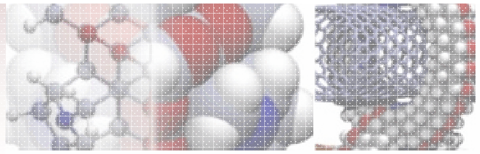

Oxides nanotubes and their applications

Maria Zaharescu

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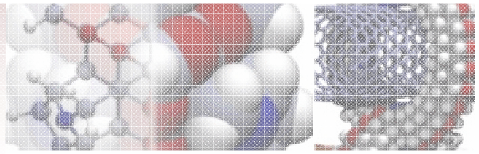
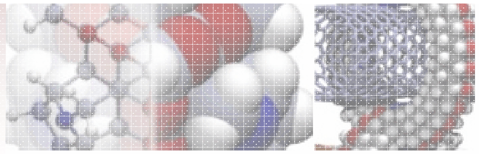


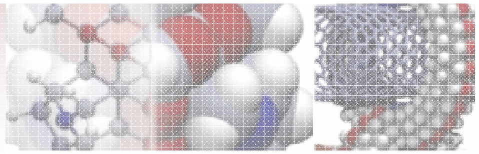
Introduction

- Carbon nanotubes (CNT) were discovered in 1991
- Since then, the interest for inorganic nanotubes increased intensively and **nanotubes of numerous inorganic compounds** were synthezised:
  - layer d-metal dichalcogenides MX_2 (M = Mo, W; Ta; X= S, Se)
  - other type of chalcogenides: InS, ZnS, Bi_2S_3, TiS_2, $TiSe_2$, CdS, CdSe, Ag_2S,
  - boron nitride (BN), carbide (BC_x) and carbonitride ($B_xC_yN_z$)
  - semiconducting materials, such as: SiGe, InGe/GaAs, InGaAs/GaAs, SiGe/Si, InGeAs/GaAs
  - nanotubes of metals: Co, Sb, Se, Bi,
  - **p-**, **d-, f-metal** (Al, **Si,** Ge, **Ti, Zn,** Nb, Ta, Zr, V, Mo, Dy, Tb) **oxides**



Introduction

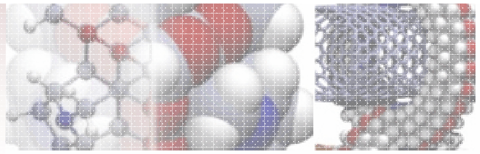
- Graphene was descovered in 2004
- In 2011 inorganic monoatomic layers are reported:
  - BN, MoS_2, Mg_3B_2, WSe_2
  - $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$



Introductionn

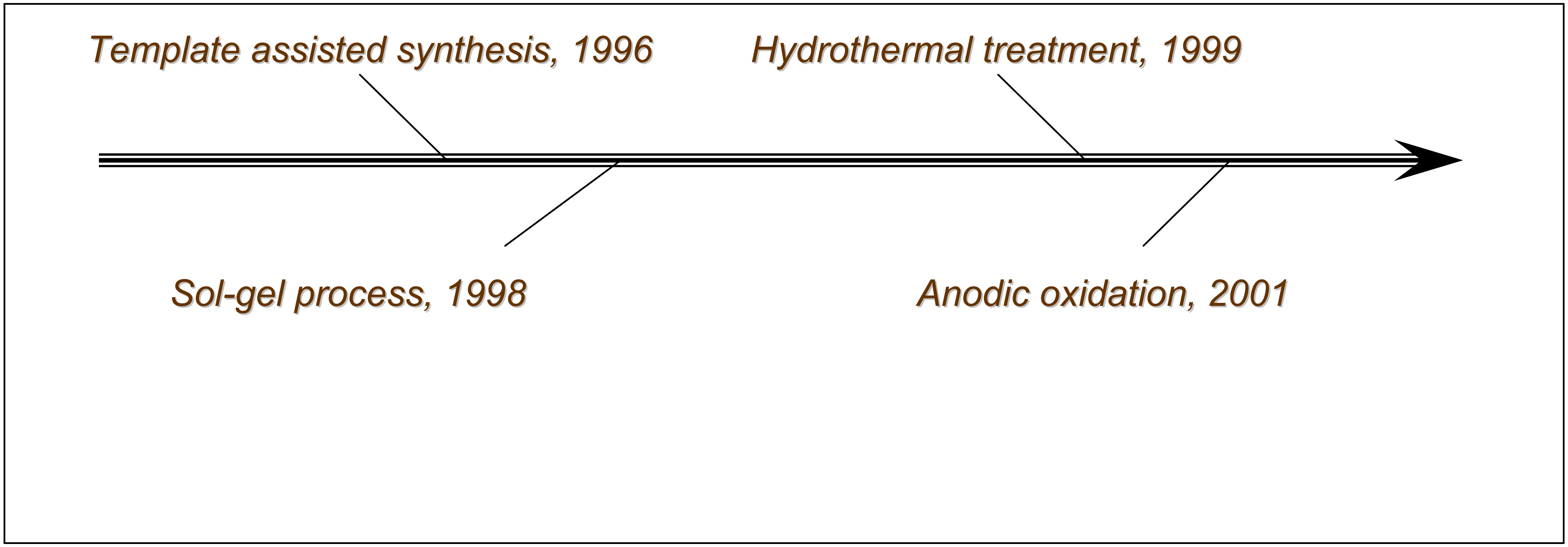
Potential application of oxide nanotubes:

- catalysis
- biochemistry
- separation science and nanotechnology
- sensors
- solar cells
- immobilization and stabilization of biologically active compounds like enzymes, antibodies, microorganisms and drugs



TiO$_2$ based nanotubes

Evolution of TiO$_2$ nanotubes preparation methods



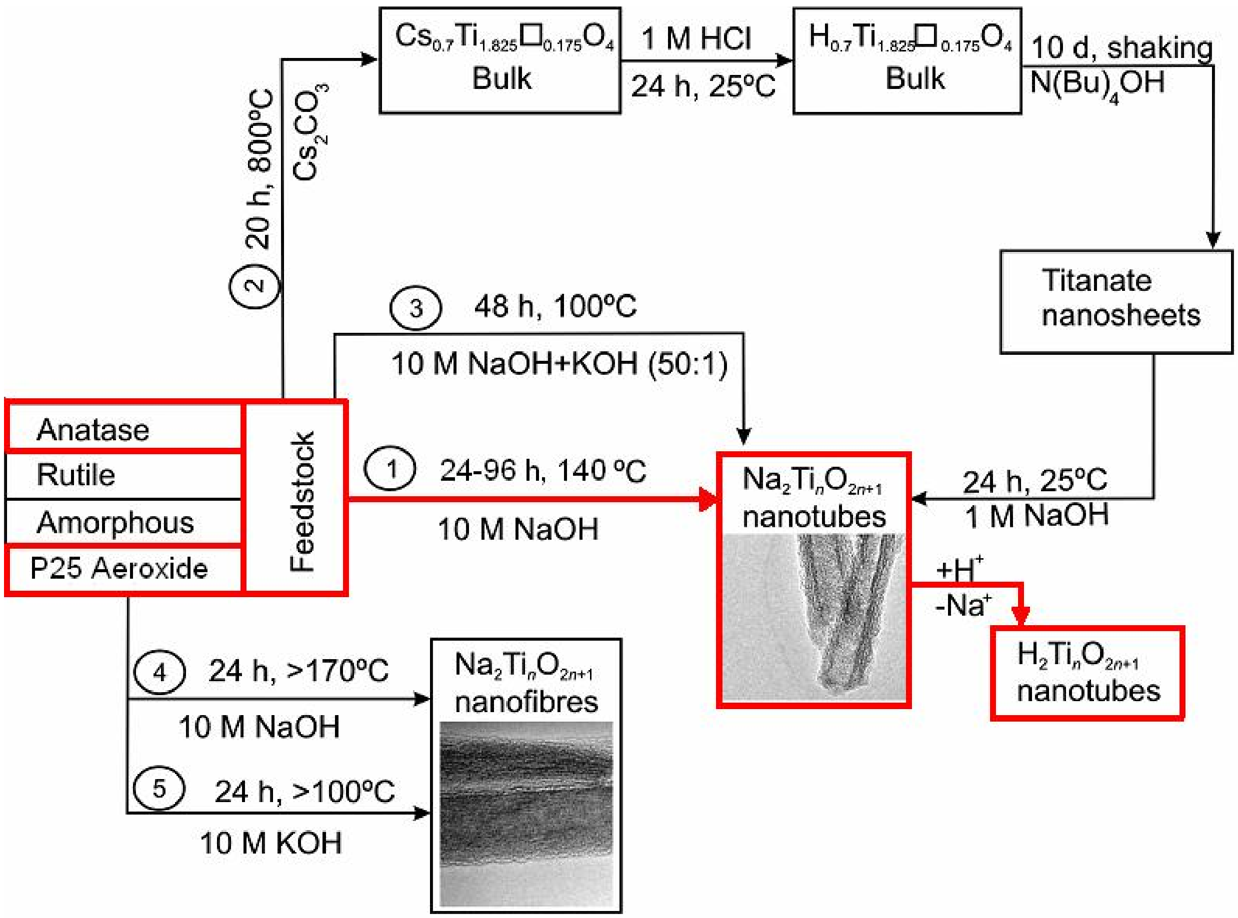
Template assisted synthesis, 1996

Hydrothermal treatment, 1999

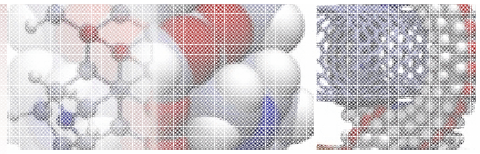
Sol-gel process, 1998

Anodic oxidation, 2001

TiO_2 based nanotubes



D. V. Bavykin, Frank C. Walsh, Elongated Titanate Nanostructures and Their Applications, *Eur. J. Inorg. Chem. 2009, 977–997*



TiO_2 based nanotubes

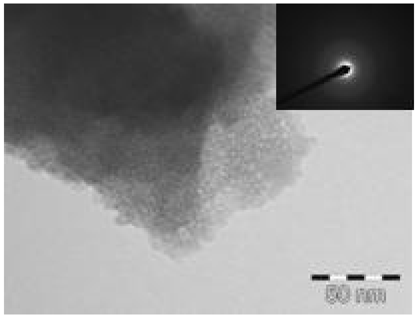
- **PRECURSORS**:

  - TiO_2 P25 Aeroxide Degussa (D),
  - Anatase Aldrich (A) and
  - Amorphous and sol-gel TiO_2 powder (SGA)
  - Nano-crystalline sol-gel TiO_2 powder (SG)

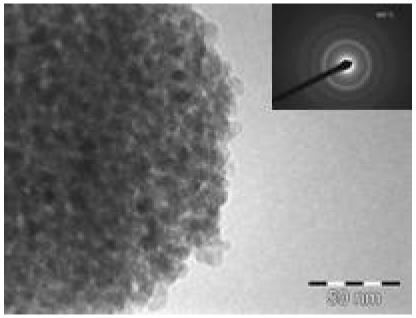
- **EXPERIMENTAL CONDITIONS**:

  1. Hydrothermal treatment at 140°C for various times (from 26-96 hours) in the presence of 10 M NaOH solution

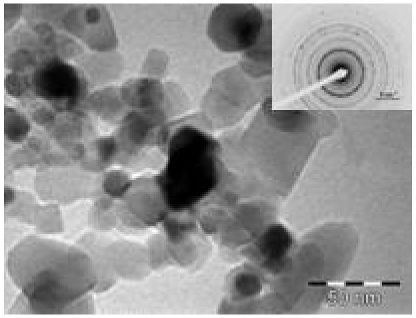
TiO_2 based nanotubes



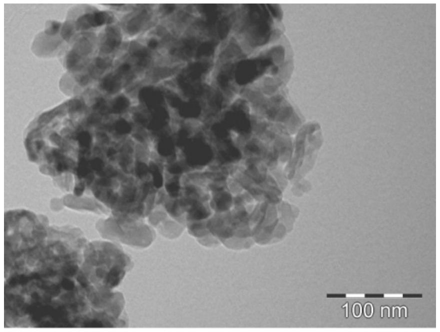
Sol-gel TiO_2 dried powder



Sol-gel TiO_2 thermally treated powder at 400°C

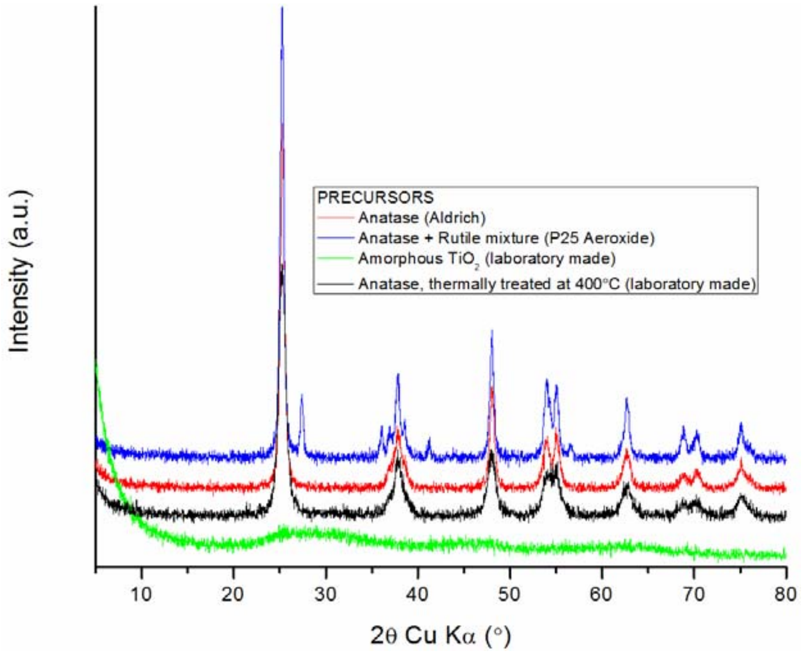


Commercial TiO_2 P25 Aeroxide



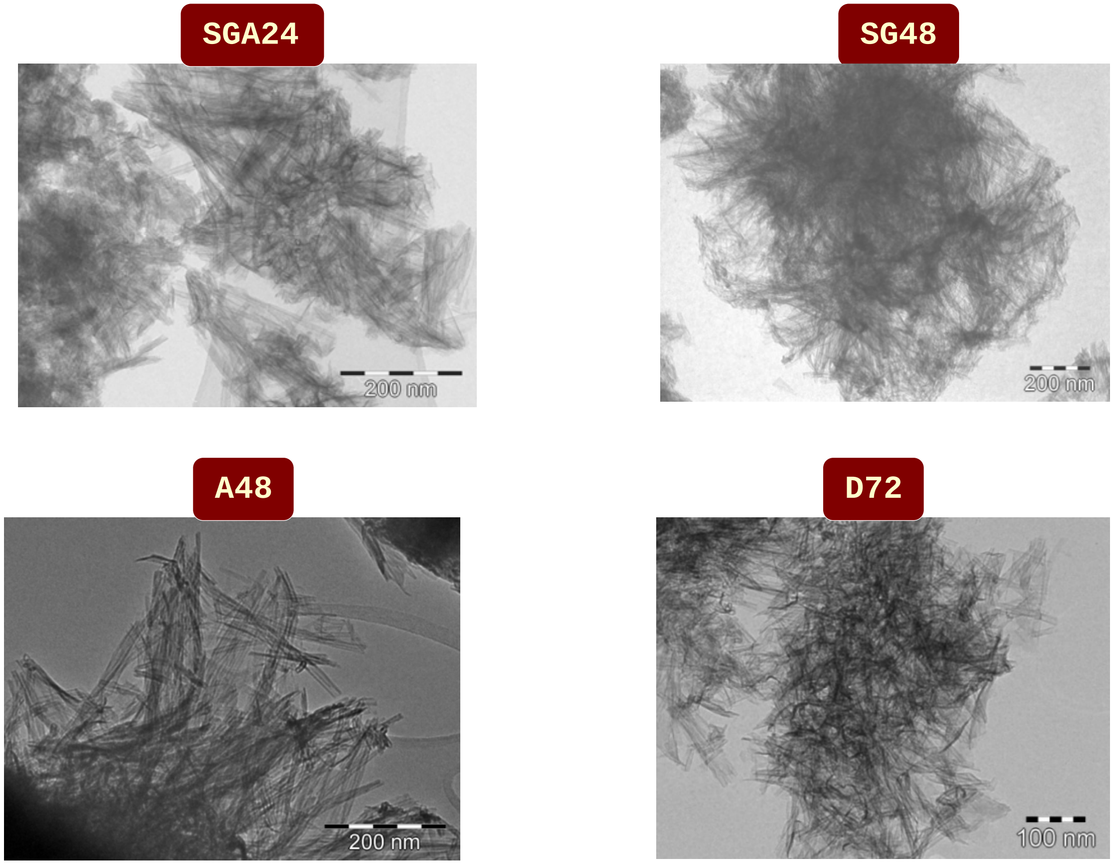
Commercial TiO_2 Aldrich

TEM and SAED images of the precursors



XRD patterns of the precursors

TiO_2 based nanotubes

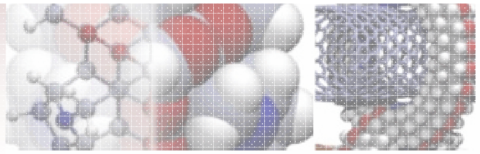

SGA24

SG48

A48

D72

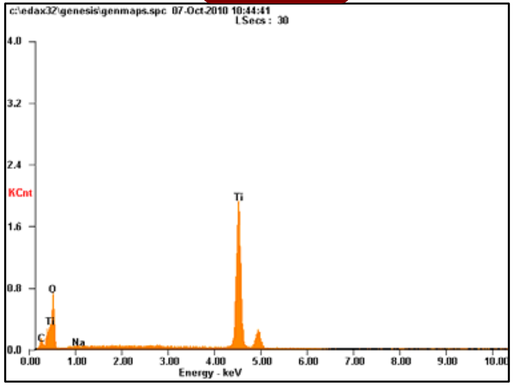
TEM images of the synthesized nanotubes



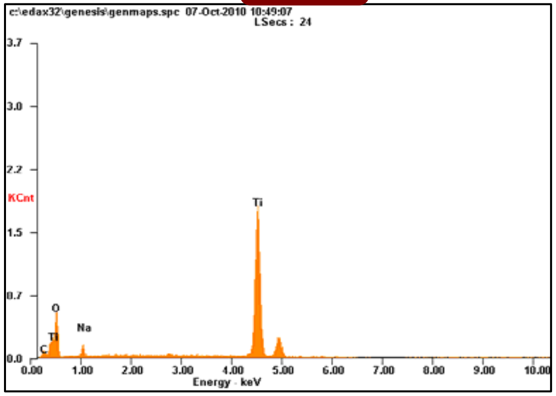
TiO_2 based nanotubes

SGA24

Element	Wt%	At%
CK	06.95	13.38
OK	42.83	61.86
NaK	**01.01**	**01.02**
TiK	49.20	23.74



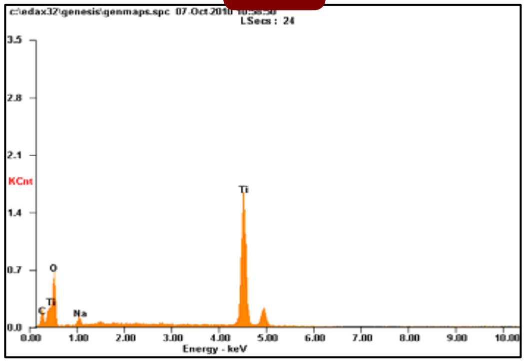
SG48



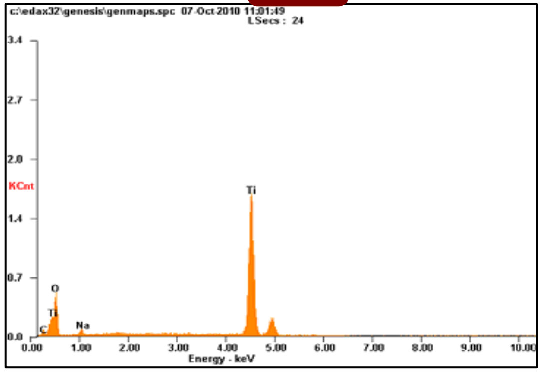
Element	Wt%	At%
CK	05.23	10.55
OK	39.14	59.28
NaK	03.69	03.89
TiK	51.94	26.28

A48

Element	Wt%	At%
CK	12.71	22.96
OK	40.10	54.40
NaK	02.55	02.41
TiK	44.64	20.23

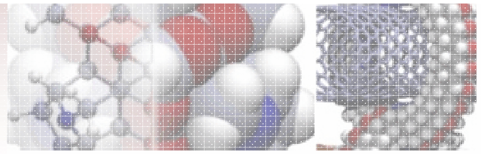


D72

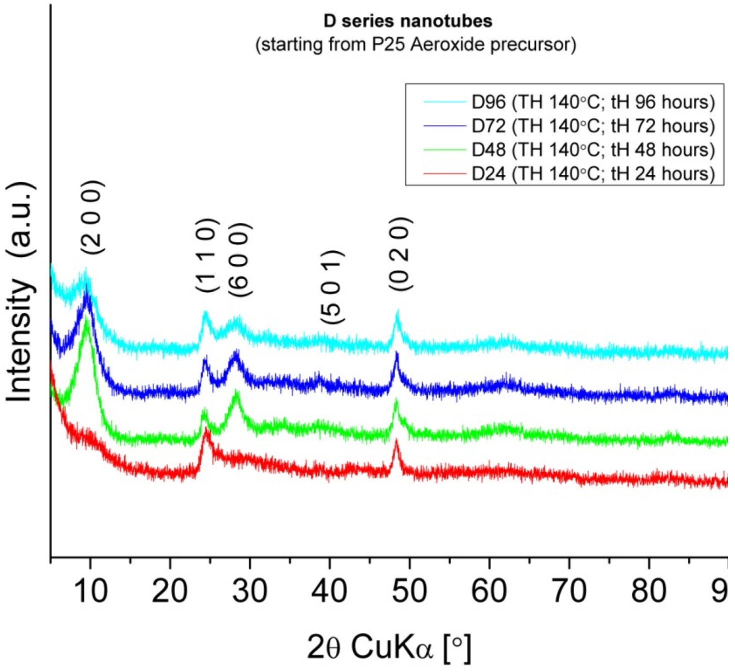


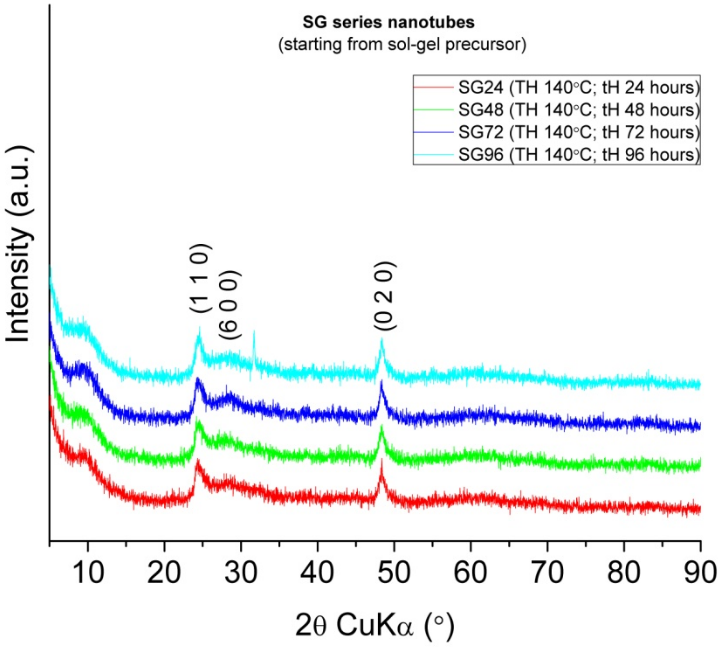
Element	Wt%	At%
CK	04.48	09.15
OK	39.76	60.99
NaK	02.33	02.48
TiK	53.44	27.38

Natrium content of the synthetised nanotubes

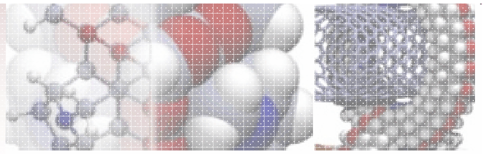


TiO_2 based nanotubes



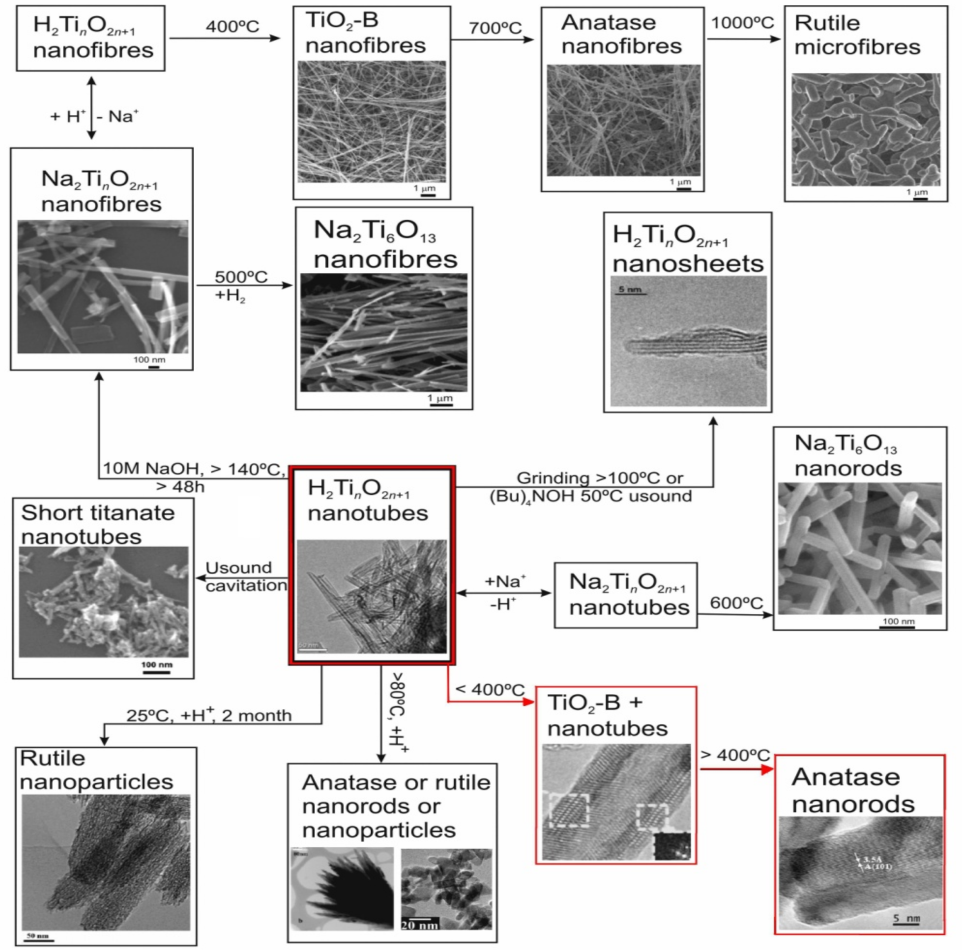


✓The titanate based nanotubes obtained from the both precursors present a similar phase composition of $Na_2Ti_2O_4(OH)_2$



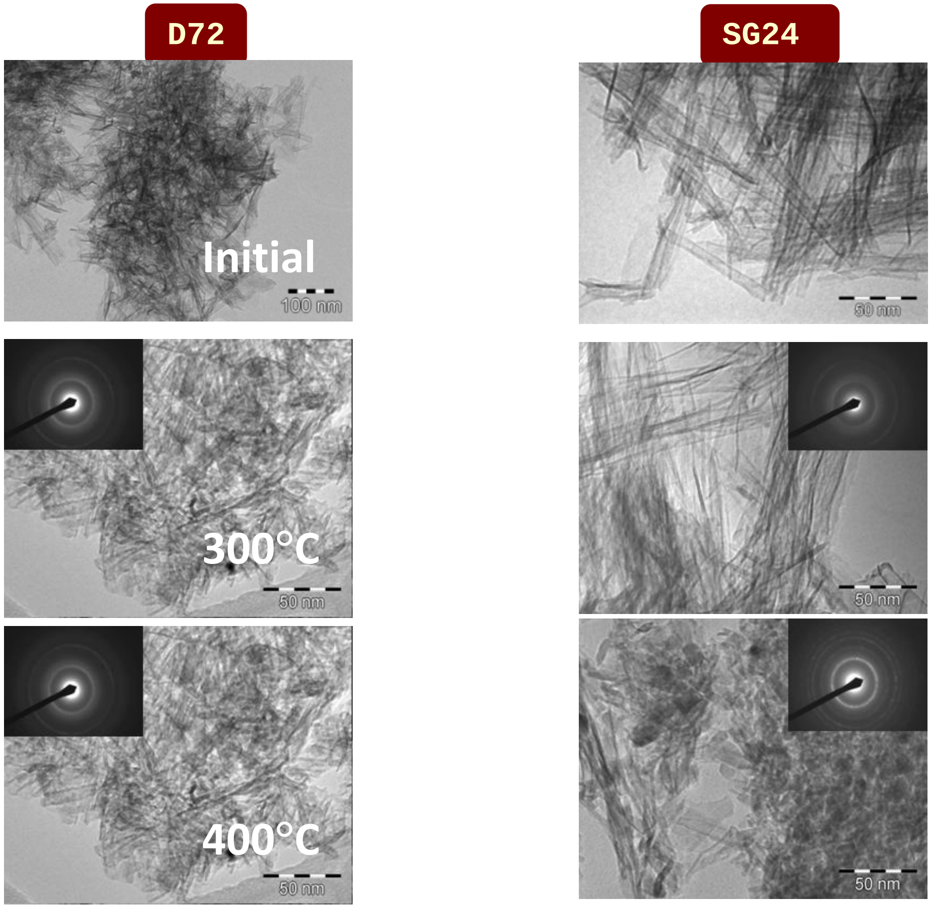
TiO_2 based nanotubes

Thermal behaviour

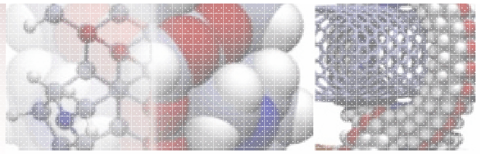


D. V. Bavykin, Frank C. Walsh, Elongated Titanate Nanostructures and Their Applications, *Eur. J. Inorg. Chem. 2009, 977–997*

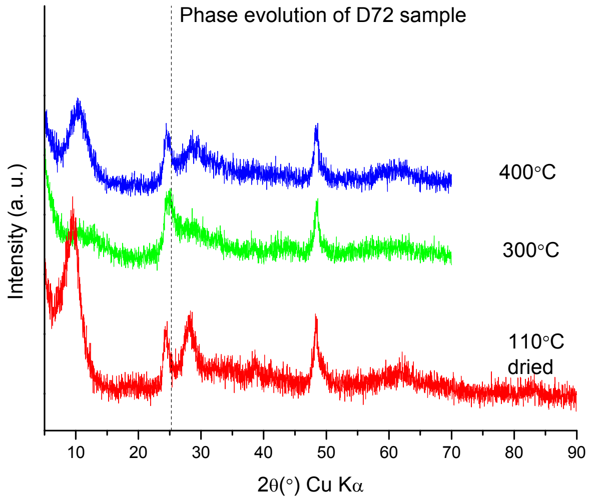
TiO_2 based nanotubes

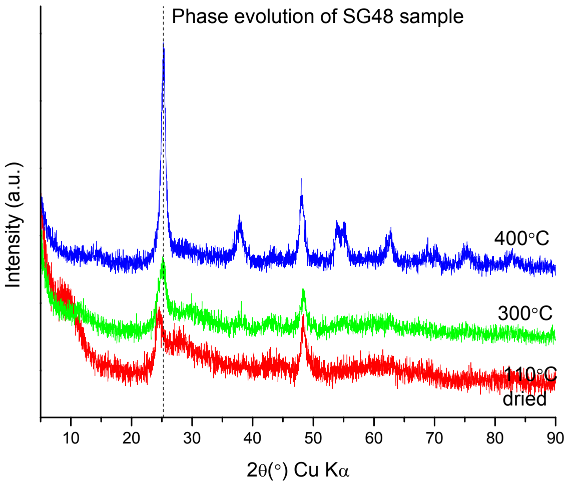


Thermal stability of the synthetised nanotubes



TiO_2 based nanotubes





Structural evolution of synthesized nanotubes by thermal treatment

TiO$_2$ based nanotubes

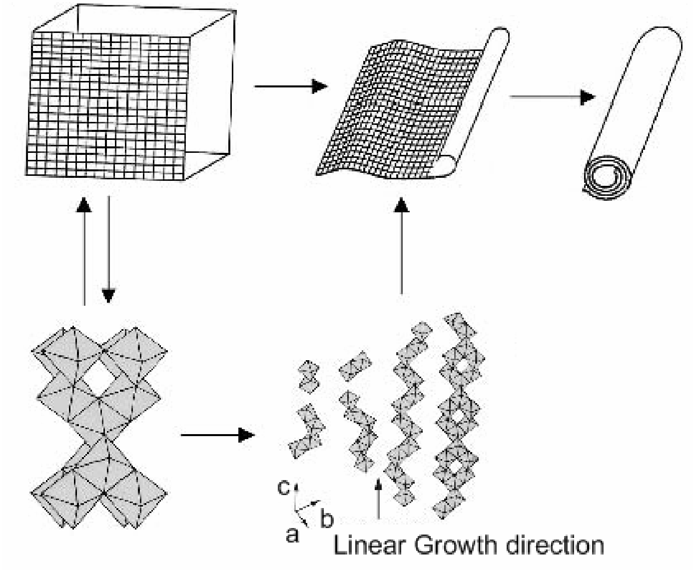
Possible mechanism of nanotubes formation

The formation mechanism takes places in three stages during hydrothermal treatment:

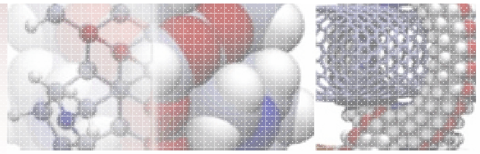
1. The 3D structure of the precursors (crystalline or amorphous) transforms under alkaline attack in 2D lamellae structure

2. The boundaries of the lamellae (nanosheets) have free bonds and the free energy

3. The tube structure, 1D, is forming by rolling the nanosheets and saturation of the free bonds from the nanosheets boundary



The modeling of the nanotube formation from nanopowders is under evaluation



TiO_2 based nanotubes - conclusions

- 1D tubular nanosized structures were obtained by hydrothermal treatment under alkali attack

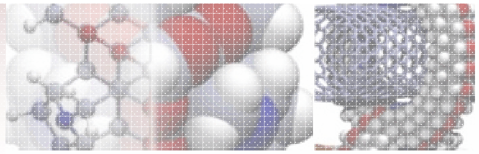
- The degree of crystallinity of the precursors influences the formation and the morphology of the nanotubes

- The amorphous sol-gel precursor is much efficient as precursor than crystalline P25 Aeroxide because it skips the dissolution stage of the crystalline phase and it has high reactivity

- The best nanotube ratio has been obtained for 72 hours hydrothermal treatment when starting from P25 Aeroxide Degussa and for 24 hours when started with sol-gel powder

- The structure and chemical composition of the nanotubes could be assigned to $Na_xH_{2-x}Ti_3O_7\cdot nH_2O$ based on EDAX and XRD analysis

- The presence of the sodium enhanced the thermal stability of the nanotubes



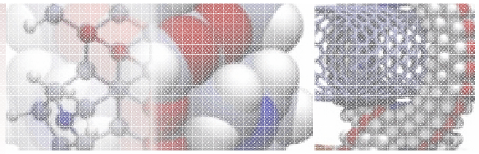
SiO_2 microtubes

- ***Previous preparation methods:***

  - Th.Nemetscheck and U.Hofmann (1954): - high temperature SiO disproportionation reaction
    - reaction of silica and silicon metal in high vacuum at 1200^0C

- ***Sol-gel preparation methods:***

  - H.Nakamura, Y. Matsui (1995): DL-tartaric acid
  - A.R.Lim et at (1999): DL-tartaric acid
  - E.M. Mokoena et al (2003): DL-tartaric acid
  - Q. Ji et all. (2004): peptidic lipids template method
  - C.H. Ruescher et all. (2007): metal salts template method
  - C.Anastasescu et al. (2009): DL-tartaric acid



SiO_2 microtubes

- **SiO_2 hollow tubes preparation**

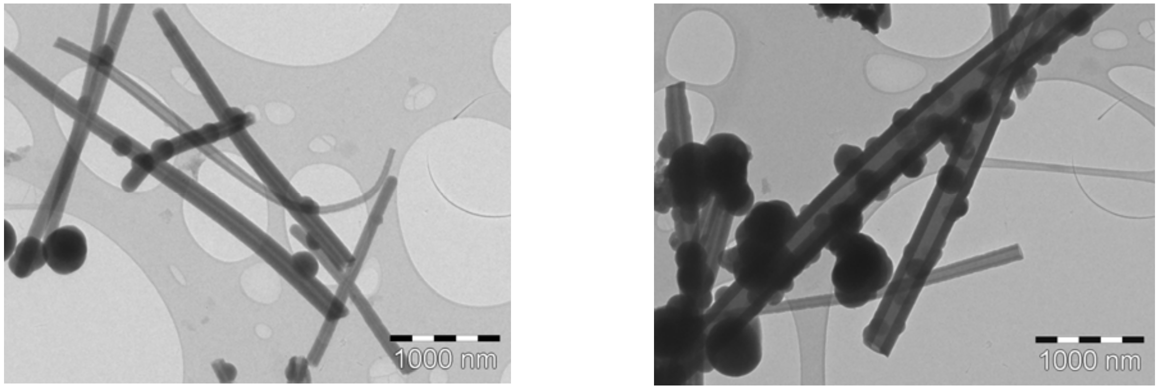
[TEOS:*DL*-tartaric acid:EtOH]:NH4OH = [1:0.04:25]:16

- Aging 1(T), 2 hrs(1T) and drying: 100^0C, 5 hs

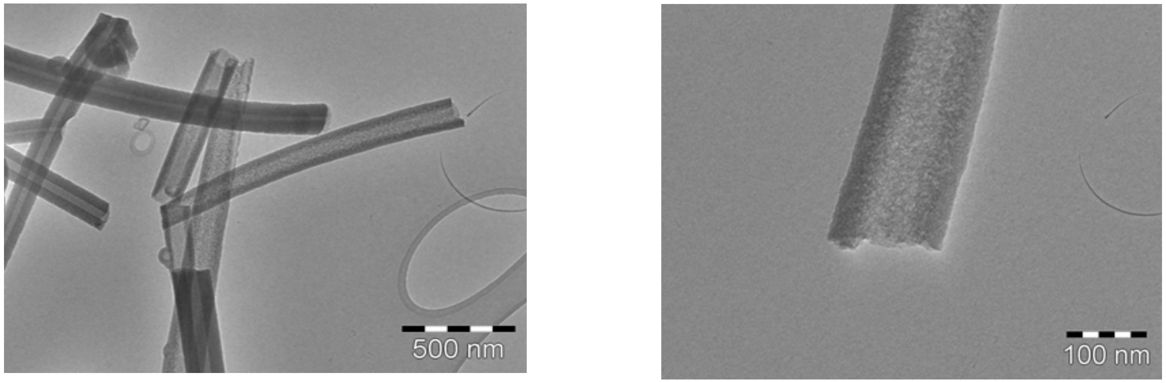
- Thermal treatment: 1 h, 400^0C, heating rate 10//min (2T)

- ***Meso-tartaric*** acid used as tempating agent (S)

SiO_2 microtubes



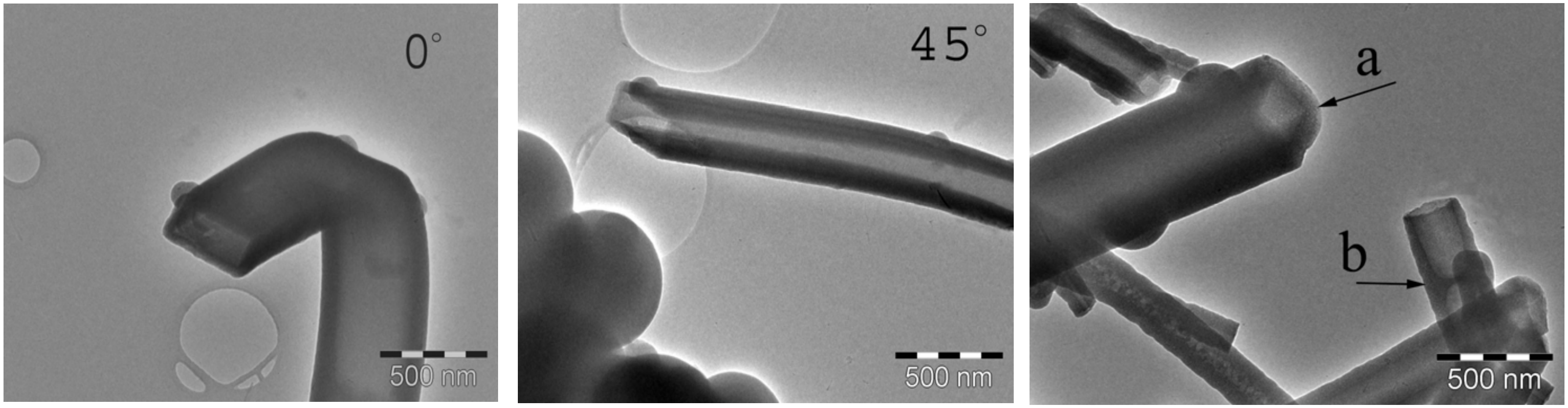
Sample SiO_2-2T (dried 1000C)



Sample SiO_2-2T (dried 100^{0}C, TT 450^{0}C)

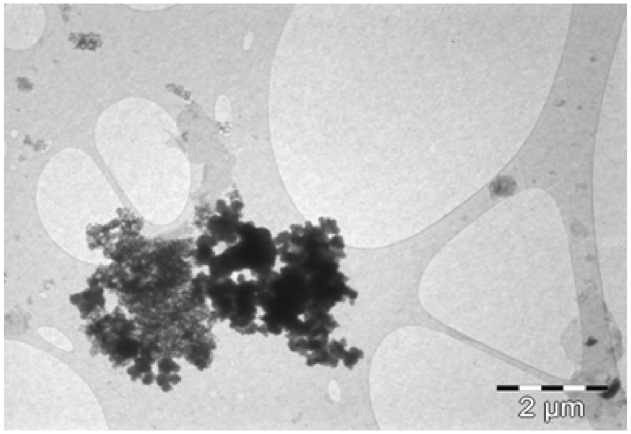
TEM images of samples with different thermal treatment

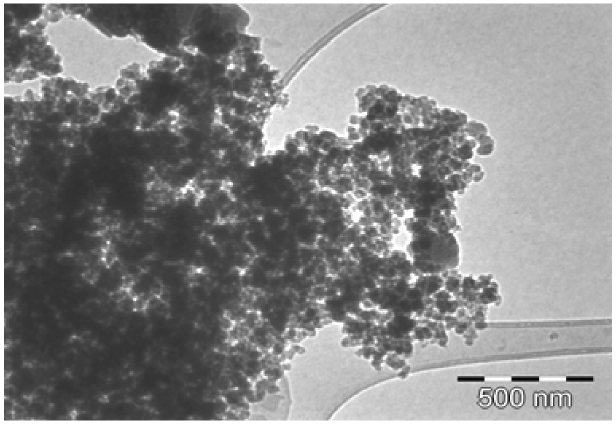
SiO_2 microtubes



SiO_2 tubes cross sections

SiO_2 microtubes

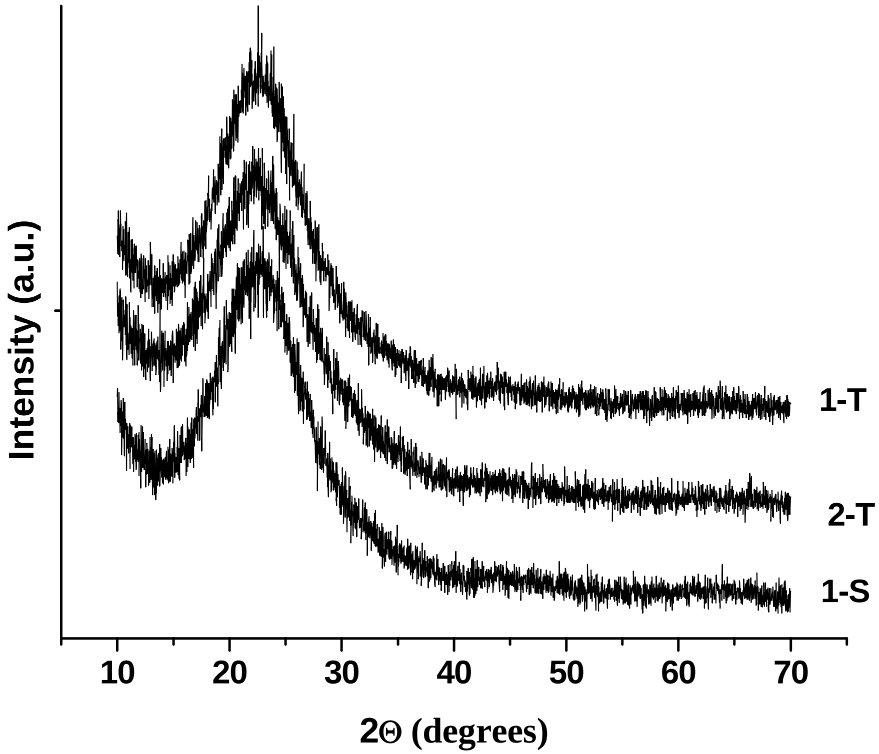




Meso-tartaric acid as templating agent

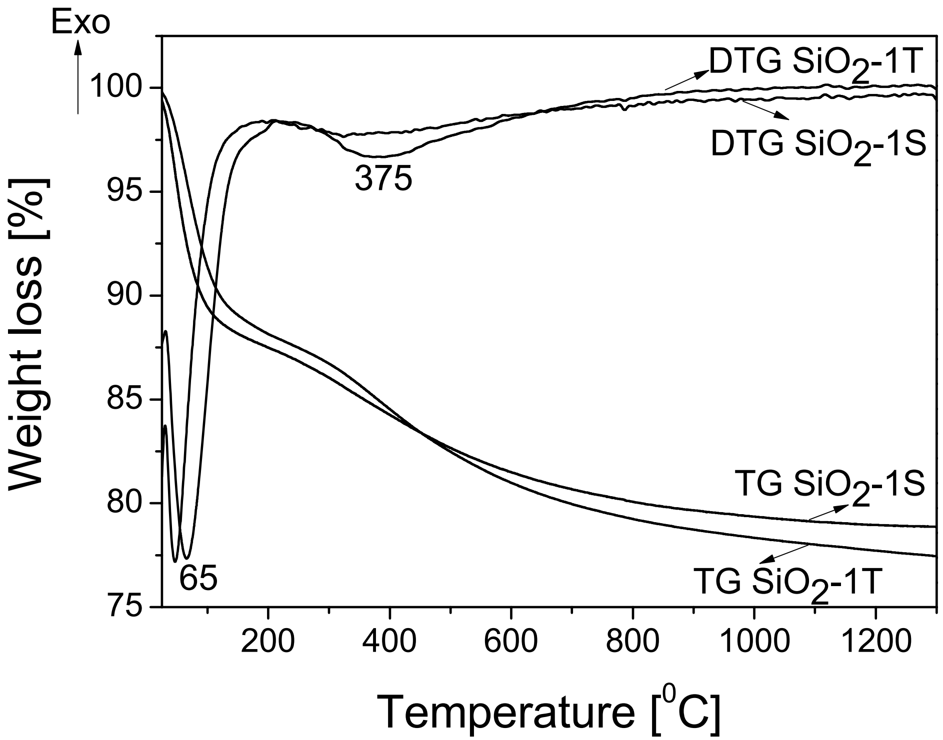
C. Anastasescu, M. Anastasescu, V.S. Teodorescu, M. Gartner, M.Zaharescu, J. Non-Cryst. Solids, 356 (2010) 2634-2640

SiO_2 microtubes

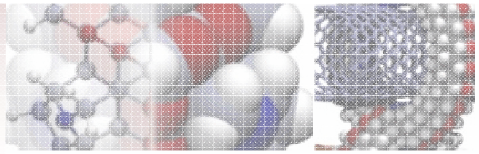


XDR patterns of the SiO_2 tubes and spheres

SiO_2 microtubes

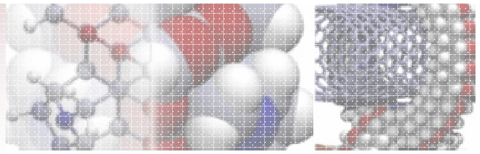


DTA/TGA curves of the SiO_2 tubes and spheres



SiO_2 microtubes - conclusions

- SiO_2 spheres and hollow tubes were prepared by sol-gel method in the presence of DL-tartaric or *meso*-tartaric acid used as templating agent
- SiO_2 tubes could be obtained only in the presence of DL-tartaric acid
- The spheres obtained in the presence of meso-tartaric acid have identical structure but different morphology as compared to the hollow tubes
- Due to their specific morphology, specific properties of the SiO_2 tubes are expected the SiO_2 tubes present the SiO_2 tubes present



Nanotubes applications

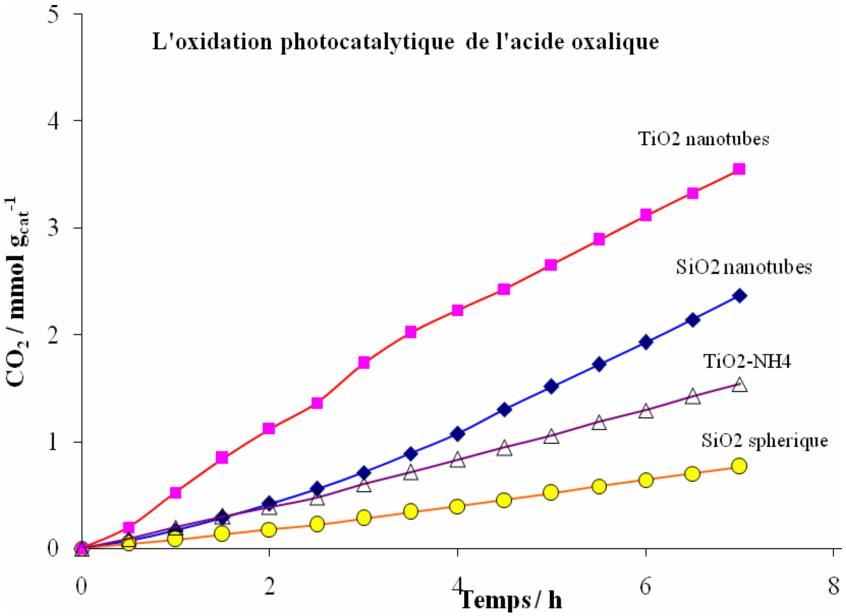
Photocatalytic activity of TiO_2 and SiO_2 tubes and spheres

TiO_2 and SiO_2 tubes and spheres were used for photocatalytic testing for the oxidation of oxalic acid to CO_2 in liquid phase at 20°C

- as prepared and
- platinum impregnated with H_2PtCl_6 to a final loading of 1%.

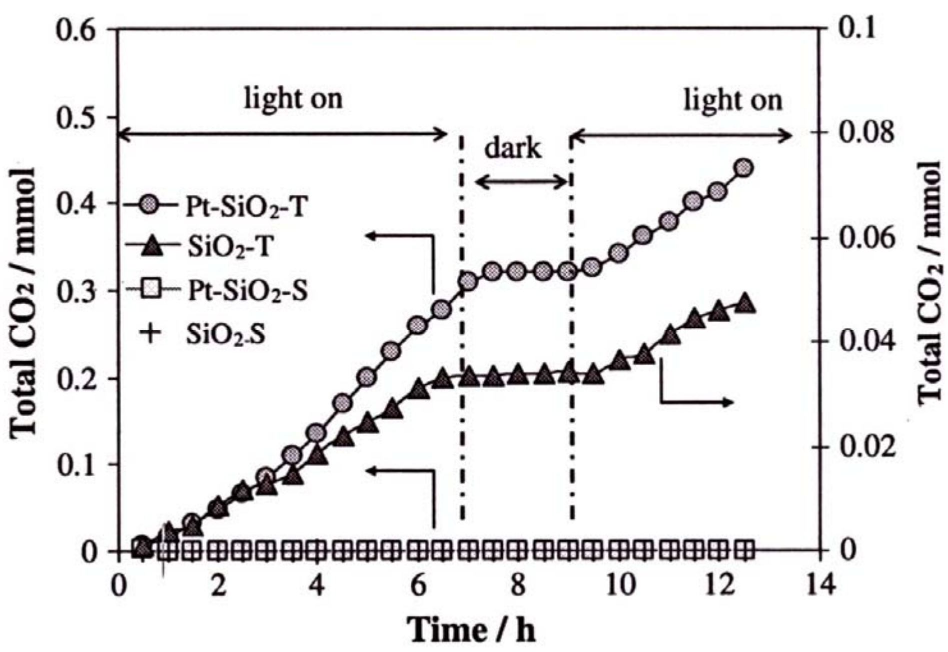
Nanotubes applications

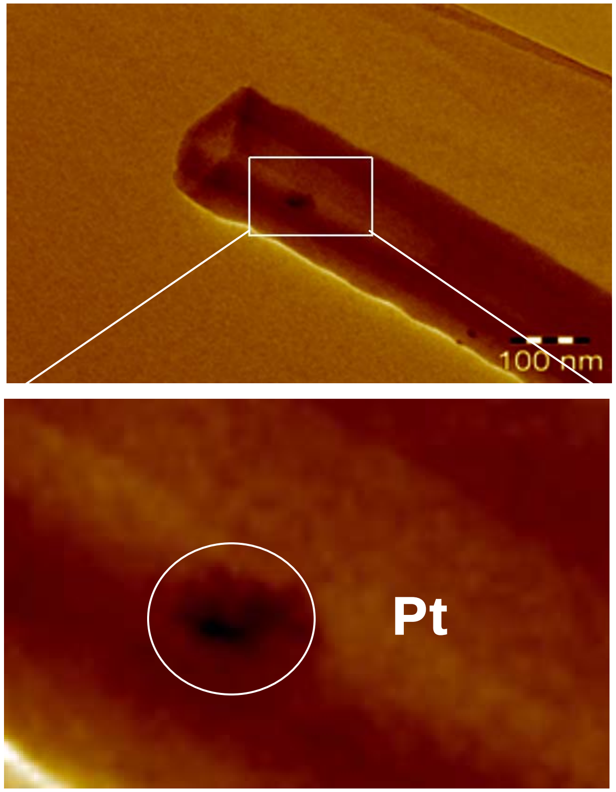
Comparative Photocatalytic activity of the TiO_2 and SiO_2 tubes and spheres



Photocatalytic oxidation of oxalic acid
(silica hollow tubes and spheres were Pt-doped)

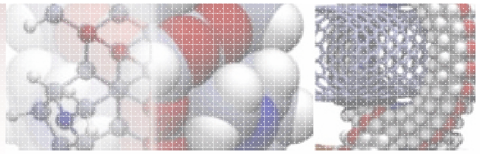
Nanotubes applications



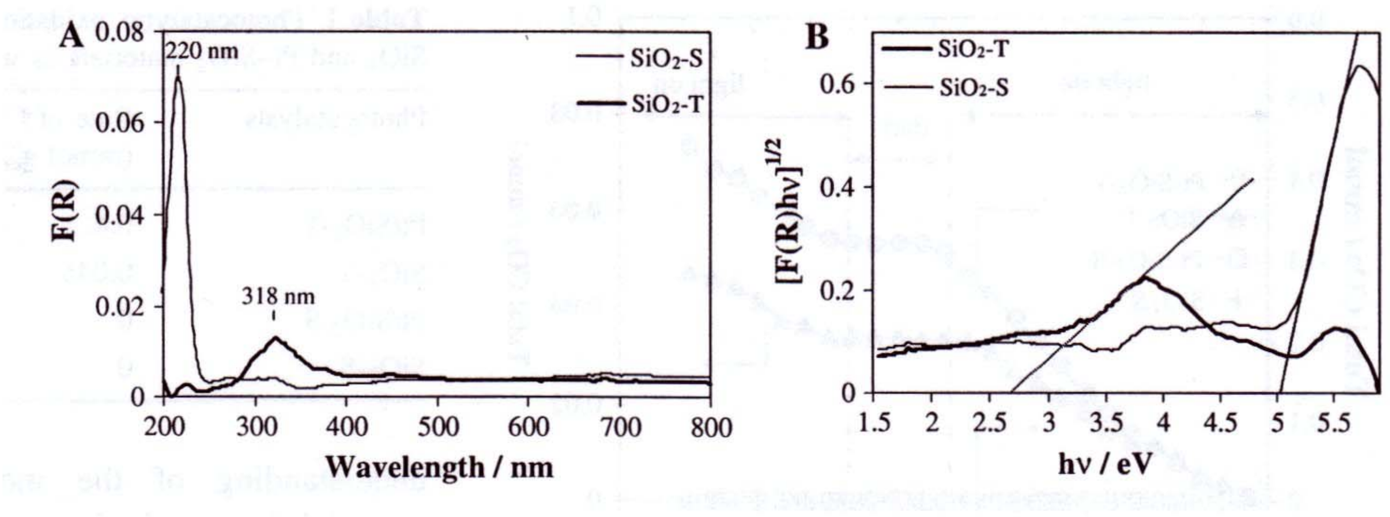


SiO_2 materials for the oxidation of oxalic acid to CO_2 in liquid phase at 20^oC

C. Anastasescu, M. Zaharescu, I. Balint, Catal Lett., 132, 81-86 (2009)



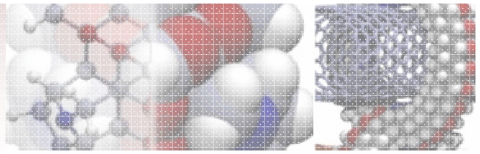
Nanotubes applications



A. The diffuse reflectance spectra of **SiO_2-NT** (**thick line**) and **SiO_2-S**

B. The plot of the transformed diffuse reflectance spectra used to determine the band gap energy

The values of the band gap energies derived form the UV-Vis plots were:
2.7 eV for SiO_2-T and 5.1 ev for SiO_2-S



Nanotubes applications

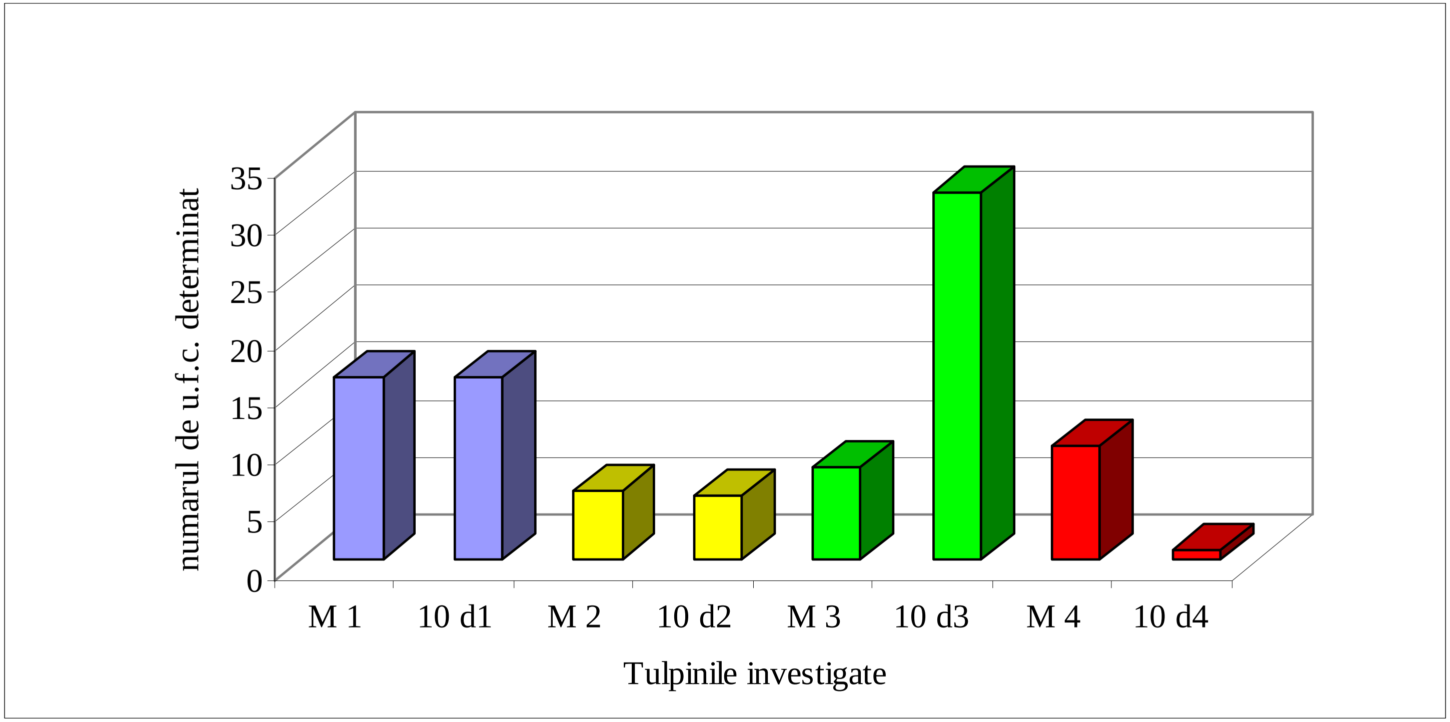
The biological activity of the SiO_2 nanotubes was studied on the following microorganisms:

- *Escherichia coli (M1)* (isolated from effluent of wastewater treatment plant)

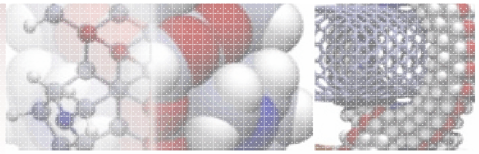
- *Virgibacillus halodenitrificans (M2)* and *Bacillus subtillis (M3)* (isolated from the surface of subterranean rock salt)

- *Bacilus sphericus (M4) (*DSMZ 369)

Nanotubes applications



Total c.f.u. number quantified after 24 hours in the presence of SiO_2 nanotubes



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Ph.D student Silviu Preda
Ph.D student Cristian Andronescu
Ph.D student Adriana Rusu

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