Synthesis of Vanadium Oxide Nanotubes (VO_X-NTs)

Vanadium(V) oxide precursor + Template

1. **Hydrolysis**
2. **Aging (Polycondensation)**
3. **Hydrothermal treatment (180°C for ~ 1 w)**

Vanadium oxide nanotubes

Vanadium(V) oxide precursor: VOR_3, V_2O_5, $VOCl_3$, HVO_3

Template: monoamine ($C_nH_{2n+1}NH_2$ with $4 \leq n \leq 22$)

or α,ω-alkyldiamine ($H_2N[CH_2]_nNH_2$ with $14 \leq n \leq 20$)

Spahr, Bitterli, Nesper, Müller, Krumeich, Nissen, *Angew. Chem. Int. Ed.* 37 (1998) 1263

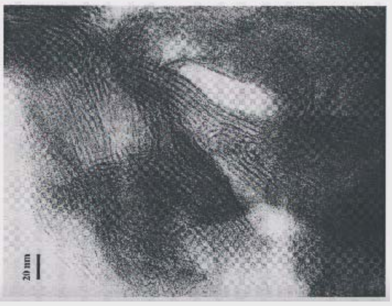
Niederberger, Muhr, Krumeich, Bieri, Günther, Nesper, *Chem. Mater.* 12 (2000) 1995

Vanadium Oxide Nano Tubes

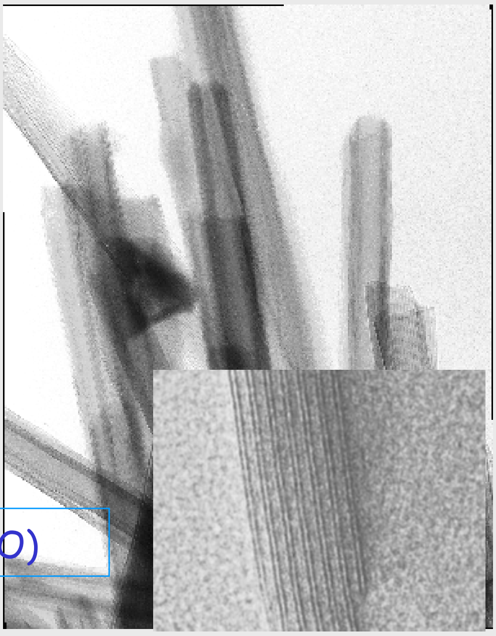
$VO(I\text{-}prop)_3$ + $C_nH_{2n+1}NH_2$

new: $VOCl_3$ +

new: V_2O_5 +

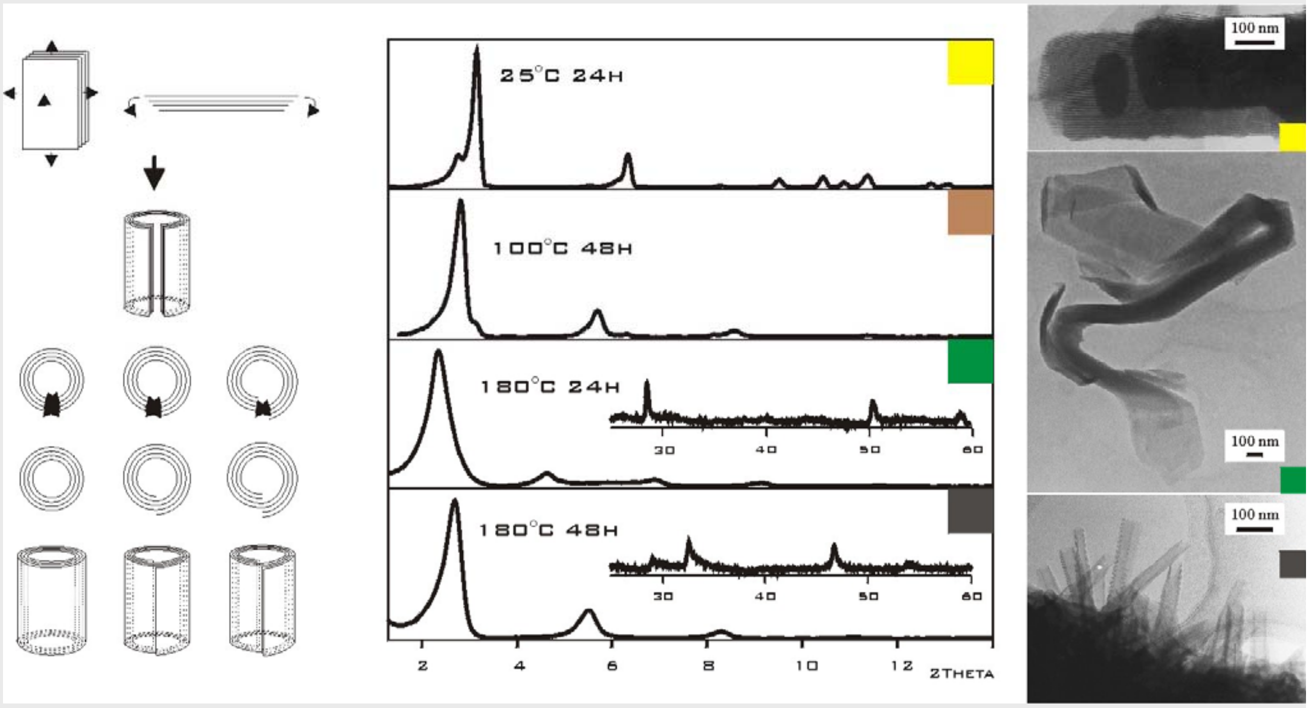


autoclave (CH_3OH/H_2O)

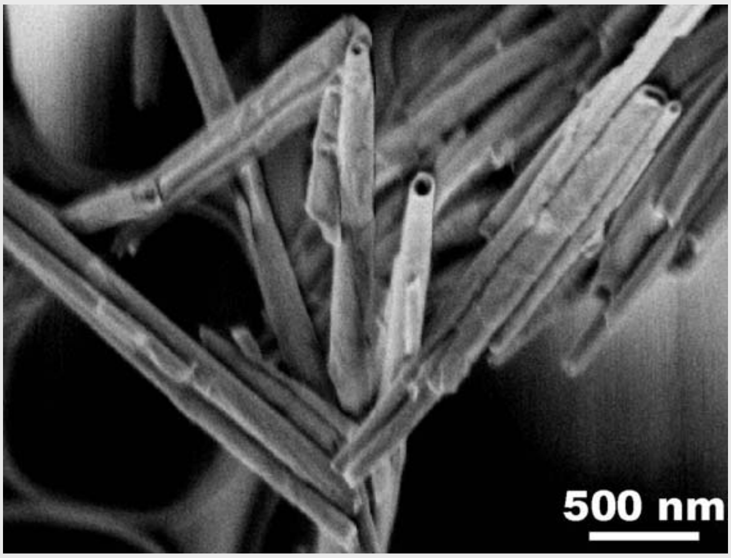


M. E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, H. U. Nissen, *Angew. Chem. Int. Ed.* **1998**, ***37***, 1263

Vanadium oxide NTs - Formation Process

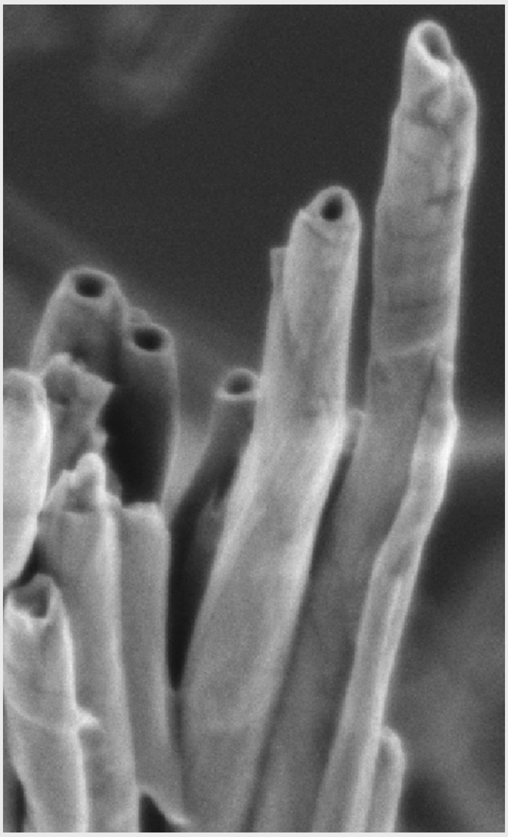


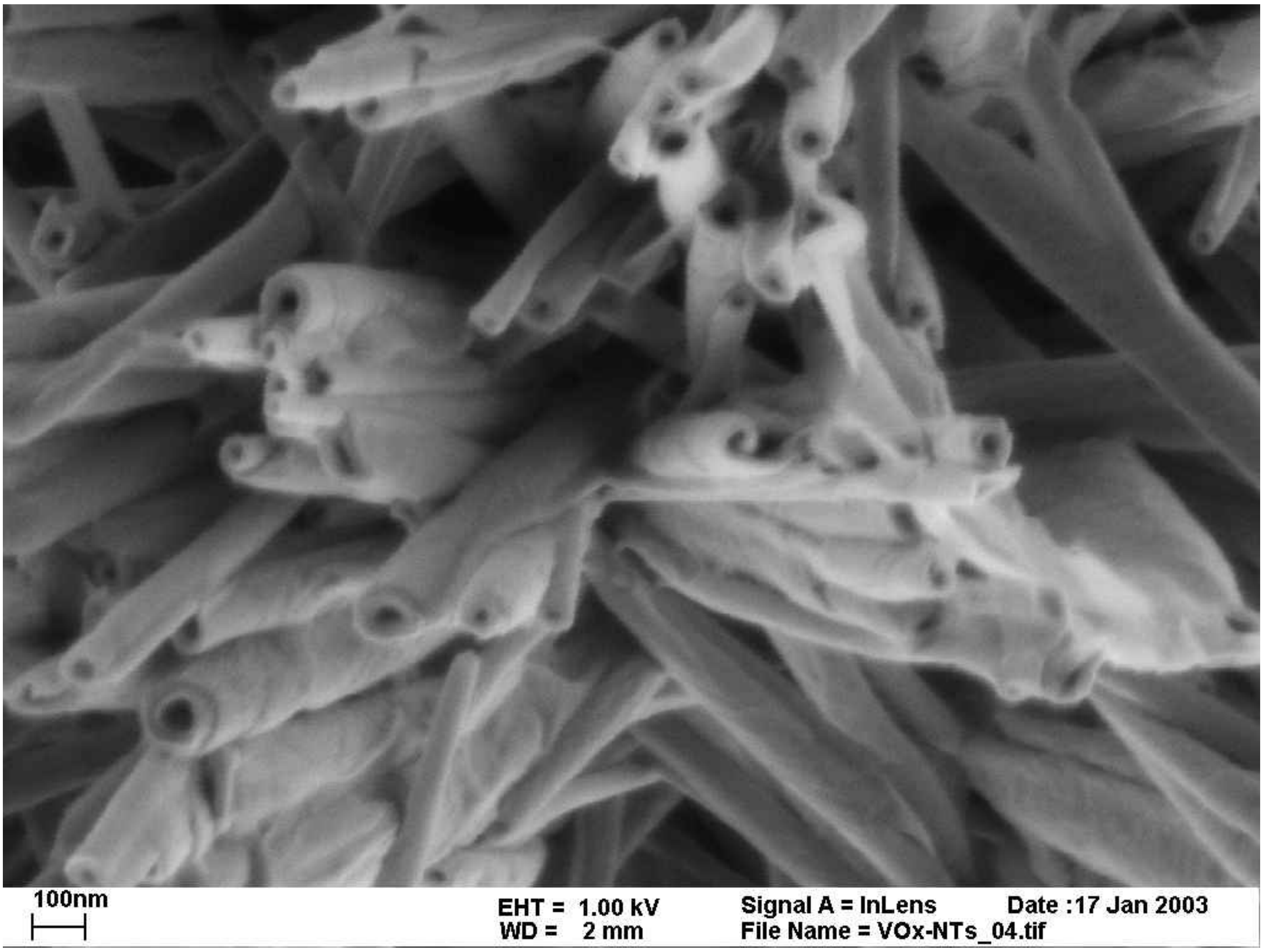
Morphology



SEM images

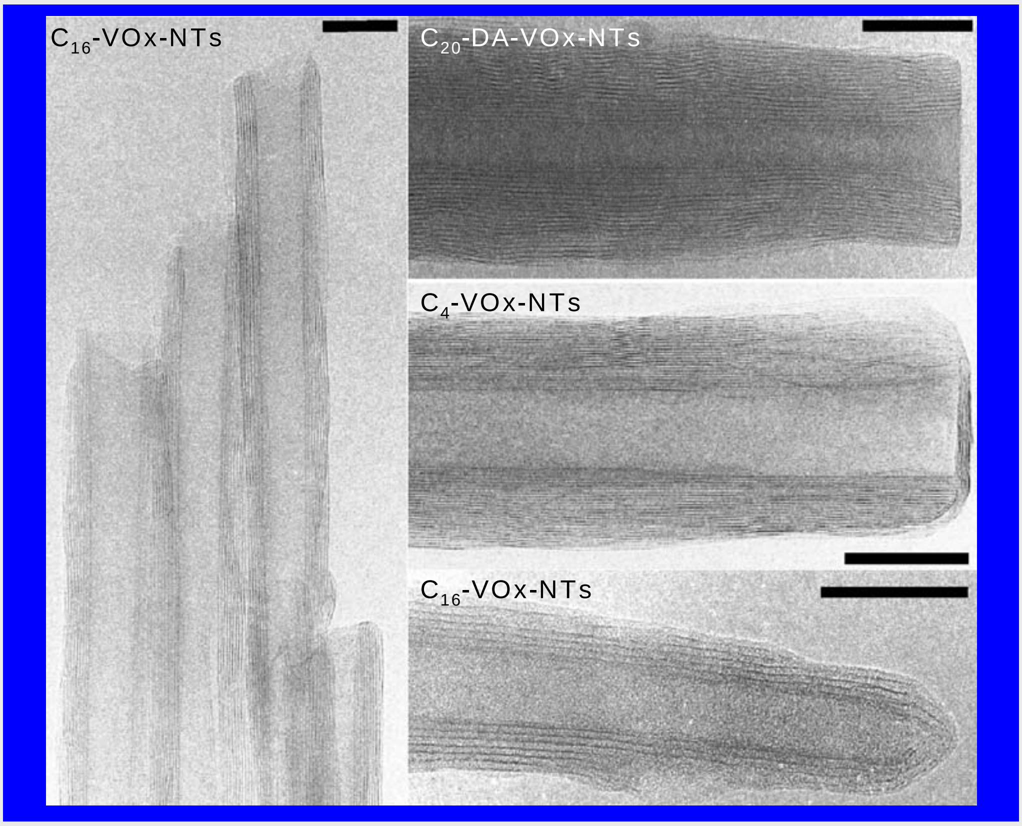
(LEO 1530 Gemini, V_{acc} = 1kV)





VO$_x$-NTs

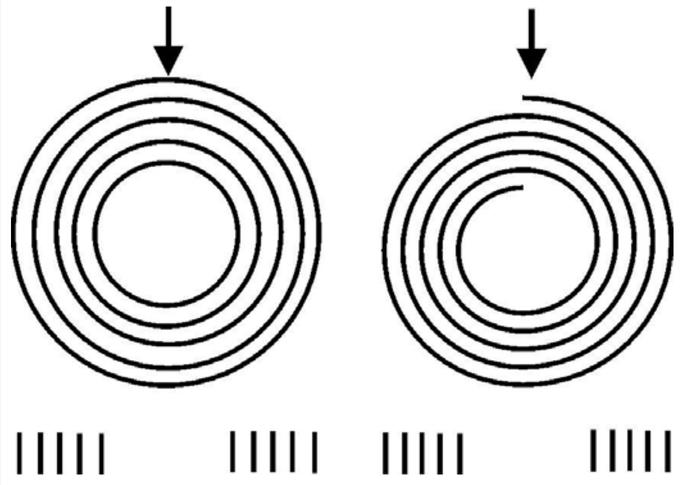
TEM Characterization



Krumeich, Muhr, Niederberger, Bieri, Schnyder, Nesper *J. Am. Chem Soc.* **121** (1999) 8324

Scrolls or Cylinders?

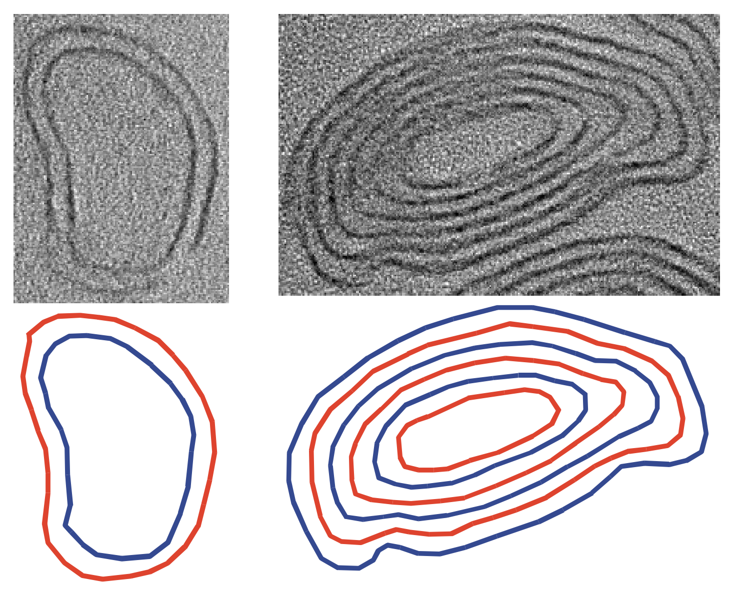
electron beam



schematic
TEM images

Cross-sectional TEM Investigation

Different types of layer structures built up the tube walls

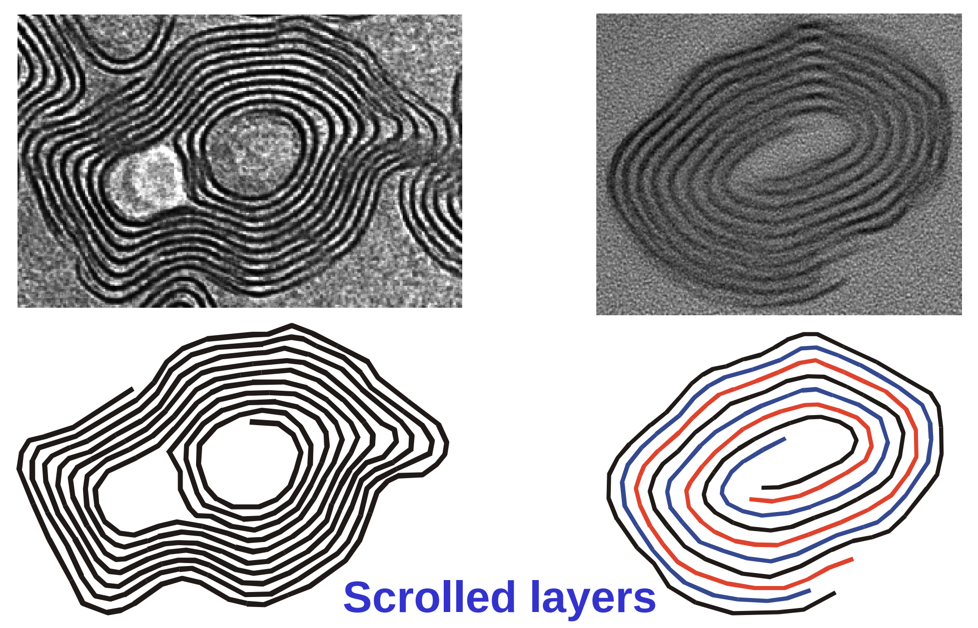


Closed, concentric cylinders

VO_x-NTs

Cross-sectional TEM Investigation

Different types of layer structures built up the tube walls



Scrolled layers

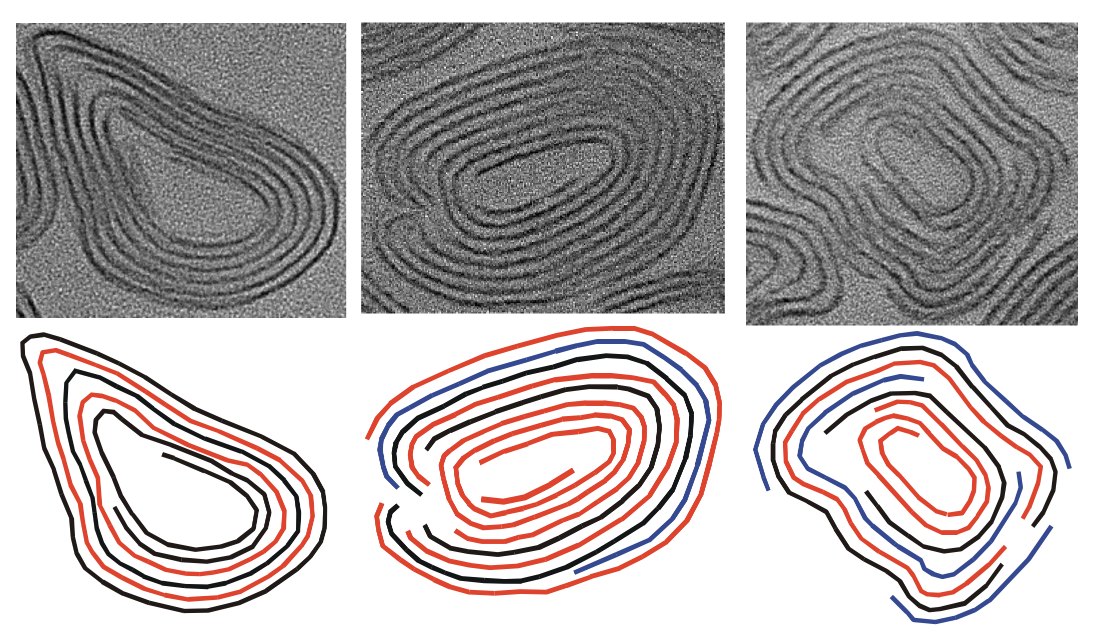
Single layer scroll

Triple layer scroll

VO_x-NTs

Cross-sectional TEM Investigation

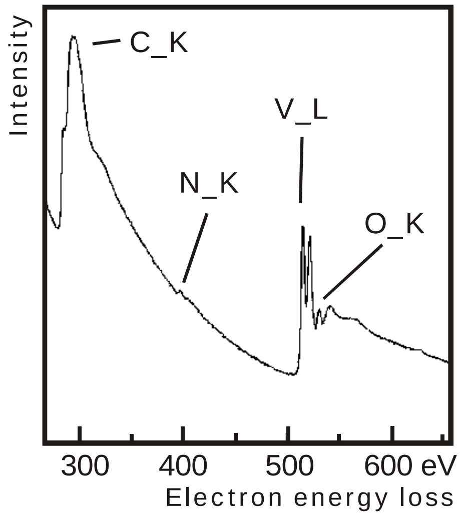
Different types of layer structures built up the tube walls



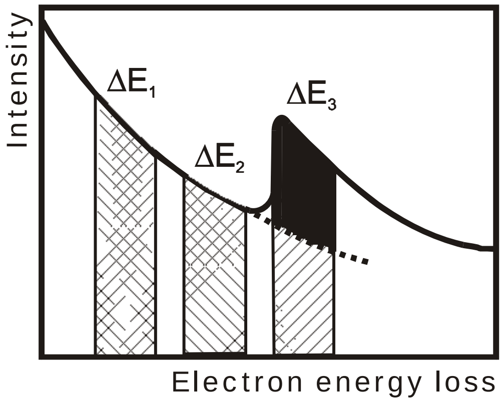
Defective combinations of scrolled and concentric layers

VO_x-NTs

Elemental Maps by Electron Spectroscopic Imaging



Section of the Electron Energy Loss Spectrum (EELS) of C_{12}-VO_x-NTs

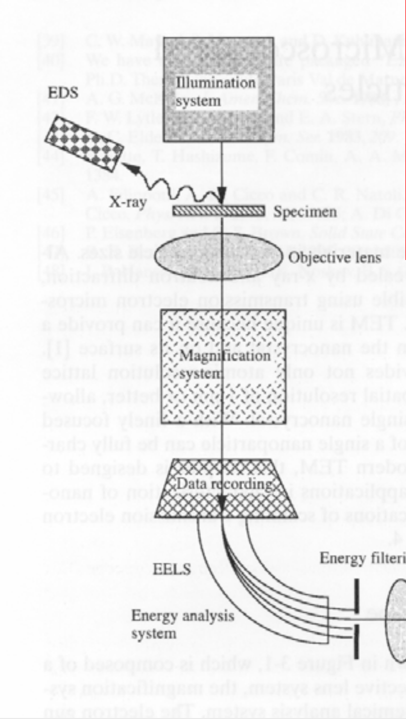


Three window method

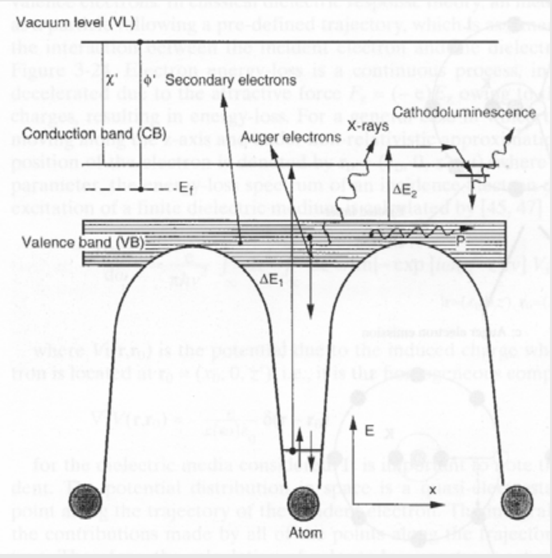
V and C, respectively, are located at the sides that with appear bright contrast.

Krumeich, Muhr, Niederberger, Bieri, R. Nesper *Z. Anorg. Allg. Chem.* 626 (2000) 2208

Transmission Electron Microscopy



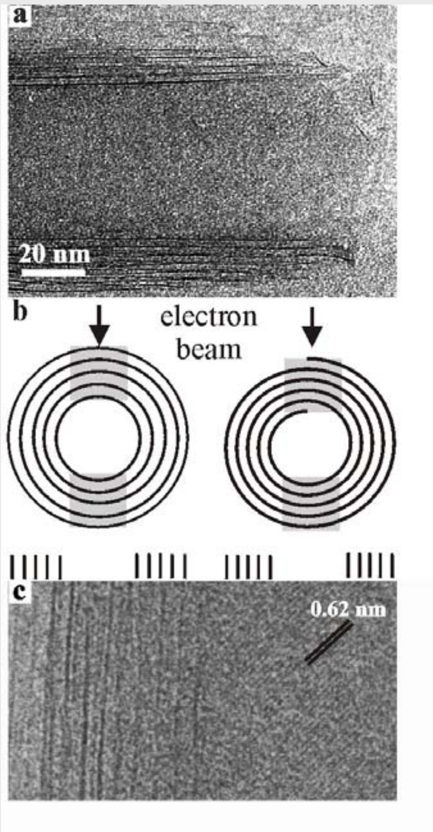
surface analysis 1-10nm

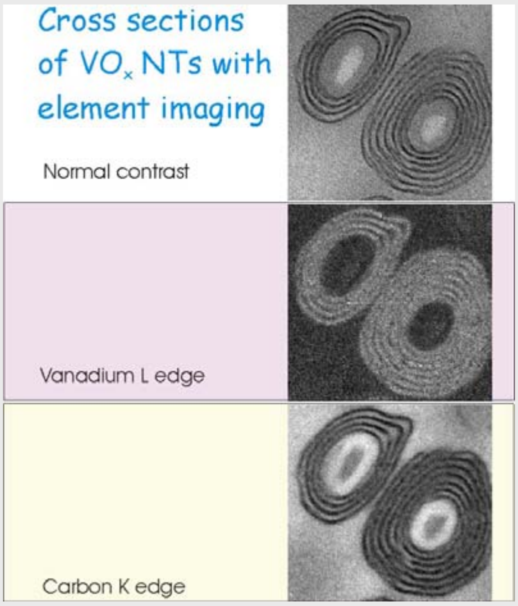


VO_x NTs – layers+componets

templates:
primary amines
C_n n=4-22

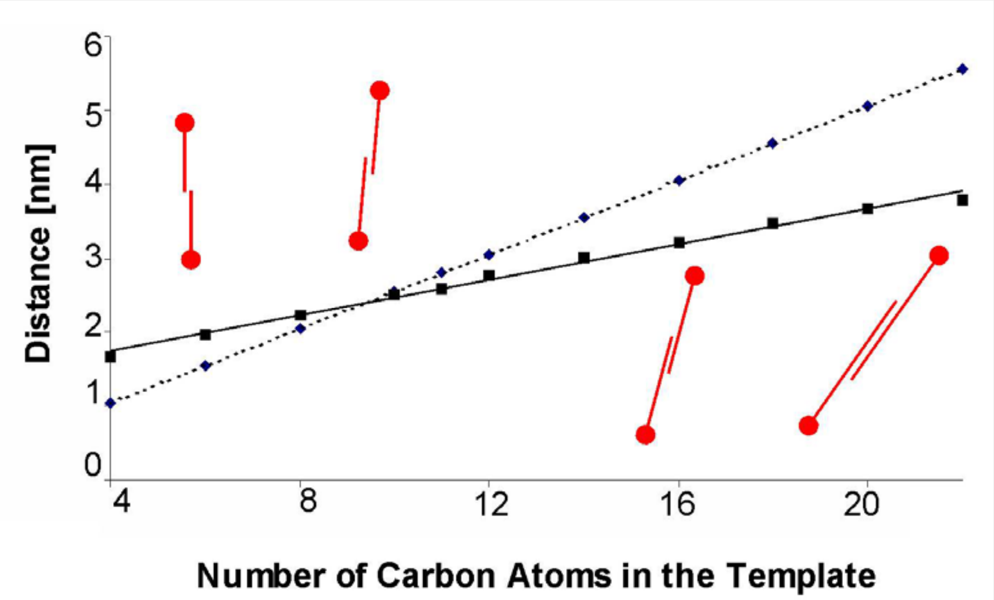
ESCA:
ammonium cations




Cross sections of VO_x NTs with element imaging

VO_x-NTs

Inter-layer distance and template size



Interlayer distances increase proportional to the length of the carbon chain (solid line).

Calculated distances increase with different inclination (dotted line).

STM Structure of the Walls

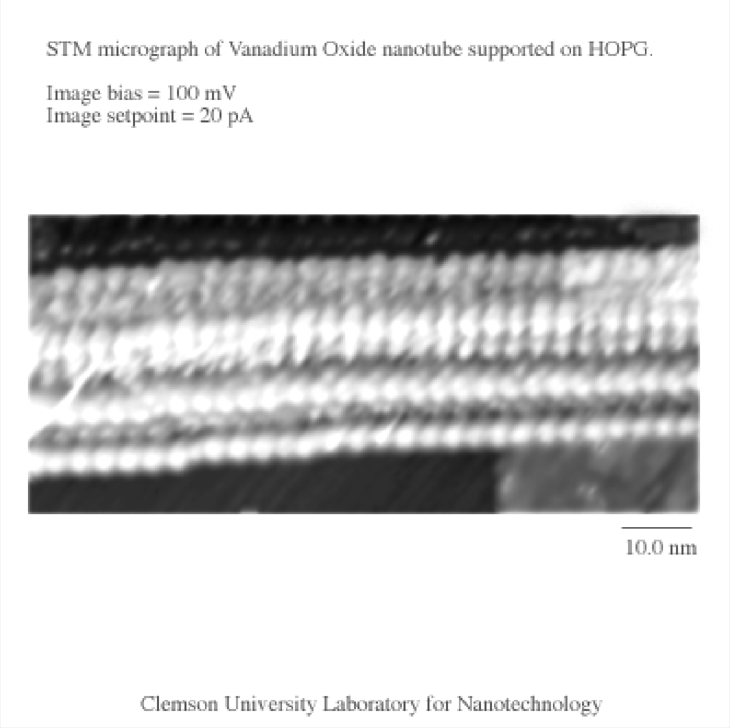
Prof. D. Carroll

Clemson Univ.

structure 1x2 nm

semiconductor

E_G=0.6 eV



STM micrograph of Vanadium Oxide nanotube supported on HOPG.

Image bias = 100 mV
Image setpoint = 20 pA

Clemson University Laboratory for Nanotechnology

Vanadiumoxid NTs - Some Properties

C/H/N/V-Analysis
magnet. measurement
electrical measurement

black powder
hardly wettable by H_2O
response to electrical fields

$VO_{2.45}[R\text{-}NH_3]_{0.27}$ R = C_4 - C_{22}

$VO_{2.45}[NH_3\text{-}R\text{-}NH_3]_{\sim 0.18}$ R = C_4 - C_{12}

paramagnetic $V^{4.63+}$

semiconductor E_G=0.6eV

thermally stable to max. 250°C

VO_x-NTs

Determination of Nanotube Structures

1. **Characterization of morphology**
2. **Characterization of layer arrangement inside the tube walls**
3. **Determination of atomic arrangement**

Problem: **No three-dimensional periodicity!**

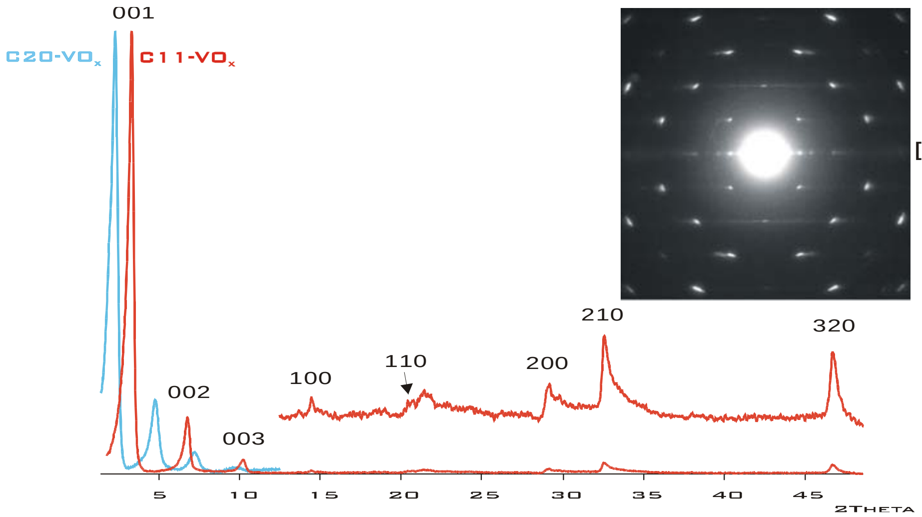
Solution: **Discussion in relation to well-characterized crystal structures**

Structure(s)

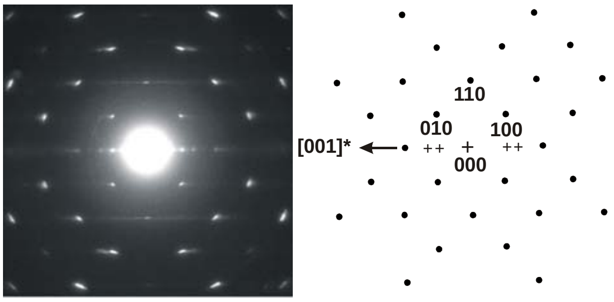
Sharp reflections 00l
- well-ordered layers in the tube walls
- inter-layer distance varies with template size

Square arrangement (a = 0.615 nm) of reflections hk0
- structure within the layers
- independent of template size

X-ray powder diffraction



Electron diffraction



M.Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, U. Nissen, *Angew. Chem. Int. Ed.* 37 (1998) 1263

M. Niederberger, H.-J. Muhr, F. Krumeich, F. Bieri, D. Günther, R. Nesper, *Chem. Mater.* 12 (2000) 1995

Crystalline Phase: (en)V_7O_{16}

Synthesis

$VO(OiPr)_3$ + ethylenediamine

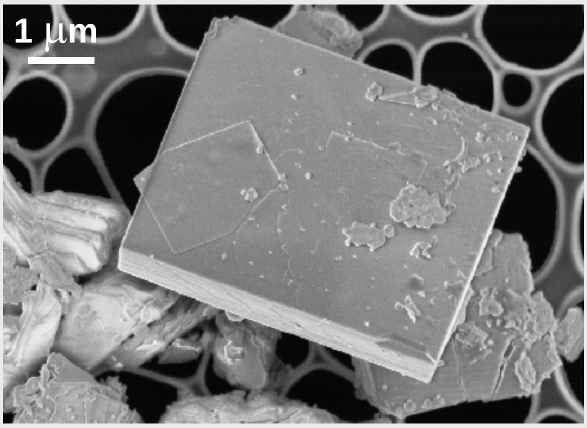
Hydrolysis

Polycondensation

Hydrothermal treatment

(en)V_7O_{16} +
(en)V_4O_{10} (minor by-product)

Morphology



SEM image of a typical plate-like crystal of (en)V_7O_{16}

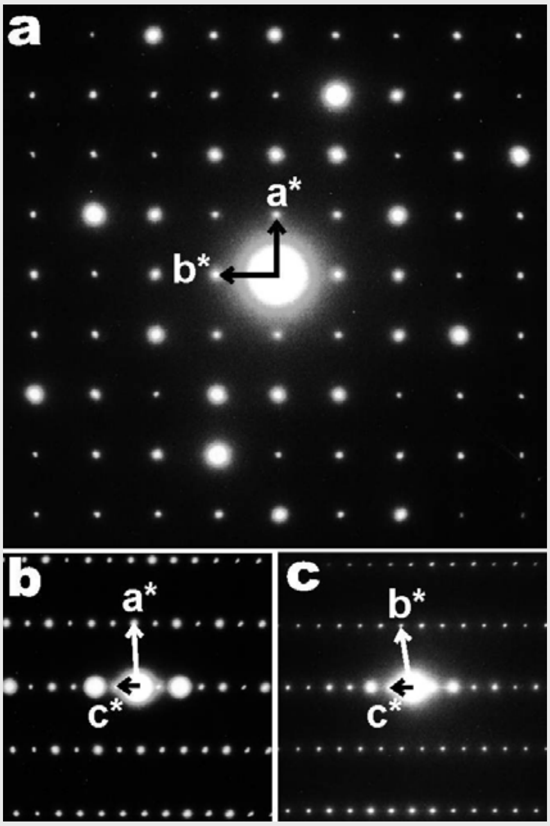
Crystalline Phase: (en)V_7O_{16}

Electron diffraction

triclinic cell

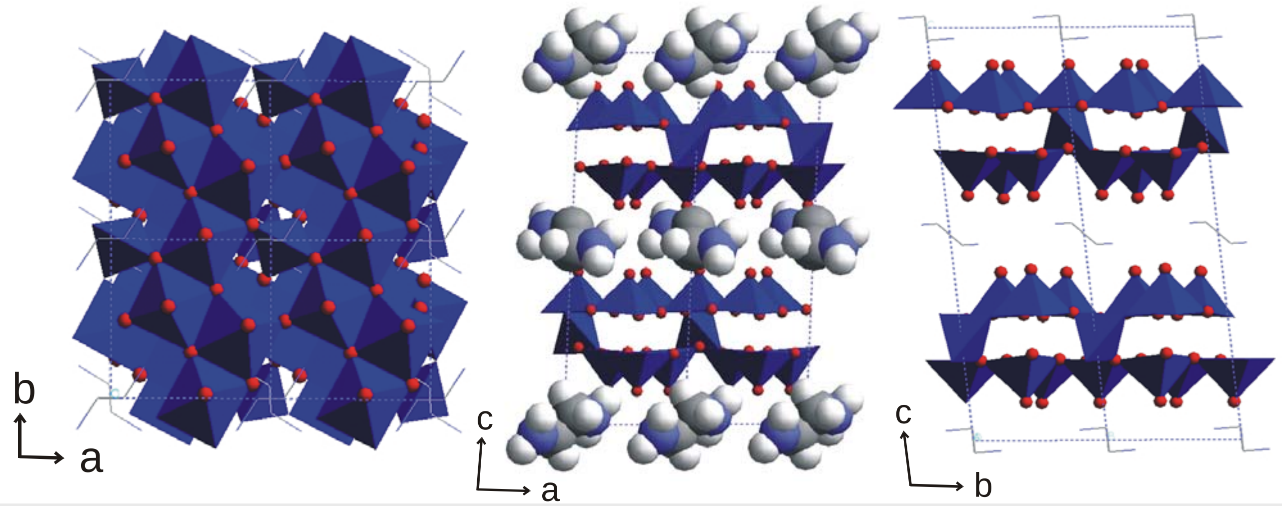
$a \approx b \approx 0.62$ nm, $c \approx 1.85$nm

$\alpha \approx 98°, \beta \approx 93°, \gamma \approx 90°$



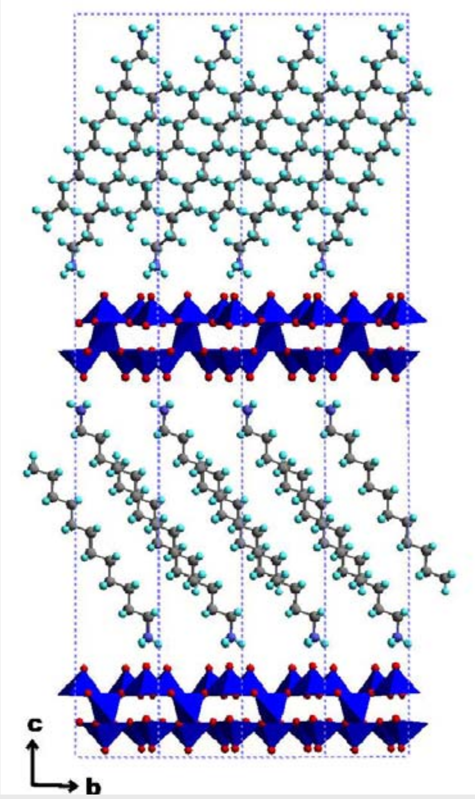
Structure of (en)V_7O_{16}

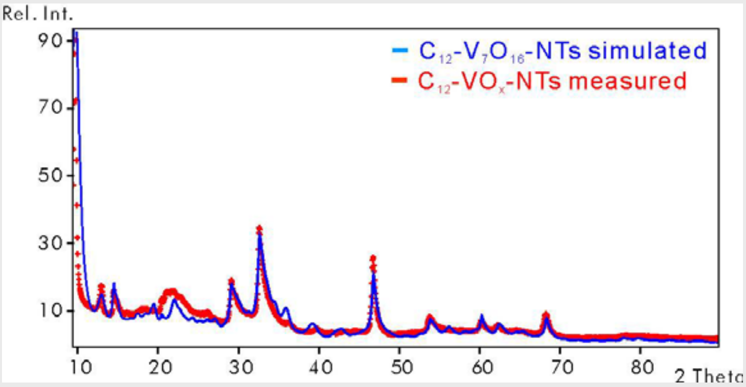
$P\bar{1}$: a=0.616, b=0.617, c=1.91 nm, α=96.14, β=92.82, γ=90.07



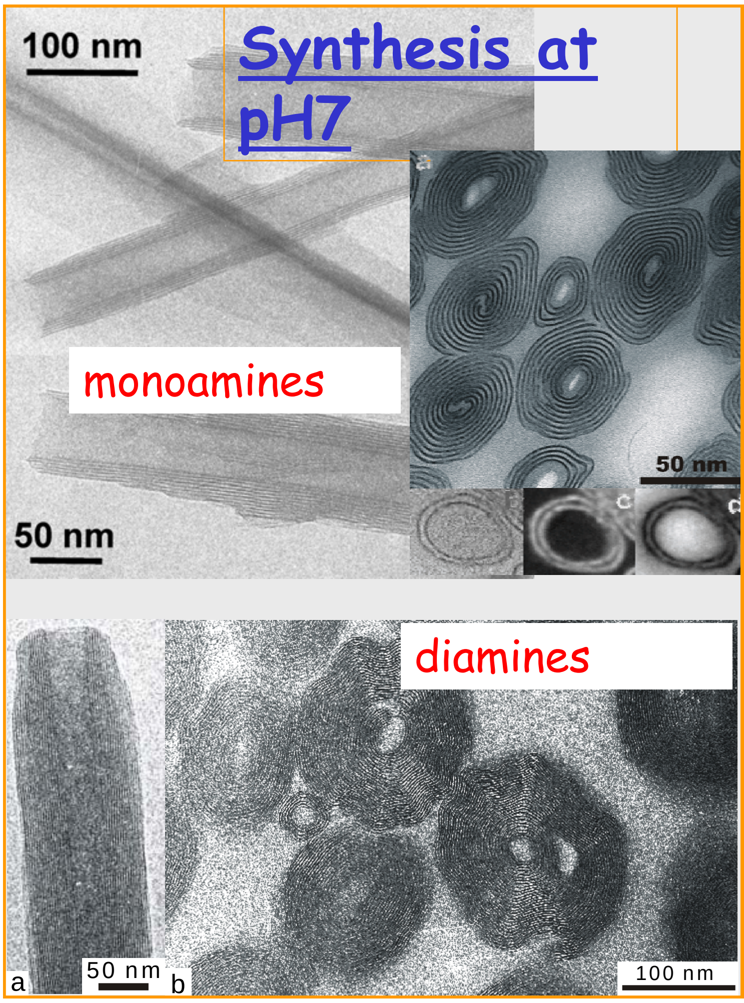
- Ethylene diamine (en) molecules are embedded between V_7O_{16} layers.
- Two sheets of VO_5 square pyramids with the apices pointing in opposite directions.
- VO_4 tetrahedra connect the two VO_5 sheets.

Model for the Wall Structure of VOx-NTs





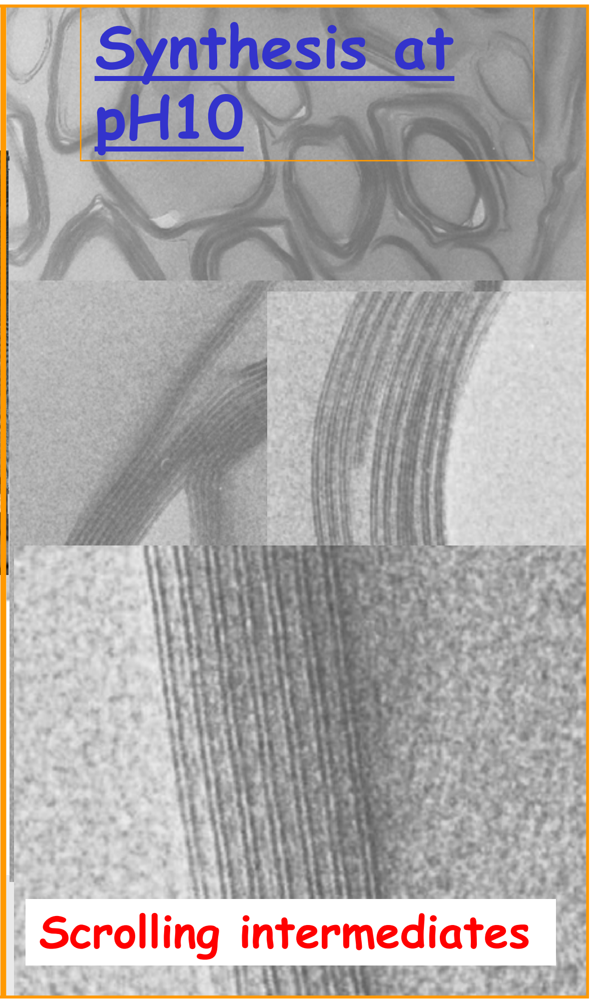
- **Model derived on the basis of the VO_x layer structure present in the related crystalline phases (en)V_7O_{16} and BaV_7O_{16}.**
- **Simulated and observed XRD patterns agree well.**
- **As in the structure of (en)V_7O_{16}, the long c axis is twice as long as the layer distance.**



Synthesis at pH7

monoamines

diamines



Synthesis at pH10

Scrolling intermediates

Modified VO_x-NTs

Synthesis

$VO(OiPr)_3 + C_nH_{2n+1}NH_2$ (n=12-14)

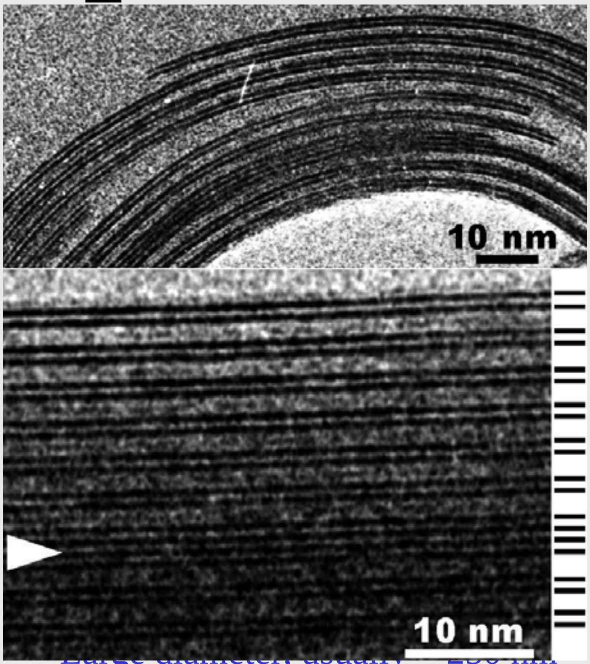
Hydrolysis

Addition of ammonia

Polycondensation

Hydrothermal treatment

Novel type of VO_x-NTs



- Large diameter, usually ~ 250 nm
- Length 2-5 mm
- Relatively small aspect ratio

Unique layer structure inside tube walls:

Long (~2 nm) and short (~0.9 nm) inter-layer distances occur alternately.

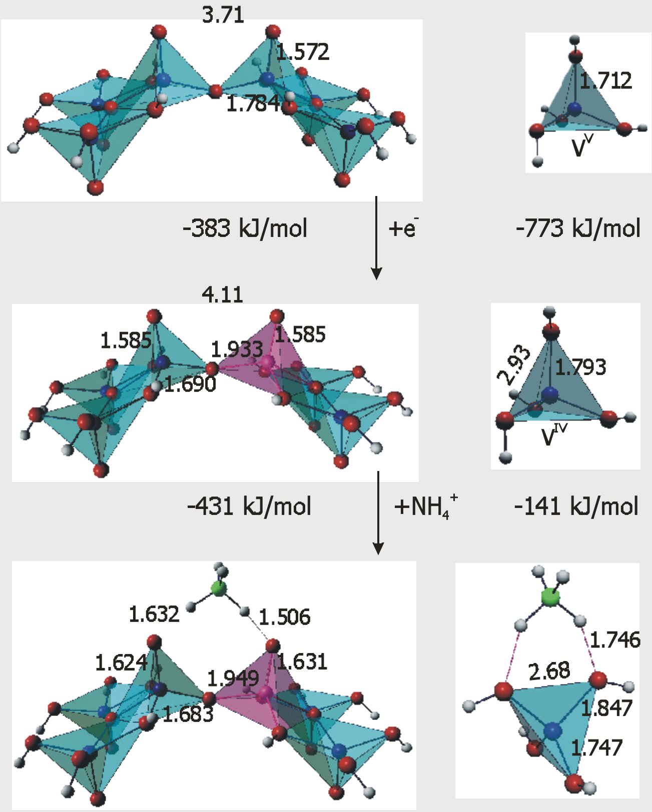
Pillai, Krumeich, Muhr, Niederberger, Nesper, *Solid State Ionics* 141-142 (2001) 185

Calculated Curvature Changes

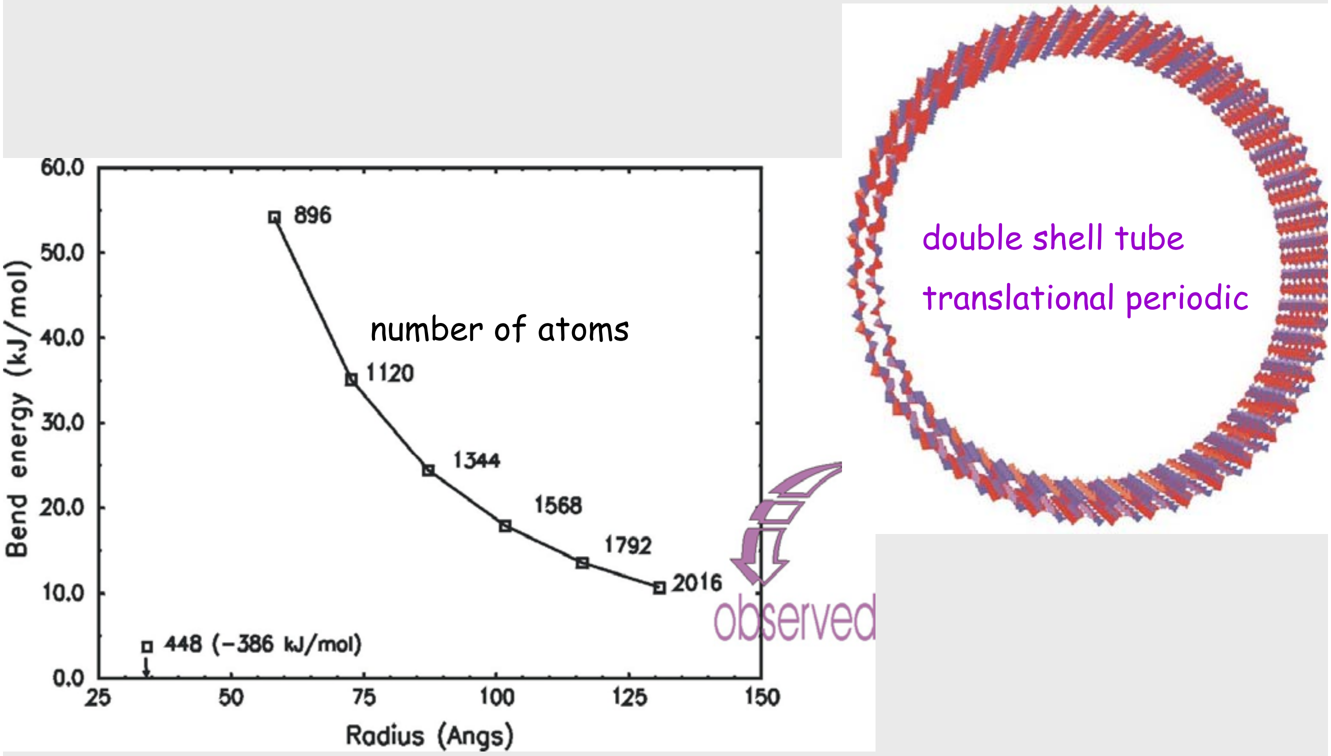
Structure and energy changes

upon reduction

and NH_4^+ adsorption



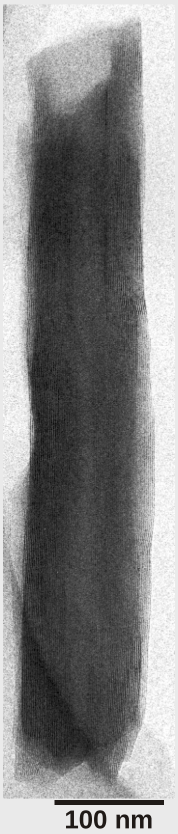
Modelling of VO_x -NTs

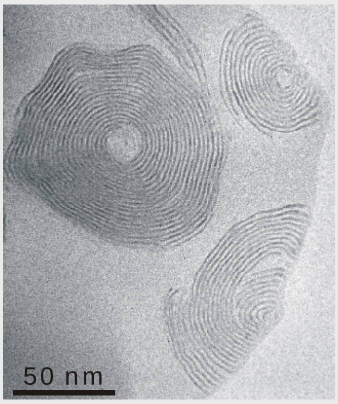


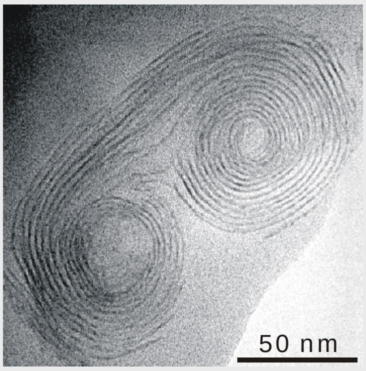
double shell tube

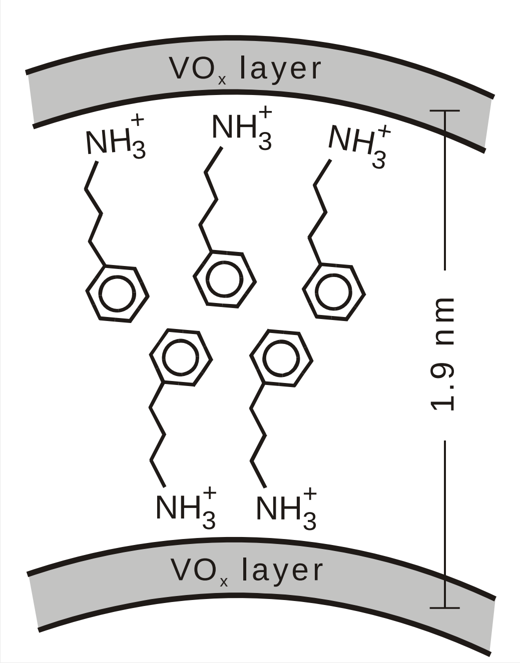
translational periodic

3-Phenylpropylamine as template



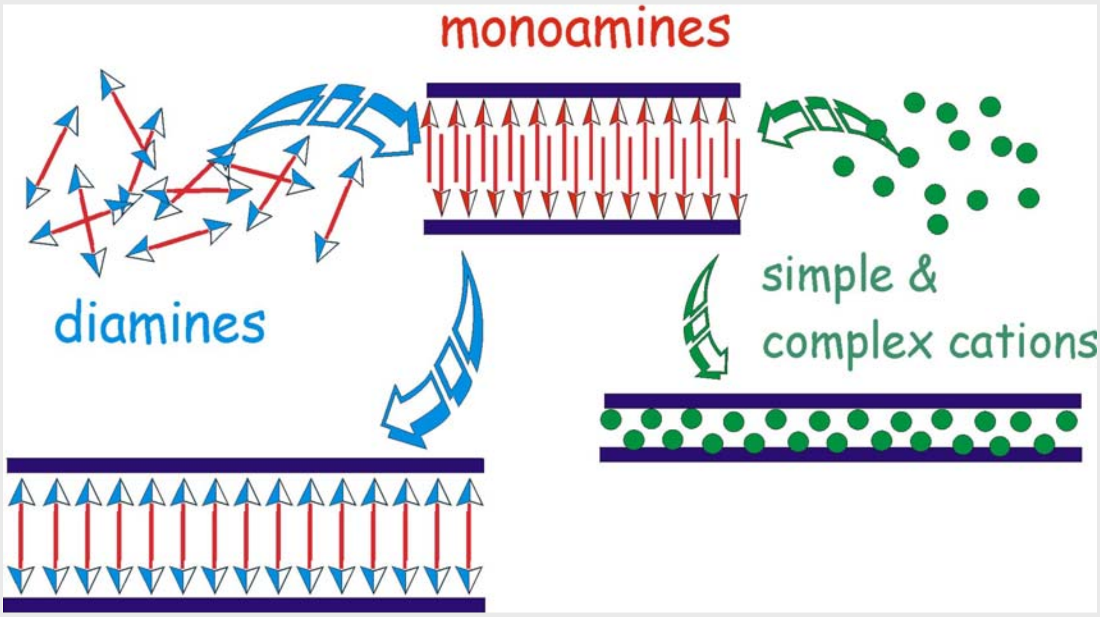




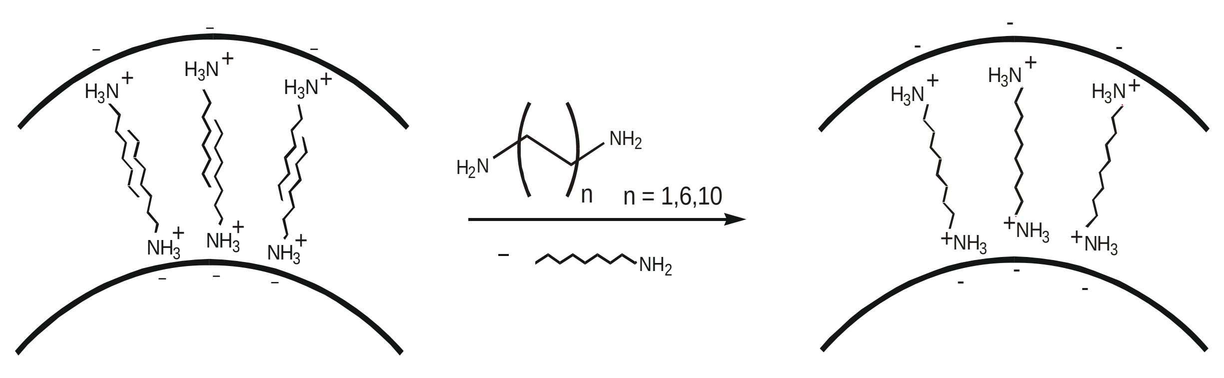


Bieri, Krumeich, Muhr, R. Nesper *Helv. Chim. Acta* 84 (2001) 3015

Exchange Reactions

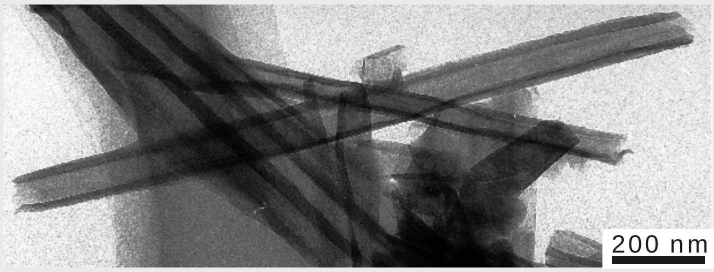


Exchange Rections:
Substitution of Monoamine Templates by α,ω-Diamines



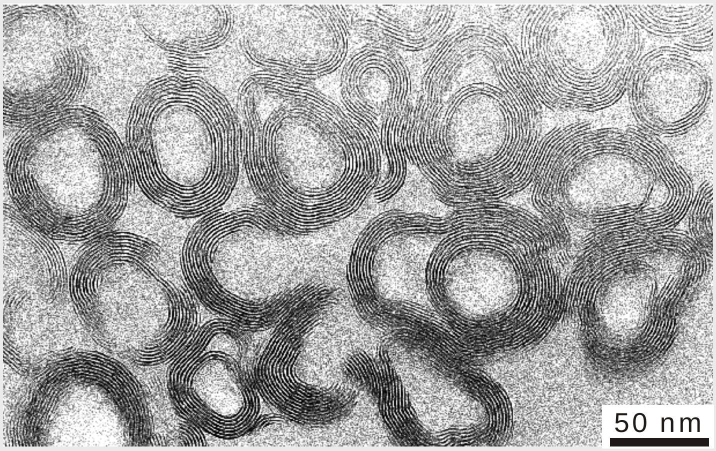
Krumeich, Muhr, Niederberger, Bieri, Reinoso, Nesper, *Nanophase and Nanocomposite Materials III*, MRS Proc. 581 (2000) 393

Exchange Rections:
Substitution of Monoamine Templates by α,ω-Diamines



C_2-DA-VO_x-NTs, obtained from C_{11}-VO_x-NTs by exchange with ethylene diamine

Interlayer distance:
2.62 → 1.7 nm

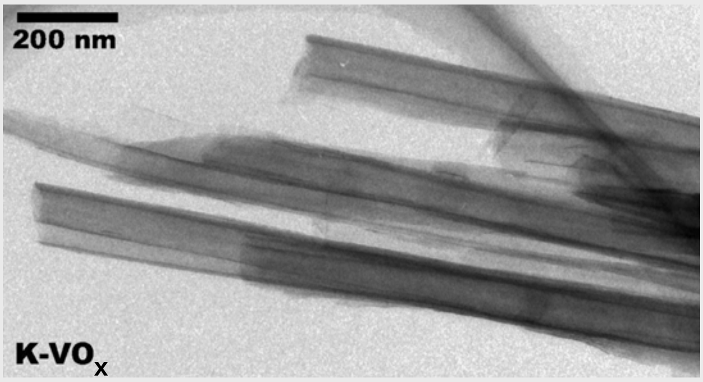


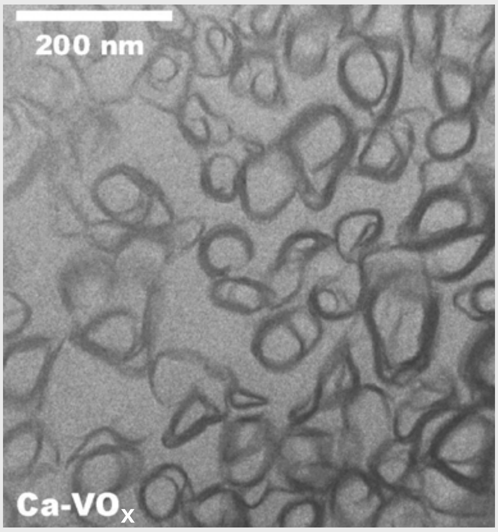
C_{12}-DA-VO -NTs, obtained from C_{11}-VO -NTs by exchange with 1,12-dodecylamine.

inter-layer distance:
2.62 → 1.83 nm.

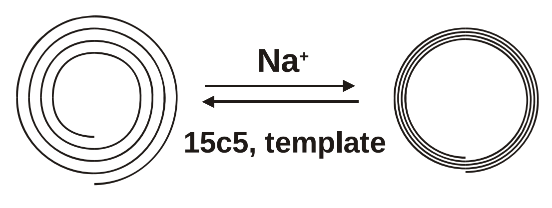
Krumeich, Muhr, Niederberger, Bieri, Reinoso, Nesper, *Nanophase and Nanocomposite Materials III*, MRS Proc. 581 (2000) 393

Exchange Rections:
Substitution of Monoamine Templates by Cations





Tubular structure is preserved.
Inter-layer distance decreases to 0.9 – 1 nm,
e.g., C_{12}-VO_x ⟶ Na-VO_x: 2.75 ⟶ 0.97 nm.



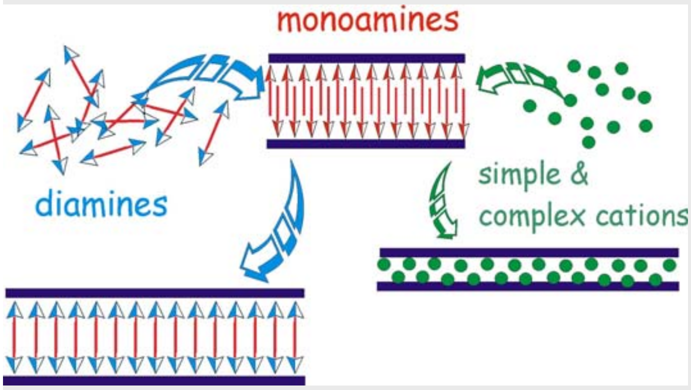
Na^+ $\rightleftarrows$ 15c5, template

Ion selectivity: K/Na = 10

Reversible cation uptake and release.

Reinoso, Muhr, Krumeich, Bieri, R. Nesper *Helv. Chim. Acta* 83 (2000) 1742

Cation Exchange Reactions



exchanged	not exchanged
Na^+, K^+	Li^+, Rb^+, Cs^+
Mg^{2+}, Ca^{2+},Sr^{2+}	Ba^{2+}
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}	
Sm^{3+}, Tb^{3+}	

Ion1	ion2	selectivity
Na^+	K^+	1 : 16
Na^+	Mg^{2+}	3 : 1
Na^+	Ca^{2+}	1 : 5
Na^+	Sr^{2+}	1 : 23

Topotactic redox reactions of copper(II) and iron(III) salts within VO_x Nanotubes

Novel Cu- and Fe-containing nanotubes of composition VO1.53 -2.1 (C12H28N)0.21Cu0.08(H2O)v0.56Clv0.01 and VO2.08vxv2.68

(C12H28N)0.13Fe0.19(H2O)v0.33Clv0.01 have been obtained by exchange of the protonated template in dodecylamine-Vox nanotubes with Cu(II) and Fe(III) salts. The exchanged materials have quite different characteristics in respect to the parent nanotubes, namely a wider inner diameter and thinner walls, owing to reduced interlayer spacings in their multiwalled structure.

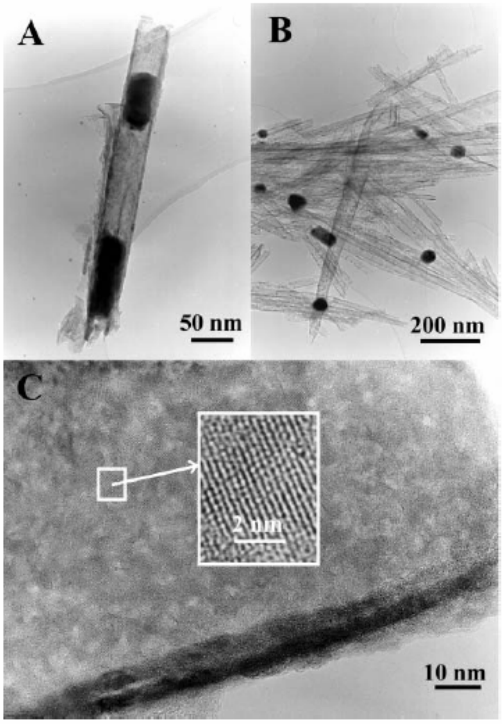
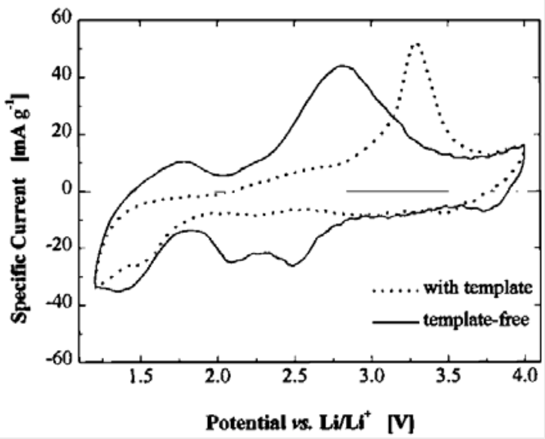


Fig. 11 HRTEM micrographs of the Cu-containing VO_x nanotubes after thermolysis at 650 °C under N_2. A: copper nanoparticles within a V_2O_3 nanotubes; B: enlarged view of VO_x nanotubes and isolated copper nanoparticles outside of the tubes; C: high magnification image of the tube walls composed mainly of 3–5 nm V_2O_3 crystallites and small Cu nanoparticles.

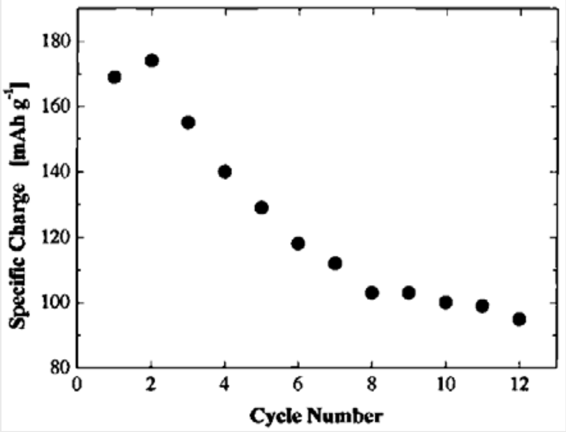
VO_x-NTs

Electrochemistry

Cyclic voltammogram of VO_x-NTs recorded at 50 mV/s in $LiClO_4$/ propylene carbonate.



Dependence of specific charge on the cycle number.



- **Electrochemical insertion of Lithium in VO_x-NTs is possible.**
- **Specific capacities of up to 200 mAh/g have been achieved.**
- **Rapid decay of tube structure causes drop of specific capacity.**

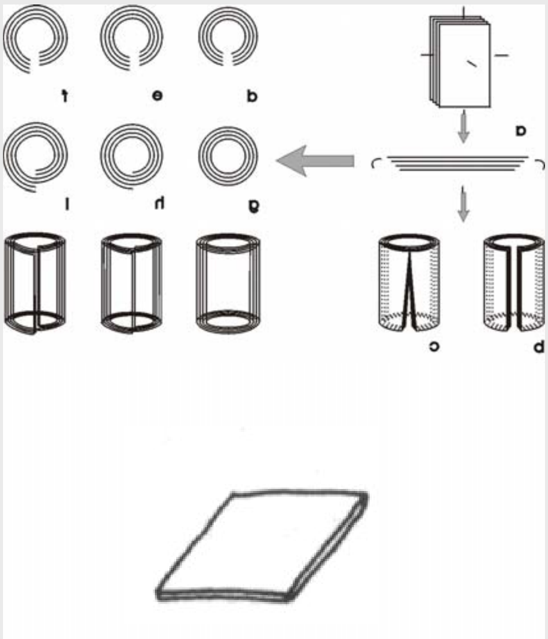
Spahr, Stoschitzki-Bitterli, Nesper, Haas, Novák, *J. Electrochem. Soc.* 146 (1999) 2780

Summary

- First tubular vanadate nanophase
- Simple synthesis: sol-gel reaction + hydrothermal treatment
- Morphology depends on template
- Mixed valency: 45% V^{4+} , semiconductor, band gap ~ 0.60 eV
- Layer structure in VO_x-NTs is isostructural to that in $(en)V_7O_{16}$
- Topochemically active nanosystem
- Reversible intercalations / electrochemisty
- Ion selectivity
- optical limiting properties

A Multitude of Nanotubes ?

stability of layers ?



=>> Scrolling of layers

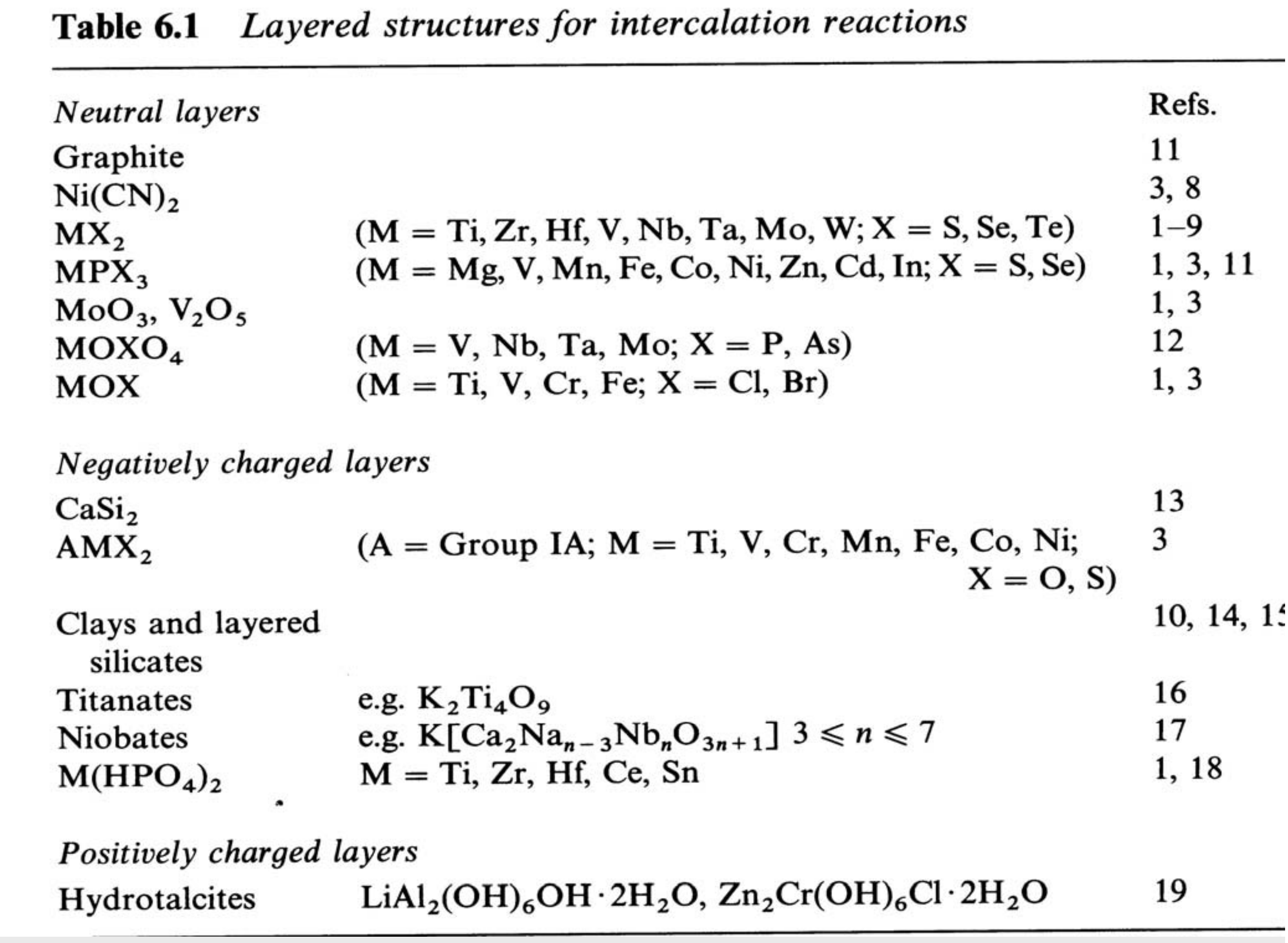


Table 6.1 *Layered structures for intercalation reactions*

		Refs.
Neutral layers		
Graphite		11
$Ni(CN)_2$		3, 8
MX_2	(M = Ti, Zr, Hf, V, Nb, Ta, Mo, W; X = S, Se, Te)	1–9
MPX_3	(M = Mg, V, Mn, Fe, Co, Ni, Zn, Cd, In; X = S, Se)	1, 3, 11
MoO_3, V_2O_5		1, 3
$MOXO_4$	(M = V, Nb, Ta, Mo; X = P, As)	12
MOX	(M = Ti, V, Cr, Fe; X = Cl, Br)	1, 3
Negatively charged layers		
$CaSi_2$		13
AMX_2	(A = Group IA; M = Ti, V, Cr, Mn, Fe, Co, Ni; X = O, S)	3
Clays and layered silicates		10, 14, 1
Titanates	e.g. $K_2Ti_4O_9$	16
Niobates	e.g. $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ $3 \leqslant n \leqslant 7$	17
$M(HPO_4)_2$	M = Ti, Zr, Hf, Ce, Sn	1, 18
Positively charged layers		
Hydrotalcites	$LiAl_2(OH)_6OH \cdot 2H_2O$, $Zn_2Cr(OH)_6Cl \cdot 2H_2O$	19

Optical Properties of VO_x Nanotubes and VO_x Nanotube-Composites

Optically active nanoparticles

1. tremendous importance for optical limiting purposes
   (very little Rayleigh scattering in the visible spectrum)
2. particular interest in multiphoton or excited state absorptions
   (very fast optical limiting phenomena in semiconductors like ZnO, ZnSe, InSb etc.)

Nonlinear Optical Transmission in VO_x Nanotubes and VO_x Nanotube-Composites

Two different absorption processes

1. 532 nm : ablation
2. 1064nm: unscrolling of tubes

J.-F. Xu, R. Cerw, S. Webster, D. L. Carroll, J. Ballato, R Nesper, *Appl. Phys. Lett*. 81 (2002) 1711

S. Webster, R. Cerw, R. Nesper, J. DiMaio, J.-F. Xu, J. Ballato, D. L. Carroll, *J. Nanosci. Nanotechnol. 4 (2004) 260* application

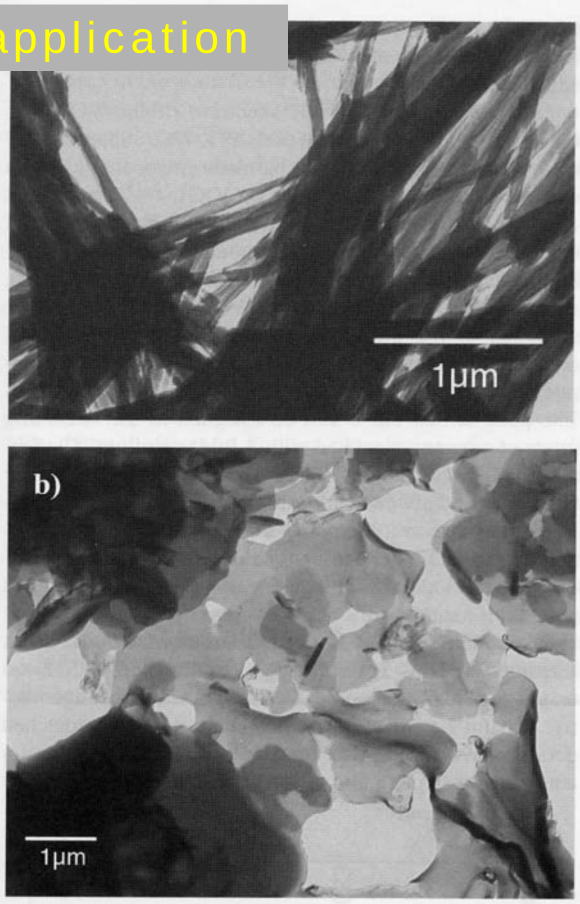


Fig. 1. (a) TEM image of VO_x nanotubes. (b) TEM image of unrolled nanotubes (platelets).

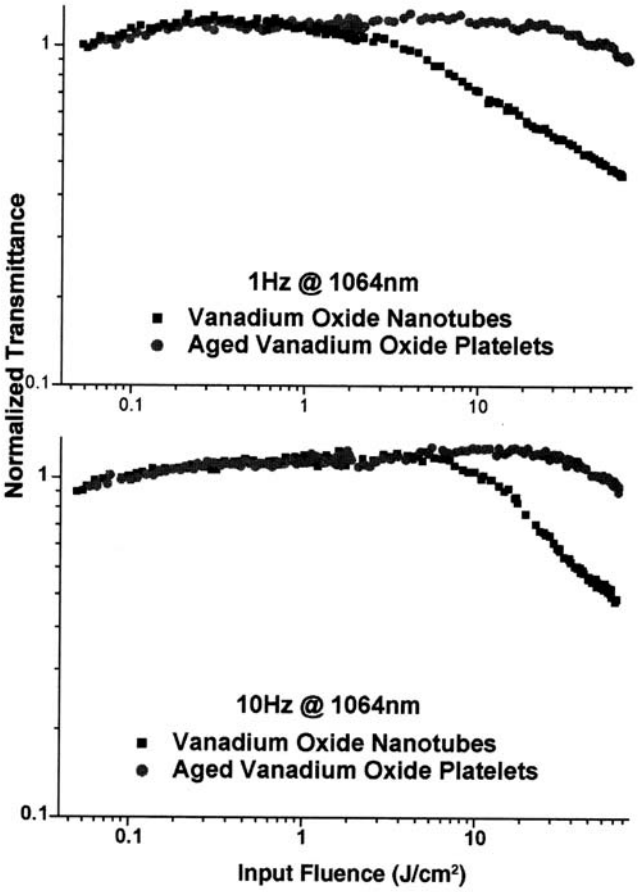


Fig. 7. Optical limiting of VO_x-NTs (black) and aged VO_x-NTs (red) at 1064 nm with a pulse repetition rate of (a) 1 Hz and (b) 10 Hz.

Electrochemistry of VO_x-NTs

S. Nordlinder, K. Edström, T. Gustafsson, *Electrochemical and Solid-State Letters*, **4 (2001)** A129-A131

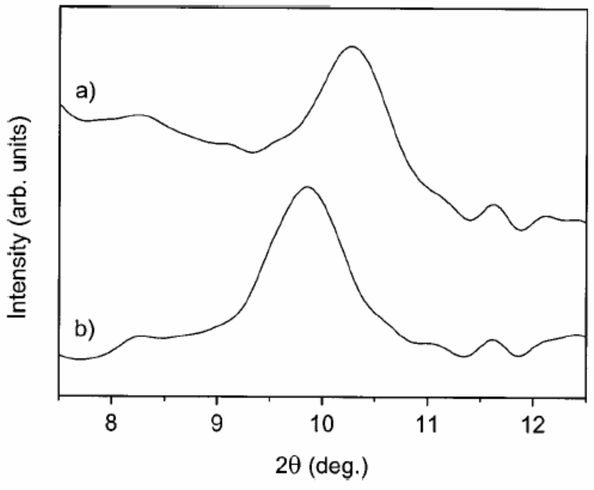


Figure 5. *Ex situ* XRD patterns for (a) Na-VO_x nanoroll cell cycled 100 times with LiTFSI salt in the electrolyte. (b) Uncycled Na-VO_x nanoroll cell.

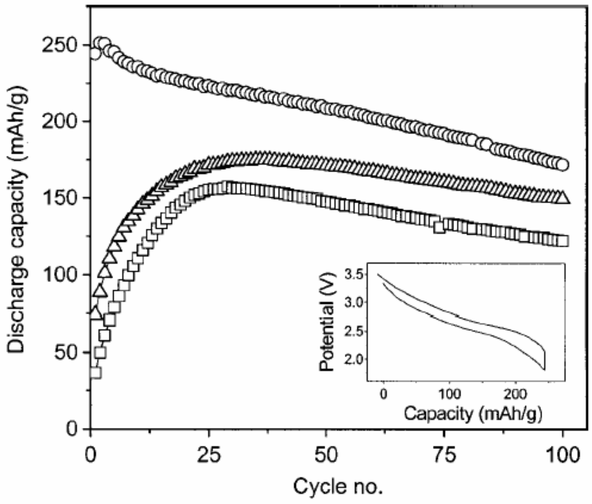


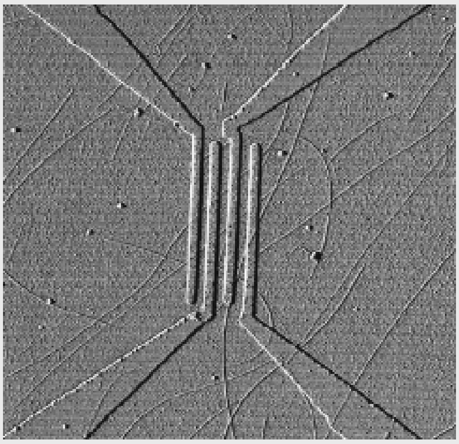
Figure 3. Discharge capacities for cells cycled with three different salts in the electrolytes; LiTFSI (○), $LiBF_4$ (△), $LiPF_6$ (□). The inset displays the first discharge/charge cycle for the cell cycled with LiTFSI-electrolyte. The potential is given *vs.* Li/Li^+.

VO_x-rods

Transistor

S. Roth et al., APPLIED PHYSICS LETTERS VOLUME 76, 2000, 1875

J. Muster et al. Adv. Mater. 2000, 12, No. 6



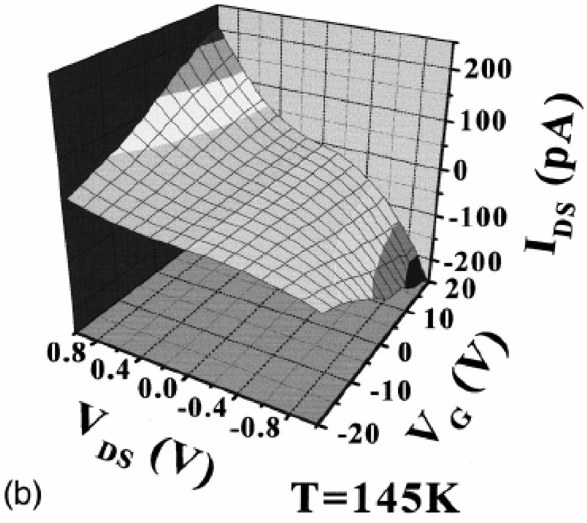


FIG. 2. (a) Current–voltage characteristics obtained from the middle two electrodes (see Fig. 1) with zero gate voltage ($V_G = 0$ V) at different temperatures $T = 131$, 145, 160, 192, 294 K. (b) 3D plot of I/V curves in dependence of gate voltage at $T = 145$ K.

Nonlinear Optical Transmission in VO_x Nanotubes and VO_x Nanotube-Composites

J.-F. Xu, R Nesper, and D. L. Carroll

Optically active nanoparticles have gained tremendous importance for optical limiting purpose because they exhibit very little Rayleigh scattering in the visible spectrum. It is now widely known that different phenomena may lead to optical limiting. Light scattering in carbon black suspensions ~CBS, beam fanning in photorefractive materials and nonlinear optical absorption in C60, as a reverse saturable absorber, are all different examples of optical limiting mechanisms that have shown excellent performance for fast eye protection in the visible portion of the spectrum. Of particular interest in nanophotonic materials are mechanisms that involve multiphoton or excited state absorptions. An example of such a mechanism includes twophoton absorption ~TPA, which generally involves a transition from the ground state of a system to a higher-lying system by simultaneous absorption of two photons, and is well known to lead to very fast optical limiting phenomena in semiconductors, such as ZnO, ZnSe, InSb, as well as in some organic materials.

Nonlinear Optical Transmission in VO_x Nanotubes and VO_x Nanotube-Composites

J.-F. Xu, R. Czerwa, S. Webster, D. L. Carroll, J. Ballato, R. Nesper, APPLIED PHYS. LETT. 2002, 81, 1711

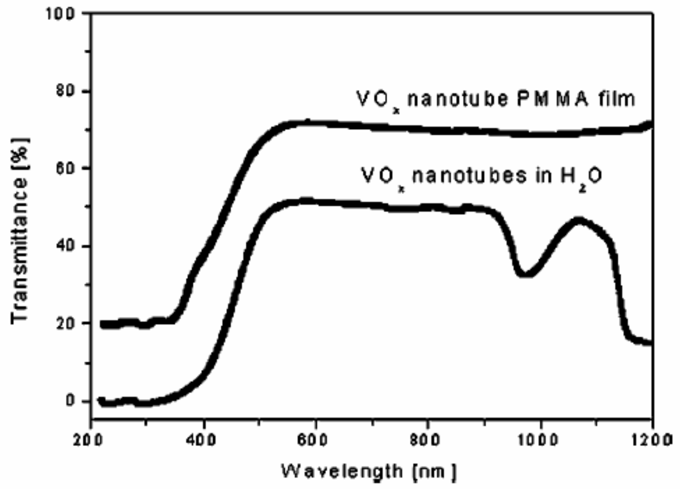


FIG. 2. Linear transmittance of VO_x nanotubes in water and PMMA film. The spectrum for the film is shifted vertically by 20% for presentation.

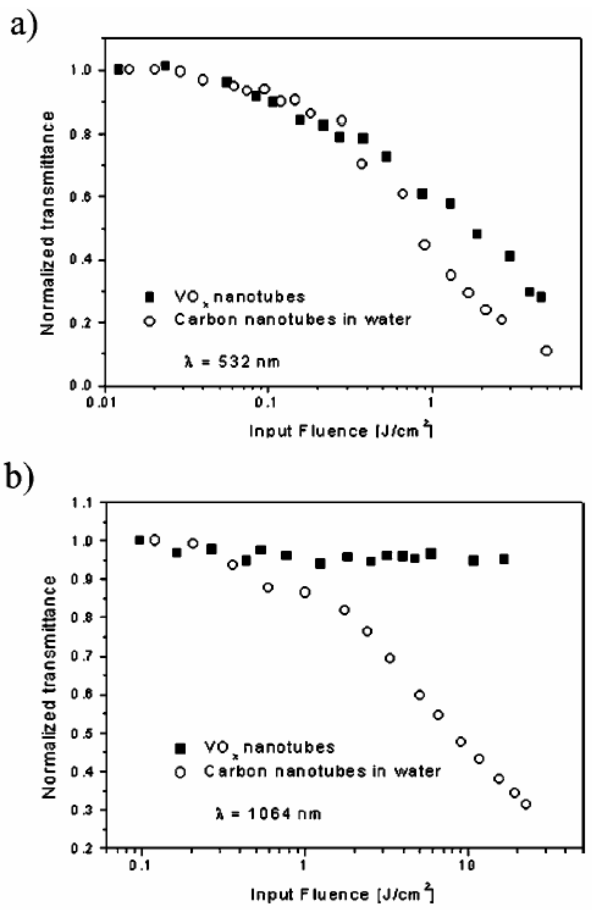


FIG. 3. (a) Comparison of the optical limiting performance of VO_x nanotubes and MWNTs at 532 nm. (b) comparison of the optical limiting performance of VO_x nanotubes and MWNTs at 1064 nm.