

AMIANTO

**DA TERRORE AMBIENTALE
A PROSPETTIVA TECNOLOGICA
DEL FUTURO**

Prof. Norberto Roveri



bea

BIO • ECO • TECHNOLOGY

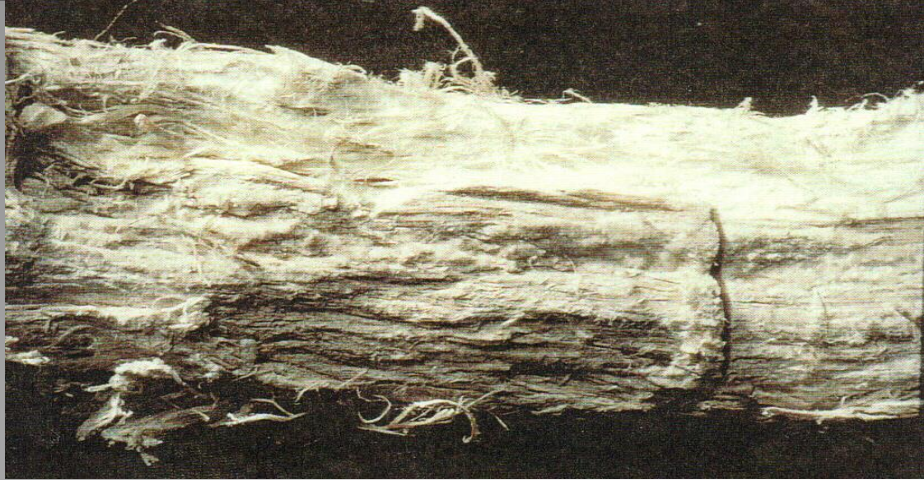
www.bioecoactive.it

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AMIANTO



MINIERA di BALANGERO (TO)

2.000.000 ton. di amianto estratte annualmente dal 1975 al 1990

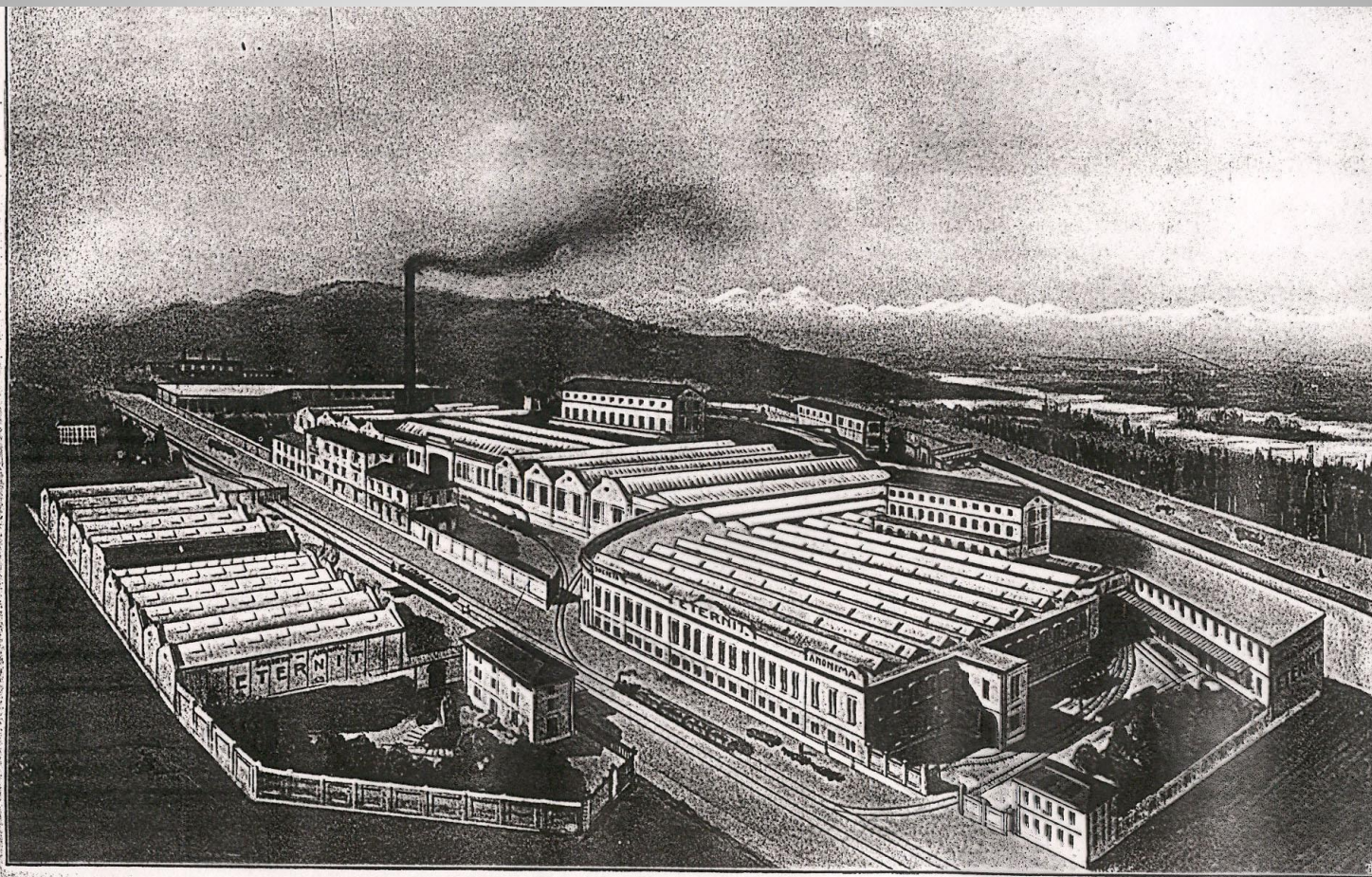


**Miniera di amianto, Balangero (TO)
foto RSA srl, Balangero**

ETERNIT

- Nel 1901 l' austriaco Ludwig Hatschek brevettò il composito “CEMENTO AMIANTO” chiamandolo Eternit (dal latino aeternitas, eternity). Un anno dopo Alois Steinmann compra il brevetto per produrre Eternit.
- Nel 1928 inizia la produzione in Eternit di tubi per il trasporto di acqua
- Nel 1933 inizia la produzione di onduline in Eternit per i tetti

LO STABILIMENTO ETERNIT DI CASALE MONFERRATO COME ERA RIPORTATO SUL DEPLIANT DELL' ETERNIT



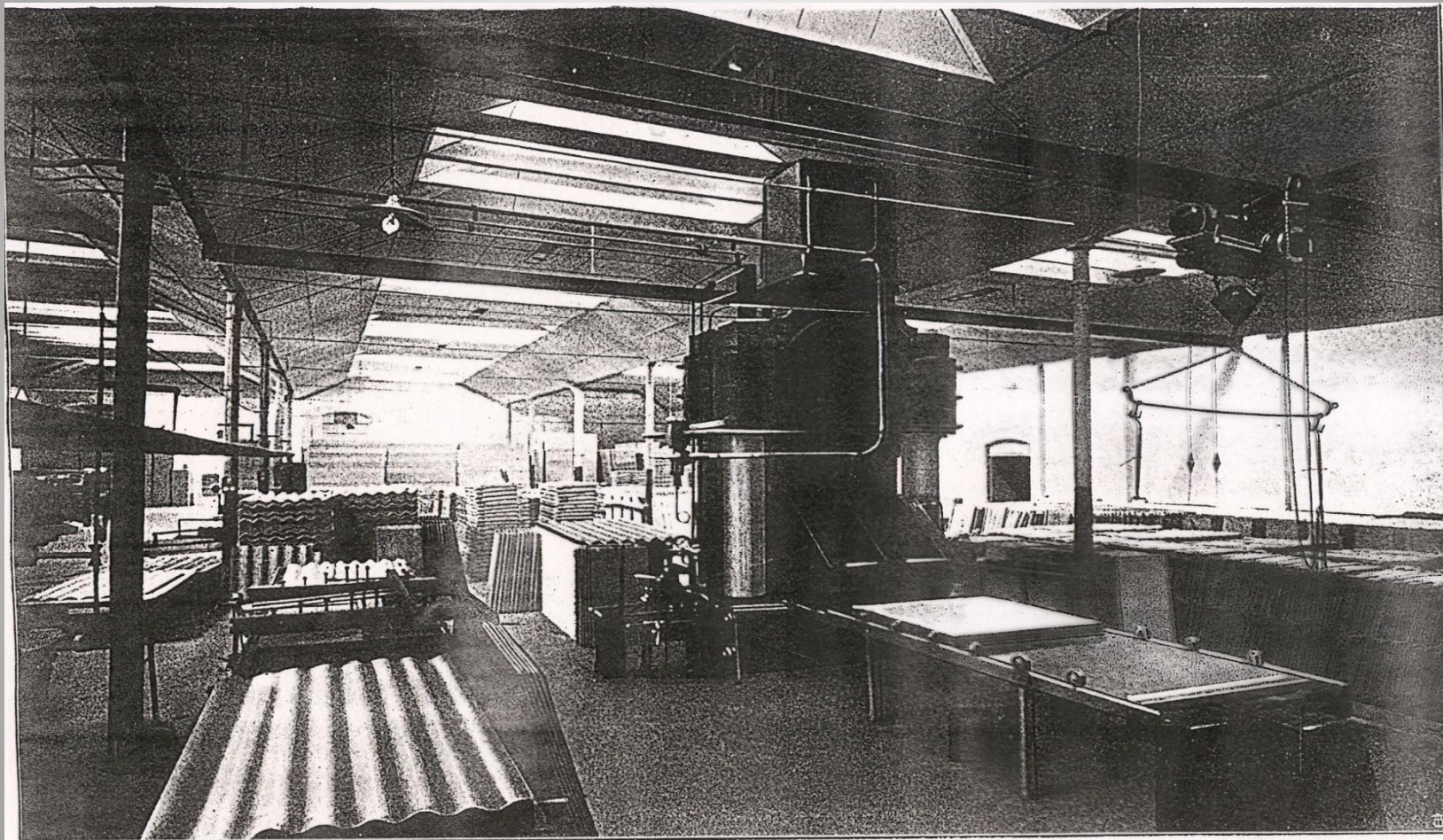
Veduta generale degli Stabilimenti di
CASALE MONFERRATO. (Area
coperta mq. 40.000).

Vue Générale des Usines de CASALE
MONFERRATO. (Superficie cou-
verte 40.000 m²).

General View of the WORKS at
CASALE MONFERRATO (40.000
square Meters of covered area).

Gesamtansicht des Werkes in CASALE
MONFERRATO. (Bebaute Fläche
etwa 40.000 m²).

ONDULINE IN ETERNIT



Grande pressa idraulica per preparazione lastre ondulate.

Grande presse hydraulique pour la preparation des plaques ondulées.

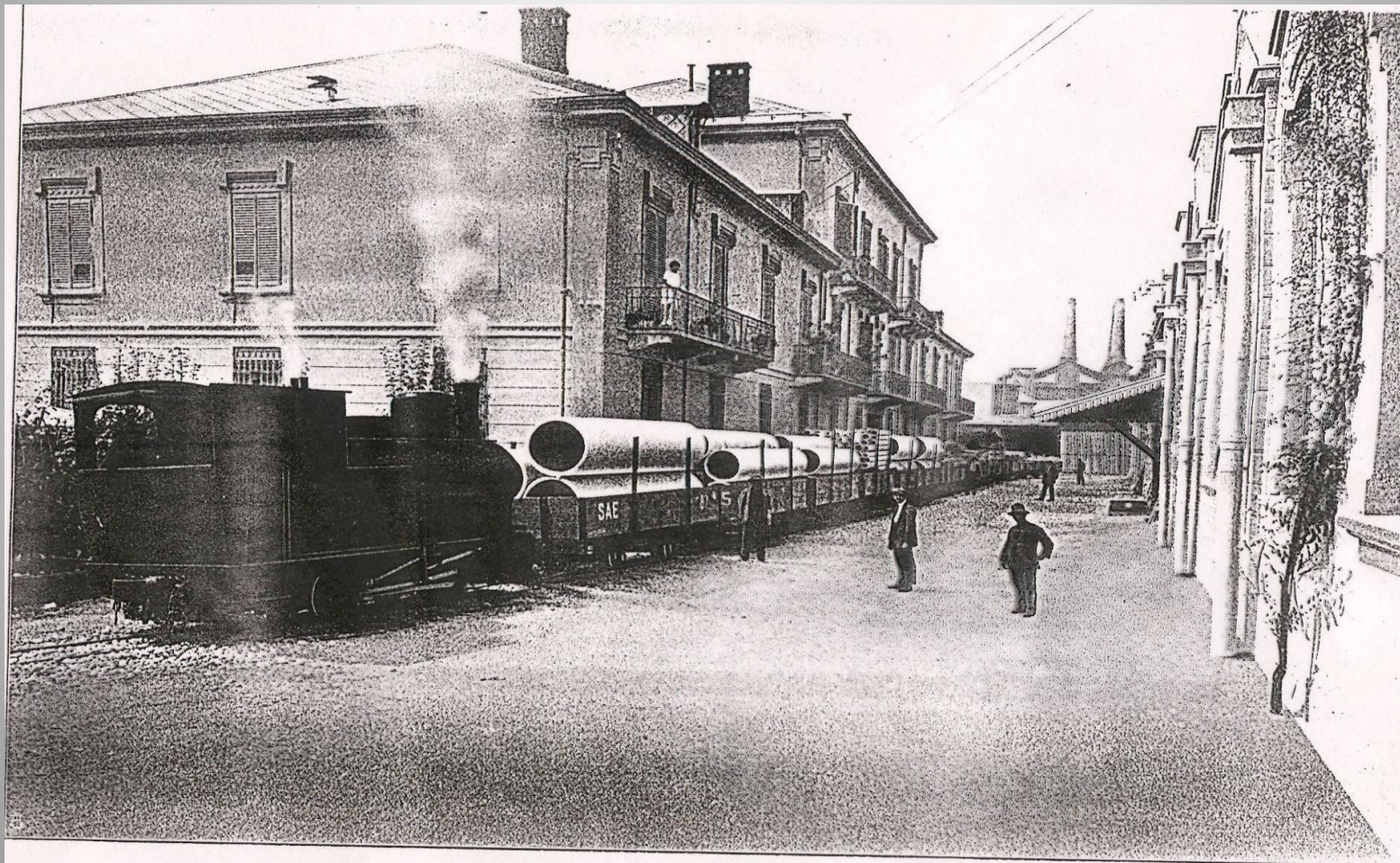
Large Hydraulic Press for preparing Corrugated Sheets.

Grosse hydraulische Presse für die Vorbereitung gewellter Platten.

OPERAI AL LAVORO PER LA PRODUZIONE DI ONDULINE DI ETERNIT



TUBI IN ETERNIT VENGONO CARICATI SU I TRENI DIRETTAMENTE NELLA FABBRICA



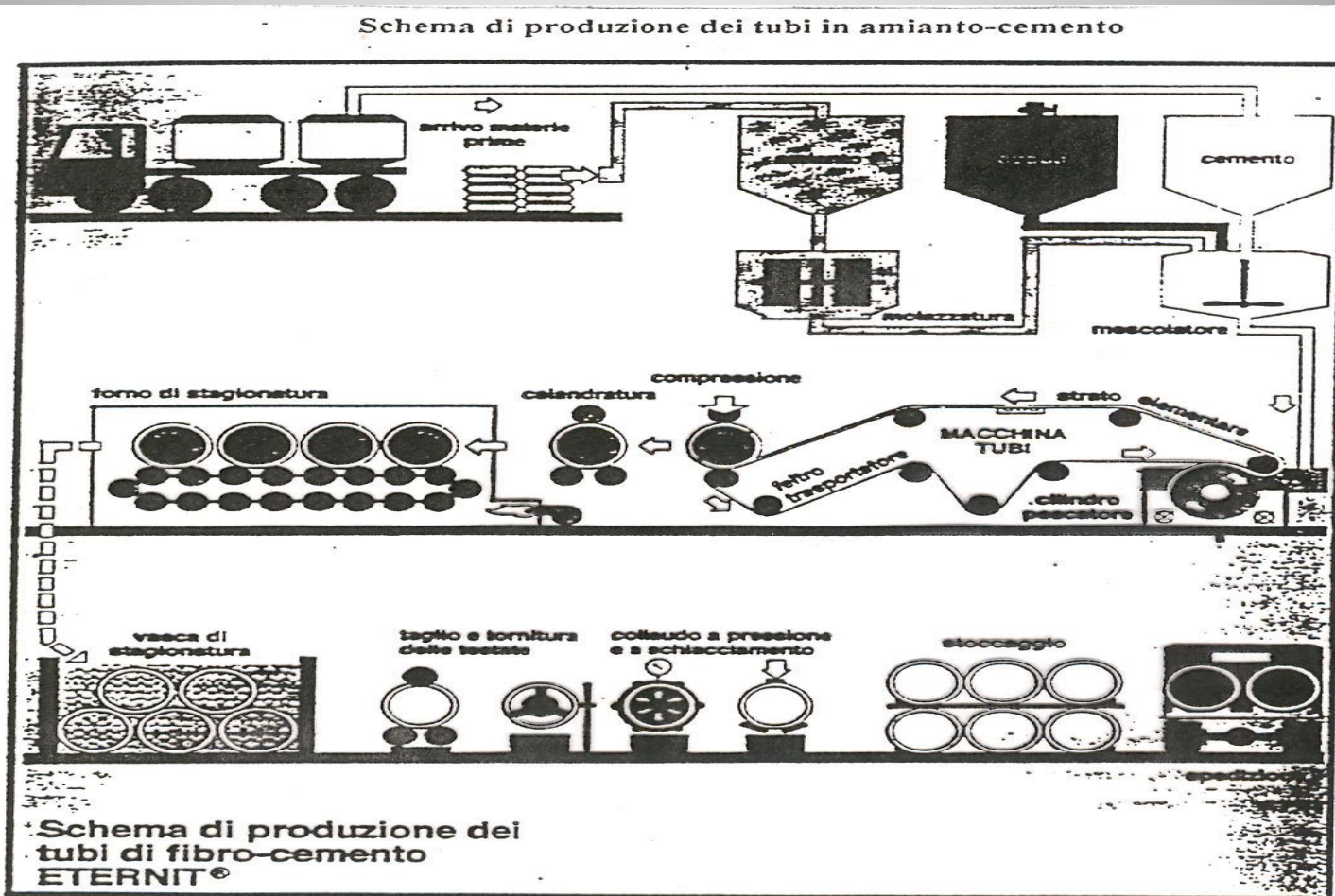
Treno di materiali Eternit in partenza
dallo Stabilimento.

Train de matériaux en Eternit au départ
de l'Etablissement.

Train leaving Works with a load of
Eternit goods.

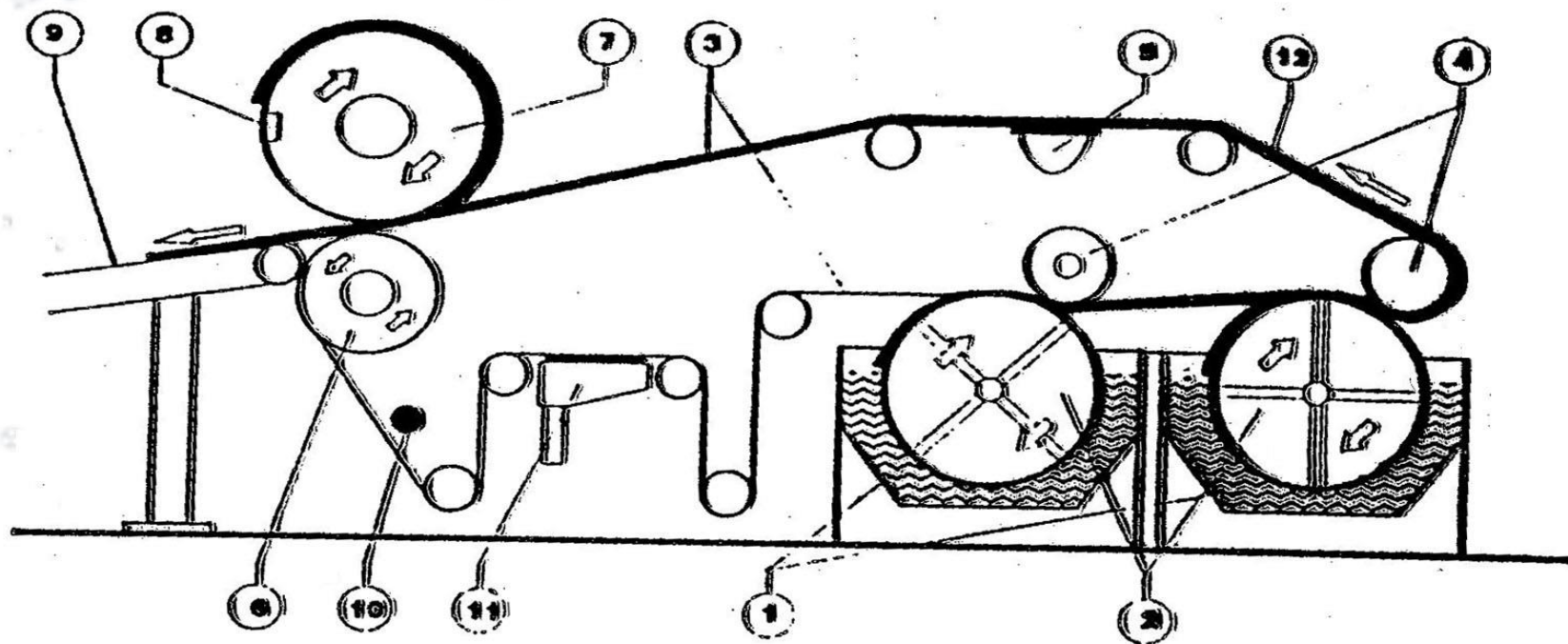
Ein mit Eternit beladener Zug verlässt
das Werk.

SCHEMA DEL PROCESSO INDUSTRIALE PER LA PRODUZIONE DI TUBI IN ETERNIT



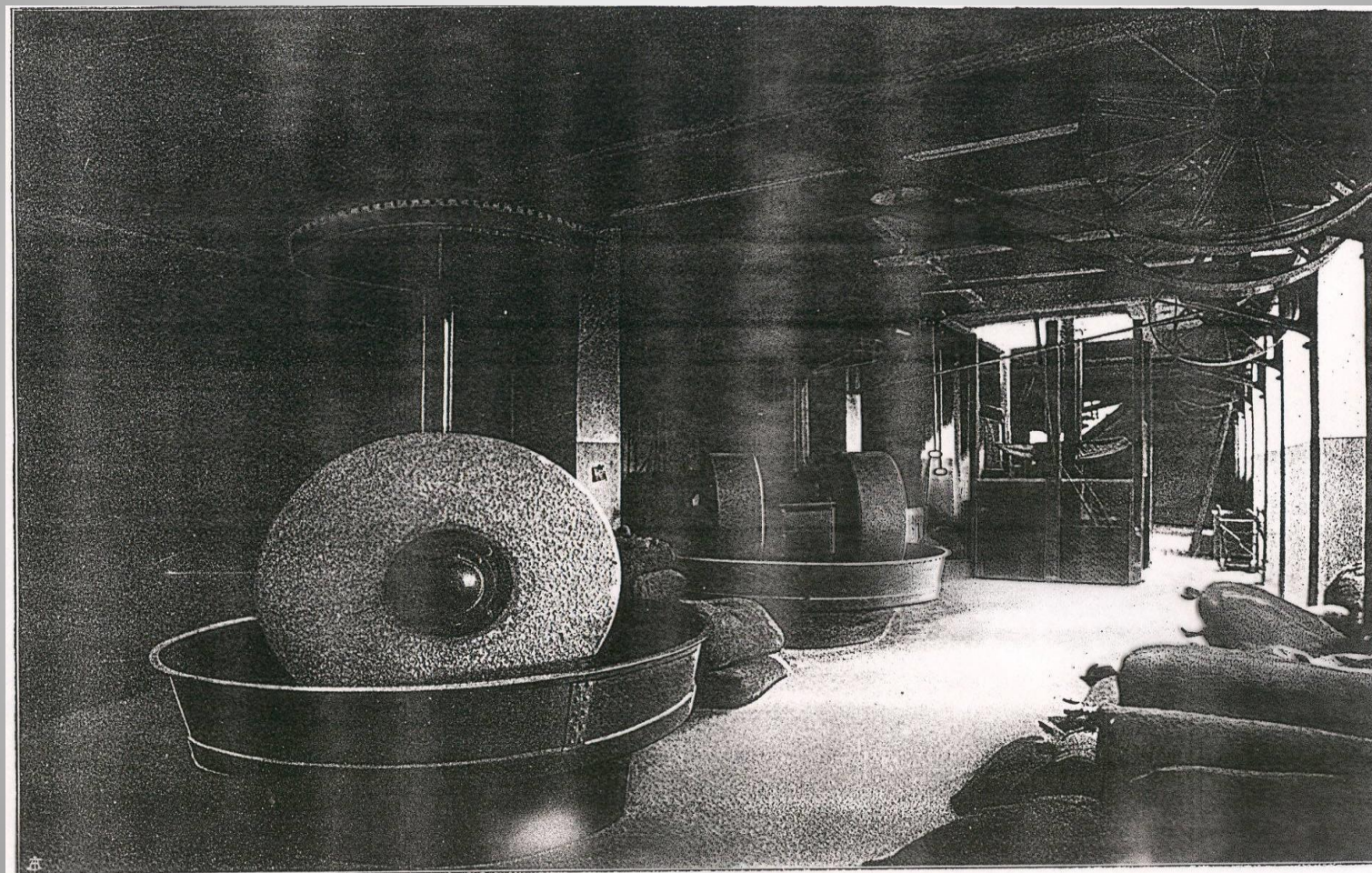
SCHEMA DEL PROCESSO INDUSTRIALE PER LA PRODUZIONE DI ONDULINE IN ETERNIT

Schema di produzione di lastre in AC



- | | | |
|----------------------|-----------------------------|---------------------------------|
| ① Vasche impasto | ⑤ Cassa aspirante vuoto | ⑨ Tappeto trasporto sfoglia |
| ② Cilindro pescatore | ⑥ Cilindro comando | ⑩ Spruzzatori acqua lava-feltro |
| ③ Feltro | ⑦ Cilindro formatore | ⑪ Cassa asciugaggio feltro |
| ④ Rullo ponitore | ⑧ Apparecchiatura di taglio | ⑫ Strato sfoglia |

LE FIBRE DI AMIANTO VENGONO MACINATE ALL' ARIA

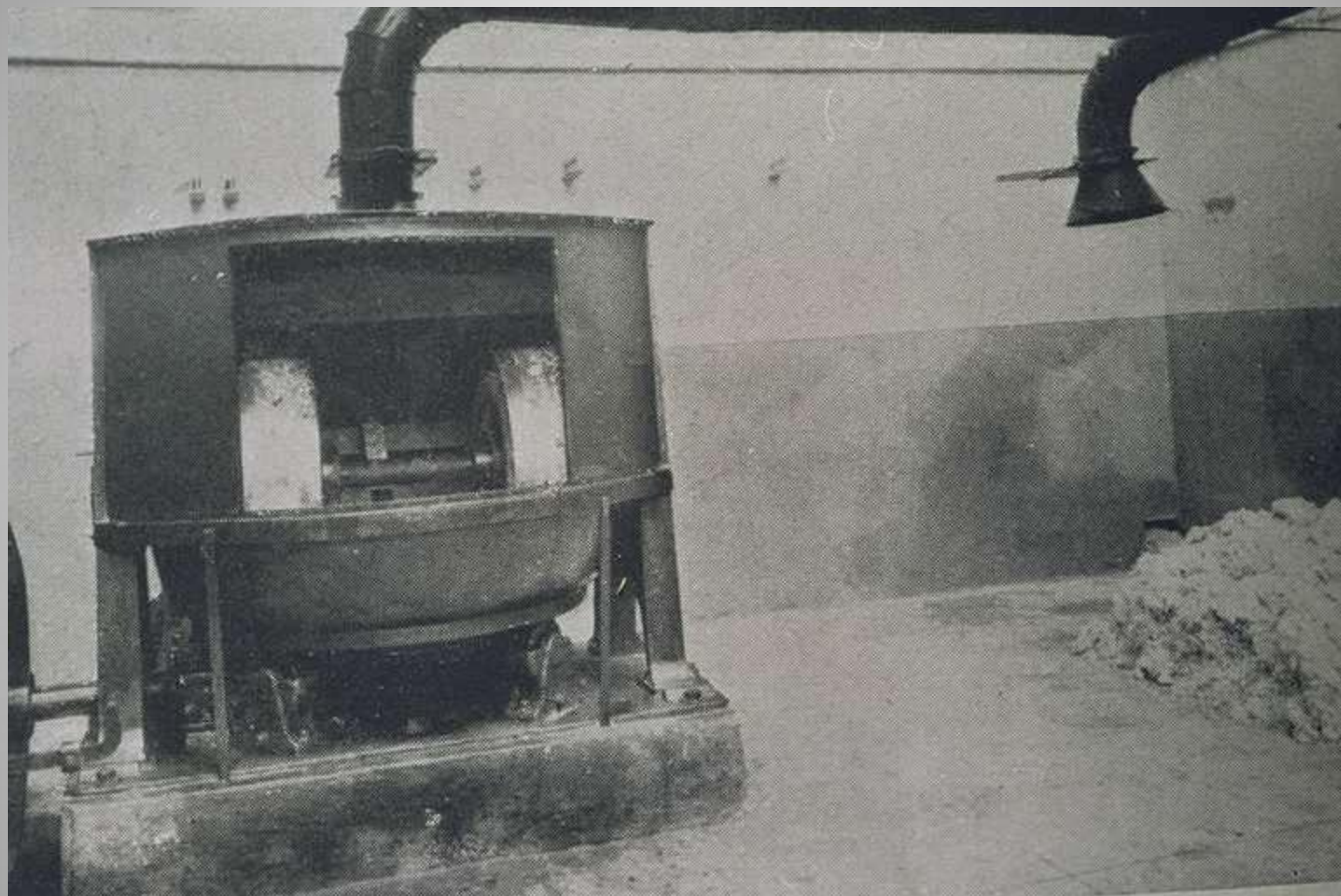


Zwei von den acht Asbest-Kollergängen.

Two of the eight Asbestos - Fibre
"Tessers".

Deux des huit meules pour l'amiante.

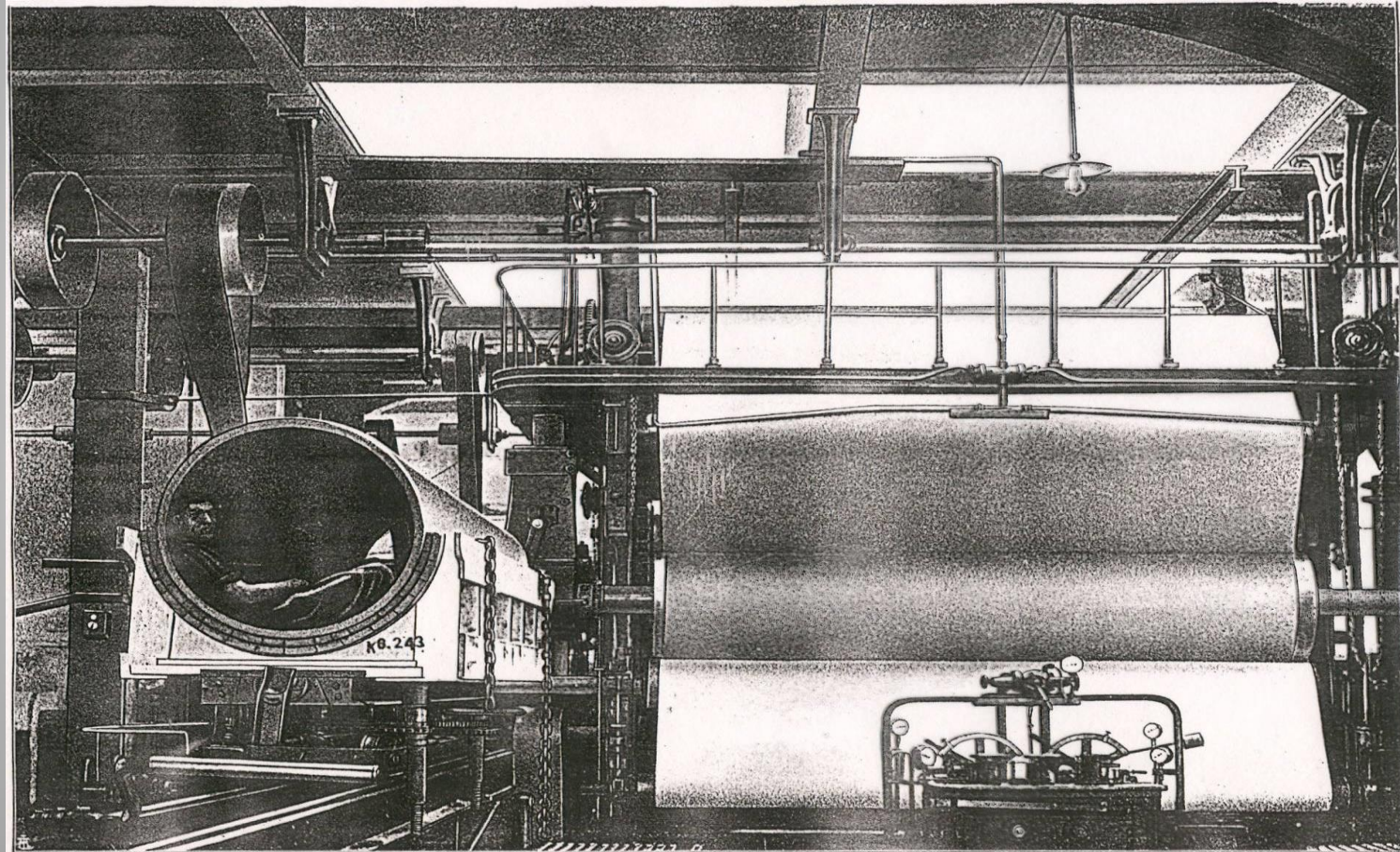
Due delle otto molasse per l'amiante.







IMPIANTO DI PRODUZIONE DEI TUBI IN ETERNIT



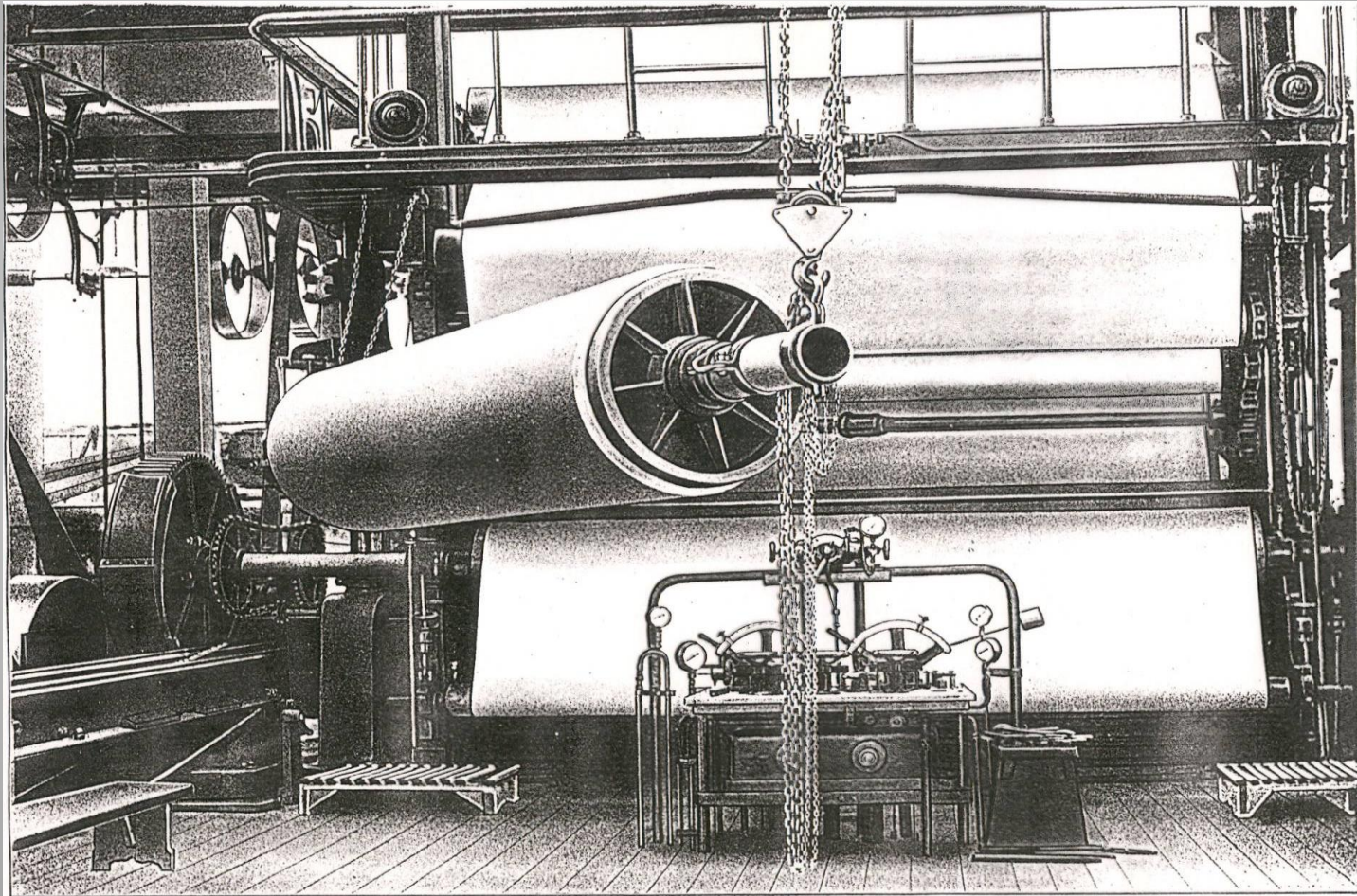
Macchina per la fabbricazione dei tubi Eternit. (Il tubo fabbricato adagiato sul sostegno a culla per il trasporto). Altro tubo già in formazione.

Machines pour la fabrication des tubes Eternit. (Le tube fabriqué est logé sur le support à berceau pour le transport); un autre tube en formation.

Machine for making Eternit Pipes (the manufactured Pipe is transferred to a cradle, to be removed). Another pipe is already in the making.

Eine der Maschinen für die Herstellung der Eternit-Röhre. Das fertige Rohr ist auf die Transport-bahn gebracht. Die Maschine hat bereits ein neues

IMPIANTO DI PRODUZIONE DEI TUBI IN ETERNIT



Macchina per la fabbricazione dei tubi Eternit (il tubo estratto dalla macchina mediante asse a cerniera).

Machine pour la fabrication des tubes Eternit (le tube extrait de la machine au moyen d'un axe à charnière).

Machine for making Eternit Pipes (the Pipe is pulled out of the Machine on a hinged axis).

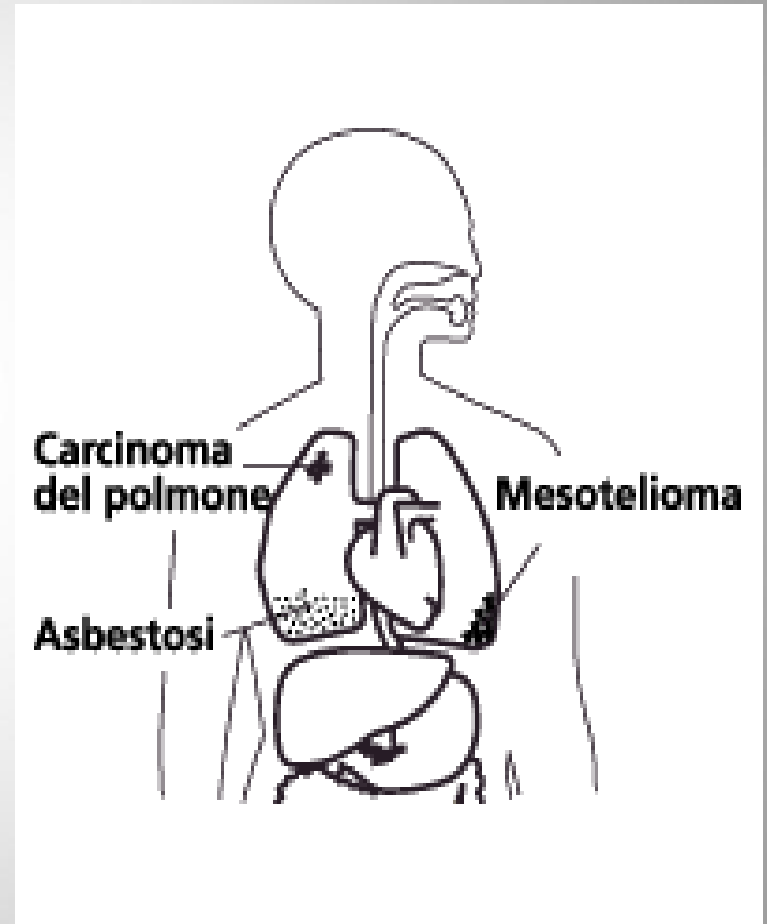
Eine der Maschinen für die Herstellung der Eternit-Rohre Das Rohr ist mittels einer in Scharnieren schwenkbaren Achse aus der Maschine herausgenommen.

PATOLOGIE CONNESSE ALL'INALAZIONE DI FIBRE DI AMIANTO

**ASBESTOSI,
CARCINOMA POLMONARE,
MESOTELIOMA PLEURICO**

Ipotesi di azione chimica
dell'asbesto nei polmoni:

(reazione di Fenton)





DISCARICHE



DISCARICHE



Amianto o Asbesto

Serpentini (Fillosilicati)

- **Crisotilo**



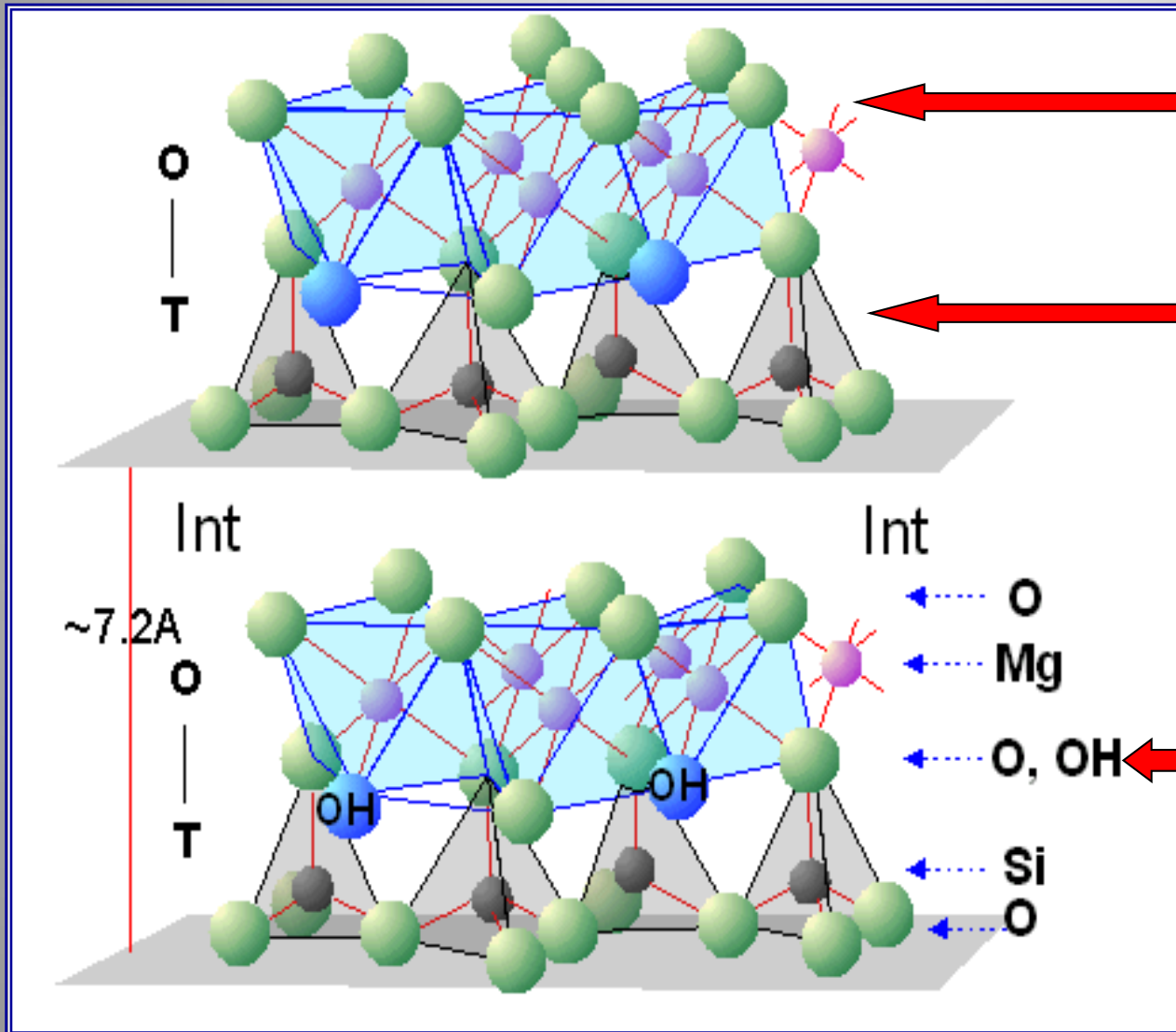
(95%)

Anfibolo (Inosilicati)

- **Amosite** $(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
- **Crocidolite**
 $\text{Na}_2(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH,F})_2$
- **Altri meno importanti:**
Antofillite, Tremolite, Actinolite

(5%)

STRUTTURA DEL CRISOTILO



LUNGHEZZA LUNGO
L'ASSE $b = 9,43 \text{ \AA}$

LUNGHEZZA LUNGO
L'ASSE $b \sim 9,1 \text{ \AA}$

GLI STRATI SONO
LEGATI DALLA
CONDIVISIONE DI
OSSIGENI APICALI

**SEZIONE TRASVERSALE
PERPENDICOLARMENTE ALL'ASSE DI FIBRA
DI UN FASCIO DI FIBRE DI CRISOTILO**





**arabesques
de serpentine**

**LIZARDITE E
CRISOTILO**

10 nm



LA DISOMOGENEITA' COMPOSIZIONALE E STRUTTURALE DEL CRISOTILO MINERALE NE RENDE DIFFICILE LO STUDIO CHIMICO

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ASBESTOS AND OTHER FIBROUS MATERIALS

Table 2.3 Chemical Analyses and Calculation of Formulas for Commercial Chrysotile Asbestos Samples from Four Countries

	Origin of Samples ^a			
	Canada (1)	USSR (2)	Zimbabwe (3)	Swaziland (4)
SiO ₂	38.75	39.00	39.70	39.93
Al ₂ O ₃	3.09	4.66	3.17	3.92
Fe ₂ O ₃	1.59	0.54	0.27	0.10
FeO	2.03	1.53	0.70	0.45
MnO	0.08	0.11	0.26	0.05
MgO	39.78	38.22	40.30	40.25
CaO	0.89	2.03	1.08	1.02
K ₂ O	0.18	0.07	0.05	0.09
Na ₂ O	0.10	0.07	0.04	0.09
H ₂ O ⁺	12.22	11.37	12.17	12.36
H ₂ O ⁻	0.60	0.77	0.64	0.92
CO ₂	<u>0.48</u>	<u>1.83</u>	<u>2.13</u>	<u>1.04</u>
	99.79	100.20	100.51	100.22

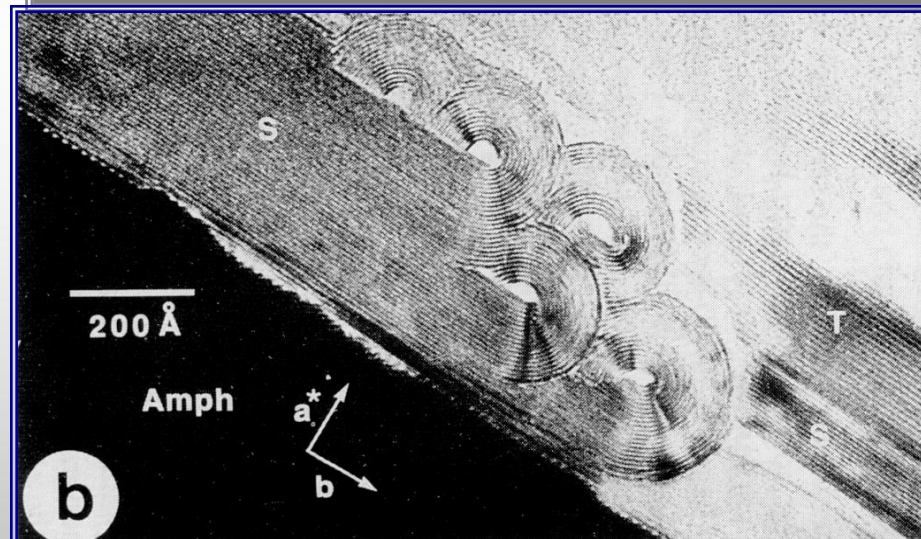
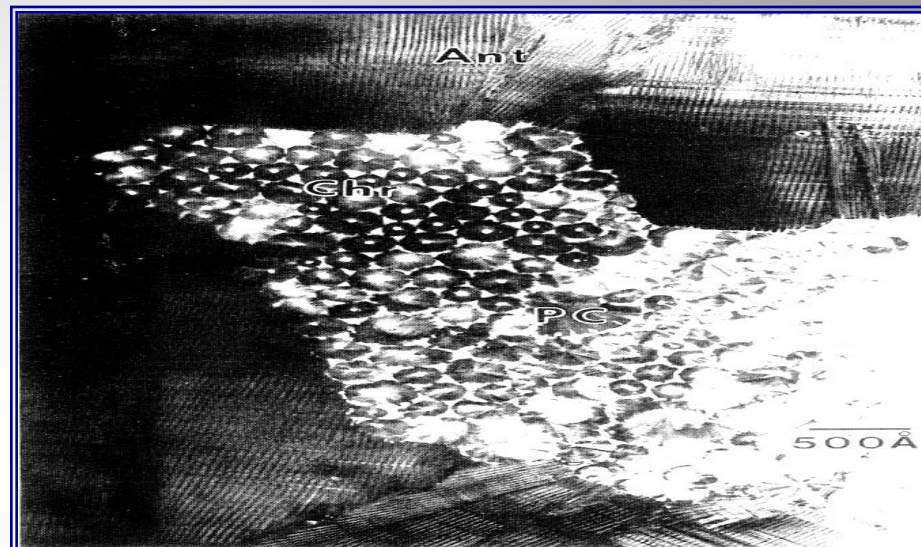
number of ions on basis of the ideal formula Mg₃Si₂O₅(OH)₄^b

Si	1.845	} 2.000	1.851	} 2.000	1.885	} 2.000	1.882	} 2.000
Al	0.155		0.149		0.115		0.118	
Al	0.018	} 3.047	0.112	} 3.013	0.062	} 3.025	0.100	} 3.016
Fe ⁺³	0.057		0.019		0.010		0.004	
Fe ⁺²	0.081		0.061		0.028		0.018	
Mn	0.003		0.004		0.010		0.002	
Mg	2.823	} 3.047	2.704	} 3.013	2.853	} 3.025	2.827	} 3.016
Ca ^c	0.045		0.103		0.055		0.052	
K ^c	0.011		0.004		0.003		0.005	
Na ^c	0.009		0.006		0.004		0.008	

^aKey to country of origin of four sample: (1) King Beaver Mine, Thetford Mines, Quebec; (2) Asbest, Urals, USSR; (3) Shahani Mines, Zimbabwe; (4) Havelock Mine, Swaziland.

^bTo express mineral chemical formulas the cations or anions substituting in a unique site in the structure are combined.

^cThese cations may be the result of adventitious inclusion of other minerals.

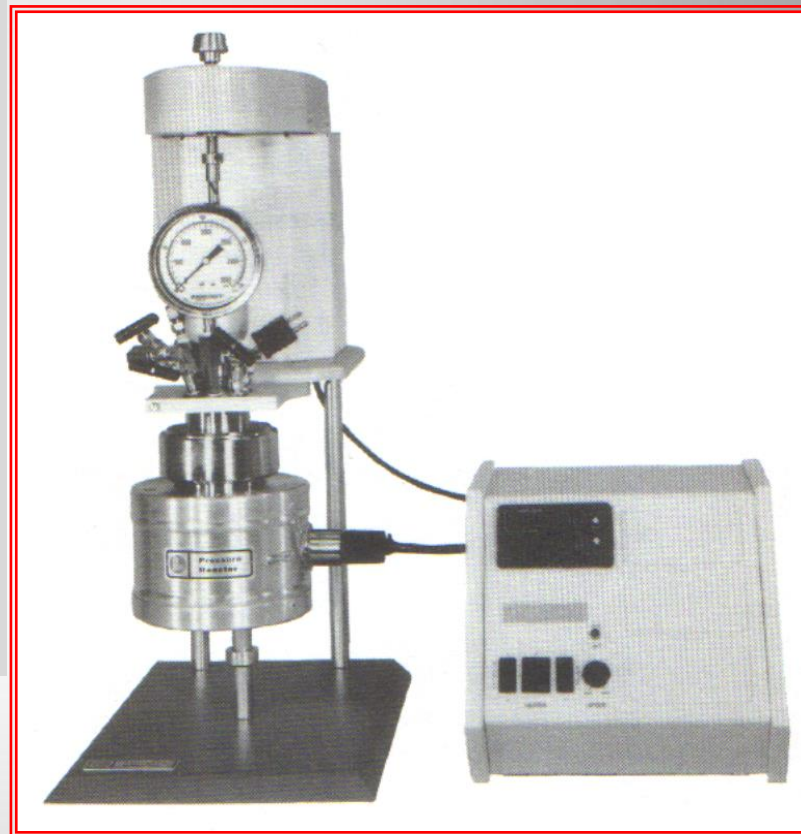


SINTESI DEL CRISOTILO GEOMIMETICO

**LA SINTESI DEL CRISOTILO E' STATA
TENTATA LA PRIMA VOLTA NEGLI
ANNI 1920-1930**

**FINO AGLI ANNI 1980, PER LA GRANDE
DISPONIBILITA' DI CRISOTILO MINERALE A
BASSO COSTO, SINTETIZZARLO ERA
VERAMENTE UNA GRANDE INCONGRUITA'**

Abbiamo messo a punto una nuova sintesi per via idrotermale, con reazioni nel sistema $\text{MgO-SiO}_2\text{-H}_2\text{O}$, per ottenere **CRISOTILO GEOMIMETICO PURO** e nanometrico, da utilizzare come standard di riferimento per lo studio della citotossicità e cancerogenicità dell'amianto minerale.



G. Falini, E. Foresti, I.G. Lesci, and N. Roveri: Structural and morphological characterization of synthetic chrysotile single crystals.

***Chem. Commun.* 14, 1512 (2002).**

1. NANOTUBI di CRISOTILO STECHIOMETRICO

Sintesi:

MgCl₂·6H₂O e SiO₂ in rapporto stechiometrico 3 : 2 dalla formula Mg₃Si₂O₅(OH)₄

pH = 13

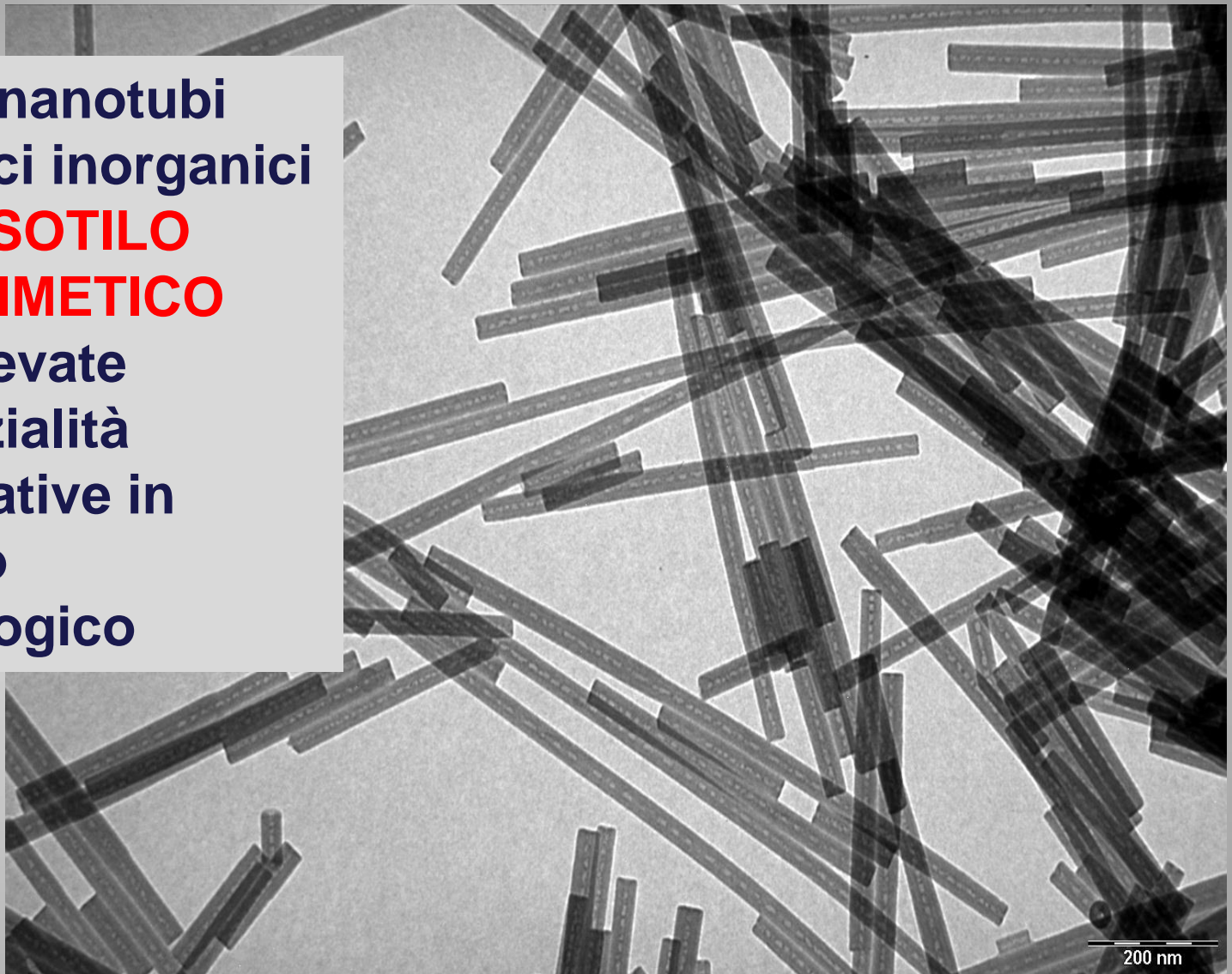
T = 300 °C

Pressione = 82 atm

Tempo di reazione = 24 h

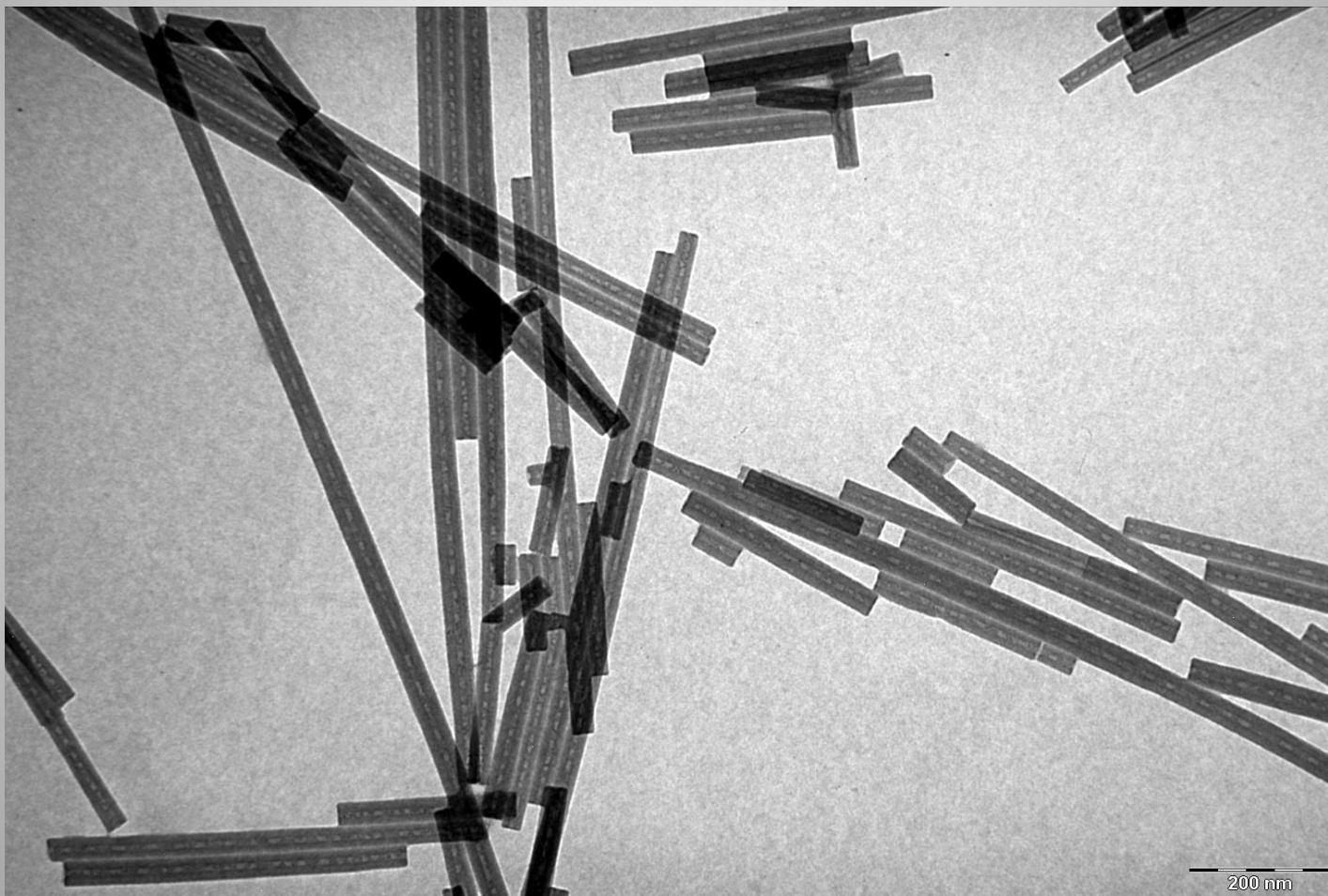


**Nuovi nanotubi
sintetici inorganici
di CRISOTILO
GEOMIMETICO
con elevate
potenzialità
applicative in
ambito
tecnologico**

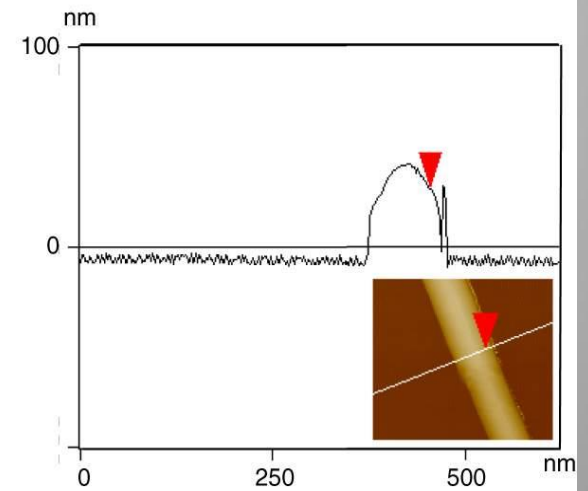
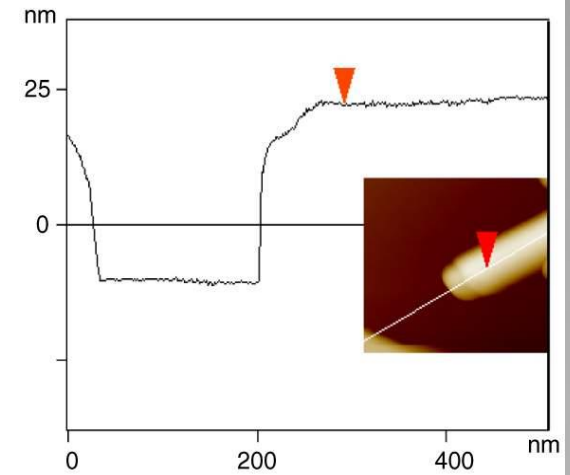
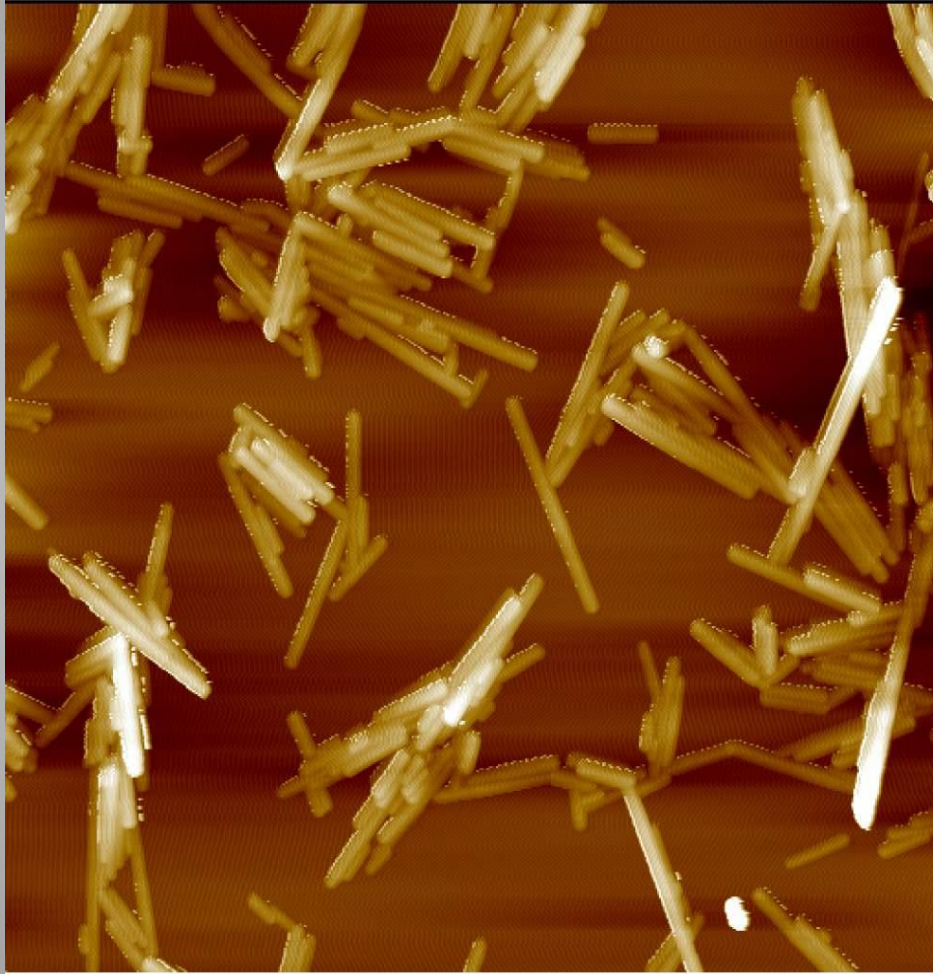


G. Falini, E. Foresti, M. Gazzano, A.F. Gualtieri, M. Leoni, I.G. Lesci, and N. Roveri: Tabular-shaped stoichiometric chrysotile nanocrystals. *Chem.-Eur. J.* 10, 3043 (2004).

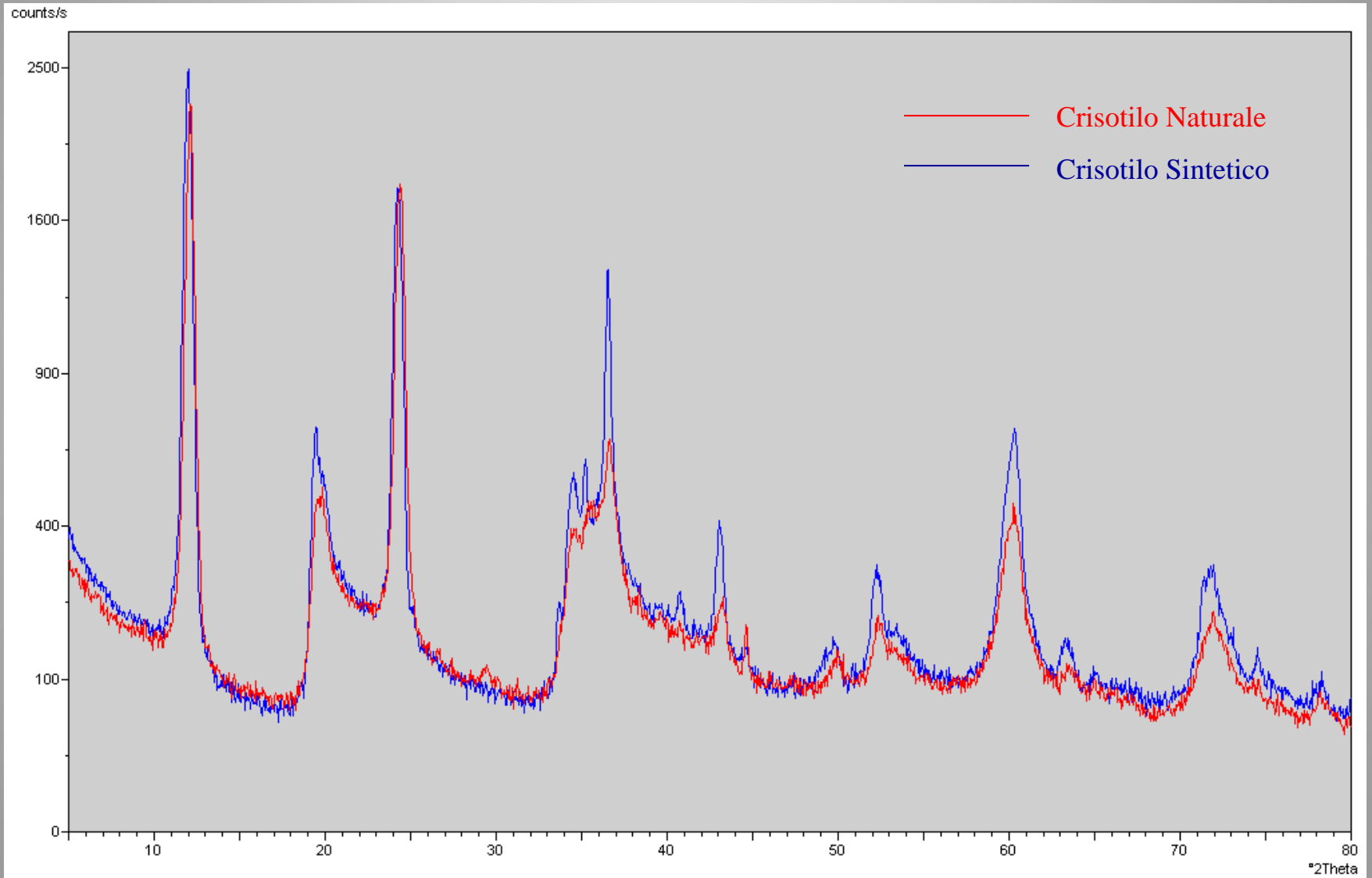
NANOTUBI INORGANICI DI CRISOTILO GEOMIMETICO



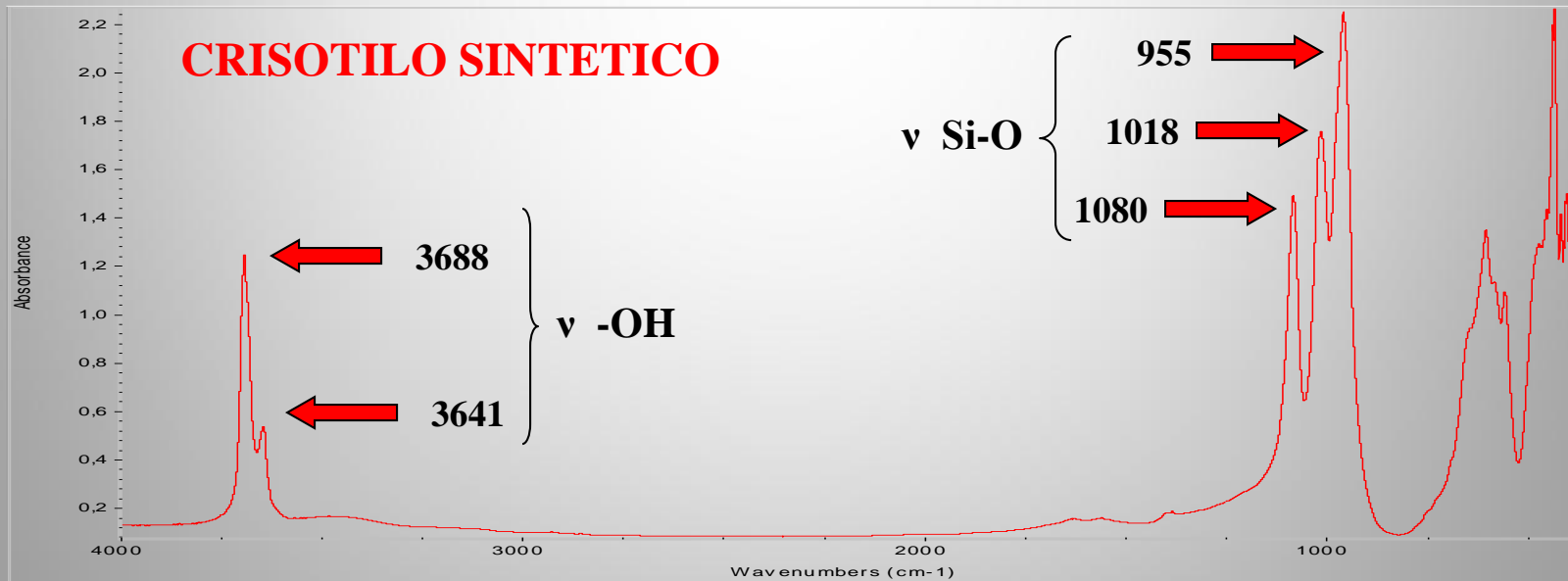
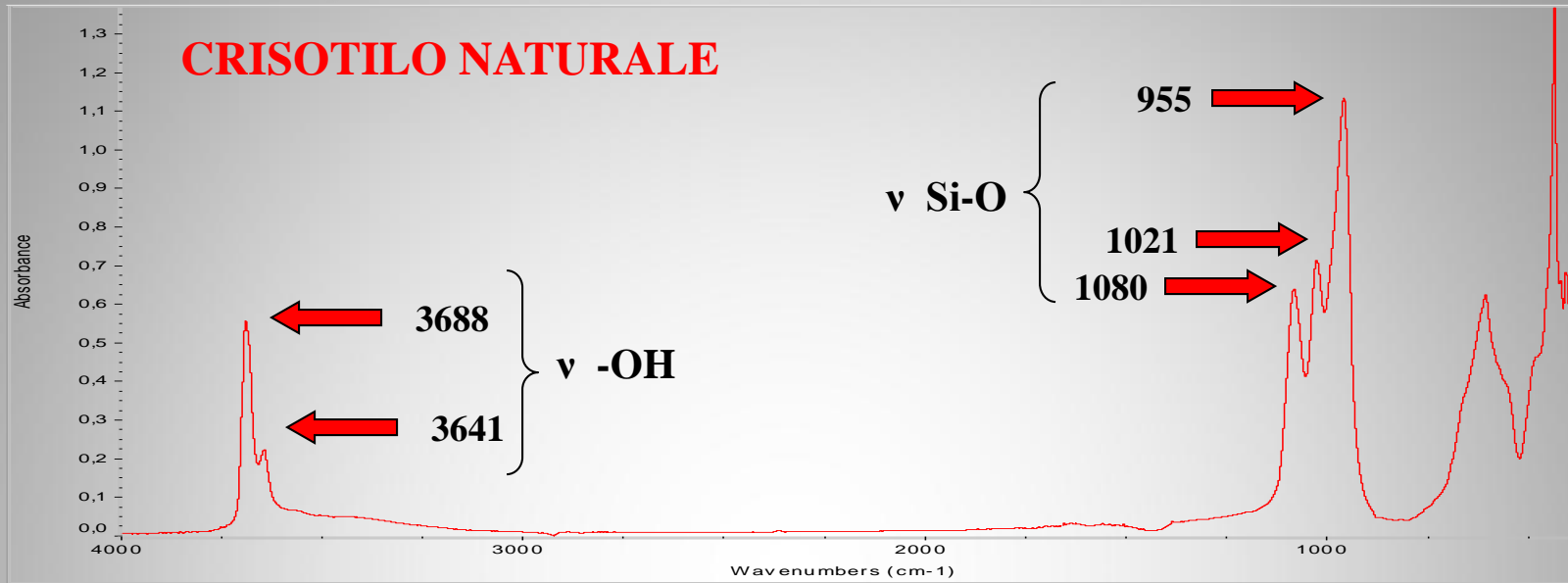
Microscopio a forza atomica (AFM)



Diffrazione ai raggi X



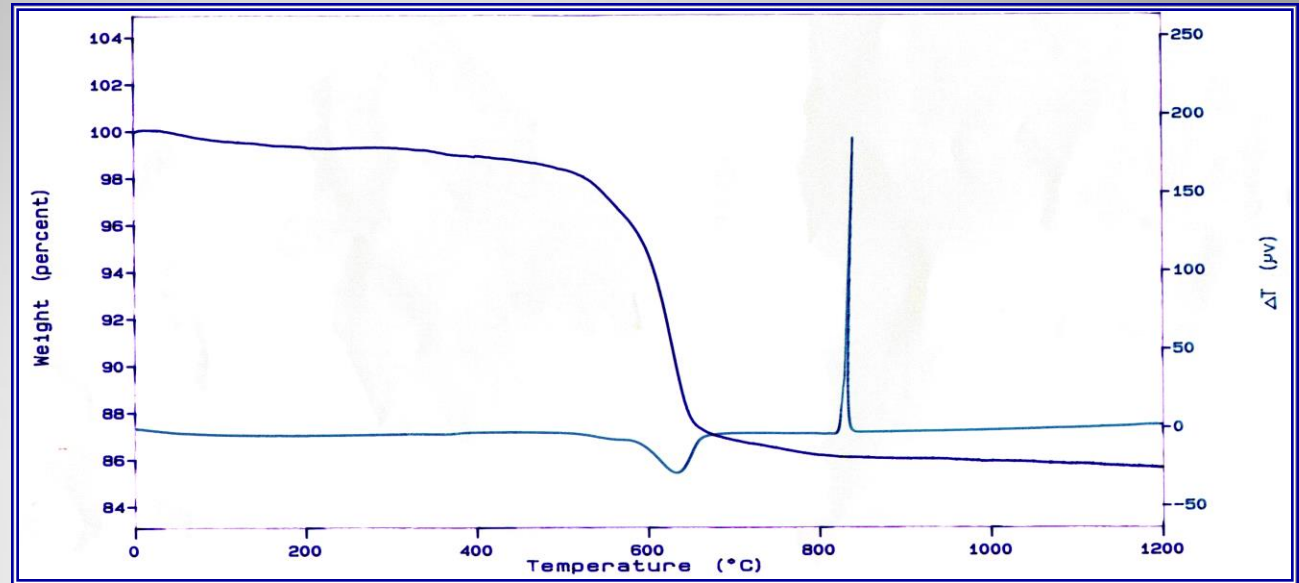
Spettro FT-IR del crisotilo



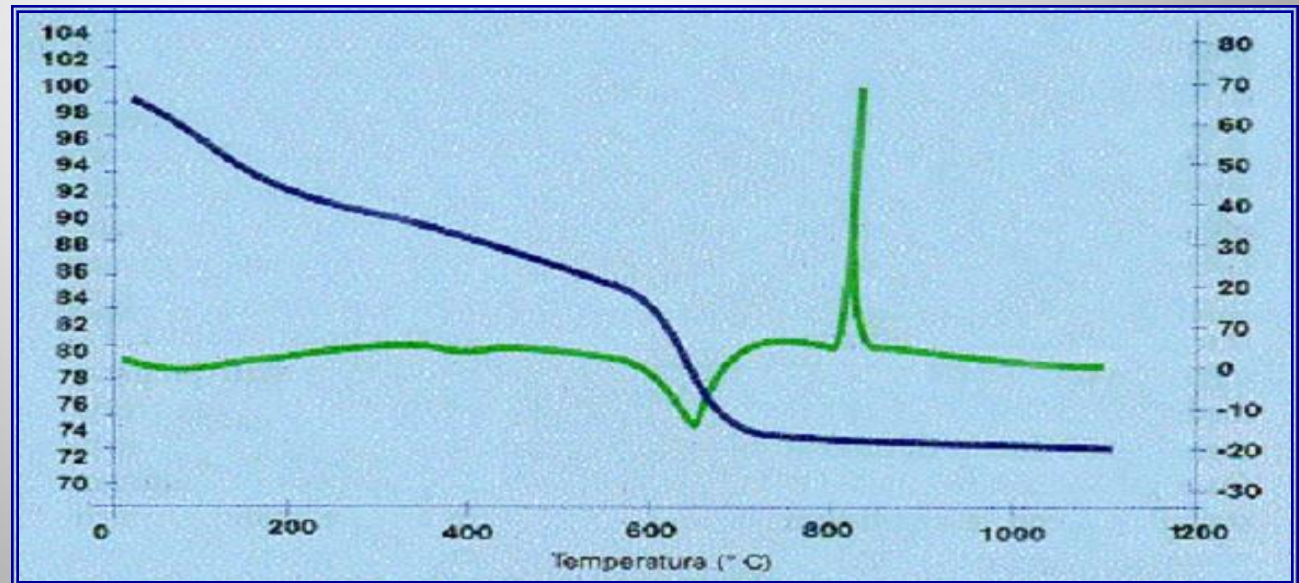
Campioni preparati in pasticca di KBr

Analisi termica

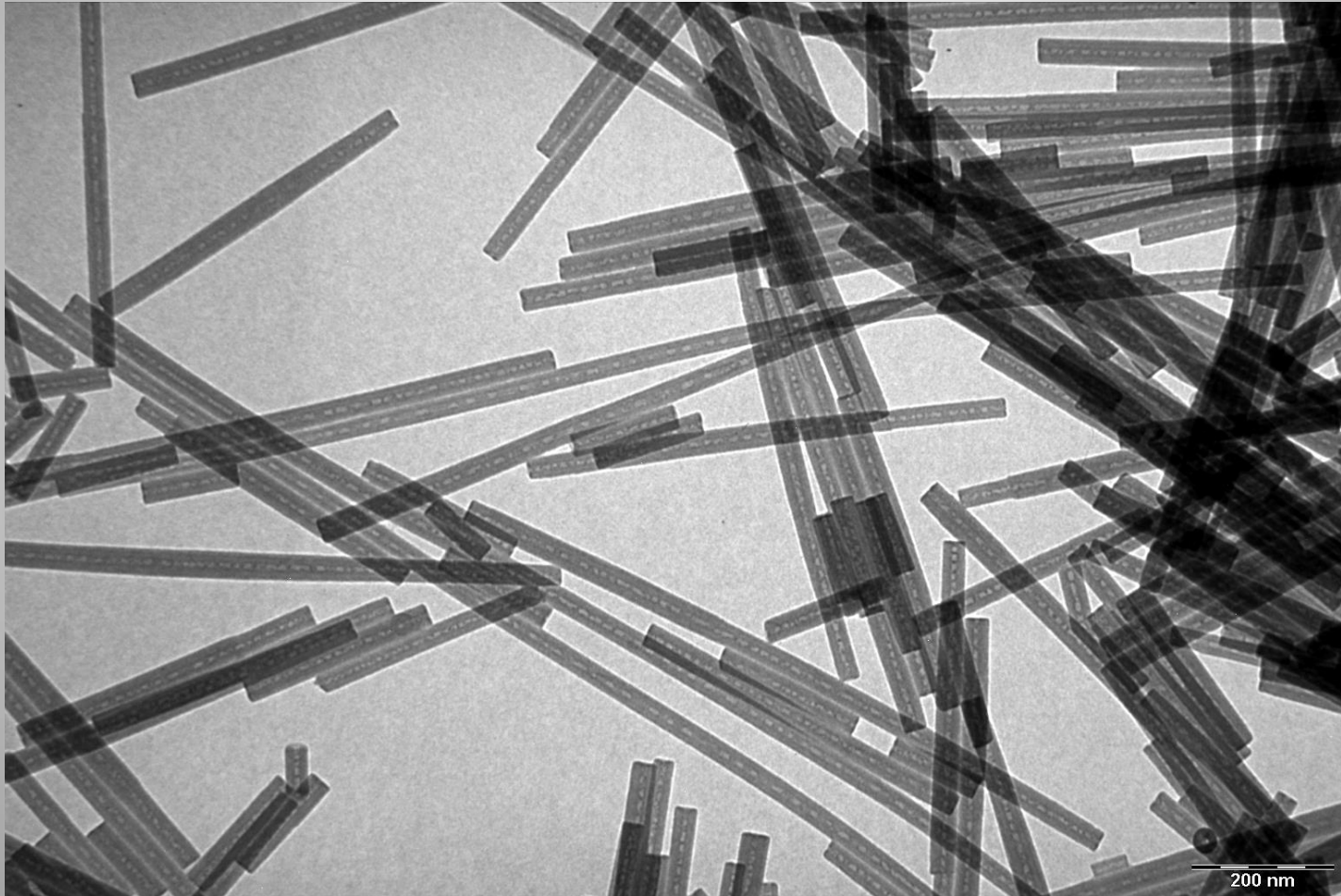
**CRISOTILO
SINTETICO**

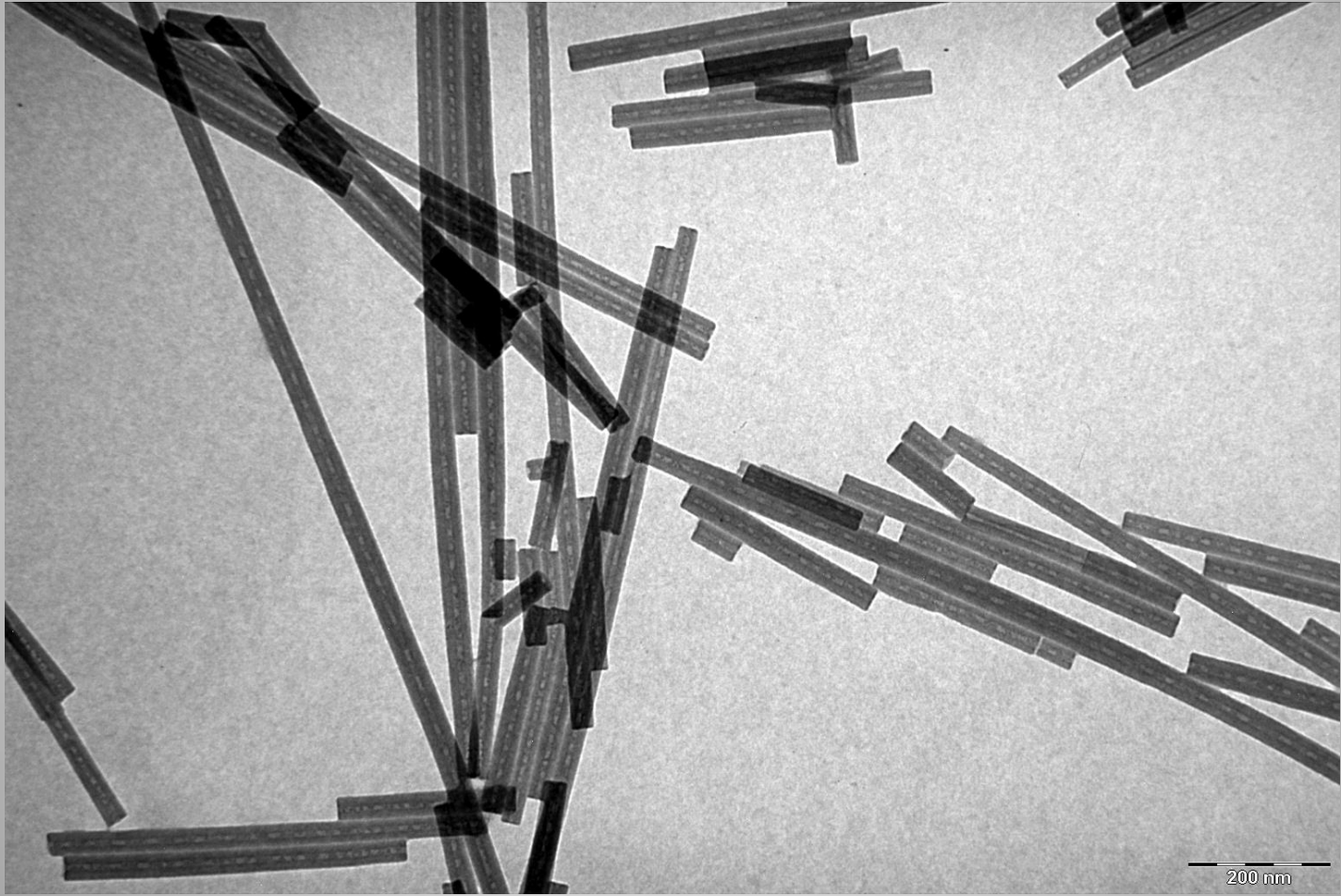


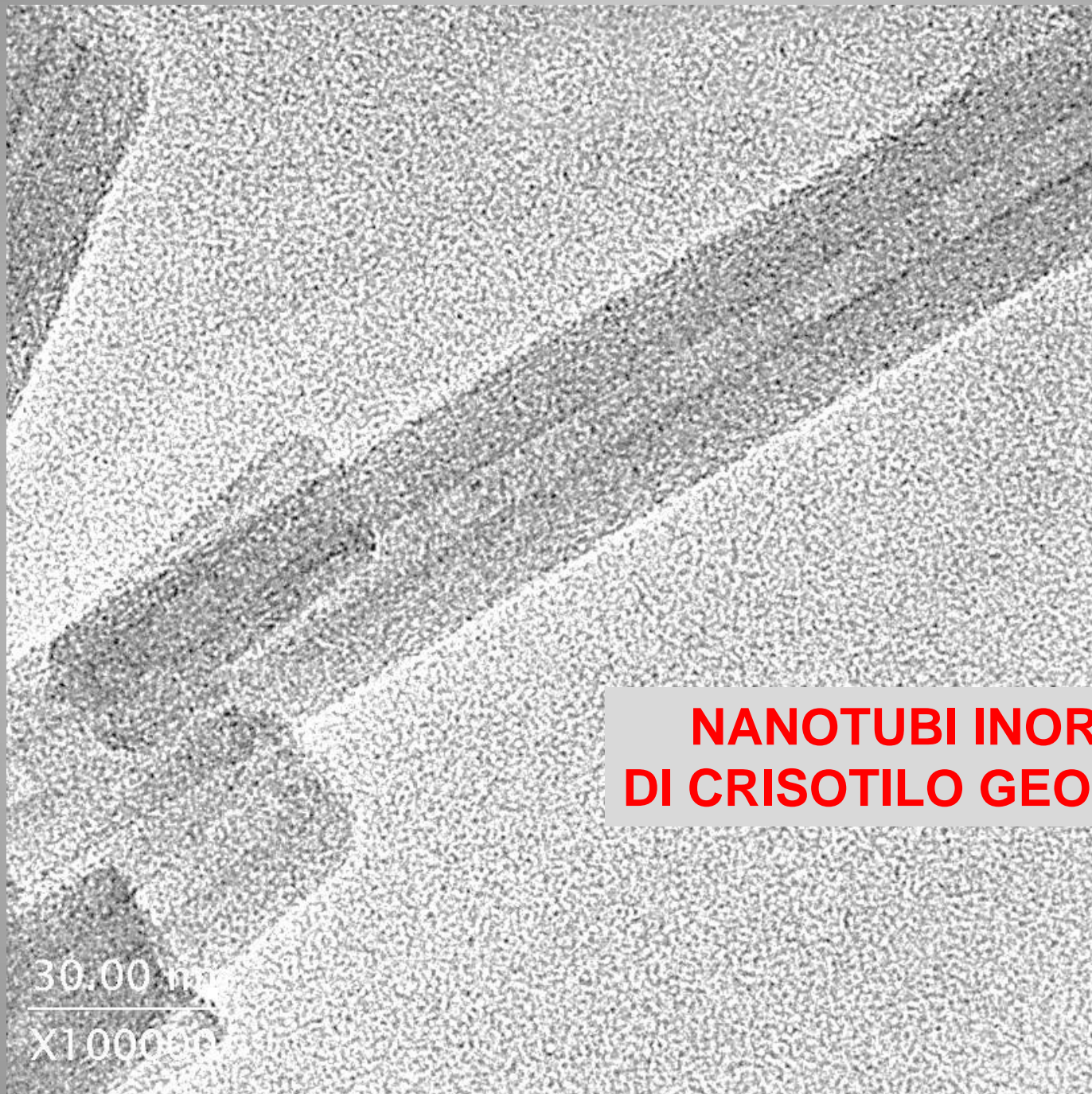
**CRISOTILO
NATURALE**



Sintesi e caratterizzazione di “Geoinspired” nanotubi e “Quantum Wires” per nanotecnologie innovative.

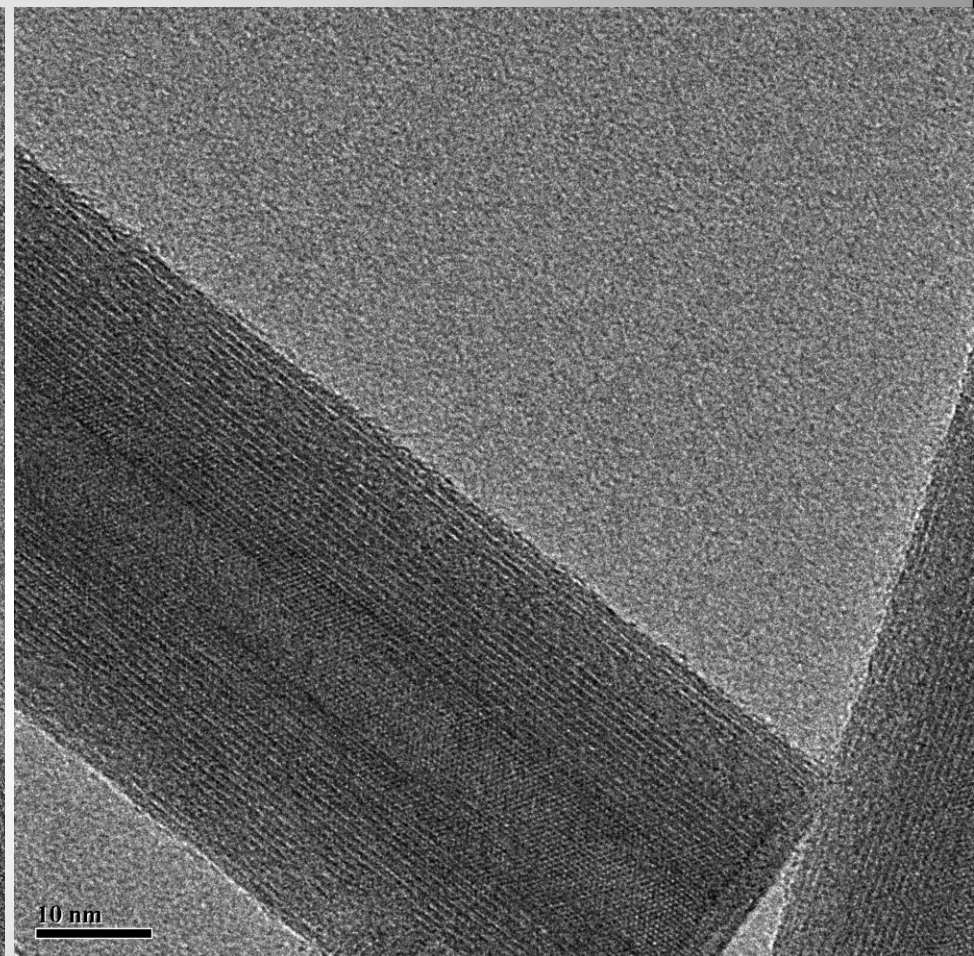
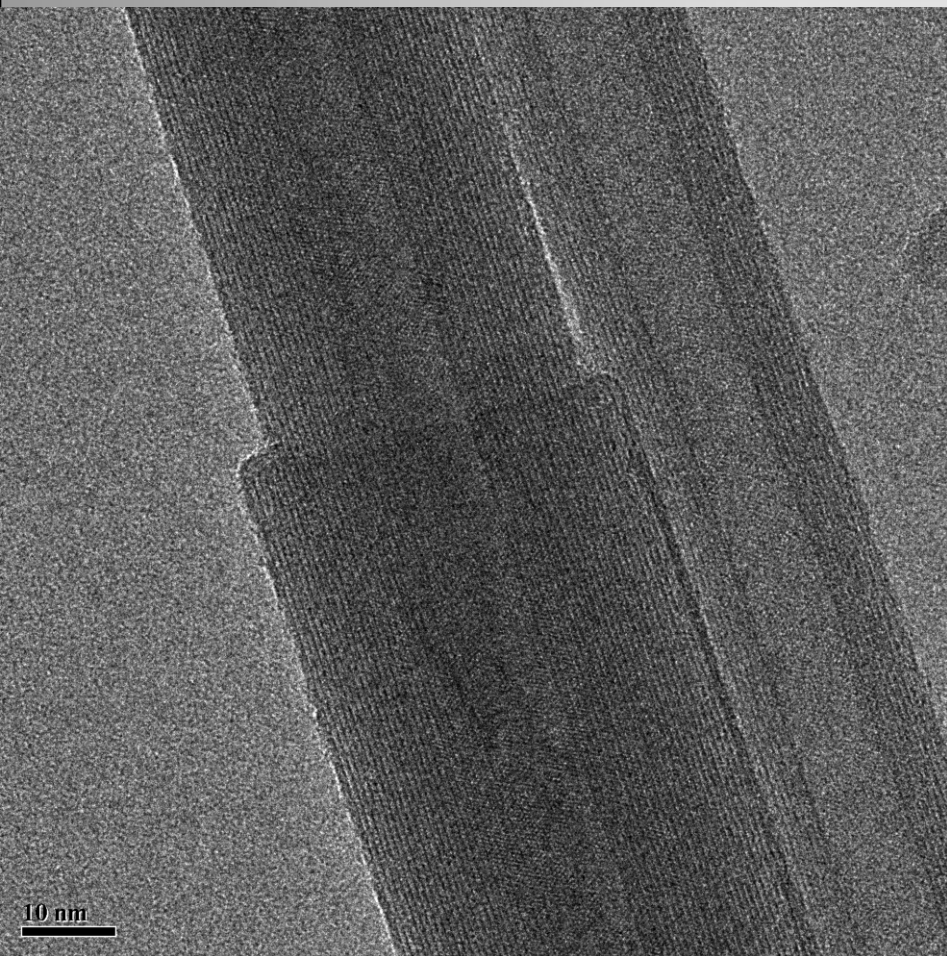






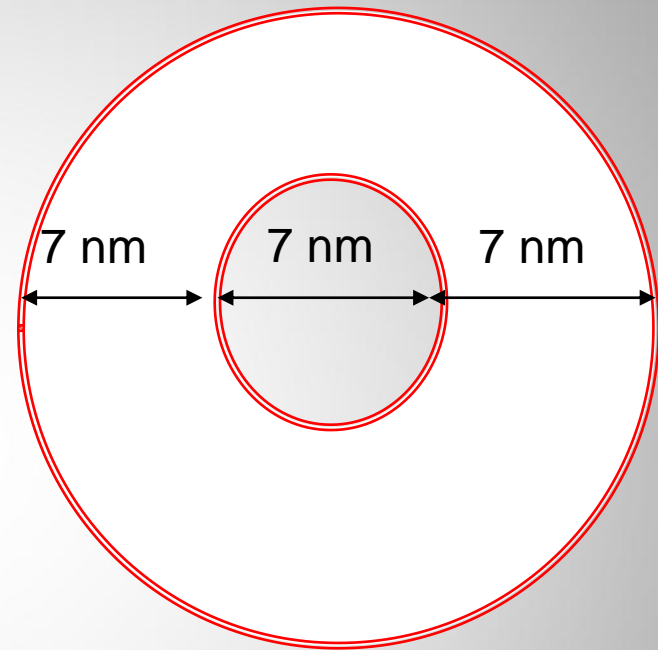
**NANOTUBI INORGANICI
DI CRISOTILO GEOMIMETICO**

30.00 nm
X100000

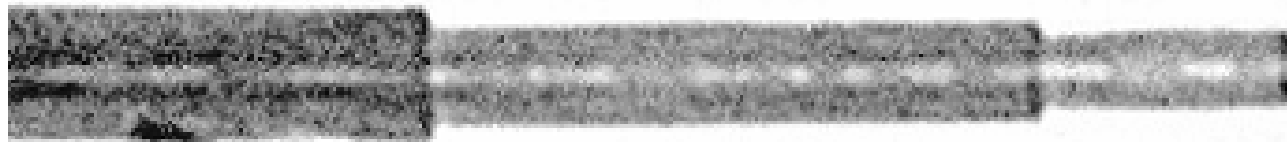


SCHEMA DELLA SEZIONE DI UN NANOTUBO DI CRISOTILO SINTETICO A PARETE SINGOLA

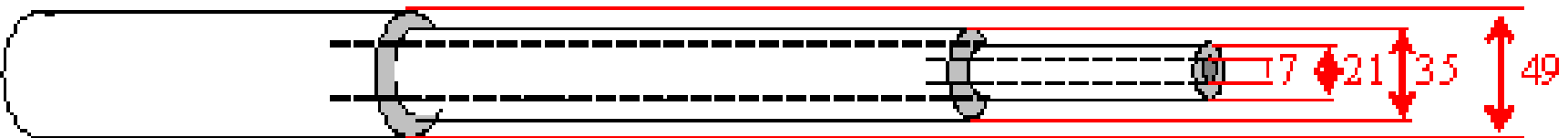
Geoinspired synthetic $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ nanotubes, which have similar radial dimensions as multiwalled carbon nanotubes (e.g., 7 nm and about 20 nm of inner and outer diameter respectively) are considerably longer (up to a few millimeters) than carbon nanotubes and are constituted of an insulating material.



CRISOTILO SINTETICO CON STRUTTURA TUBO IN TUBO (nanotubi inorganici a multiparete)



200 nm

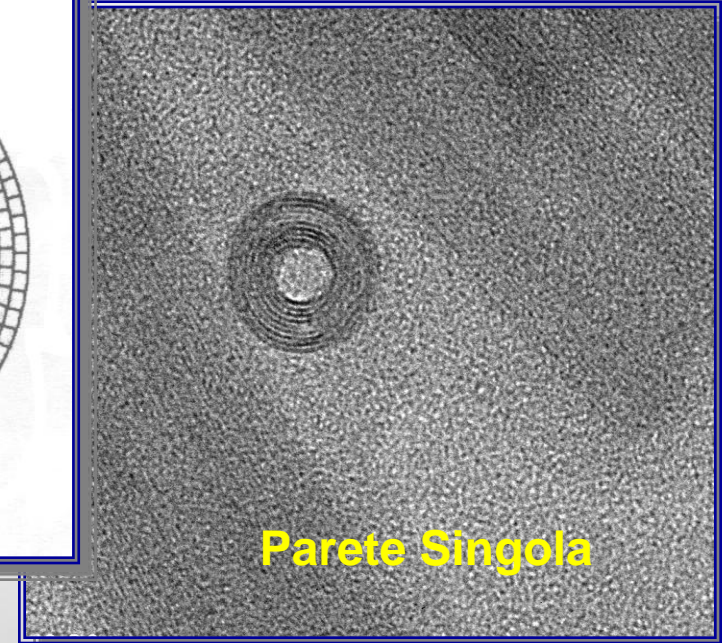
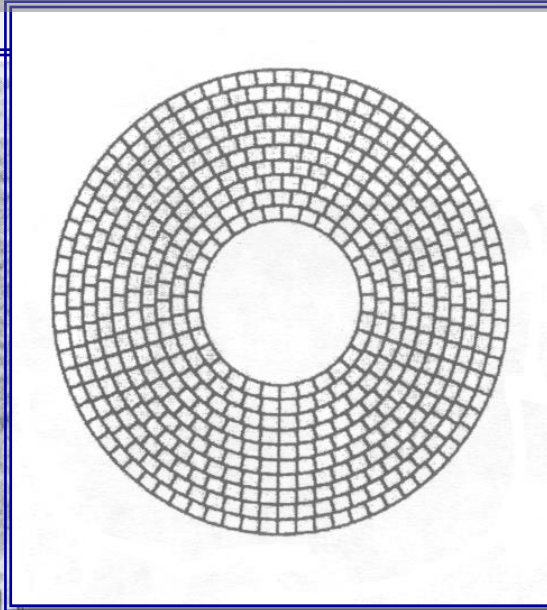
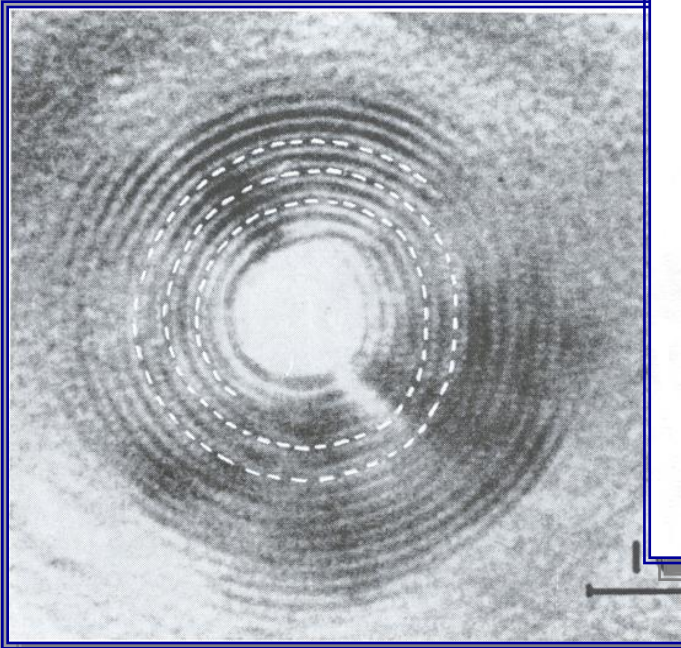
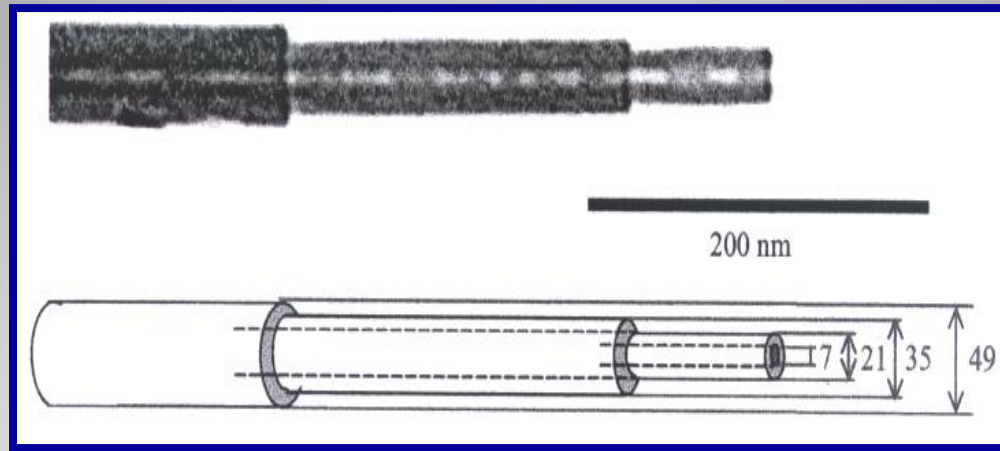


Rappresentazione grafica dei nanotubi con dimensioni in nm.

M. Leoni, A.F. Gualtieri, and N. Roveri:

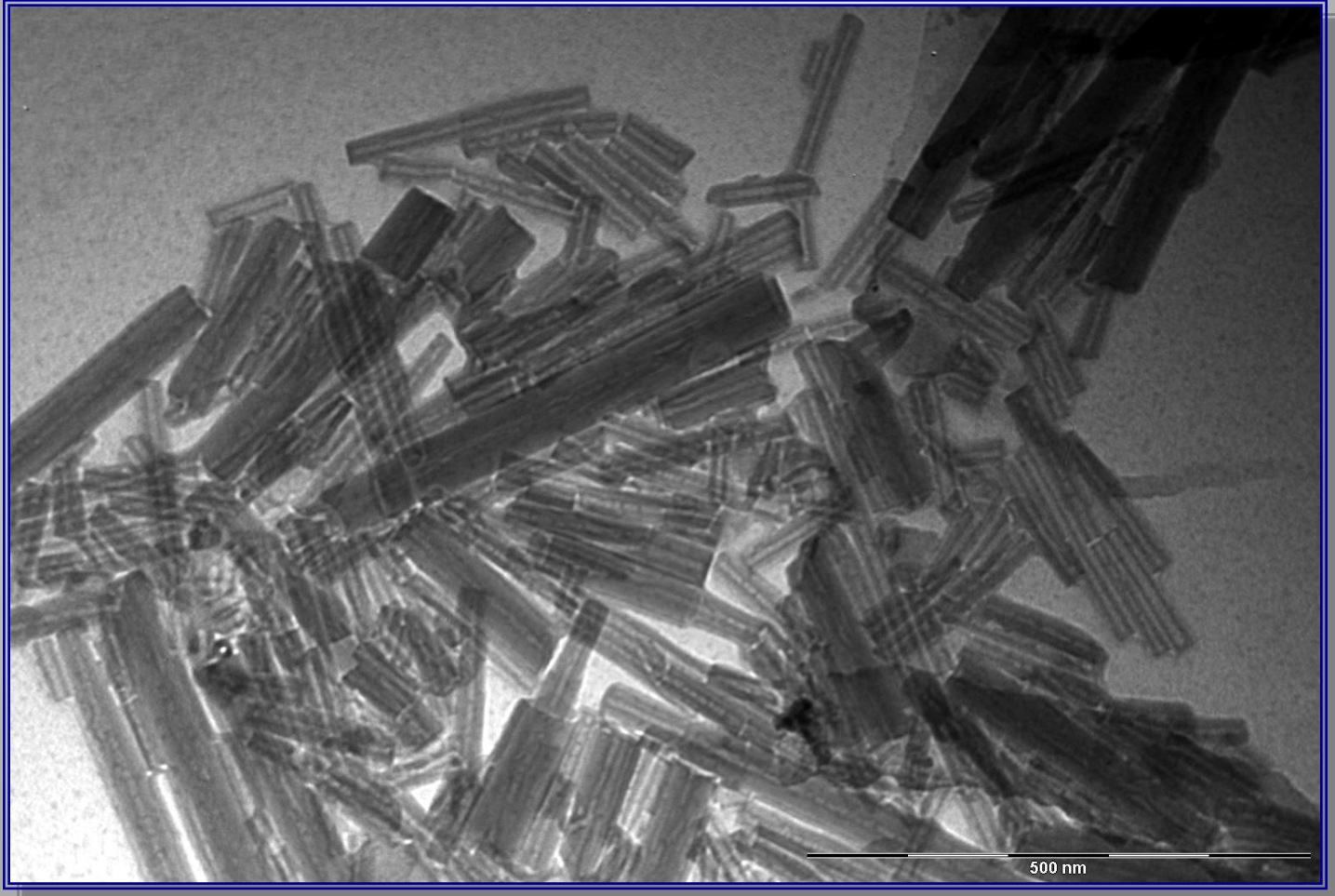
Simultaneous refinement of structure and microstructure of layered materials.

J. Appl. Crystallogr. 37(1), 166 (2004).

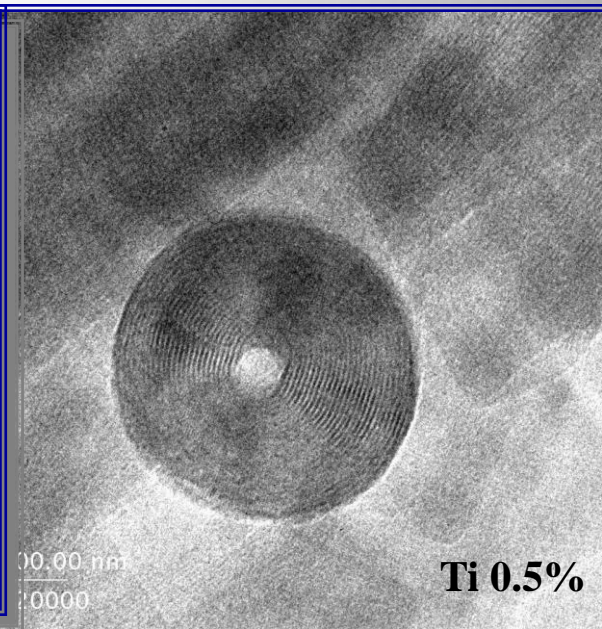
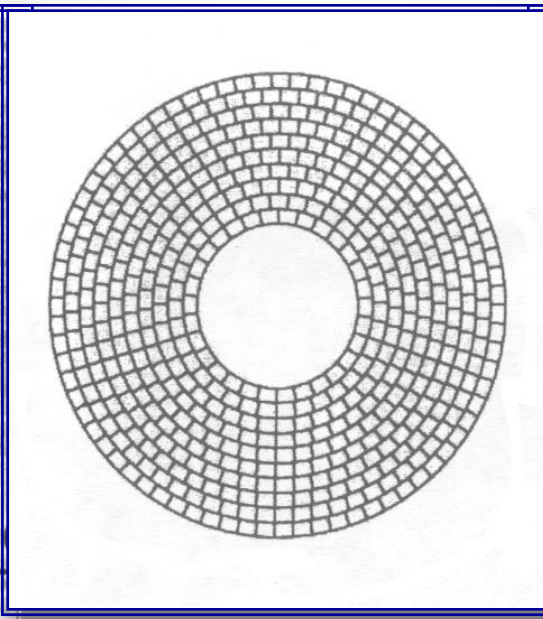
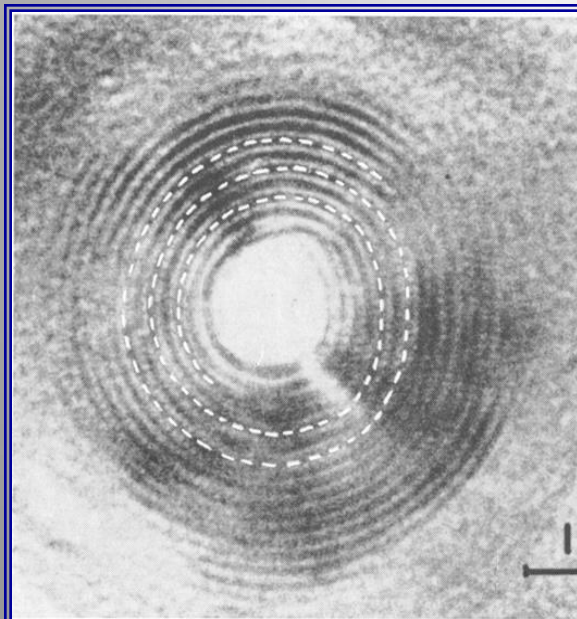
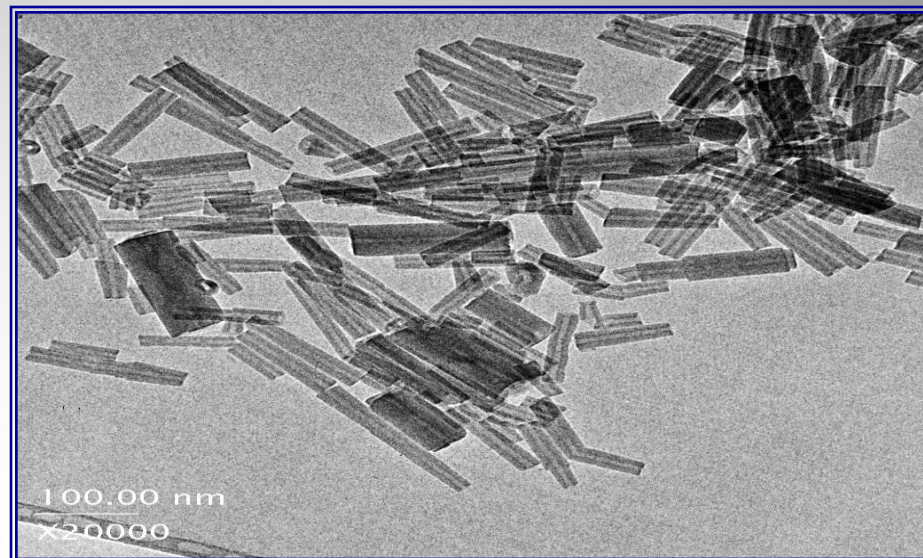


E. Foresti, M.F. Hochella, Jr., H. Kornishi, I.G. Lesci, A.S. Madden, N. Roveri, and H. Xu: **Morphological and chemical/physical characterization of Fe-doped synthetic chrysotile nanotubes.** *Adv.Funct. Mater.* 15(6), 1009 (2005).

NANOTUBI GEOMIMETICI DI CRISOTILO A MULTIPARETE

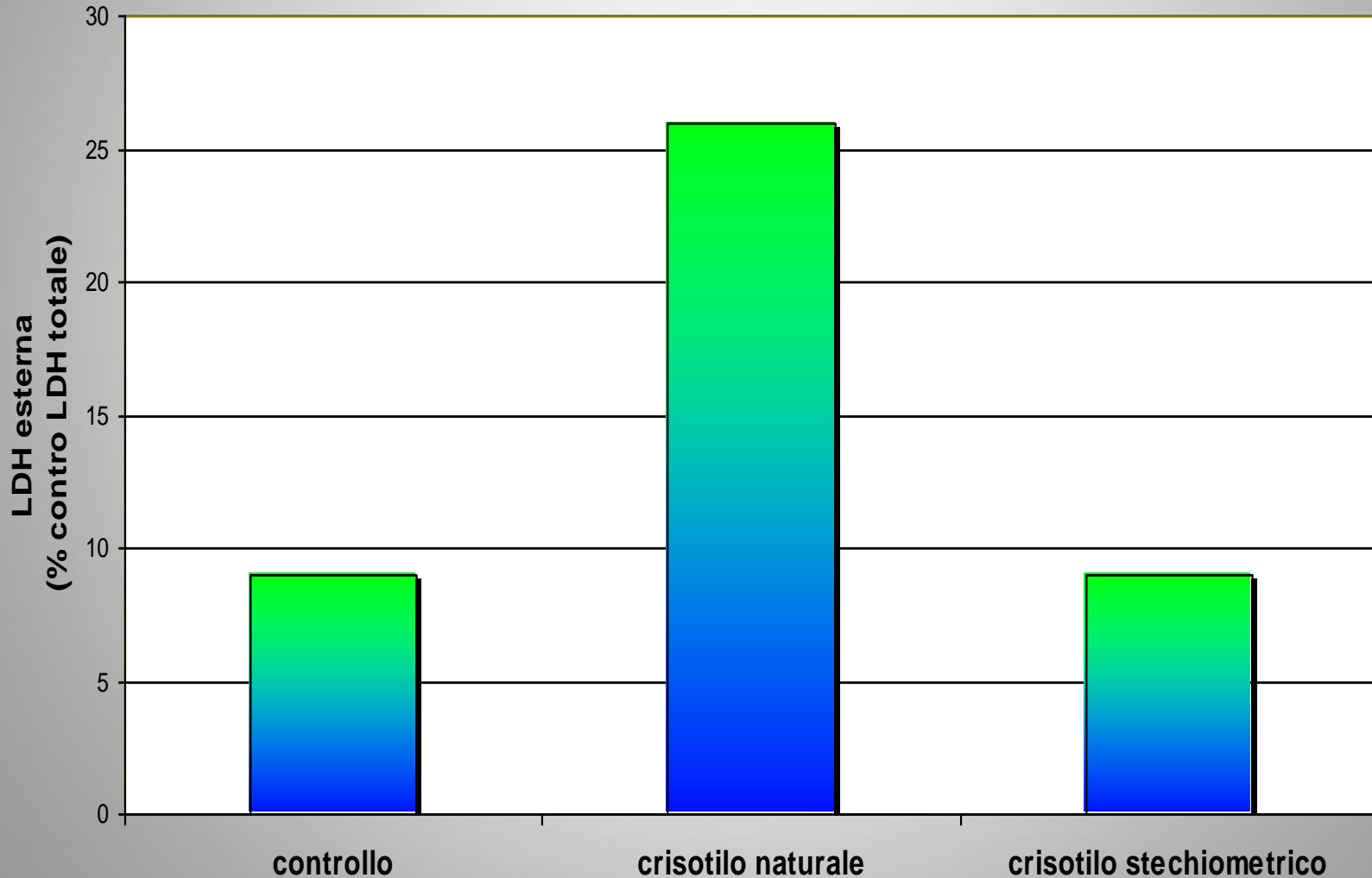


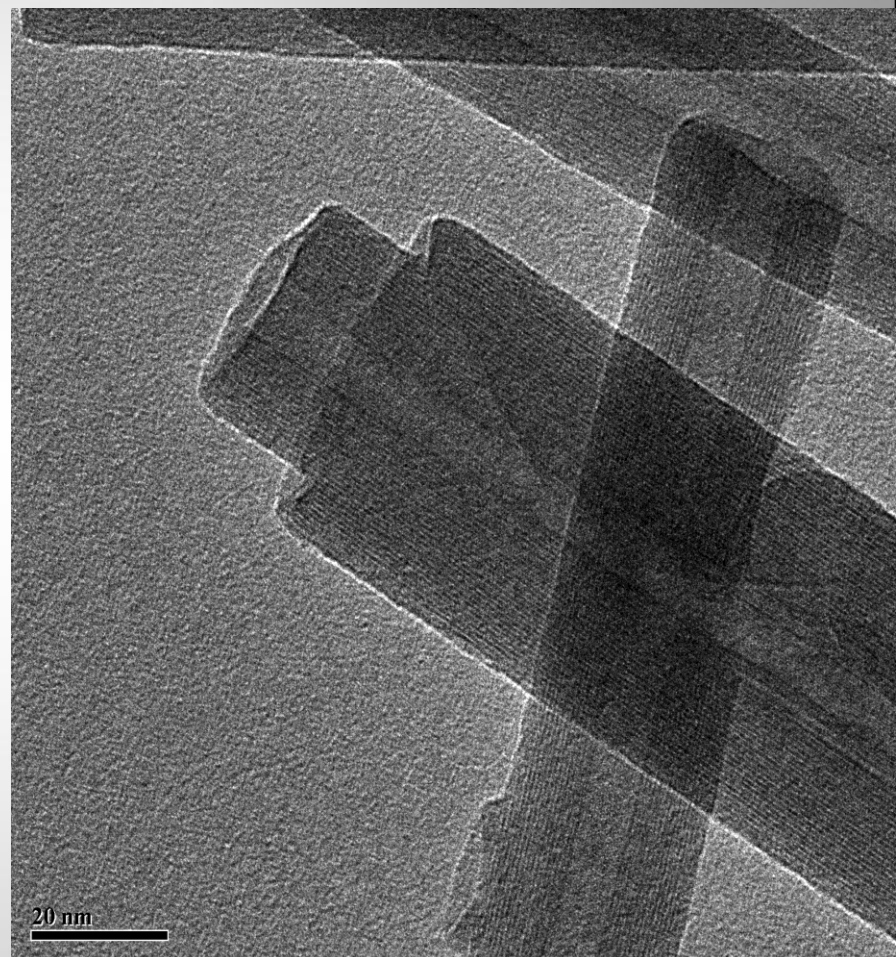
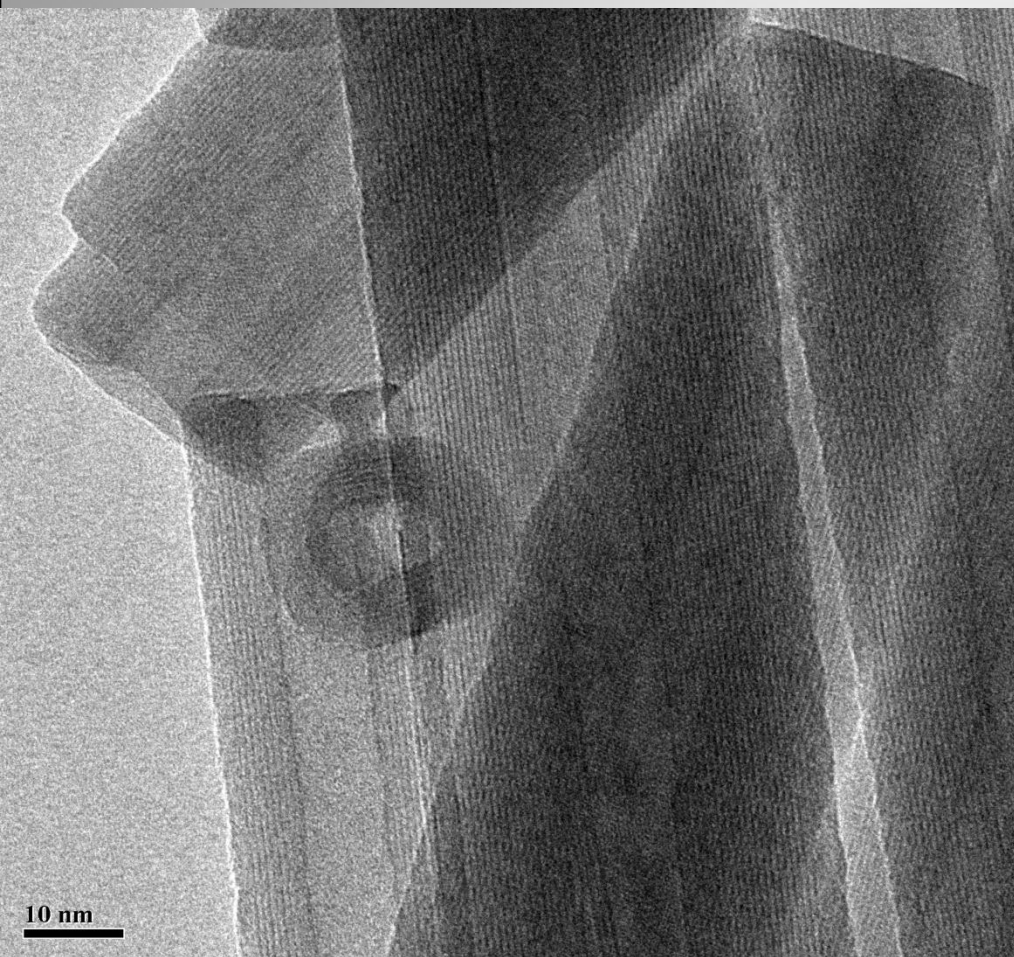
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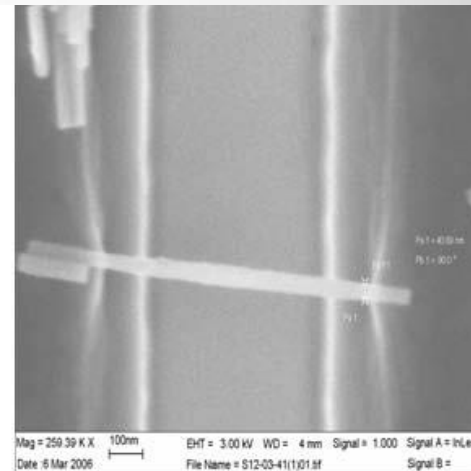
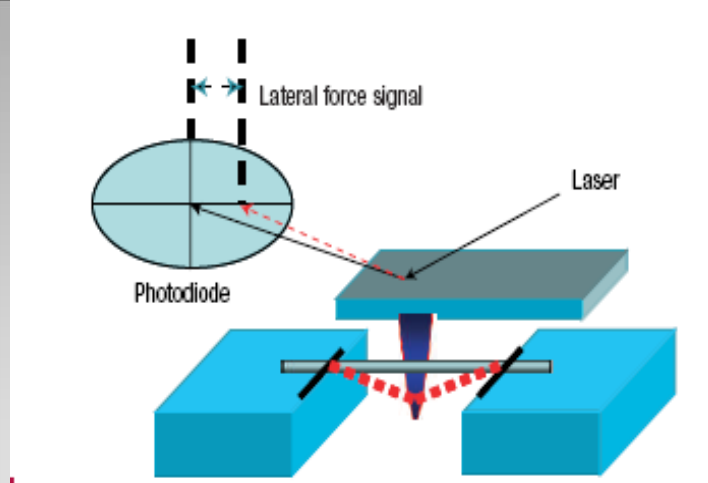


IL CRISOTILO SINTETICO BIOMIMETICO NON E' TOSSICO

E. Gazzano, E. Foresti, I.G. Lesci, M. Tomatis, C. Riganti, B. Fubini, N. Roveri, and D. Ghigo:
**Different cellular responses evoked by natural and stoichiometric
synthetic chrysotile asbestos.** *Toxicol. Appl. Pharmacol.* 206(3), 356 (2005).





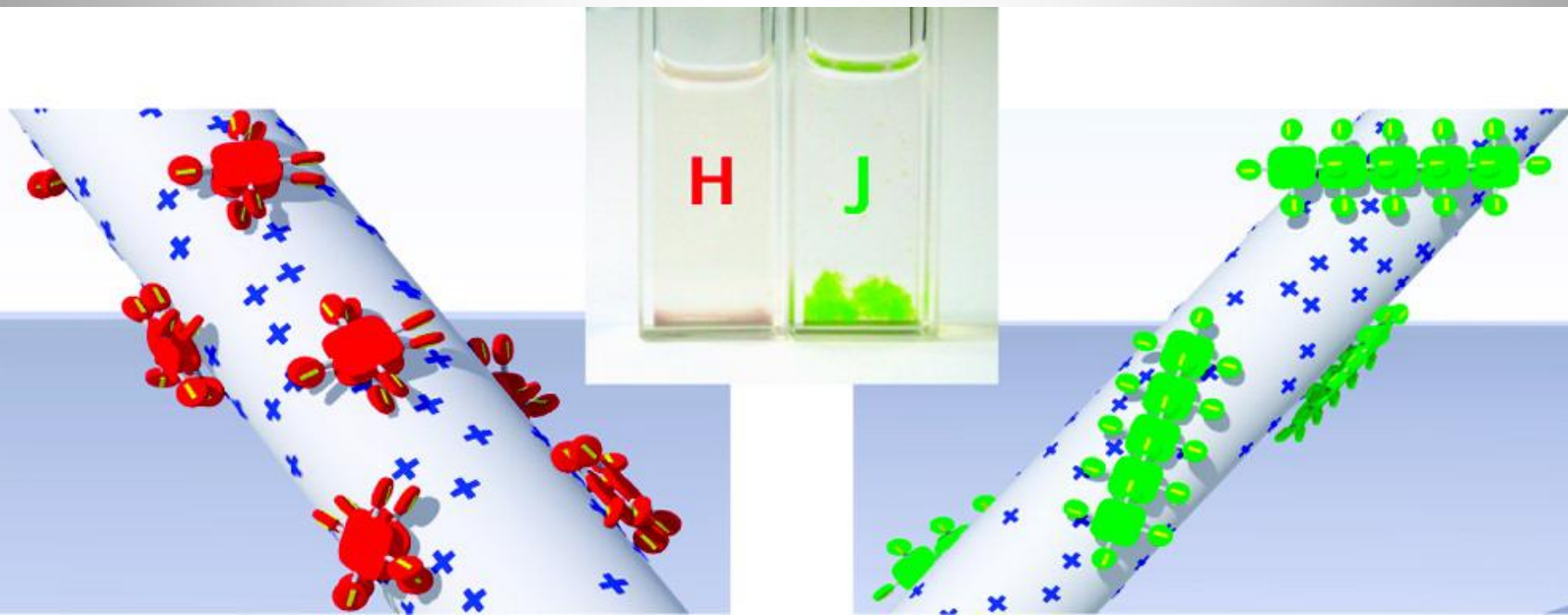


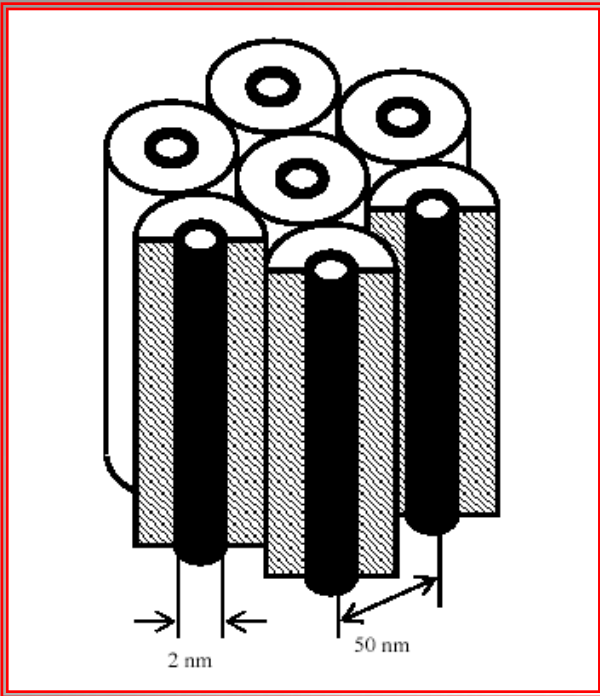
	Diameter (nm)	Length (nm)	maximum distance (nm)	Young's modulus(GPa) (1st)	Young's modulus(GPa) (2nd)
1	40	620	5	271	302
2	33	650	5	336	212
3	41	655	5	16	14

Self-Organizing Functional Materials via Ionic Self Assembly: Porphyrins H- and J-Aggregates on Synthetic Chrysotile Nanotubes

G. De Luca, A. Romeo, V. Villari, N. Micali, I. Foltran, E. Foresti, I.G. Lesci, N. Roveri, T. Zuccheri, and L. Monsu Scolaro

J. Am. Chem. Soc., Article ASAP • DOI: 10.1021/ja901273h • Publication Date (Web): 30 April 2009





Nanotubi di crisotilo naturale come **NANOWIRES**

Materiali utilizzati:

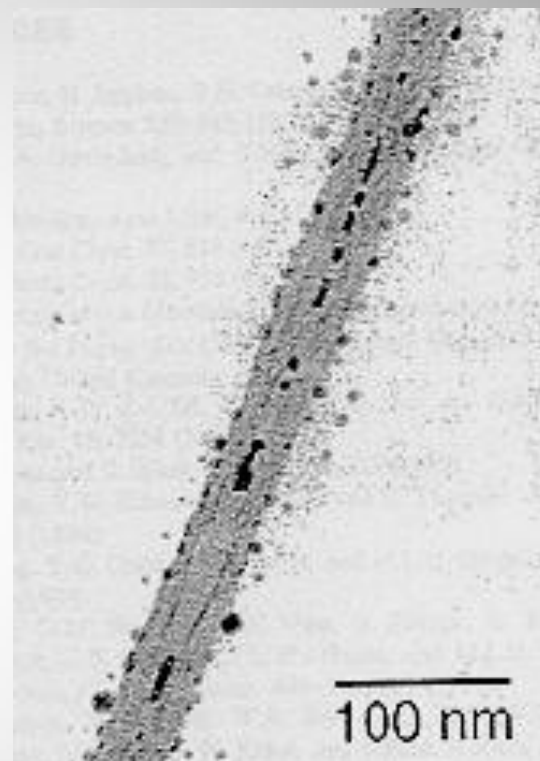
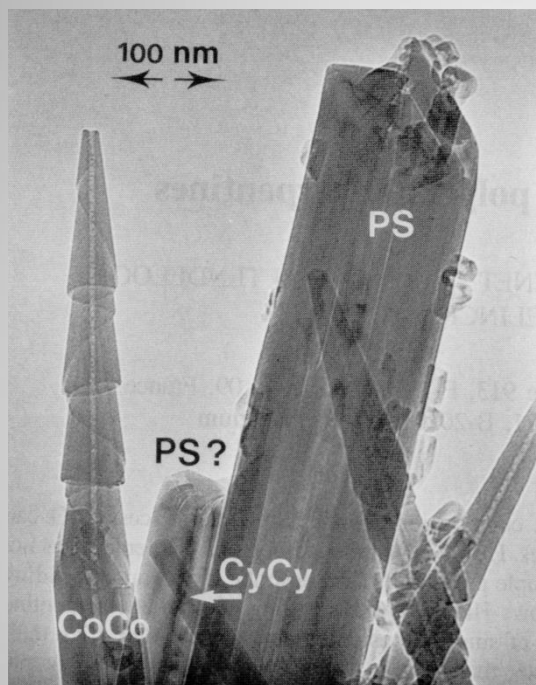
- Metalli – Hg Pb Sn
- Semiconduttori – InSb CdSe GaAs InP

Tecniche utilizzate:

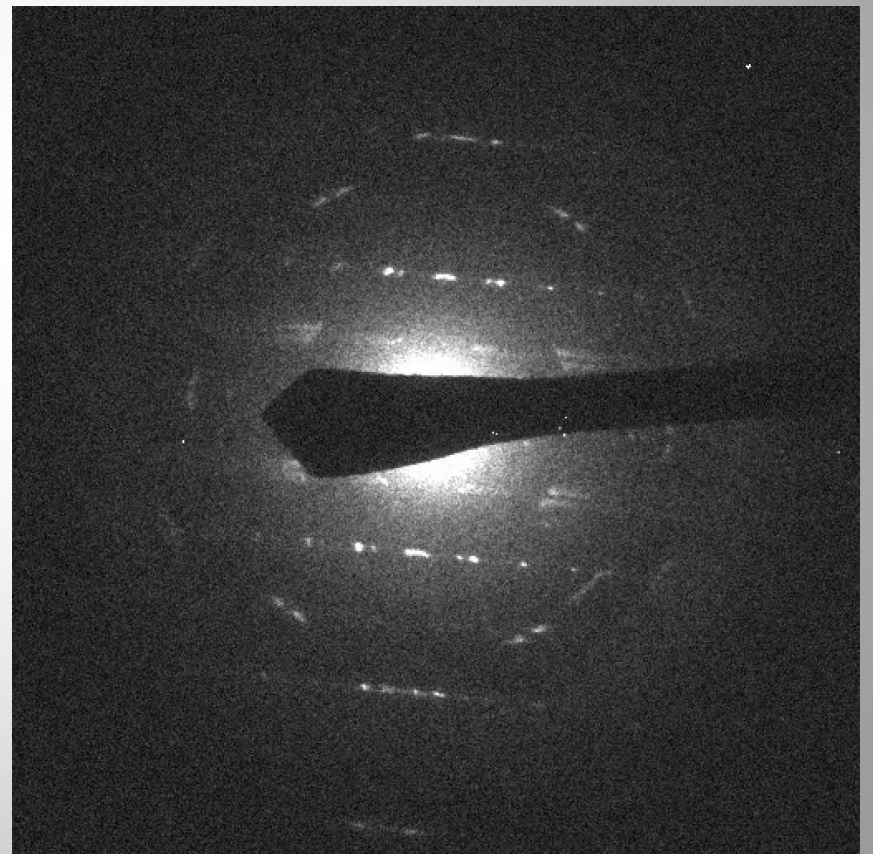
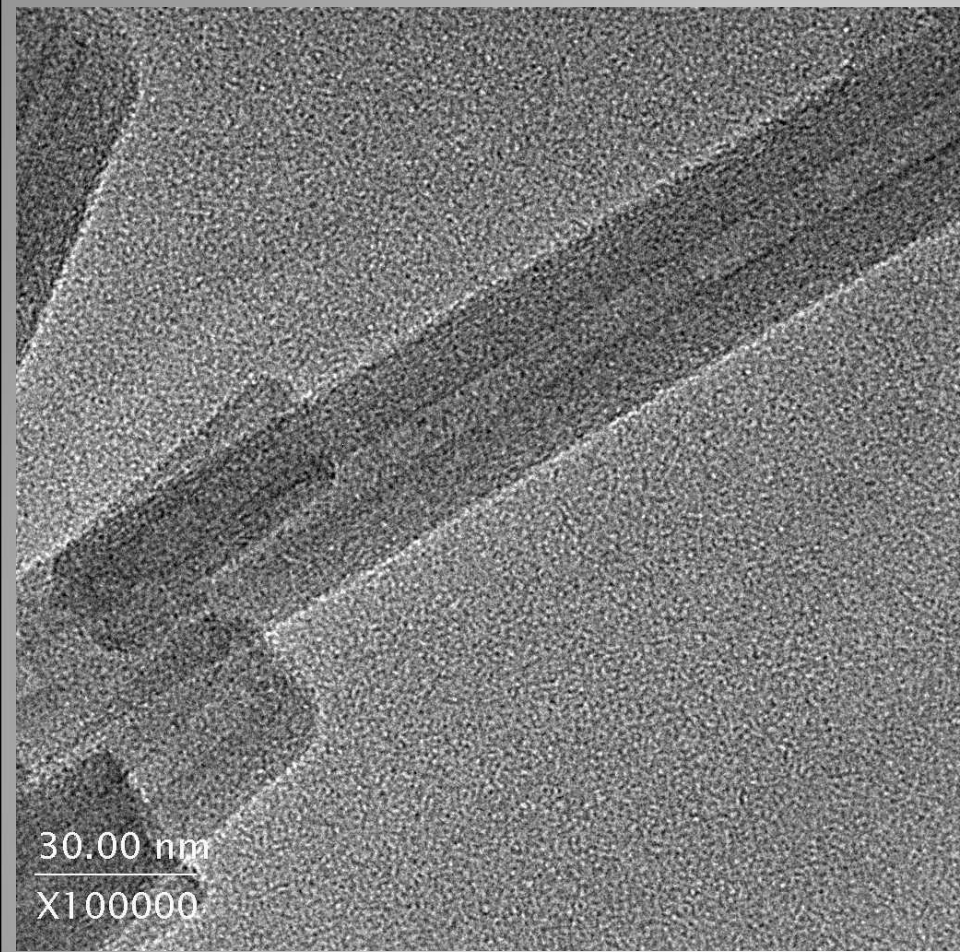
- alta pressione (10-15 Kbar)
- Metal Organic Chemical Vapor Deposition (MOCVD)

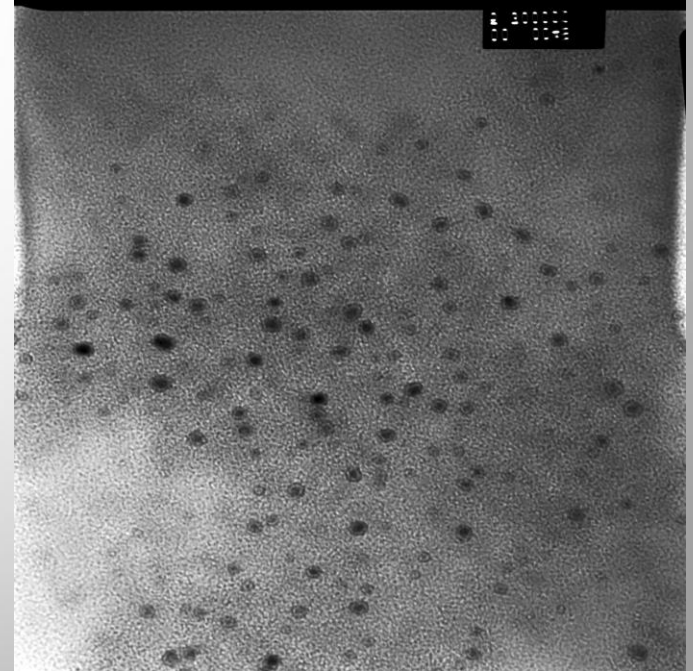
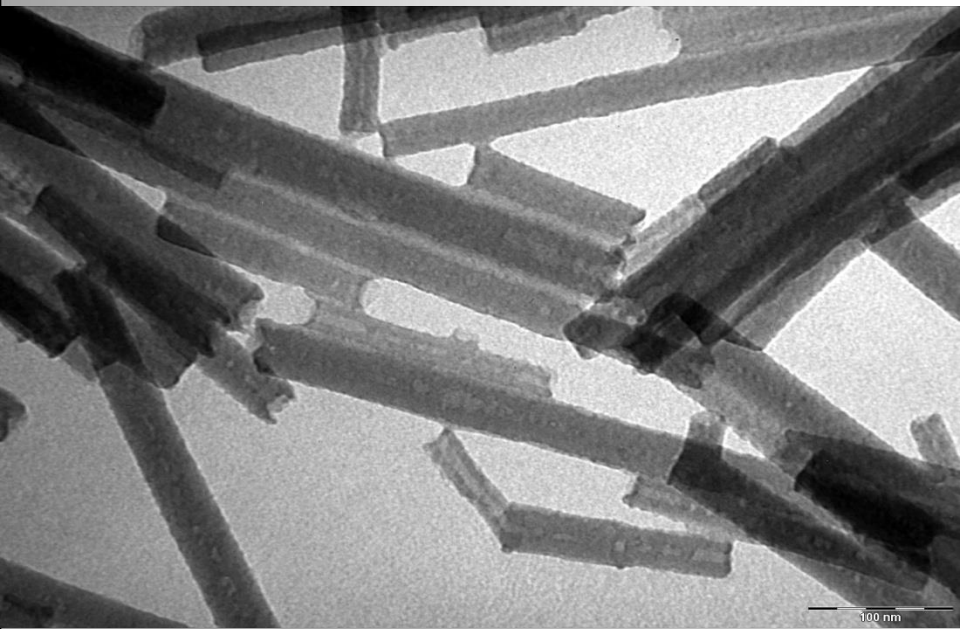
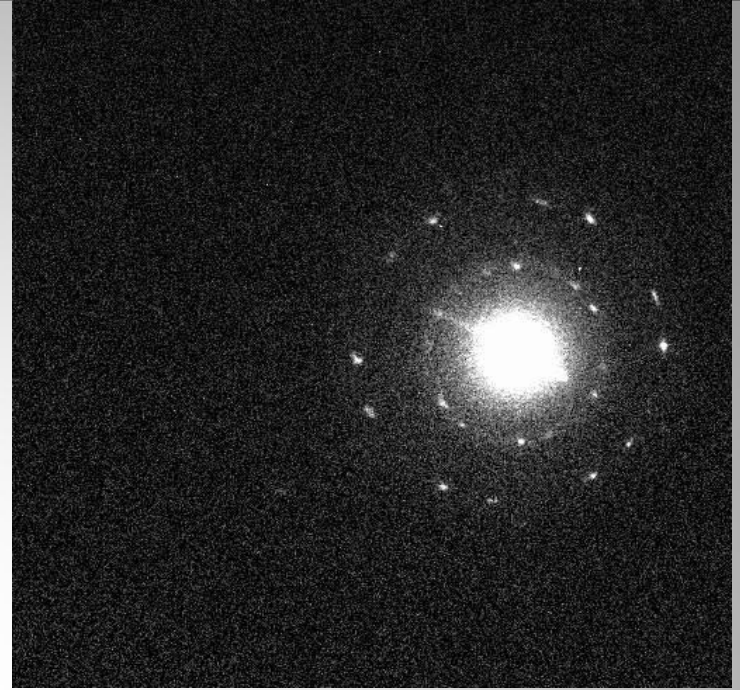
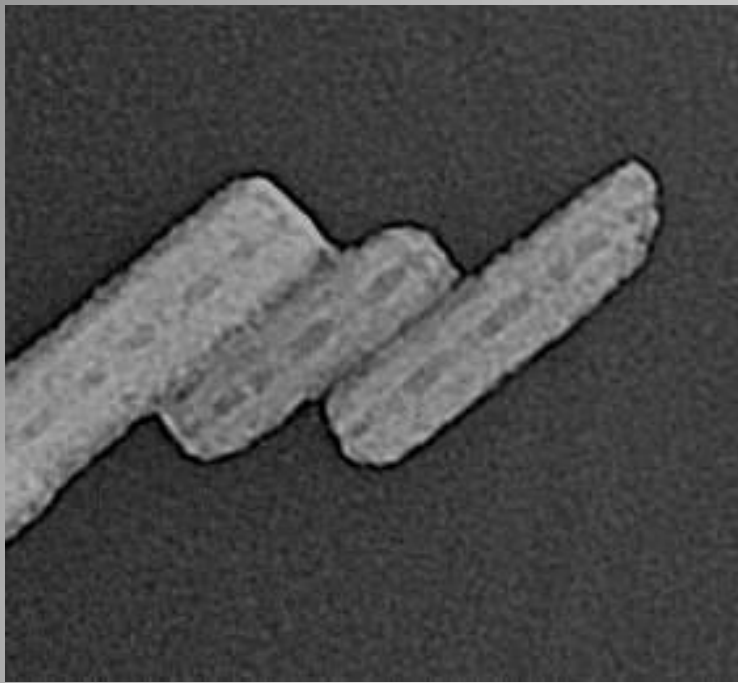
I sistemi così ottenuti mostrano degli svantaggi:

- disomogeneità del campione naturale:



- tossicità delle fibre di crisotilo naturale per lo più dovuta alla contaminazione da parte di ioni estranei nella struttura.





Nanoparticelle *Au/Ag* cappate con *decanetiolo*

SINTESI bifasica acqua bidistillata / toluene:

AgNO_3 e $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in diversi rapporti molari

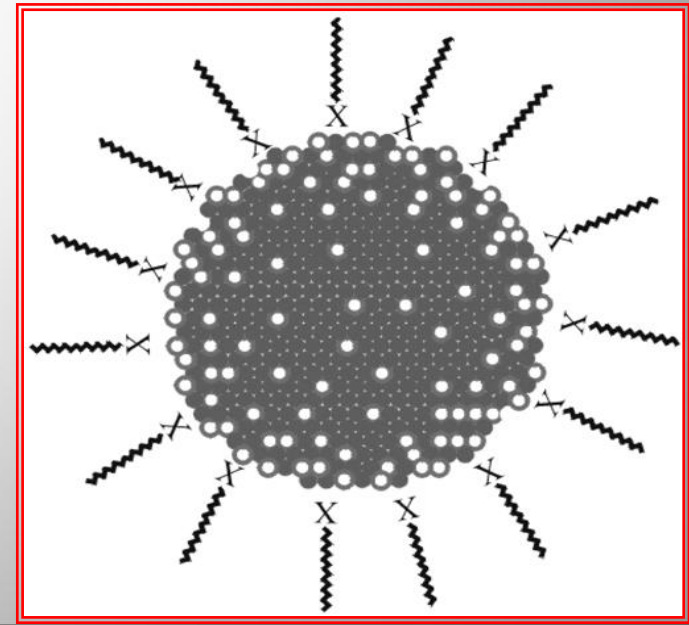
Agente riducente – NaBH_4

Agente cappante – Decanetiolo

Tensioattivo – Tetraoctilammoniobromuro (TOAB)

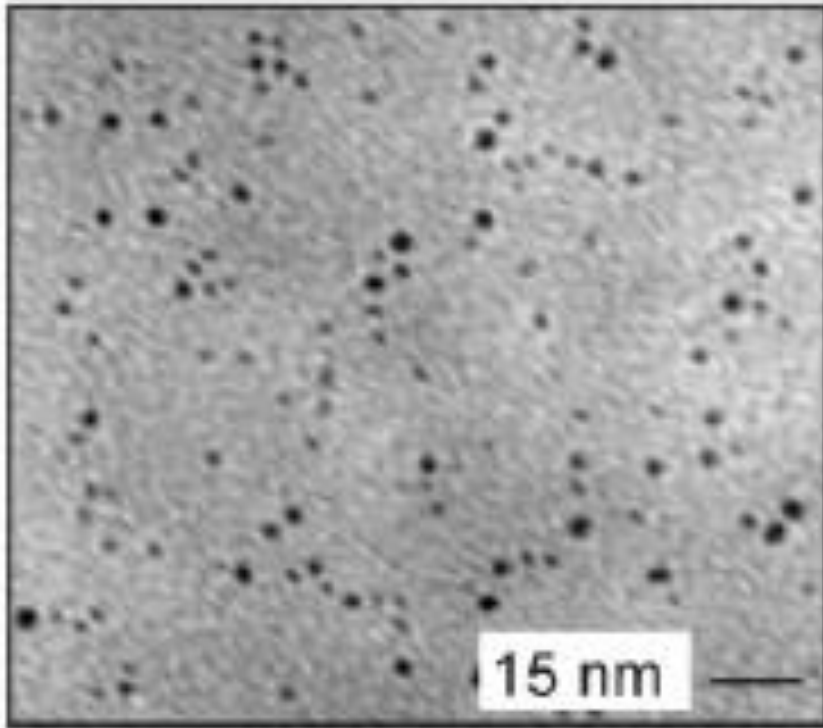
Tempo di reazione – 4 ore

Solvente finale – Esano

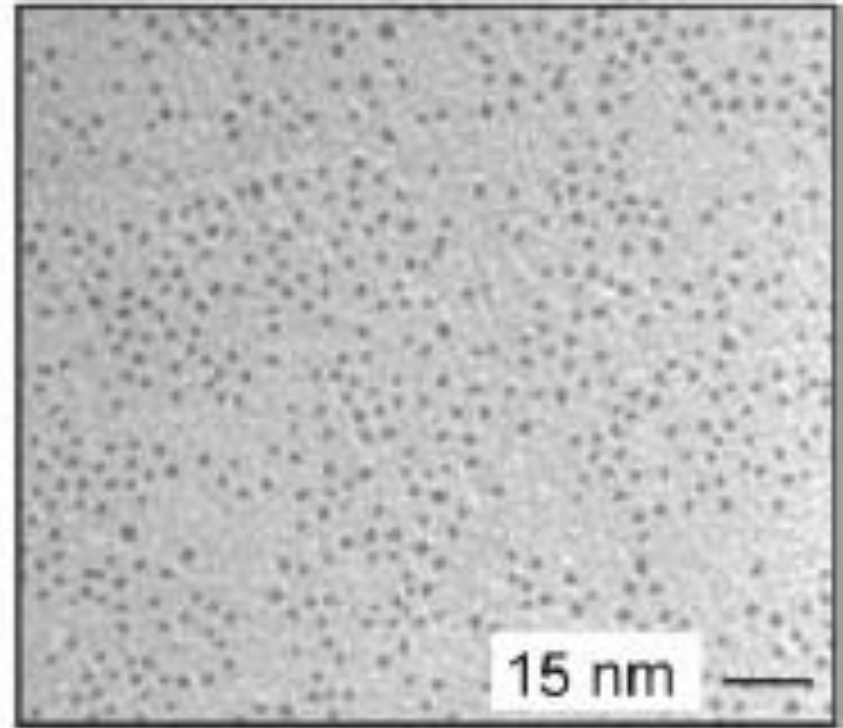


Nanoparticelle *Au/Ag* cappate con *decanetiolo*

Caratterizzazione:



TEM Au/Ag 1/4 2.7 nm



TEM Au/Ag 4/1 – 2.3 nm

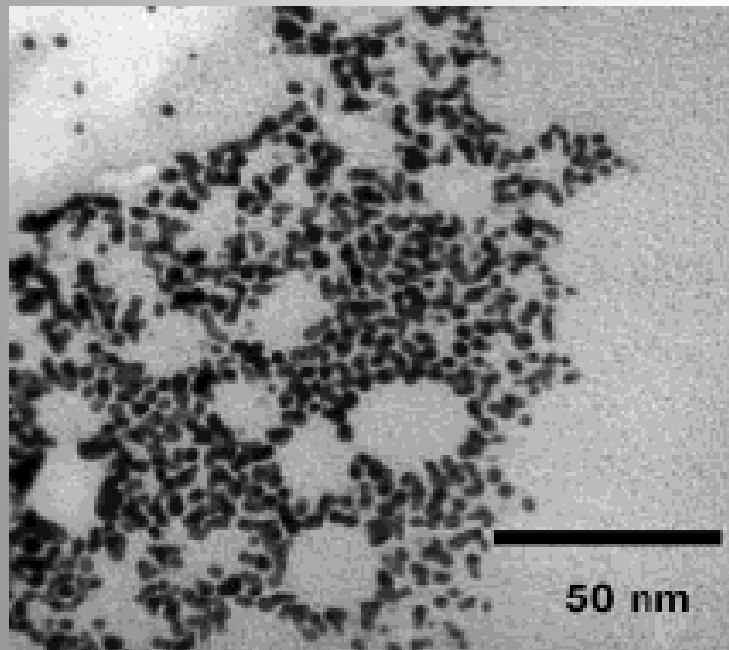
Se il rapporto *Au/Ag* aumenta, diminuiscono le dimensioni delle nanoparticelle.

Nanoparticelle *Au/Ag* cappate con *cisteina*

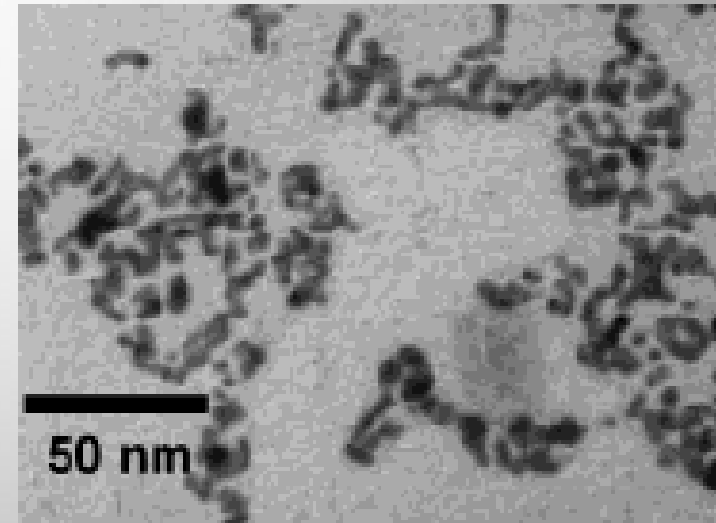
Sintesi: la medesima - agente cappante cisteina

Caratterizzazione:

Medesimo comportamento in spettroscopia di assorbimento UV-Vis (la lunghezza d'onda del max aumenta all'aumentare della % di Au)



dopo 5 giorni

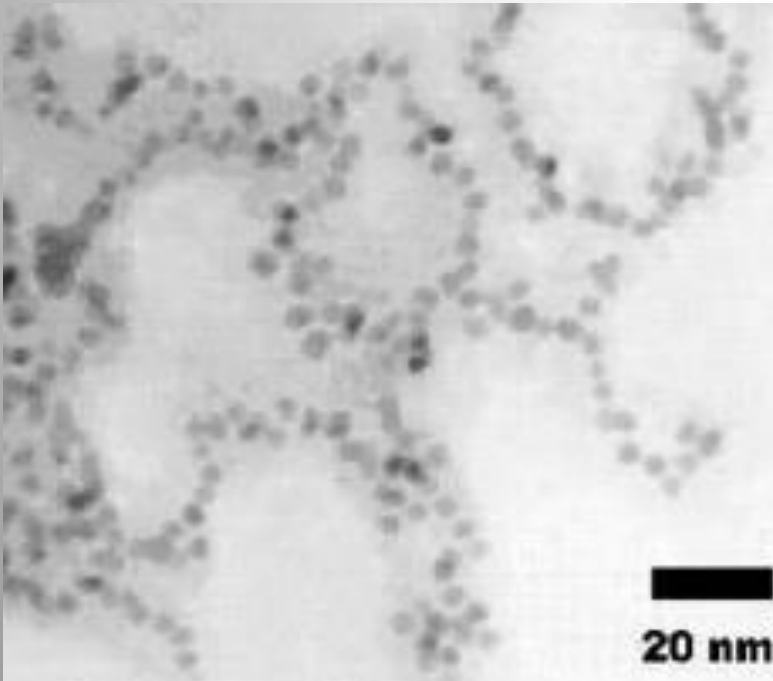


Nanoparticelle *Au/Ag* cappate con *acido tiomalico*

Sintesi: la medesima - agente capping acido tiomalico

Caratterizzazione:

Medesimo comportamento in spettroscopia di assorbimento UV-Vis



Diametro medio -- 2.5 nm

pH (nanoparticelle) = 3.6

pH (nanotubi) > 8

Nanoparticelle di *Si* cappate con *eptene*

Sintesi:

SiCl_4 – Tetracloruro di Silicio

Solvente di reazione – Toluene su setacci molecolari

Agente riducente – LiAlH_4 in soluzione 1 M di THF

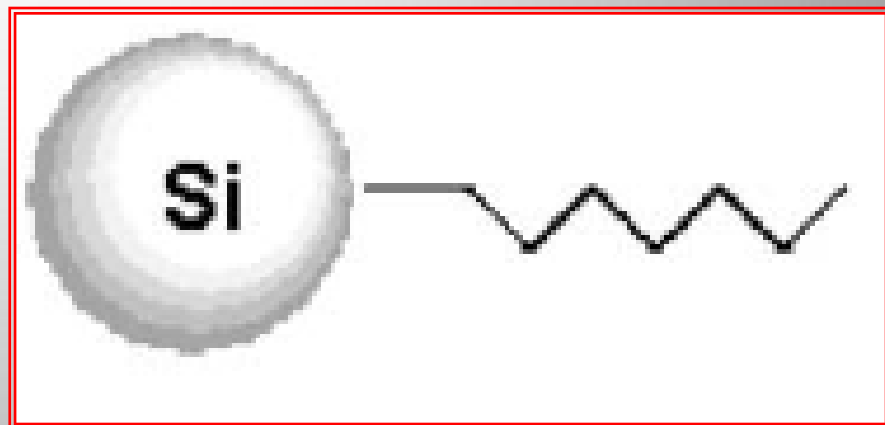
Agente cappante – 1-eptene

Tensioattivo – Tetraoctilammoniobromuro (TOAB)

Catalizzatore – soluzione acquosa 0.1 M di $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$

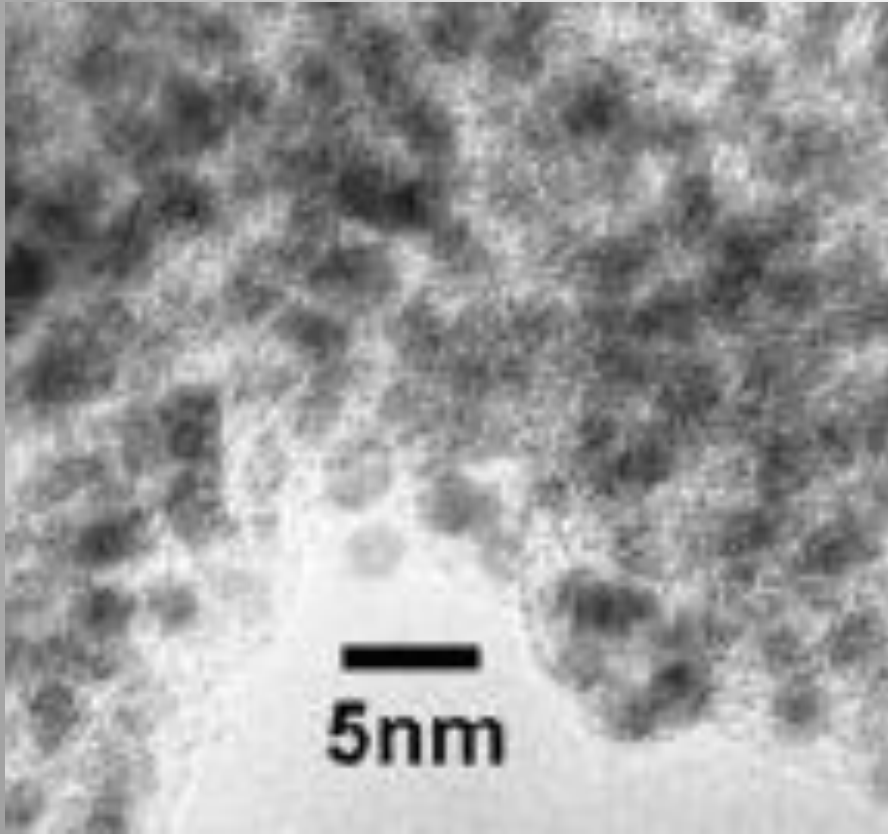
Tempo di reazione – 12 ore

Solvente finale – Esano



Nanoparticelle di *Si* cappate con *eptene*

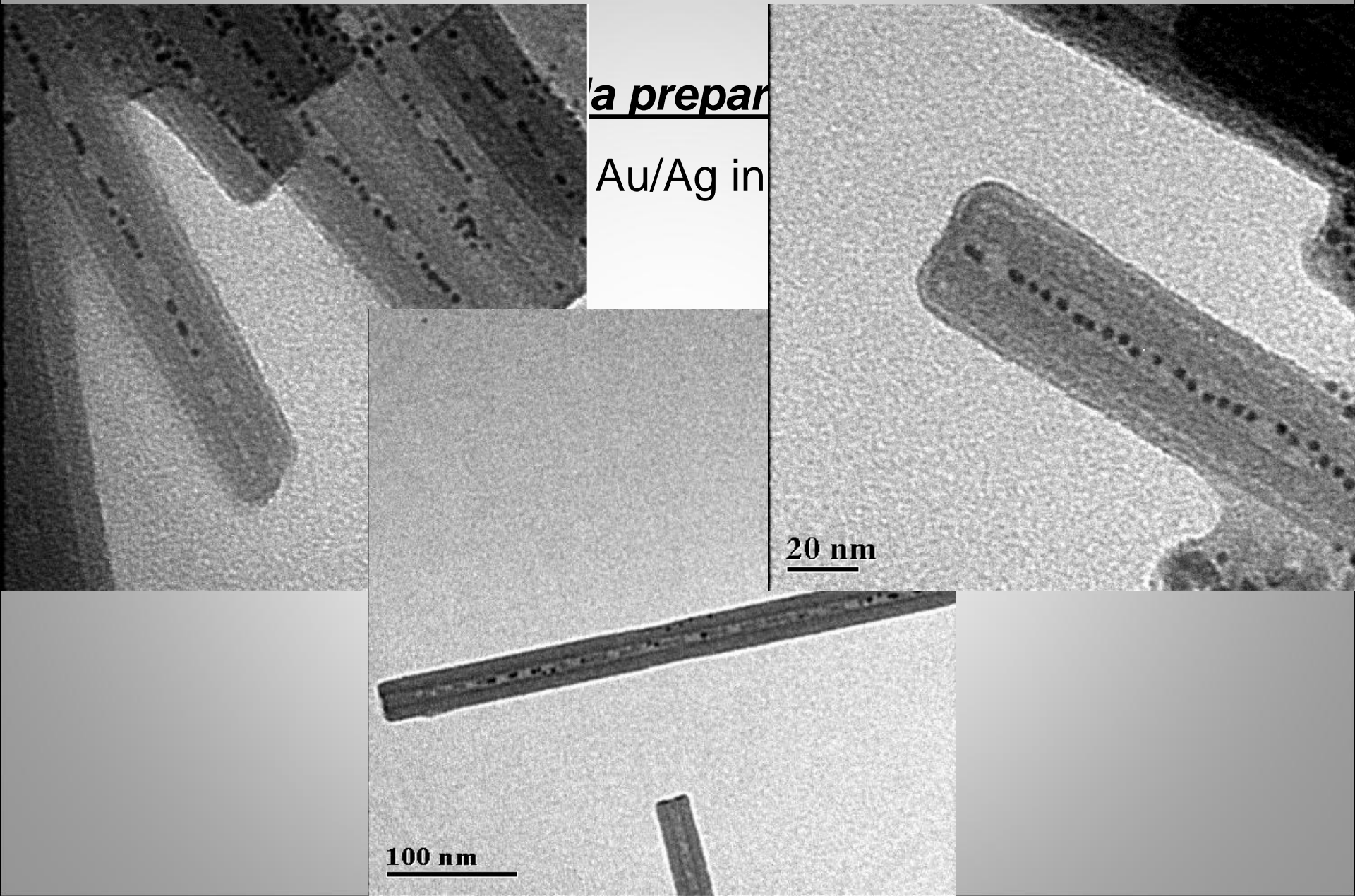
Caratterizzazione:

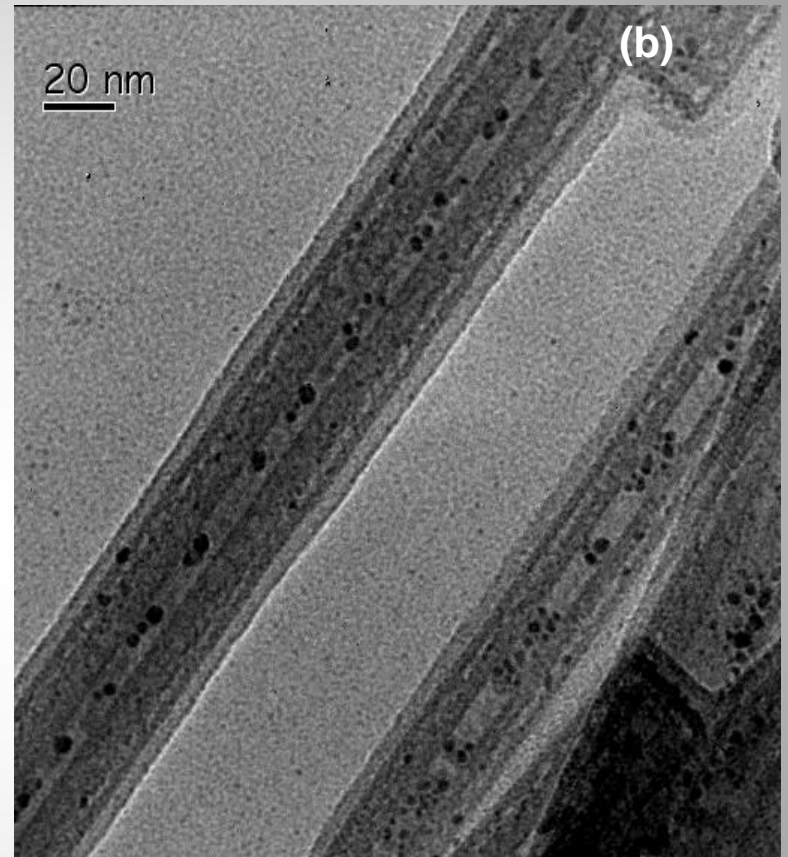
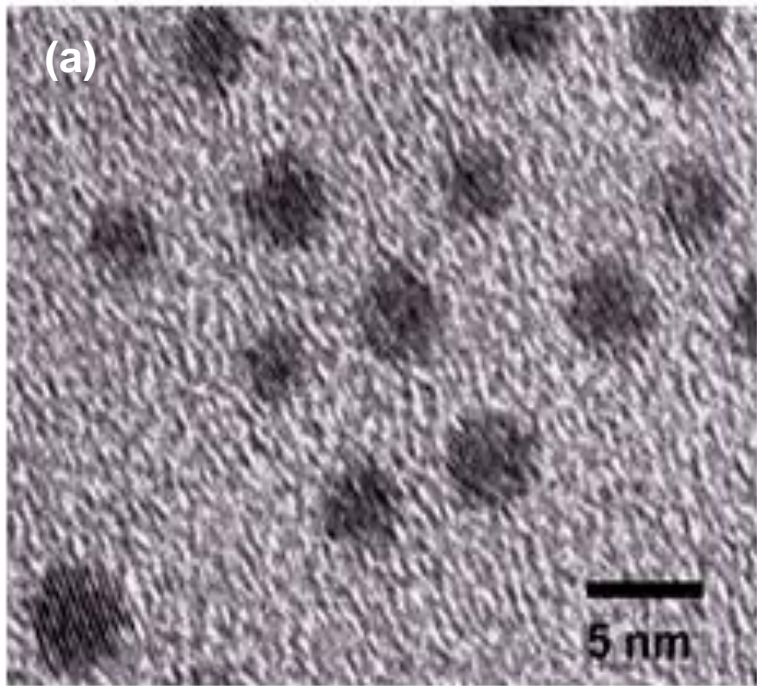


Diametro medio – 2 nm

Tendenza a formare clusters di dimensioni pari a multipli di 2 nm

NWs di Au/Ag rivestiti da isolante

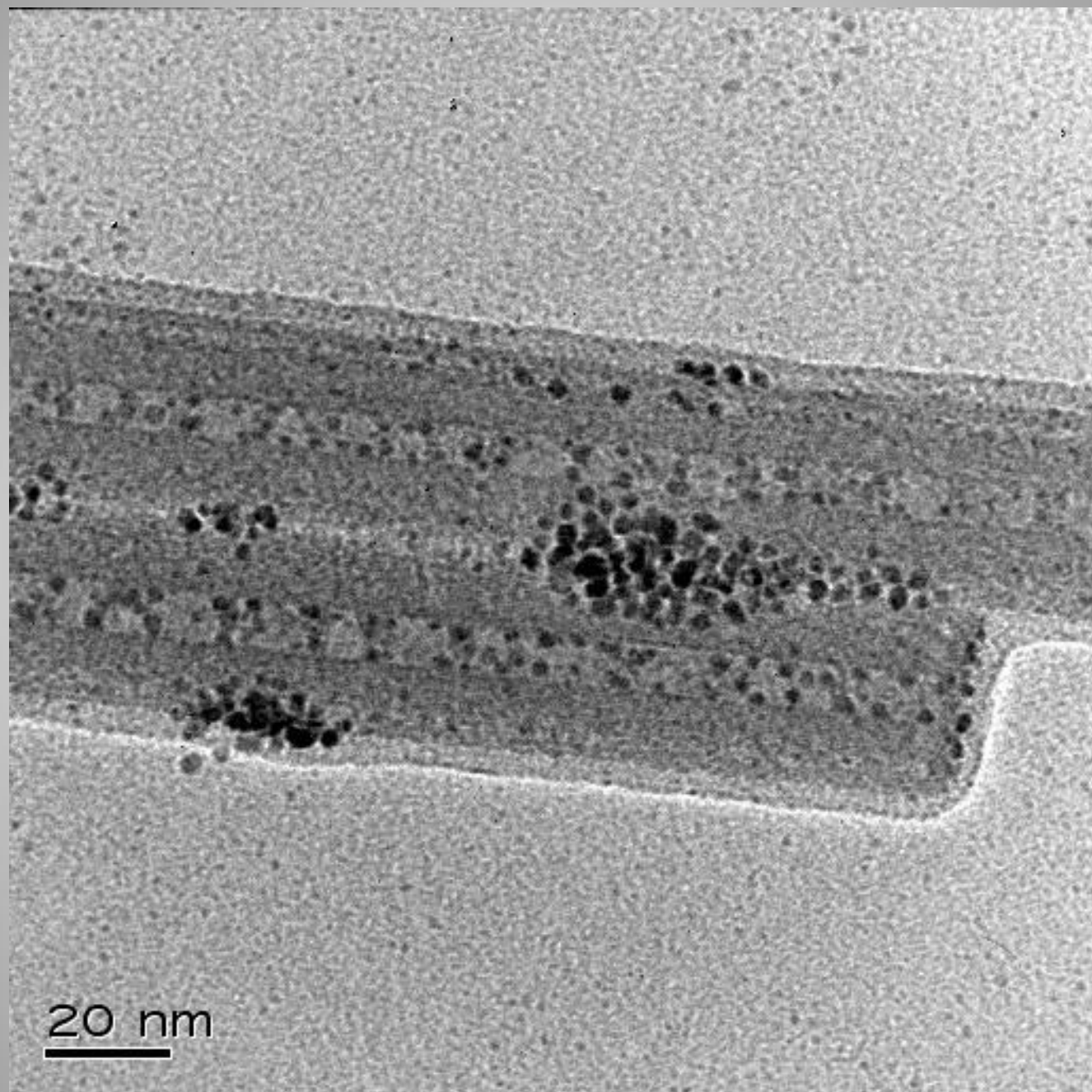


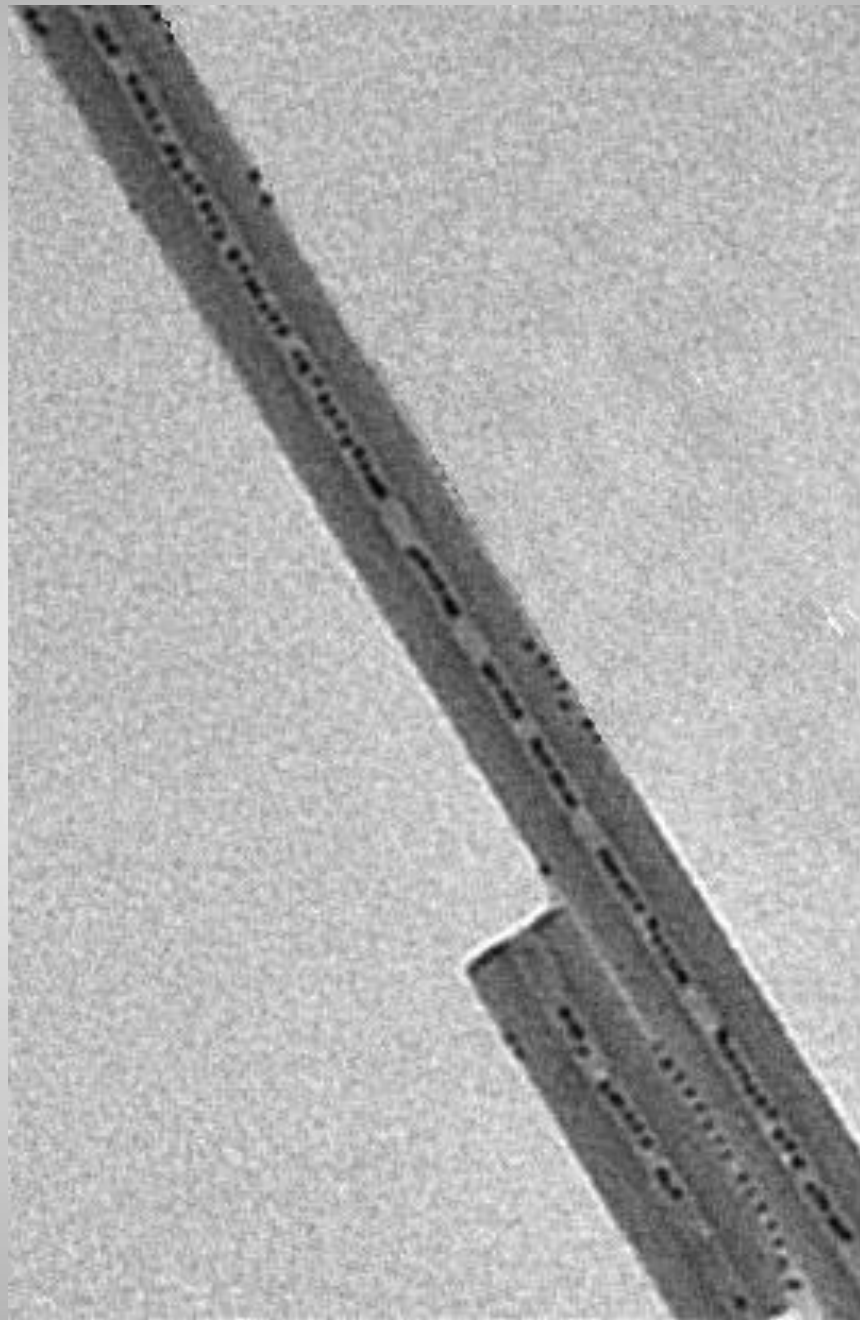


Geoinspired Synthetic Chrysotile Nanotubes

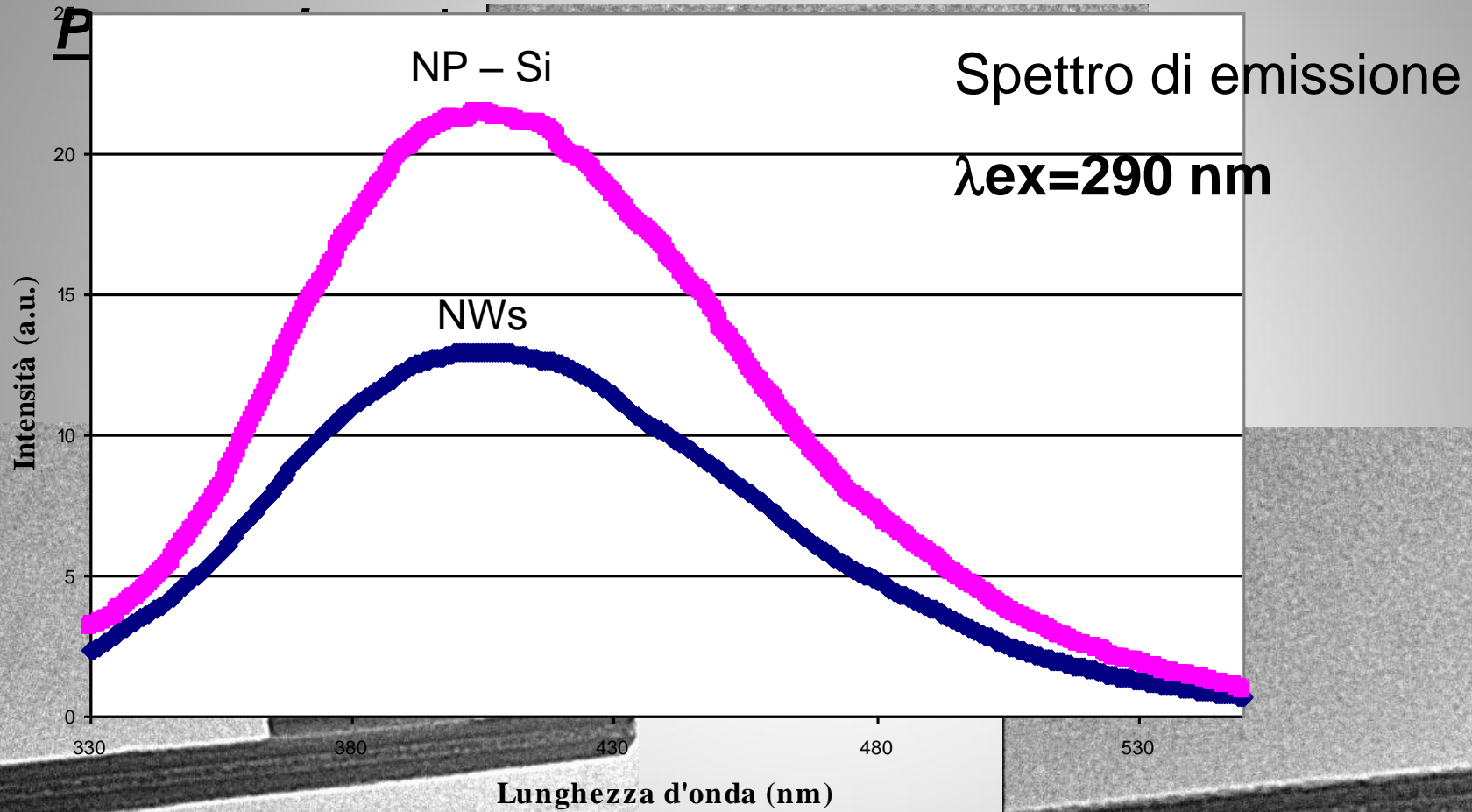
N. Roveri, G. Falini, E. Foresti, G. Fracasso, I.G. Lesci, P. Sabatino

J. Mat. Research, 2006 in press



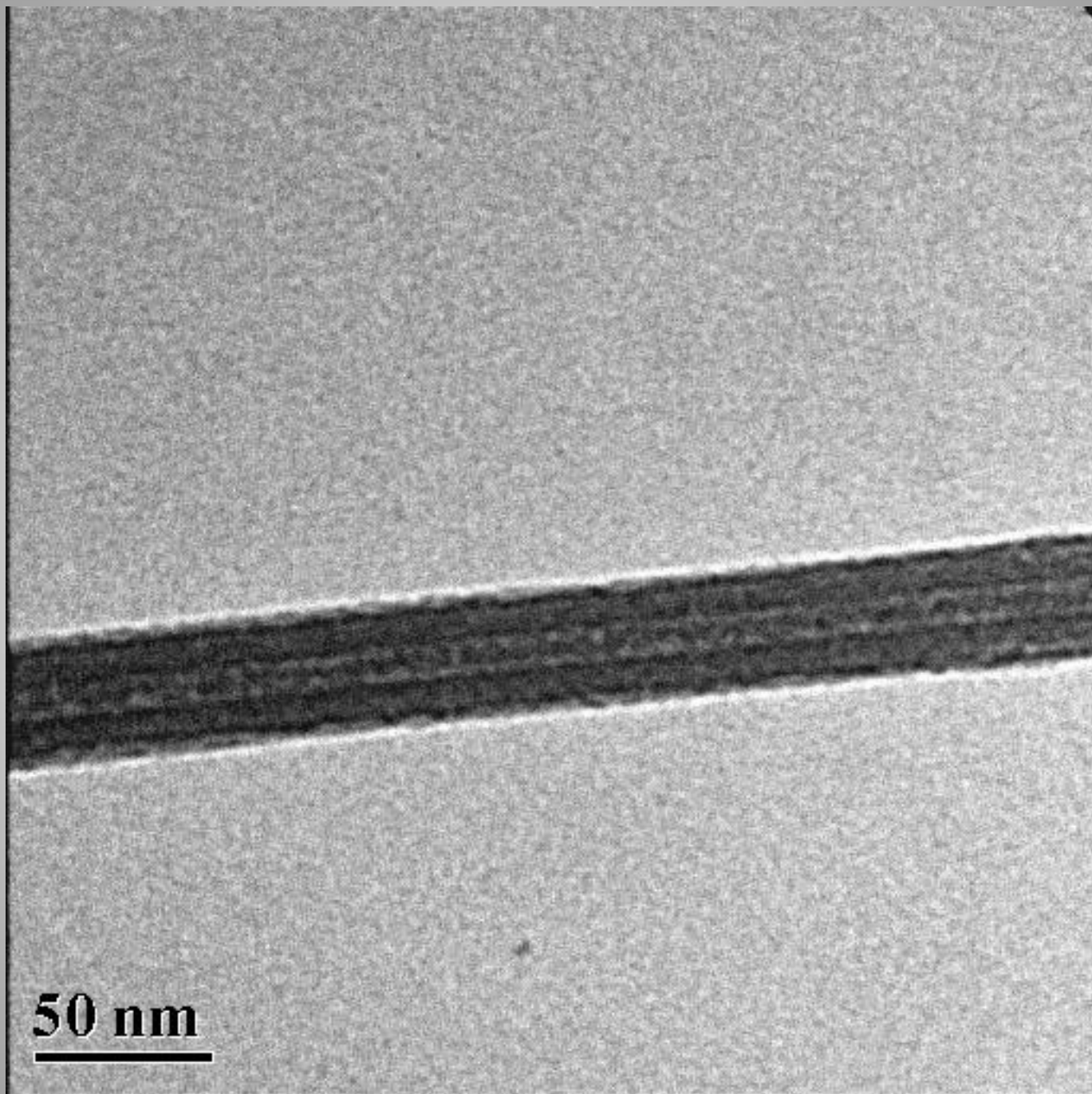


NWs di Si rivestiti da isolante

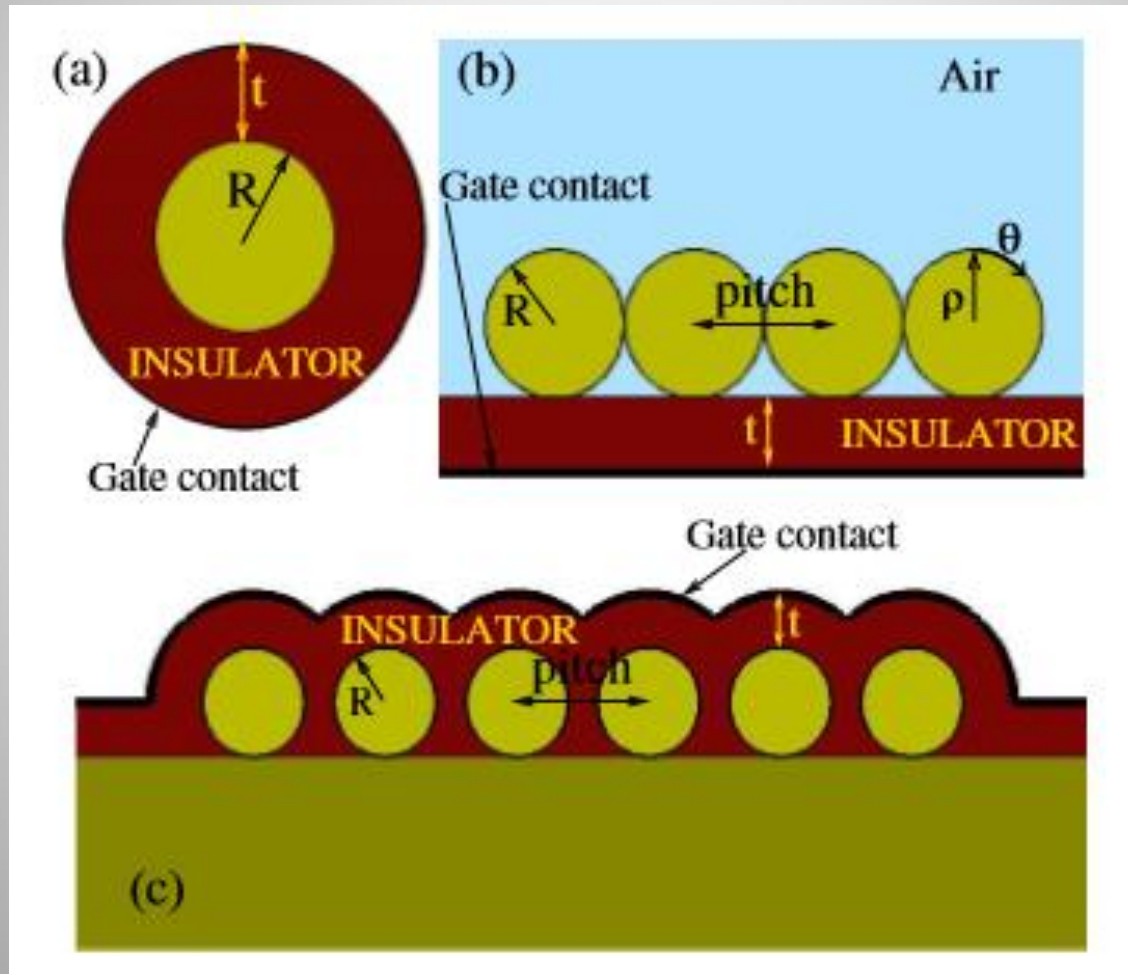


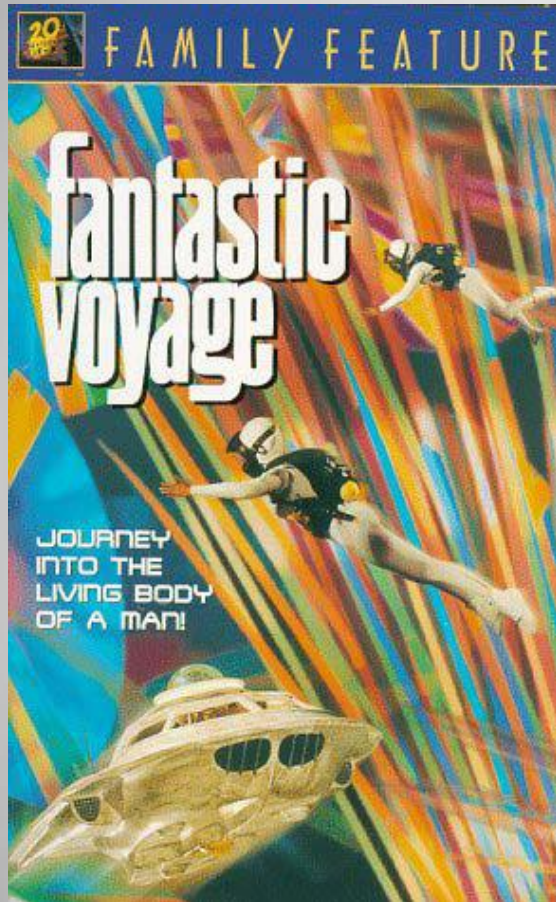
50 nm

50 nm

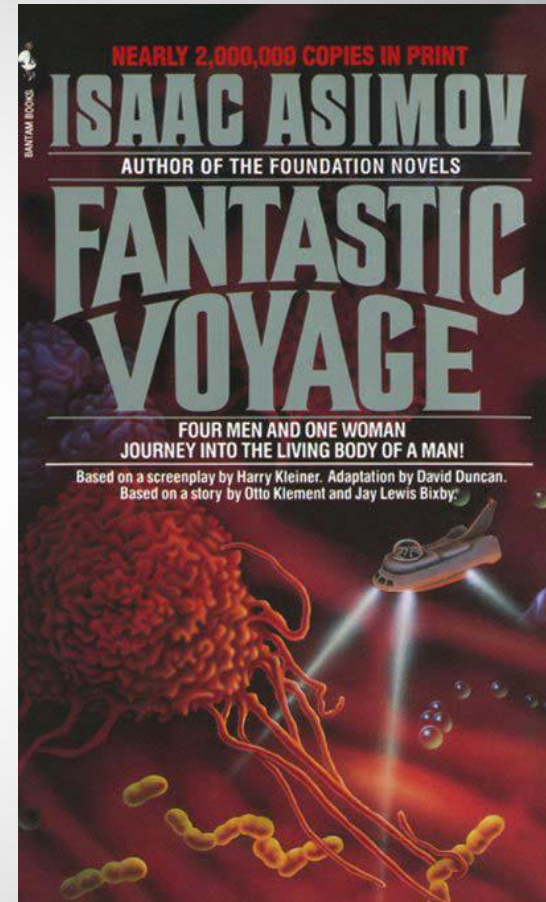


NUOVI TRANSISTOR





**Fantastic Voyage,
1966**



**Isaac Asimov, 1987
Fantastic Voyage**