

CHEMISTRY

ON

SURFACES

SURFACES

B. L. V. Prasad and Team
National Chemical Laboratory

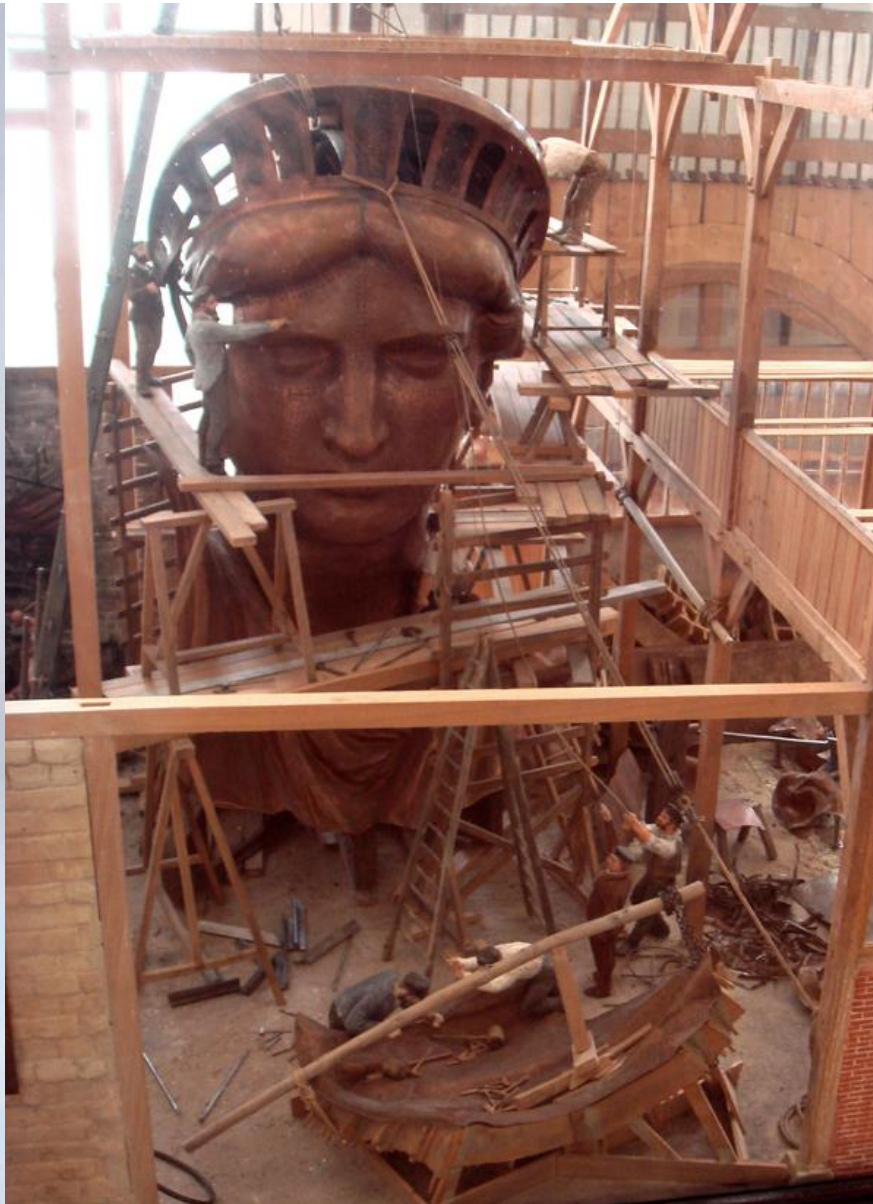
What is Surface?



IUPAC Definition:

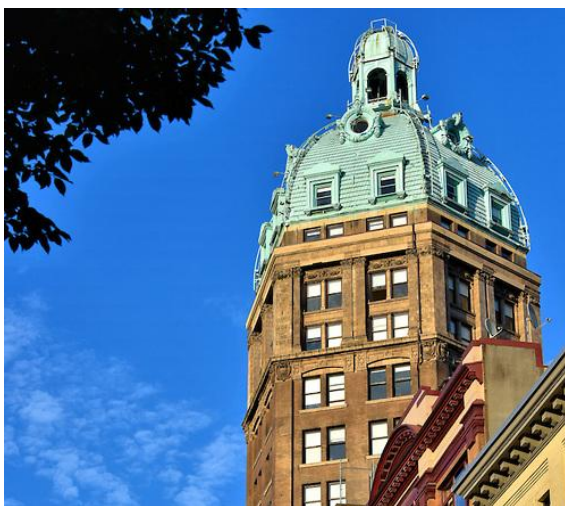
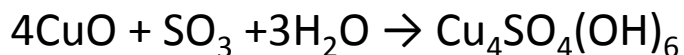
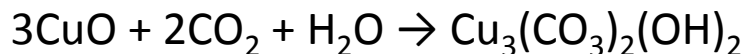
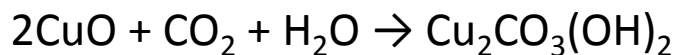
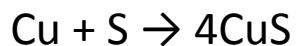
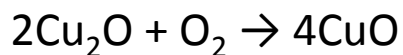
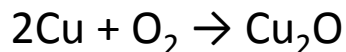
A boundary between two phases is called a ***surface*** or ***interface***. The two words are often used synonymously, although interface is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly, e.g. the solid/gas interface. On the other hand if we are referring to only one phase we say surface e.g. the surface of a solid.

Why should we care about surfaces?

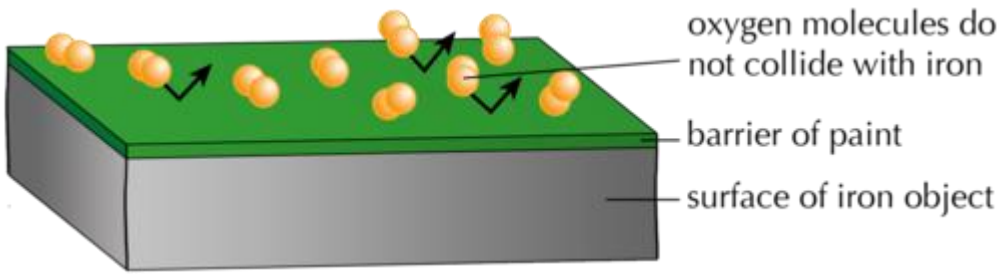
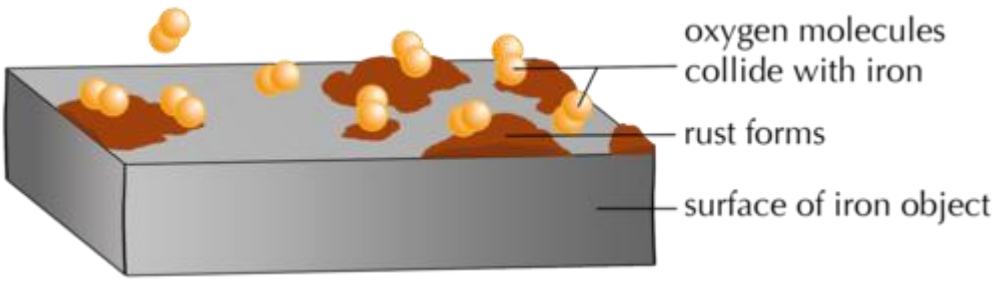


Then how did the Statue of Liberty turn green?

The Statue of Liberty gets its blue-green color from patina formed on its copper surface mainly through oxidation along with several other chemical reactions. The main constituent of patina contains a mixture of 3 compounds: $\text{Cu}_4\text{SO}_4(\text{OH})_6$ in green; $\text{Cu}_2\text{CO}_3(\text{OH})_2$ in green; and $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ in blue. The following reactions are involved.



What would have happened if Statue of Liberty was made of iron?



To Do

1. What other metals/materials are protected by native oxide from further corrosion/rusting?
2. What other metals/materials are not protected by native oxide from corrosion/rusting?

<http://www.instructionbooks.co.za/natural-sciences/g9/g9-nm-09.html>

What way we can protect these metals from further damage?



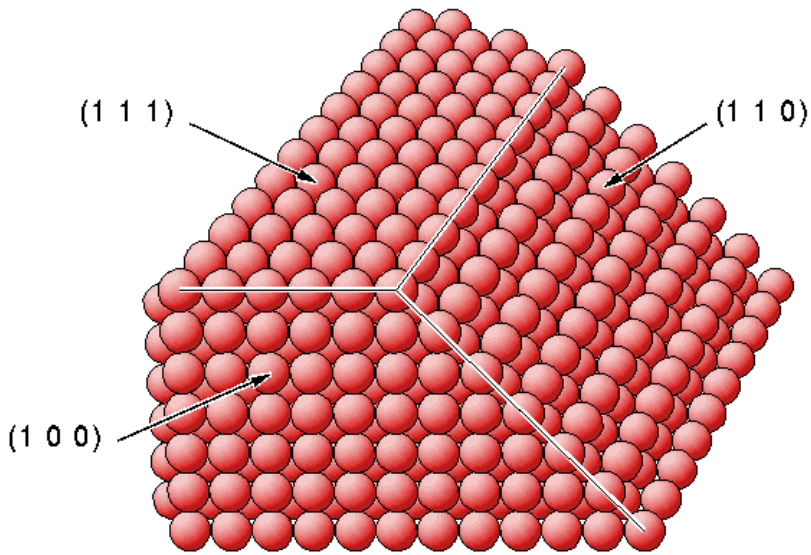
<https://www.youtube.com/watch?v=EqMJMifNTIs>



To Do

1. Read more about Delhi iron pillar. Why it doesn't get rusted?
2. What is electroplating? Can you do it at home??

Okay surfaces are different, but why?

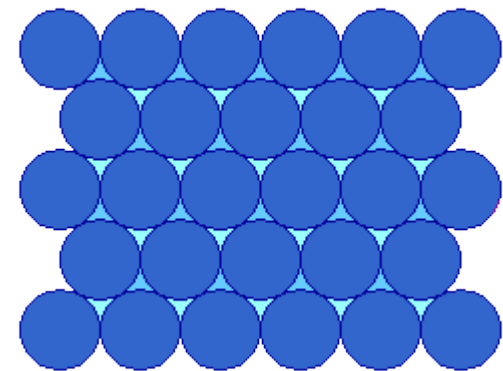


fcc lattice : different net planes

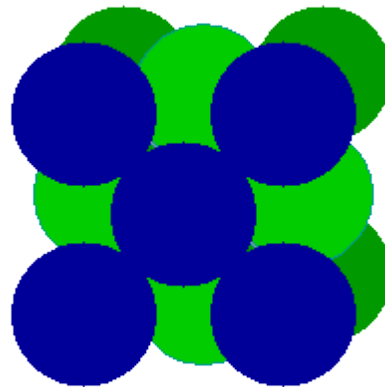
REACTIVITY

➤ The surface atoms that have less number of nearest neighbours feel unsatisfied.

➤ So crystal planes having such becomes more reactive.

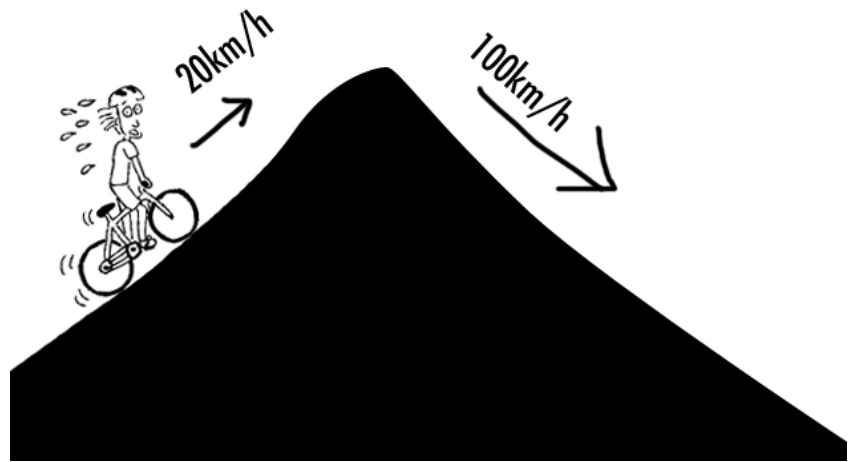
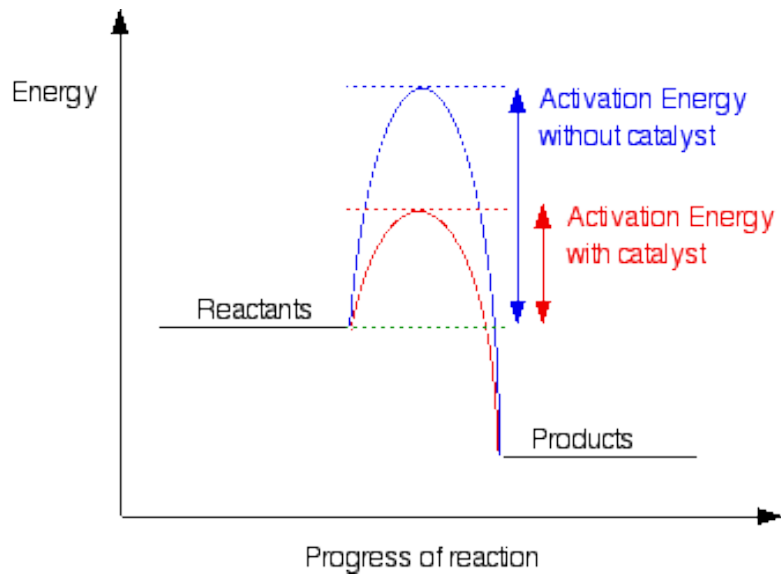


111 plane



100 plane

➤ We use such reactive metal species as catalysts.



Catalyst: a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.



Let's do one catalysis experiment



<https://www.youtube.com/watch?v=UTfMrx7275w>



https://www.youtube.com/watch?v=o1_D4FscMnU

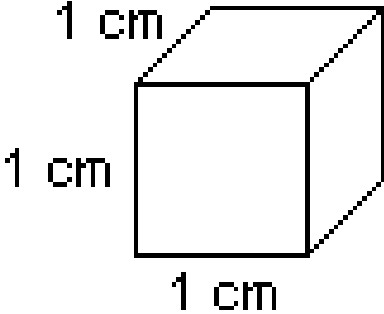
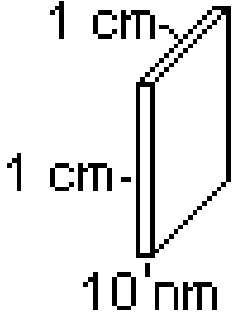
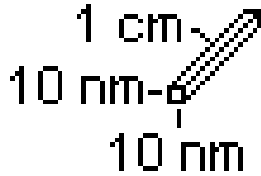
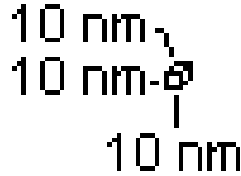
https://www.youtube.com/watch?v=uMkzxV_y7tY



What was the most important discovery of last century?

1. Internet
2. Mobile phone
3. $E = mc^2$
4. None of the above

How to improve the catalyst's efficiency?

	State of Subdivision			
	mass	laminated	fibrillar	corpuseular
				
N	1	10^6	10^{12}	10^{18}
A_1, m^2	6×10^{-4}	2×10^{-4}	4×10^{-10}	6×10^{-16}
A, m^2	6×10^{-4}	200	400	600

State of Subdivision and Total Area

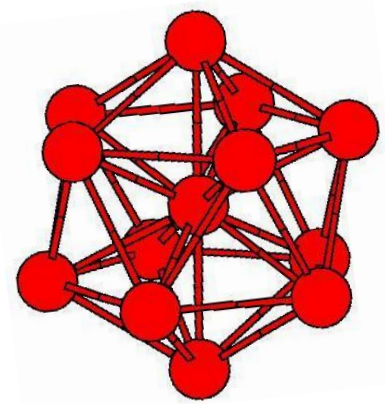
Why smaller particles behave better?

$$T = \frac{10}{3}n^3 + 5n^2 + \frac{11}{3}n + 1$$

$$n \geq 0$$

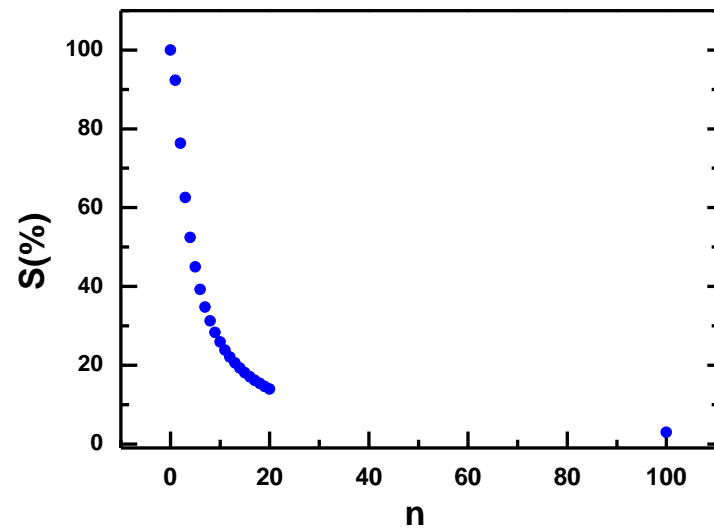
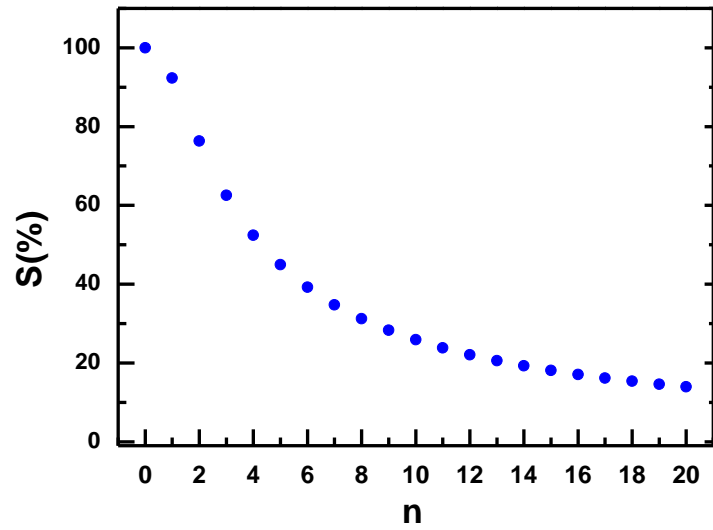
$$S = 10n^2 + 2$$

$$n \geq 1$$



N = shell number
 T = total number of atoms
 S = atoms on surface

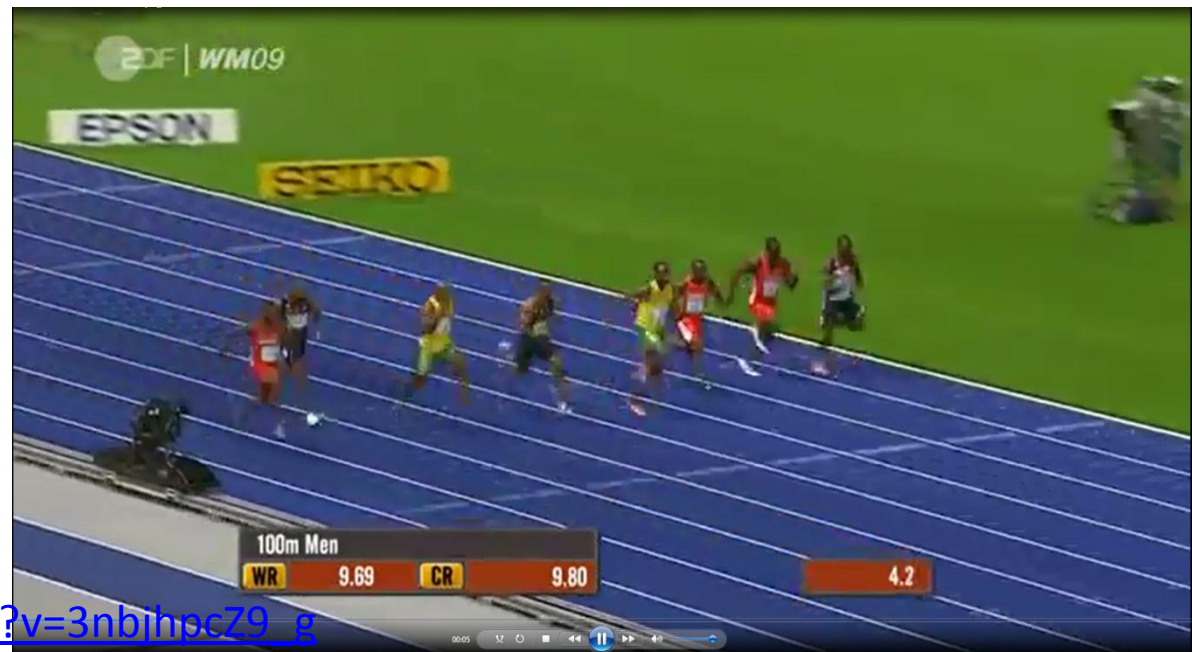
n	T	S	%S
0	1	1	100
1	13	12	92.3
2	55	42	76.3
3	147	92	62.5
4	309	162	52.4
5	561	252	44.9
6	923	362	39.2
7	1415	492	34.7
8	2057	642	31.2
9	2869	812	28.3
10	3871	1002	25.8
11	5083	1212	23.8
12	6525	1442	22.0
13	8217	1692	20.5
14	10179	1962	19.2
15	12431	2252	18.1
16	14993	2562	17.0
17	17885	2892	16.1
18	21127	3242	15.3
19	24739	3612	14.6
20	28741	4002	13.9
100	3.3837E6	100002	2.9554



Other applications of surface interactions



<https://www.youtube.com/watch?v=0m8bWKHmRMM&t=5s>



https://www.youtube.com/watch?v=3nbjhpzc79_g

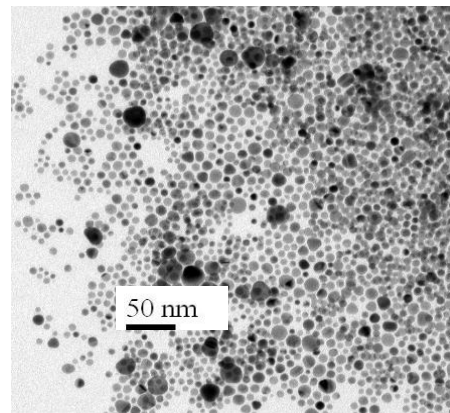
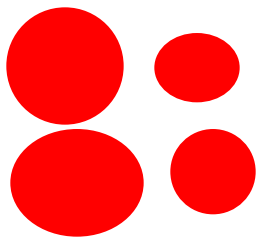
Any other?



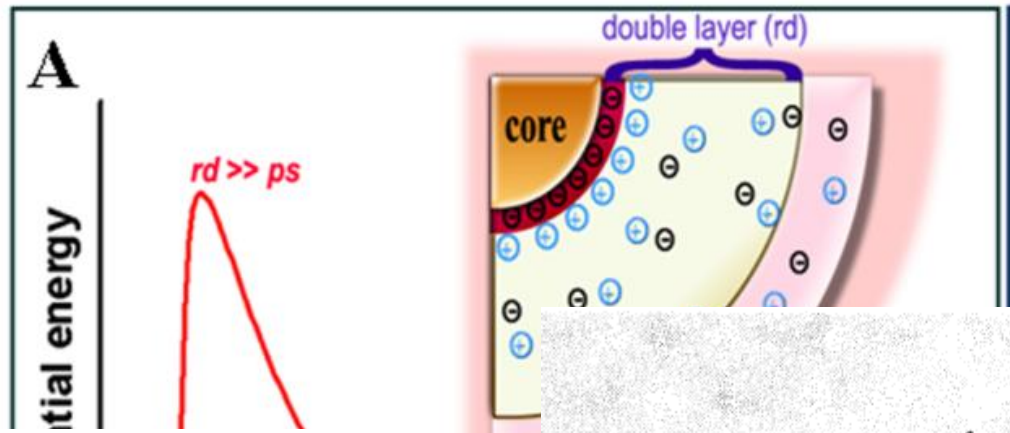
Metal ions
(in water)



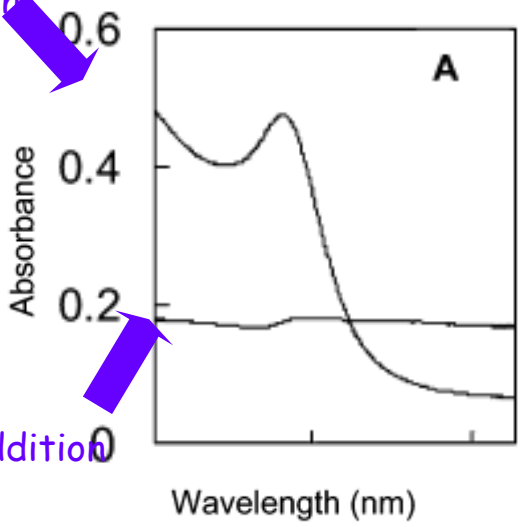
Reduction



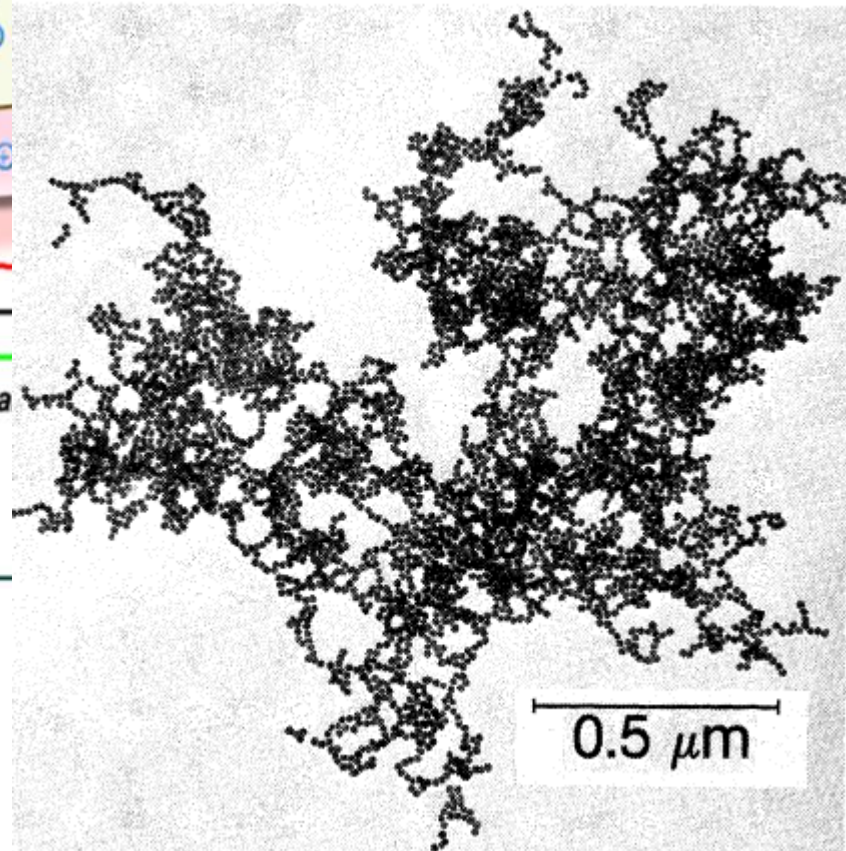
Aqueous (citrate, bio synthesis etc.)
Turkevich et al J. Discuss. Faraday Soc.
1951, 11, 55.



Before salt addition



after salt addition



"Naked to protected" state



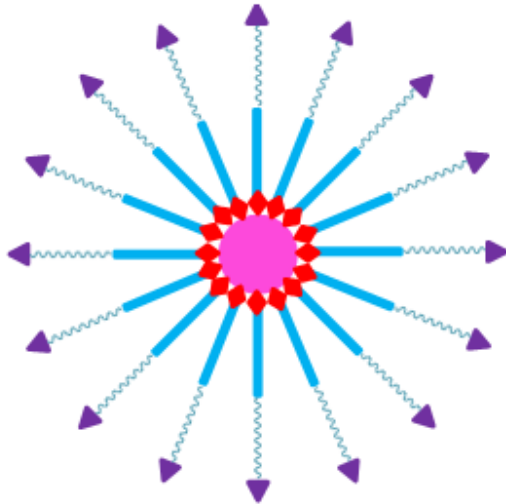
"Dress" consciousness



"Dress" consciousness



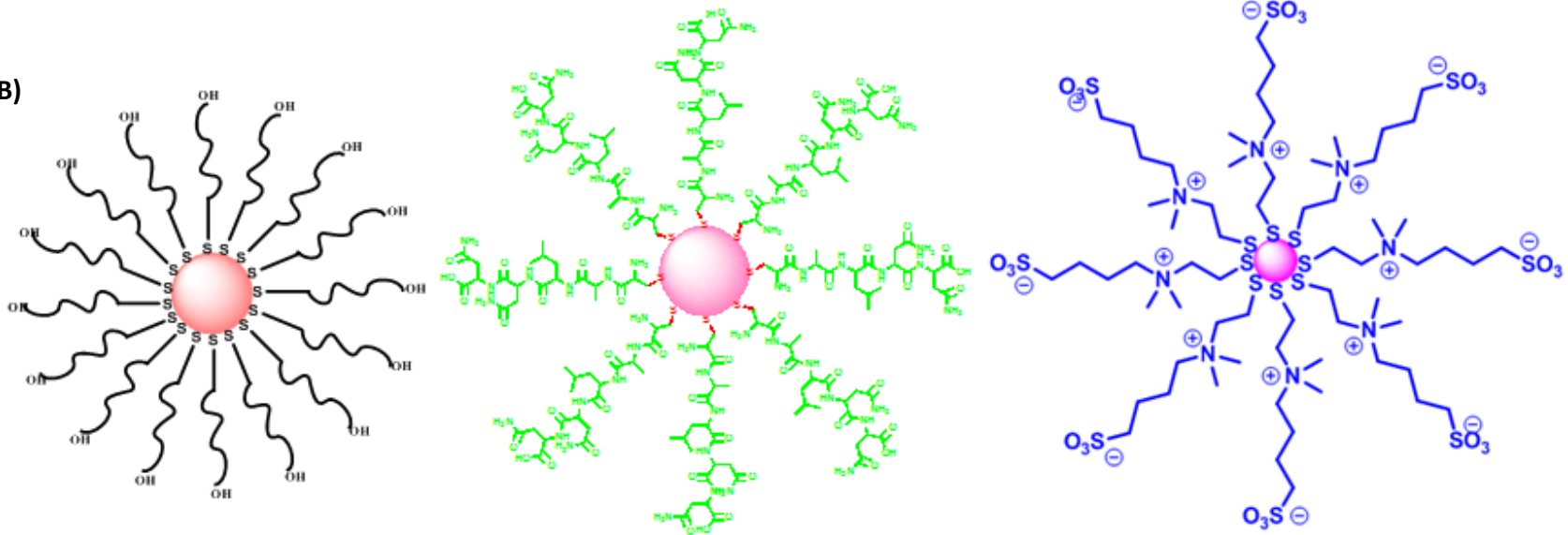
(A)



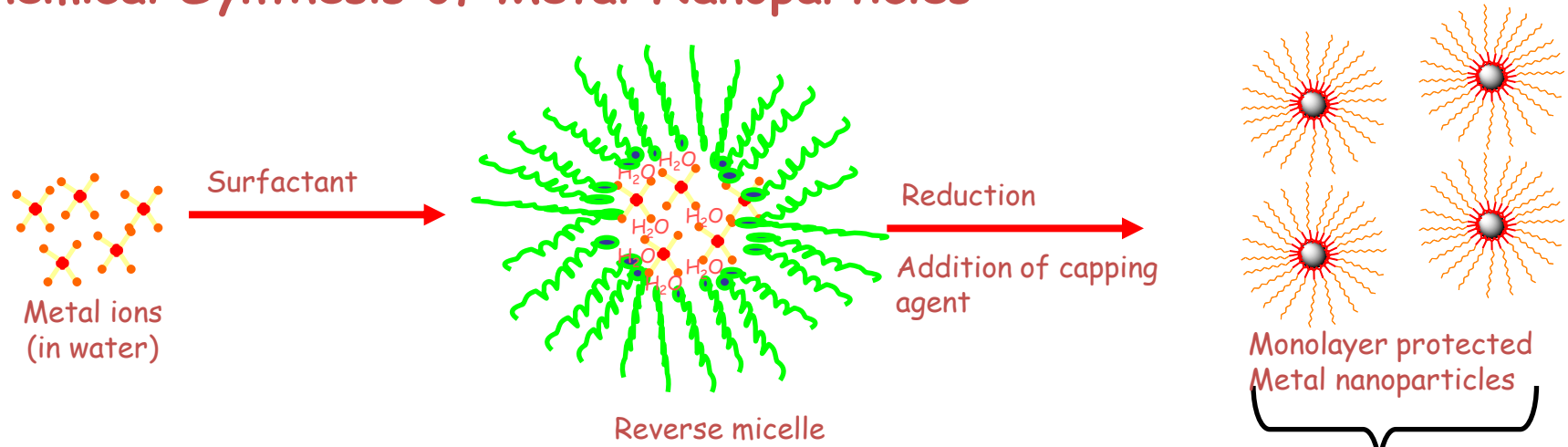
▲=Exposed functional group ($-\text{SO}_3^-$, $+\text{NH}_3$, $-\text{COOH}$ etc.) which directs dispersion stability in aqueous media

◆=Head functional group ($-\text{SH}$, NH_2 etc.) which is attached to metal surface.

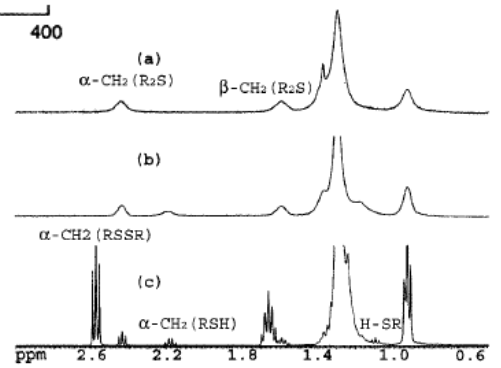
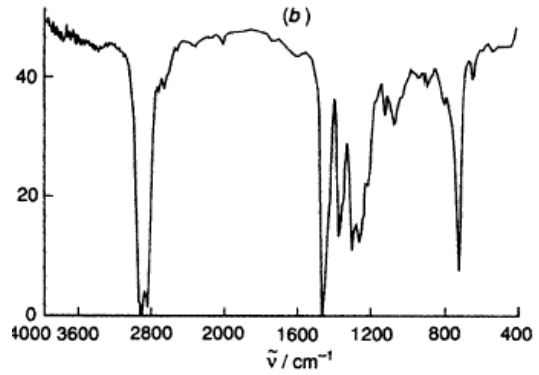
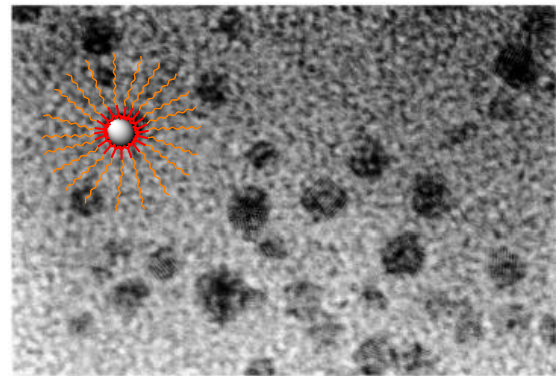
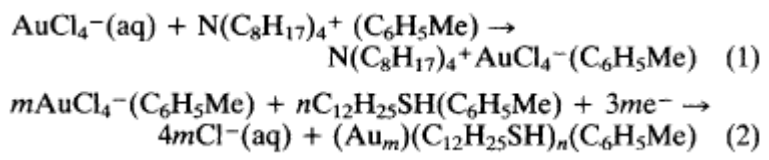
(B)



Chemical Synthesis of Metal Nanoparticles



Organic (Brust-Schiffrin method, reverse micelle process etc.) Brust et. al. 1994, Chem. Commun. 801.



"Appropriate" dresses



Mountaineer

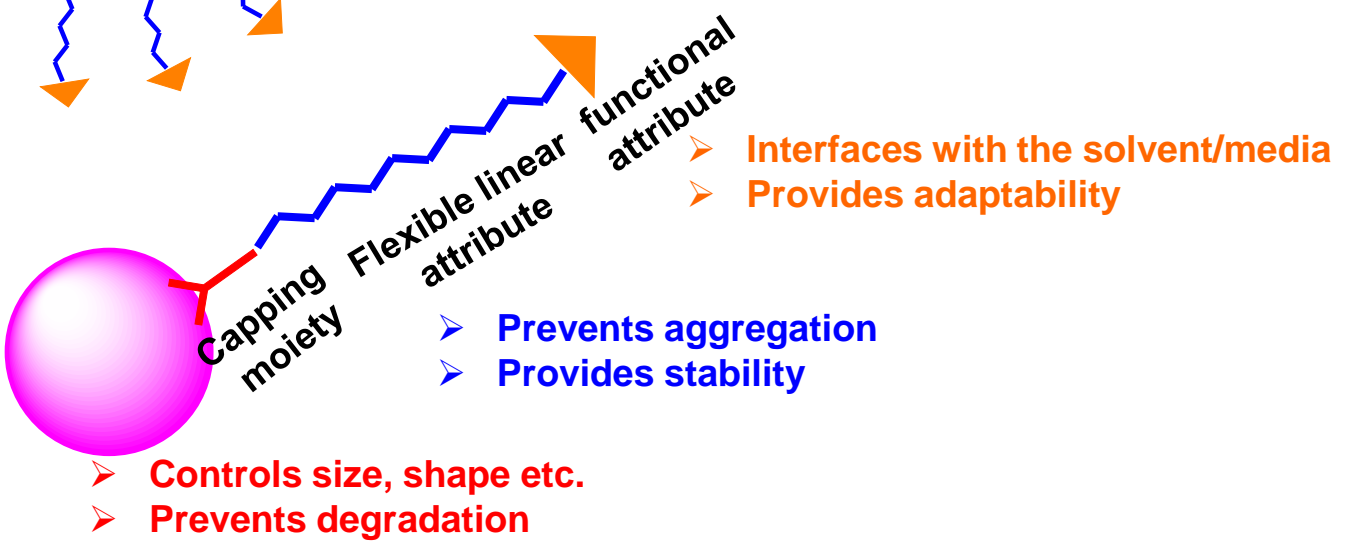
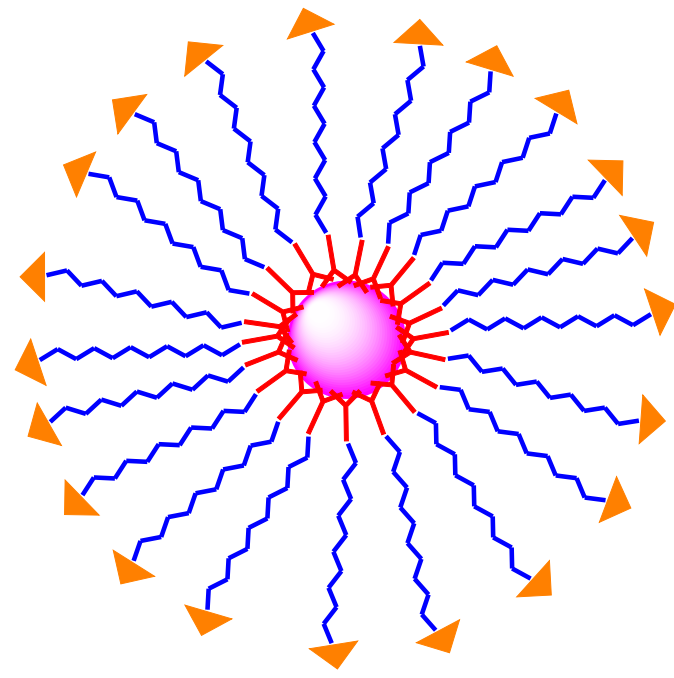


Soldier

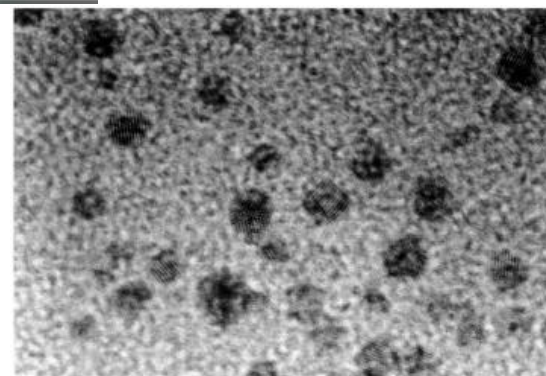
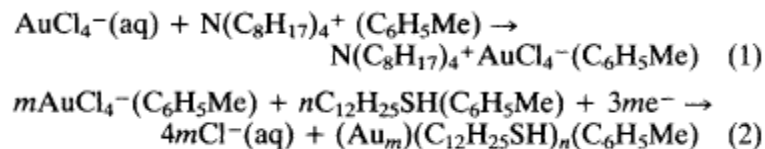


Bridegroom

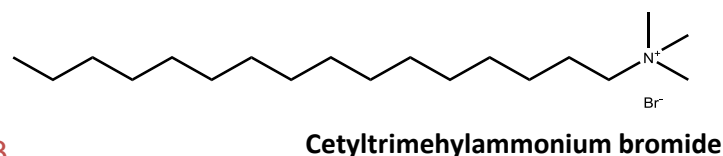
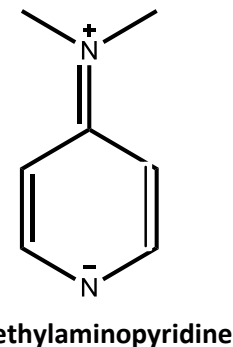
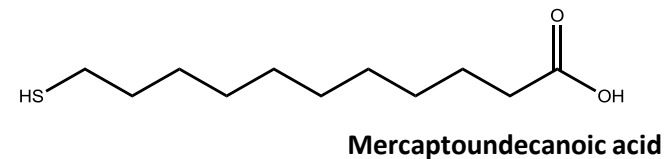
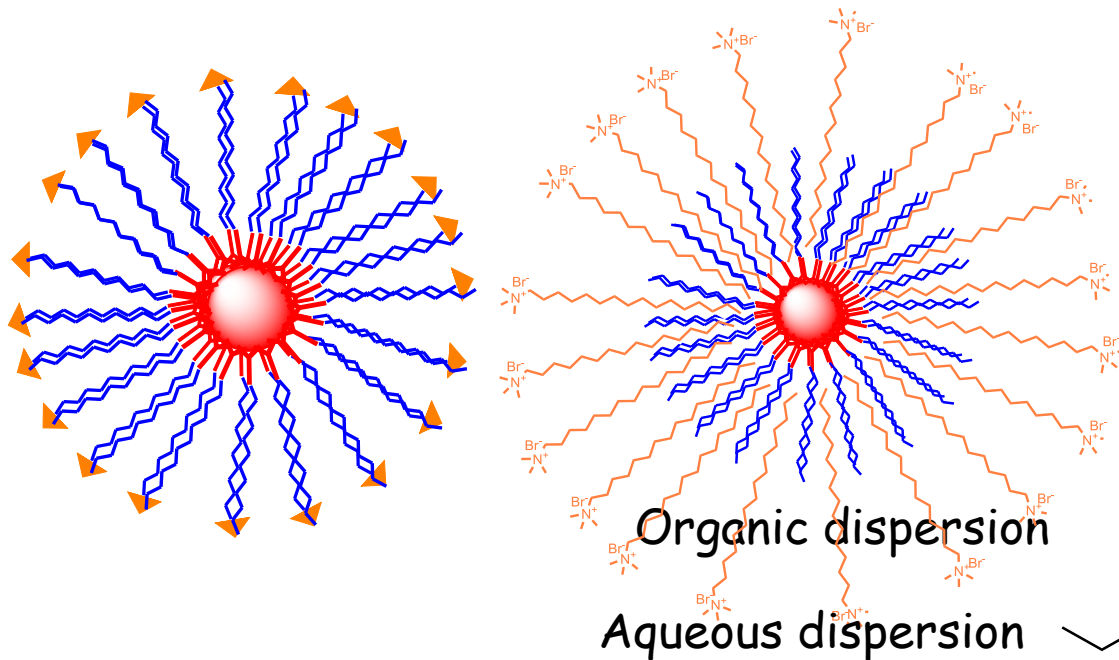
Nanomaterial synthesis/modifications - role of molecular tools



Synthesis of nanoparticles in organic media and their transfer to aqueous media



M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *Chem. Commun.* 1994, 801



J. Simard, C. Briggs, A. K. Boal, V. M. Rotello, *Chem. Commun.* 2000, 1943

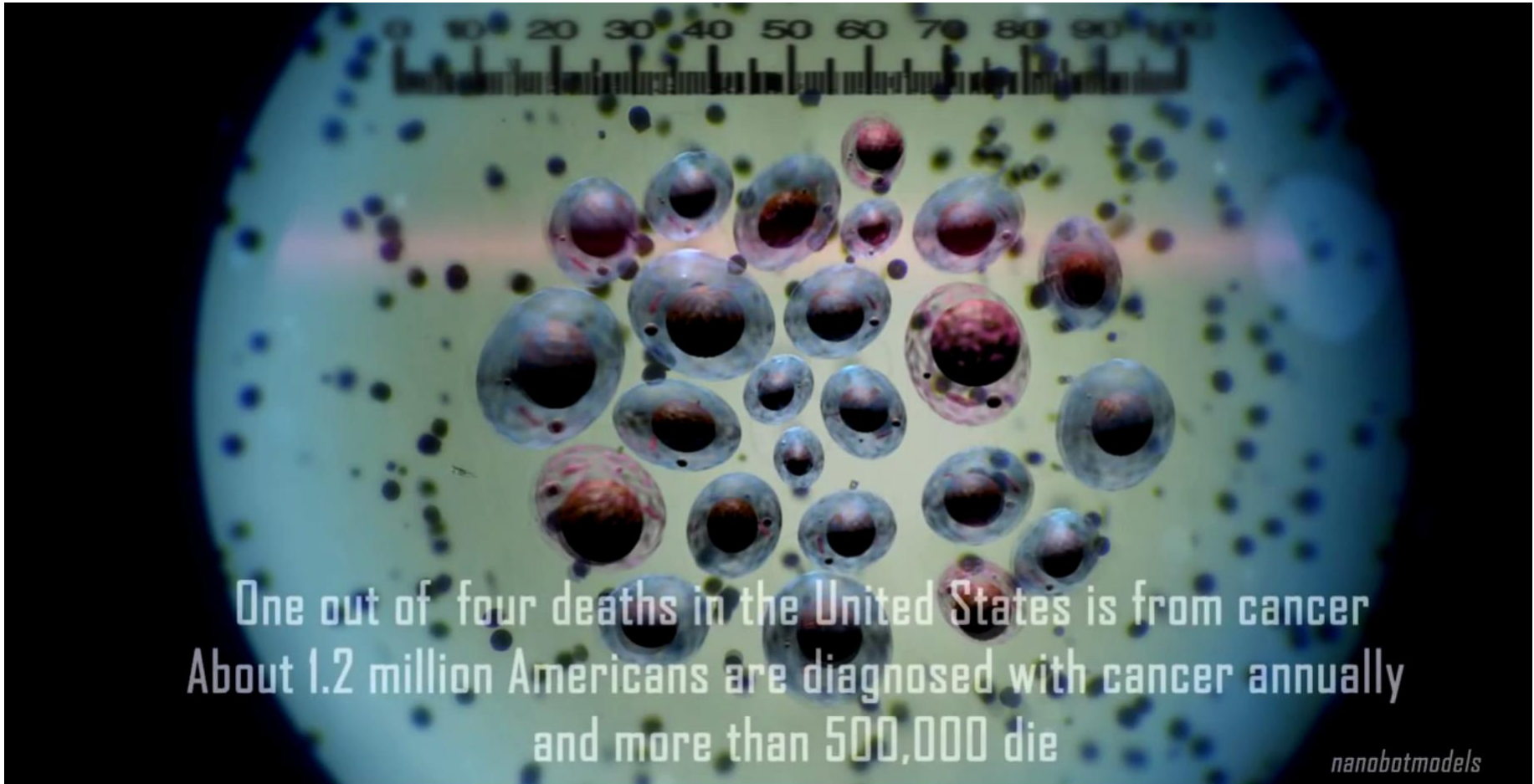
D. I. Gittins and F. Caruso, *Angew. Chem. Int. Ed.* 2001, 40, 3001

A. Swami, A. Kumar and M. Sastry, *Langmuir*, 2003, 19, 1168.

"Functional" Dresses



Targeted therapy



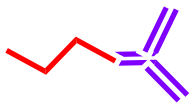
One out of four deaths in the United States is from cancer
About 1.2 million Americans are diagnosed with cancer annually
and more than 500,000 die

nanobotmodels

<https://www.youtube.com/watch?v=emEua2eJp1U>



= fluorescent label



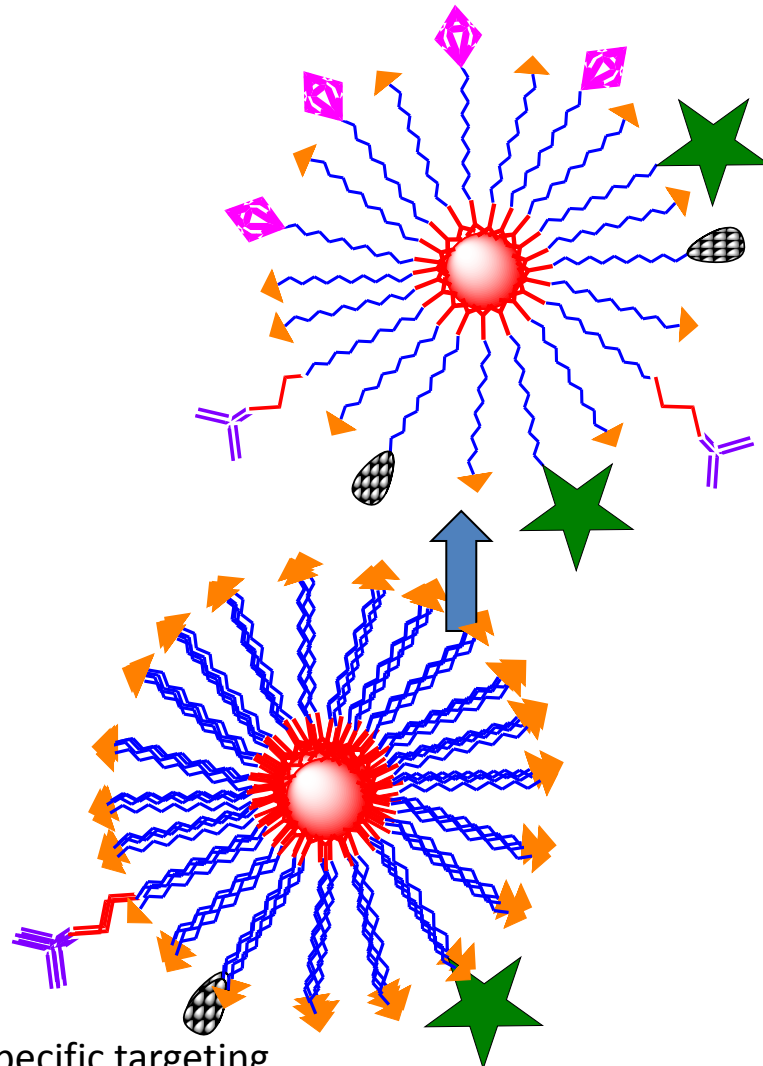
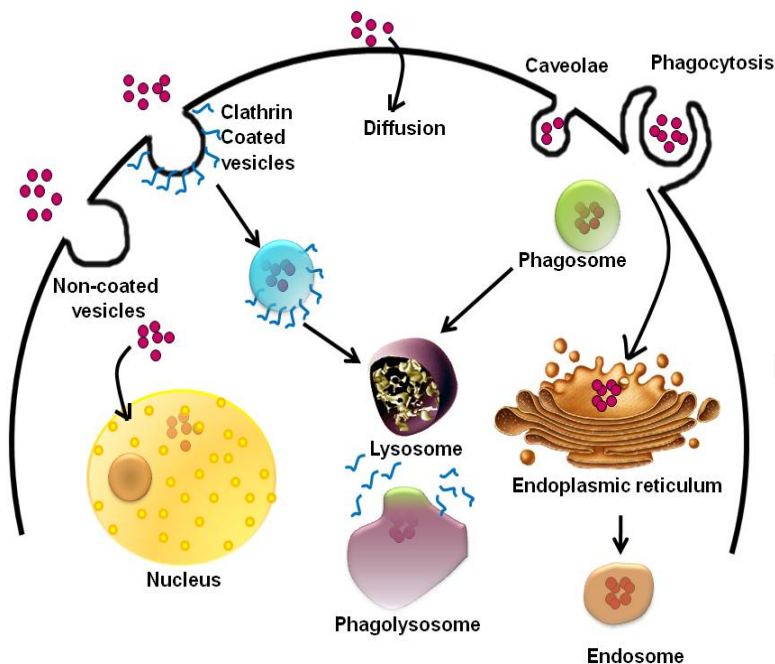
= antibody or other targeting molecule (eg. folic acid)



= molecules that assist preferential uptake (nutrients/BSA like proteins) etc.



= drugs



Highly specific targeting

Preferential uptake

Fluorescent labelling

Functionalized nanoparticles (aqueous dispersions)

- Better stability
- Higher retention
- Bio-compatibility

Chimreic nanoparticles

Chimera

The Chimera, according to Greek mythology, is a monstrous fire-breathing hybrid creature



Chimera



Mahakali

Thank you



Synthesis Assembly and Applications of Materials (SAAM) Group



Dr. Guruswamy Kumaraswamy



Dr. Arunarka Valli Turaga