Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2024, **34**, 893–895

Mendeleev
Communications

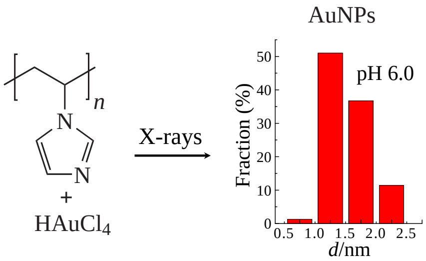
Effect of pH on radiation-induced synthesis of gold nanoparticles in solutions of poly(1-vinylimidazole)–Au^{III} complexes

Alexey A. Zharikov,*[a] Elena A. Zezina,[a] Anastasia V. Bolshakova,[a] Andrey V. Sybachin,[a]
Alexander S. Pozdnyakov,[b] Vladimir I. Feldman[a] and Alexey A. Zezin[a,c]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.*
E-mail: garikov-aleksey@mail.ru
[b] *A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,*
664033 Irkutsk, Russian Federation
[c] *N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow,*
Russian Federation

DOI: 10.1016/j.mencom.2024.10.039

Irradiation of an aqueous ethanol solution of poly(1-vinylimidazole) containing Au^{III} ions with X-rays leads to the generation of gold nanoparticles (AuNPs) with an average size determined by the pH value of the medium. The results obtained demonstrate a prominent example of the formation of stable ultrasmall AuNPs (<2 nm) at neutral pH.



Keywords: gold nanoparticles, poly(1-vinylimidazole), radiation-chemical synthesis, metal–polymer complexes, plasmon resonance, pH control.

Ultrasmall gold nanoparticles (AuNPs) exhibit unique catalytic,[1,2] electrochemical[1,2] and optical[2–4] properties. The bottom-up approach, based on reduction of Au^{III} ions in solutions in the presence of a suitable stabilizing agent, is a common method for preparing AuNPs with controlled size distribution, including sufficiently stable small NPs.[1,5] Chemical synthesis and efficient stabilization of ultrasmall AuNPs typically involves the use of molecules containing sulfur atoms, which are known to have a strong affinity to the Au surface through the formation of Au–S bonds.[1] However, in such cases, the available metal surface area is significantly reduced, and therefore, potential applications are limited. From this point of view, special attention should be paid to the use of polycations and nonionic polymers containing functional groups with nitrogen atoms as templates for the synthesis of AuNPs.[6,7] In this case, macromolecules do not form a dense layer around ultrasmall NPs (*i.e.*, some segments of the macromolecule are adsorbed on the surface of the NP, while other segments of the chain may form loops and tails or interact with another NP).

The radiation-chemical method is based on the reduction of metal ions by radical species (solvated electrons, hydrogen atoms, alcohol radicals, *etc.*) formed as a result of radiolysis of the medium. This approach makes it possible to control the kinetics of NP formation by adjusting such irradiation parameters as the absorbed dose and dose rate.[8] Furthermore, the radiation-chemical approach ensures the preparation of chemically pure nanocomposites, since typical chemical reducing agents are not used.[8,9] It is worth noting that a variation of the pH value of the medium leads to an alteration of the chemical nature and radiation-chemical yields of the main reducing agents involved in the redox reactions of NP formation,[10] which may strongly affect the competition between the processes of nucleation and growth. This work presents preliminary results of the radiation-chemical reduction of Au^{III} ions in the solutions of poly(1-vinylimidazole) (PVI),[†] a non-toxic and biocompatible polymer with the properties of a weak polybase.[11]

The UV-VIS spectra of PVI–Au^{III} complexes at pH 2.2 and pH 6.0 are shown in Figure 1(*a*). Mixing solutions of HAuCl$_4$ and PVI leads to the disappearance of the bands at 305 and 223 nm, corresponding to the ligand-to-metal charge transfer in complex AuCl$_4^-$ ions.[12] This fact clearly indicates the replacement of chloride ions by imidazole groups in the first coordination sphere of Au^{III} ions and suggests the formation of a metal–polymer complex in both acidic and neutral media. A similar effect was previously observed in the case of poly(1-vinyl-1,2,4-triazole).[7]

[†] To prepare AuNPs, an aqueous solution of 3 mM HAuCl$_4$ was added with continuous stirring to an aqueous solution of 21 mM (based on monomer unit) PVI (M_w = 25 kDa, synthesized at the Favorsky Irkutsk Institute of Chemistry, Irkutsk, Russia). Macromolecules in protonated or non-protonated forms were prepared by adding hydrochloric acid or potassium hydroxide to achieve pH 2.2 or 6.0, respectively. Before irradiation, 10 vol% of ethanol was added to the solutions as a scavenger of hydroxyl radicals. To remove atmospheric oxygen dissolved in the water–ethanol medium, the samples were bubbled with argon (extra pure grade). X-ray irradiation was carried out using a 5-BKhV-6 tube with a tungsten anode, as described in detail previously.[7] UV-VIS spectra of the initial and irradiated samples were recorded on a Perkin Elmer Lambda 9 spectrophotometer using quartz optical cells with a 1 mm optical path. Electrophoretic mobility measurements were performed in a thermostatic cell using Brookhaven ZetaPlus equipment. The structure of the resulting AuNPs was examined using a Karl Zeiss Leo-912 AB OMEGA transmission electron microscope (TEM) with a resolution of 0.3 nm, operating at 120 kV.

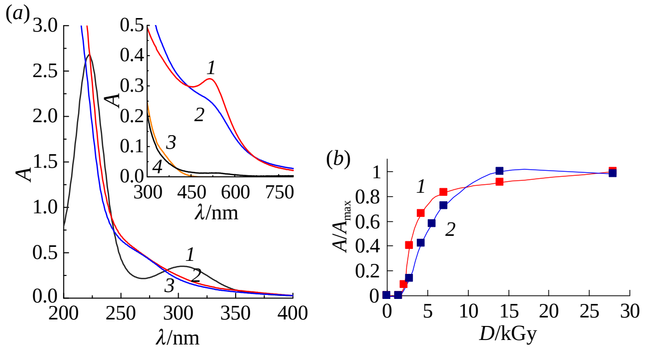


Figure 1 (*a*) UV-VIS spectra of (*1*) $HAuCl_4$ solution and initial aqueous PVI–Au^{III} solutions with (*2*) pH 2.2 and (*3*) pH 6.0. Inset: UV-VIS spectra of PVI–Au^{III} solutions with (*1*),(*3*) pH 2.2 and (*2*),(*4*) pH 6.0, either (*1*),(*2*) irradiated with X-rays to an absorbed dose of 14 kGy or (*3*),(*4*) not. (*b*) Dose dependence of the normalized optical density A/A_{max} of the AuNP absorption band at λ = 515 nm and absorbed dose rate of 1.4 kGy min^{-1} for solutions with (*1*) pH 2.2 and (*2*) pH 6.0.

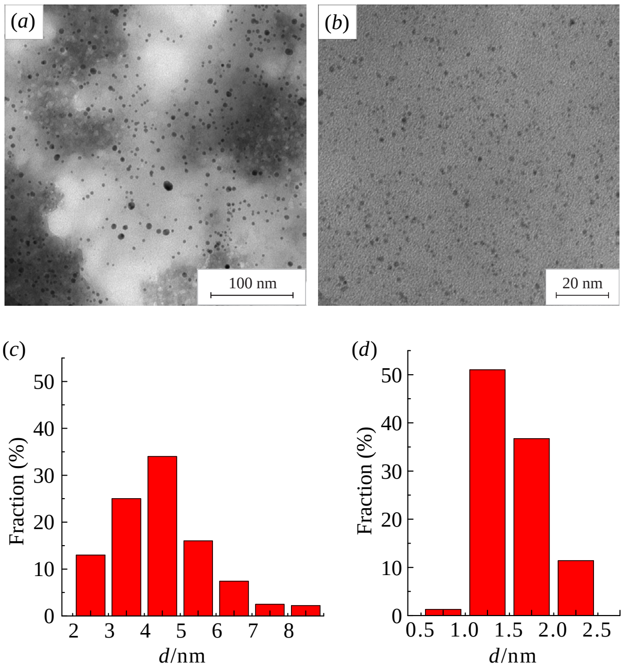


Figure 2 (*a*),(*b*) TEM images of samples with (*a*) pH 2.2 and (*b*) pH 6.0 irradiated with X-rays to an absorbed dose of 14 kGy. (*c*),(*d*) Size distributions of AuNPs obtained at (*c*) pH 2.2 and (*d*) pH 6.0.

The electrophoretic mobility (EPM) of PVI–Au^{III} aggregates has a significantly positive value of +4.1 × 10^{-4} cm^2 V^{-1} s^{-1} at pH 6.0. Obviously, the positive charge of this aggregates is associated with the formation of complex ions $[Au(Im)_xL_{4-x}]^{(x-1)+}$ ($x > 1$, Im is an imidazole group, and L is a low molecular weight Cl^- or OH^- ligand), since PVI macromolecules are not protonated at neutral pH (the EPM for PVI samples is close to zero at pH 6.0).

During irradiation, the initially colorless solutions with pH 2.2 and pH 6.0 acquired red and brown colors, respectively, which qualitatively indicate the formation of AuNPs with different average sizes. UV-VIS spectra of samples irradiated to an absorbed dose of 14 kGy, which corresponds to an irradiation time of 10 min, are shown in the inset to Figure 1(*a*). It is noteworthy that the absorption band corresponding to the surface plasmon resonance of AuNPs prepared at pH 2.2 is significantly more intense than that of the complex irradiated at pH 6.0. In the latter case, the typical plasmon peak at *ca.* 520 nm, characteristic of AuNPs, is practically absent. Instead, a shoulder appears in the range from 400 to 600 nm, suggesting the formation of AuNPs with an average size of less than 2 nm.[2] The intensity of the absorption bands increases with increasing absorbed dose due to the gradual conversion of Au^{III} ions into AuNPs, reaching a plateau value at *ca.* 7 and 10 kGy for solutions with pH 2.2 and pH 6.0, respectively [Figure 1(*b*)].

TEM data for samples irradiated to an absorbed dose of 14 kGy showed that AuNPs with the smallest size and narrowest size distribution (number average diameter D_n = 1.5 nm, weight average diameter D_w = 1.8 nm, D_w/D_n = 1.20) are formed at neutral pH, when PVI macromolecules are non-protonated [Figure 2(*b*),(*d*)], while irradiation at pH 2.2 leads to the formation of relatively large AuNPs (D_n = 4.2 nm, D_w = 5.7 nm, D_w/D_n = 1.36) [Figure 2(*a*),(*c*)]. Thus, the results obtained demonstrate the high efficiency of PVI as a stabilizing matrix for AuNPs, which in neutral and, apparently, acidic media is achieved due to the specific adsorption of non-protonated imidazole groups on the Au surface.[7,13] Indeed, it can be assumed that imidazole groups replace chloride ions adsorbed on the Au surface by analogy with ligand substitution in the $AuCl_4^-$ complex, which effectively occurs even at pH 2.2.

It is well known that the radiation-chemical reduction of multiply charged metal ions is a complex process and proceeds through the formation of ions in intermediate oxidation states.[8,14] Analysis of the basic scheme[8] of radiation-chemical processes leading to the formation of metal NPs shows that a decrease in pH to 2.2 leads to a significant decrease in the radiation-chemical yield of hydrated electrons (e_{aq}), the strongest reducing agent (E^0 = −2.87 V *vs.* NHE),[15] which is crucial for the formation of isolated solvated Au^0 atoms ($Au^+ + e_{aq} \longrightarrow Au^0$),[14] *i.e.*, for the nucleation stage. It should be emphasized that the standard potential of the Au^+/Au^0 pair is much lower (−1.5 V *vs.* NHE)[16] than that corresponding to the formation of bulk Au metal (+1.69 V *vs.* NHE),[16] and therefore the reduction of Au^I ions limits the formation of NPs.[13] In an acidic medium, most of e_{aq} is actually replaced by hydrogen atoms. At first glance, hydrogen atoms (E^0 = −2.3 V *vs.* NHE)[15] are also strong reducing agents that can provide the nucleation stage (see above). However, in contrast to e_{aq}, hydrogen atoms should preferentially react with ethanol molecules. The resulting $Me(HO)HC^{\bullet}$ radicals exhibit much weaker reducing properties (E^0 = −1.1 V *vs.* NHE)[15] and are capable of reducing Au^I ions only on the metal surface, thereby ensuring the growth of NPs. Thus, from a kinetic point of view, a decrease in the pH value leads to a decrease in the rate of the nucleation stage. Consequently, at the same initial Au^{III} concentration, larger AuNPs are formed.

In summary, the results obtained demonstrate a prominent example of the use of pH adjustment for highly efficient control of AuNP size in radiation-induced synthesis, which is associated with the specific mechanism of radiation-chemical processes in aqueous alcohol media. Finally, it can be assumed that the resulting AuNP–PVI nanocomposites may be of potential interest for medical applications.[11]

This work was carried out with financial support from the Russian Science Foundation (project no. 22-73-00054). E. S. Shiryaeva and V. V. Shorokhov are gratefully acknowledged for valuable discussions.

References

1 M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293; https://doi.org/10.1021/cr030698+.

2 V. Amendola, R. Pilot, M. Frasconi, O. M. Maragò and M. A. Iatì, *J. Phys.: Condens. Matter*, 2017, **29**, 203002; https://doi.org/10.1088/1361-648X/aa60f3.

3 E. A. Karpushkin, N. K. Ivanova, E. A. Mesnyankina and V. G. Sergeyev, *Mendeleev Commun.*, 2024, **34**, 78; https://doi.org/10.1016/j.mencom.2024.01.023.

4 N. K. Ivanova, E. A. Karpushkin, L. I. Lopatina and V. G. Sergeyev, *Mendeleev Commun.*, 2023, **33**, 346; https://doi.org/10.1016/j.mencom.2023.04.016.

5 J. Koetz and S. Kosmella, *Polyelectrolytes and Nanoparticles*, Springer, Berlin, 2007; https://doi.org/10.1007/978-3-540-46382-5.

6 A. B. R. Mayer and J. E. Mark, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 1997, **34**, 2151; https://doi.org/10.1080/10601329708010040.

7 A. A. Zharikov, R. A. Vinogradov, E. A. Zezina, A. S. Pozdnyakov, V. I. Feldman, A. L. Vasiliev and A. A. Zezin, *Colloid Interface Sci. Commun.*, 2022, **47**, 100602; https://doi.org/10.1016/j.colcom.2022.100602.

8 J. Belloni, *Catal. Today*, 2006, **113**, 141; https://doi.org/10.1016/j.cattod.2005.11.082.

9 A. A. Zezin, A. I. Emel'yanov, G. F. Prozorova, E. A. Zezina, V. I. Feldman, S. S. Abramchuk and A. S. Pozdnyakov, *Mendeleev Commun.*, 2019, **29**, 158; https://doi.org/10.1016/j.mencom.2019.03.013.

10 A. Zezin, G. Danelyan, A. Emel'yanov, A. Zharikov, G. Prozorova, E. Zezina, S. Korzhova, T. Fadeeva, S. Abramchuk, N. Shmakova and A. Pozdnyakov, *Appl. Organomet. Chem.*, 2022, **36**, e6581; https://doi.org/10.1002/aoc.6581.

11 I. A. Shurygina, G. F. Prozorova, I. S. Trukhan, S. A. Korzhova, N. N. Dremina, A. I. Emel'yanov, O. V. Say, N. P. Kuznetsova, A. S. Pozdnyakov and M. G. Shurygin, *Nanomaterials*, 2022, **12**, 16; https://doi.org/10.3390/nano12010016.

12 O. R. Miranda and T. S. Ahmadi, *J. Phys. Chem. B*, 2005, **109**, 15724; https://doi.org/10.1021/jp0514832.

13 A. V. Meltonyan, A. H. Poghosyan, S. H. Sargsyan, K. S. Margaryan and A. A. Shahinyan, *J. Polym. Res.*, 2020, **27**, 91; https://doi.org/10.1007/s10965-020-02075-8.

14 G. R. Dey, A. K. El Omar, J. A. Jacob, M. Mostafavi and J. Belloni, *J. Phys. Chem. A*, 2011, **115**, 383; https://doi.org/10.1021/jp1096597.

15 P. Wardman, *J. Phys. Chem. Ref. Data*, 1989, **18**, 1637; https://doi.org/10.1063/1.555843.

16 S. Mosseri, A. Henglein and E. Janata, *J. Phys. Chem.*, 1989, **93**, 6791; https://doi.org/10.1021/j100355a042.

Received: 13th May 2024; Com. 24/7495