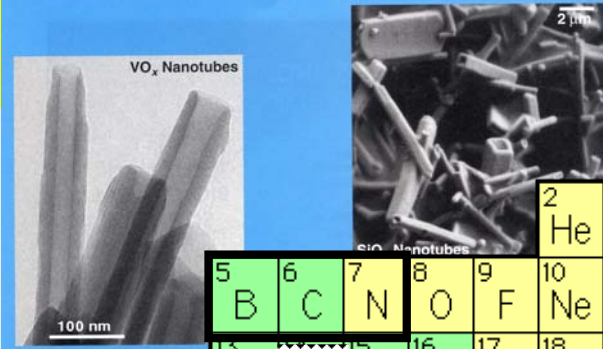


# Inorganic Nanotubes

G. R. Patzke, F. Krumeich, R. Nesper, *Angew. Chem. Int. Ed. Engl.* 14 (2002) 2447



|       |        |          |              |           |        |        |        |        |        |        |         |         |         |         |         |         |         |  |  |     |      |       |       |      |       |       |       |
|-------|--------|----------|--------------|-----------|--------|--------|--------|--------|--------|--------|---------|---------|---------|---------|---------|---------|---------|--|--|-----|------|-------|-------|------|-------|-------|-------|
| 1 H   | Oxides |          | Carbon-based |           |        |        |        |        |        |        |         |         |         |         |         |         |         |  |  |     | 2 He |       |       |      |       |       |       |
| 3 Li  | 4 Be   | Chalco.  |              |           |        |        |        |        |        |        |         |         |         |         |         |         |         |  |  | 5 B | 6 C  | 7 N   | 8 O   | 9 F  | 10 Ne |       |       |
| 11 Na | 12 Mg  | Metallic |              | Semicond. |        |        |        |        |        |        |         |         |         |         |         |         |         |  |  |     |      | 13 Al | 14 Si | 15 P | 16 S  | 17 Cl | 18 Ar |
| 19 K  | 20 Ca  | 21 Sc    | 22 Ti        | 23 V      | 24 Cr  | 25 Mn  | 26 Fe  | 27 Co  | 28 Ni  | 29 Cu  | 30 Zn   | 31 Ga   | 32 Ge   | 33 As   | 34 Se   | 35 Br   | 36 Kr   |  |  |     |      |       |       |      |       |       |       |
| 37 Rb | 38 Sr  | 39 Y     | 40 Zr        | 41 Nb     | 42 Mo  | 43 Tc  | 44 Ru  | 45 Rh  | 46 Pd  | 47 Ag  | 48 Cd   | 49 In   | 50 Sn   | 51 Sb   | 52 Te   | 53 I    | 54 Xe   |  |  |     |      |       |       |      |       |       |       |
| 55 Cs | 56 Ba  |          | 72 Hf        | 73 Ta     | 74 W   | 75 Re  | 76 Os  | 77 Ir  | 78 Pt  | 79 Au  | 80 Hg   | 81 Tl   | 82 Pb   | 83 Bi   | 84 Po   | 85 At   | 86 Rn   |  |  |     |      |       |       |      |       |       |       |
| 87 Fr | 88 Ra  |          | 104 Rf       | 105 Db    | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Uub | 113 Uut | 114 Uuq | 115 Uup | 116 Uuh | 117 Uus | 118 Uuo |  |  |     |      |       |       |      |       |       |       |
|       |        |          | 57 La        | 58 Ce     | 59 Pr  | 60 Nd  | 61 Pm  | 62 Sm  | 63 Eu  | 64 Gd  | 65 Tb   | 66 Dy   | 67 Ho   | 68 Er   | 69 Tm   | 70 Yb   | 71 Lu   |  |  |     |      |       |       |      |       |       |       |
|       |        |          | 89 Ac        | 90 Th     | 91 Pa  | 92 U   | 93 Np  | 94 Pu  | 95 Am  | 96 Cm  | 97 Bk   | 98 Cf   | 99 Es   | 100 Fm  | 101 Md  | 102 No  | 103 Lr  |  |  |     |      |       |       |      |       |       |       |

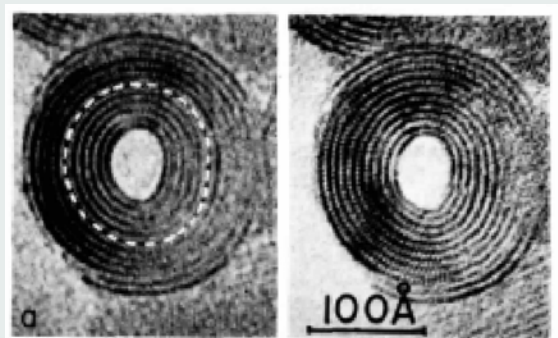
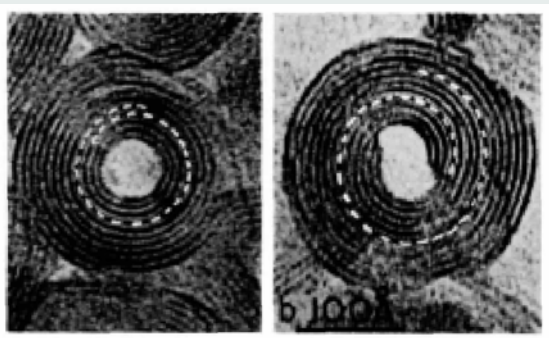
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## History

### Tubular Silicate minerals

TEM investigation of the cross-sections of Chrysotile



**Scrolls of one or more layers**

**But:** also closed, concentric cylinders

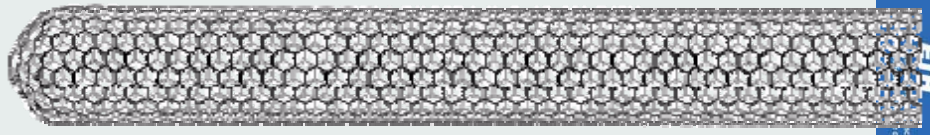
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Yada, *Acta Crystallogr. A* 27 (1971) 659

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ETH  
Department of Chemistry, Institute of Physical Chemistry  
Swiss Federal Institute of Technology Zurich

# Nanotubes



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*CRYSOTILE, Bi-Nb-S*

carbon

boron nitride

(BN,  $B_xC_yN_z$ )

boron carbide

( $B_xC$ )

silicon dioxide

(amorphous)

transition metal oxide

( $VO_x$ ,  $TiO_2$ )

metal sulfide

( $MoS_2$ ,  $WS_2$ ,  $NbS_2$ ,  $InS$ ,  $CdS(e)$ )

transition metal halide

( $NiCl_2$ )

metal

(Au, Ni, Bi, Te)

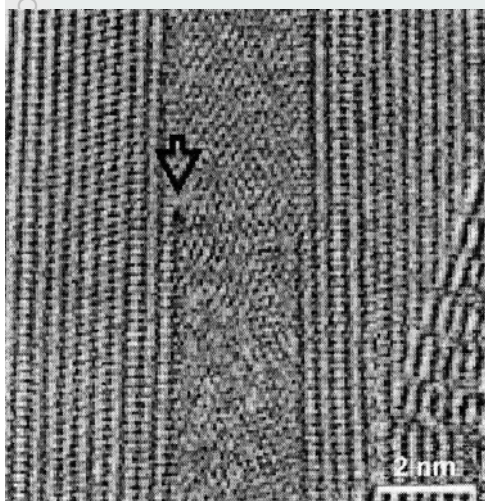


## BN Nanotubes

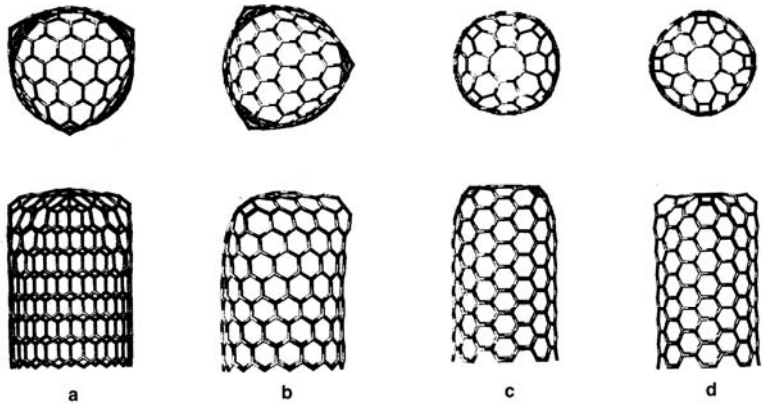
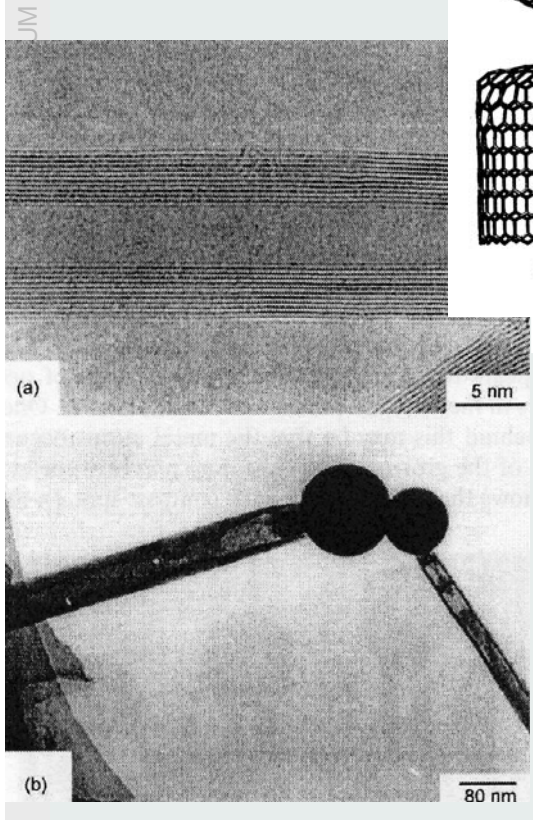
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Fig. 36 HREM image of single-walled BN nanotubes adhering on a W substrate. (Reproduced with permission from ref. 110).



# BN Nanotubes



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# BC<sub>x</sub> Nanotubes

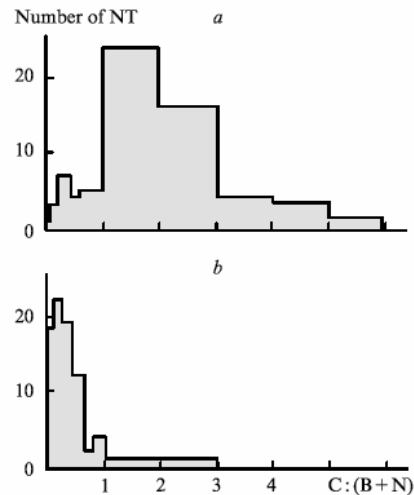
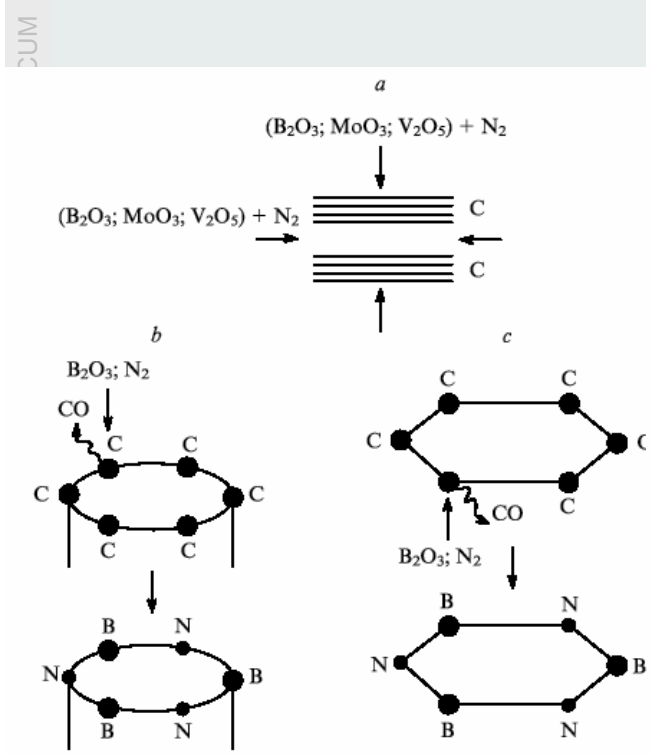


Figure 3. Composition histogram of multilayer BCN-nanotubulenes synthesised by chemical substitution from carbon NT (at 1773 K in a flow of nitrogen);<sup>63</sup> (a) without oxides, (b) in the presence of MoO<sub>2</sub>.

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# B-C-N Nanotubes

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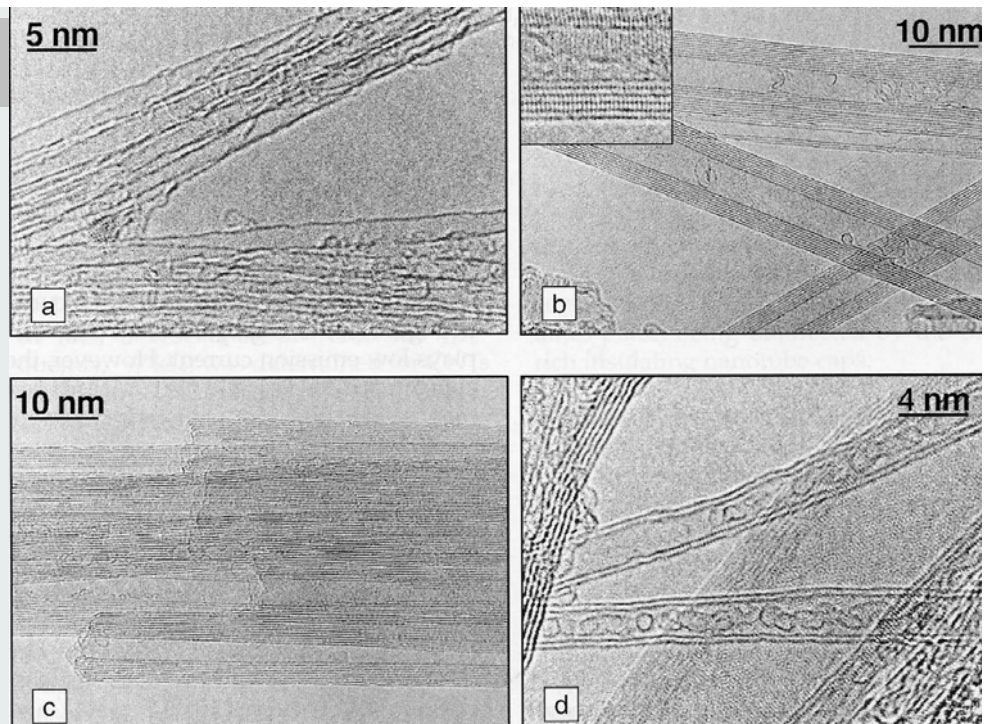
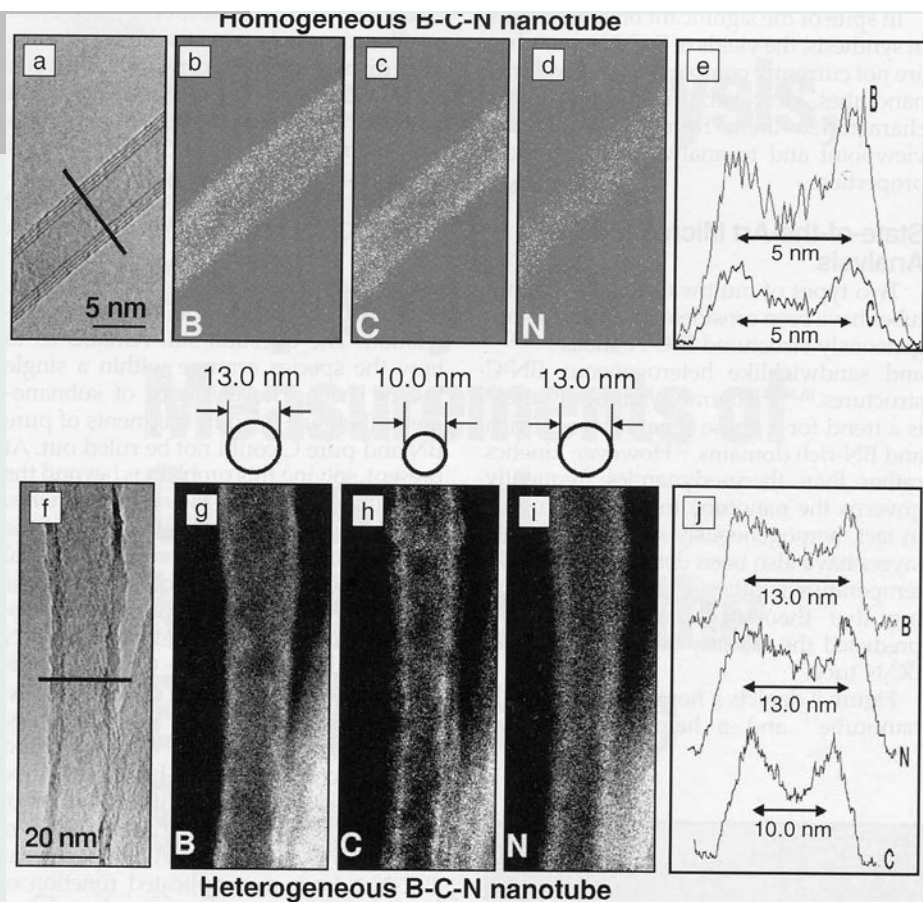


Figure 1. High-resolution transmission electron microscopy (TEM) images of B-C-N nanotubes converted from carbon nanotubes (CNTs) by means of high-temperature chemical reactions:<sup>16–22</sup> (a) B/N-doped C single-walled nanotube bundles; (b) BN-rich multiwalled B-C-N nanotubes; (c) ropes made of dozens of open-ended BN-rich B-C-N nanotubes; and (d) double-walled BN-rich B-C-N nanotubes with C buckyballs in their cores. Inset in (b) shows a high-resolution TEM micrograph of a BN-rich B-C-N multiwalled nanotube wall fragment exhibiting atom column separation of  $\sim 0.21$  nm along the shells; this is peculiar to “zigzag”-oriented shells (tube axis parallel to the  $[10\bar{1}0]$  orientation of a graphitic sheet).

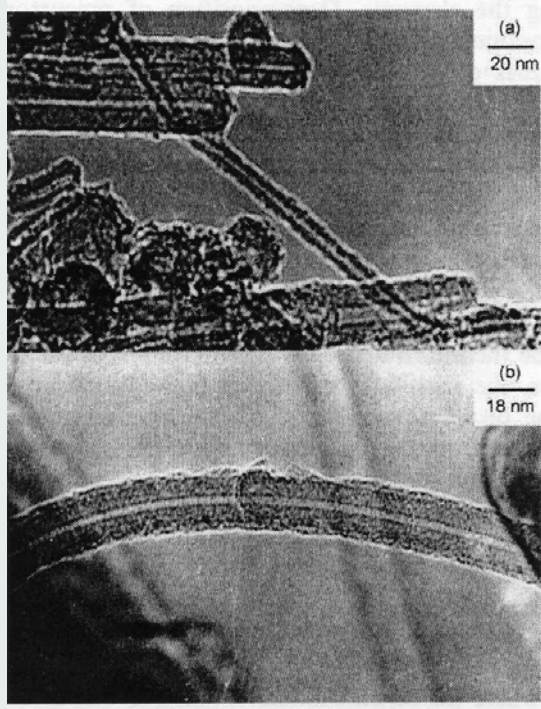
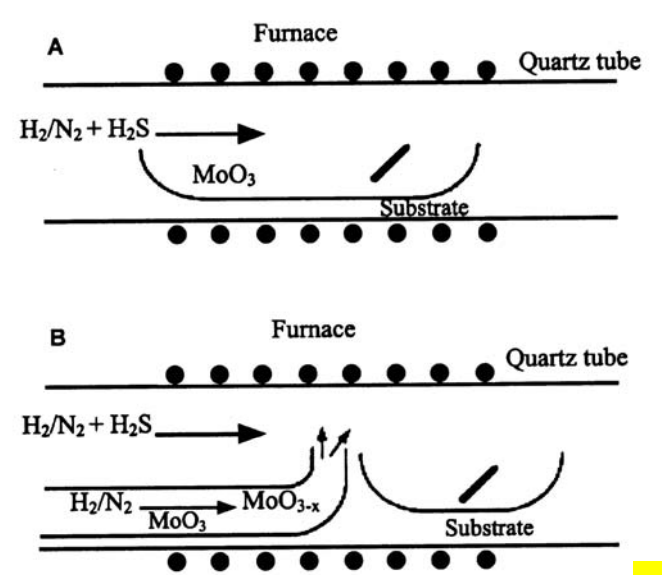
# B-C-N Nanotubes

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# Nanotubes of Dichalcogenides– MoX<sub>2</sub>

IM HELVETICUM

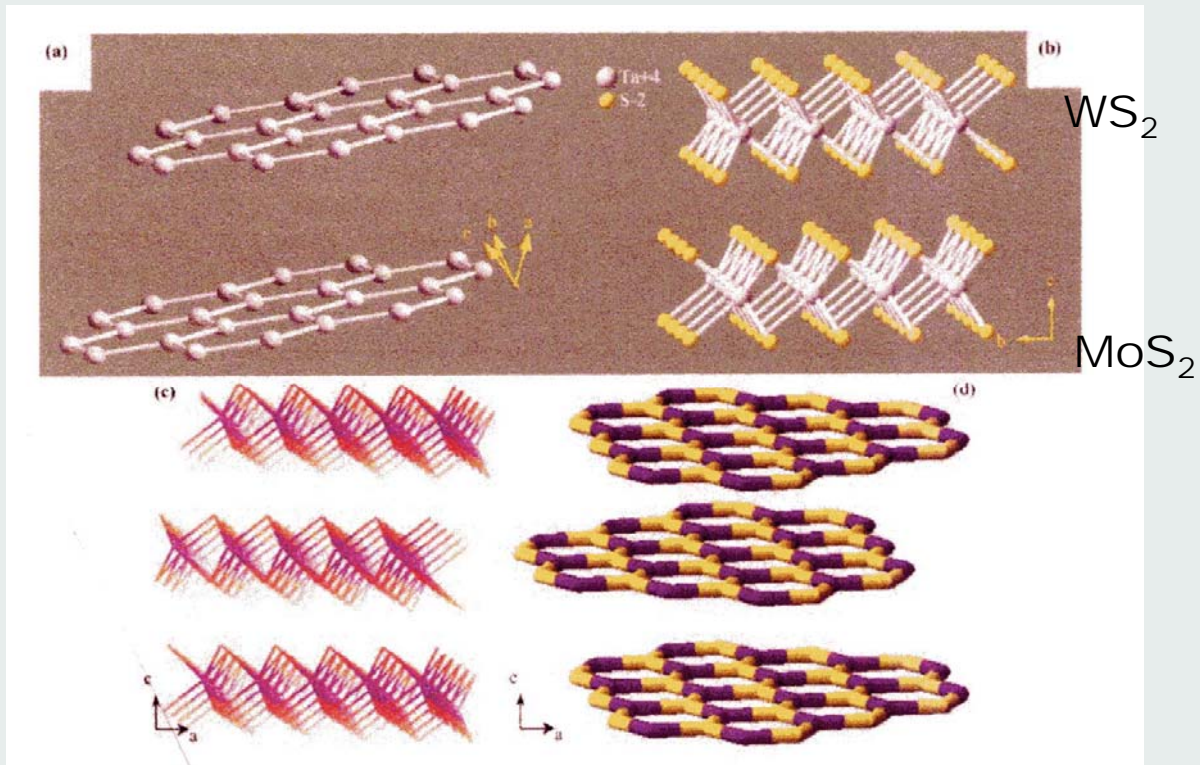


TH Zürich  
 Tenne, Margulis, Genut, Hodes, *Nature* 360 (1992) 444

Nanoch

# Nanotubes of Layered Materials

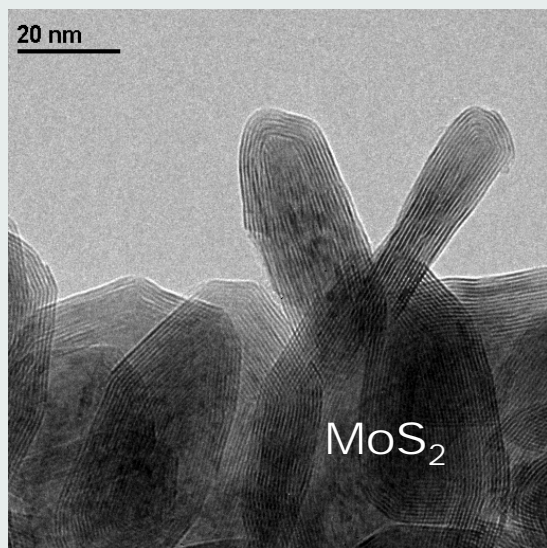
R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM



ETH  
 Eidgenössische Technische Hochschule Zürich  
 Swiss Federal Institute of Technology Zürich

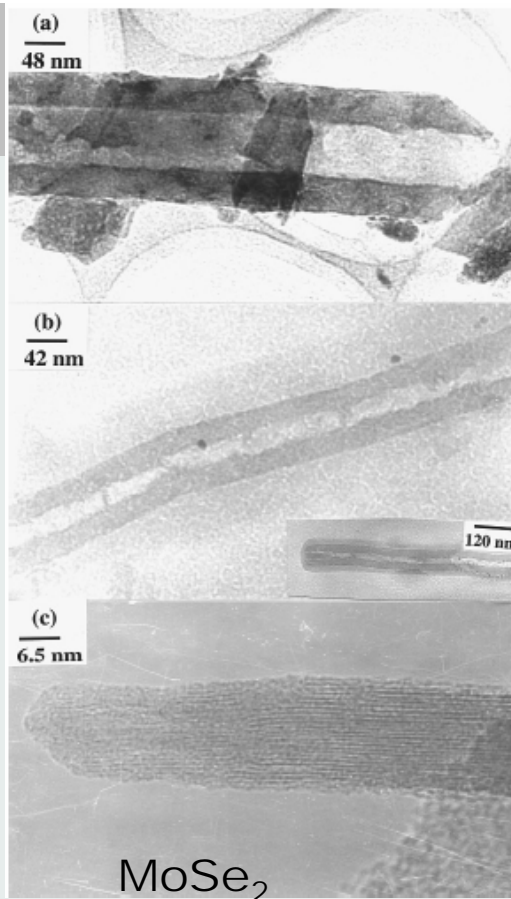
# Nanotubes of Dichalcogenides– $\text{MoX}_2$

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Tenne, Margulis, Genut, Hodes, *Nature* 360 (1992) 444

C.N.R. Rao et al, *Chem. Commun.*, 2001, 2236–2237



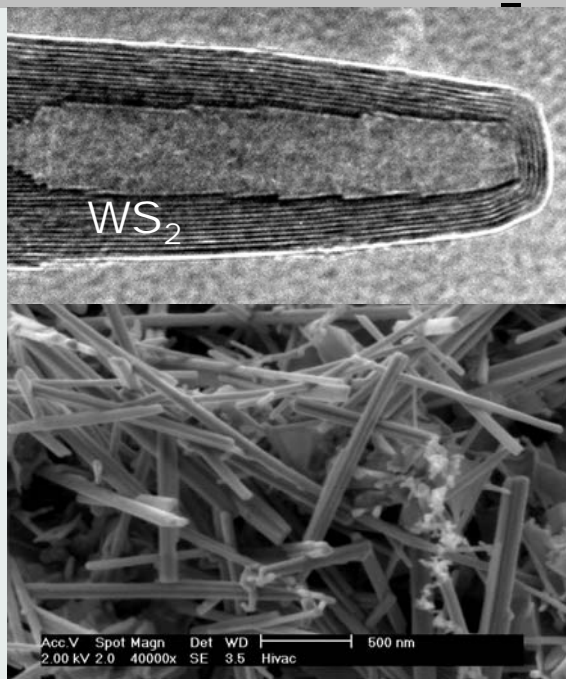
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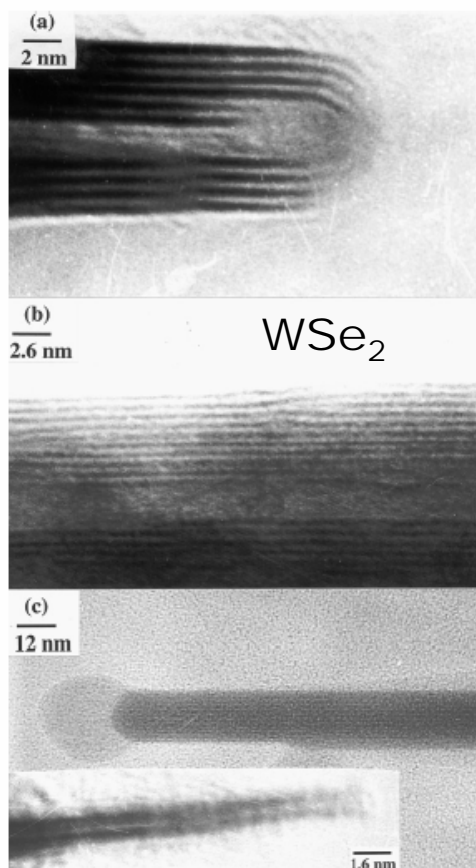
# Nanotubes of Dichalcogenides– $\text{WX}_2$

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Tenne, Margulis, Genut, Hodes, *Nature* 360 (1992) 444

C.N.R. Rao et al, *Chem. Commun.*, 2001, 2236–2237



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# Nanotubes of Dichalcogenides– W/Nb/X<sub>y</sub>

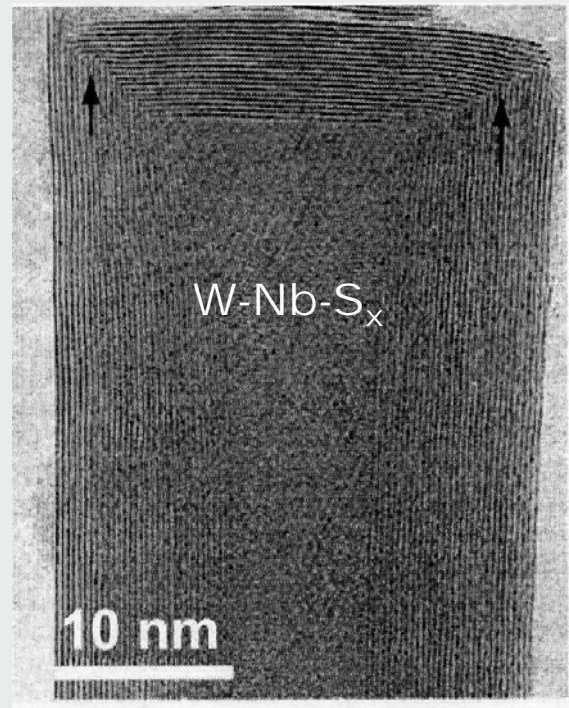
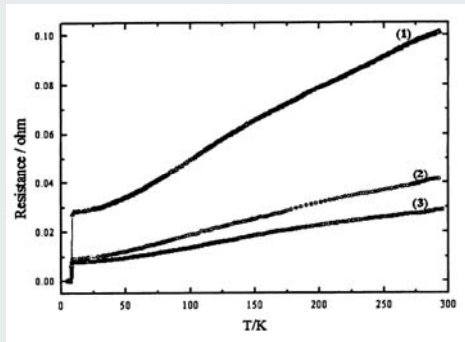
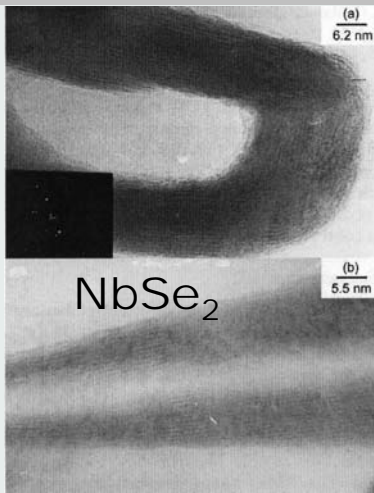


Fig. 18 TEM image showing the sharp 90° bend observed in the W–Nb–S nanotubes. (Reproduced with permission from ref. 41a).

# Nanotubes of Dichalcogenides– ReS<sub>2</sub>

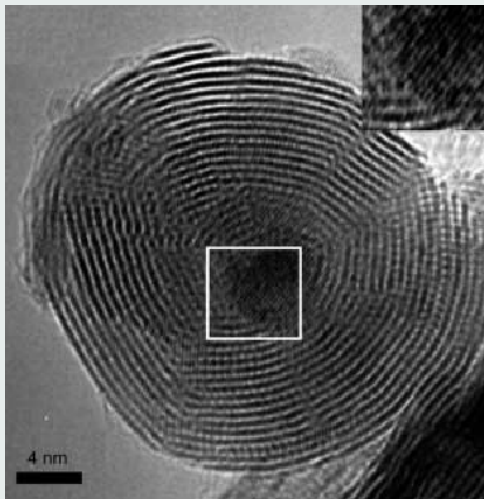


Abbildung 5. HRTEM-Aufnahme eines kleinen ReS<sub>2</sub>-Partikels, in das ein ReO<sub>2</sub>-Nanopartikel eingeschlossen ist. Die 0.29 nm breiten Gitterstreifen (Einschub) entsprechen den ReO<sub>2</sub>-{111}-Ebenen.

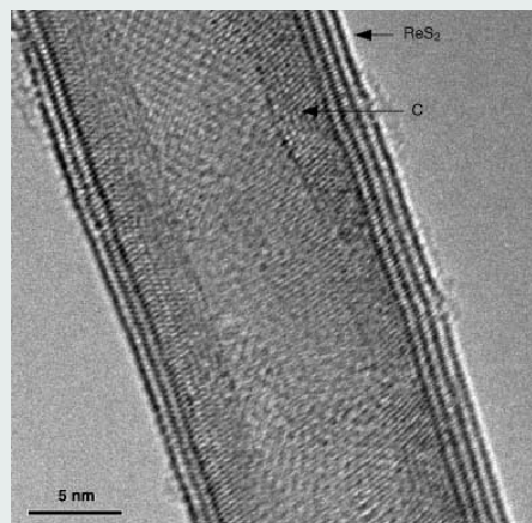
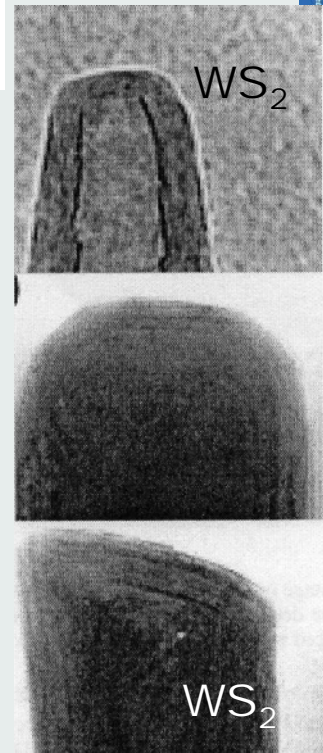
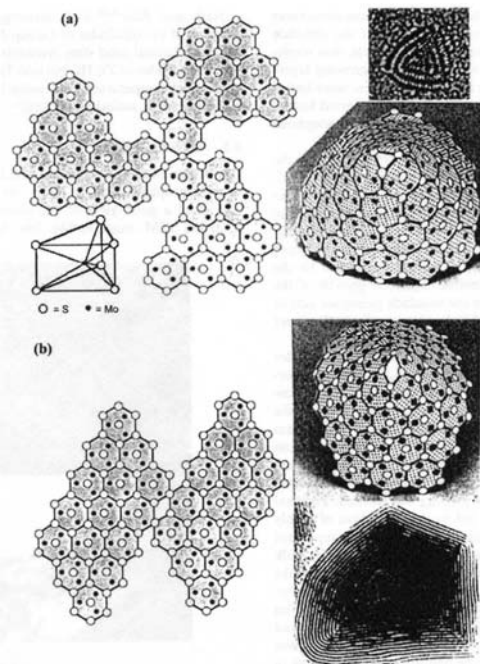


Abbildung 6. HRTEM-Aufnahme einer ReS<sub>2</sub>-Nanoröhre, die auf einer MWCNT als Templat gewachsen ist. Die ReS<sub>2</sub>-Röhrenwände sieht man als sehr dunkle parallele Linien mit relativ großen Abständen dazwischen. Die Kohlenstoffwände der darunter liegenden MWCNT sind weniger deutlich zu erkennen, und die Abstände zwischen ihnen sind sehr viel geringer.

# Nanotube Tips of Dichalcogenides– $WX_2$

**Fig. 16** Various closed tips observed in  $WS_2$  tubes possibly containing square or octagonal defects. (Reproduced with permission from ref. 47).



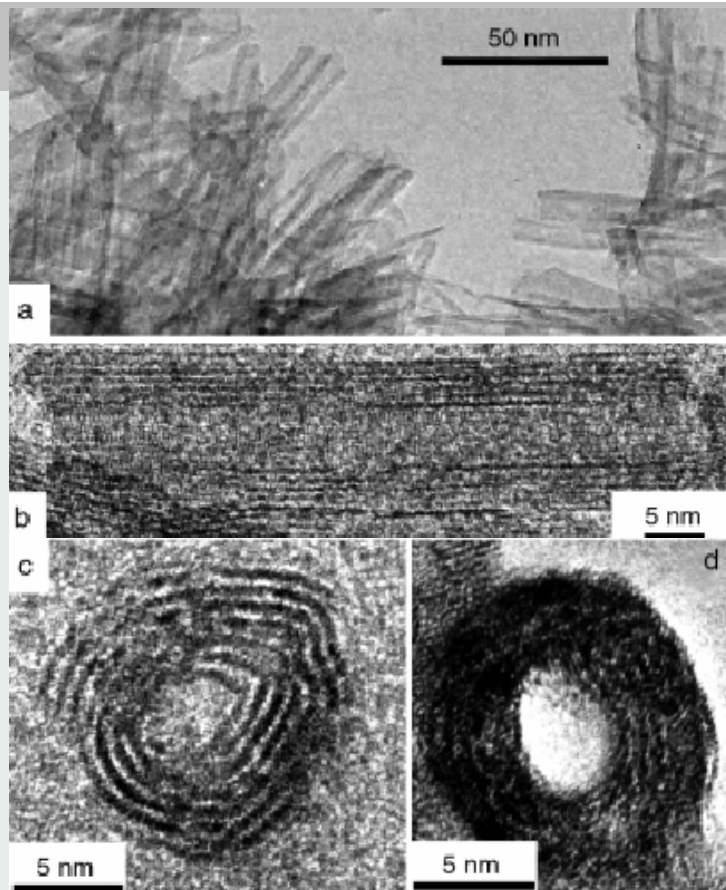
**Fig. 17** Illustration of various point defects which exists in the vertices of IF  $MoS_2$ : (a) a triangular point defect; (b) a rhombohedral point defect. Insets show IF structures that are likely to contain such point defects. (Reproduced with permission from ref. 19).

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# “ $TiO_2$ ” Nanotubes

Kasuga, Hiramatsu, Hoson,  
Sekino, Niihara,  
*Langmuir* 14, (1998) 3160

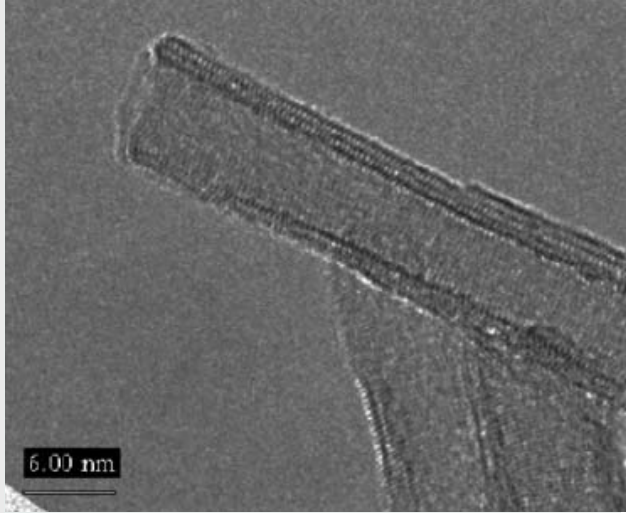


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# “TiO<sub>2</sub>” Nanotubes



G. H. Du, Q. Chen, R. C. Che, Z. Y. Yuan, L.-M. Peng, **APPLIED PHYSICS LETTERS VOLUME 79 (2001) 3702**

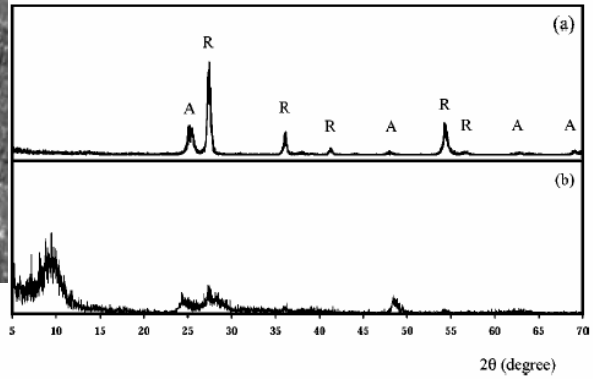


FIG. 4. XRD profiles taken from (a) a TiO<sub>2</sub> sample formed by sol-gel procedure and (b) titanium oxide nanotubes (sample B). In (a) peaks resulting from the anatase phase are denoted by A and those from the rutile phase are denoted by R.

# NiCl<sub>2</sub> Nanotubes

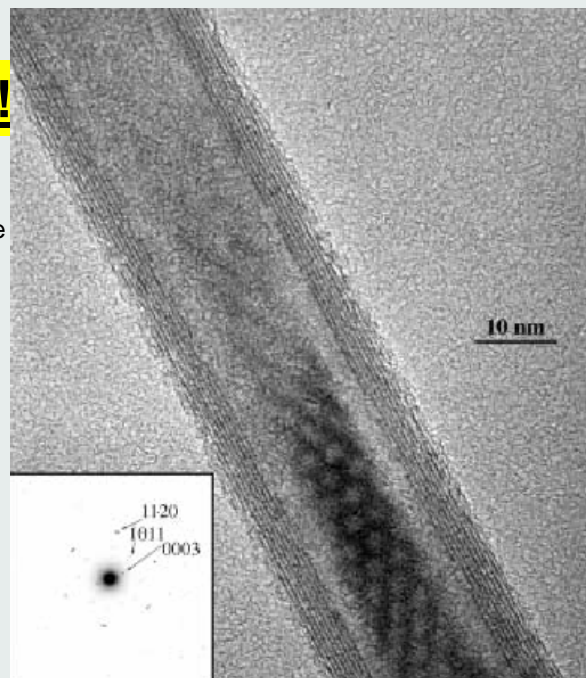
Y. R. Hachon, E. Grunbaum, R. Tenne, J. Sloan, J. L. Hutchison, **Nature (London) 395 336 (1998)**

## CdCl<sub>2</sub> structure types !

Multilayer NT were obtained; their cross-sections were up to ~7 nm, while the lengths were several micrometres.

The tubular structures remained stable for a few days. It is assumed that the most interesting applications of such structures may be related to their unusual magnetic characteristics.

It should be noted that it is compounds which form phases with quasi-2D structures under equilibrium conditions that are usually considered as potential candidates for the synthesis of NT.



# Tb(OH)<sub>3</sub>, Tb<sub>4</sub>O<sub>7</sub>, Y(OH)<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub> nanotubes

Fig. 7. A) An SEM image of the as-synthesized Y(OH)<sub>3</sub> product. B) TEM image of a single Y(OH)<sub>3</sub> nanotube. C) An HRTEM image of the outside part of the tube wall, clearly showing resolved fringes of (100) planes (spacing  $d = 0.542$  nm). Inset: The SAED pattern recorded from the [010] zone axis.

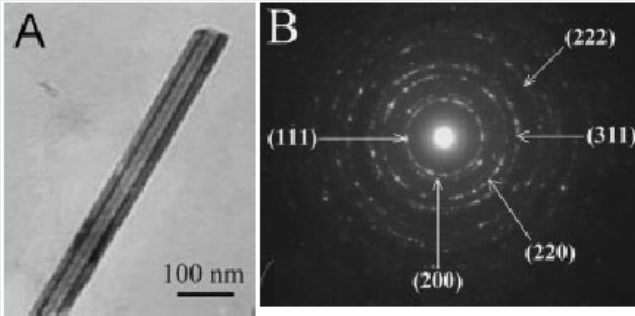
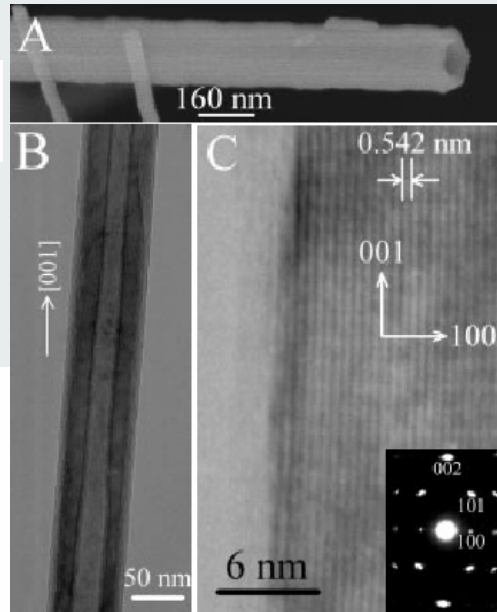


Fig. 5. A) A typical TEM image of a single Tb<sub>4</sub>O<sub>7</sub> nanotube. The Tb<sub>4</sub>O<sub>7</sub> product was obtained by calcination of the as-synthesized Tb(OH)<sub>3</sub> at 450 °C for 6 h in air. B) ED pattern of the Tb<sub>4</sub>O<sub>7</sub> nanotubes.

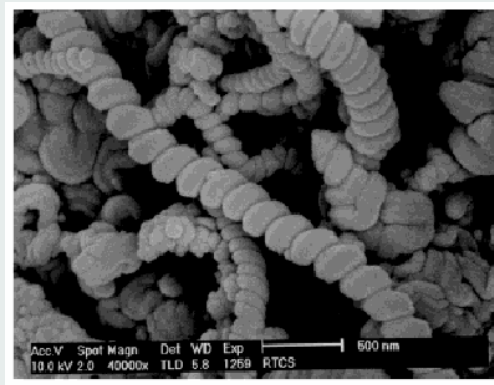
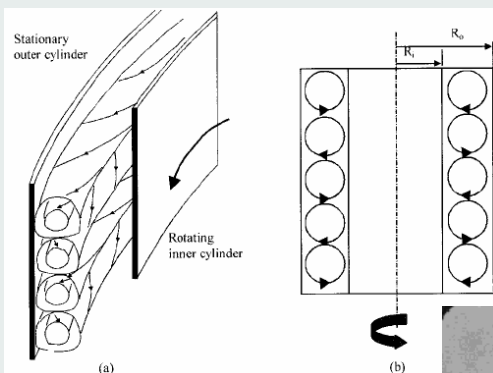
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## Helical Mesostuctured Tubules from Taylor Vortex-Assisted Surfactant Templates\*\*

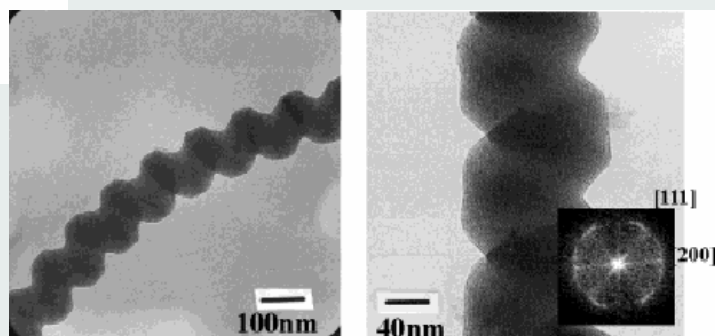
*Adv. Mater.* 2001, 13, No. 15, August 3

By Won-Jong Kim and Seung-Man Yang\*

Schematic illustration of the coil-spring flow between a stationary outer cylinder and a rotating inner cylinder. The two cylinders are aligned coaxially. The inner and outer cylinders are 10 cm in length, and 4 and 4.4 cm in radius, respectively.



Synthesis: Cetyltrimethylammonium bromide (CTAB; Sigma) and sodium salicylate (NaSal; Aldrich) were used to prepare the wormlike micelles, which served as the template. Tetraethylorthosilane (TEOS; Aldrich) in hydrochloric acid (HCl; Junsei) was used as a precursor of the silica substrate used to form the silica±surfactant meso-structure.

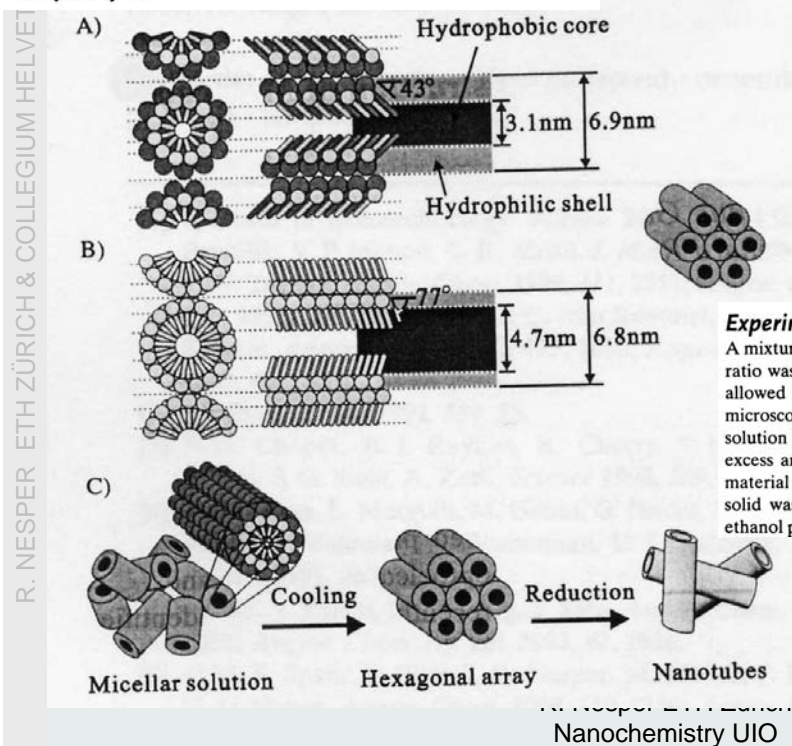


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## Noble-Metal Nanotubes (Pt, Pd, Ag) from Lyotropic Mixed-Surfactant Liquid-Crystal Templates\*\*

Tsuyoshi Kijima,\* Takumi Yoshimura, Masafumi Uota, Takayuki Ikeda, Daisuke Fujikawa, Shinji Mouri, and Shinji Uoyama

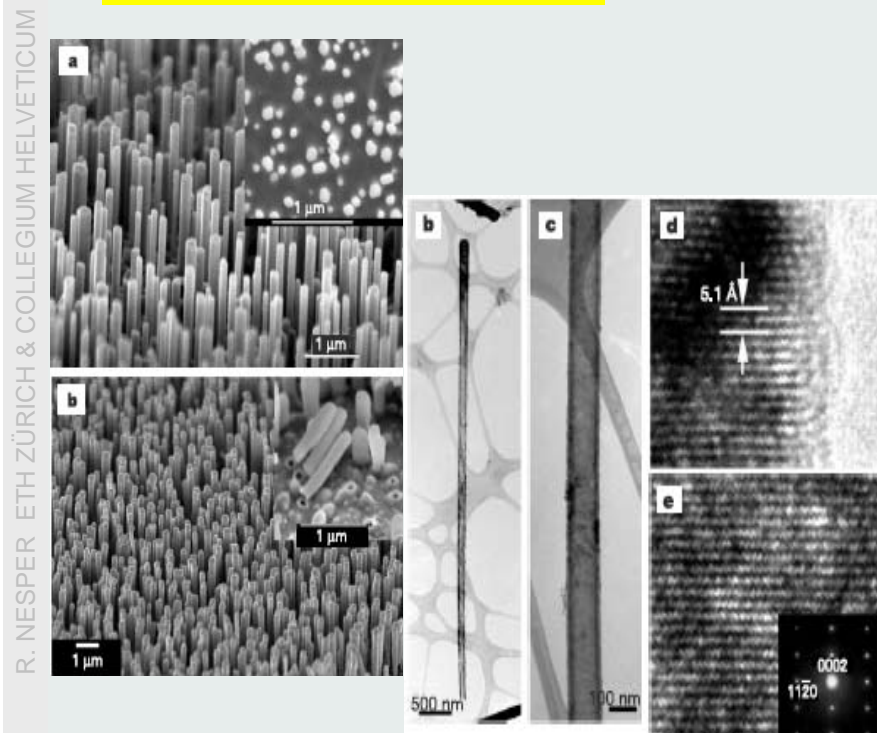
**Figure 4.** Schematic models for the formation of platinum nanotubes in the mixed surfactant templating system: A) Mixed ( $C_{12}EO_9$ /Tween 60) and B) single ( $C_{12}EO_9$ ) surfactant cylindrical rodlike micelles. C) Pathway from micellar solution to metal nanotubes by the reduction of metals salts confined to the aqueous shell of mixed-surfactant cylindrical micelles. The metal salts and water molecules are omitted from the models.



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## Semiconductor Nanotubes

NATURE | VOL 422 | 10 APRIL 2003



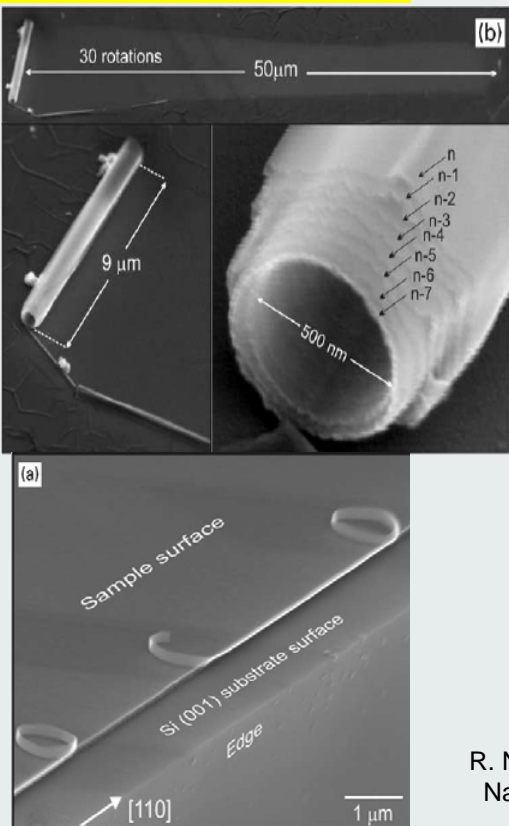
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# Semiconductor Nanotubes

Physica E 13 (2002) 969 – 973

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