

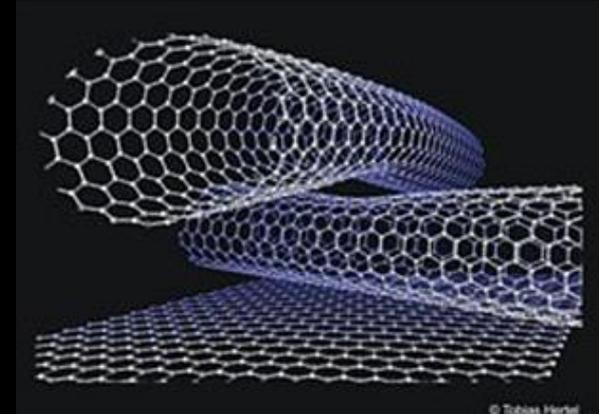
An aerial photograph of a winding asphalt road that curves through a lush, green, hilly landscape. The road is dark grey with white lane markings and is bordered by a low concrete wall. The surrounding terrain is covered in dense green vegetation, including trees and shrubs. The sky is not visible, and the overall scene is bright and clear.

**Una storia delle
nanoscienze
per tappe**

**Luigi Fabbrizzi
Università di Pavia**

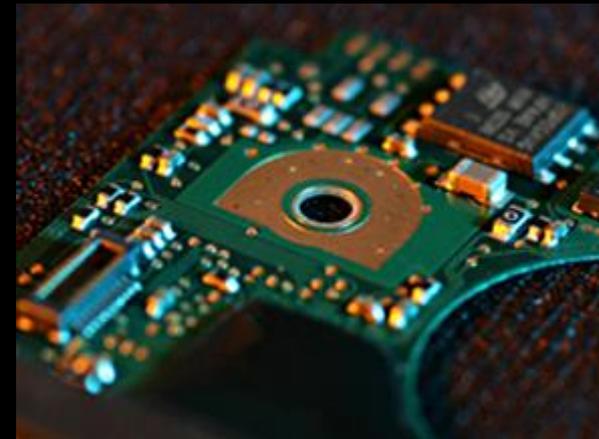
Nanoscienza: studio e manipolazione della materia nella scala nano (1-100 nm).

Chimica – Fisica - Biomedicina



Nanotecnologia: applicazione dei principi della nanoscienza alla produzione di nanomateriali e componenti in scala nano, utili alla società.

Ingegnerie



**Chi è nata prima?
La nanoscienza o la nanotecnologia?**



Licurgo

Dioniso

Ambròsia

Coppa di Licurgo, Roma, **IV sec. d.C.**
vetro scolpito, h 16.5 cm, Ø 13.2 cm
Department of Greek and Roman
Antiquities, The British Museum,
London

Bacco
Dioniso
(Διόνυσος)



Pan



**Ambròsia
(Άμβροσία)**

satiro





illuminazione dall'esterno



illuminazione dall'interno

Come stanno le cose

1965: il vetro contiene minime quantità di Au (40 ppm) e di Ag (300 ppm)

1990: la microscopia elettronica a trasmissione (TEM) mostra la presenza di nanoparticelle di una lega Ag/Au (ca. 70:30) delle dimensioni di 50-100 nm, disperse nel vetro

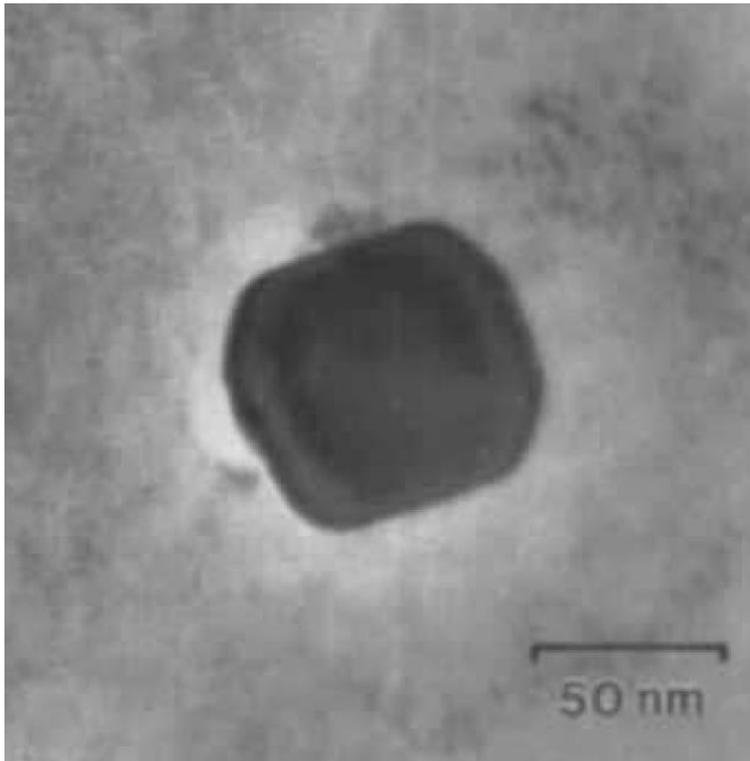


Figure. TEM image of a gold-silver alloy particle. The slightly rounded polygonal form indicates that it is a single crystal. The crystalline nature of the Ag/Au particles and their fine dispersion in the glass suggests that they are colloidal metal precipitated from solution by heat treatment.

D. J. Barber, I. F. Freestone, An investigation of the origin of the colour of the Lycurgus Cup by analytical TEM, *Archaeometry* 2007, 32, 33–45.

Quando sono colpiti dalla luce gli elettroni sulla superficie della nanoparticella vibrano in modo di alterare il colore a seconda della posizione dell'osservatore

Come erano riusciti i Romani del IV secolo d.C. a colorare il vetro della Coppa di Licurgo con nanoparticelle di oro?

The process used remains unclear, and it is likely that it was not well understood or controlled by the makers and was probably discovered serendipitously by accidental "contamination" with minutely ground gold and silver dust left on the desk after other works (British Museum's note).



Serendipity

(scoperta fortunata e inattesa)



**PURO
CASO**

FALSO



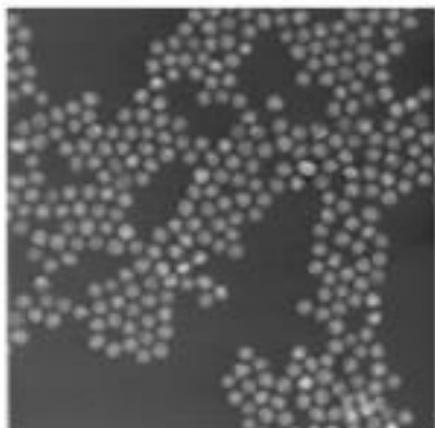
Mosaico della Basilica di Santa Prudenziana, Roma (IV sec. d.C.). Il colore rosso carnicino delle tesserae di vetro è dovuto alla presenza di nanoparticelle di una lega Au-Ag.

M. Verità, P. Santopadre, Analysis of Gold-Colored Ruby Glass Tesserae in Roman Church Mosaics of the Fourth to 12th Centuries, *Journal of Glass Studies* 2010, 52, 11-24

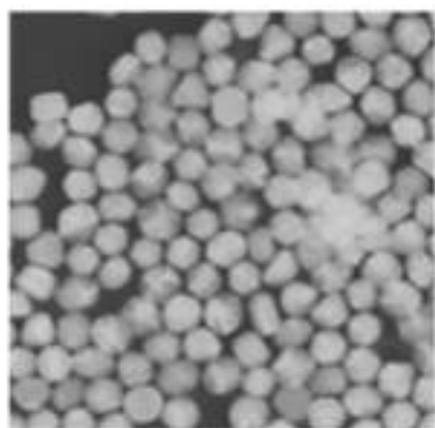


The Annunciation to the Virgin, ca. 1340.
From the Church of St. John the Baptist,
Hadzor. Now in the Stained Glass
Museum, Ely.

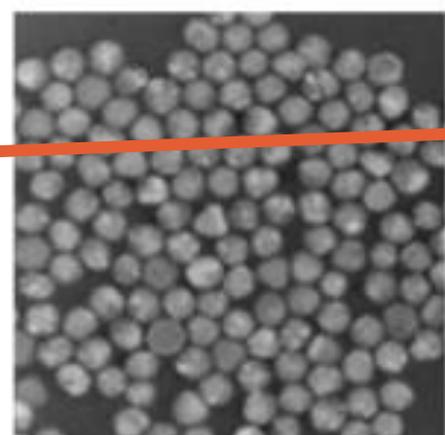




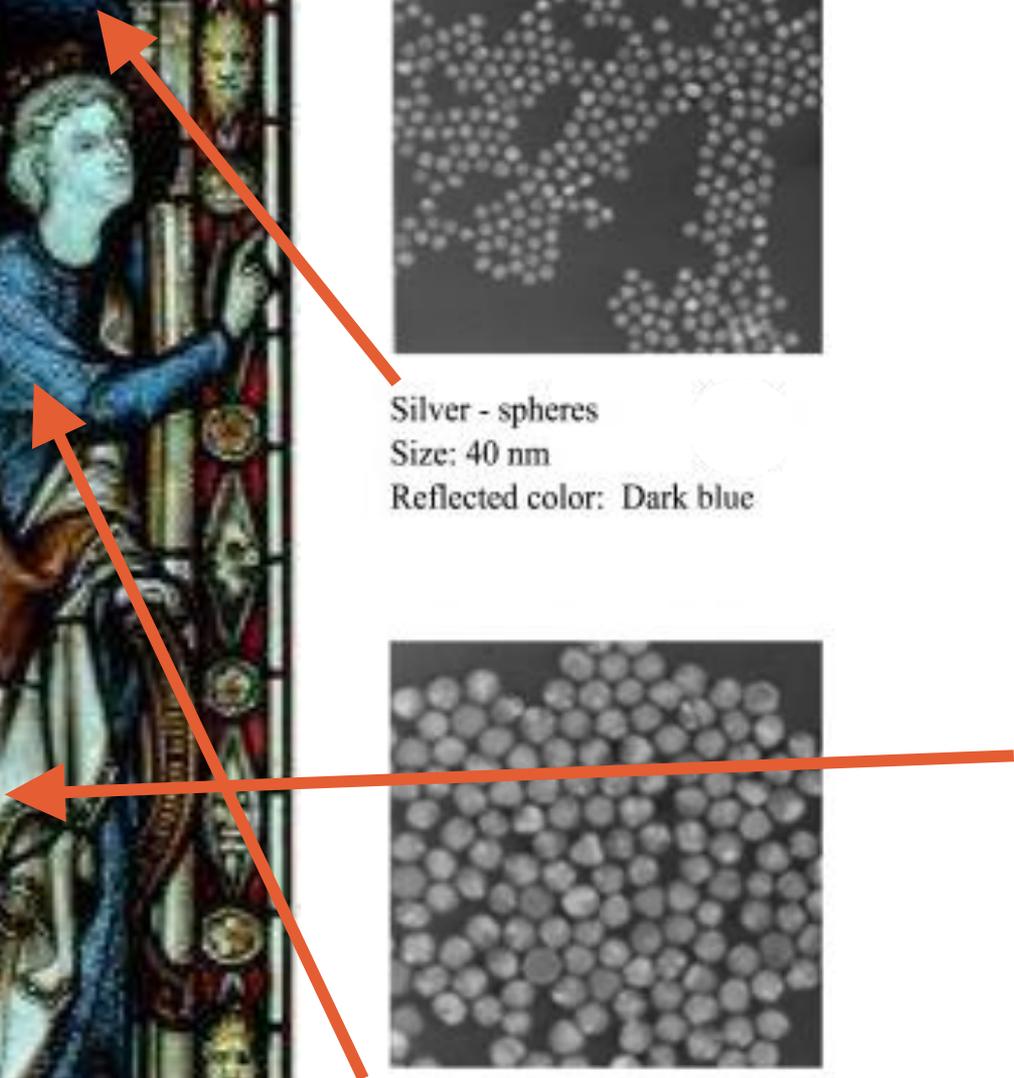
Silver - spheres
Size: 40 nm
Reflected color: Dark blue

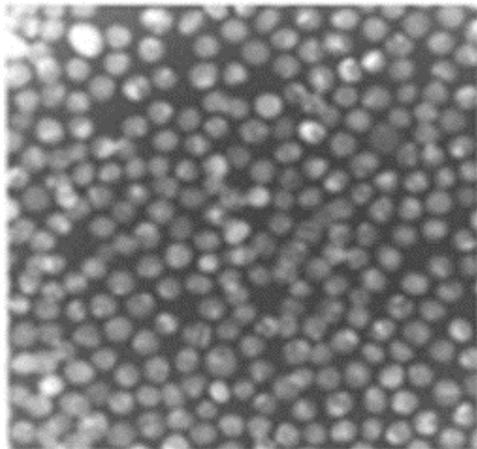


Silver - spheres
Size: 100 nm
Reflected color: Shiny gold

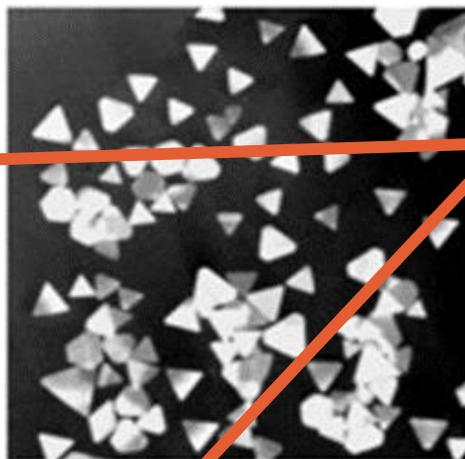


Silver - spheres
Size: 80 nm
Reflected color: Celestial blue

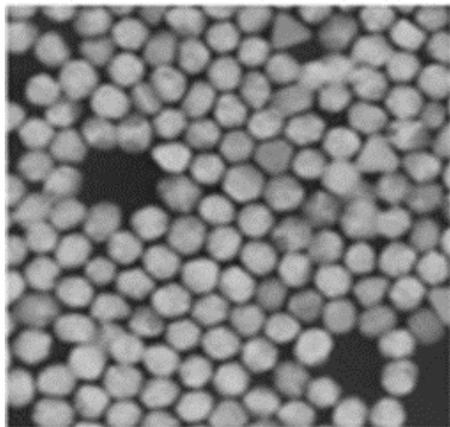




Gold - spheres
Size: 50 nm
Reflected color: Yellowish green



Silver - prisms
Size: 100 nm
Reflected color: Red



Gold - spheres
Size: 100 nm
Reflected color: Coral



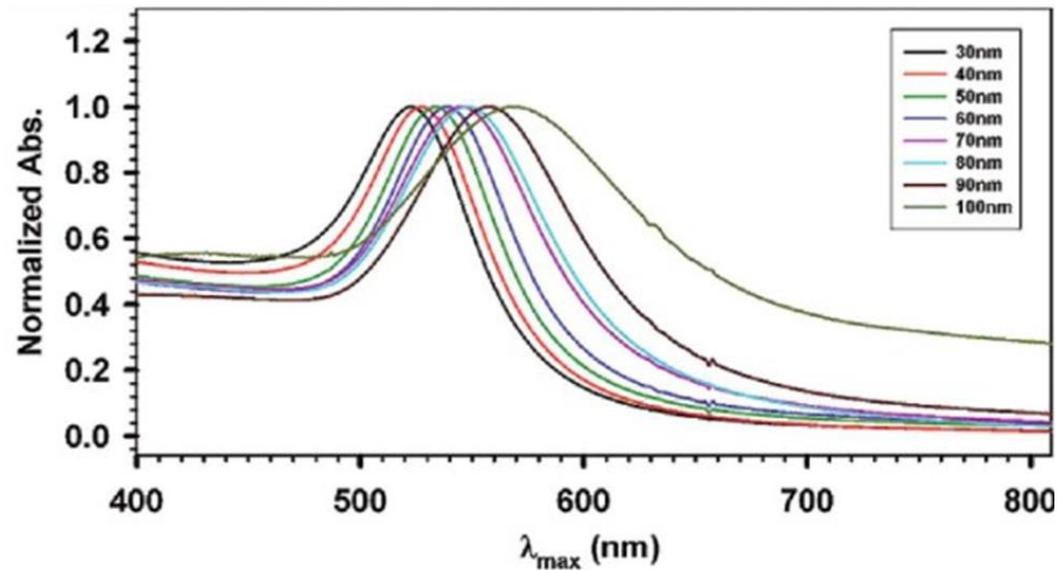
Il colore delle nanoparticelle varia con le dimensioni - Au



30 nm



100 nm



Au



Ag



La prima sintesi documentata
di un pigmento di oro:
la porpora di Cassio (1685)

ANDRÆ CASSII D:
HAMBURGENSIS
DE EXTREMO ILLO ET
PERFECTISSIMO
NATURÆ OPIFICIO

AC
PRINCIPE TERRÆ
NORUM SIDERE

AURO

De admirandâ ejus naturâ, ge-
neratione, affectionibus, effectis, atque
ad operationes artis habi-
tudine.

COGITATA

Nobilioribus experimentis illustrata.

Aurum & Adamas typi æternitatis.

HAMBURGI,

Sumptibus GEORGII WOLFFI,
ANNO M DC LXXXV.

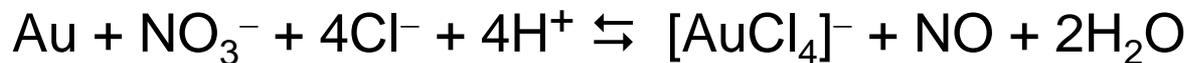
Andrea Cassius
di Amburgo

Pensieri sull'ultimo e
perfettissimo lavoro
della Natura e sul
Principe dei metalli,
l'Oro, e sulla sua
ammirevole natura,
produzione, condizioni ed
effetti ai fini delle opere
artistiche, illustrati dai
più nobili esperimenti.

Amburgo, 1685

La 'recepta' di Cassius

Sciolgo una dracma (4.4 g) di oro in una soluzione di due parti di 'aqua fortis' (HNO₃ ndr) e una parte di spirito di sale (HCl ndr).

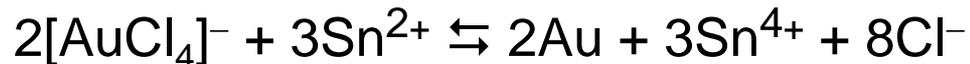


Aggiungo una soluzione di spirito di sale a stagno metallico, a poco a poco, così che il metallo si scioglia senza sviluppare troppo calore e troppo 'gas silvestre' (CO₂ ??? ndr).



*H₂, Cavendish (1766)

Verso una piccola parte della 1^a soluzione e una piccola parte della 2^a soluzione in un recipiente che contiene una grande quantità di acqua. Loro precipita nella forma di un cristallo rosso porpora.





XVII sec. (D)



Epoca Vittoriana (GB)



Art Nouveau (D)



Meissen, 1735



Volkstedt, 1770



Porcellane della 'Famille rose', Cina XVIII sec.



Porpora di Cassio: da cosa è costituita

- 1857: Michael Faraday, *The Bakerian Lecture. Trans. R. Soc.* **1857**, 147, 17
"I believe the Purple of Cassius to be essentially **finely divided metallic gold** associated with more or less of oxide of tin."
- 1872 Henri Debray, *Comptes Rendus de l'Académie des Science* **1872**, 76, 1025. "Purple of Cassius consisted of **finely divided gold** that had been absorbed by stannic acid".
- 1898 Richard Zsigmondy, ultramicroscopio: dispersione di particelle di oro in acido stannico colloidale; in soluzione, le particelle di Au sono separate alla dialisi su pergamena; la soluzione dà il cono di Tyndall.

La prima preparazione consapevole delle nanoparticelle di oro - 1857



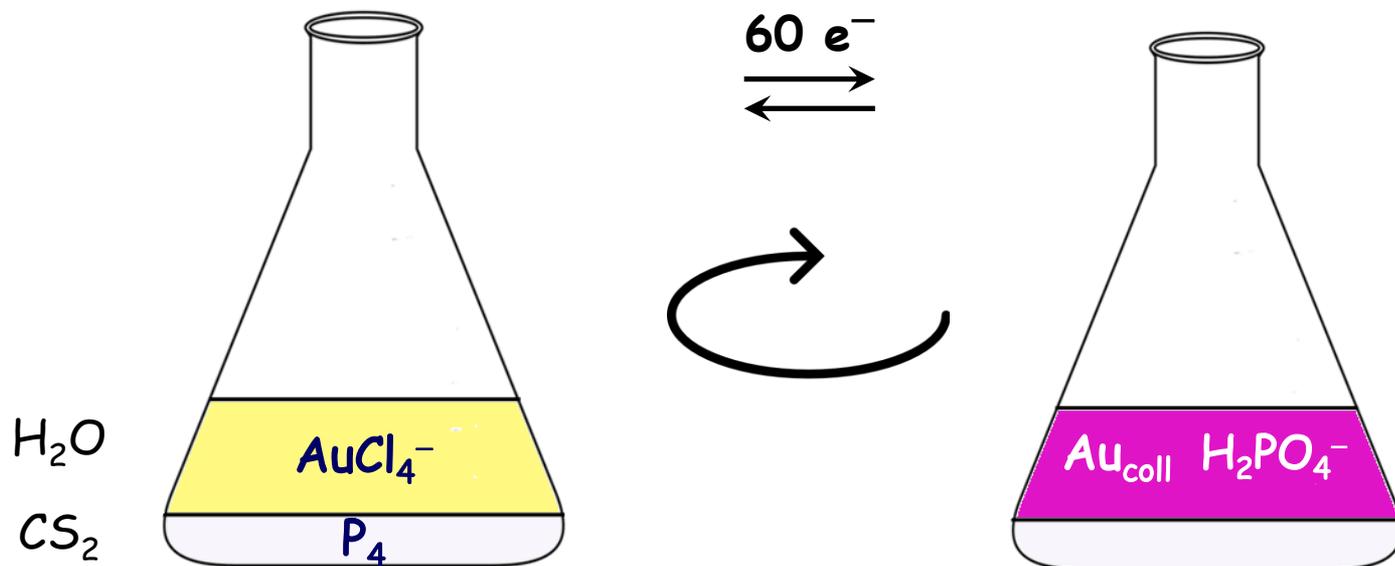
Michael Faraday (1791 –1867)
Professore alla Royal Institution
of Great Britain

- Liquefazione dei gas.
- Elettrochimica. Leggi dell'elettrolisi.
- Elettromagnetismo. Induzione elettromagnetica. Generatori di corrente elettrica. Motore elettrico.

Michael Faraday nel suo laboratorio alla Royal Institution, acquerello su carta di Harriet Jane Moore, 1852. Royal Institution of Great Britain, London.

M. Faraday, "The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light", *Philosophical Transactions of the Royal Society of London*, 1857, 147, 145–181

A quick and ready mode of producing the ruby fluid, is to put a quart of the yellow weak solution of gold (containing about 0.6 of a grain of metal) into **40 mg** a clean bottle, to add a little solution of phosphorus in sulphide of carbon, and then to shake it well for a few moments: a beautiful ruby or amethystine fluid is immediately produced, which will increase of tint by a little time. The process of reduction appears to consist in a transfer of the the gold to the phosphorus, and the formation of phosphoric or phosphorous hydrochloric acid, by the further action of the water.



“... these fluids often remain unchanged for **many months** and have all the appearance of solutions.”

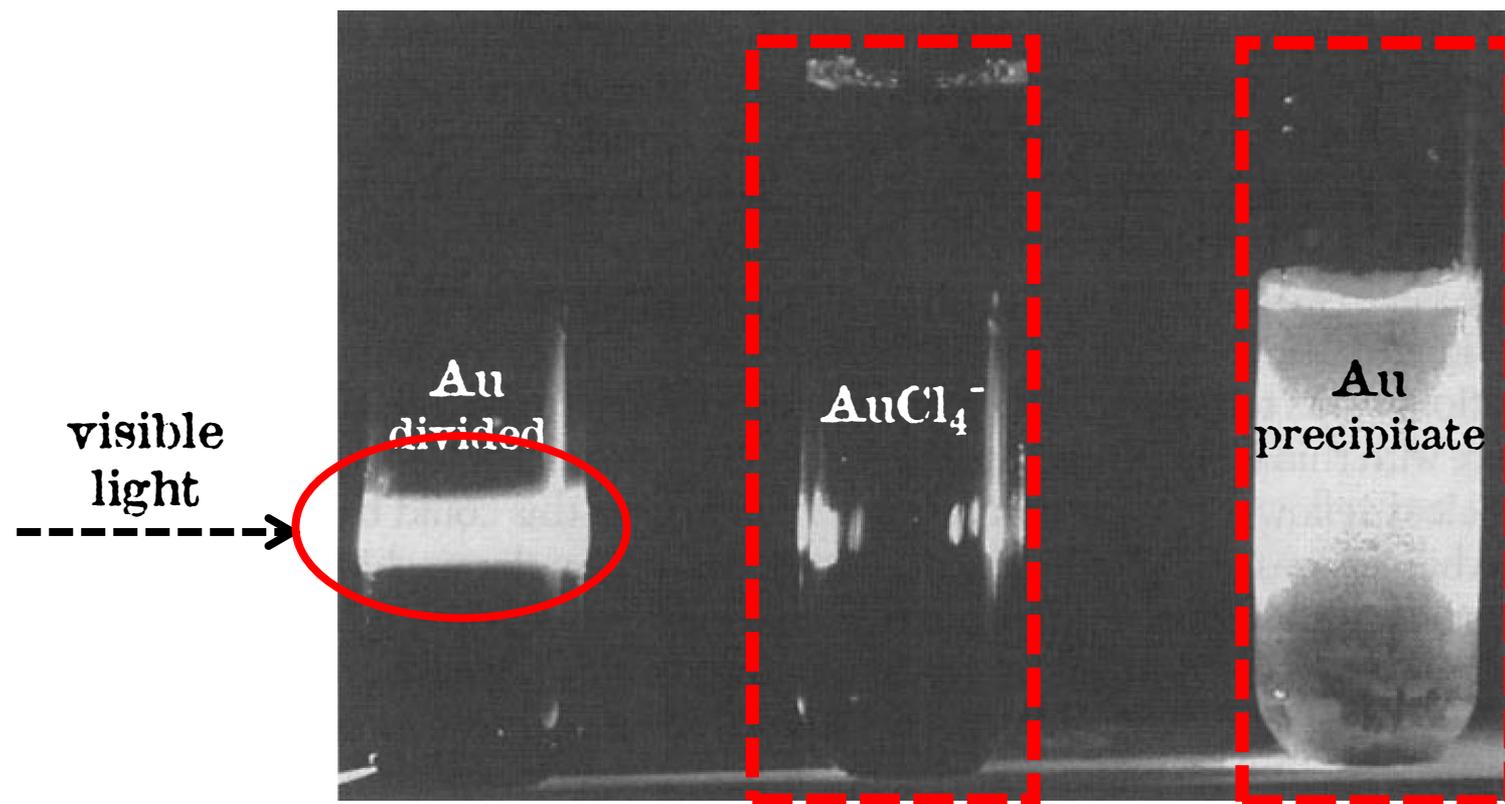
many = 1920 \approx 2000



Michael Faraday's Gold Colloids sample
(1856)

Credit: Paul Wilkinson. April 2016.
Place: Basement laboratory at the Ri

“... these fluids often remain unchanged for many months and have all the appearance of solutions. But they never are such, containing in fact no dissolved, but gold. The particles are easily rendered evident, by gathering the rays of the sun (or of lamp) into a cone by a lens and sending the part of the cone near the focus into the fluid; the cone becomes visible, and though the illuminated particles cannot be distinguished because of their minuteness, yet the light they reflect is golden and seen to be abundant in proportion to the quantity of the gold present.”

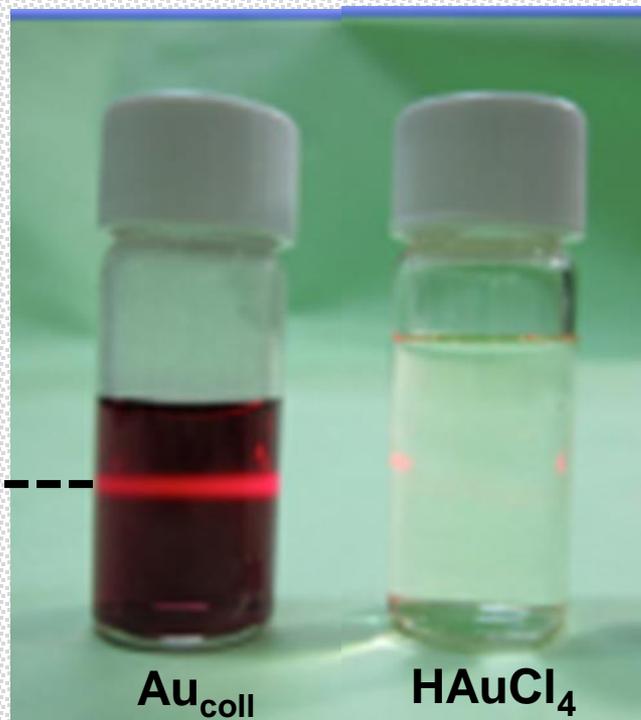


Tweney, R. D., Mears, R. P., & Spitzmüller, Replicating the Practices of Discovery: Michael Faraday and the Interaction of Gold and Light. In M. E. Gorman, R. D. Tweney, D. C. Gooding, & A. P. Kincannon (Eds.), *Scientific and technological thinking*, **2005**, pp. 137–158.

*Un'esercitazione didattica
sulle proprietà ottiche delle
nanoparticelle d'oro (AuNPs)*

- Preparazione di una soluzione
acquosa di AuNPs*
- Dimostrazione ottica della natura
colloidale della soluzione*

Sgocciola in un vial 2.0 mL (40 goccioline) di 1.0 mM HAuCl_4 e 0.5 mL di una soluzione 0.1 M di sodio citrato. Chiudi il vial col tappo di plastica e tienilo a bagno in un becher di acqua bollente per 10 min. Togli il tappo e lascia raffreddare.



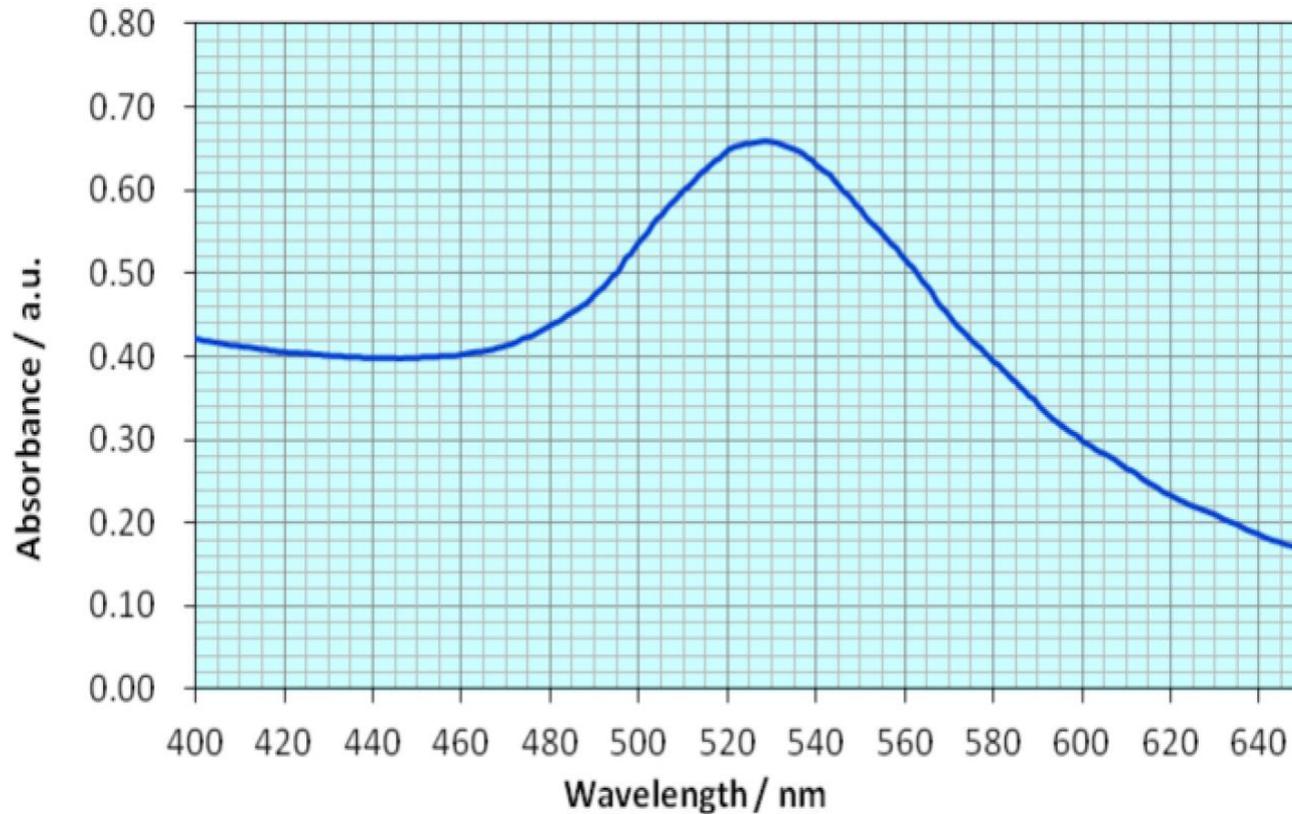
Costo dell'esperimento per studente

2.0 mL of 1.0 mM chlorauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, PM = 412) = 2×10^{-6} mol \rightarrow 0.82 mg

prezzo $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O} \approx \text{€}100/\text{g}$

0.82 mg \rightarrow 82 cent

Yang, S.-P., Microscale Synthesis and Characterization of Gold Nanoparticles for the Laboratory Instruction, *Chemical Education Journal* **2013**, 15. <http://chem.sci.utsunomiya-u.ac.jp/cejrnIE.html>



Affective domain: positive response

I believe that high-school students can easily synthesize, identify and understand gold nanoparticles. A student said: “I thought it was very joyful to preserve at home our own Au nanoparticles we synthesized”.

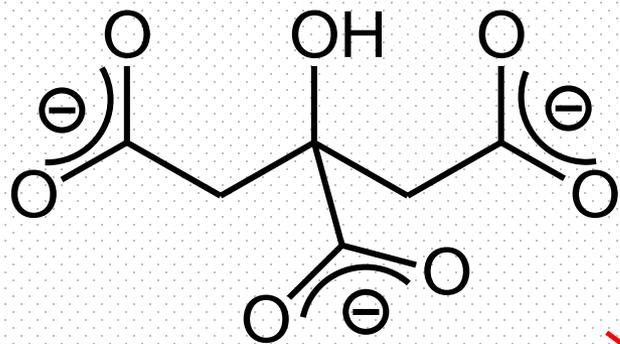
Commento socio-economico:

Tutti possono farsi le loro nanoparticelle. Anche le massaie in cucina.

PERCHE' LE
NANOPARTICELLE
NON SI AGGREGANO
A DARE IL METALLO?

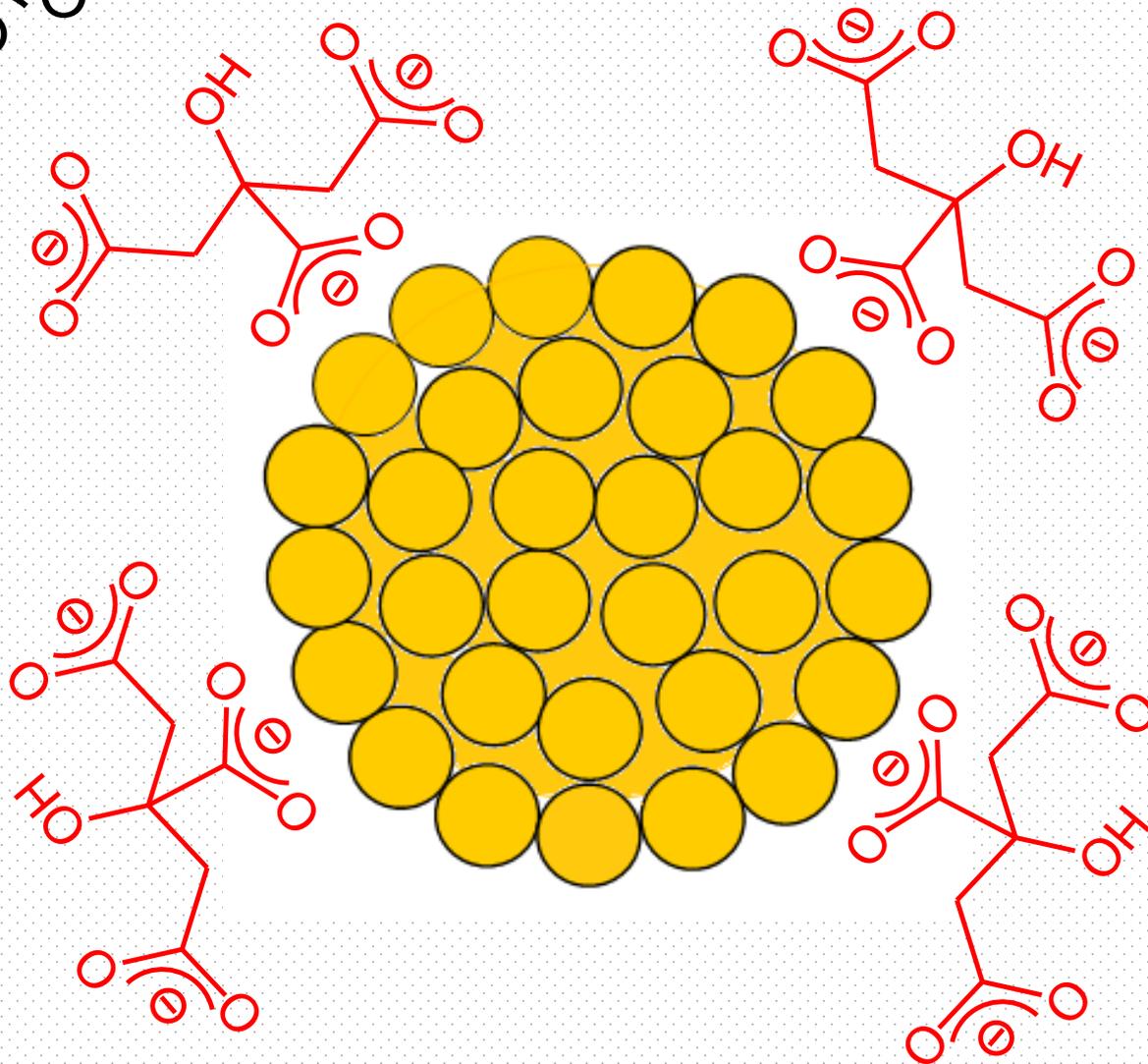
CHI GLIELO
IMPEDISCE?





citrate

($E^\circ = -0.19 \text{ V}$)



Sintesi delle nanoparticelle d'oro (AuNPs) ieri e oggi

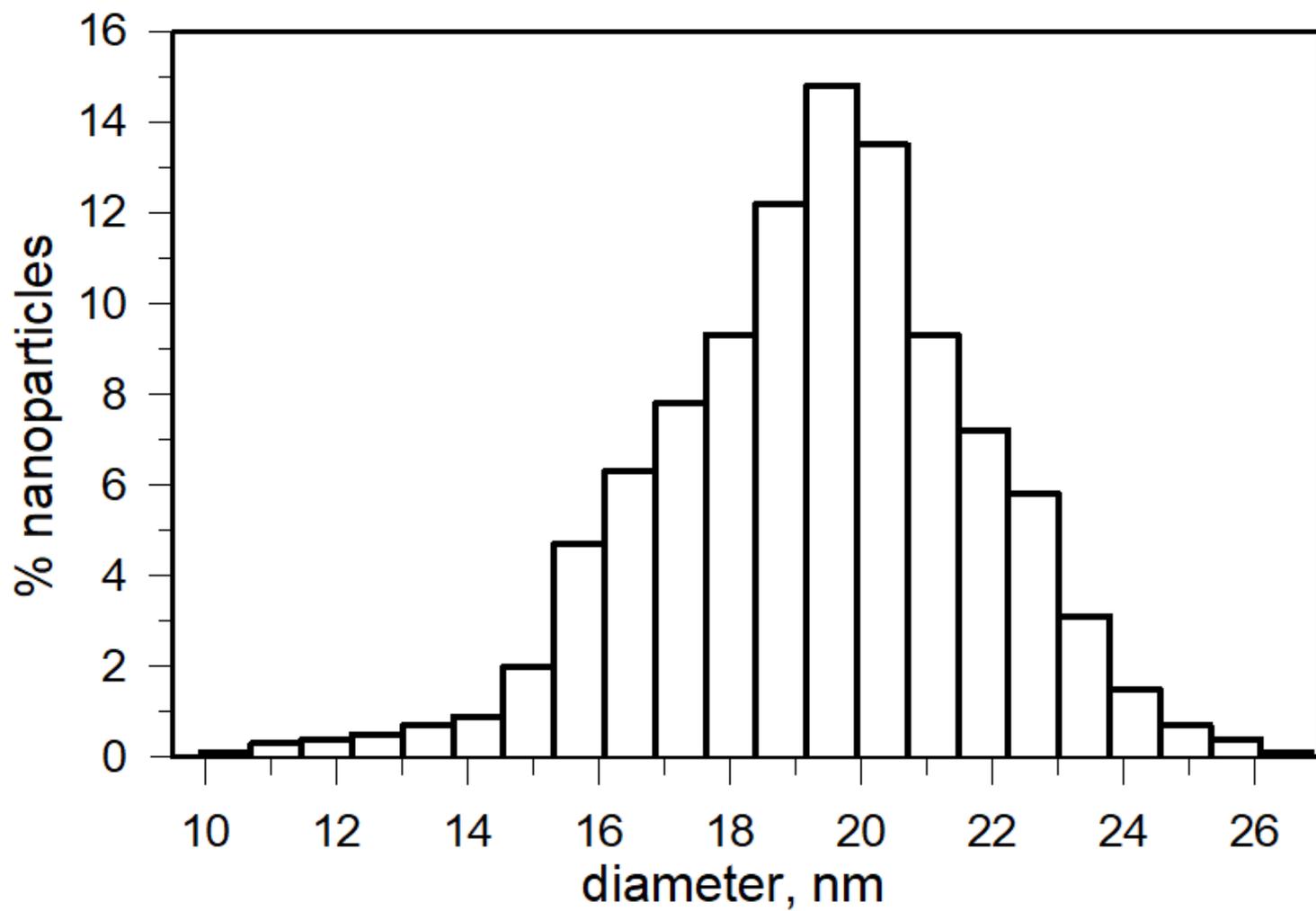
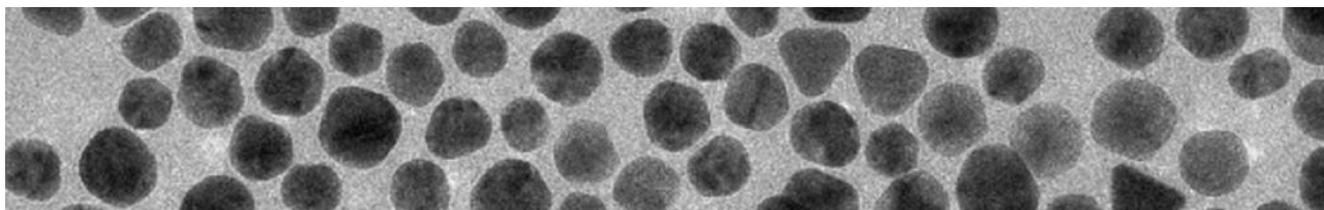
Faraday (1857)

1. Riduzione bifasica (liquido/liquido): $\text{AuCl}_4^- (\text{aq}) + \text{P}_4 (\text{CS}_2, \text{Et}_2\text{O})$
2. Riduzione in fase omogenea liquida (H_2O): $\text{AuCl}_4^- + \text{sugar}$, **tartaric acid**, protosulphate of iron (FeSO_4) and protochloride of tin (SnCl_2)

Turkevich (1951)

1. Riduzione in fase omogenea liquida (H_2O): $\text{AuCl}_4^- + \text{citrato}$, acido ossalico, idrossilammina
2. Riduzione bifasica liquid/gas: $\text{AuCl}_4^- (\text{aq}) + \text{CO} (\text{g})$, acetylene (g)

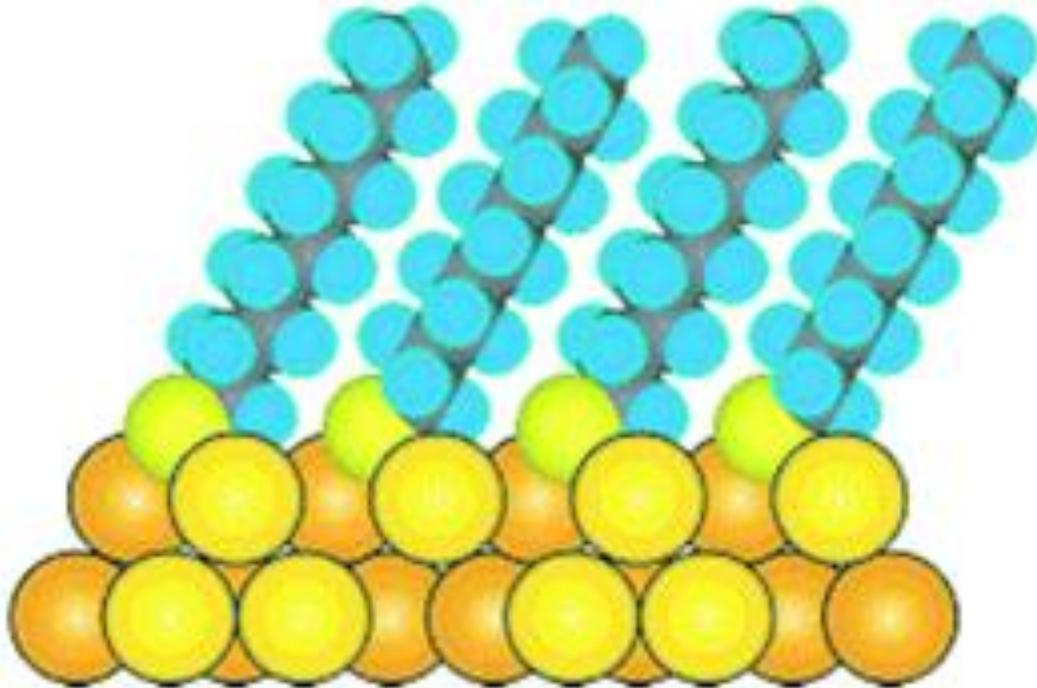
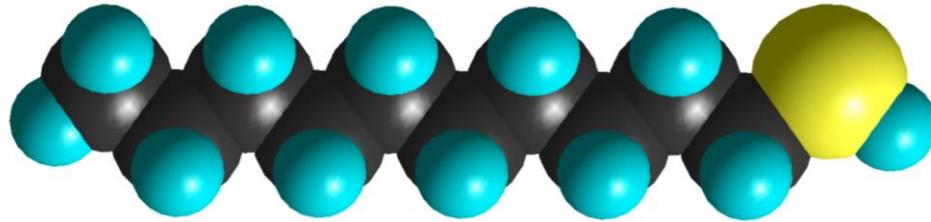
J. Turkevich, P. Cooper Stevenson, J Hillier, A study of the nucleation and growth processes in the synthesis of colloidal gold, *Discuss. Faraday Soc.* **1951**, 11, 55-75



Come si possono controllare le dimensioni delle nanoparticelle?

copiamo dai **SAMs**, Self Assembled Monolayers

decanethiol



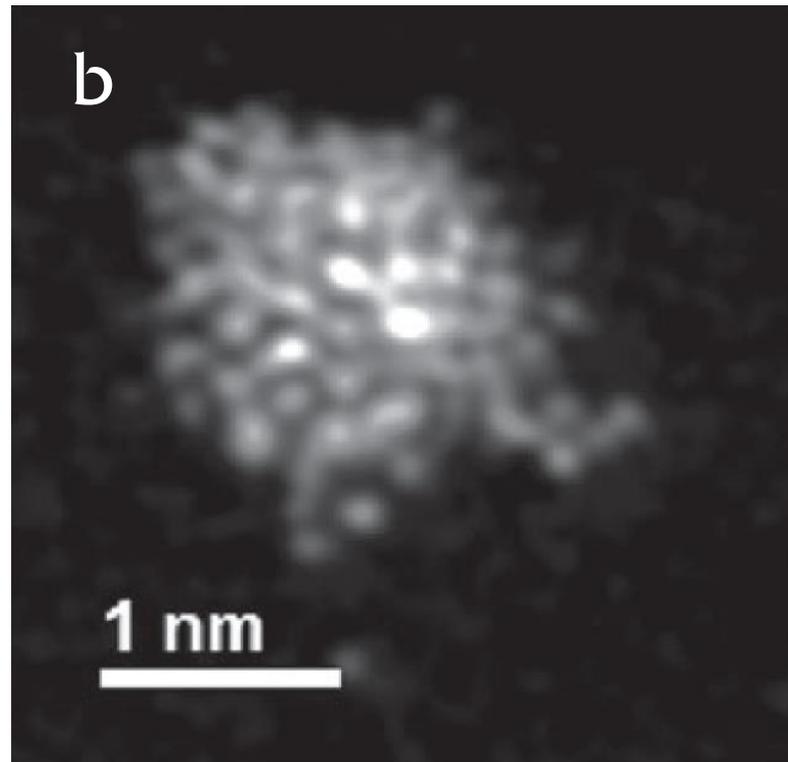
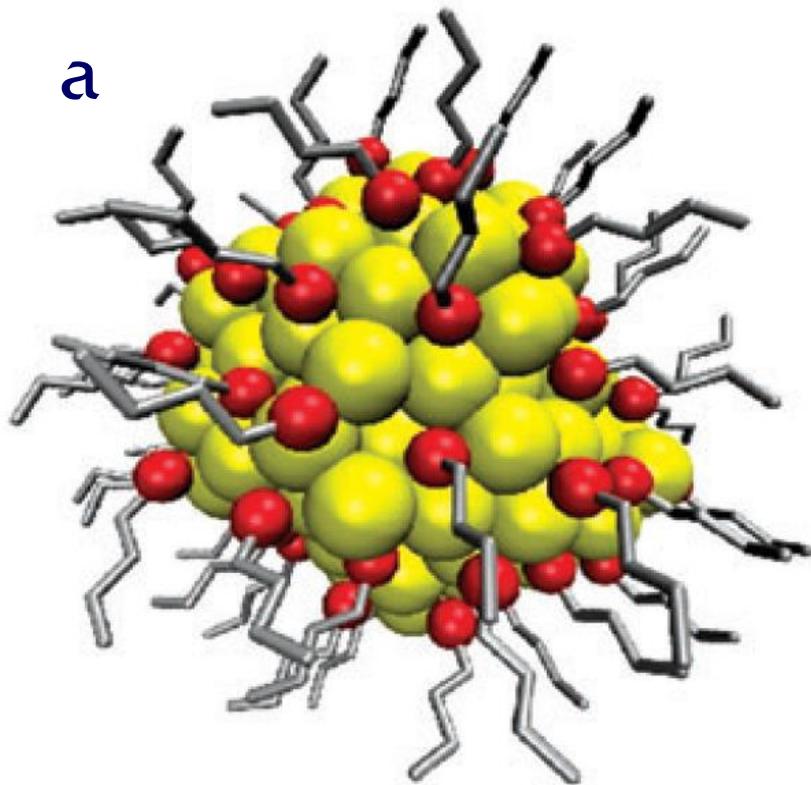


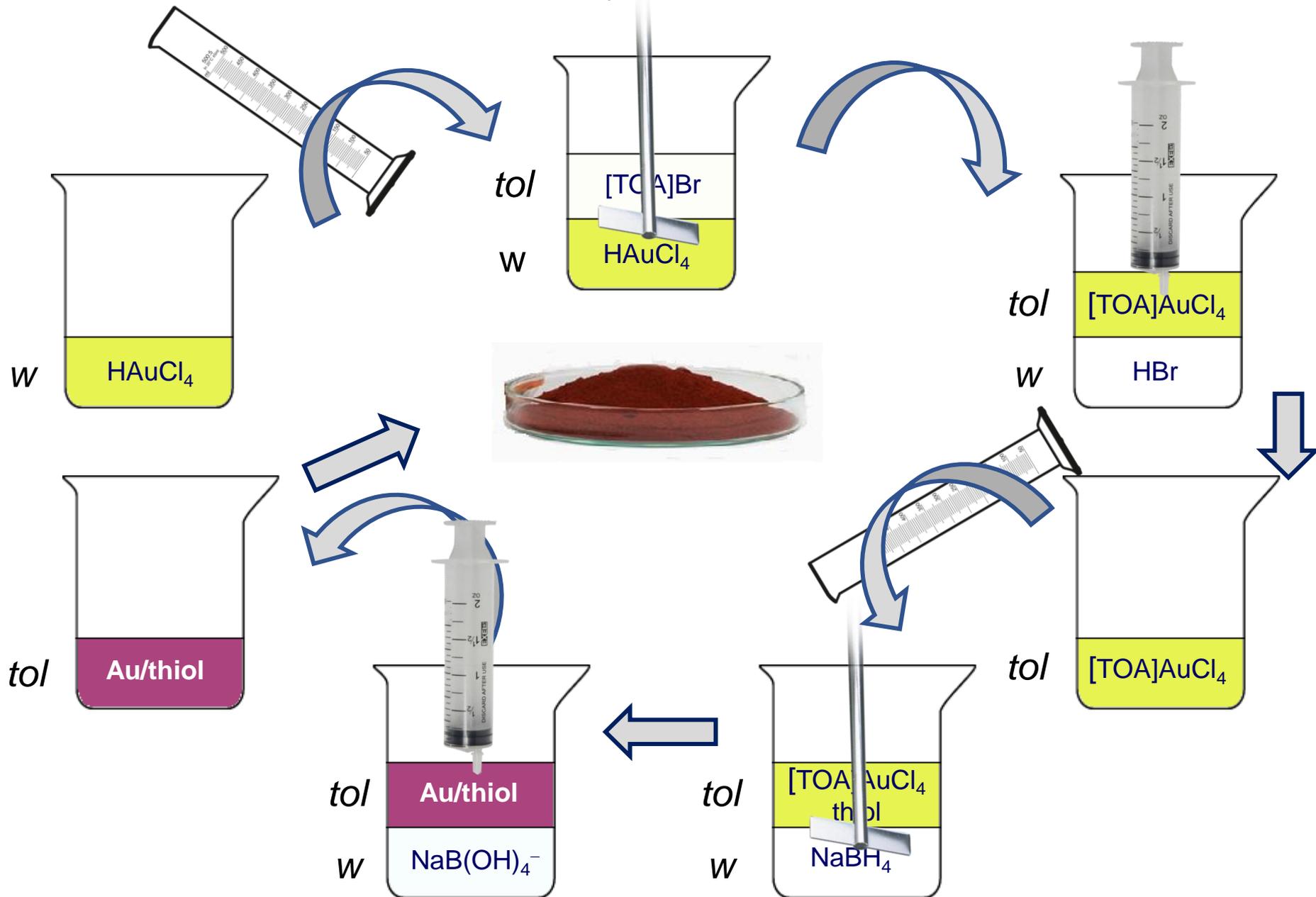
Figure. A comparison between a theoretical (a) and an experimental (b) structure of a gold nanoparticle capped by alkanethiol molecules of similar size.

M. Brust, M. Walker, D. Bethell, D J. Schiffrin, R. Whyman, Synthesis of Thiol-derivatised Gold Nanoparticles in a Two-phase Liquid-Liquid System, *J. Chem. Soc., Chem. Commun.* 1994, 801–802

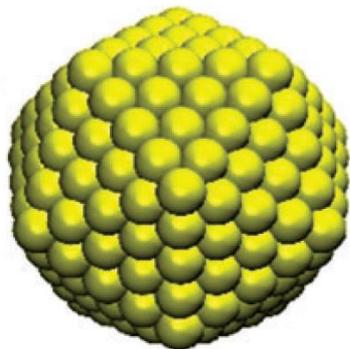
w water; *tol* toluene

[TOA]Br, tetra-octyl-ammonium Br

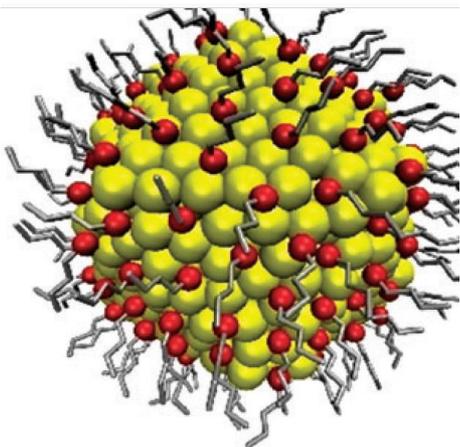
thiol, dodecanethiol



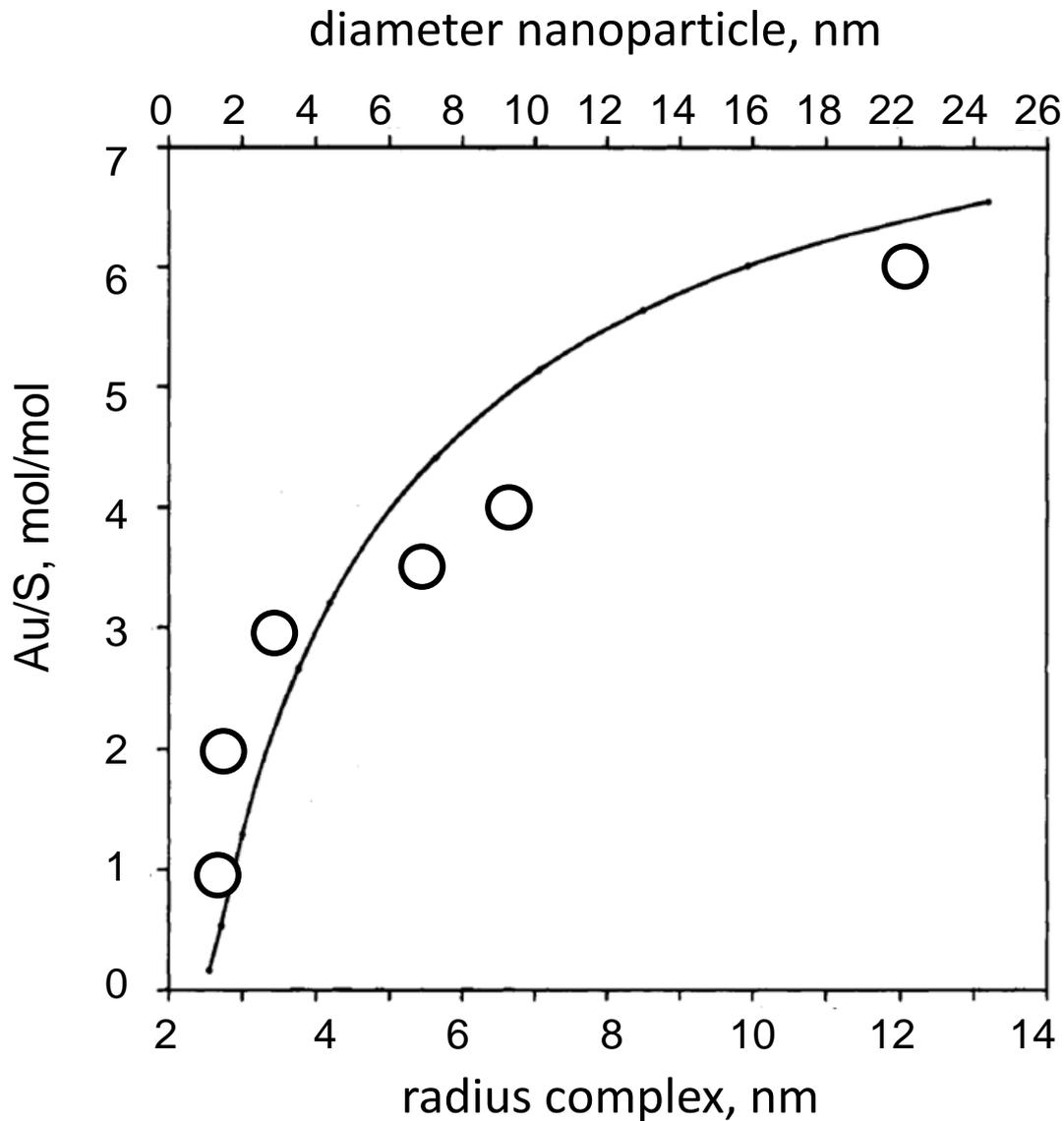
D. V. Leff, P. C. Ohara, J. R. Heath, W. M. Gelbart, Thermodynamic Control of Gold Nanocrystal Size: Experiment and Theory, *J. Phys. Chem.* 1995, 99, 7036-7041

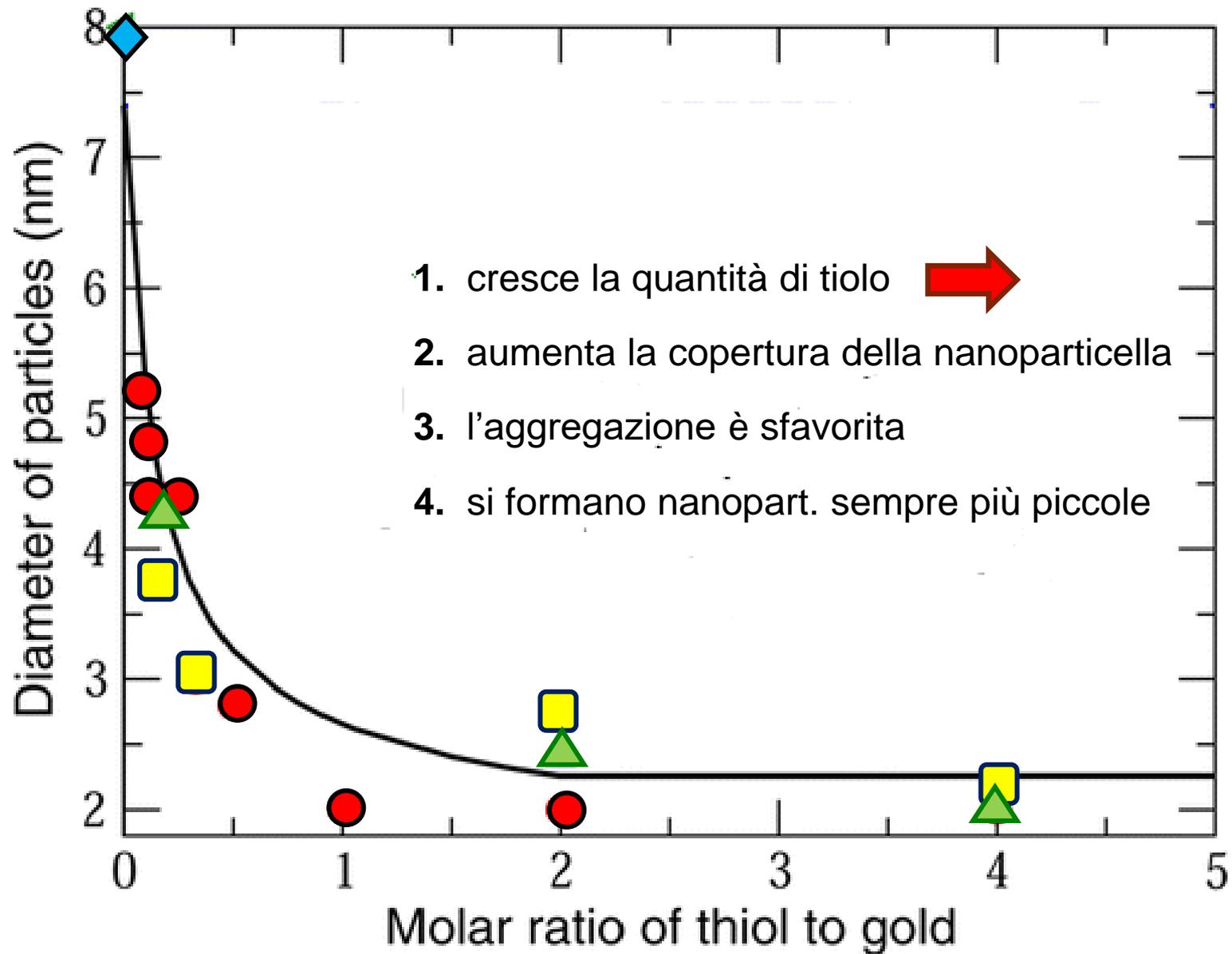


nanoparticle



complex





S. R. K. Perala, S. Kumar, On the Mechanism of Metal Nanoparticle Synthesis in the Brust-Schiffrin Method, *Langmuir* 2013, 29, 9863-9873

SCUSI PROF, MA
COSA FA LO
SCIENZIATO?

LO SCIENZIATO OSSERVA LA
NATURA E CERCA DI DARNE
UN'INTERPRETAZIONE
QUANTITATIVA



SI', MA CON COSA
LA OSSERVA?

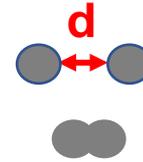
BEH, CON QUEGLI STRUMENTI
CHE LA TECNOLOGIA GLI
METTE A DISPOSIZIONE



10^5 a.C



$d = 0.2 \text{ mm}$
 $200 \mu\text{m}$
 $200\,000 \text{ nm}$



Il **potere di risoluzione** (risoluzione laterale) è quella minima distanza **d** tra due punti che permette ancora di distinguerli. Se la distanza tra i due punti è minore di **d**, essi si confondono in uno solo

1500

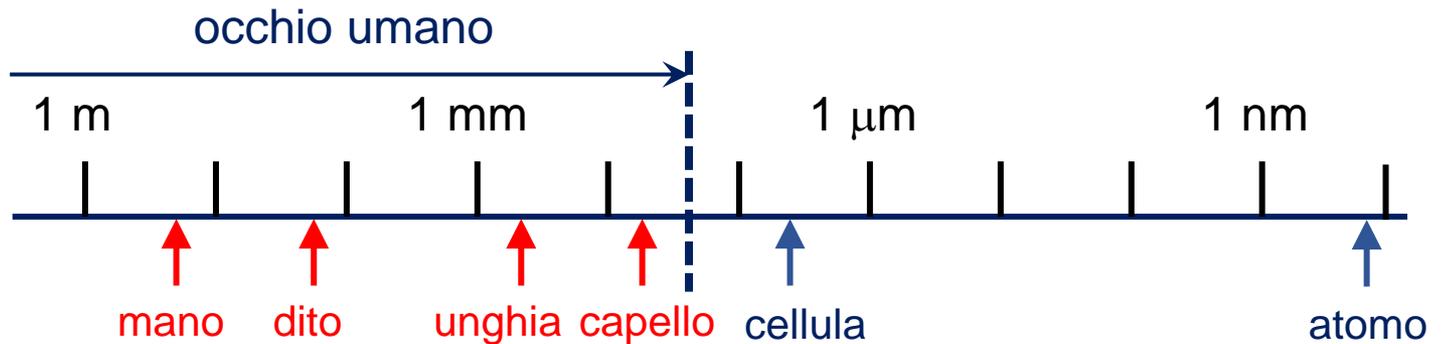
1600

1700

1800

1900

2000



10⁵ a.C



$d = 0.2 \text{ mm}$
 $200 \mu\text{m}$
 $200\,000 \text{ nm}$

I primi microscopi vennero prodotti nei Paesi Bassi alla fine del XVI secolo (Zacharias Jannsen, 1595)

Galileo ne costruì uno (1624), che inviò al principe Federico Cesi, fondatore dell'Accademia dei Lincei. Galileo definiva lo strumento un "occhialino per vedere le cose minime"

1500

1600

1700

1800

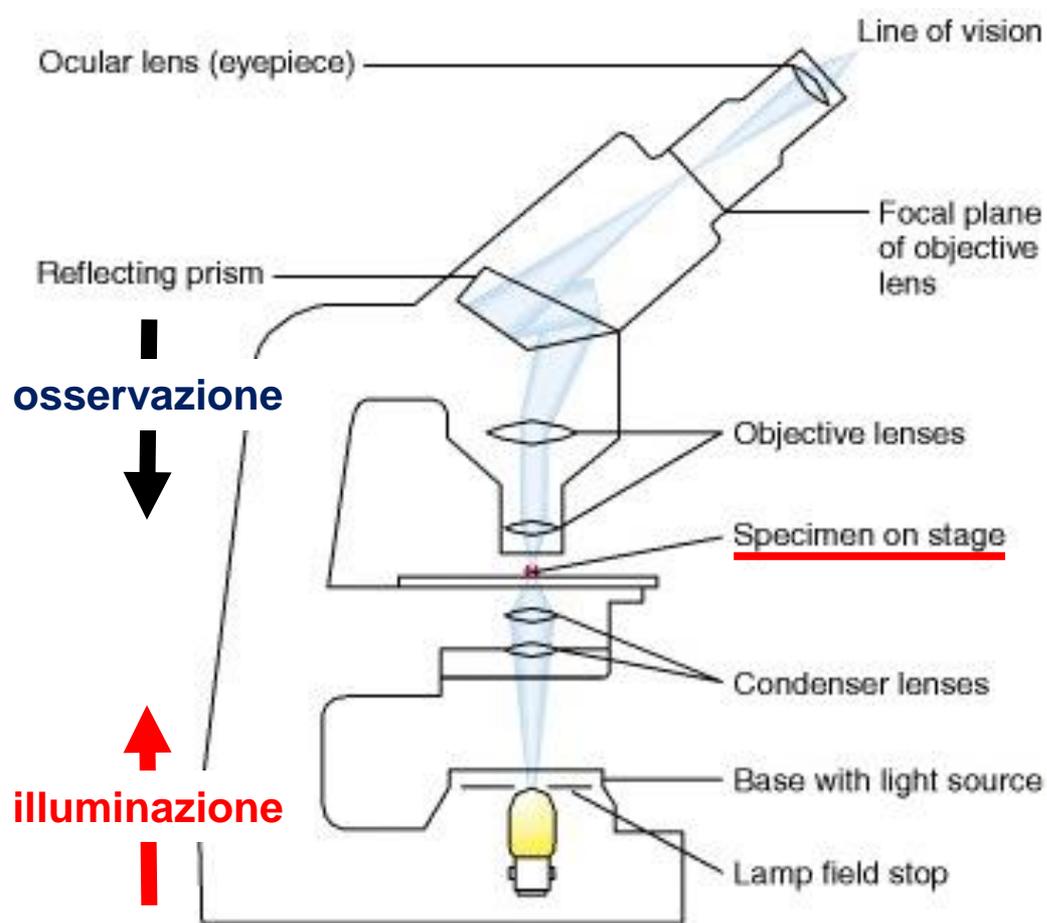
1900

2000



microscopio ottico





Il potere di risoluzione (**risoluzione laterale**) di un microscopio è quella minima distanza d tra due punti, che permette ancora di distinguerli

$$d = 0.6098 \frac{\lambda}{A_N}$$

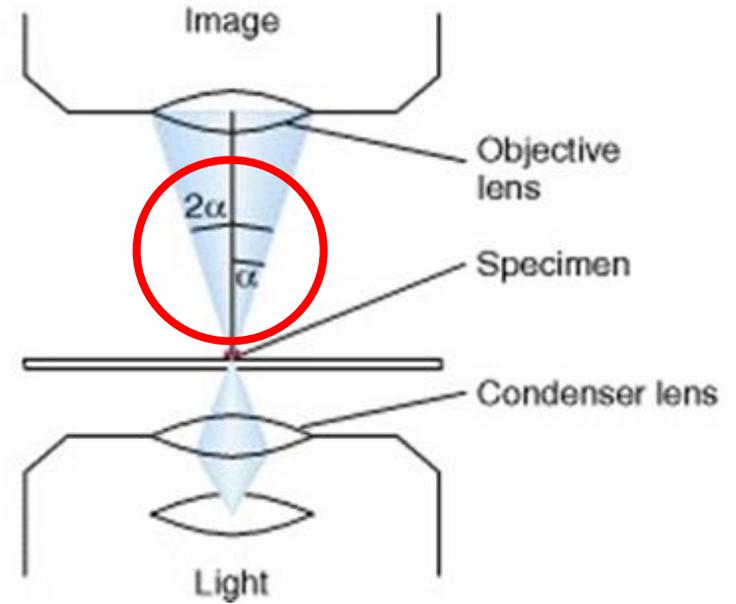
lunghezza d'onda della radiazione che illumina il campione

apertura numerica

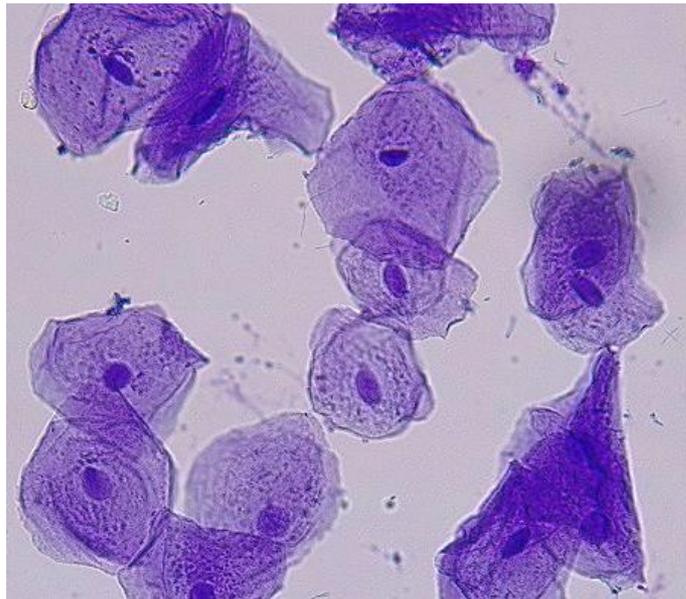
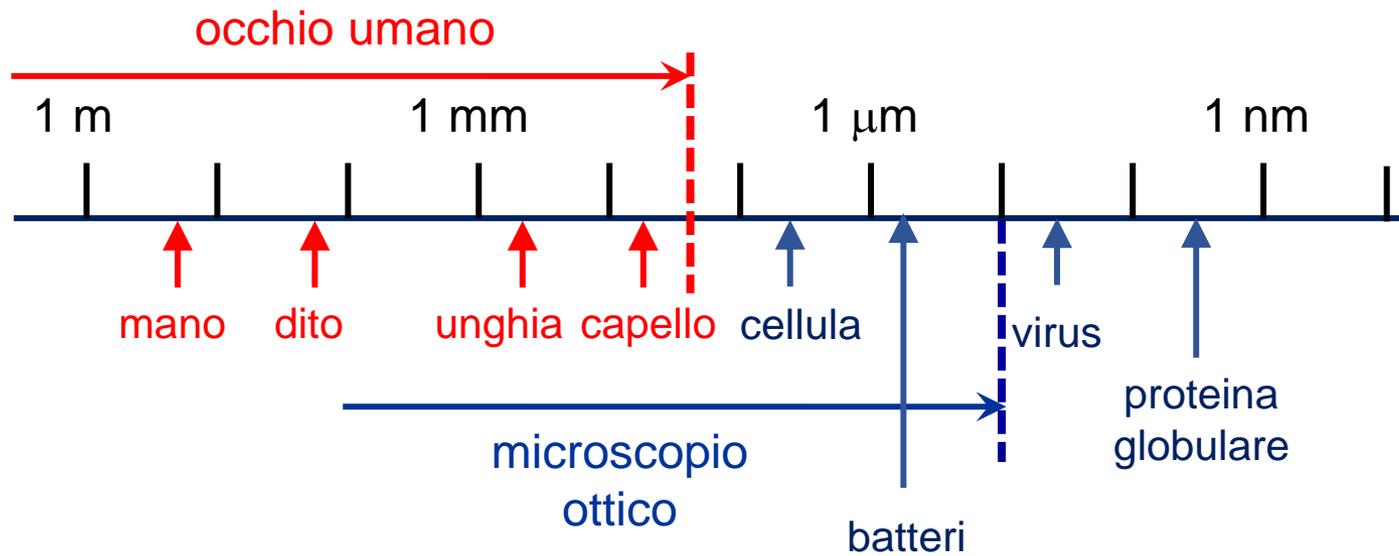
$$A_N = n \sin \alpha$$

angolo del cono di illuminazione

indice di rifrazione



$$d = 0.1 \mu\text{m}$$
$$100 \text{ nm}$$



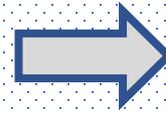
Cellule epiteliali della mucosa della bocca colorate con blu di metilene



Forme cocciche Gram-positive (streptococchi)

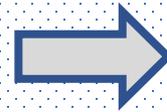
I microscopi elettronici

la risoluzione di un microscopio aumenta (d diminuisce) al diminuire della lunghezza d'onda della radiazione che illumina λ



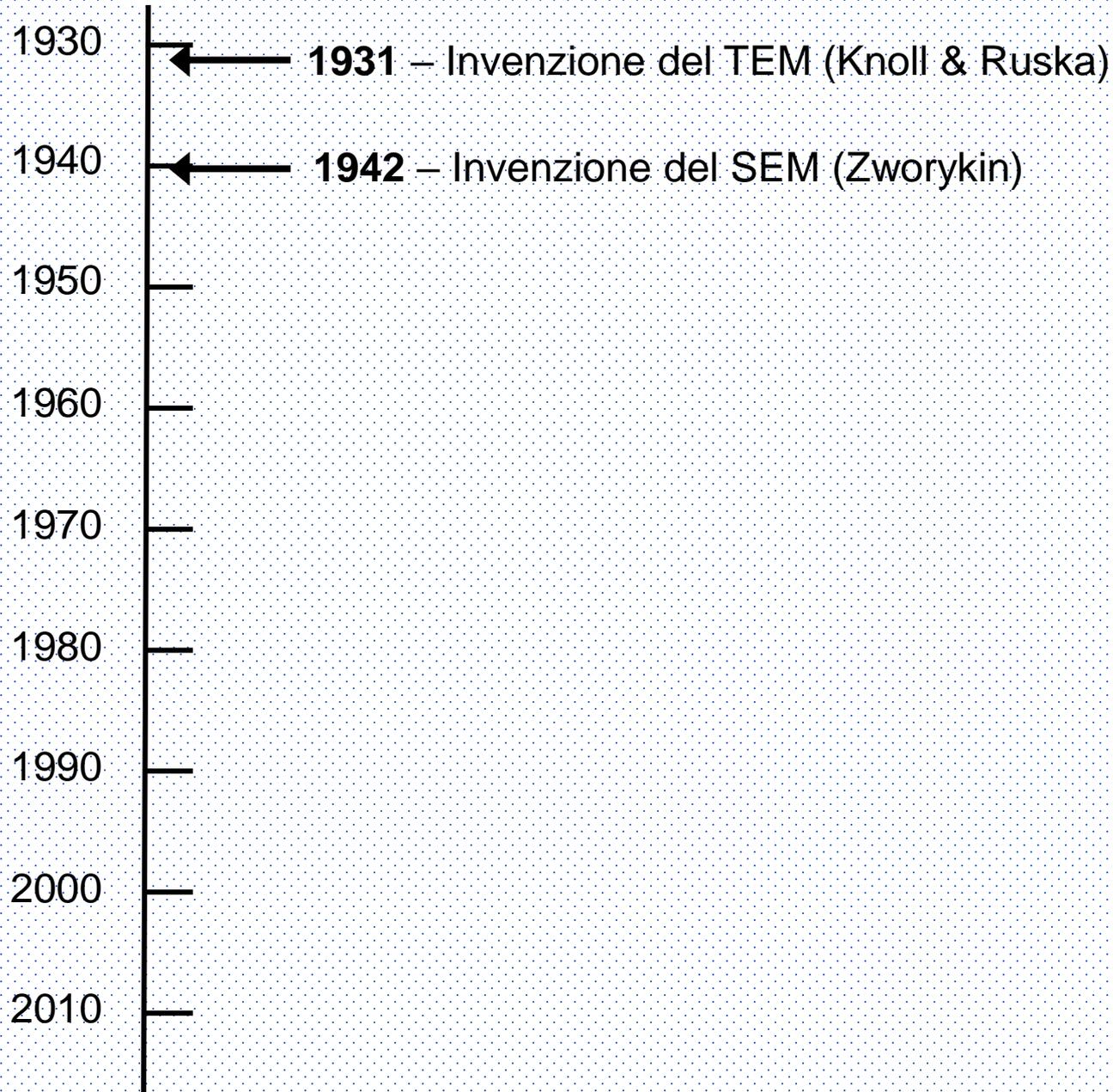
fascio di elettroni accelerato da una differenza di potenziale ΔV

La lunghezza d'onda λ diminuisce al crescere di ΔV

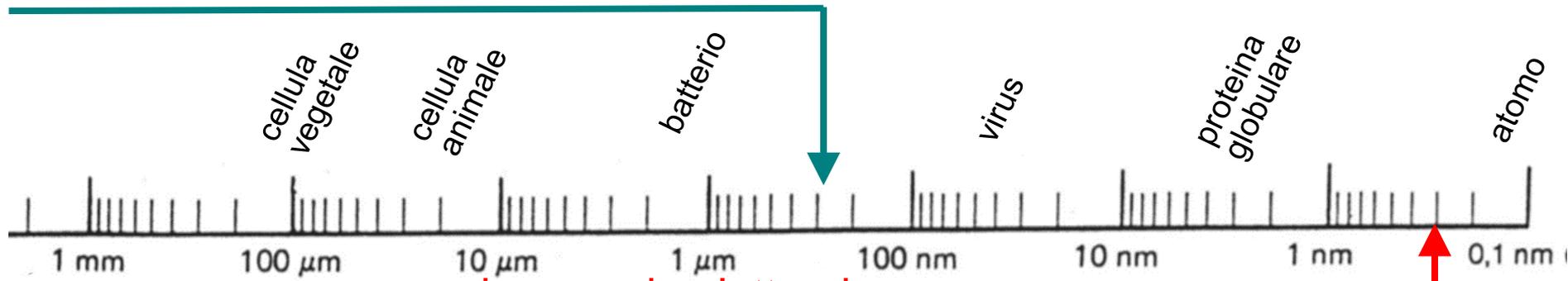


Il microscopio elettronico è un microscopio che utilizza come radiazione gli elettroni accelerati a 40-400 keV

I microscopi elettronici



microscopio ottico – 100 nm



microscopio elettronico
a trasmissione (**TEM**) – 0.2 nm

microscopio elettronico
a scansione (**SEM**) – 10 nm

TEM

€300,000 to €10,000,000



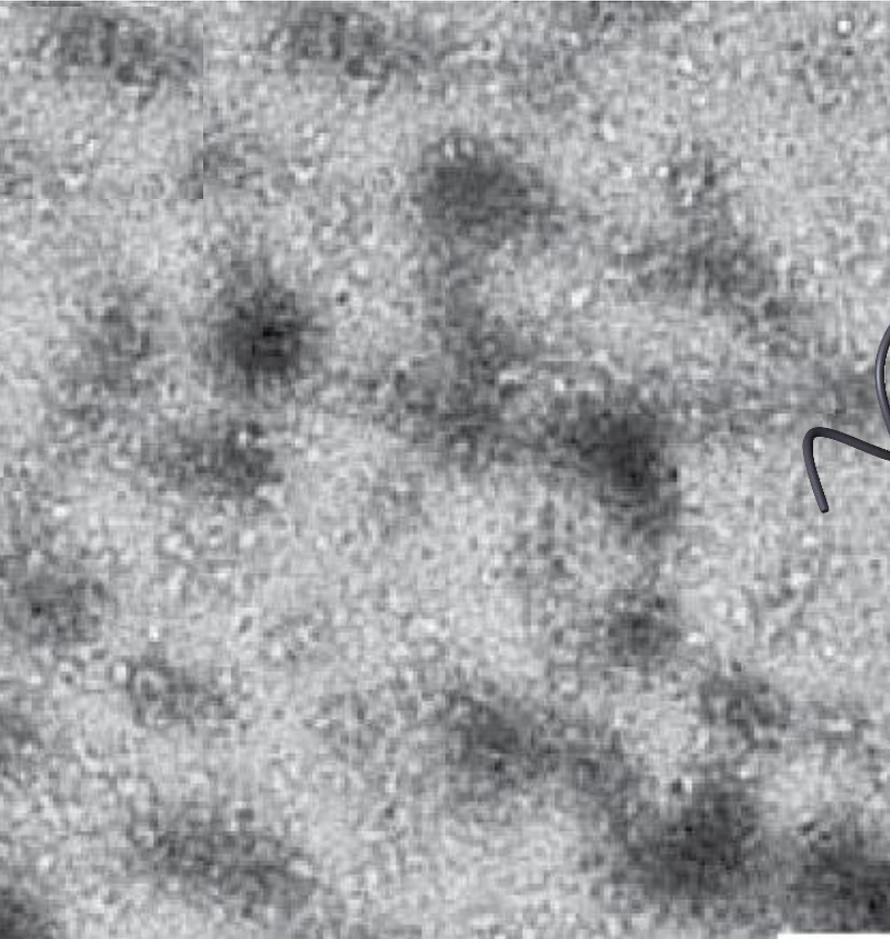
SEM

€80,000 to €2,000,000



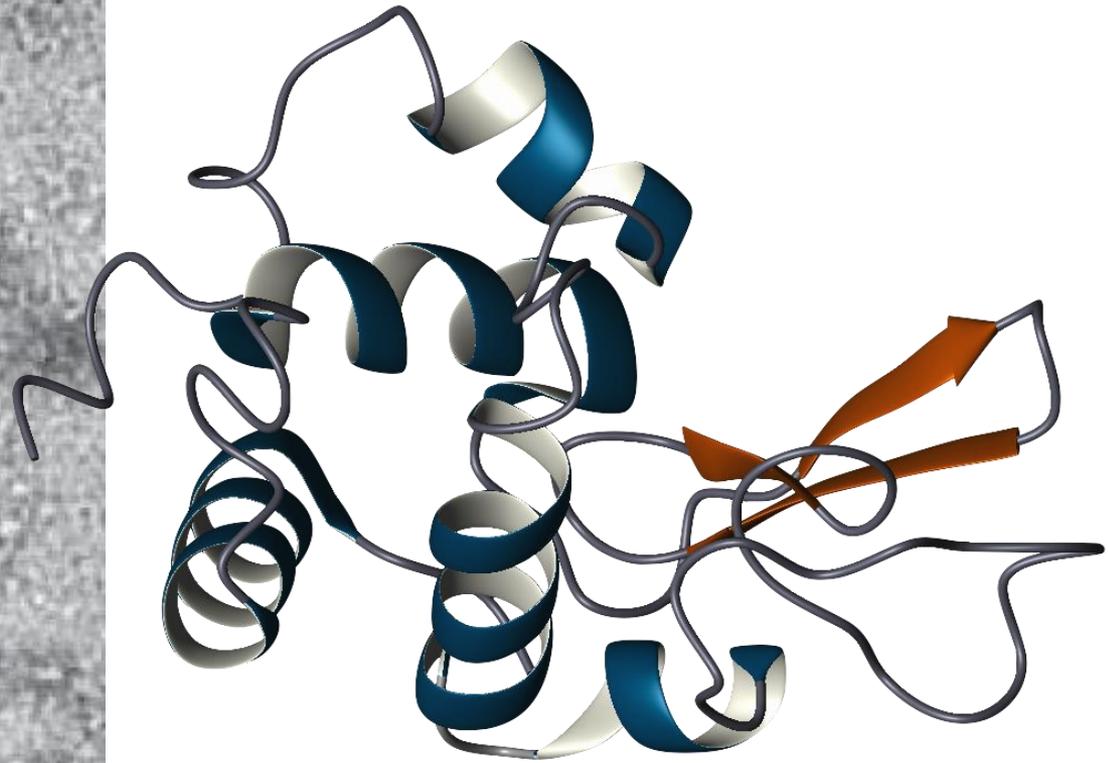
Il microscopio elettronico a trasmissione (TEM) ha un potere risolutivo è di 0.2 nm, circa 5×10^5 volte maggiore di quello dell'occhio umano. **Il microscopio elettronico a scansione (SEM) ha un potere risolutivo di 10 nm**, quindi viene in un certo senso "superato" dal TEM, ma riesce a fornire delle **immagini tridimensionali**, che permettono di apprezzare i contorni e la forma delle strutture osservate.

TEM - lysozyme, MW: 14,100



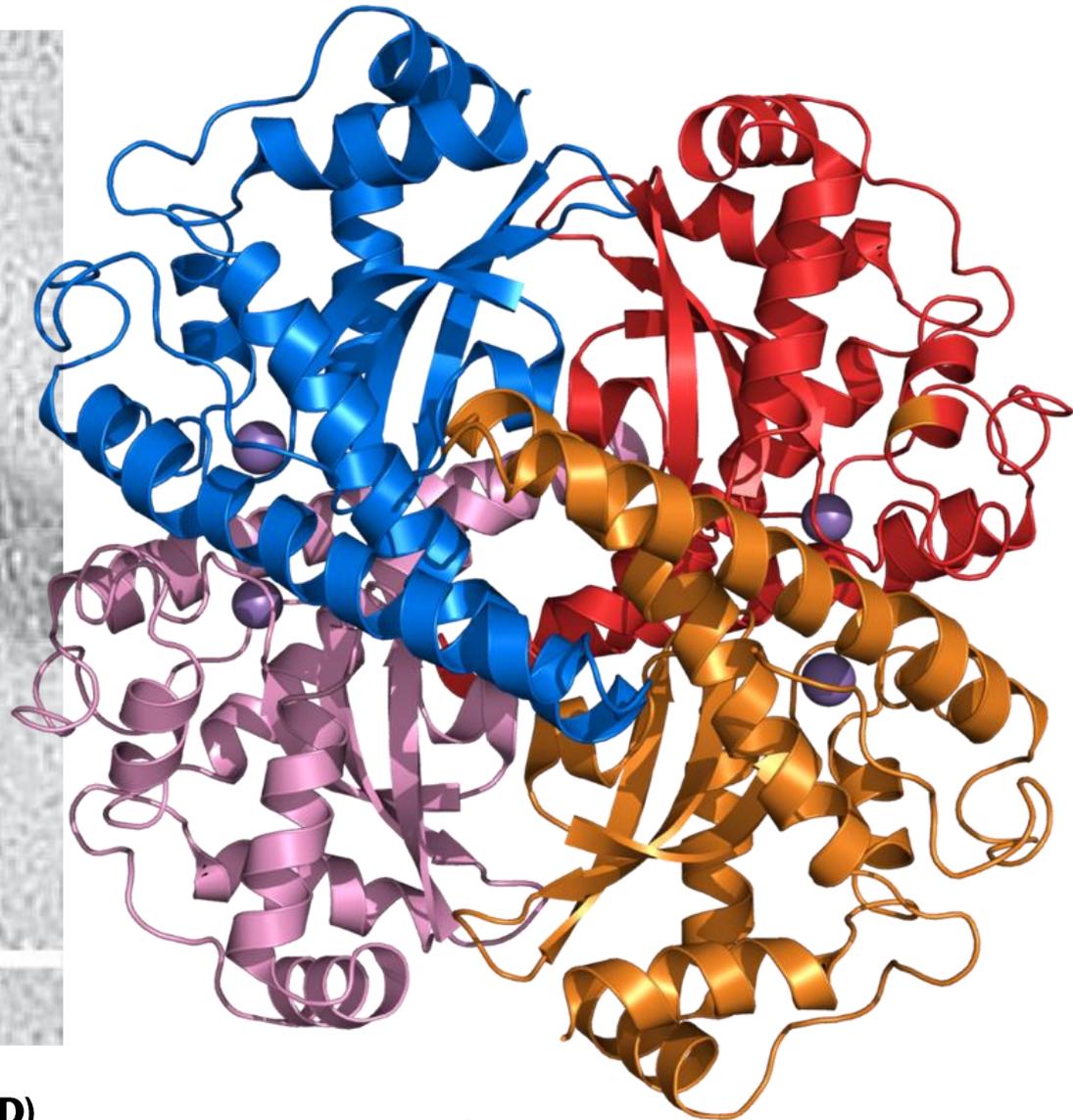
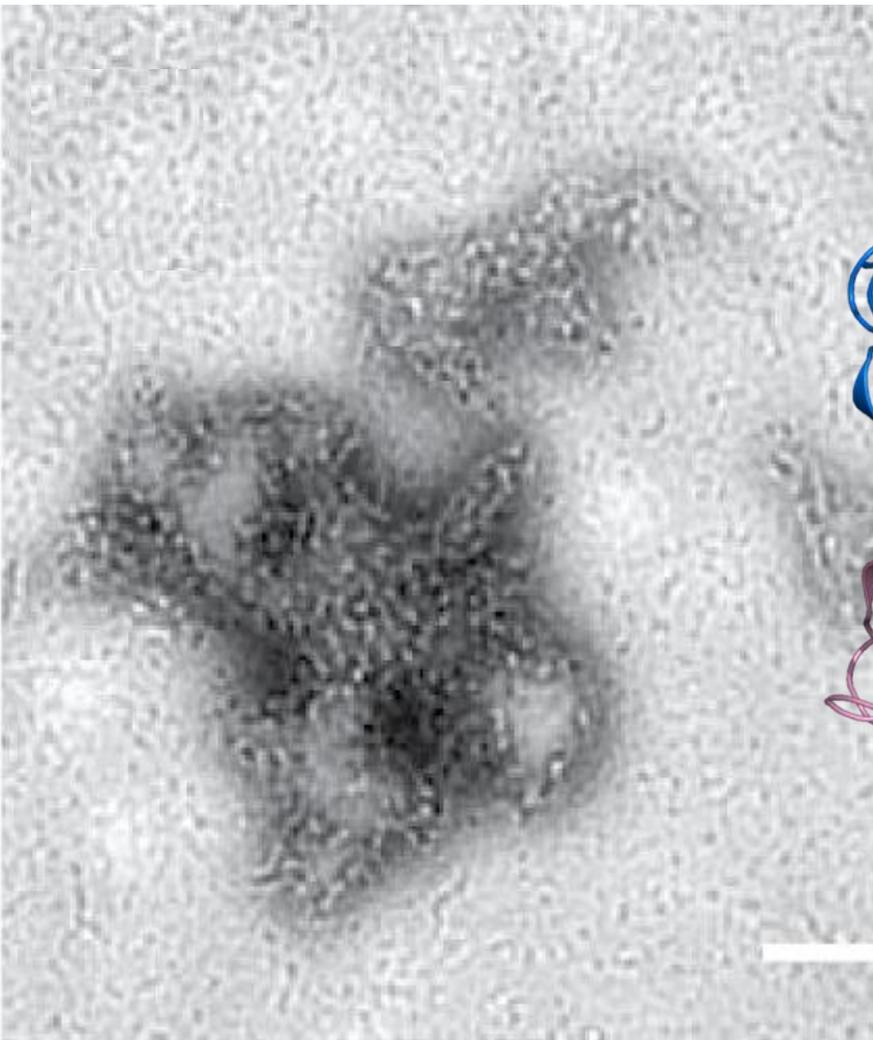
TEM image of lysozyme

Samples were negatively stained using 2% aqueous ammonium molybdate. Scale bar represents 100 nm.



Ribbon diagram of lysozyme from Bacteriophage T4. 2.5 Å crystallographic structure

TEM - Superoxide dismutase: MW: 32,500



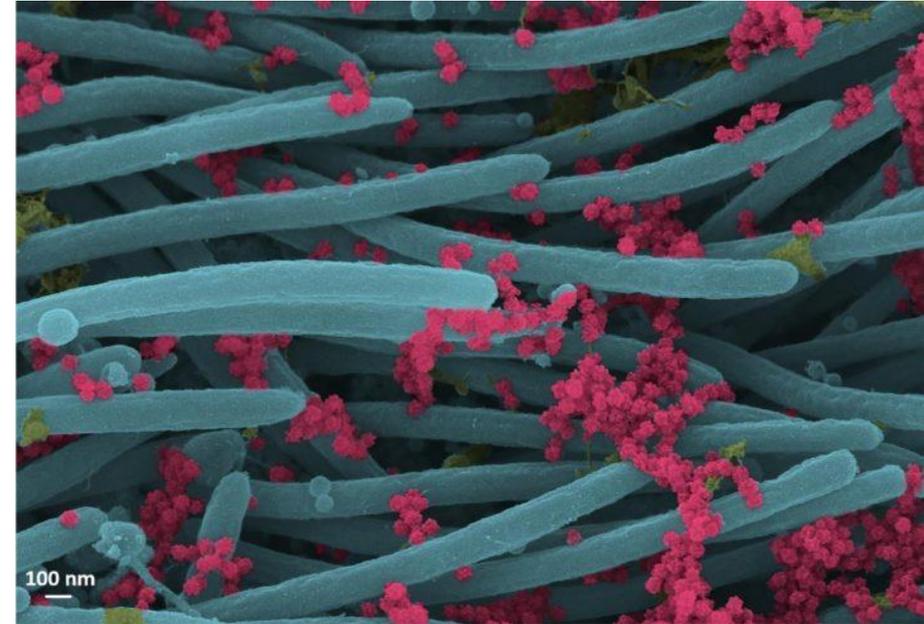
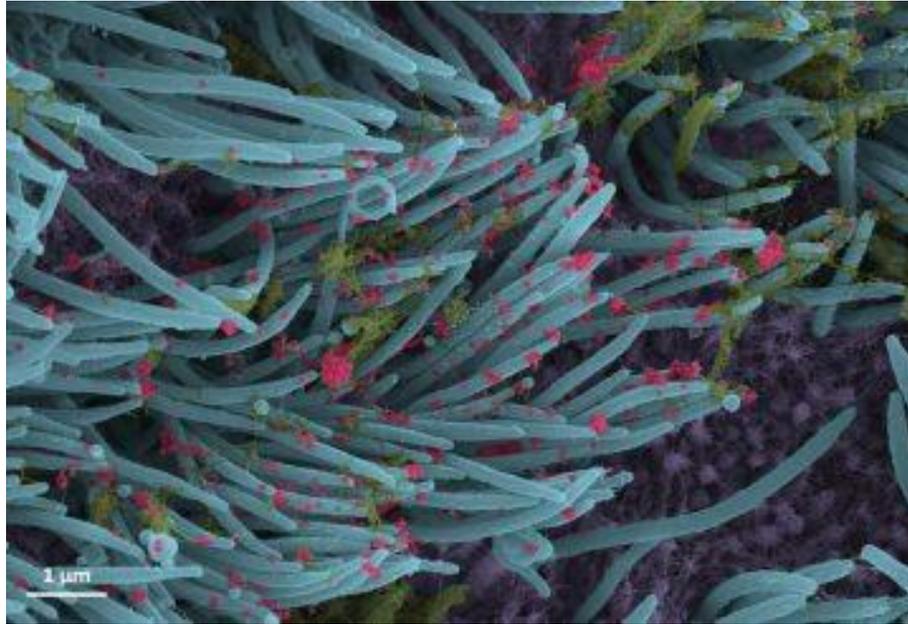
TEM image of superoxide dismutase (SOD)

Samples were negatively stained using 2% aqueous ammonium molybdate. Scale bar represents 100 nm.

Ribbon diagram of a human superoxide dismutase 2 (SOD2) tetramer. Manganese ions shown in violet. 2.5 Å crystallographic structure

SEM - SARS-CoV-2

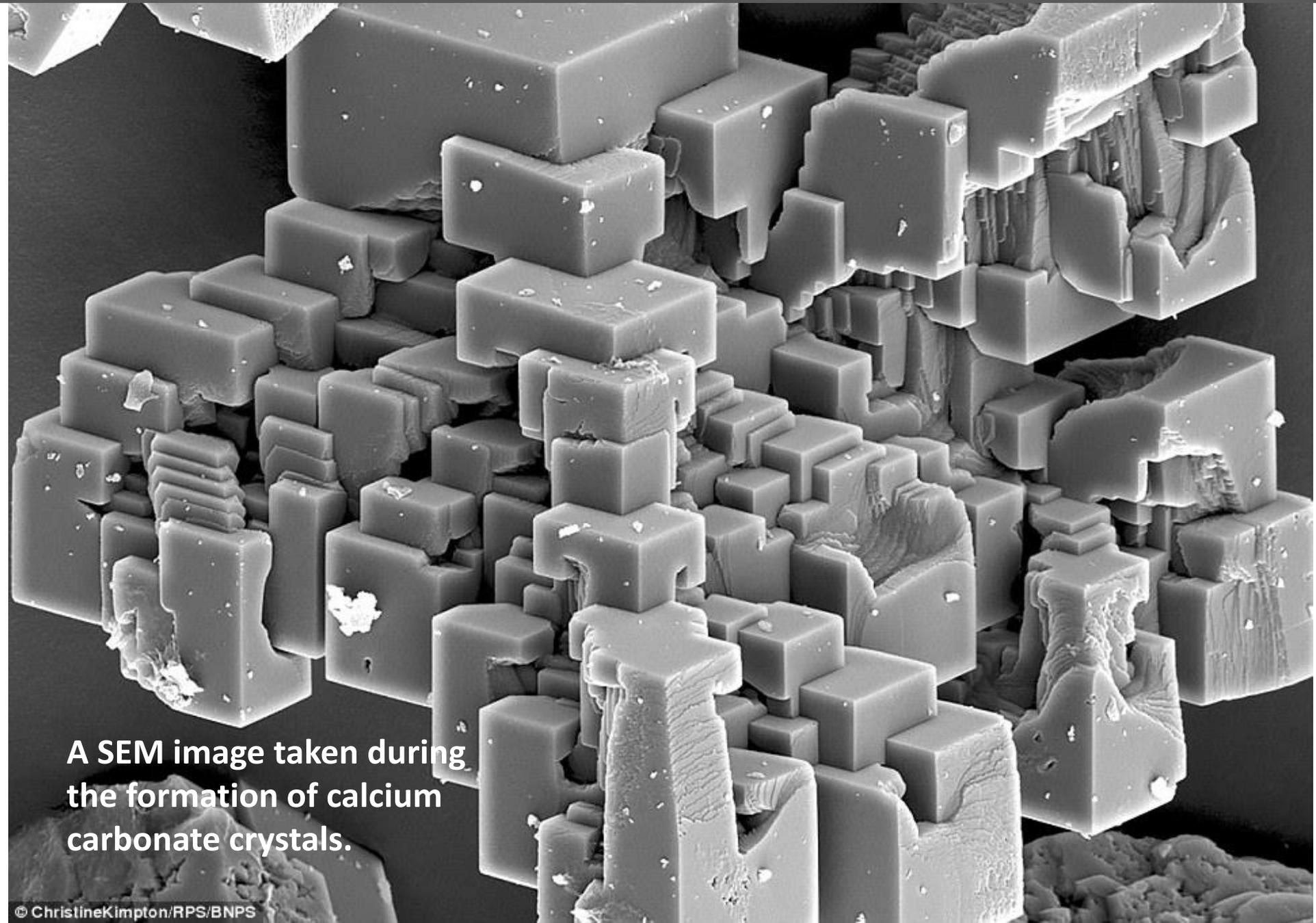
Camille Here, SARS-CoV-2 Infection of Airway Cells, *N. Engl. J. Med.* **2020**, 383, 969.



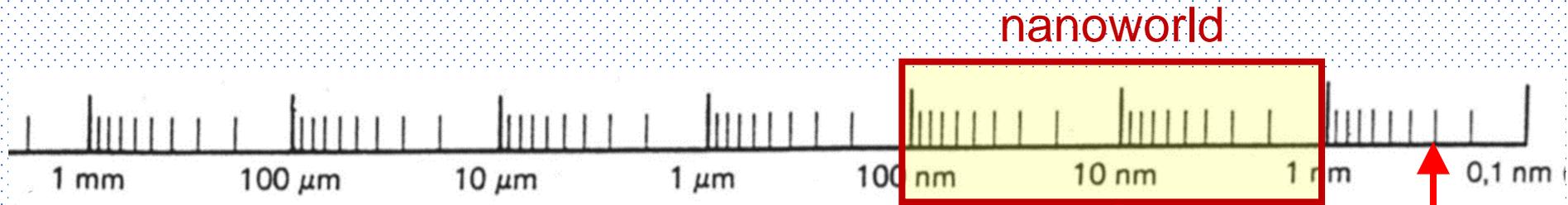
A higher power magnification image shows the structure and density of SARS-CoV-2 virions (red) produced by human airway epithelia

SARS-CoV-2 virions (red)

SEM in mineralogia- CaCO_3



A SEM image taken during the formation of calcium carbonate crystals.

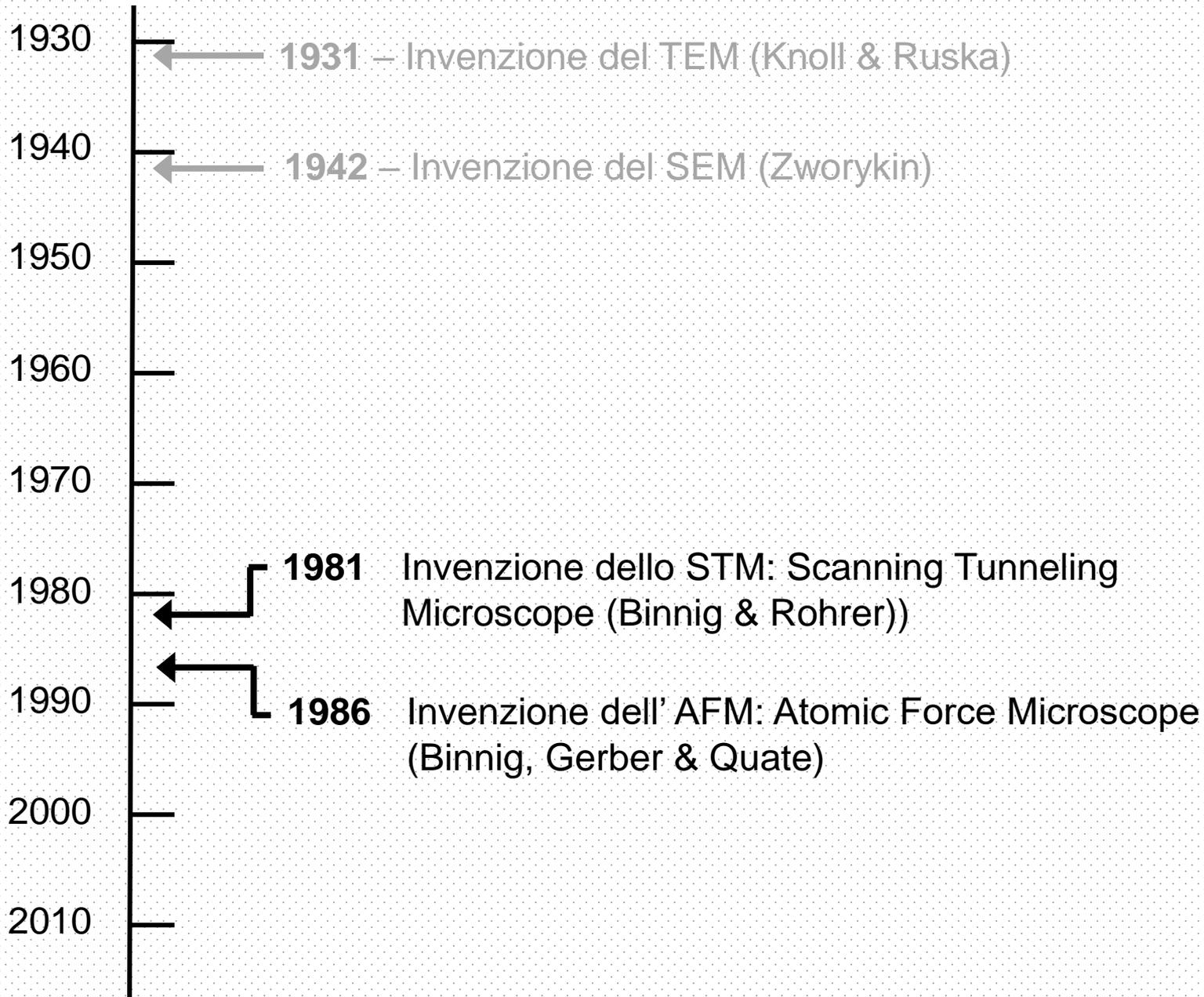


microscopio elettronico
a trasmissione (**TEM**)

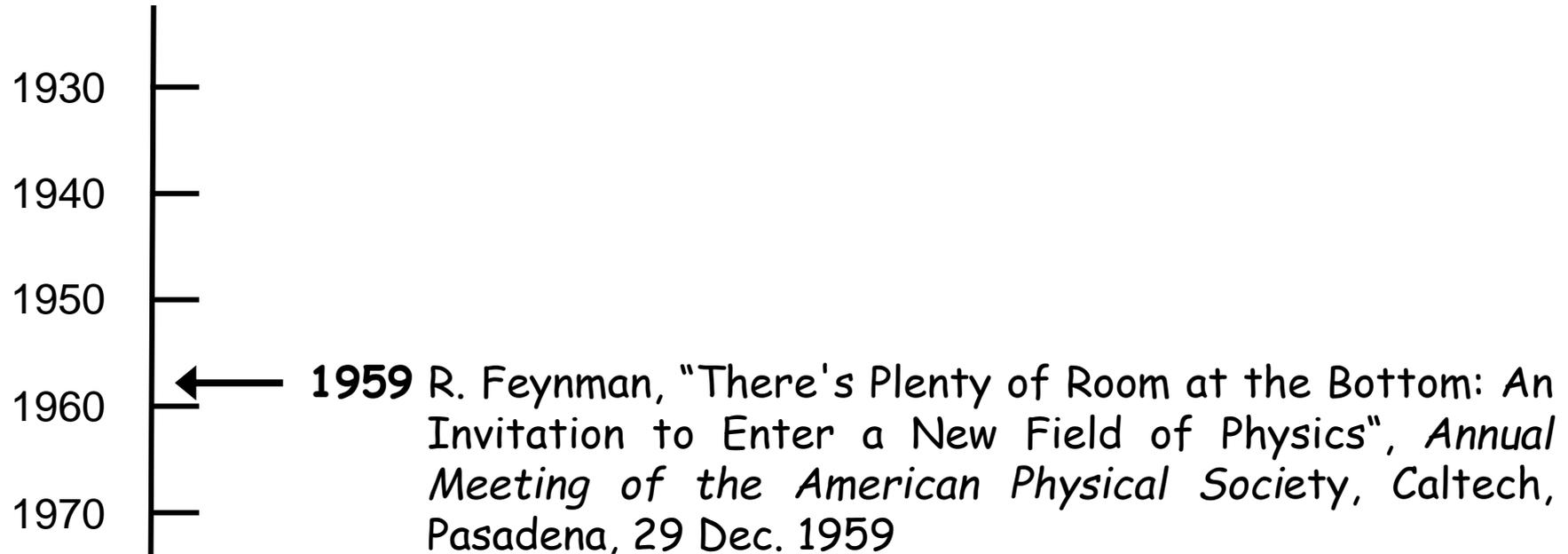
microscopio elettronico
a scansione (**SEM**)



I microscopi elettronici



Esiste un 'manifesto' delle nanoscienze?



Richard Feynman (1918-1988)
Fisico teorico. Premio Nobel per la
Fisica 1965 (Elettrodinamica
Quantistica)

There's Plenty of Room at the Bottom

A small world

Why cannot we write the entire 24 volumes of the *Encyclopaedia Britannica* on the head of a pin?

Molecular machines

What are the possibilities of small but movable machines? They may or may not be useful, but they surely would be fun to make.

Rearranging the atoms

The principles of physics do not speak against the possibility of manoeuvring things atom by atom. Ultimately, we can arrange the atoms the way we want; the very atoms, all the way down!

$S \triangle CAB$

$$m = \iiint \rho(x,y,z) dv$$

$AM = MD = ?$

$$c - \frac{b^2}{4a}$$

φ
 dy

CHE ACCADREBBE SE
NOI FISICI POTESSIMO
METTERE GLI ATOMI
LINO PER LINO DOVE
VOGLIAMO?

MA QUESTO E'
UN COMPITO
DEI CHIMICI!

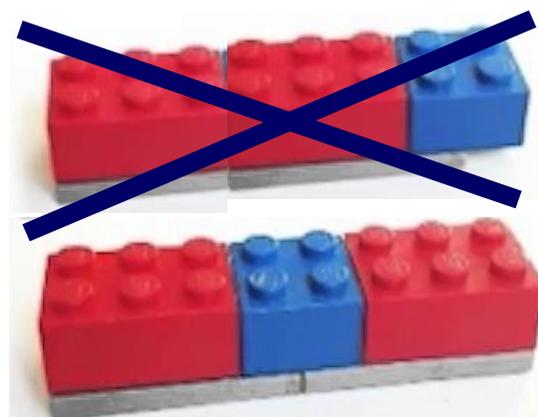
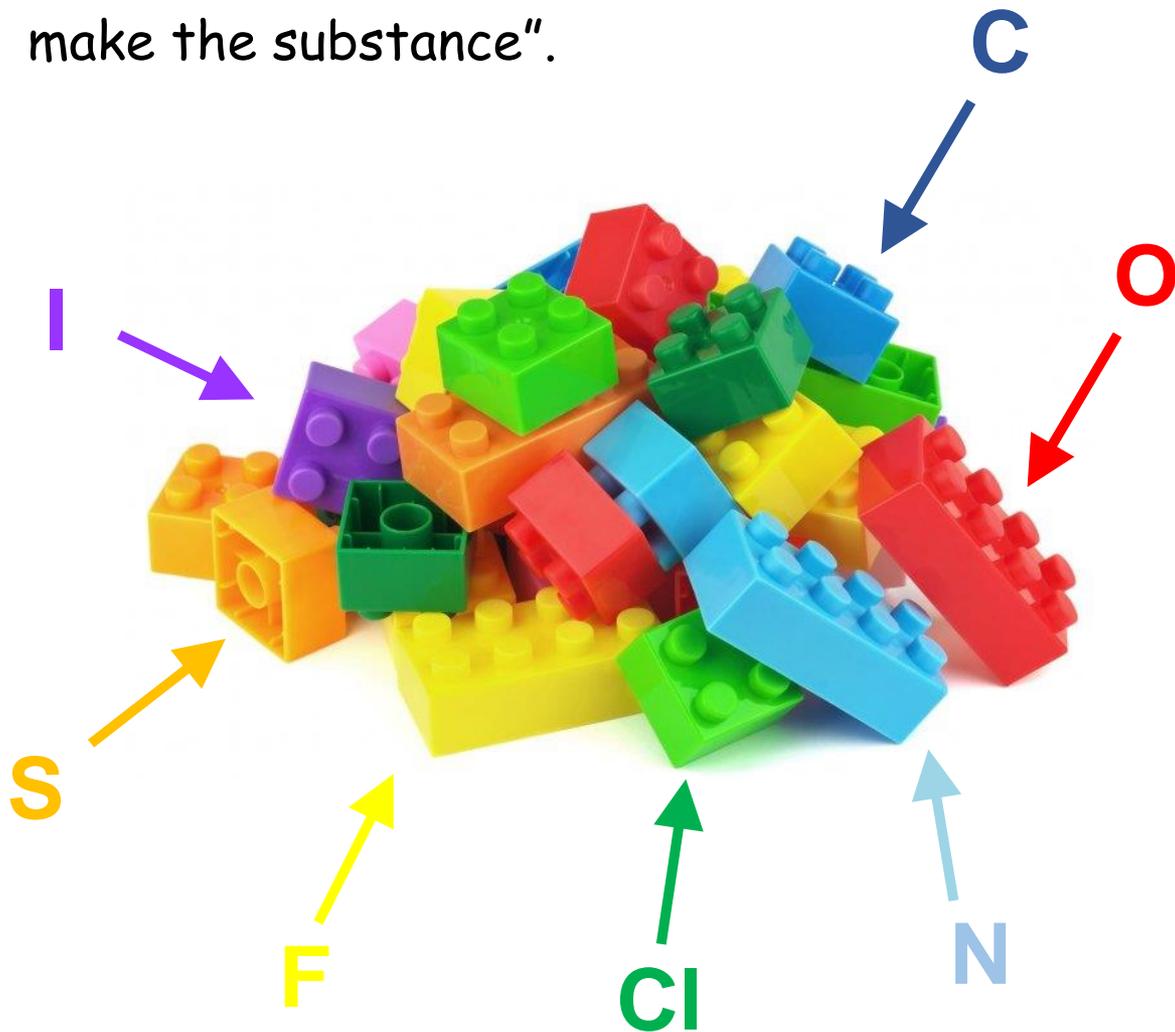
$\sin(x-y)$

$\sqrt{5-x} \quad 3n$

$(m-n)^2$

$$V = \sqrt{\frac{2gh}{1 + \frac{1}{MR}}}$$

"But it is interesting that it would be, in principle, possible (I think) for a physicist to synthesize any chemical substance that the chemist writes down. Give the orders and the physicist synthesizes it. How? Put the atoms down where the chemist says, and so you make the substance".



Quando e da chi è stato inventato il termine 'nanotecnologia'?



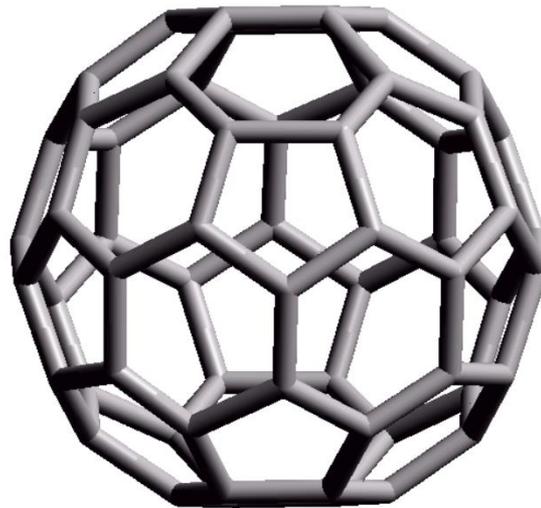
Norio Taniguchi
(1912-1999)
Tokyo University



Fullerene C₆₀ 60 atomi di carbonio (sp²) ai vertici di un **icosaedro troncato**. 32 facce: 12 pentagoni e 20 esagoni, ogni pentagono è circondato da esagoni. Nessun pentagono è legato a un altro pentagono. Struttura polienica piuttosto che aromatica: legami corti (1.38 Å) condivisi tra esagoni adiacenti, legami lunghi (1.45 Å) condivisi tra pentagoni ed esagoni adiacenti. Natura piramidale e non planare dei C sp². Solido nero cristallino, solubile in benzene (soluzione rosso violetta). Scoperto e caratterizzato nel 1985.*



icosaedro
troncato



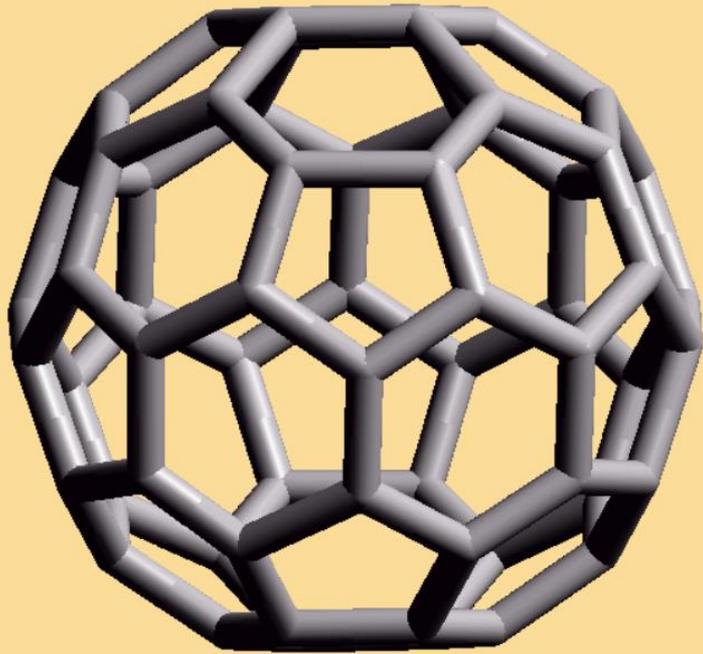
buckminster-
fullerene



footballene**

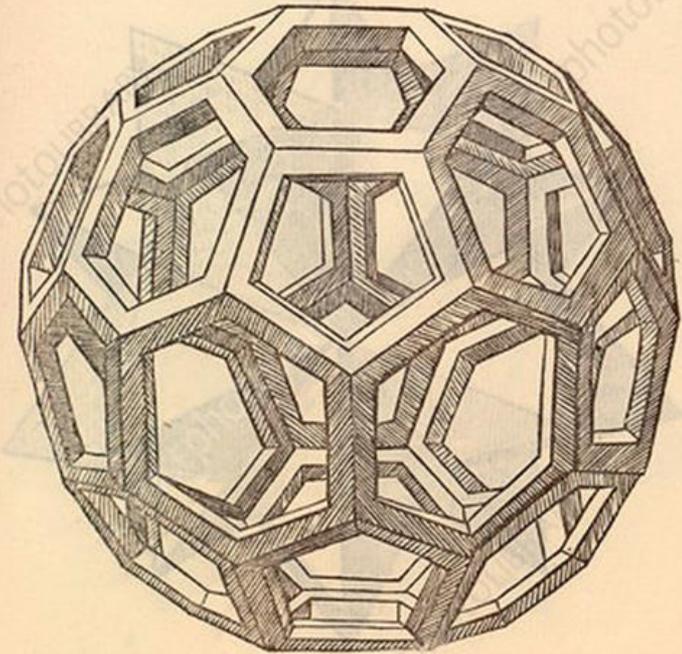
* Kroto, H.W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E., C₆₀: Buckminsterfullerene, *Nature* **1985**, 318, 162–163.

** Tango Durlast, Adidas, **1978** FIFA World Cup in Argentina.



~~fullerene~~
leonardene

W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, D. R. M. Walton, Crystal structure and bonding of ordered C_{60} , *Nature* 1991, 353, 147-149.

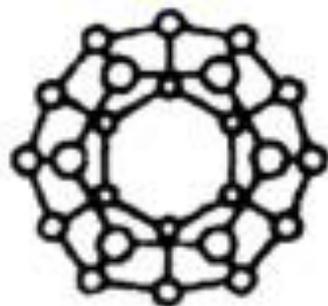


leosaedron abscisum Vacuum

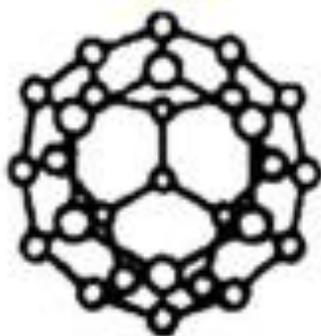
Fra' Luca Pacioli, *De Divina Proportione* (1498). Riproduzione anastatica del codice in pergamena conservato presso la Biblioteca Ambrosiana di Milano, 130 fogli.

Disegni di Leonardo da Vinci

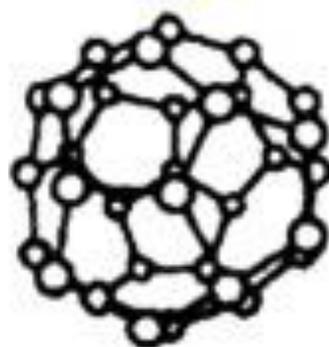
C_{24}



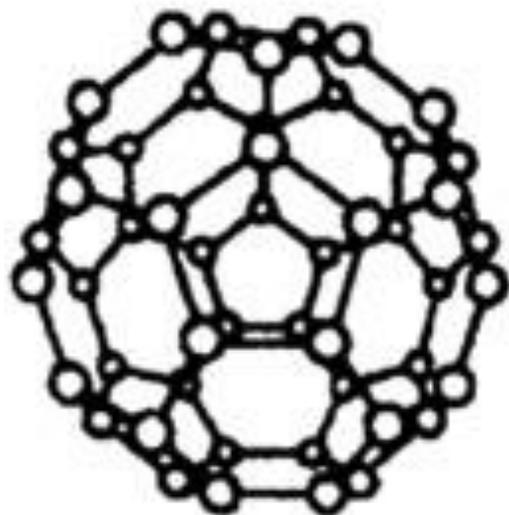
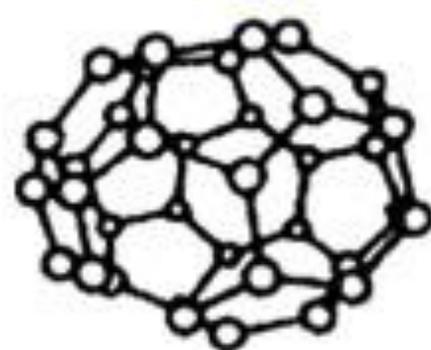
C_{28}



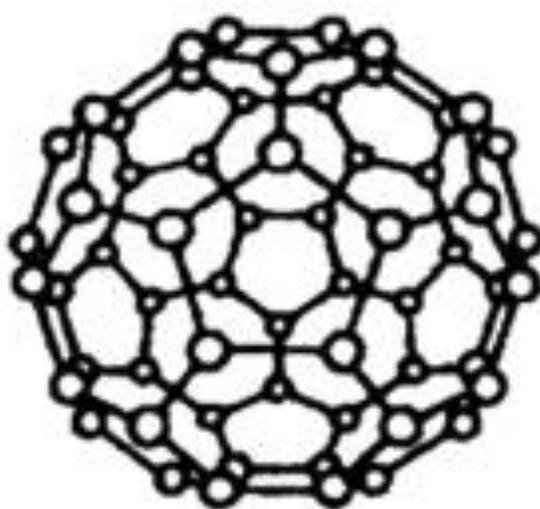
C_{32}



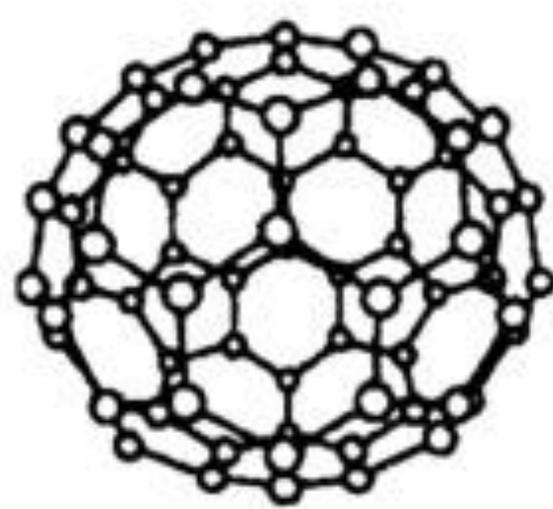
C_{36}



C_{50}



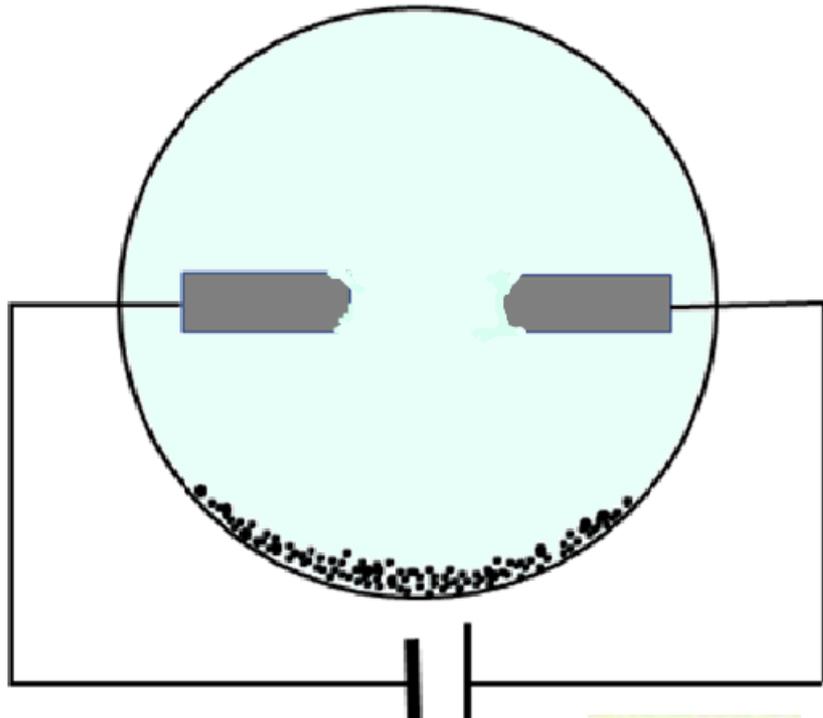
C_{60}



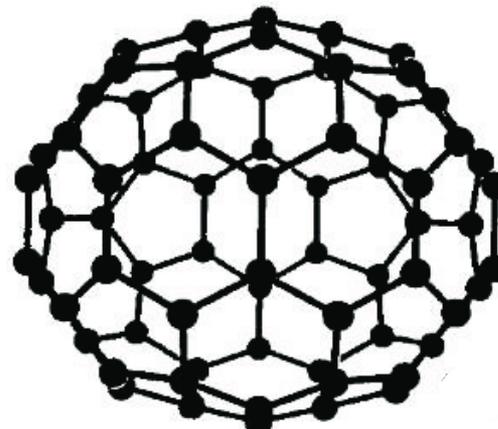
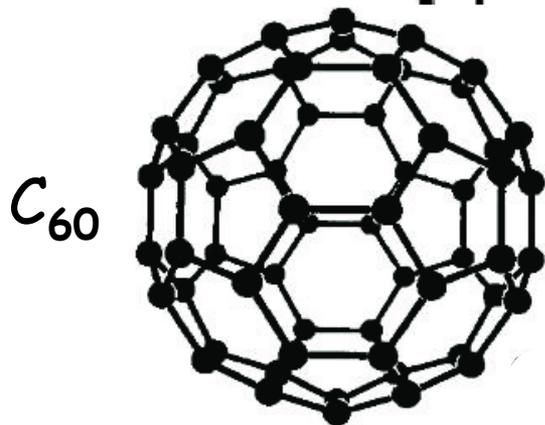
C_{70}

Come si prepara il fullerene C_{60} ?

Krättschmer, W., Lamb, L., Fostiropoulos, K., Huffman, D. R., "Solid C_{60} : a new form of carbon" *Nature* **1990**, 347, 354–358.



C_{60} and other fullerenes are now routinely made by a **low pressure method** in which an electric discharge is passed across the gap between 2 **graphite electrodes** in a **helium atmosphere (100 torr)**. The resulting soot is collected and mixed with a solvent such as benzene; the fullerenes dissolve, are extracted, then separated by chromatography.



C_{70}



Tutte le immagini (2)

Documenti

[↓ SDS](#)

[🔍 CdO/CdA](#)

[📄 Scheda delle specifiche](#)

379646 ▶ **Sigma-Aldrich**

Fullerene-C₆₀

99.5%

Sinonimo/i:

Buckminsterfullerene

Empirical Formula (Hill Notation):

C₆₀

Numero CAS: **99685-96-8**

Peso molecolare: 720.64

Beilstein:

Numero MDL: **MFCD00151408**

NACRES: NA.23

SKU	Taglio della confezione	Disponibilità	Prezzo
379646-1G	1 G	✓ Spedizione prevista il 15 novembre 2021 - DA	221,00 €
379646-5G	5 G	✓ Spedizione prevista il 15 novembre 2021 - DA	705,00 €



Tutte le immagini (2)

Documenti

[↓ SDS](#)

[🔍 CdO/CdA](#)

[📄 Scheda delle specifiche](#)

482994 ▶ **Sigma-Aldrich.**

[5,6]-Fullerene-C₇₀

98%

Sinonimo/i:

Buckminsterfullerene C₇₀, Fullerene-C₇₀

Empirical Formula (Hill Notation):

C₇₀

Numero CAS: **115383-22-7**

ID PubChem: **24871859**

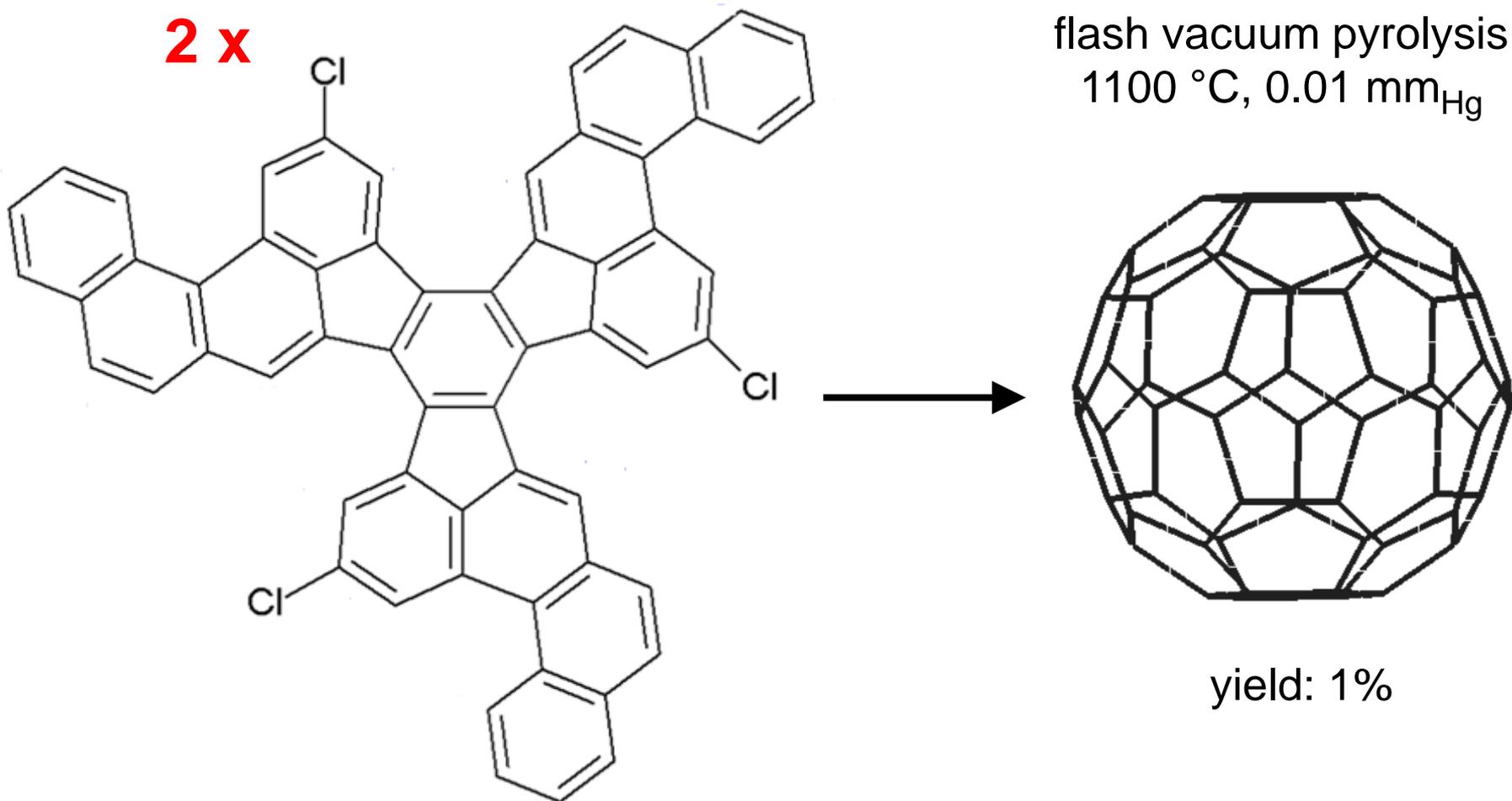
Peso molecolare: 840.75

NACRES: NA.23

Numero MDL:

SKU	Taglio della confezione	Disponibilità	Prezzo
482994-100MG	100 MG	 Spedizione prevista il 15 novembre 2021 - DA	141,00 €
482994-500MG	500 MG	 Spedizione prevista il 15 novembre 2021 - DA	465,00 €

Si può preparare il C_{60} per sintesi organica?

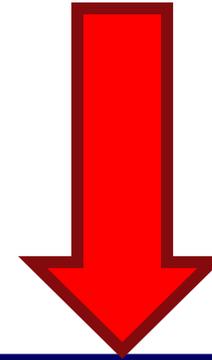


Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; De Meijere, A. "A Rational Chemical Synthesis of C_{60} ", *Science* **2002**, 295, 1500–1503.

I due paradigmi per la preparazione delle nanoparticelle

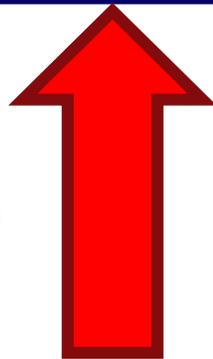
*materiale
macroscopico*

top-down

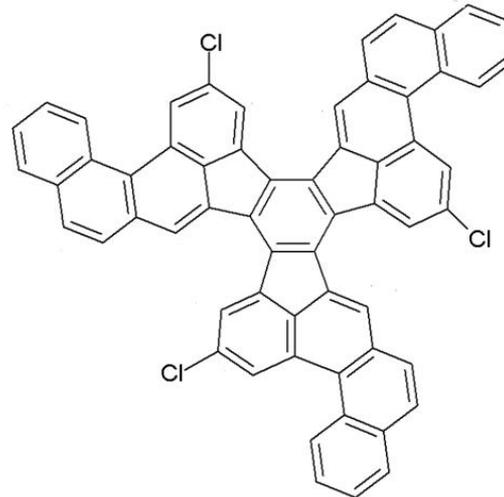


nanoparticelle

bottom-up



*atomi e
molecole*

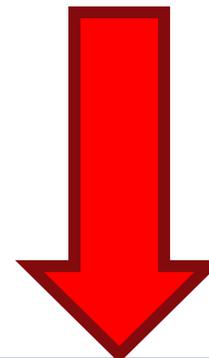


Faraday conosceva i due paradigmi?

*materiale
macroscopico*

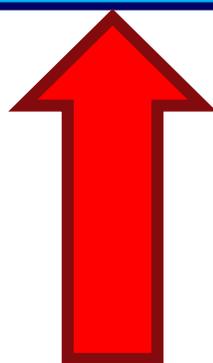


top-down

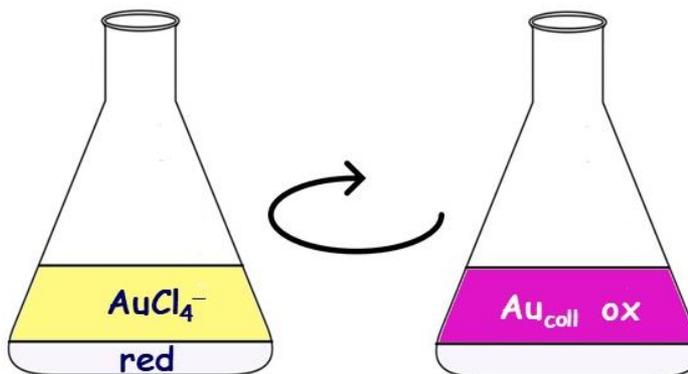


nanoparticelle

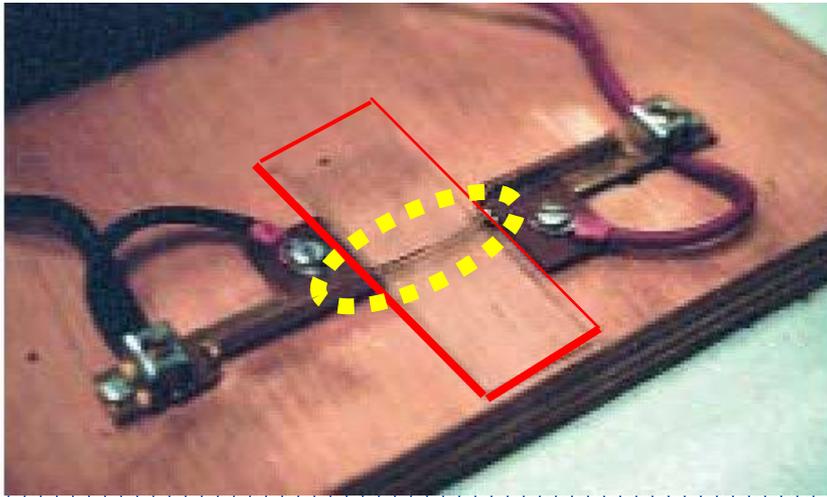
bottom-up



*atomi e
molecole*



Deflagrazione di un filo di oro sottoposto a scarica elettrica



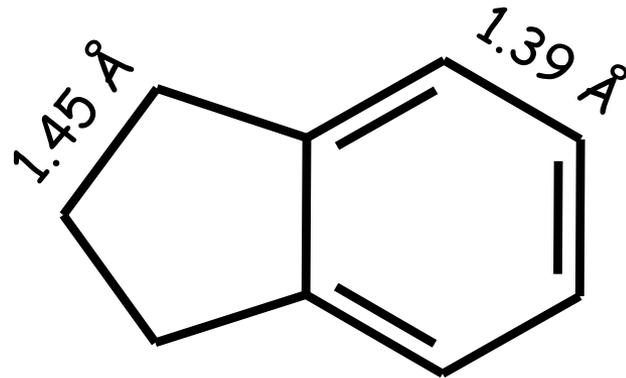
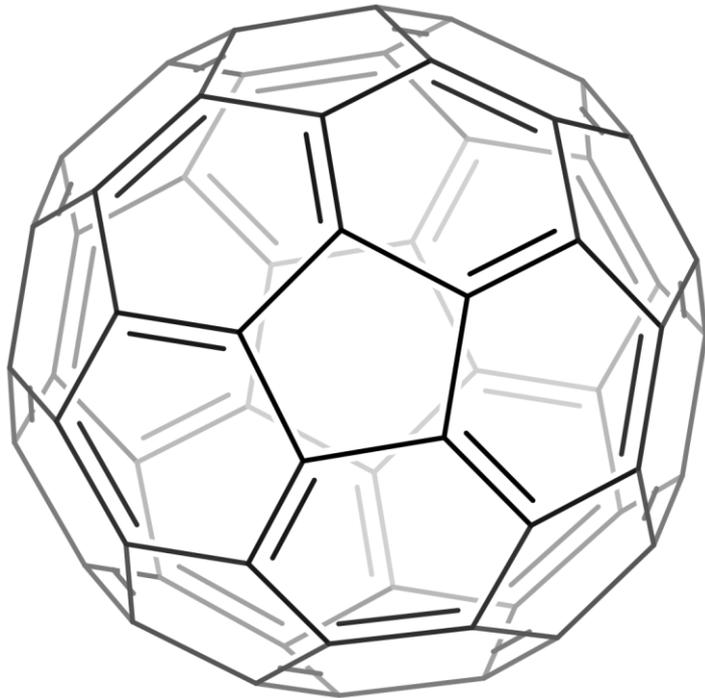
Faraday's deflagration apparatus. The gold wire (center) is mounted above a glass slide and connected to a battery of 6 Leyden jars (in parallel). [Courtesy of the Royal Institution].



One of Faraday's "deflagrations" (No. 321, Faraday's numbering). [Courtesy of the Royal Institution].

Esiste una chimica del fullerene?

Reattività tipica di poliolefine localizzate ed elettrone-deficienti più che di sistemi aromatici. La piramidalizzazione dei $C(sp^2)$ introduce forti tensioni e il rilascio di queste tensioni sta alla base della reattività dei fullerene (ca. 80% del $\Delta H^\circ_{\text{react}}$).



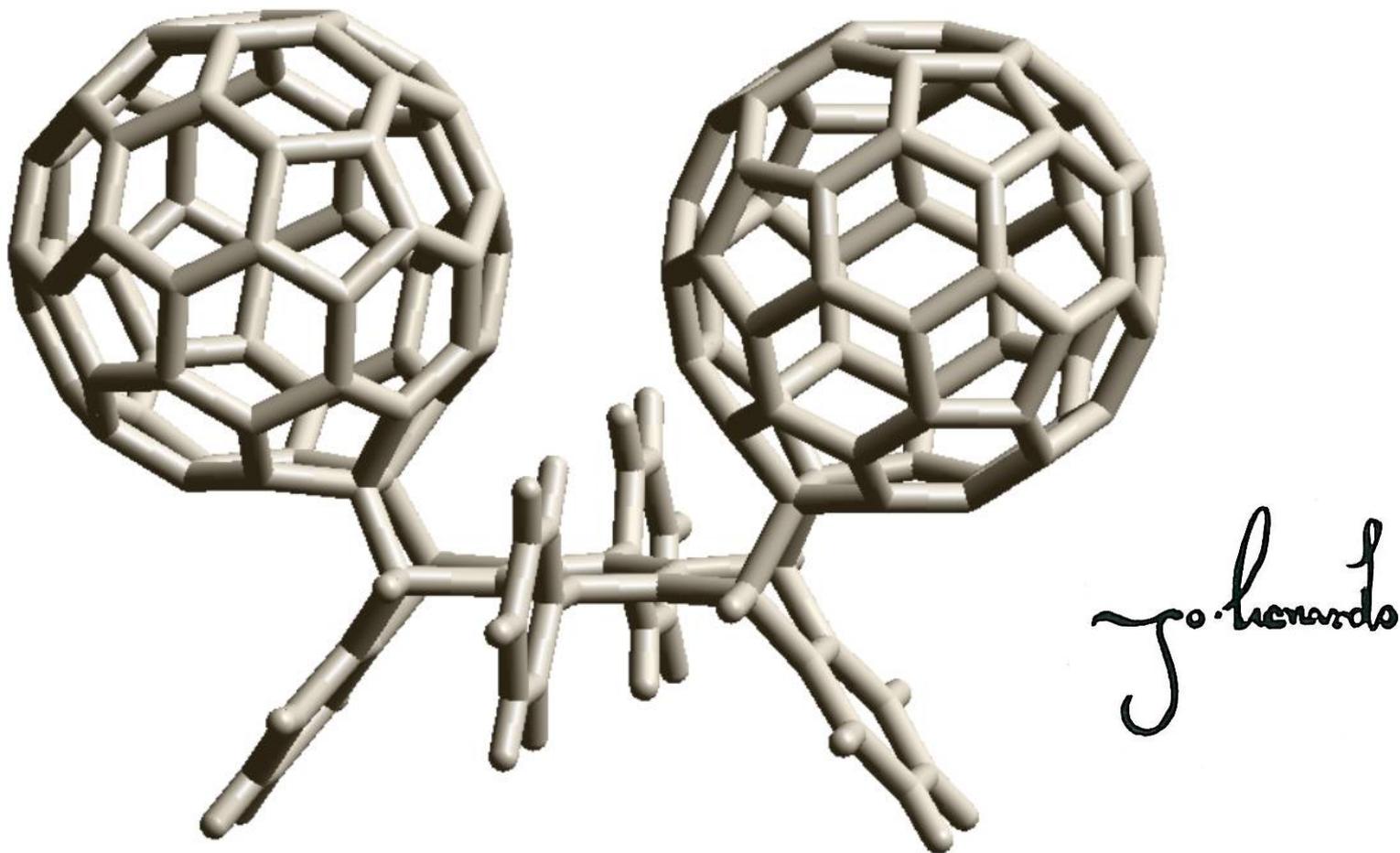
C—C singolo 1.54 Å

C=C doppio 1.33 Å

C \equiv C benzene 1.40 Å

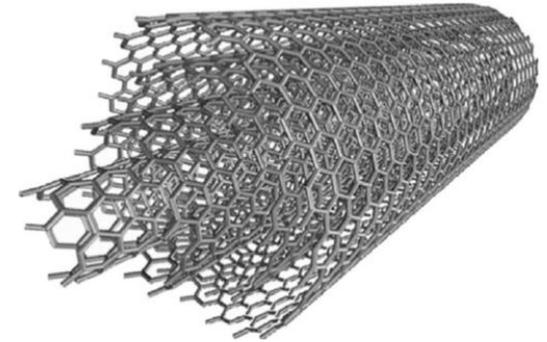
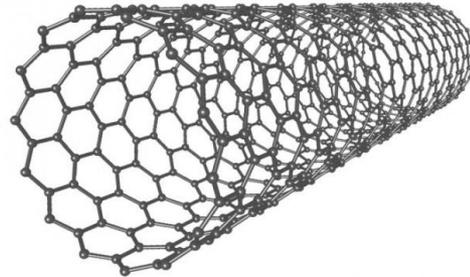
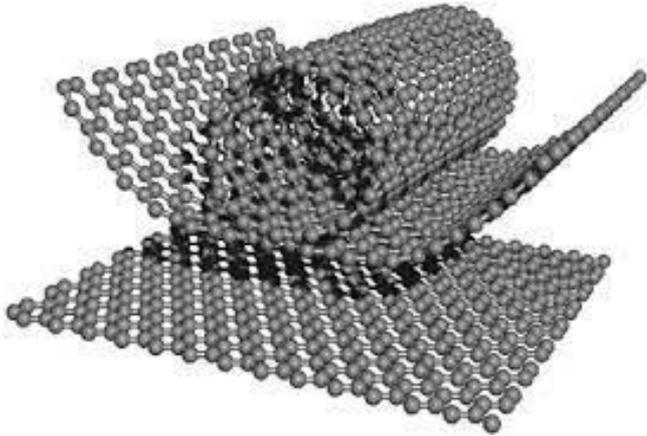
Reazioni: addizioni nucleofile, reazioni pericicliche, idrogenazioni, ossidazioni, idrossilazioni, reazioni di eliminazione, reazioni di Diels-Alder, addizioni radicaliche

Una doppia cicloaddizione di Diels-Alder di due C_{60} con 6,13-difenilpentacene a dare una molecola che sarebbe piaciuta anche a Leonardo

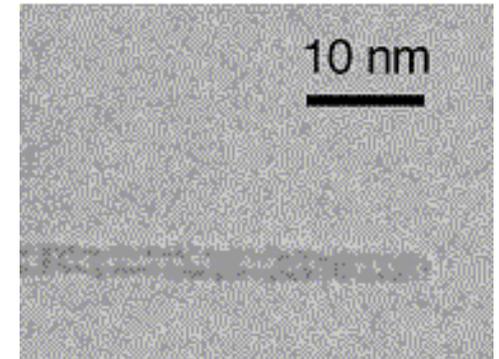


G. P. Miller, J. Briggs, J. Mack, P. A. Lord, M. M. Olmstead, and A. L. Balch, Fullerene-Acene Chemistry: Single-Crystal X-ray Structures for a [60]Fullerene-Pentacene Monoadduct and a *cis*-Bis[60]fullerene Adduct of 6,13-Diphenylpentacene, *Org. Lett.* **2003**, *5*, 4199–4202

I nanotubi. Un'altra forma allotropica del carbonio, struttura cilindrica, virtualmente monodimensionale, formalmente ottenuta dall'avvolgimento di uno o più fogli di grafite (di grafene).

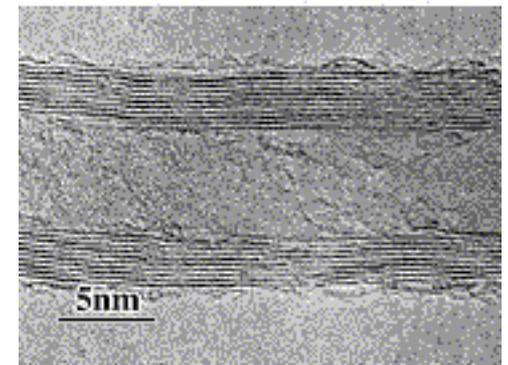
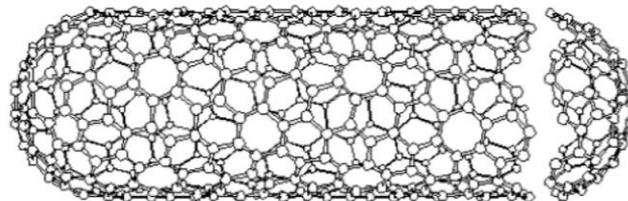


I nanotubi a parete singola. Diametro tra 0.7 e 10 nm, in genere < 2 nm. Lunghezza da pochi nm a mm. Ne consegue un elevato rapporto lunghezza/diametro ($\approx 10^4$): per questo i nanotubi possono essere considerati delle strutture *quasi monodimensionali*.



I nanotubi a parete multipla. Costituiti da più cilindri concentrici. Diametro fino a 100 nm.

Sono chiusi alle estremità da calotte emisferiche di tipo fullerenico



1980

← **1985** Il fullerene: Kroto et al. *Nature* **1985**, 318, 162–163.

1990

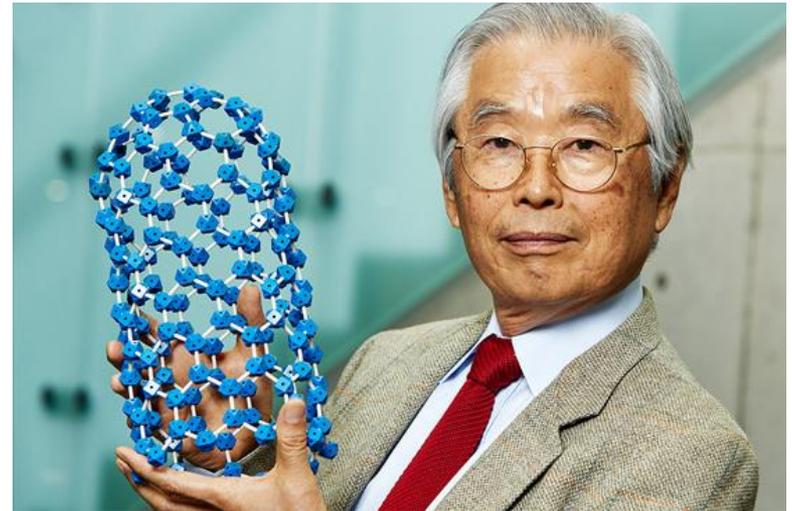
← **1991** I nanotubi: Iijima, *Nature* **1991**, 354, 56–58.

2000

Sumio Iijima (1939-)
Fisico
NEC Corporation
Meijo University

2010

2020



Iijima, S., Helical microtubules of graphitic carbon, *Nature* 1991, 354, 56-58.

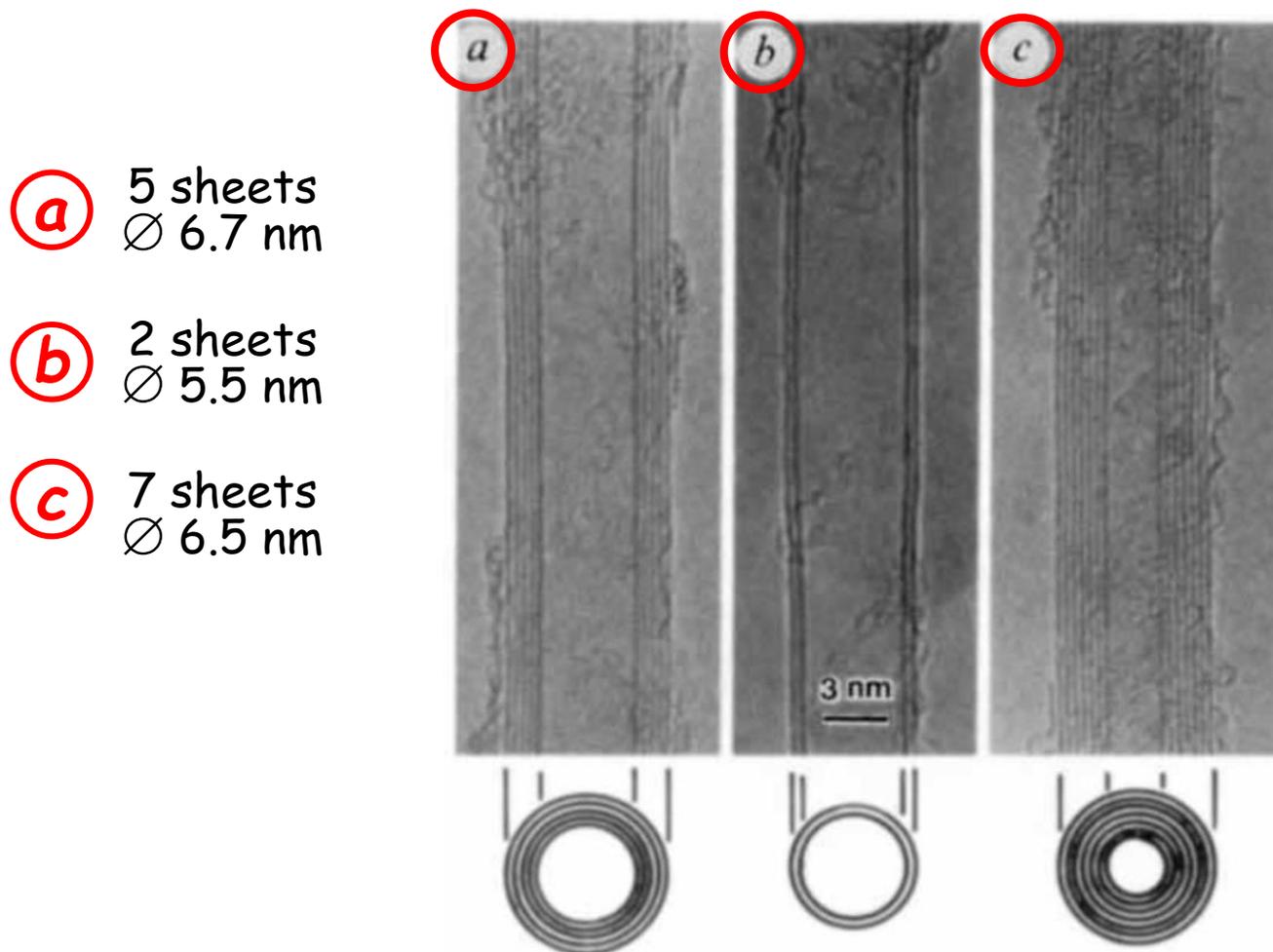
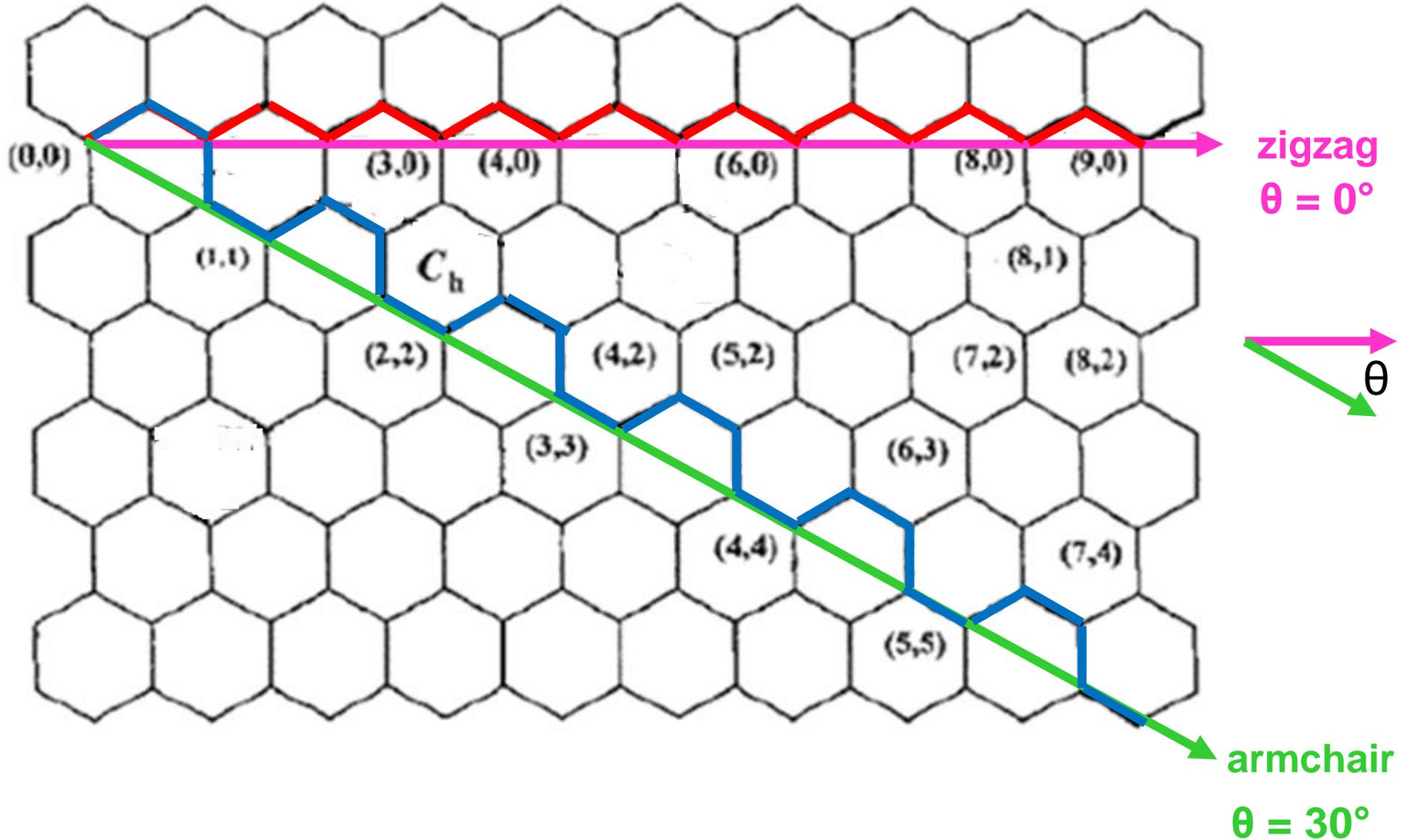
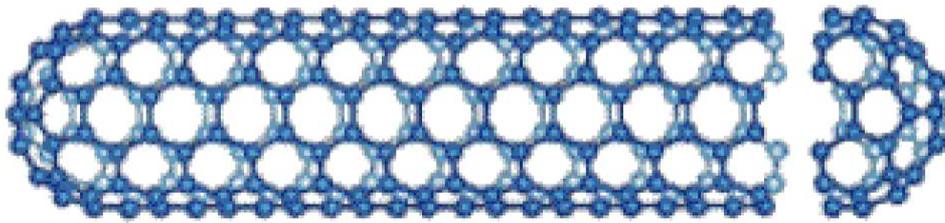


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet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

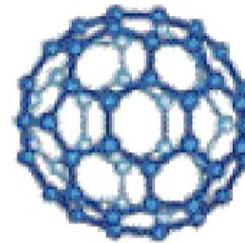
Un foglio di grafene si può avvolgere in due modi limite: 1. in maniera parallela all'asse del rotolo (detta a zigzag); 2. in maniera obliqua (detta a armchair). Le due forme hanno proprietà fisiche diverse.



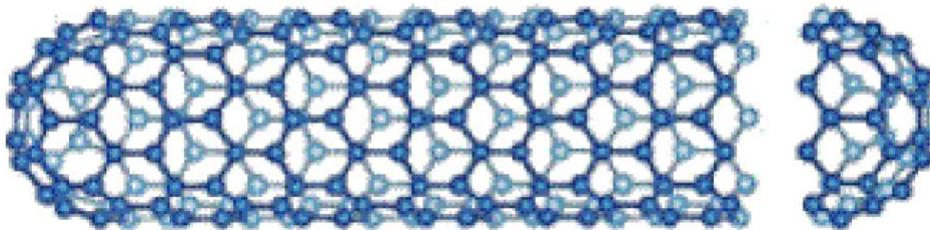


armchair nanotube $\theta = 30^\circ$

conduttore metallico

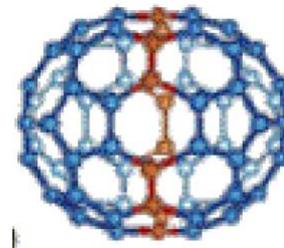


C_{60}



zigzag nanotube $\theta = 0^\circ$

semiconduttore



C_{70}

Nanoparticelle: il favorevole rapporto superficie/volume

$$S = 4\pi r^2$$

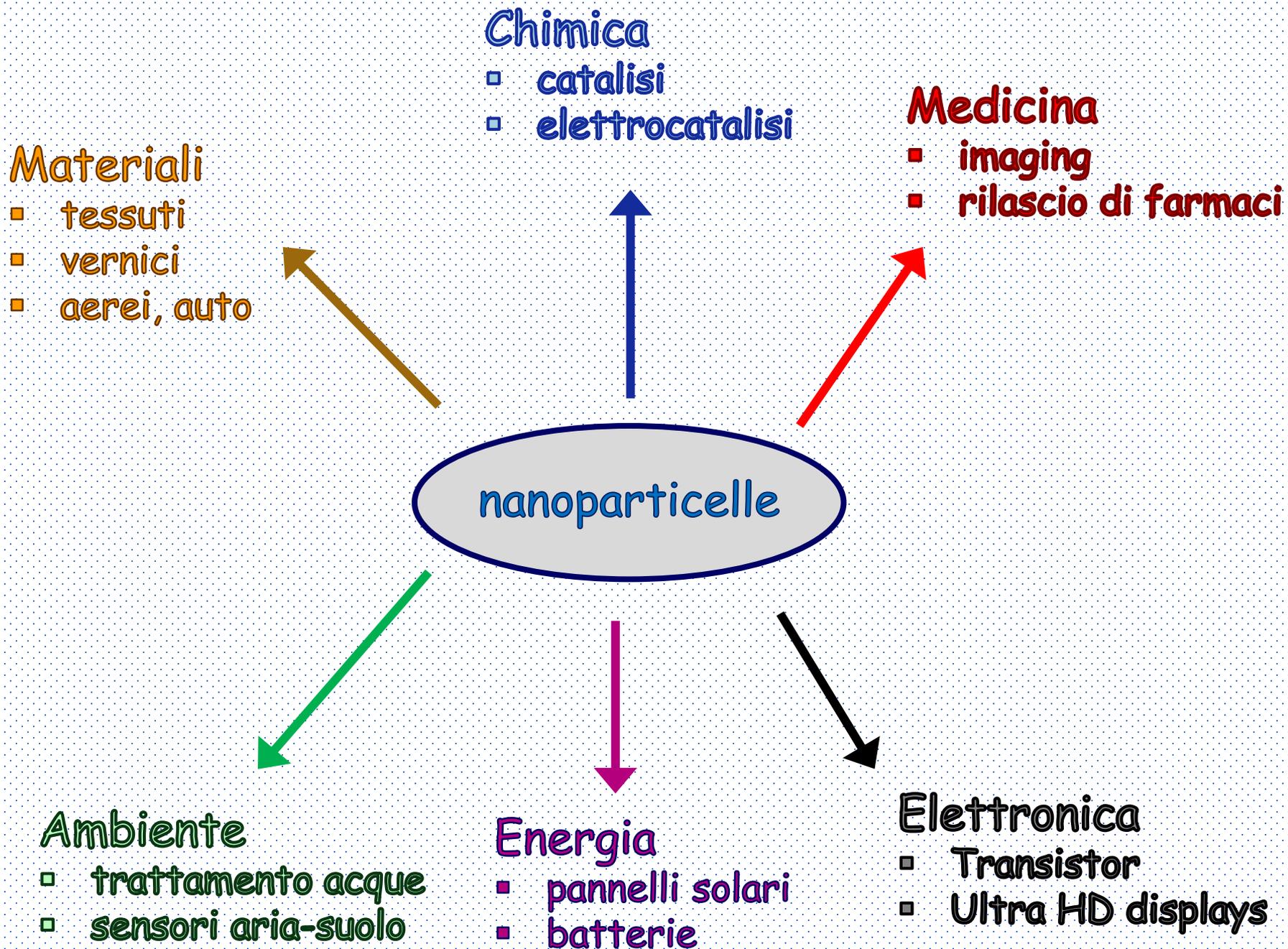
$$V = \frac{4}{3}\pi r^3$$

$$\frac{S}{V} = \frac{3}{r}$$

	raggio, nm	S/V, nm ⁻¹
	1	3
	10	0.3
	100	0.03
1 μm	1000	0.003
	10000	0.0003
	100000	0.00003
1 mm	1000000	0.000003
	10000000	0.0000003
	100000000	0.00000003
1 m	1000000000	0.000000003



1 kg di granuli del volume di 1 mm³
ha la stessa superficie di 1 mg di
nanoparticelle del volume di 1 nm³.





LA TAPPA NON E'
MICA FINITA, MA
D'ORA IN POI E'
TUTTA DISCESA