RADIOLYTICAL SYNTHESIS OF GOLD NANOPARTICLES AND MECHANISM OF THEIR FORMATION

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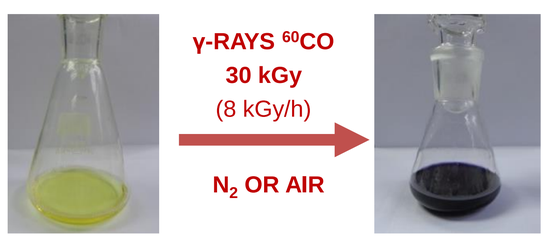
Introduction

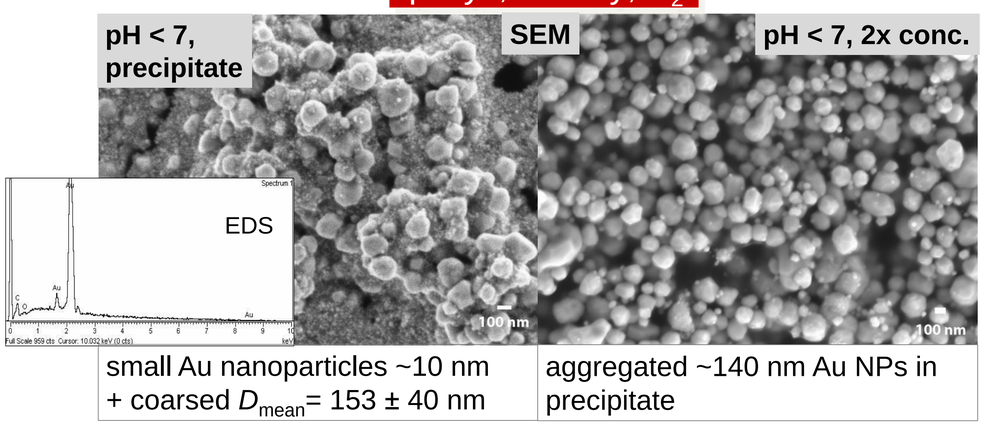
Gold nanoparticles (AuNPs) are widely used in analytical chemistry, in biomedicine and catalysis. Classical method for AuNPs synthesis is a citrate method, where citrate ions act both as reducing and stabilizing agents, but it requires high temperatures (~100 ^{O}C). γ-irradiation synthesis provides an excellent control over nanoparticle shape and size. The main advantage is its high energy and high reductive power, it yields a mass of reductive radicals (solvated electrons etc.), homogeneously in the whole volume of the sample. On the other hand, microemulsion synthesis has the advantage of preparing very small and uniform nanoparticles with control of their size and shape, thus defining their chemical and physical properties. Ideally, the water droplets (aqueous core of microemulsion) are completely enveloped by protective monolayer of surfactant and therefore are well dispersed in the oil phase. In such well-dispersed aqueous phase, the dissolved metal cations can be hydrolyzed, precipitated or reduced. The reducing agent is very important parameter in the synthesis of AuNPs. In this work, different systems with different reducing conditions were used. **The goal of this work was to study the influence of reducing and/or oxidizing conditions on the formation of gold nanoparticles**. **The hypothesis is that AuNPs could be synthesized without using reducing agents, *i.e.* due to very low affinity of gold for oxygen, AuNPs could be synthesized under highly oxidizing conditions.**

RADIATION INDUCED MICROEMULSION SYNTHESIS

56 ml cyclohexane
6 ml Triton X-100
1 ml 4 wt% $HAuCl_4 \cdot 3H_2O$ + 1 ml H_2O
or 1 + 1 ml 0.4 M NaOH
2 ml 1-pentanol



γ-rays, 30 kGy, N_2



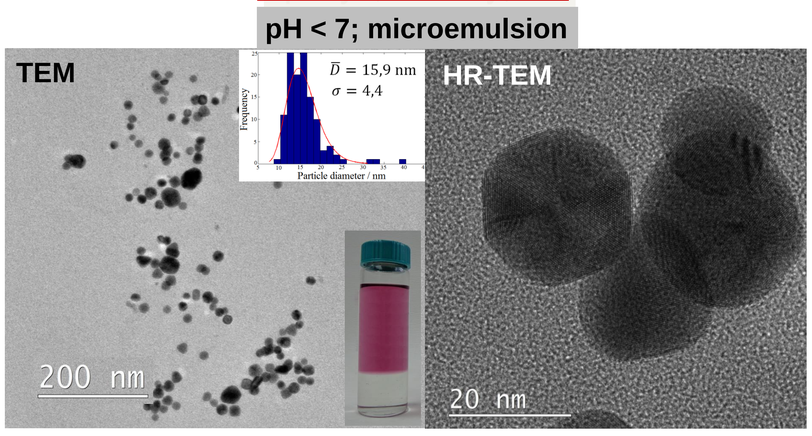
small Au nanoparticles ~10 nm + coarsed D_{mean}= 153 ± 40 nm

aggregated ~140 nm Au NPs in precipitate

- Reducing power of γ-rays tuned by atmosphere (N_2 ,air)
- **γ-irradition produced AuNPs even in the presence of air**
- Reduction by e^-_{aq}, organic radicals and H_2 formed by water and organic phase radiolysis
- In air more oxidizing species ($O_2^{\bullet -}$, $HO_2^{\bullet}$)

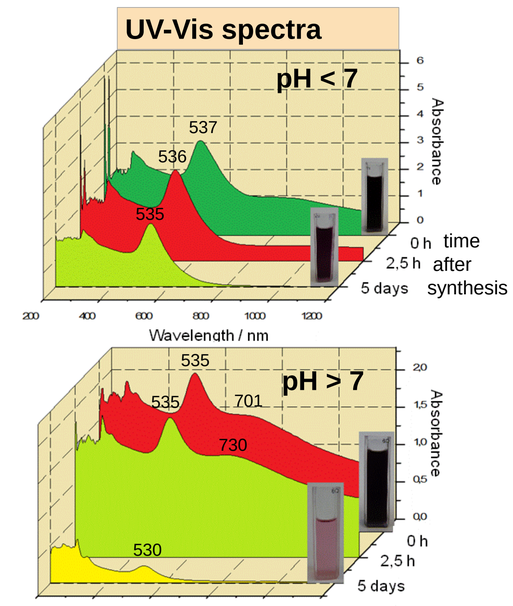
γ-rays, 30 kGy, air

pH < 7; microemulsion



discrete, well-dispersed, uniform Au NPs (D_{mean}=15.9 nm)

Au NPs synthesized at acidic pH being more stable.



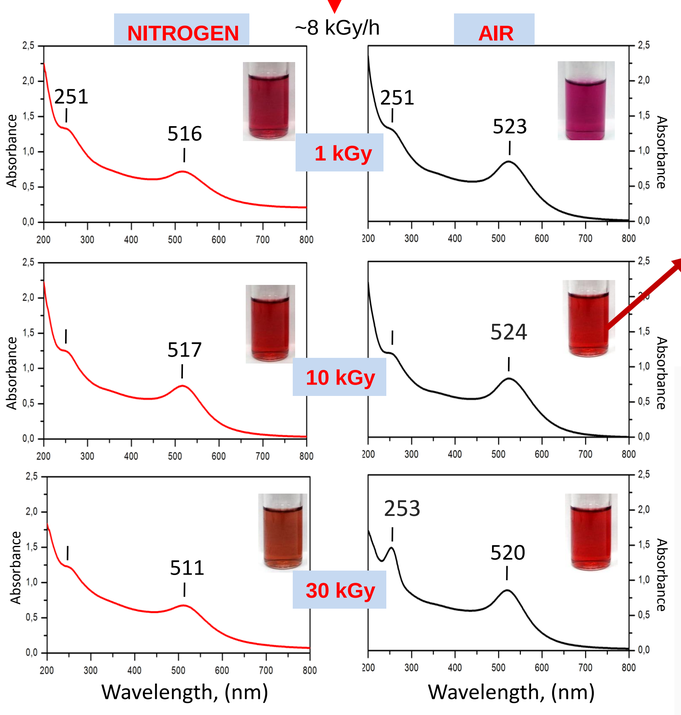
- **AuNPs can be formed in air-saturated microemulsions under highly oxidizing conditions**

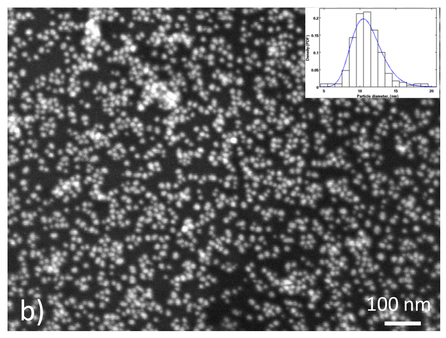
REFERENCES: 1) T. Jurkin, M. Guliš, G. Dražić, M. Gotić, Gold Bull. 49 (2016) 21.
2) N. Hanžić, T. Jurkin, A. Maksimović, M. Gotić, Radiat. Phys. Chem. 106 (2015) 77.

SYNTHESIS BY A CITRATE-RADIOLYTICAL METHOD

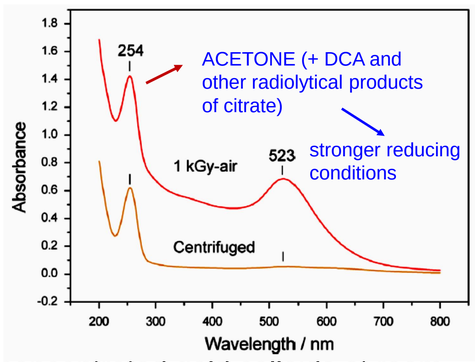
EXPERIMENTAL:
20.5 μL 4 wt% $HAuCl_4 \cdot 3H_2O$ + 10 ml MQ-H_2O + 200 μL 1 wt% citrate

^{60}Co γ-rays, ~8 kGy/h





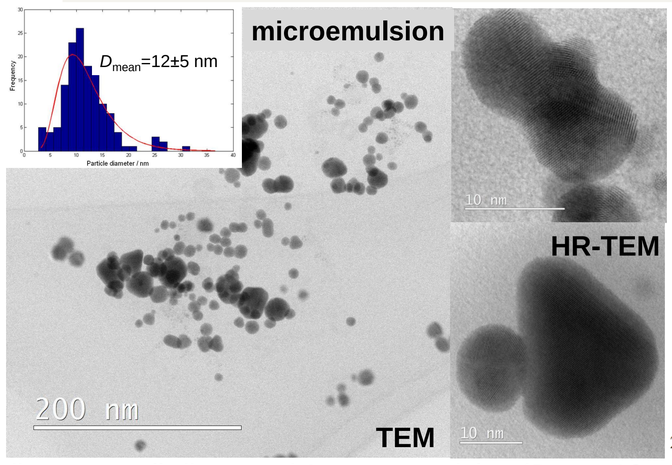
AuNP size controlled by atmosphere air (~10 nm), nitrogen (~5 nm)

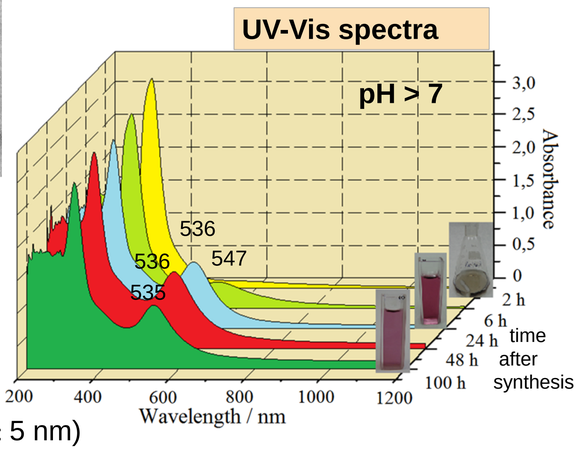


- γ-irradiation produced well-dispersed and highly concentrated gold colloids at room temp. in the presence of oxygen
- **Enhanced radiolytical degradation (oxidation/decarboxylation) of citrate** by dissolved O_2 and catalysed by gold → advantage effect in formation of AuNPs
- Radiolytical products of citrate (DCA etc.) - stronger reducing agents than citrate ions→ reduction at room temp.

Microemulsion without γ-rays, Oxidizing conditions, pH > 7

CONFIRMATION





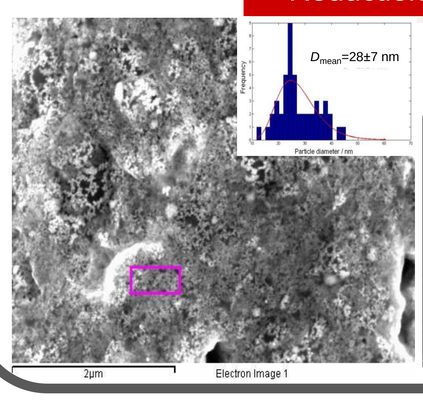
discrete, well-dispersed Au nanoparticles (D_{mean}=12 ± 5 nm)

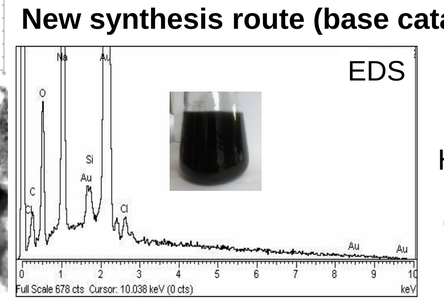
The reduction by oxidation of alcohol and Triton X-100:

CONFIRMATION

$$3\ R\text{-}OCH_2CH_2\text{-}OH + 2\ Au^{3+} \rightarrow 2\ Au + 3\ R\text{-}OCH_2CHO + 6\ H^+$$

Reduction in alcohol aq. solution, pH > 7





Au NPs synthesized using oxidation of 1-pentanol.

New synthesis route (base catalysed oxidation of alcohols):

(1) base catalysed

$$H_\beta R\text{-}OH_\alpha \overset{HO^-,\ pH>7}{\rightleftarrows} H_\beta R\text{-}O^- + H_\alpha^+$$

(2) base and Au catalysed

$$H_\beta R\text{-}O^- \rightarrow R{=}O + H_\beta^+ + 2e^-$$

Conclusions

- Size and size distribution of gold nanoparticles, their aggregation, dispersion and stability in the microemulsions depend on the strength of the reducing agent.
- Rather small and monodisperse AuNPs were obtained using γ-irradiation of microemulsion; stability depended on the pH. The reducing power of γ-irradiation was controlled by saturated gases. γ-irradiation was able to produce AuNPs in air-saturated microemulsions under oxidizing conditions. Generally, smaller AuNPs were obtained in the presence of N_2 in comparison to the air.
- At oxidizing conditions in microemulsion (NaOH aq.solution) AuNPs formed near the surfactant layer and are relatively uniform and well-dispersed. This can be explained by oxidation of hydroxyl (alcohol and Triton X-100) to carbonyl group with the aid of the catalytic action of hydroxyl ions and gold. In parallel with the catalytic oxidation of alcohol groups, Au^{3+} ions were reduced to elemental gold (Au^0). Mechanism is confirmed by synthesis of AuNPs in pure 1-pentanol (without microemulsion).
- **The base-catalyzed oxidation of alcohols can be used as new, simple synthesis route for obtaining AuNPs.**
- γ-irradiation of Au(III)/citrate solutions produced well-dispersed and highly concentrated gold colloids at room temp. An easy radiolytical reduction of Au^{3+} in the presence of oxygen can be explained by enhanced radiolytical oxidation/decarboxylation of citrate to dicarboxyacetone, acetone and other products.
- **We confirmed that classical approach of using a reducing agent to synthesize AuNPs is not a determining factor, since diametrically different approach can be used, namely in stimulating the oxidation of organic molecules in proximity to gold ions.**