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Photochemical Synthesis of Colloidal Metals

Anatol V. Loginov*, Tatiana B. Boitsova, Valentina V. Gorbunova

Department of Inorganic Chemistry, Russian State Pedagogical University, Moyka 48,
191186, St. Petersburg, Russia

SUMMARY: New photochemical method for preparation of colloidal metal particles (Cu, Ag, Au) as a films on the quartz surface and colloidal dispersion in different matrixes has been devised. Possibilities to control the properties of photogenerated colloidal metal particles are discussed.

Introduction

The unique properties of colloidal metals are of great interest both for the theory and for the technology of creation of the new nanophase materials and catalysts. The phenomenon is based on their specific electronic structure, charge distribution and large size of the surface. Study and practical application of these highly reactive particles are presently limited by the lack of reproducible method, which allows controlling the donor-acceptor properties and dispersity of metal colloidal system.

Morphology

Photoreduction of metal complexes in solution and at the liquid-solid interface[1-4] is a promising method for metal colloid preparation:

$$\begin{tikzcd}
{[M^ZL_n]_s} \arrow[r, shift left, "h\nu\ (CTTM)"] & \{M^{(Z-1)+}L_{n-1},L^\bullet\}_s \arrow[l, shift left] \arrow[r] & {[M^{(Z-1)+}L_{n-1}] + (L)_s + (S^\bullet)_s} \arrow[dl, dashed, shift right, "h\nu,\ s"'] \\
{(M^O{}_N)_{ads} \text{ or } (M^O{}_N)_s} & (M^O)_s \arrow[l, dashed] \arrow[ur, shift right] &
\end{tikzcd}$$

By this means we have synthesized very stable Cu, Ag, Au and bimetallic Au/Cu, Au/Ag and Ag/Cu colloids in the form of:

- nanophase films on the quartz and glass surface 150 nm and up in thickness;
- dispersions in porous glasses, Nafion membrane, solid polymers (PVA, PEG, gelatin), glycerol and ethylene glycol solutions.

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Unlike colloids prepared by traditional methods (chemical reduction, gas evaporation, ultrasonic and electric discharge) photogenerated colloidal are characterized by:

- high degree of their monodispersity. Typical size of particles – 5-20 nm.
- high stability. For example, gold, silver and copper nanophase films on quartz surface and particles in porous glasses are stable under air condition at room temperature over to 2 years. Colloidal dispersion in glycerol and ethylene glycol stable over 6 months.

It is significant that photochemical method does not require the introduction of stabilizers (surfactants, π-acceptor and micelles) which decrease the catalytic activity of colloidal particles.

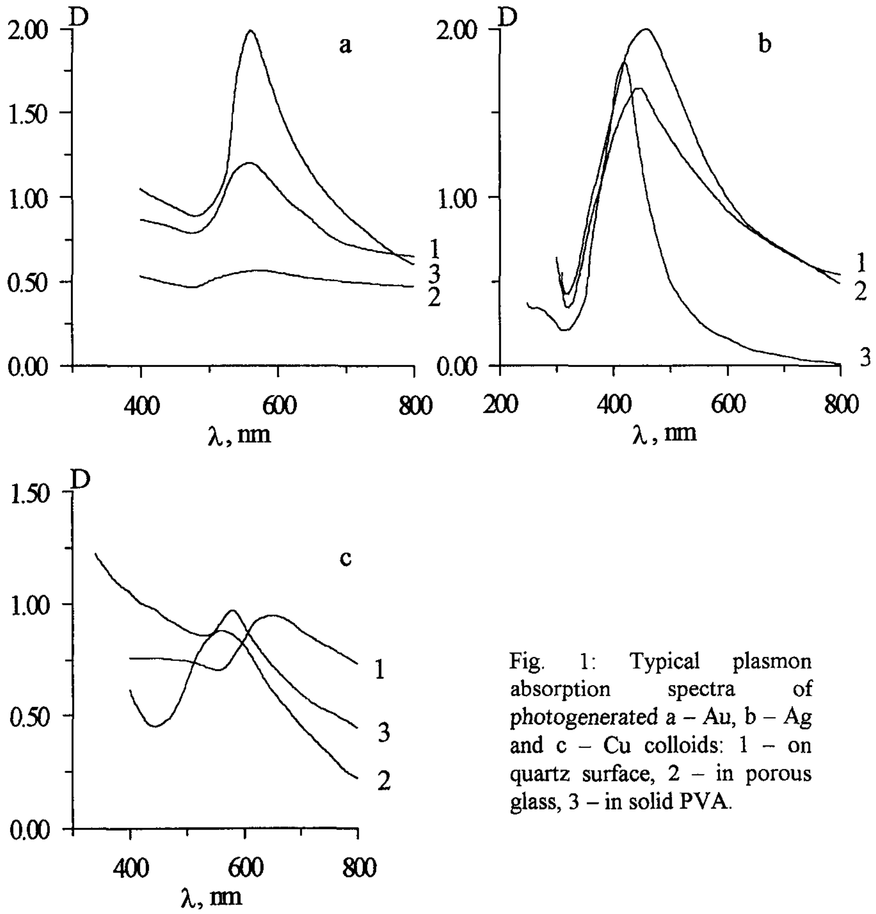

Fig. 1: Typical plasmon absorption spectra of photogenerated a – Au, b – Ag and c – Cu colloids: 1 – on quartz surface, 2 – in porous glass, 3 – in solid PVA.

All systems have intense narrow plasmon band in visible or near UV-region (Fig. 1).

All initial steps of colloid formation proceed in liquid (or pseudoliquid) phase. We have shown that photosynthesis of copper, silver and gold colloids include formation of Cu(I) and Au(I) intermediates, small nonmetallic clusters (limited stage) and metastable colloidal metal particles and aggregates. Generation of intermediates brings into existence the induction period in the kinetic curve. The subsequent growing of colloid particle includes coalescence of clusters and autocatalytical reduction on their surface of Cu(I), Ag(I) and Au(I)-complexes from the photolyte. Dissolved oxygen, Cu(II) and Au(III) ions oxidize the clusters and intermediates. Their stabilization is achieved by adsorption on the solid surface (in the case of colloidal films) and by increasing of photolyte viscosity (in the case of liquid colloidal dispersions). UV-irradiation acts as initiator of Cu(II,I), Au(III,I) and Ag(I) single electron reduction and as accelerator of adsorption and growing of unstable clusters.

Photodeposition of colloidal metal films on quartz in the initial stages of their formation is well described by Folmer-Veber mechanism$^{5)}$. Growth of island-type films is attended by transformation of amorphous to crystalline structure of colloidal particles, but unlike the gas evaporation method it does not lead to the structure of bulk metal.

Variations in experimental conditions (light energy and intensity, nature and concentration of initial metal complexes, photolyte viscosity, geometry of photochemical cell) influence on the photochemical formation and properties of colloidal metals. For example, all processes are characterized by well-defined threshold of intensity ($<10^{15}$ quantum cm^{-2} s^{-1}). Induction period is decreased (Fig. 2) and quantum yield of colloidal metals is increased (Tab. 1) with increasing of the light intensity. This indicates that the mechanism is multiquantum. From the table it will be observed the greater the light intensity and the quantum yields, the smaller size of particles and the narrower their size distribution.

Tab.1. Dependence of average size (d), effective quantum yield (Φ) and relative monodispersity (δ) of gold particles in photodeposited film from light intensity (I)

I_{light}, quantum cm$^{-2}\cdot$s^{-1}	d, nm	Φ_{col}	δ
$4.2\cdot10^{16}$	10-20	0.10	5.0
$1.2\cdot10^{16}$	20-30	0.08	1.5
$7.0\cdot10^{15}$	30-40	0.05	0.6

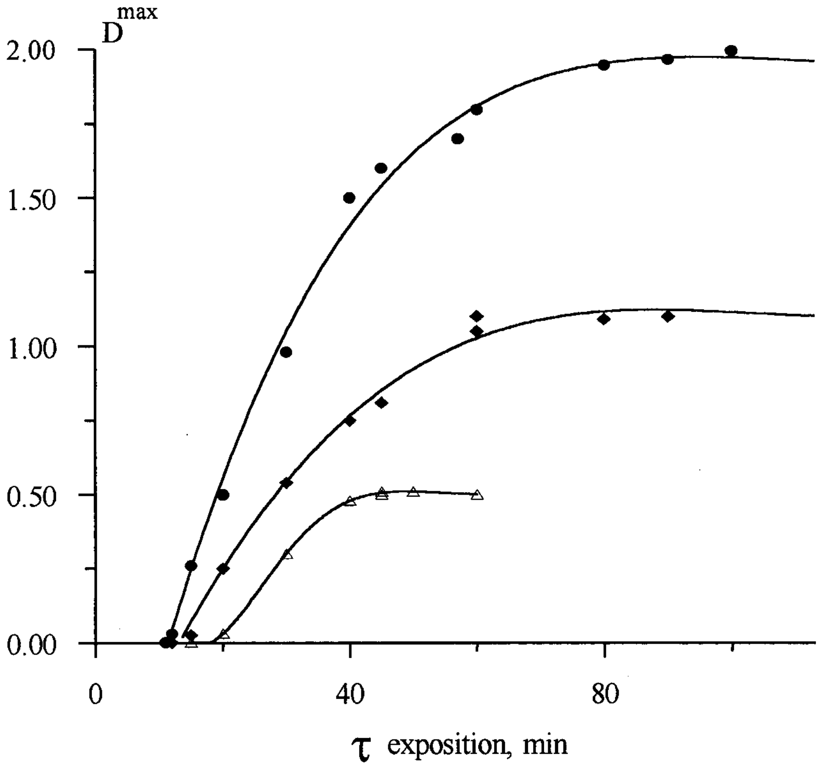

Fig. 2: Kinetic curves of photochemical generation of colloidal gold films on quartz under irradiation UV-light (λ 254 nm). Light intensity: ● = 4.2 × 10^{16}, ◆ = 1.2 × 10^{16}, Δ = 7.0 × 10^{15} quantum cm^{-2} s^{-1}.

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References

[1] Torigoe K., Esumi K., *Langmuir.* **8**, 59 (1992)

[2] Loginov A.V., Gorbunova V.V., Boitsova T.B., *Appl. Chem.* **5**, 804 (1994)

[3] Loginov A.V., Gorbunova V.V., Boitsova T.B., *J. General Chem.* **2**, 189 (1997)

[4] Boitsova T.B., Loginov A.V., Gorbunova V.V., *Appl. Chem.* **10**, 1585 (1997)

[5] Ievlev V.M., Trusov L.I., Kholmyansky V.A., "Structural transformation in the thin films", Metallurgy, Moscow 1982, p.20.