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On the stability of metal nanoparticles synthesized by laser ablation in liquids

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On the stability of metal nanoparticles synthesized by laser ablation in liquids

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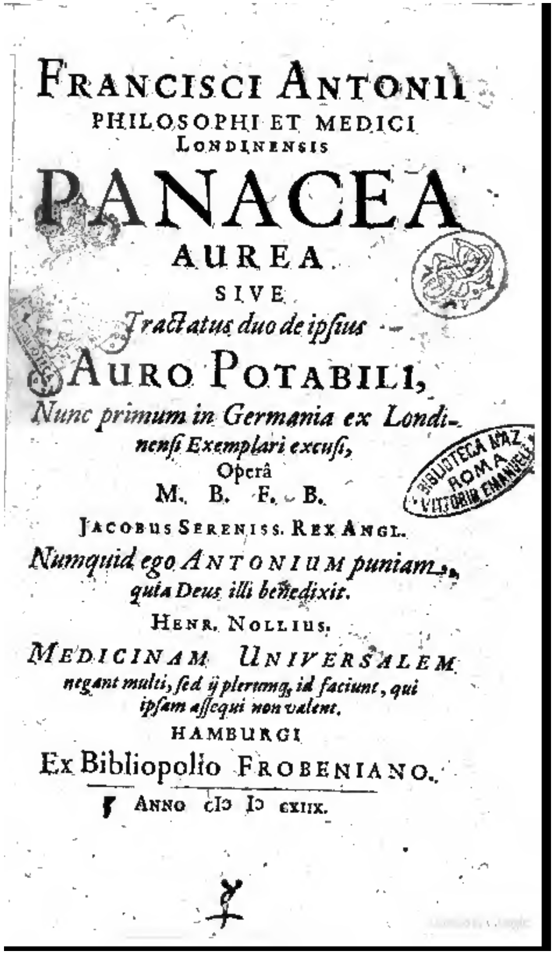
Association in Solution IV

July 31 - August 4, 2017, Memorial University
St. John's, Newfoundland, Canada

gold nanoparticles (AuNPs)are known by centuries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LONDINENSIS
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Tractatus duo de ipsius
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Nunc primum in Germania ex Londi-
nensi Exemplari excusi,
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M. B. F. B.
JACOBUS SERENISS. REX ANGL.
Numquid ego ANTONIUM puniam,
quia Deus illi benedixit.
HENR. NOLLIUS.
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negant multi, sed ij plerumq; id faciunt, qui
ipsam assequi non valent.
HAMBURGI
Ex Bibliopolio FROBENIANO.
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1618

X. THE BAKERIAN LECTURE.—*Experimental Relations of Gold (and other Metals) to Light.* By MICHAEL FARADAY, *Esq., D.C.L., F.R.S., Fullerian Prof. Chem. Royal Institution, Foreign Associate of the Acad. Sciences, Paris, Ord. Boruss. pour le Mérite, Eq., Memb. Royal and Imp. Acadd. of Sciences, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, Munich, Bruxelles, Vienna, Bologna, Commander of the Legion of Honour, &c. &c.*

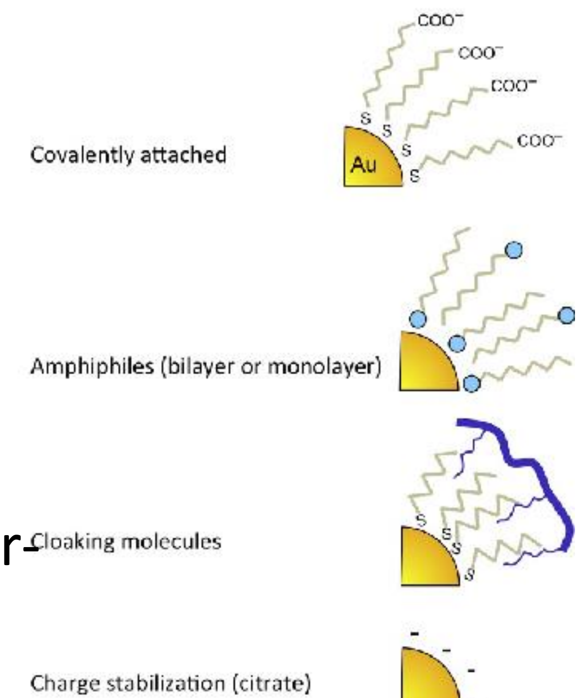
Received November 15, 1856,—Read February 5, 1857.

Chemically synthesized NPs are stabilized by a surface layer of capping agents.

These molecules:

1) avoid the infinite growth of the solid phase,

2) impart a repulsive inter-particle interactions.



a purification step is always required to separate chemical products and unreacted reagents from the AuNps and there are also several conditions in which the presence of molecules bound to the AuNP surface is detrimental.

Pulsed Laser ablation in liquid (PLAL)

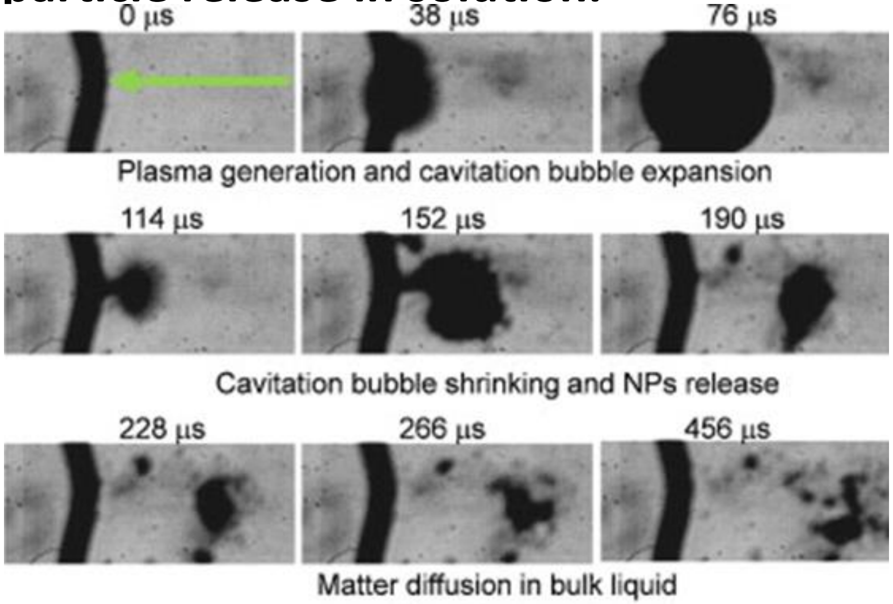
or

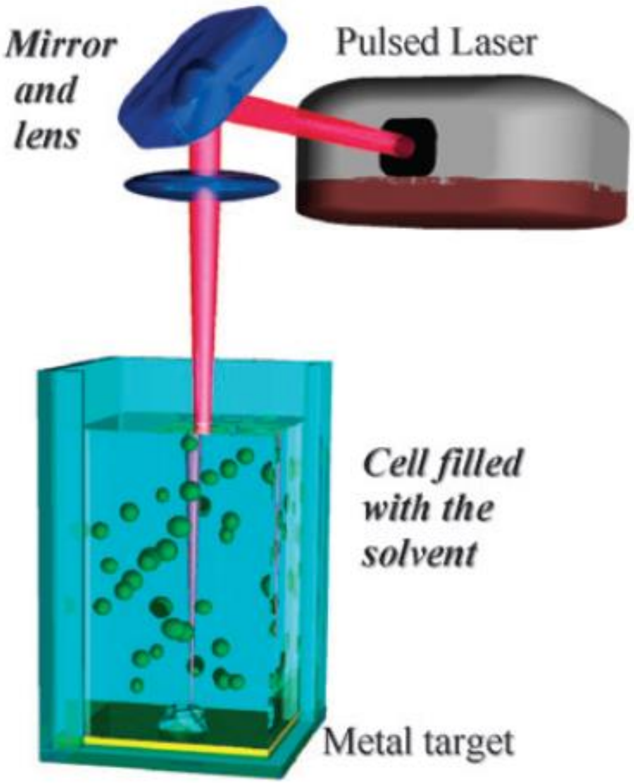
Laser Ablation Synthesis in Solution (LASiS)

is an alternative technique for forming metal nanoparticles (NPs) in pure liquids (NO stabilizers!!)

Barcikowski , Compagnini *Phys.Chem. Chem. Phys.*, 2013, **15**, 3022
Zhang D., Gökce B., Barcikowski S., *Chem. Rev.*, **2017**, *117*, 3990

PLAL involves focused laser pulsed irradiation of a bulk metal target in a liquid.
It consits of four stages: Laser-matter interaction, plasma induction, cavitation bubble formation and particle release in solution.

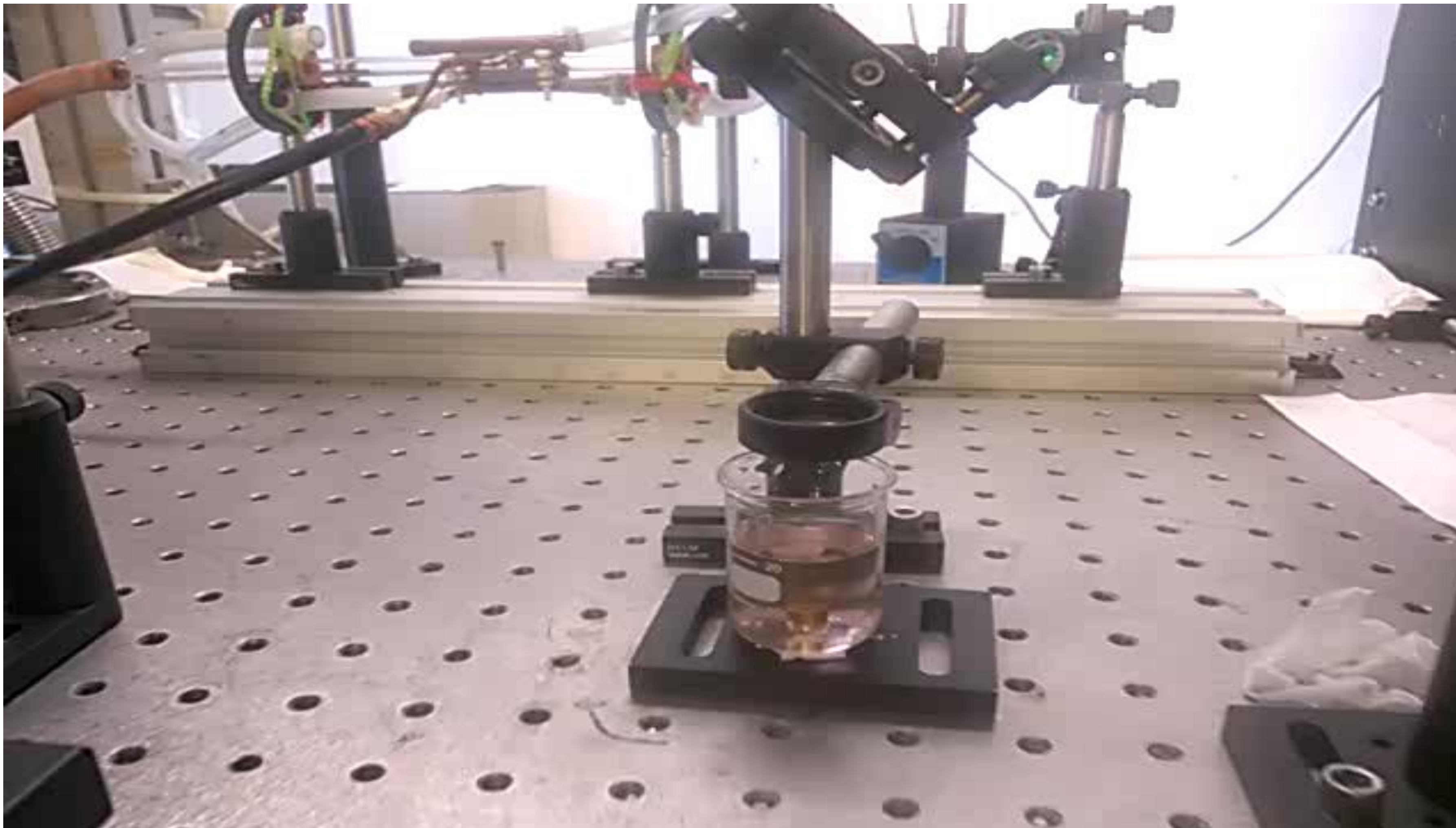





Alessandro De Giacomo


Marcella Dell'Aglio

PLAL is environmental friendly and has an easy experimental set-up.



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Industrial & Engineering Chemistry Research
Article
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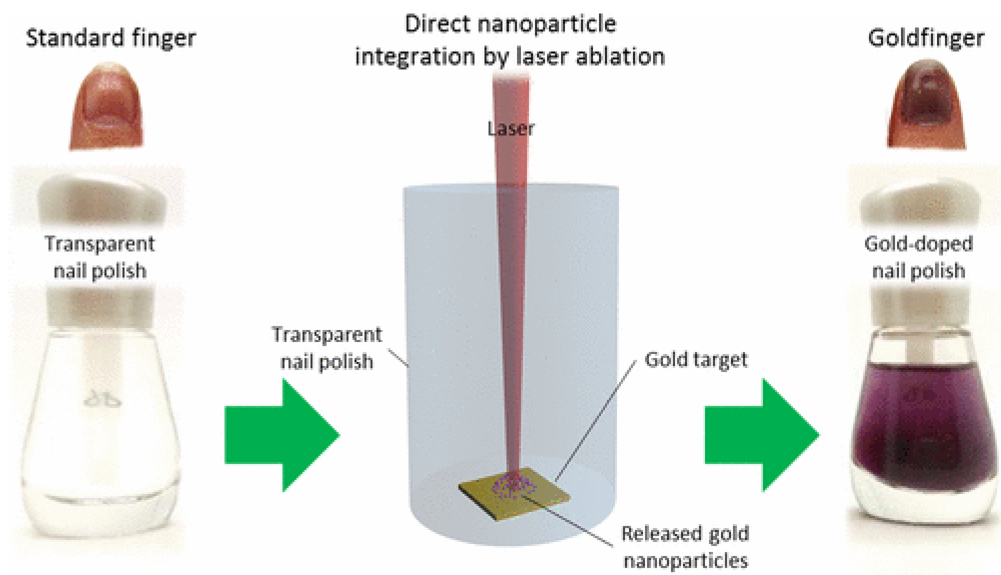
Direct Integration of Laser-Generated Nanoparticles into Transparent Nail Polish: The Plasmonic "Goldfinger"

Marcus Lau,[†,‡] Friedrich Waag,[†,‡] and Stephan Barcikowski*[,†,‡]

Antibacterial, durable nail polish

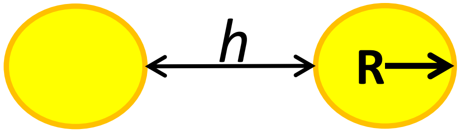


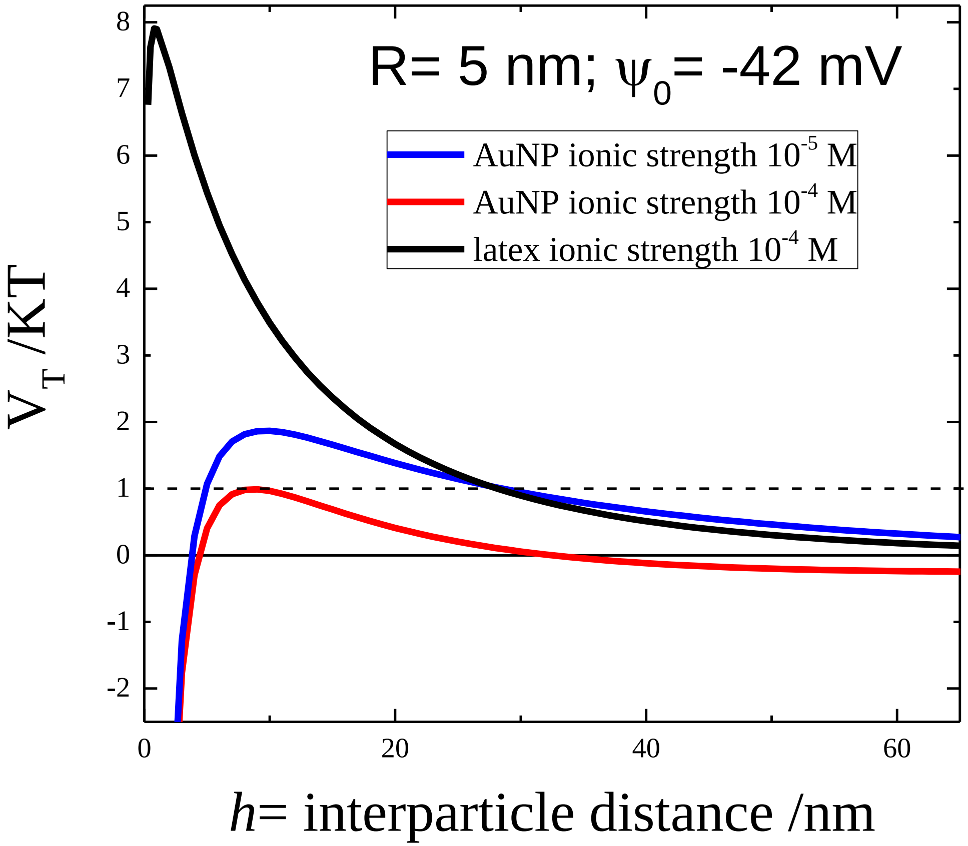
Antibacterials for:
- food packaging
- Couches & Sofas

“naked” NPs synthesized by PLAL are long standing for months

Colloidal stability of metal nanoparticles

$$V_T = V_A + V_R$$



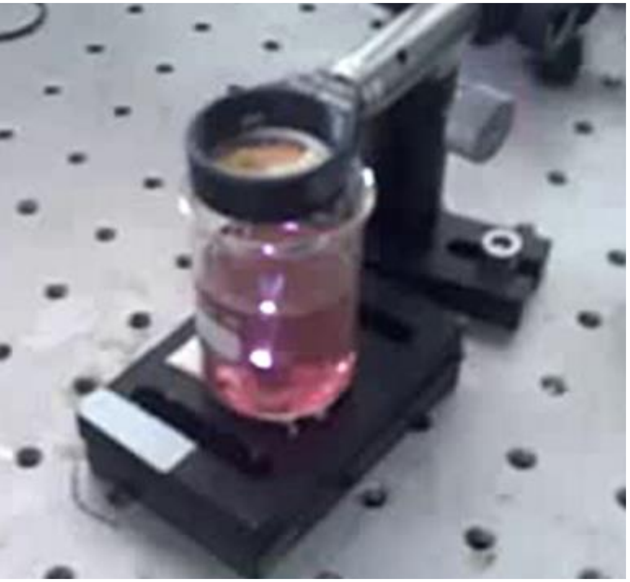


Hamaker constant H

- gold H ~ 100 k_bT
- polystyrene H~2 k_bT

Israelachvili *Intermolecular and surface forces*, Academic Press 1992

“naked” NPs synthesized by PLAL are long standing for months



Gold is a noble metal that is inert under most conditions but, as a matter of fact, AuNPs prepared by PLAL in pure water have a large negative zeta-potential.

small particles in solution at low ionic strength (R/λ_D<<1) → Huckel limit

The question is what is the origin of these surface charges?

Common explanations for this phenomenon involve the presence of gold oxides and/or the anion adsorption

Sylvestre et al. *J. Phys. Chem. B*, **2004**, *108*, 16864; Muto et al. , *J. Phys. Chem. C* **2007,** *111,* 17221
Merck et al . *Langmuir*, **2013**, **30**, 4213

although evidences against such a explanation are growing in recent years. Fong et al. *Langmuir,* **2013, 29**, 12452

Some facts

$$-AuOH_2^+ \overset{K_{a1}=3.9}{\longleftrightarrow} -AuOH + H^+$$

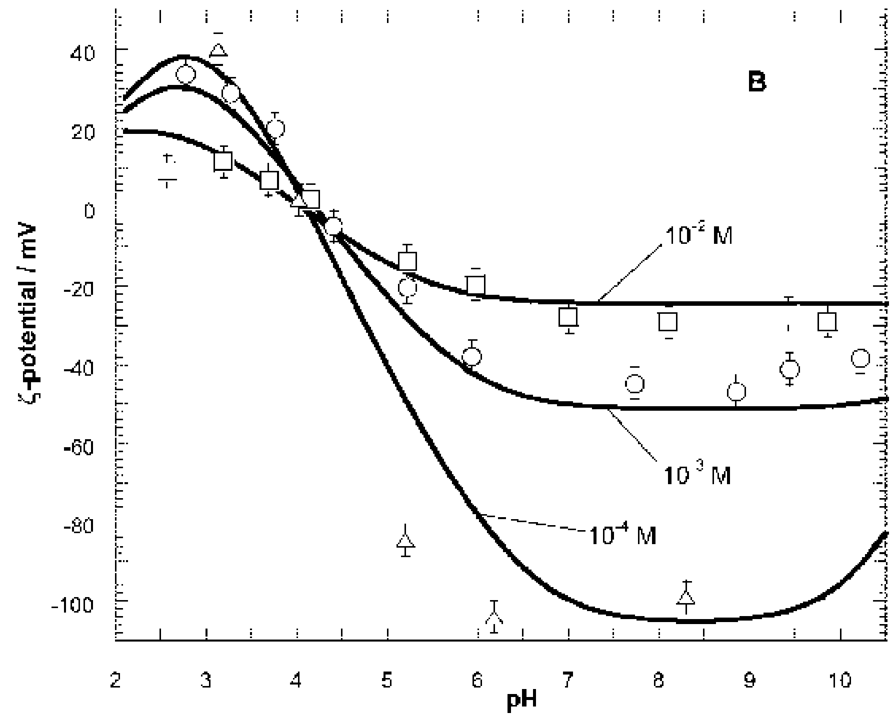
$$-AuOH \overset{K_{a2}=4.2}{\longleftrightarrow} -AuO^- + H^+$$

Journal of Colloid and Interface Science 260 (2003) 95–106

Faradaic depolarization in the electrokinetics of the metal–electrolyte solution interface

Jérôme F.L. Duval,* Geertje K. Huijs, Wim F. Threels, Johannes Lyklema, and Herman P. van Leeuwen

Stable AuNPs have been successfully synthesized by means of PLAL also in solutions of acids (HCl, H_2SO_4, HNO_3) at pH= 3



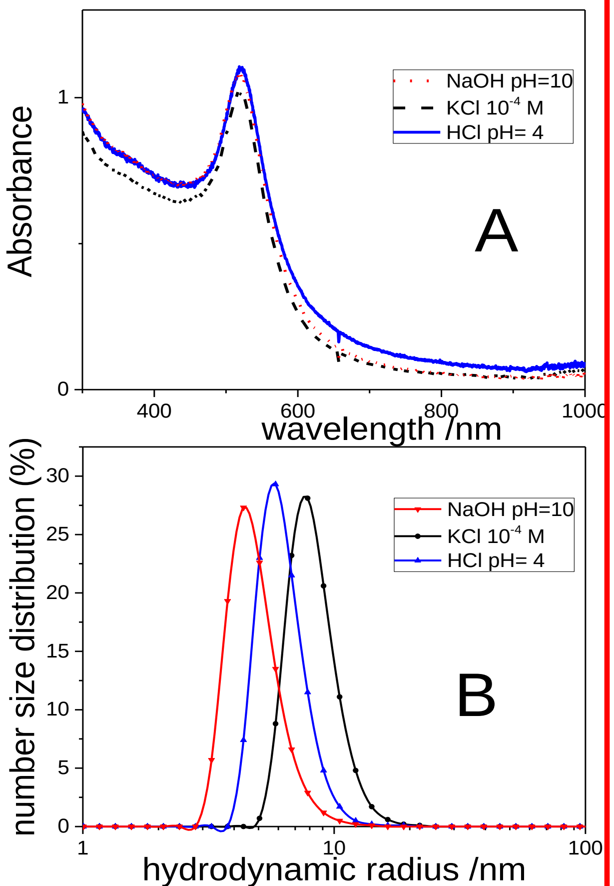
metallic core (R_c) and hydrodynamic (R_h) radius and ζ-potential of AuNPs ablated in acidic and in KCl solutions			
Ablation medium	R_c /nm (SPR)	Rh /nm (DLS)	ζ /mV
HCl pH=3	6 ±3	7 ± 1	-57 ± 3
HNO_3 pH=3	6±3	6±3	-60 ± 3
H_2SO_4 pH=3	6±3	7 ± 2	-66± 6
KCl 10^{-4} M	5±3	6 ±2	-67 ± 3

marginal role of the surface oxides (HNO_3 is an oxidant much stronger)

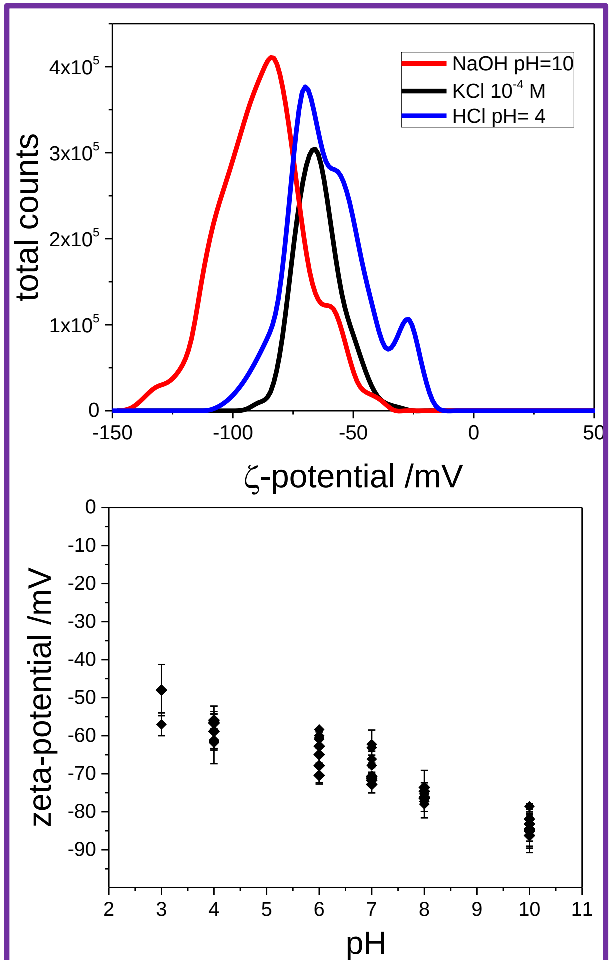
the formation of stable NPs at pH 3 excludes any role of carbonates in the stabilization of AuNPs

Some facts (AuNPs)

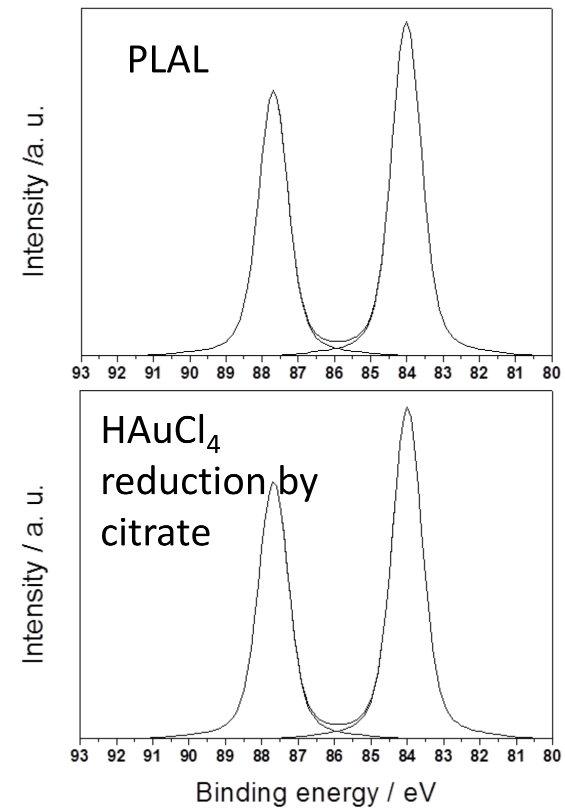
AuNPs prepared in in 10^{-4} M solutions of HCl, KCl and NaOH.



NO effect of pH on the size and on the concentration



Only small effect of pH on ζ-potential .
Δζ~25 mV over 7 pH-units crossing the pK_as of -AuOH

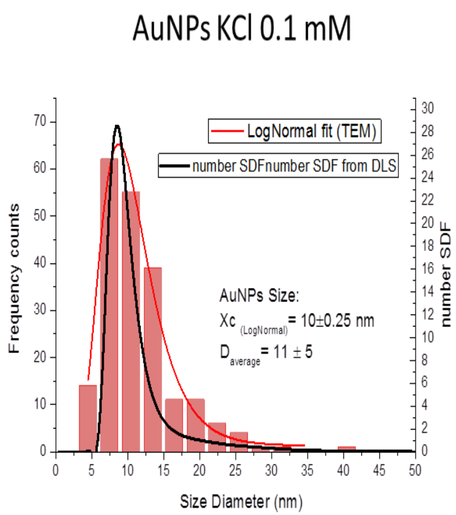


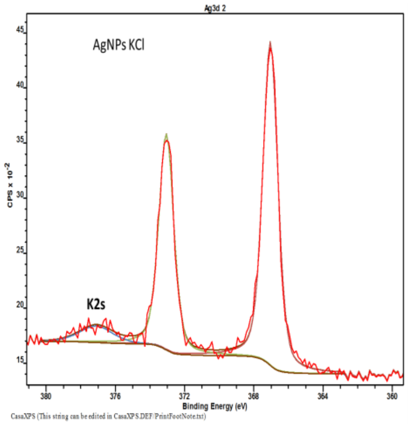
NO oxidized gold (only Au^0)

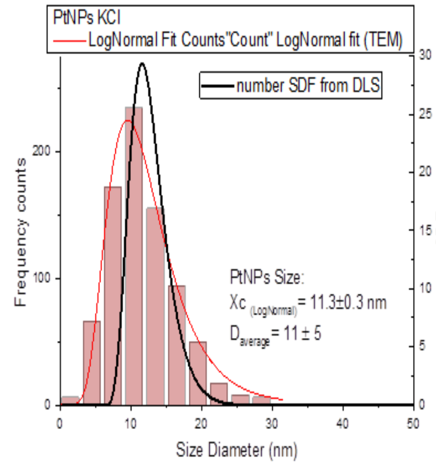
NO contribution of ion adsorption to the AuNPs stabilization

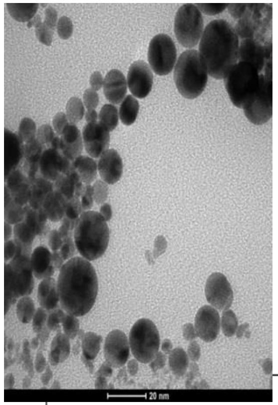
NO contribution of gold oxides to the AuNPs stabilization

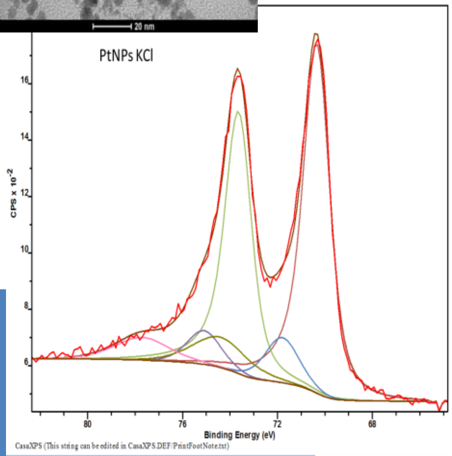
Some facts (gold, platinum, silver)









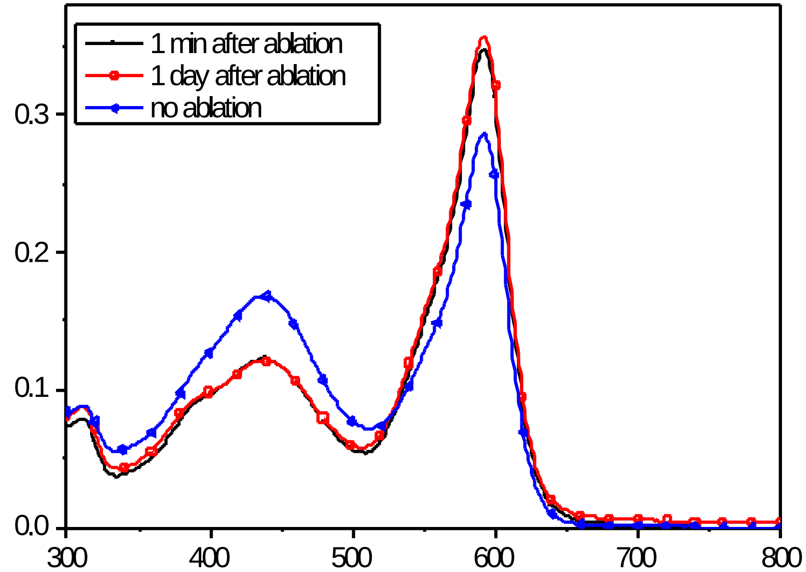


	SPR /nm diameter	DLS 7nm diameter	TEM/ nm		Z-pot /mV	XPS
			LogNormal Fit	$D_{average}$		
AuNPs	14±2	13±3	12±0.2	13±6	-39.7±0.3	--
AuNPs+KCl	9±2	10.2±0.6	10.2±0.2	11±5	-62±7	Au(0) 97.1% BE = 83.4 eV Au^{+} 2.9% BE = 85.4 eV
PtNPs	-	20±6	19.4±0.3	20±7	-45±1	--
PtNPs+KCl	-	14±2	11.3±0.3	11±5	-58±3	Pt(0) 77.6% (BE = 70.3 eV) Pt(II) 10.8% (like hydroxide) BE = 71.8 eV Pt(IV) 11.6% (PtO2) BE = 74.4 eV
AgNPs	12±2	13±2	-	-	-42±0.6	--
AgNPs+KCl	8±2	13±2	10.6±0.4	11±5	-59±2	Ag(0) 100% BE = 367.0 eV

Some facts

The ablation process causes an increase of 0.2 pH unit

bromophenol blue spectra before and after PLAL.



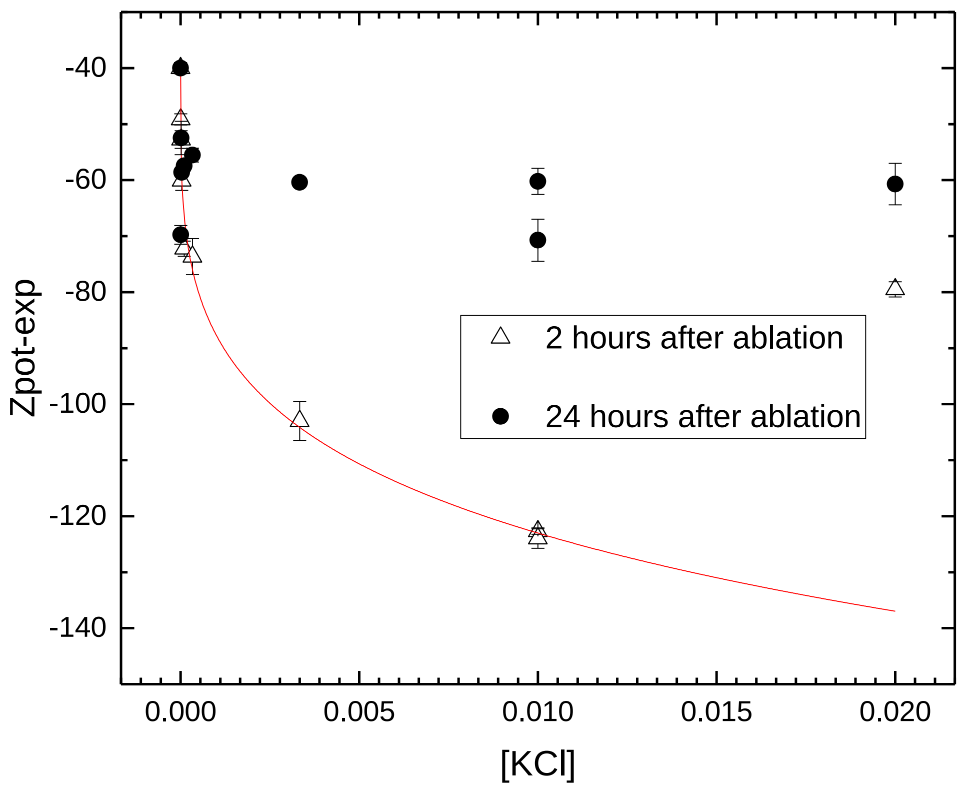
incompatible with the formation of -Au-OH

Ablation in MQ water results in unstable particles (??)

Langmuir
Article
pubs.acs.org/Langmuir

In Situ Non-DLVO Stabilization of Surfactant-Free, Plasmonic Gold Nanoparticles: Effect of Hofmeister's Anions

Vivian Merk,[†,#] Christoph Rehbock,[†,#] Felix Becker,[‡] Ulrich Hagemann,[‡] Hermann Nienhaus,[‡] and Stephan Barcikowski*[,†]



Ablation in different salts (after equilibration) results in mutually close size and charge

Minor role of ion adsorption

These evidences suggest that the gold oxidation and/or the anion adsorption have only a minor role on building the negative surface potential

Who could be the next candidate ?

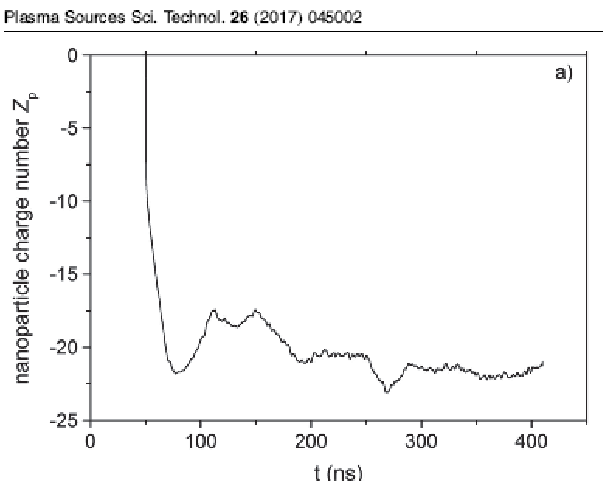
What is the most abundant negatively charged species found in the laser-induced plasma ?

The electrons!!!

The NPs nucleate in the plasma phase and the nuclei are negatively charged and this induces their growth by ions attraction.

The produced NP could save its negative charge

Taccogna , Dell' Aglio, Rutigliano, Valenza, De Giacomo, *Plasma Sources Sci. Technol*. **2017**, *26*, 045002



Z~-20

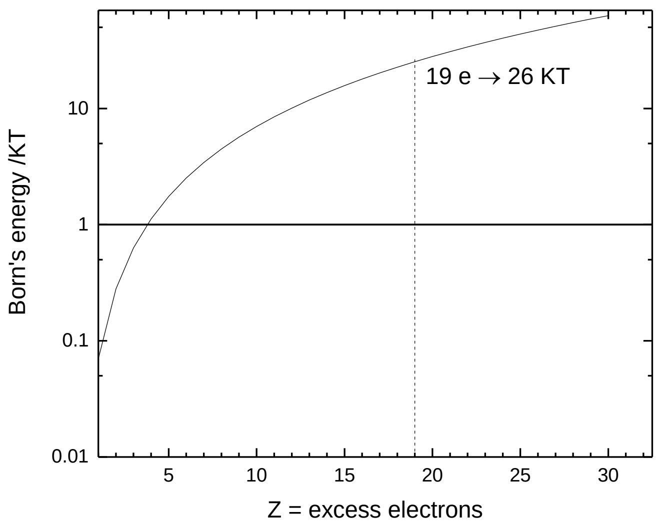
$$\psi_0 = Z \frac{l_B}{R} \frac{KT}{e} \sim \text{-70 mV}$$

The free-energy of Z extra electrons on a metallic sphere equals the Born energy

$$\Delta G = \frac{Z^2 e^2}{8\pi\varepsilon\varepsilon^\circ} \frac{1}{R} = z^2 \frac{l_B}{2R} KT$$

the Bjerrum length l_B in water is 0.7 nm and the free energy of one excess electron staying on a NP of 5 nm in radius is only 0.07 KT

$\Delta G \propto Z^2$; above a certain amount of electrons (Z) the reaction of the electrons with other species become competitive



In pure water

$$NP^{(Z)-} + H^+(aq) \rightarrow NP^{(Z-1)-} + \tfrac{1}{2} H_2(g)$$

$$\tfrac{1}{2}\mu_{H_2} + \mu_{NP(Z-1)} = \mu_{NP(Z)} + \mu_{H^+}$$

$$ln\left(\frac{C(Z)}{C(Z-1)}\right) = +\tfrac{1}{2}\, lnP_{H_2} - ln[H^+] + \frac{l_B}{R}\frac{(1-2z)}{2(1+\frac{R}{\lambda_D})}$$

$$ln\left(\frac{C(Z)}{C^\circ - C(Z)}\right) = -7.22 - ln[H^+] + \frac{l_B}{R}\frac{(1-2z)}{2(1+\frac{R}{\lambda_D})}$$

$$[H^+] = [H^+]_{bulk} exp\left(-\frac{e\Phi^\circ}{KT}\right)$$

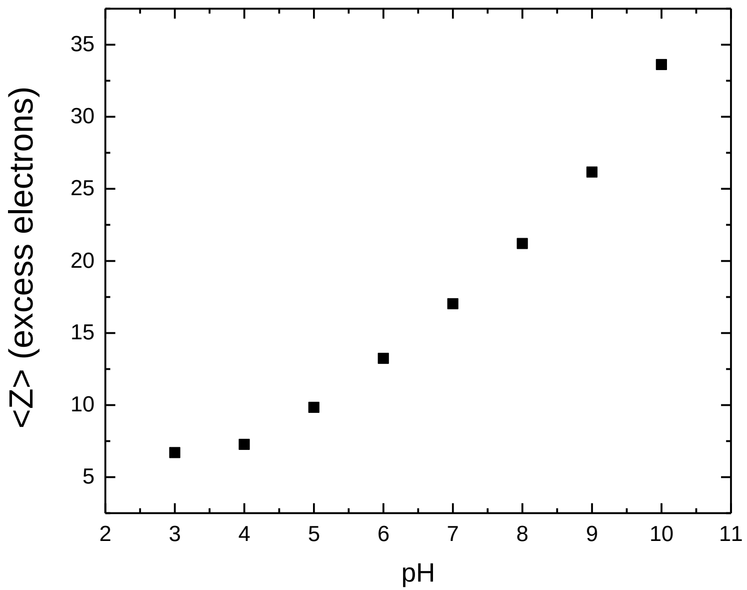
$$\Phi^\circ = -z\frac{l_B}{R}\frac{KT}{e(1+\frac{R}{\lambda_D})}$$

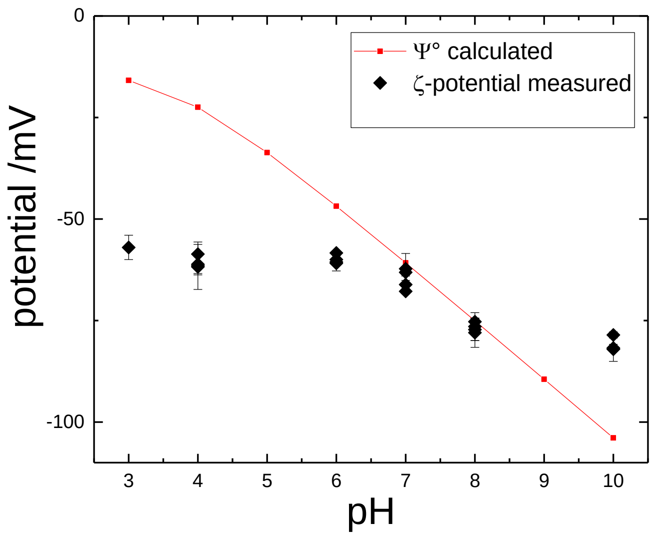
$$\rho(Z) = (1-\rho(Z))exp\left\{-\frac{l_B}{R}\frac{2Z}{\left(1+\frac{R}{\lambda_D}\right)} - 7.22 + 2.3pH - ln[H^+] + \frac{l_B}{R}\frac{1}{2\left(1+\frac{R}{\lambda_D}\right)}\right\}$$

$$= (1-\rho(Z))e^{\Psi(Z,pH)}$$

it is possible to evaluate the average charge carried by the NP as

$$\langle Z\rangle = \frac{\sum_{Z=1}^{\infty} Z\rho(Z)}{\sum_{Z=1}^{\infty} \rho(Z)}$$





the colloidal size of the NPs is very important:

i) the particles must be large enough to reduce the Born energy of charging to a level that doesn't allow direct reaction with the hydrated H^+ present in solution.

ii) the particles must be so small that small number of excess electrons (5-10) is enough to build a strongly negative ζ-potential that assures the stability against aggregation.

Conclusions

Stabilization by metal oxides and anion adsorption seems improbable.

"electron-stabilized nanoparticles" ?

Thanks to
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