Clusters as precursors of nano-objects

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Nano-particles

Since long ago man has used the properties of particulate materials in an empirical manner.

In the VIIIth century the Chinese discovered the « black powder », which later gave birth to fireworks, then to military uses about the year 1000, well before it was understood that the speed of the combustion was inversely proportional to the grain size.

Man created hand stencils by blowing pigments onto a hand against the wall, which has survived to the ages. (30000 years ago, grotte Chauvet)
Stained-glass for cathedrals

The origin of these colours, due to pigmented grains which are insoluble in their surroundings, was invoked by Michael Faraday (1791-1867) in 1853.

In 1907 Gustav Mie (1868-1957) explained the colours by showing how light in medium gets scattered by particles.
Nano-grains (of carbon) exist in interstellar medium.

Horse-head nebula in Orion cloud.

Anglo-Australian observatory
Clusters as precursors of nano-objects

In fact, it is only over the years that the idea has emerged of an object whose size, less than the length scale of characteristic to a physical phenomenon, gives it its original and unique properties.

• Optical response
• Reactivity

Deposition of clusters on surface for building new architectures
I. Total Mie extinction

Total Mie extinction (plasmon polariton)

- Dipolar mode
  - Absorption $A_1$
  - Scattering $S_1$
- Quadrupolar mode
  - Absorption $A_2$
  - Scattering $S_2$
- Higher mode

Graphical representation:

- Intensity vs. $R$ for $A_1$, $S_1$, $A_2$, and $S_2$.
- 2R indicated on the graph.
Absorption: evolution with size

R↑ optical response shows a blue shift
Intensity ↓ ⇒ reflection
Experimental set-up

Absorption cross section: \[ \frac{I(X_{n-p})}{I(X_n)} = f(h\nu) \]
Optical response of mass-selected free metallic clusters

\[ \lambda \gg R \]

Mie resonance

Photo-absorption depletion spectroscopy

The absorption cross section probes the shape of the particle

Chem. Phys. Lett. 189, 28 (1992); 190, 42 (1992)
Dipolar Mie Absorption of Ag$_n$

The colour of metallic nano-clusters

Experimental absorption profile of the Mie plasmon resonance of Li$^{+}_{1500}$.

Comparison with the Mie resonance of a Lithium macroscopic sphere in the long wavelength limit $R \ll \lambda$.

$$\sigma(\omega) = \frac{4\pi\omega}{c} R^3 \text{Im} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2}$$

The similarity between these two resonances suggests that a local description of the dielectric function is relevant

PRL 70, 1492 (1993)
\( h \omega_p (N^{-1/3}) \)

Electron spill out

Mie plasmon, surface plasmon and volume plasmon

$$\sigma(\omega) = \frac{4\pi\omega}{c} R^3 \text{Im} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + a}$$

- \(a = 2\) Mie plasmon  free e\(^{-}\) confine in a sphere
- \(a = 1\) surface plasmon  free e\(^{-}\) confine in 2D
- \(a = 0\) volume plasmon  free e\(^{-}\) no confinement
Plasmon resonance in Potassium

\[ \sigma(\omega) = \frac{4\pi\omega}{c} R^3 \text{Im} \left[ \frac{\varepsilon(\omega)}{\varepsilon(\omega) + a} \right] \]

\( h\nu_{s}(q) \)

\( h\nu_{M}(R^{-1}) \)

\( R << \lambda \)

Mie plasmon, surface plasmon and volume plasmon

\[
\sigma(\omega) = \frac{4\pi\omega}{c} R^3 \text{Im} \left( \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + a} \right)
\]

- \(a = 2\) Mie plasmon  \(\text{free } e^- \text{ confine in a sphere}\)
- \(a = 1\) surface plasmon  \(\text{free } e^- \text{ confine in 2D}\)
- \(a = 0\) volume plasmon  \(\text{free } e^- \text{ no confinement}\)
Te nanowire

20 nm
EELS analysis

Photodiode Counts x 1000

Energy Loss (eV)

plasmon of Te

Zero loss

Te (N45)

Inner shell 4d→5p

SP 11.4 eV  VP 17.5 eV
Te plasmons mapping

Nanowire surfaces

SP

VP

Te N$_{45}$

C. Colliex C. Bréchignac to be published
II. Reactivity of metallic clusters
The reactivity of a finite reservoir of electrons

How does the electronic shell structure of the reservoir influence the reactivity?
- Physisorption (geometrical)
- Chemisorption (electronic)
- Dissociation-reaction (with temperature)
Experimental set-up

Patrick Martin
Martin Schmidt
Physisorption of $N_2$ on silver

Adsorption of $N_2$ on Ag surface is known to be very weak. At 77K $N_2$ molecules do not stick on Ag(110) $N_2$ molecules physisorbed at 45K. Teillet-Billy et al. Surf.Sci. 465(2000)

On charged clusters, the charge may enhance the adsorption
\[ \text{Ag}^+_n (\text{N}_2)_p \]

\( n = 9, 10, 11, 12, 13 \)

\[ \text{T} = 77K \]

Sticking and evaporation of \( \text{N}_2 \) during \( t \) at \( T \)

\[ \text{Ag}^+_n (\text{N}_2)_p + \text{N}_2 \leftrightarrow \text{Ag}^+_n (\text{N}_2)_{p+1} \]
Interaction between oxygen and surfaces


\[
O_{2g} \leftrightarrow O_{2P} \leftrightarrow O_{2a} \leftrightarrow 2O_{a}
\]
Silver nano-clusters $\text{Ag}_n^+$ and oxygen

$\text{Ag}_{12}^+ \ (\text{Ag}_{12}\text{O}_2)^+$

Schmidt et al.

$e^-$ transferred from the metal cluster to the $\text{O}_2$ antibonding $\pi^*$ orbital
Chemisorption of O₂ on Agₙ⁺

Since the number of e⁻ that can be extracted is limited, a chemisorbed O₂ protects the cluster against further chemisorption.

A chemisorption charges the cluster by additionally one charge.

Ratio: \( I(O₂)/I(N₂) \)

Since the number of e⁻ that can be extracted is limited, a chemisorbed O₂ protects the cluster against further chemisorption.
Chemisorption of $O_2$ on $Ag_n^+$
Chemisorption of O$_2$ on Ag$_n^+$ and Ag$_n^-$

Kim, Ganteför CPL 383, 80 (2004)
Laser heating
dissociative chemisorption

\[ \text{Ag}_{15} \text{Ag}_{16} \text{Ag}_{17} \]

\[ \text{Ag}_{16} \text{O}_2 \]

1600  1650  1700  1750  1800  1850

\[ \text{hv} \]

\[ \text{Ag}_{15} \text{Ag}_{15} \text{O} \]

\[ \text{Ag}_{16} \text{O} \]

\[ \text{Ag}_{17} \text{O} \]
Stability of Ag$_n$O$^+$

Shift $\Delta n=2$
Oxygen atom traps two electrons O$^-$, which can no longer contribute to the electron glue.

$\text{Ag}_n\text{O}_y^+$?


Up to $y=5$
At 77K

Brechignac et al.
Cluster dissociation

Dissociative chemisorption:
Two e⁻ transfer to O⁻

Physisorption

Chemisorption:
One e⁻ transfer.

O⁻ is not observed so far

Schematic potential energy diagram
$N_2$ sticking on $Ag_3^+$

Schmidt et al.  
The mean pressure ratio $<p_1/p_2>$ as a function of cluster size. $p_1$ and $p_2$ are $N_2$-pressures, which lead to the same amount of sticking $N_2$ on the same silver cluster without $O_2$ ($p_1$) and with $O_2$ ($p_2$).

III. Cluster deposition
Experimental set up for cluster deposition

1) Flux measurement
Quartz microbalance

2) Flux measurement
Quartz microbalance

3) Deposition
Analysis with AFM, STEM in vacuum
TEM, STEM, after transfer in the air

n=500
\(d=3\) nm
\(\Delta d=0.5\) nm
Dynamics of the growth: non equilibrium shape, role of surface defects

The kinetic energy of the incident clusters (0.05 eV) is small as compared to its binding energy (1.5 eV). Their fragmentation is unlikely. Each cluster diffuses on the surface, until it reaches a defect, or an other cluster.

If the laps of time between two successive arrivals is smaller than the time to coalesce, the island growths in a dendritic way.

W. Mullin R. Sekarka
J. Appl. Phys. 34 323 (1963)
Morphology control of supported islands

B. Yoon et al. Surface science 76; 443 (1999)
Branch width vs incident cluster size

\[ \langle n \rangle = 2300 \]

B. Yoon et al. Surface science 76; 443 (1999)
Faceting of silver island driven by oxygen

Fractal islands as test case for studying morphological change driven by oxide impurity
On the instability of jets

With respect to instability due to capillary force, the principal problem is the determination, as far as possible, of the mode of disintegration of an infinite cylinder, and in particular of the number of masses into which a given length of cylinder may be expected to distribute itself.

Proc. Math. Soc. 10, 4 (1879)
Capillary instability of a cylindrical mass

« On the instability of jets » Rayleigh Proc. Lond. Math. Soc. 10, 4, (1879) \( \Rightarrow \lambda=4.508 \times D \) leads more rapidly the disintegration of the cylindrical mass

\[ \lambda = 4.508 \times D \]

Mass conservation:
\[ \pi D^2/4L = n4/3\pi R^3 \]

\[ R = 0.95D \]
\[ \lambda = 4.76R \]
Nanowires of copper

Annealing of a copper nanowire

\[ \lambda/D = 4.5 \pm 0.4 \]

Enhancement of the surface self-diffusion

- Surfactant as oxide molecules carried by clusters in a subsequent deposition
  - surface self-diffusion
- Assuming a fractal as a set of bars and scale invariance
Nanofractal fragmentation

\[ \frac{\lambda}{l_0} = 4.7 \pm 0.5 \]

Thermal vs chemical fragmentation
Coarsening of a 2D fractal
The paradox which consists of having the same process \textit{i.e.} surface-self-diffusion leading to antinomic behaviours, takes its origin into the critical length required for developing capillary instabilities (locally or not?)
Pearling instabilities of membrane tubes with anchored polymers

Polymer
Hydrophylic dextran

Chloroform-methanol
Fluid like state

Hollow tubular lipid vesicle
Stearyl-oleoyl-phosphatidyl-choline (SOPC)

I. Tsafrir PRL 86 1138 (2001)
Hollow tubular lipid vesicle and silver branch
A peristaltic state in a thick cylinder

Phys. Rev. E 58, 1158
Delaunay surface curvature

\[ R_c = \frac{2ay^2}{b^2 - \varepsilon y^2} \]

\[ N = y \frac{ds}{dx} = \frac{2ay^2}{b^2 + \varepsilon y^2} \]

\[ \frac{1}{R_c} - \frac{1}{N} = -\frac{\varepsilon}{a} \]

a and b are the axis of ellipse
\[ \varepsilon=1 \text{ ellipse} \]
\[ \varepsilon=-1 \text{ hyperbola} \]

J. Math. Pures Appl. 6, 309 (1841)
Spherodization of carbon nanotubes in TEM

Irradiation of CNT in a high resolution TEM

No morphological changes are observed up to 1600°C when the bulk sample is heated in the furnace.
Neurons and fractals
M. Schmidt; A. Lando; S. Benrezzak; N. Kébaïli, Ph. Cahuzac, A. Masson; C. Bréchignac.
Collaboration with C. Colliex’s group at LPS