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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gold nanoparticles (AuNPs) are known by centuries.

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 interparticle interactions.
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
PLAL involves focused laser pulsed irradiation of a bulk metal target in a liquid. It consists of four stages: Laser-matter interaction, plasma induction, cavitation bubble formation and particle release in solution.
PLAL is environmental friendly and has an easy experimental set-up.
Direct Integration of Laser-Generated Nanoparticles into Transparent Nail Polish: The Plasmonic “Goldfinger”

Marcus Lau,†,‡,§ Friedrich Waag,†,‡ and Stephan Barcikowski*†,‡,§

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 \( H \sim 100 \, k_B T \)
- polystyrene \( H \sim 2 \, k_B T \)

Israelachvili *Intermolecular and surface forces*, Academic Press 1992

R = 5 nm; \( \psi_0 = -42 \, mV \)

\( h = \) interparticle distance /nm

<table>
<thead>
<tr>
<th></th>
<th>AuNP ionic strength 10^{-5} M</th>
<th>AuNP ionic strength 10^{-4} M</th>
<th>latex ionic strength 10^{-4} M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

"Hamaker constant \( H \) - gold \( H \sim 100 \, k_B T \) - polystyrene \( H \sim 2 \, k_B T \)"
“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 \((R/\lambda_D<<1)\) → 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

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

\[-AuOH_2^+ \xrightleftharpoons{K_{a1}=3.9}^- AuOH + H^+\]

\[-AuOH \xrightleftharpoons{K_{a2}=4.2}^- AuO^- + H^+\]

Stable AuNPs have been successfully synthesized by means of PLAL also in solutions of acids (HCl, H$_2$SO$_4$, HNO$_3$) at pH = 3

<table>
<thead>
<tr>
<th>Ablation medium</th>
<th>$R_c$ /nm (SPR)</th>
<th>$Rh$ /nm (DLS)</th>
<th>$\zeta$ /mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl pH=3</td>
<td>6 ±3</td>
<td>7 ± 1</td>
<td>-57 ± 3</td>
</tr>
<tr>
<td>HNO$_3$ pH=3</td>
<td>6±3</td>
<td>6±3</td>
<td>-60 ± 3</td>
</tr>
<tr>
<td>H$_2$SO$_4$ pH=3</td>
<td>6±3</td>
<td>7 ± 2</td>
<td>-66±6</td>
</tr>
<tr>
<td>KCl 10$^{-4}$ M</td>
<td>5±3</td>
<td>6 ±2</td>
<td>-67 ± 3</td>
</tr>
</tbody>
</table>

Metallic core ($R_c$) and hydrodynamic ($R_h$) radius and $\zeta$-potential of AuNPs ablated in acidic and in KCl solutions.

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**
- **NO contribution of ion adsorption to the AuNPs stabilization**
- Only small effect of pH on $\zeta$-potential. $\Delta \zeta \sim 25$ mV over 7 pH-units crossing the pK$_a$s of -AuOH
- **NO oxidized gold (only Au$^0$)**
- **NO contribution of gold oxides to the AuNPs stabilization**
### Some facts (gold, platinum, silver)

#### AuNPs KCl 0.1 mM

<table>
<thead>
<tr>
<th>SPR /nm diameter</th>
<th>DLS 7nm diameter</th>
<th>TEM/ nm LogNormal Fit</th>
<th>D\text{average}</th>
<th>Z-pot /mV</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuNPs</td>
<td>14±2</td>
<td>13±3</td>
<td>12±0.2</td>
<td>13±6</td>
<td>-39.7±0.3</td>
</tr>
<tr>
<td>AuNPs+KCl</td>
<td>9±2</td>
<td>10.2±0.6</td>
<td>10.2±0.2</td>
<td>11±5</td>
<td>-62±7</td>
</tr>
<tr>
<td>PtNPs</td>
<td>-</td>
<td>20±6</td>
<td>19.4±0.3</td>
<td>20±7</td>
<td>-45±1</td>
</tr>
<tr>
<td>PtNPs+KCl</td>
<td>-</td>
<td>14±2</td>
<td>11.3±0.3</td>
<td>11±5</td>
<td>-58±3</td>
</tr>
<tr>
<td>AgNPs</td>
<td>12±2</td>
<td>13±2</td>
<td>-</td>
<td>-</td>
<td>-42±0.6</td>
</tr>
<tr>
<td>AgNPs+KCl</td>
<td>8±2</td>
<td>13±2</td>
<td>10.6±0.4</td>
<td>11±5</td>
<td>-59±2</td>
</tr>
</tbody>
</table>
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 (??)
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.


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

\[ Z \sim -20 \]

The free-energy of \( Z \) extra electrons on a metallic sphere equals the Born energy.

\[ \Delta G = \frac{Z^2 e^2}{8\pi \varepsilon \varepsilon_0 R} \frac{1}{2} = Z^2 \frac{l_B}{2R} KT \]

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

\[ \text{NP}^{(Z)^-} + \text{H}^+(\text{aq}) \rightarrow \text{NP}^{(Z-1)^-} + \frac{1}{2} \text{H}_2(g) \]

\[ \frac{1}{2} \mu_{H_2} + \mu_{\text{NP}(Z-1)} = \mu_{\text{NP}(Z)} + \mu_{\text{H}^+} \]

\[ \ln \left( \frac{C(Z)}{C(Z-1)} \right) = \frac{1}{2} \ln P_{H_2} - \ln [H^+] + \frac{L_B}{R} \frac{(1 - 2z)}{2(1 + R \lambda_D)} \]

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

\[ \Phi^o = -z \frac{L_B}{R} \frac{KT}{e(1 + R \lambda_D)} \]

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

\[ = (1 - \rho(Z)) e^{\Psi(Z,pH)} \]
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 a small number of excess electrons (5-10) is enough to build a strongly negative $\zeta$-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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Marcella Dell’Aglio, Alessandro De Giacomo, Gabriele Valenza

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Rosaria Picca, Nicola Cioffi, Helena Mateos