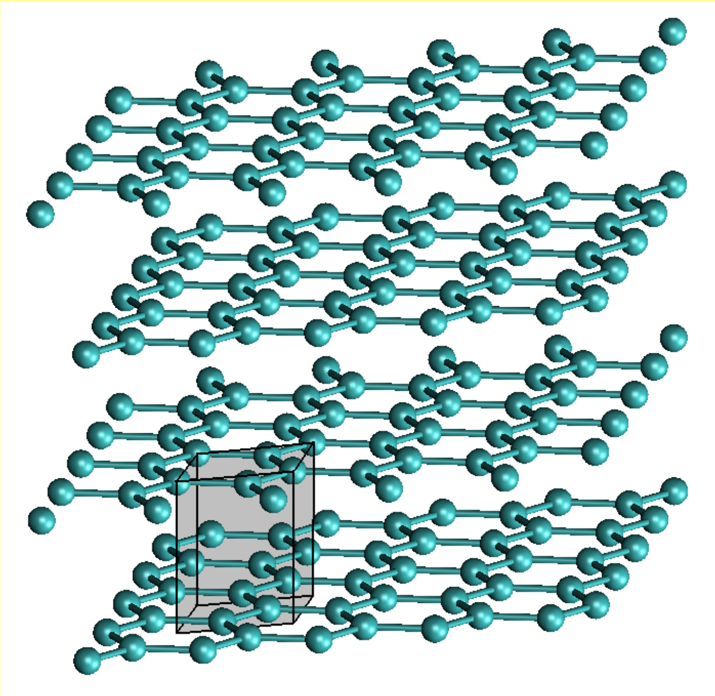
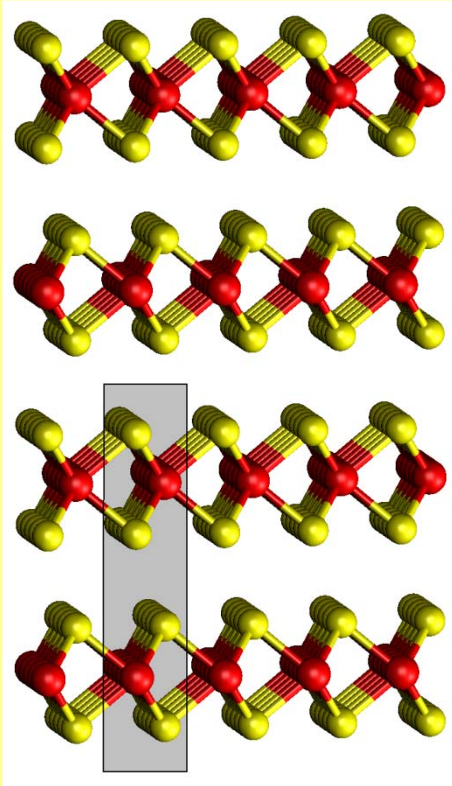



FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

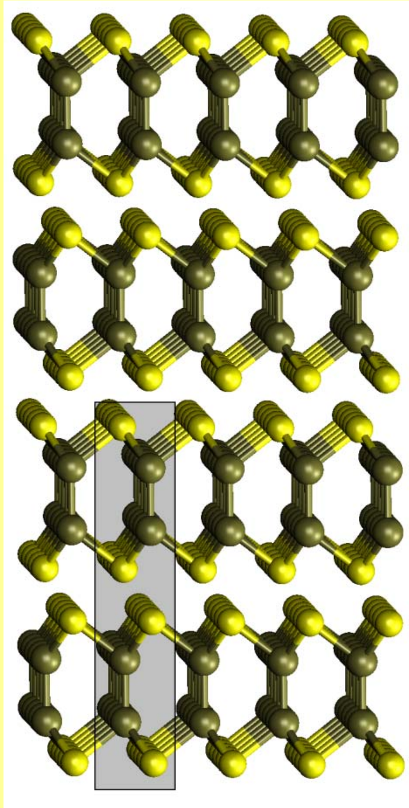
# חומרים (תרכובות) שכבתיים



Graphite



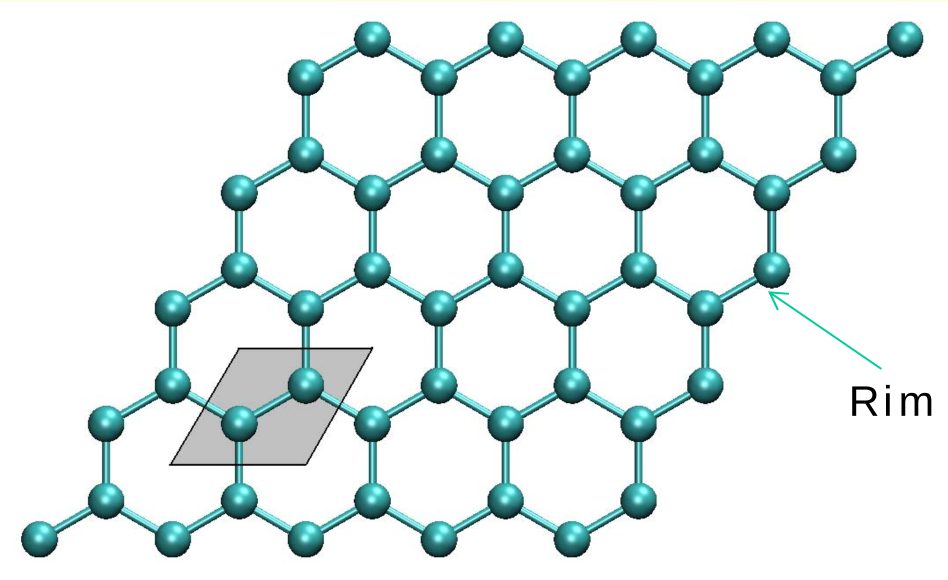
$MoS_2$



GaS

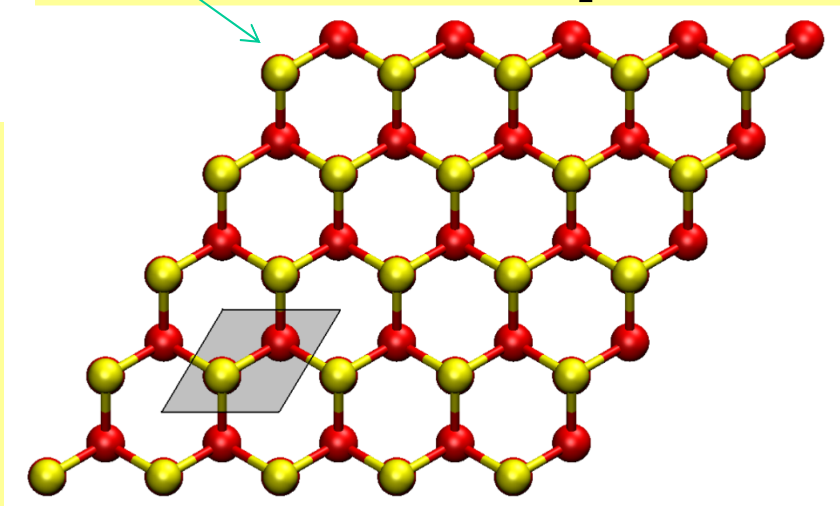
# שכבה יחידה (מבט מלמעלה)

## מה מקורה של אי היציבות המבנית של המבנה השטוח



Rim atoms

$MoS_2$



Graphene

# עדויות ראשונות לקיומם של מבני-ננו חלולים וסגורים של מוליבדנום דיסולפיד

R. R. Chianelli; E. B. Prestridge; T. A. Pecoraro; J. P. DeNeufville

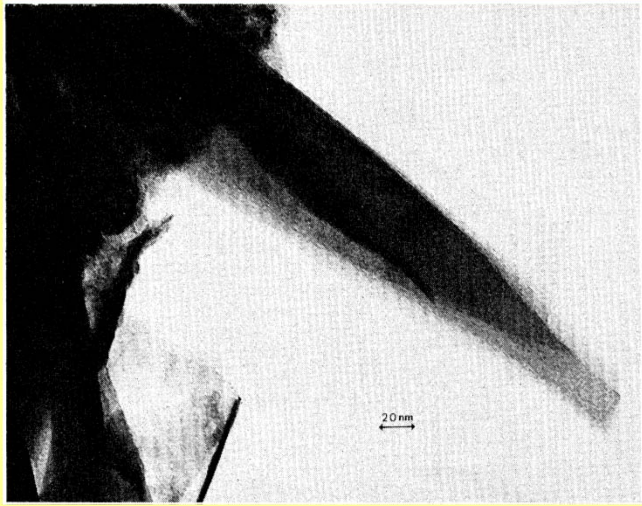
*Science*, New Series, Vol. 203, No. 4385 (Mar. 16, 1979), 1105-1107.

## Molybdenum Disulfide in the Poorly Crystalline ''Rag'' Structure

Abstract. *Molybdenum disulfide has been prepared in an unusual poorly crystalline form, termed the ''rag'' structure, consisting of several stacked but highly folded and disordered S-Mo-S layers. This previously unknown structure demonstrates the flexible and macromolecular nature of the layered transition metal dichalcogenides. The determination of this structure provides a basis for understanding its highly broadened x-ray diffraction pattern and relatively low surface area, and is a starting point for optimizing the catalytic and surface properties of molybdenum disulfide.*

structure single layers of transition metals are sandwiched between two layers of close-packed chalcogen atoms. Within these layers the transition metal atoms are bound to six sulfur atoms which are arranged trigonally ($MoS_2$) or octahedrally ($TiS_2$) about the metal. Each sulfur atom bridges three transition metal atoms within the same layer, forming the only strong bonds in the structure. Because of these strong intralayer forces, the layers can be viewed as two-dimensional macromolecules which stack, bound only by van der Waals forces, to form three-dimensional crystals (*4*). Alkali metals and organic bases can be inserted (intercalated) between these layers (*5*).

We report here another manifestation of the anisotropic and macromolecular



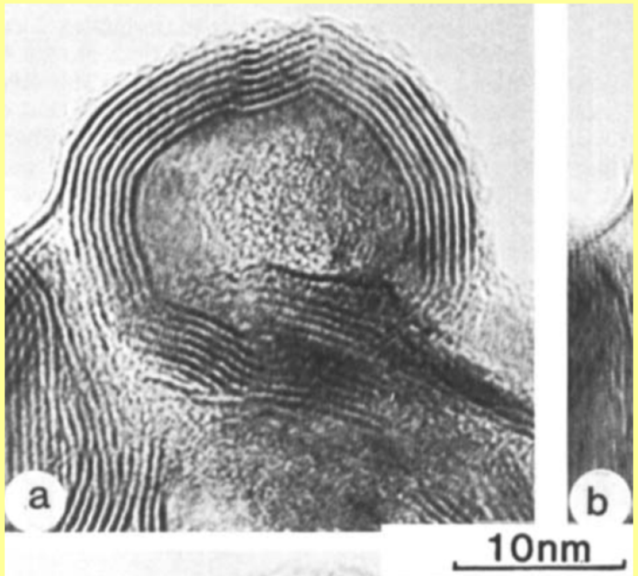

JOURNAL OF ELECTRON MICROSCOPY TECHNIQUE 3:67–93 (1986)

## Transmission Electron Microscopy of Catalysts

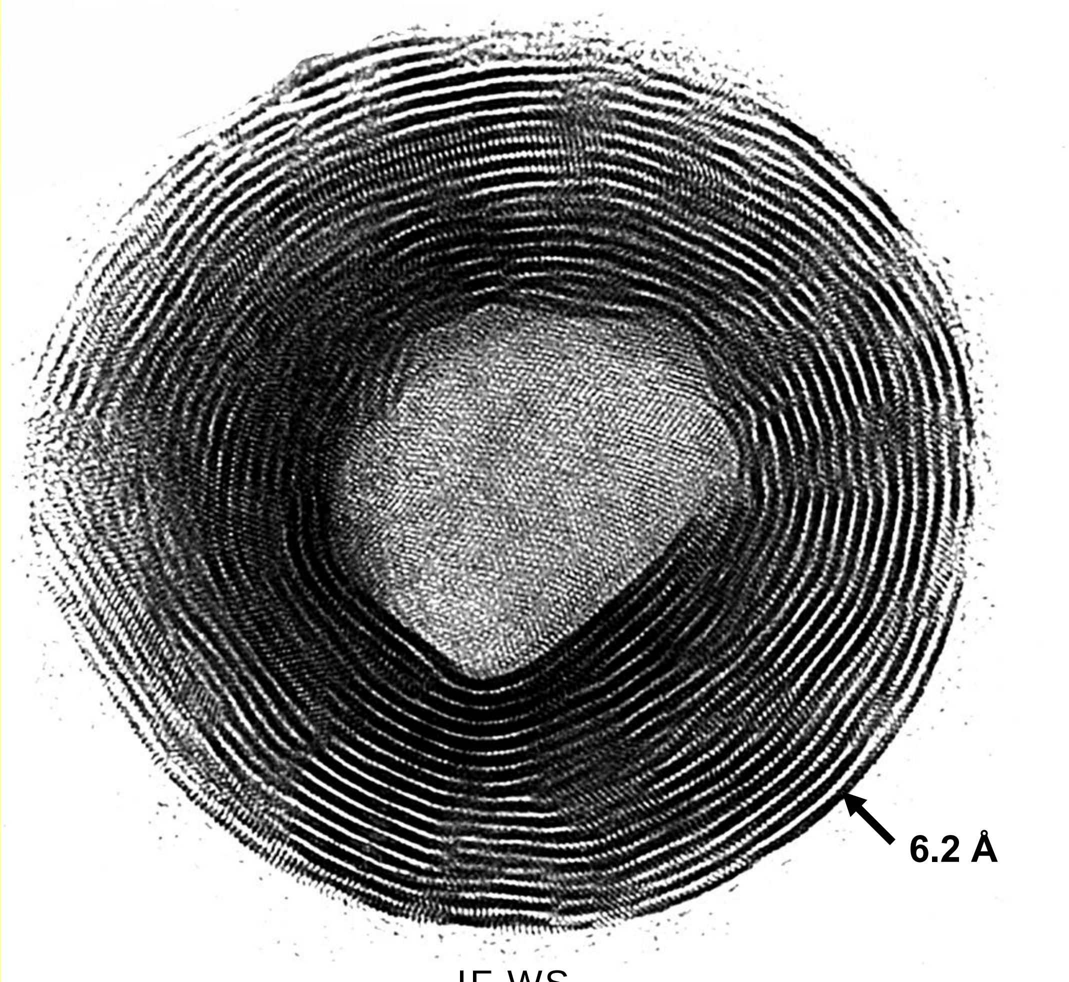
J.V. SANDERS
*CSIRO Division of Materials Science, University of Melbourne, Parkville, Victoria, Australia 3168*

***KEY WORDS*** Catalyst structure, Transmission electron microscopy, Review

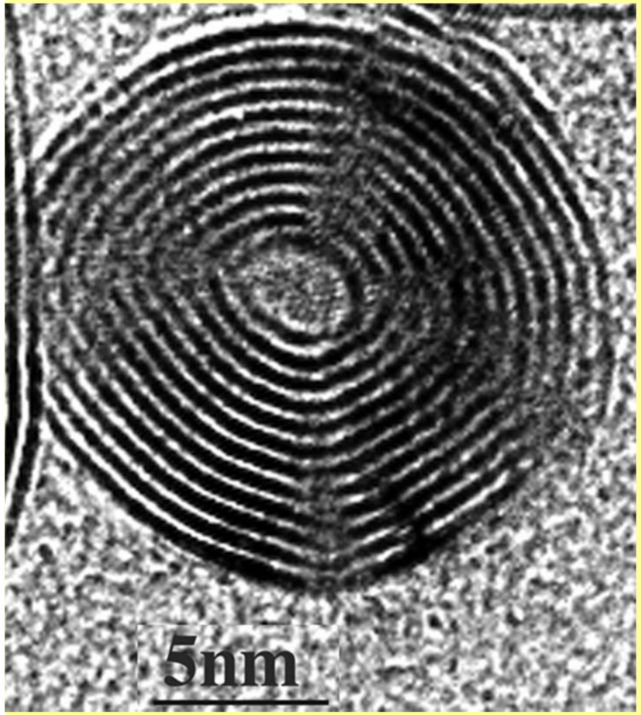
***ABSTRACT*** The determination of the structures of catalysts is an important step in understanding their behaviour and in developing new or improved catalysts. By their nature, catalysts mostly have a structure which can be resolved only by transmission electron microscopy (TEM) used near its limit of applicability. This article discusses recent selected examples of the use of TEM to examine materials used as catalysts, such as clusters of atoms, small crystalline particles, the materials (oxides) on which these are supported, zeolites, and deposits of carbon which often form on catalysts during catalytic reactions. Interpretation of the images is often aided by the techniques of image processing.



## תמונות מיקרוסקופ של צבירים רב-מולקולריים (IF)

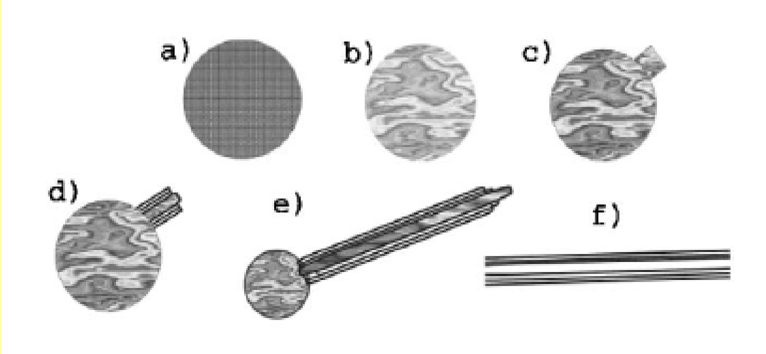



IF-$WS_2$

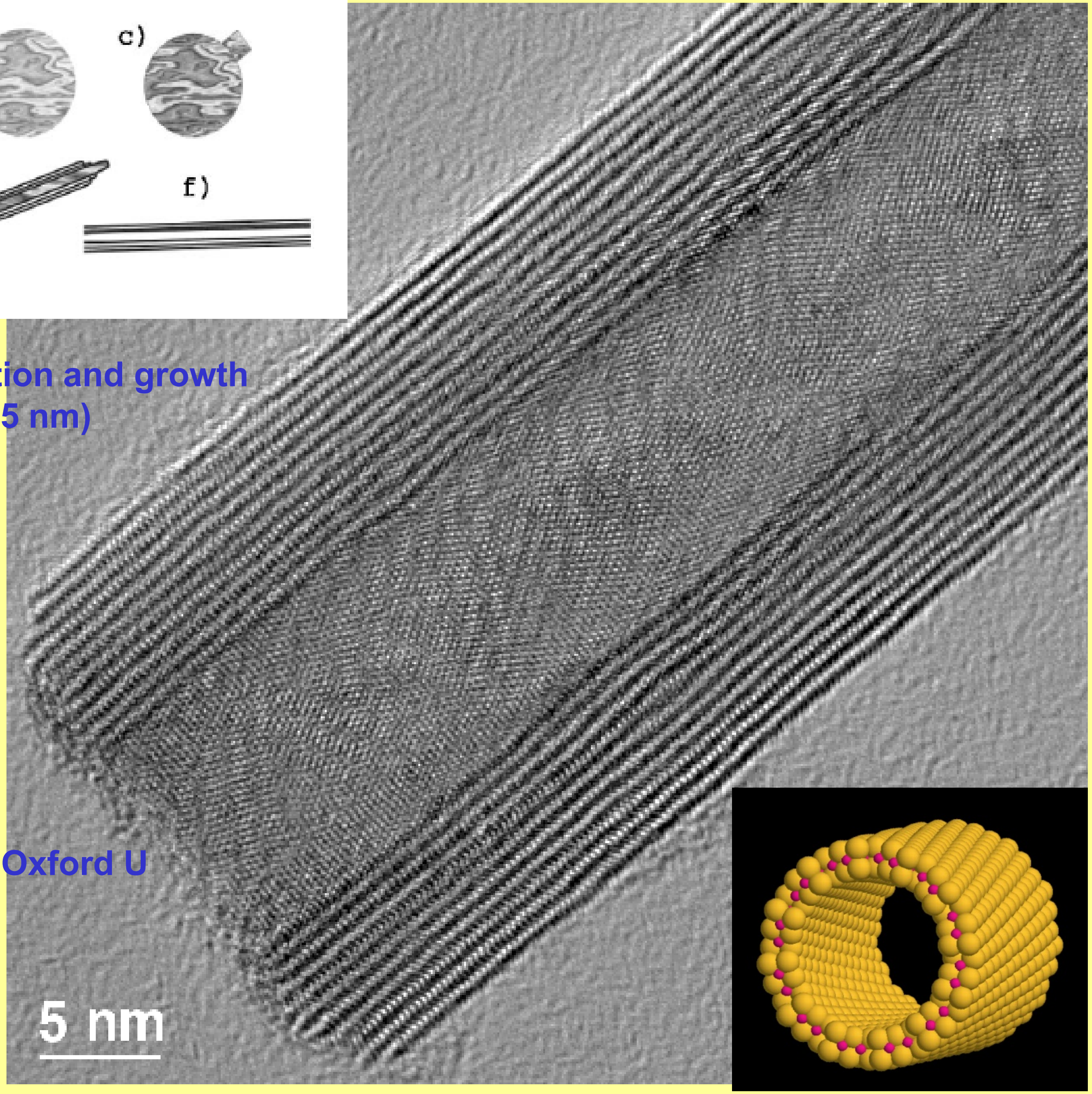



IF-$MoS_2$

# Multiwall $WS_2$ nanotubes (type I)



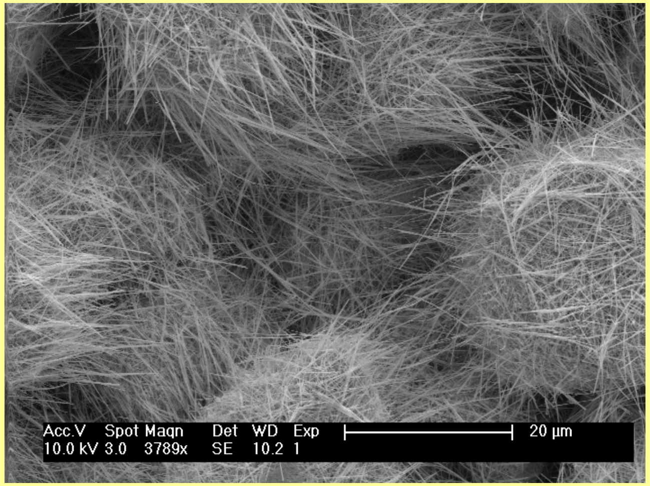

Spontaneous nucleation and growth
Thin nanotubes (20-25 nm)

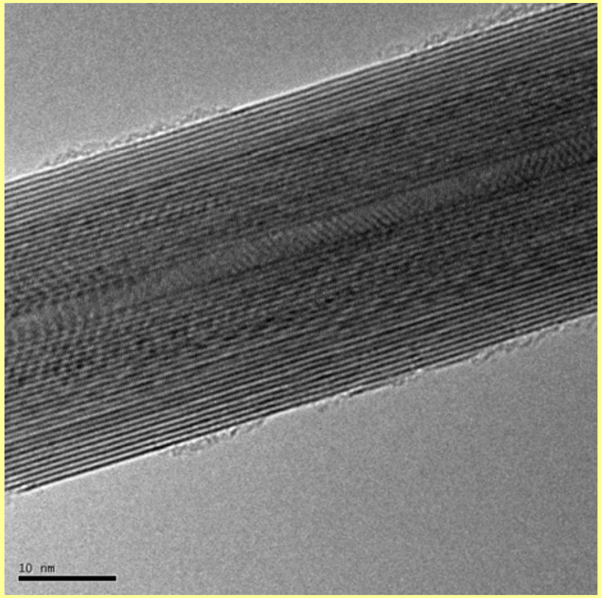


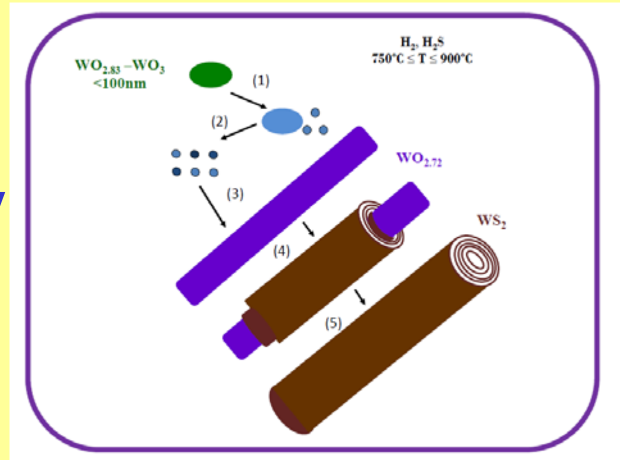

R. Dunin-Borkowski, Oxford U
1996

R. Rosentsveig et al,, *Chem. Mater*. 14, 471 (2002)
G. Seifert, Th. Köhller, and R. Tenne, *J. Phys. Chem. B* 106, 2497-2501 (2002)

# Mass production of multiwall $WS_2$ nanotube (type II)


**Oxide nanowhisker growth followed by diffusion controlled sulfidization of the oxide core (30-150 nm nanotubes)**

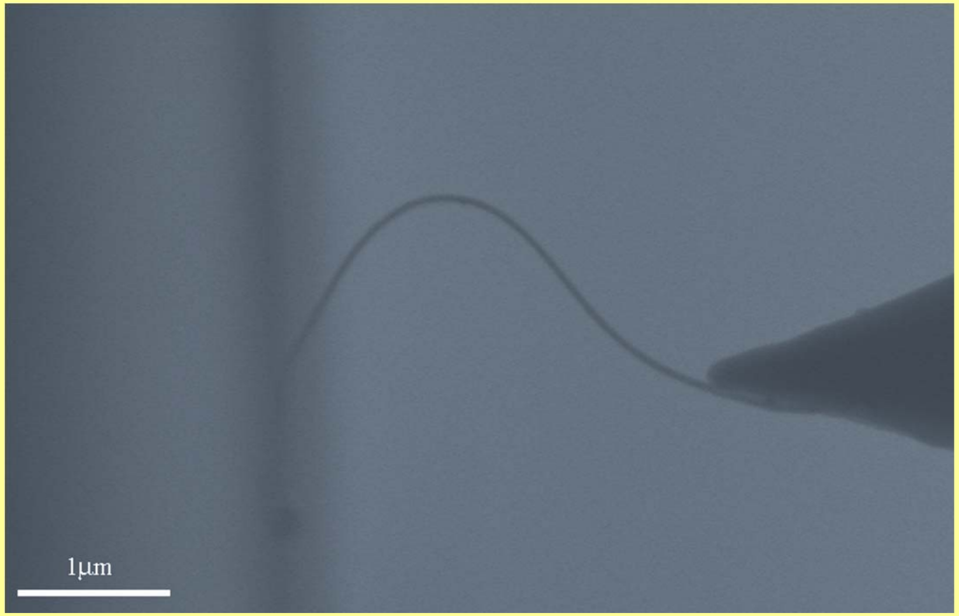
**A. Rothschild et al., *JACS* 122, 5169 (2000)**
**A. Zak. et al., *Nano* 4, 91 (2009)**
**A. Zak et al., *Sensors and Transd. J.*, in press**

**$H_2$, $H_2S$**
**750ºC ≤ T ≤ 900ºC**

**"NanoMaterials"**

# SEM view of a buckling of an individual $WS_2$ nanotube

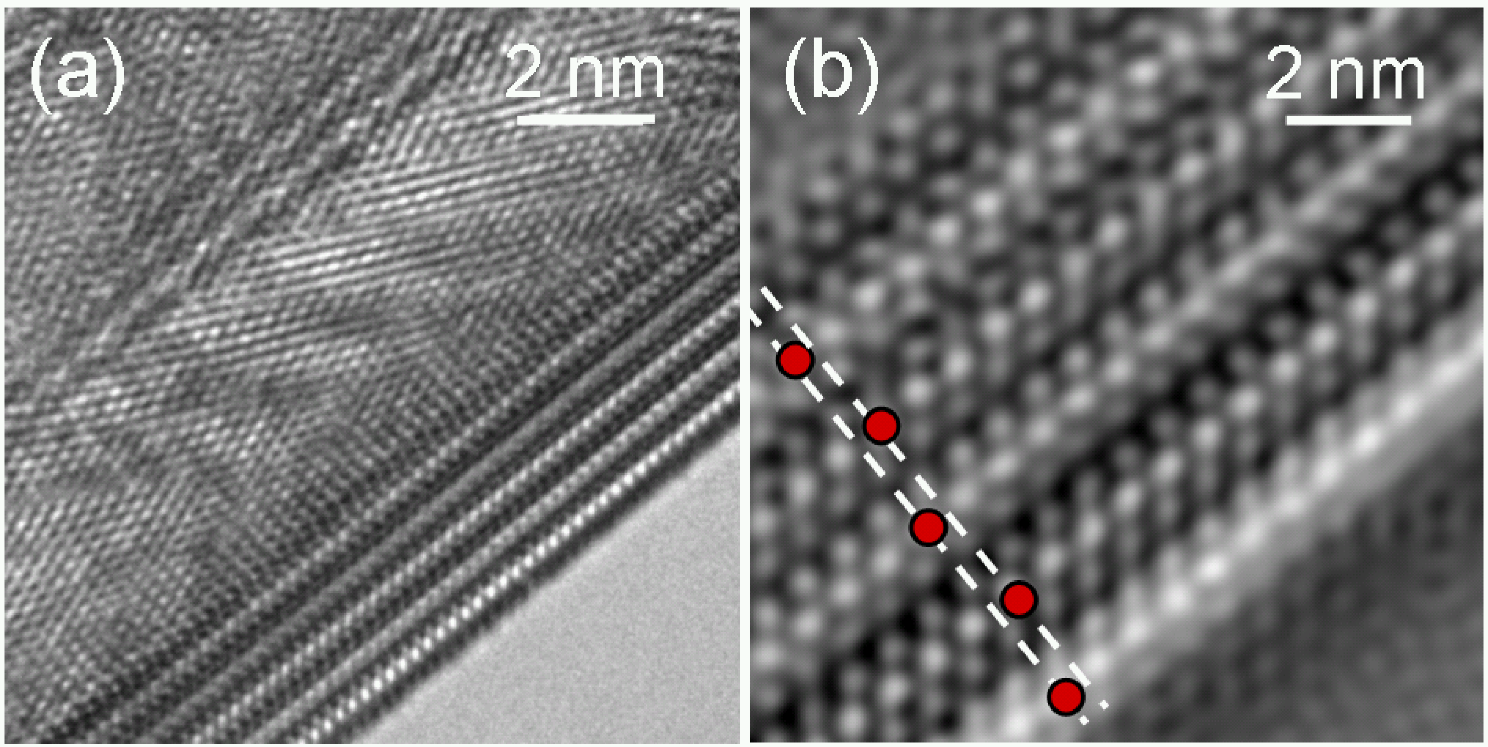
***E*=150-160 GPa**




**I. Kaplan-Ashiri, K. Gartsman, H.D. Wagner,**
**V. Ivanovskya, T. Heine, G. Seifert, and R. Tenne, *PNAS*, 103, 523 (2006)**

# Aberration corrected UHRTEM of $WS_2$ nanotube

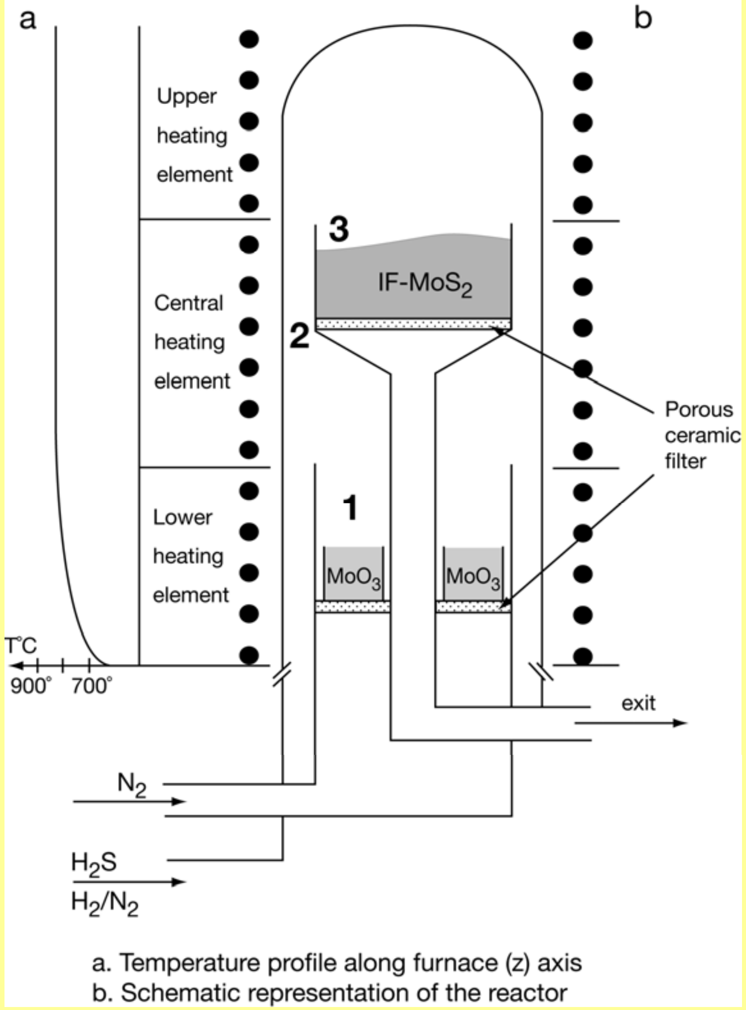
**NCSI image of $WS_2$ nanotube recorded in an aberration-corrected FEI Titan 80-300 at 80 kV. Atoms are represented as white signal over the mean background. (b) Enlarged view of the frame seen in (a), containing the phase of the exit-plane wavefunction retrieved by focal series reconstruction of the same area. Simulations show that the roll-up vectors are (0, 98) (8, 107) (0, 123) (0, 134) (0, 146) and a chiral angle of 3.6º. The relative shift of the shells against each other is demonstrated by the schematic lines, marking W atoms at the edge of the shells.**

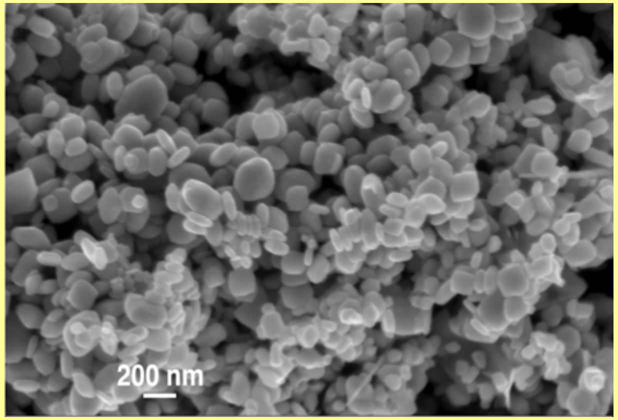


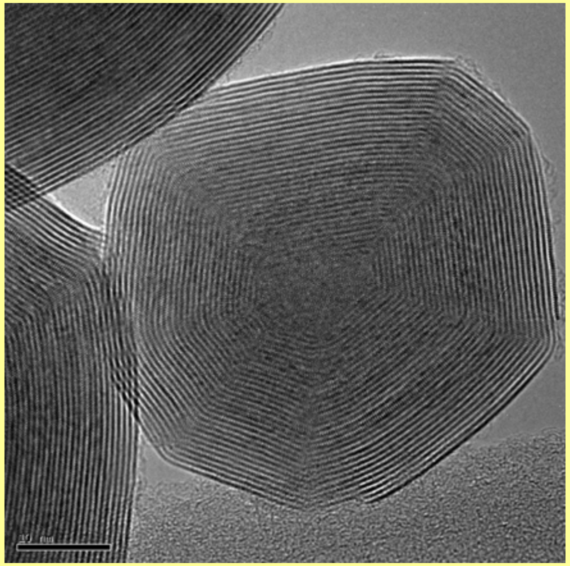

Ernst Ruska–Centrum für Mikroskopie und Spektroskopie mit Elektronen
ER-C

**M. Bar-Sadan, L. Houben, A. Enyashin, G. Seifert, and R.Tenne,**
***Proc. Natl. Acad. Sci* 105, 15643 (2008)**

# Scaling up the synthesis of IF-$MoS_2$



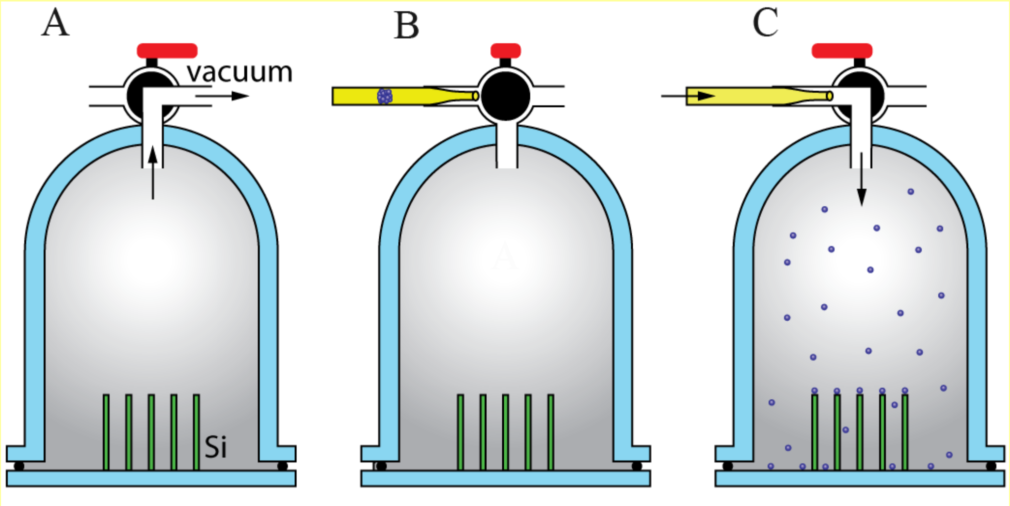



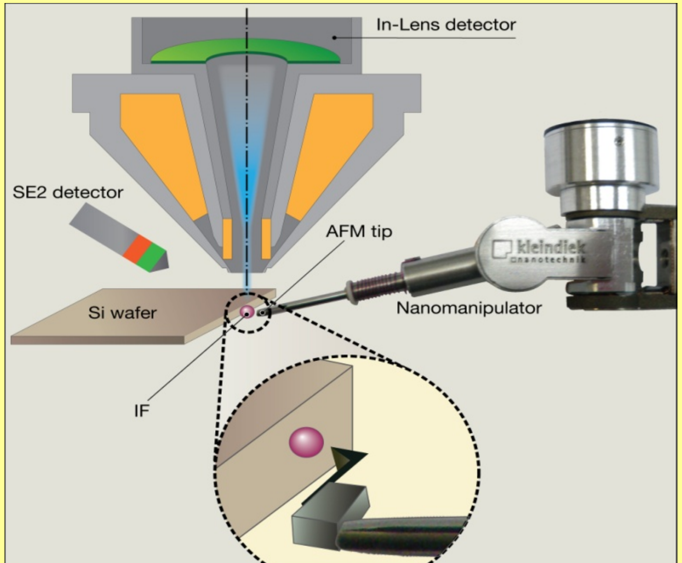
**1. evaporation; 2. condensation of suboxide; 3. sulfidization starts**

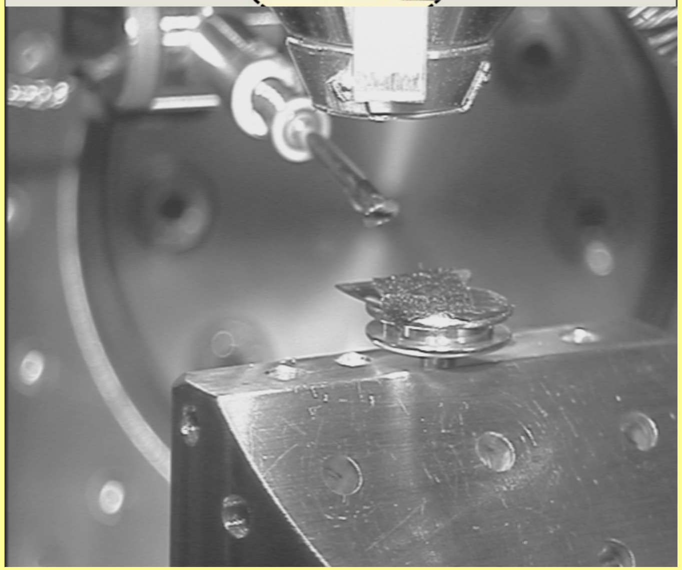
**A. Zak et al., *JACS* 122, 11108 (2000)**

**R. Rosentsvieg, Y. Novema et al., *J. Mater. Chem.*, 19, 4368 (2009)**

# Measuring the mechanics of individual IF nanoparticles in the SEM

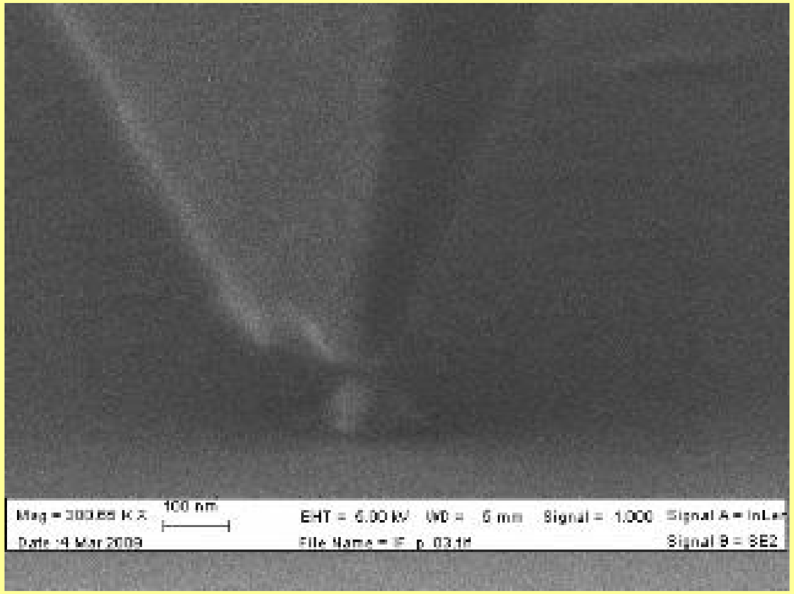


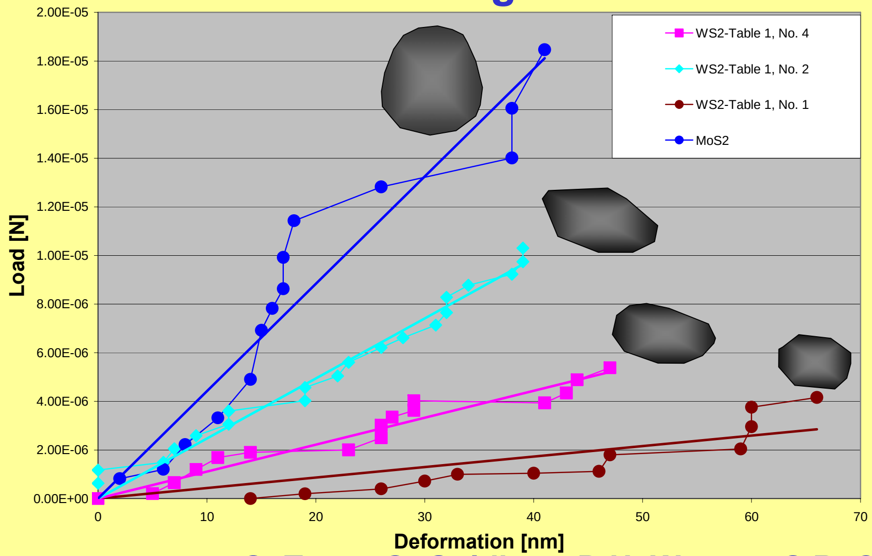



O. Tevet, O. Goldbart, H.D. Wagner and R. Tenne

# Pressing individual IF-$WS_2$ nanoparticle




## Calculated strength- 1-2.5GPa



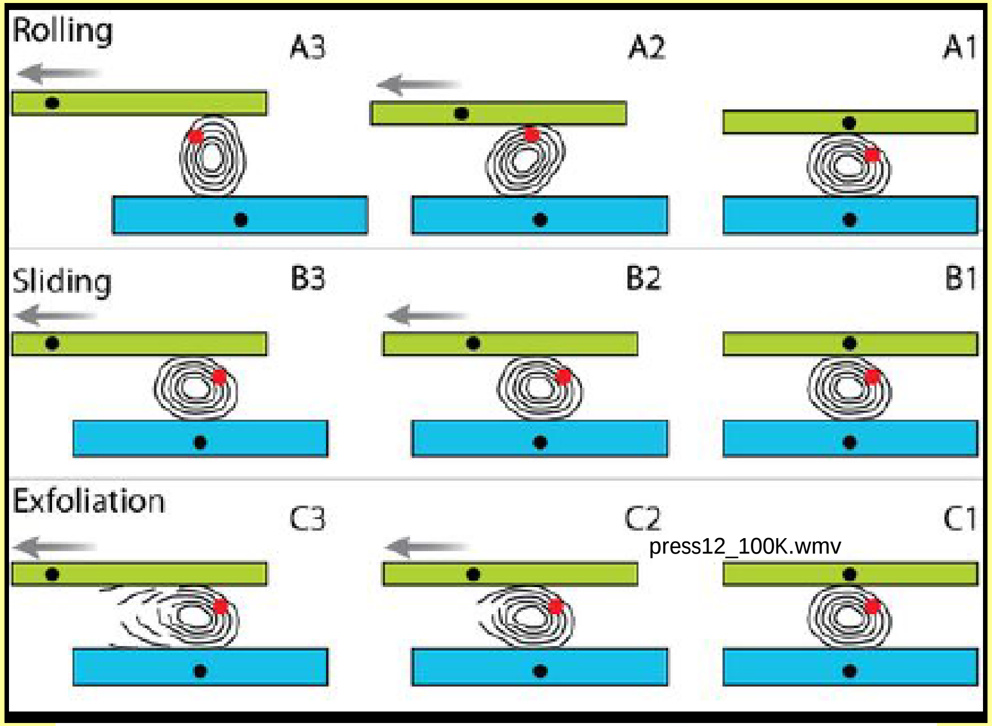

O. Tevet, O. Goldbart, D.H. Wagner, S.R. Cohen, R. Rosentzveig, R. Popovitz-Biro and R. Tenne, *Nanotechnology* 21 365705 (2010)

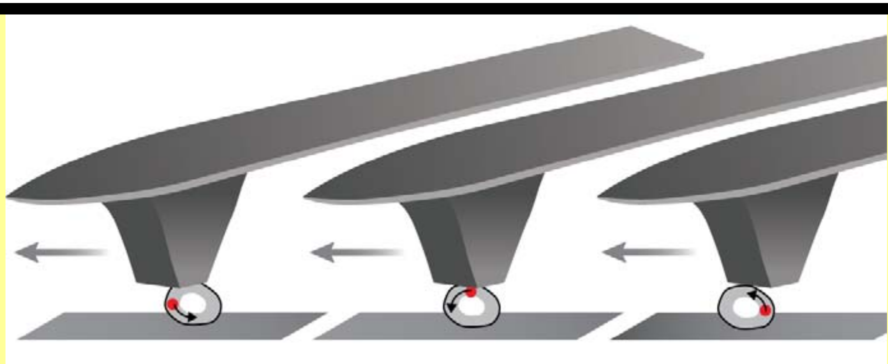
# On the mechanism of lubrication

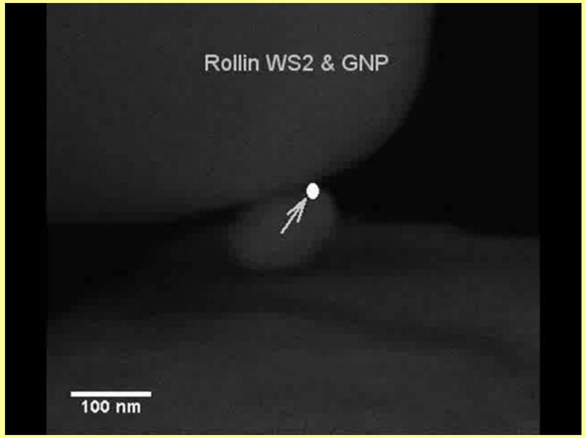
0.6 GPa

1.0 GPa

1.2 GPa



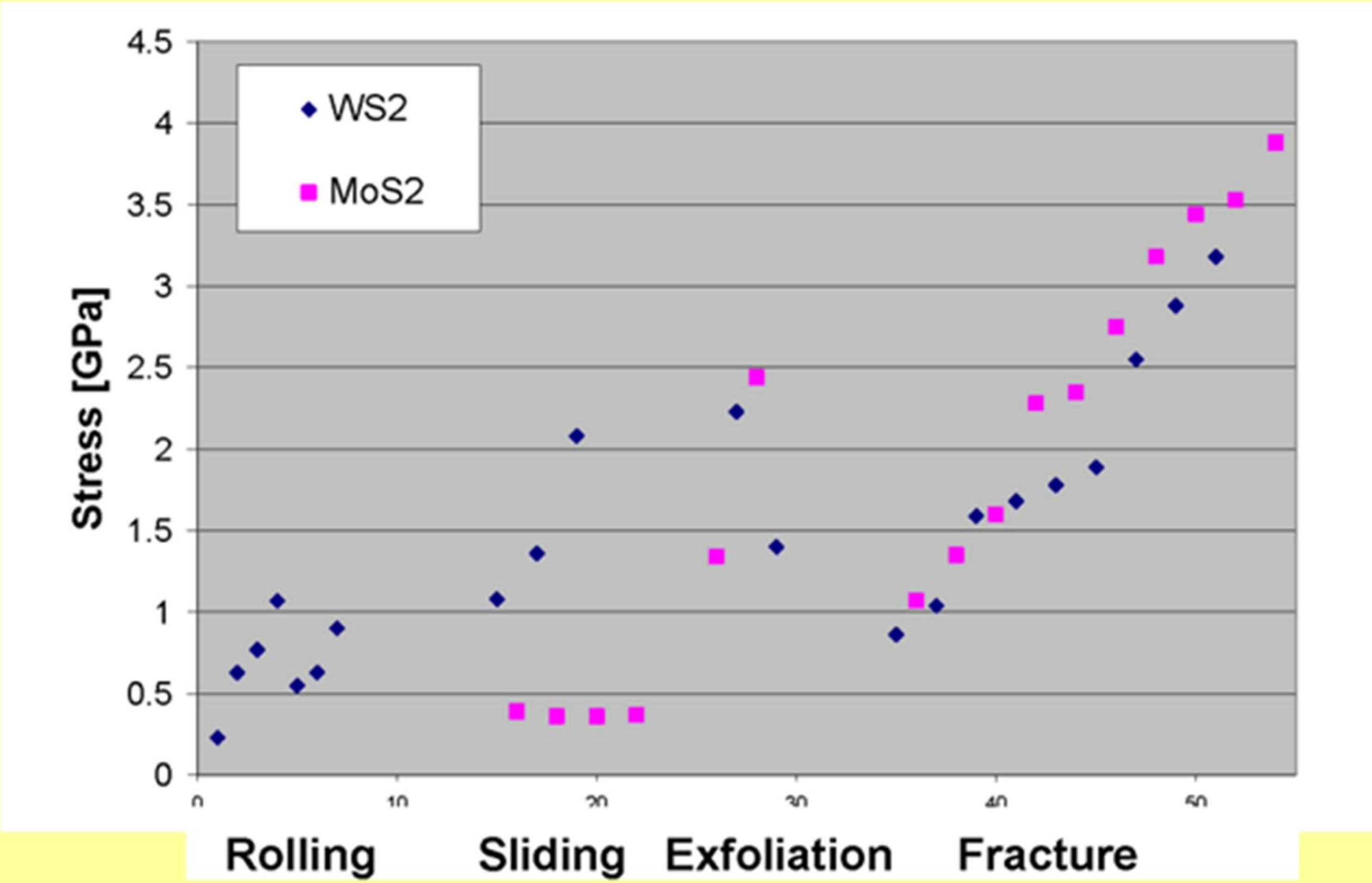



**Rolling friction**

**Exfoliation and transfer**

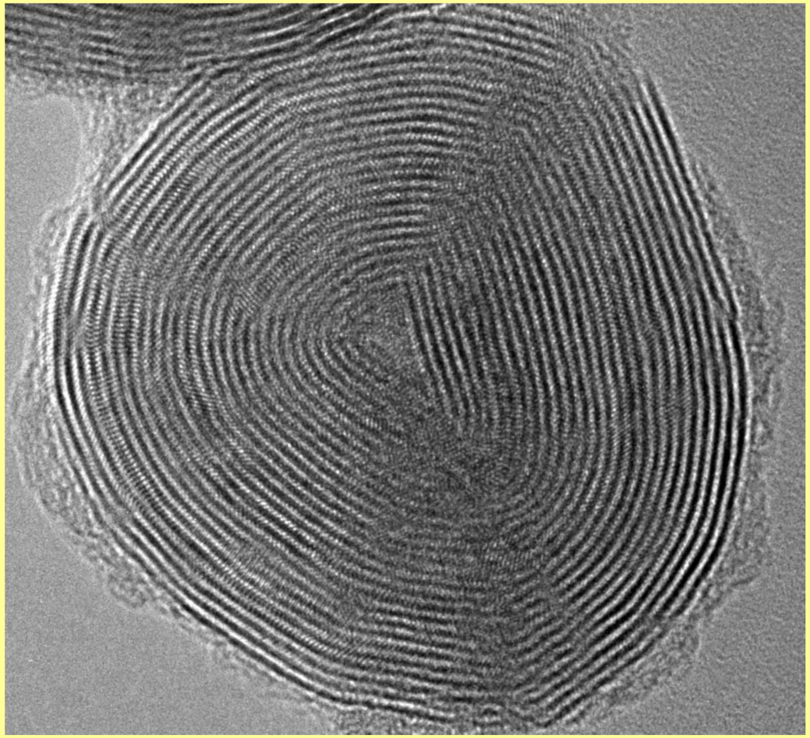
O. Tevet, P. Von-Huth, R. Popovitz-Biro, R. Rosentsveig, H. D. Wagner and R. Tenne,
*PNAS* 108, 19901 (2011)

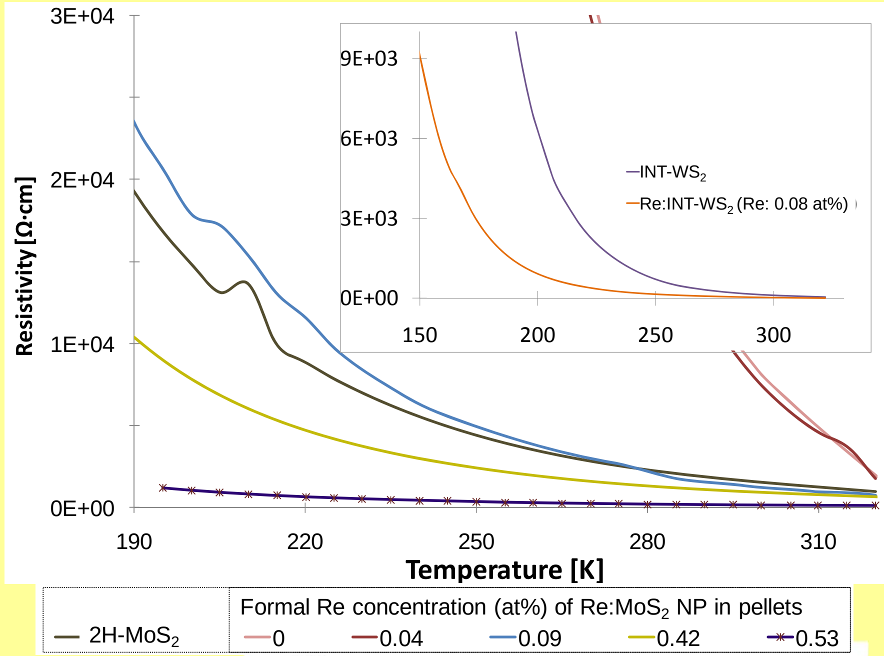
# Summary of the mechanical properties of IF NP

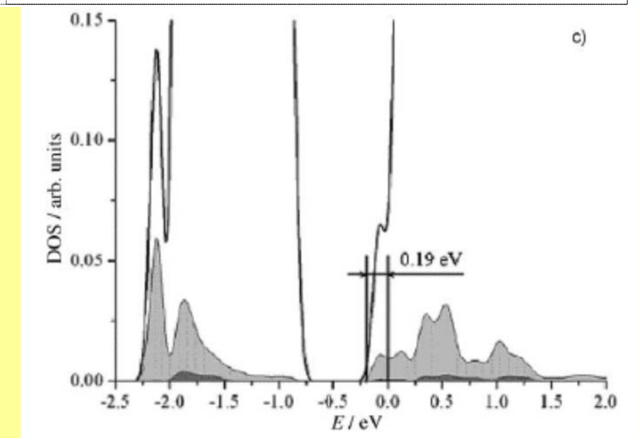



O. Tevet, P. Von-Huth, R. Popovitz-Biro, R. Rosentsveig, H. D. Wagner and R. Tenne, *PNAS* 108, 19901 (2011)

# Re (Nb) doped IF-$MoS_2$





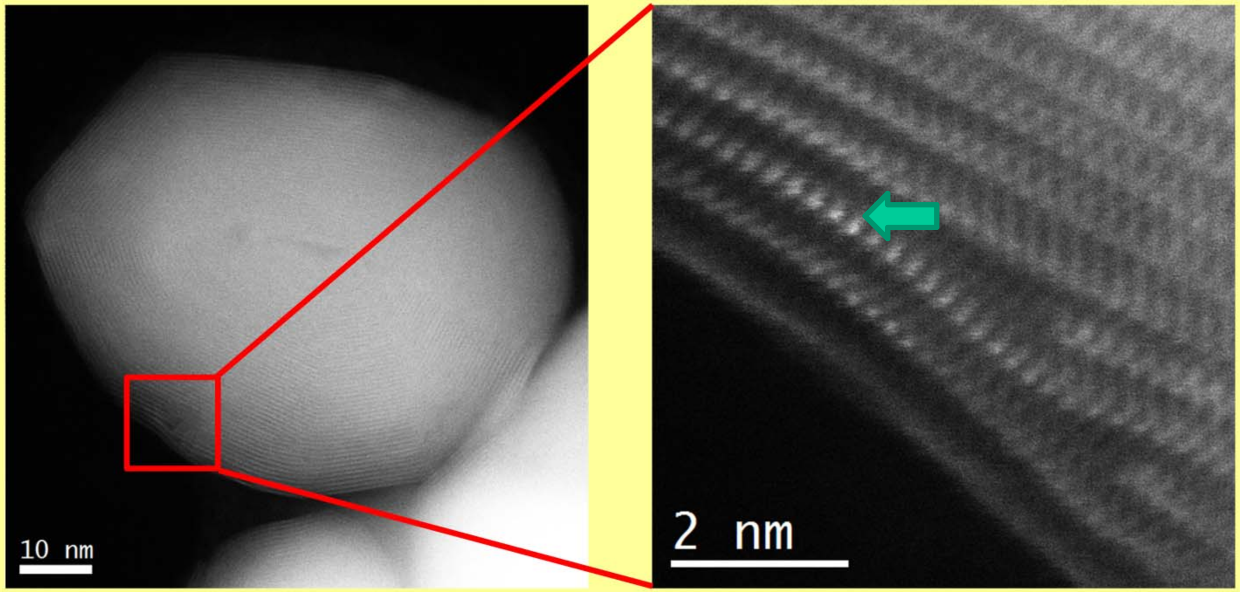



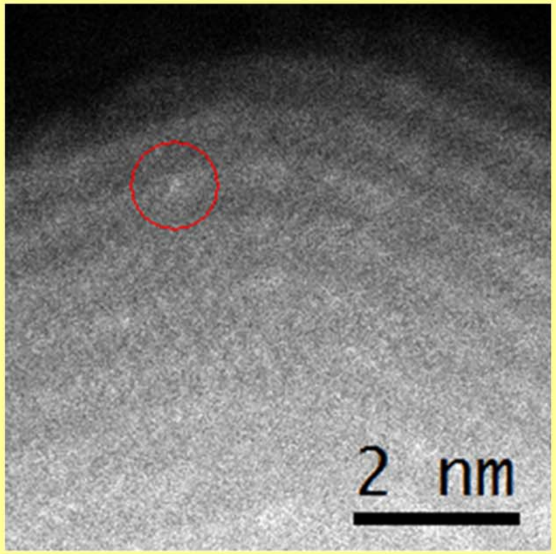

**0.3 at% Re**

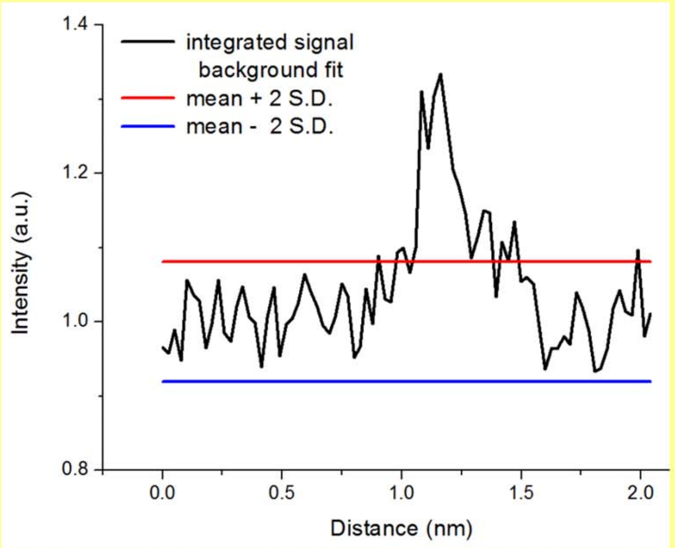
**2H-$MoS_2$ → Ea = 0.127eV**
**IF-$MoS_2$ → Ea = 0.334eV**
**IF-Mo(Re)$S_2$ → Ea = 0.077eV**

**L. Yadgarov, R. Rosentsveig, G. Leitus, A. Albu-Yaron, A. Moshkovich, V. Perfilyev, R. Vasic, A.I. Frenkel, A.N. Enyashin, G. Seifert, L. Rapoport and R. Tenne, *Angew. Chem. Intl. Ed.* 51, 1148 (2012).**

# Re atoms in IF-$MoS_2$ nanoparticles

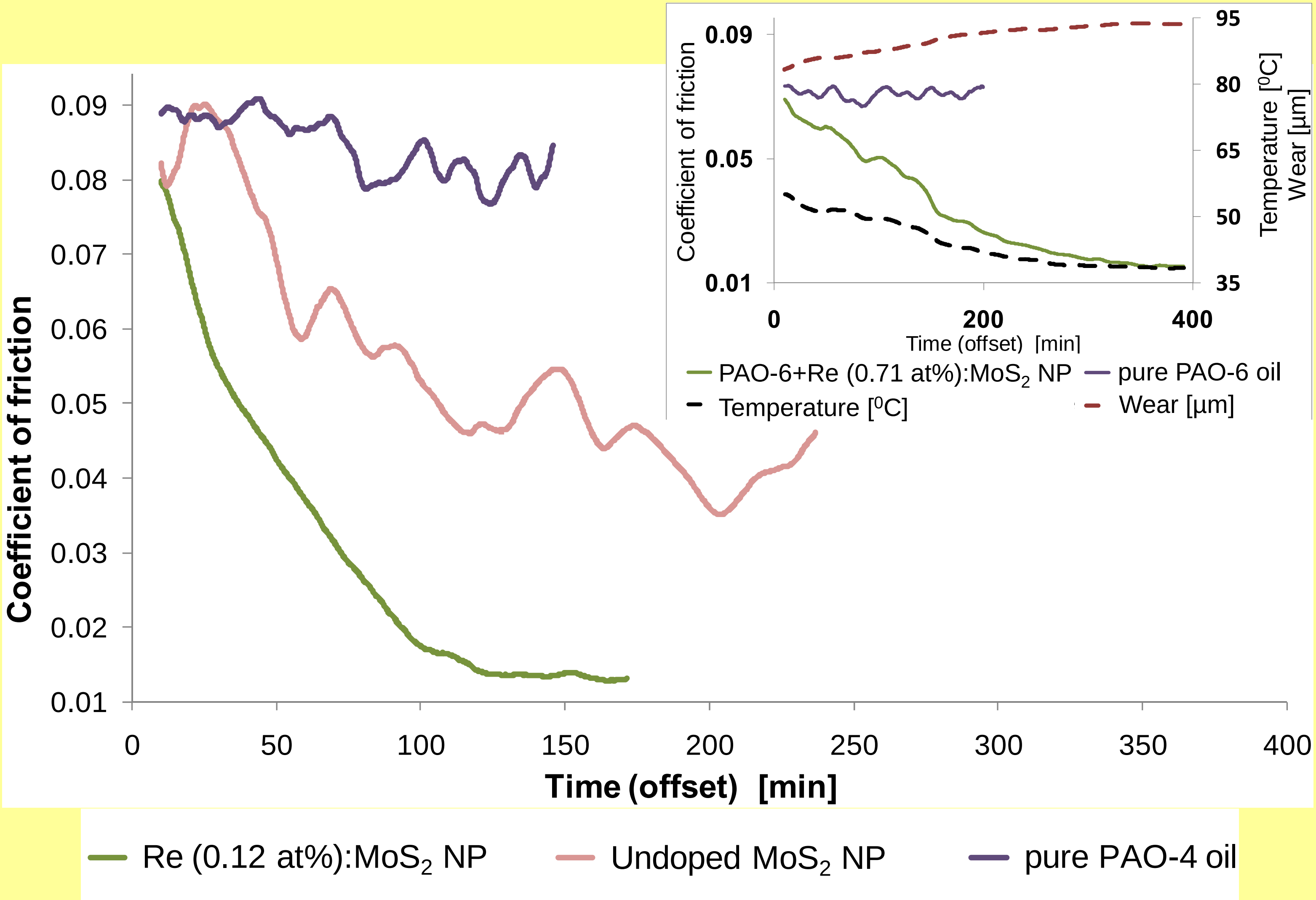


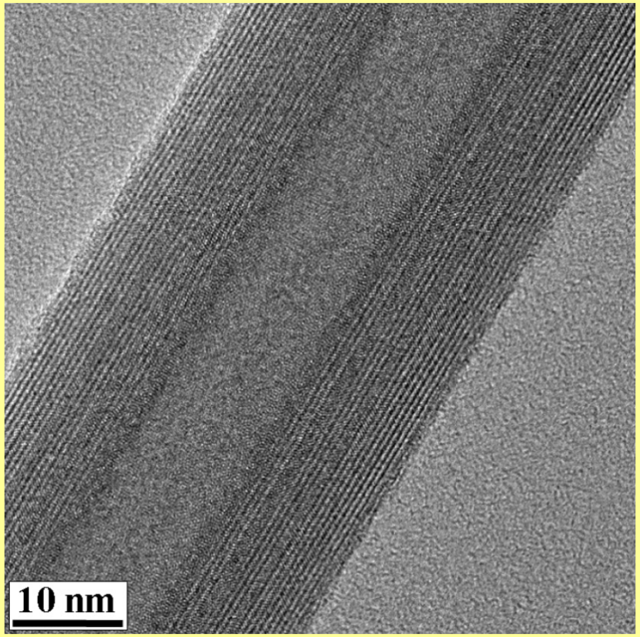

D. Stroppa and L. Houben, E-RC, Jülich

# Tribological tests in mixed lubrication conditions (PAO-4)

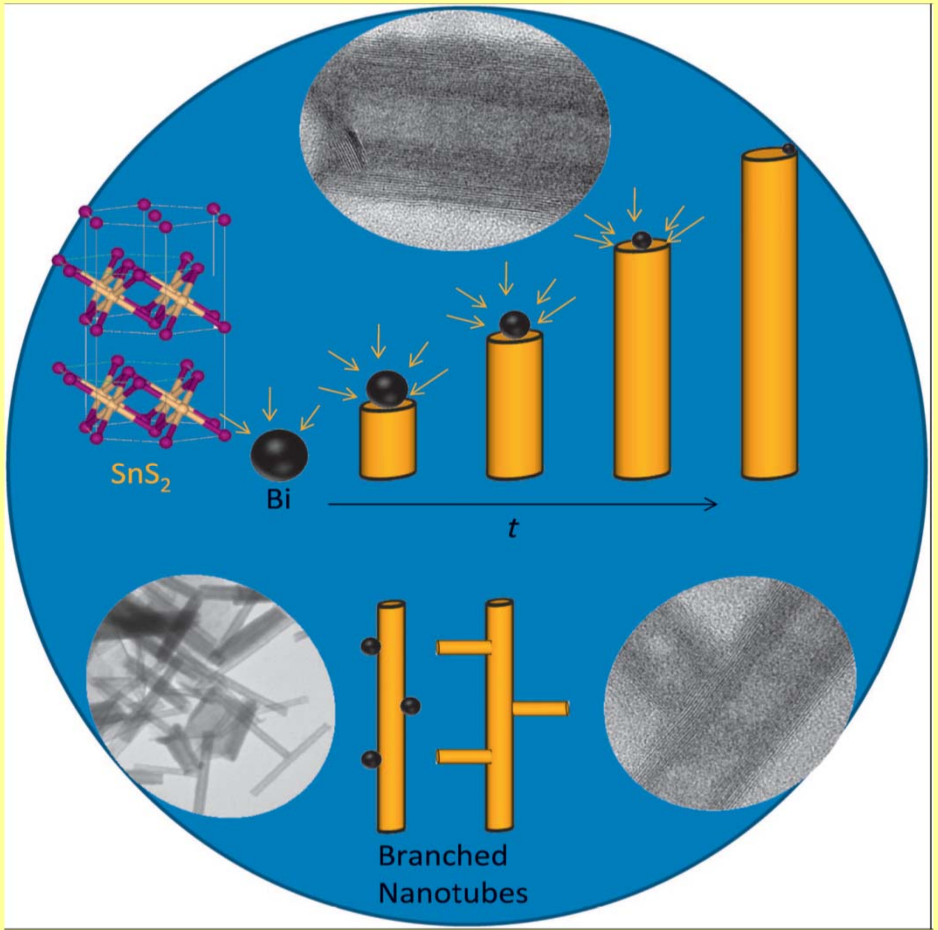


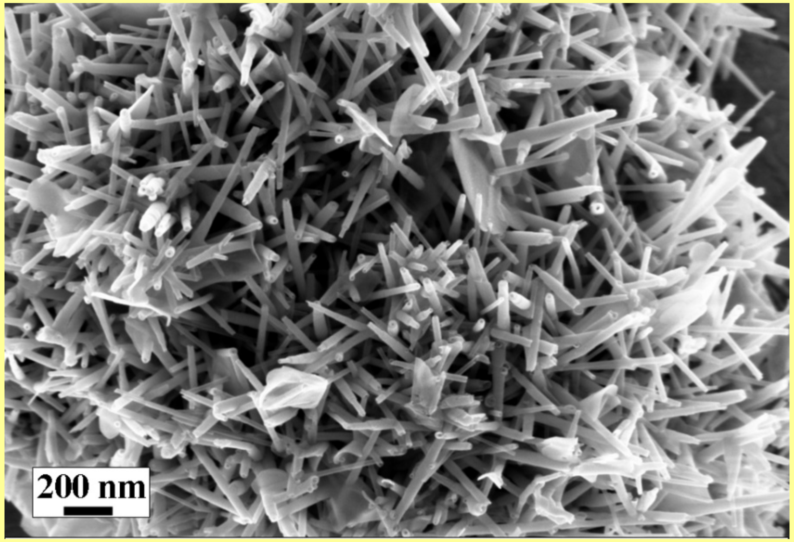

L. Rapoport, . Moshkovith, V. Perfiliev, A. Laikhtman, I. Lapsker, L. Yadgarov, R. Rosentsveig and R. Tenne, *Trib. Lett*. 45, 257 (2012)

# Vapor-liquid-solid (VLS) growth of $SnS_2$ nanotubes with Bi catalyst



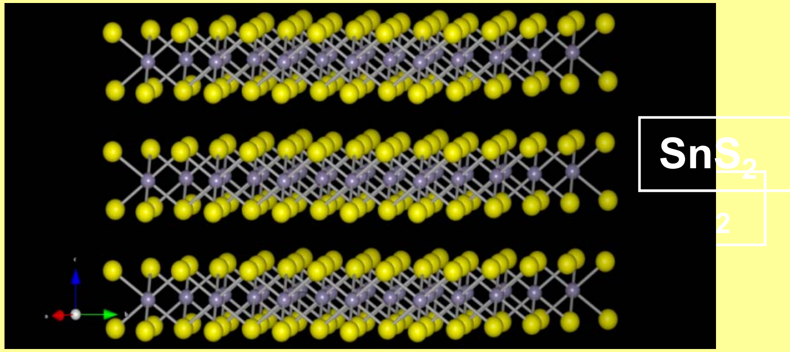

$SnS_2$ nanotube

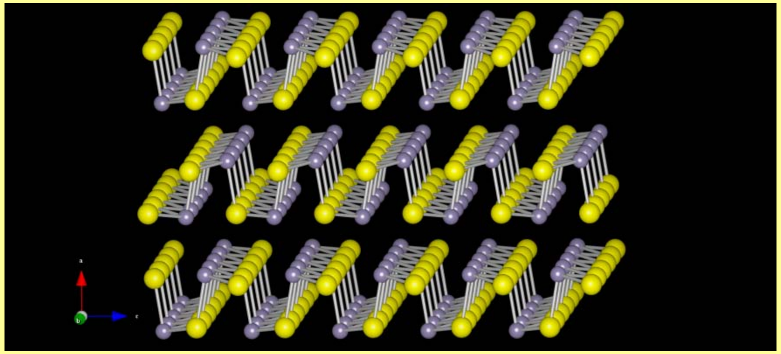


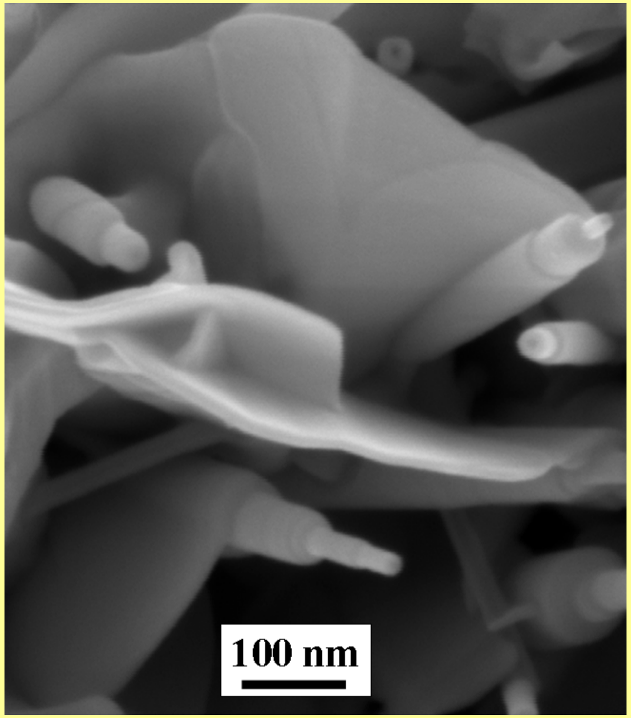




A. Yella, E. Mugnaioli, M. Panthoefer, H.A. Therese, U. Kolb and W. Tremel, *Angew. Chem. Int. Ed.* 48, 6426 (2009)
G. Radovsky, R. Popovitz-Biro, M.Staiger, K. Gartsman, C. Thomsen, T. Lorenz, G. Seifert and R. Tenne, *Angew. Chem. Intl. Ed.* (2011)

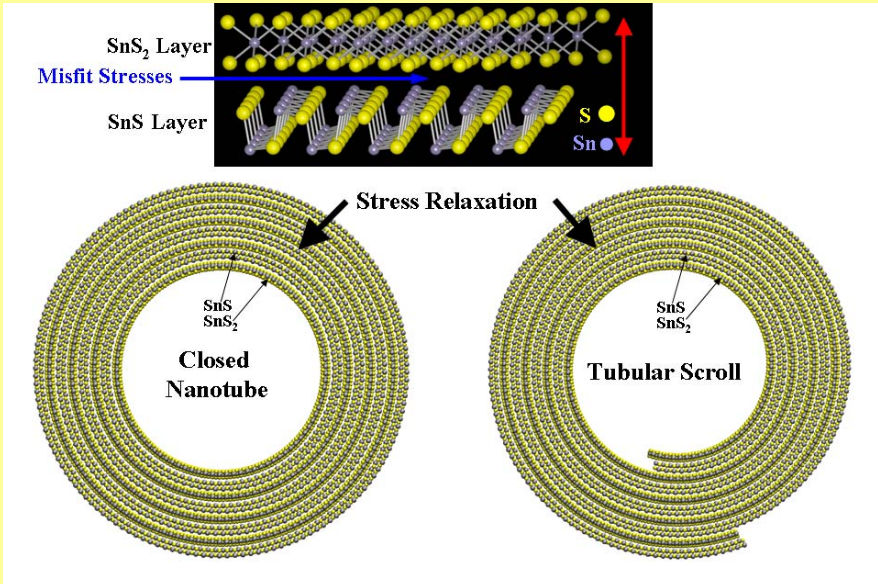
# Mechanism of formation of (misfit) $SnS_2$/SnS ordered superstructure nanotubes






SEM image of a nanoscroll




G. Radovsky, R. Popovitz-Biro, M. Staiger, K. Gartsman, C. Thomsen, T. Lorenz, G. Seifert and R. Tenne,
*Angew. Chem. Intl. Ed*. 50, 12316 (2011)