

NMR study of Au/Al nanosystems in solution

Victor Kislyuk^{*}, Andrii Melnyk^{**},
Nikolay Buryak^{***}, Volodymyr Trachevskij^{****}

Nuclear magnetic resonance spectroscopy (NMR) ^1H , ^{35}Cl , ^{27}Al and ^{13}C was applied to study underlying processes at the various stages of the synthesis of Au/Al nanoparticles. ^{35}Cl spectrum was downfield shifted by 2.6 ppm as to the reference signal of the hydrated Cl^- ion in NaCl solution. The evolution of the NMR spectra points to the formation of the stabilized shell around the gold containing nucleus. The shell restricts the supply of the reducing agents, which is the condition for the formation of Au^{2+} state at the concentration range in question. The electron paramagnetic resonance (EPR) spectra reveal formation of both Au^{2+} ($g = 2.17$) and Au^+ ($g < 2$) intermediates incompletely reduced as well as Au^0 clusters ($g = 2.062$) with odd number of atoms. The latter is coupled in many cases by the narrow signal with $g = 2.0048$ attributed to the radical in the supporting surrounding (tannin containing matrix in our case).

Key words: NMR, EPR, nanoclusters, UV-vis spectroscopy

1 Introduction

Magnetic properties of nanoparticles are used widely in many fields: biology (biosensors) [1-3], medicine (hyperthermia [4, 5], MRI – magnetic resonance imaging [6]), chemistry (waste water treatment [7]) as well as semiconductor technology (development of magnetic storage devices [8], photovoltaic cells [9, 10] *etc.*). The gold containing nanoparticles are of particular interest due to the special techniques developed for producing bio-electrical signal generated by biomolecules immobilized at the nanoparticle surface [11, 12].

Methods of the synthesis of the gold nanoparticles are based on the multistage reduction process of $\text{Au}^{3+} \rightarrow \text{Au}^0$, which *a priori* does not suggest any paramagnetic properties provided it deals with a bulk material. However, there are a set of experimental evidences of the paramagnetism in gold-containing nanoparticles [13-15] as well as nanoparticles or metal complexes containing atoms-diamagnetics in the bulk such as silver [16] and copper [17].

This study is an attempt to deepen the knowledge on the nature of the magnetism in gold-containing nanoparticles in general and in particular nanoparticles of Al/Au composite [18]. There are at least two conceptual possibilities of this phenomenon: i) stabilization of the gold intermediates (Au^{2+}); ii) transformation of the reducing molecules (tannin and/or citrate) into radical forms. The Al compounds added to the system while initiation of the

reduction of the gold ions can also provide: i) fine adjustment of the reduction degree and rate during the nanoparticle formation; ii) effective tool to monitor structure and functionality of the nanoclusters with ^{27}Al NMR-label.

To follow the underlying processes NMR spectra were registered at different stages of the synthesis from precursors (solution of HAuCl_4^- and HAICl_4^- – "metal-containing solution" and solution consisting of sodium citrate and tannin – "reducing solution") to the complete reduction and oxidation. The task concerns the system both simple (binary and ternary) and more complex compounds of $\text{AuCl}_4^- - \text{AlCl}_4^- - \text{tannin} - \text{citrate}$. ^1H , ^{35}Cl , ^{27}Al , ^{13}C NMR spectroscopic techniques allow one to study impacts of the various factors.

2 Experiment

2.1 Sample preparation

Au/Al nanocomplex was synthesized by co-reduction method [18] modified according to peculiarities of the redox processes. A water solution of the chlorine containing compounds of Au and Al (HAuCl_4 and AlCl_3) was used as a precursor ("metal containing solution"). 0.55% solution of HAuCl_4 was produced by dissolving gold (of 99,99% purity) filings at the ambience of chlorine gas [19]. The gaseous chlorine flowed from the reactor with potassium permanganate where hydrochloric acid was added with low rate (approximately 0.01 ml per 5 minutes).

^{*}G. V. Kurdyumov Institute of Metal Physics, National Academy of Sciences of Ukraine, Vernadskogo 36, 03142 Kyiv, Ukraine, viktorkislyuk@gmail.com, ^{**}Institute of Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Naumova str. 13, 03028 Kyiv, Ukraine, ^{***}V. I. Vernadskiy Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Acad. Palladina Ave. 32-34, 03680 Kyiv, Ukraine. ^{****}Technological Center, National Academy of Sciences of Ukraine, Pokrovska str. 13, 04070 Kyiv, Ukraine

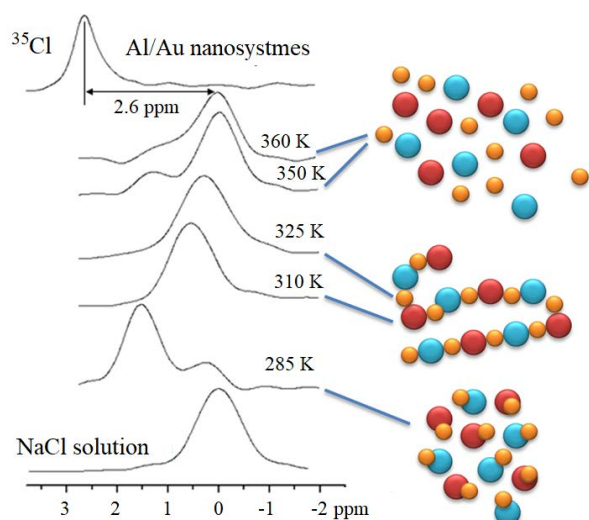


Fig. 1. ^{35}Cl NMR spectra: schematic representation for the system of Al, Cl and Au atoms in the solution

A 1% solution of the aluminum chloride was prepared from $\text{Al}(\text{OH})_3$ powder with hydrochloric acid poured slowly till stoichiometric ratio and left for a day. Then water was added in the amount corresponding to 1% concentration.

The "metal containing solution" comprised of 5.45 ml of the 0.55% solution of the gold compound and 6 ml of the 1% solution of the aluminum containing constituent. Finally, water was added till 240 ml volume. To study Al influence on the final paramagnetic properties, we used the precursor solution with sufficient excess of the aluminum content followed by the proportionally increased amount of the hydrochloric acid. In this case soda was used to regulate the pH value of the metal-containing solution.

The "reducing solution" contained the mixture of two water solutions: 3 ml of 1% tannin solution and 12 ml of 1% solution of sodium citrate; 25 mM solution of equimolar amount of sodium carbonate was added as a buffer. Then H_2O was added in amount to reach 60 ml volume of the whole mixture.

The "metal containing" and "reducing" solutions were heated separately to 45 – 50 °C and mixed together under intense stirring for 10 minutes. Then the final solution containing the Al/Au nanosystem was left to cool down to room temperature. One sample was prepared with lack (as to the reaction stoichiometry) of the "reducing solution" to check the role of the reducing agents on the magnetic properties of the final Al/Au nanosystem. The influence of temperature was observed on the NMR spectra of the "metal containing solution".

We used 0.3 M solution of tris(ethylene diamine) cobalt (III) chloride ($\text{Co}[\text{en}]_3\text{Cl}_3$) as a model object to reveal the nature of the downfield shift observed in the NMR ^{35}Cl spectra of the final Al/Au nanosystem. NMR ^{35}Cl spectrum of the solution of $\text{Co}[\text{en}]_3\text{Cl}_3$ with chlorine ions known to be linked to the outer sphere via H-bonding demonstrated the same direction of the chemi-

cal shift (with $\delta \sim 15$ ppm) as that of the Al/Au nanosystem.

The paramagnetic properties of the formed system were studied for the solid species extracted from the solution and dried at temperature not exceeding 50 °C by different methods: i) centrifugation and separation of the solid residue; ii) salting out from the Al/Au solution with dioxane; iii) liophilic drying of the solution with increased Al content; iv) liophilic drying of the solution with stoichiometry shifted toward lack of the reducing constituent.

2.2 NMR

NMR spectra were registered by NMR spectrometer Bruker Avance 400 (9.4 T magnetic field) at frequency values 400.130 MHz (^1H), 100.613 MHz (^{13}C), 39.204 MHz (^{35}Cl), 104.261 MHz (^{27}Al). The signal was accumulated after electromagnetic pulses of 6 – 10 μs duration repeated with 0.5 – 4 s period of time.

Chemical shift (δ , ppm) was determined as to the reference spectra of, respectively: NaCl solution for ^{35}Cl spectra; 6-coordination peak of aqua-Al complex [20] for ^{27}Al spectra; tetramethylsilane for ^1H and ^{13}C .

To study temperature influence on the formation of the heterometal composition ^{35}Cl NMR spectra of the solution mixture of the metallic compounds heated gradually from 285 K to 360 K were registered at various values from this range. ^1H and ^{13}C NMR spectra served to control the state of the "reducing solution".

2.3 UV-vis absorption

UV-vis electron absorption spectrum was measured for the solution in 1 cm thick cuvette with Specord.

2.4 EPR

EPR spectra were recorded on a X-band spectrometer Bruker Elexsys E580 at room temperature (295 K). The EPR spectra recording conditions were as follows: frequency - 9.87 GHz; microwave power - 4 and 16 mW; modulation intensity - 5 G with modulation frequency 100 kHz; scan width - 600 mT and 51.2 mT; resolution - 2048 points; conversion time - 117 ms; time constant - 81 ms; number of scans - 4 and 16. Before spectral investigation samples of the studied nanocomposites were placed in glass capillaries with a diameter of 1 mm and then inserted into standard 3 mm quartz ampoule (Norrell). Sample of diphenylpicrylhydrazyl (DPPH) with $g = 2.0036$ was used for the spectrometer calibration.

3 Results and discussions

^{35}Cl NMR spectra are turned to be the most informative ones (Fig. 1) as to the possibility to follow the transformations in the metallic precursor solution and final Al/Au solution within 275 – 360 K temperature range.

There are two signals observed in the spectra below room temperature, one of which with approximately 1.5

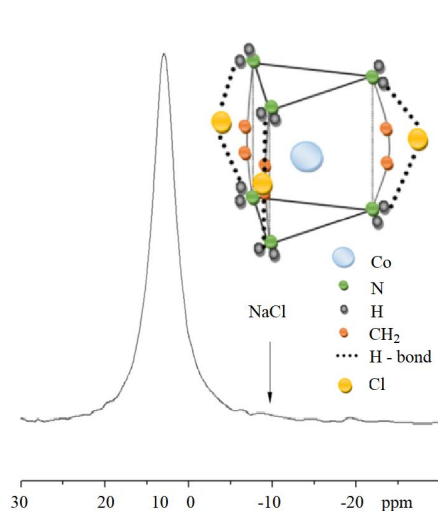


Fig. 2. NMR ^{35}Cl signal of $\text{Co}[\text{en}]_3\text{Cl}_3$ used in this research as a model system

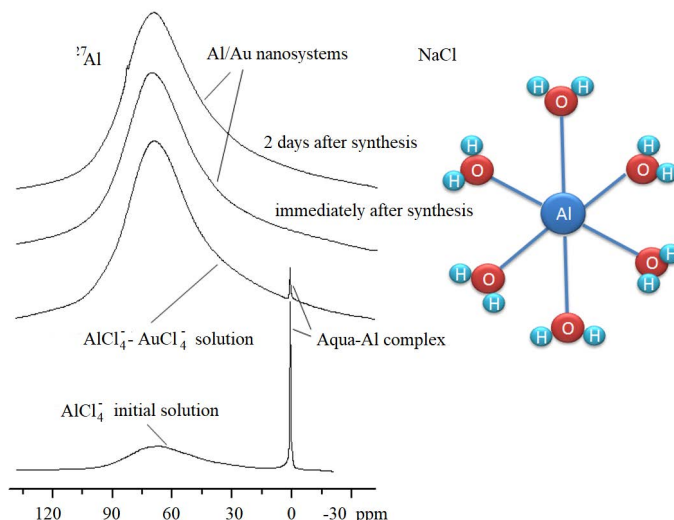


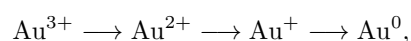
Fig. 3. ^{27}Al NMR spectra, and schematic image of 6-coordination Al aqua-complex

ppm (low field peak) relates to the chloride ions as components of some nanostructure formed under these conditions (Fig. 1, 285 K). The other one is close to that of chloride ions in NaCl solution. The signals merge under the heating. Heating induces also the upfield shift of the combined peak (curves corresponding to 310 K and 325 K). The temperature of the synthesis (near 325 K) corresponds to the state with single peak, which means intense exchange between hydrated chloride ions and outer Cl^- ions – components of the Au-Cl-Al heterometal complex newly formed in the solution. This line is observed within rather narrow temperature range near the synthesis temperature. The chlorine role in this complex is to form a bridge fragment keeping together aluminum and aurum atoms and perhaps even to participate in the formation of the chain with these atoms (Fig. 1, right). Further temperature increase destroys these links, as it follows from the position of the peaks corresponding to that of hydrated chloride ion at 350 K and 360 K temperatures of the "metal containing solution". Hence, 310 – 325 K temperature range chosen as the most appropriate for the synthesis [18] determines the best thermodynamic conditions for the further route for the formation of the metal containing nanoparticles.

The ^{35}Cl NMR spectrum of the final solution after the complete synthesis at 325 K contains peak down field shifted by 2.6 ppm as to that of the hydrated Cl^- ions. Thus, the shift observed is an evidence of the Cl-ion participation in the formation of the final nanostructure. This chlorine-ion could play a twofold role of participation in: compensation of the positive charge located inside the metal-containing core of the newly formed nanostructure (via coulomb interaction) as well as competing formation of the complex at the outer sphere. The latter relates to the hydrogen bonds with functional groups of tannin-citrate and H_2O molecules being involved. H-bonding pulls the electron cloud from the chlorine nucleus, which reduces the screening of the NMR signal of the final nanosystem, *ie* induces the downfield shift. To

explain the relation of the direction of ^{35}Cl spectrum shift of the final nanostructure with the hydrogen bonding the experiment was carried with the model object: 0.3 M solution of $\text{Co}[\text{en}]_3\text{Cl}_3$ solution with known bond structure in the crystalline state [21]. The solution of this system contains the chloride ion subjected to competing interactions: i) coulomb attraction to $(\text{Co}[\text{en}]_3)^{3+}$ ion; ii) H-bonding. The latter keeps the Cl^- apart from the attracting positive charge (Fig. 2), which ensures the stability of the system.

The location of the positive charge in the Al/Au nanosystem is rather attributed to the gold containing fragments in accordance with the theory of soft and hard acids [22]. This means that the gold can be reduced incompletely, and there are intermediate states formed at a certain step of the multistage reduction process [23]:



in particular paramagnetic state of Au^{2+} . This is consistent with the existence of the magnetic properties of the produced system of Al/Au nanoparticles.

^{27}Al NMR spectra (Fig. 3) reflect processes in the coordinate proximity of Al atom at the various stages of the synthesis. The initial spectrum of HAlCl_4 solution consists of wide line of the Al polymer form and intense narrow peak of 6-coordinated ion of aluminum in aqua-complex [20] which reduces after adding the gold compound and disappears completely after pouring the "reducing solution" with the redox parameters corresponding to the conditions of the Al transition to polymer form with tetracoordinated state. Hence, the nanoparticles synthesized in the solution contain polymer oxide hydrated form with tetracoordinated Al which is responsible for the stability function (along with the molecules of tannin and citrate). This form is known [24] to be in either neutral or negatively charged state at the conditions in question for the reaction mixture. Thus, the carriers of

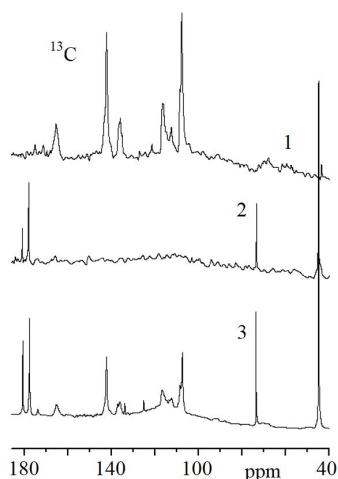


Fig. 4. ^{13}C NMR spectra of the constituents of the "reducing solution": 1 – tannin; 2 – citrate; 3 – tannin and citrate mixture in ratio used for the synthesis

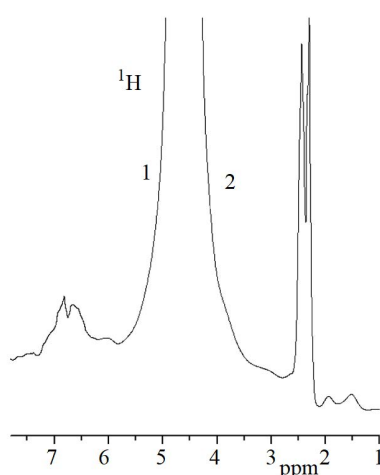


Fig. 5. ^1H NMR spectra of the constituents of the "reducing solution": 1 – tannin; 2 – sodium citrate

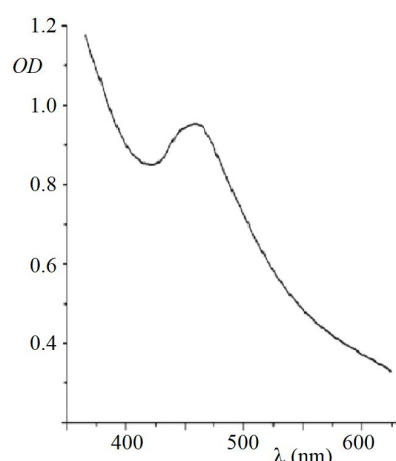


Fig. 6. UV-vis electron absorption spectrum of the Al/Au nanosystem in the solution

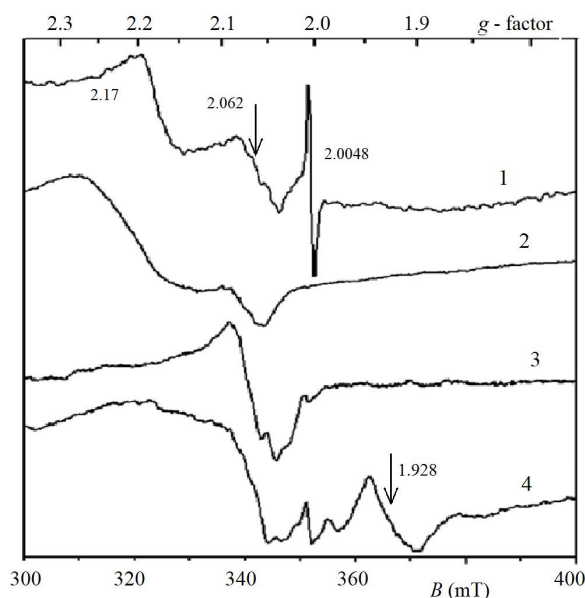


Fig. 7. EPR spectra of the samples of Al/Au nanosystems extracted from the final synthesized solution by the following methods: 1 – centrifugation; 2 – salted out with dioxane; 3 – water vaporization from the solution with aluminum excess; 4 – water vaporization from the solution with lack of the reducing agents

the positive charge in the above mechanism of the down-field shift in NMR ^{35}Cl spectra can be only Au^{2+} and Au^+ .

The signal with $\delta \sim 80$ ppm in ^{27}Al NMR spectrum appears in two days after the synthesis. This signal is outlined against the wide line of the polymer oxide form and attributed to $\text{Al}(\text{OH})_4^-$. We established that the presence of this signal is a criterion in the optimization of the conditions for the directed synthesis.

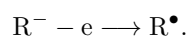
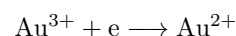
^{13}C and ^1H NMR spectra are utilized to control processes involving reducing agents. ^{13}C spectrum (Fig. 4) answers the question about the interaction of the con-

stituents in the "reducing solution". The spectrum registered after the mixing tannin and citrate (Fig. 4, curve 3) contains new features (absent in the spectra of the constituents measured separately), which is an evidence of the appearance of a supermolecular structure-formative matrix. This structure is stable due to the action of the bicarbonate buffer solution and the sequence of the bulk structurizing which is sensitive to the order in the sequence of the reagent injection. Separate addition of the buffer solution solely to tannin or citrate destroys the structure with precipitation. ^1H NMR spectra contain features of the presence of the tannin and sodium citrate in the solution.

The UV-vis spectrum of the electron absorption, Fig. 6, is typical for the plasmon band attributed to plasmon resonance for gold nanoparticles in the solution [25].

EPR spectra of all our samples (Fig. 7) contain one or several resonances (dependent on the technique used for the sample preparation) with g -factor values of 2.17, 2.062, 2.0048 and $g < 2$, while line with $g = 2.062$ is present at the spectra of all the samples prepared in this research.

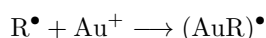
The $g = 2.17$ signal is reported by other researchers [13, 15] and is often attributed to the formation of the intermediate incompletely reduced paramagnetic state of Au^{2+} corresponding to $[\text{Xe}]4f^{14}5d^9$ electron configuration. The $g = 2.17$ signal appearance is mostly coupled with the registration of $g = 2.0048$ signal (Fig. 7, curve 1), which corresponds to the following charge transfer reaction:



In contrast, the authors studied the stabilization of the gold containing nanoparticles at the zeolite surface [15] did not reveal the narrow line with $g = 2.0048$. This line is also absent on the spectra of the other our samples

fabricated by vaporization and salting out of the stoichiometric solution in dioxane (Fig. 7, curves 2 and 3). Hence, the appearance of such a radical state is assumed to be related to the supporting environment lability preventing (due to chelate-effect) mechanical stress. In contrary, the latter can be the reason which suppresses the radical state appearance within the supporting matrix for the case of the stabilization at the zeolite surface. The sample salted out from the colloid solution does not contain the radical EPR signal due to disproportionation of the radicals – oxidation products of the organic components of the system.

The EPR signal with $g < 2$ is measured for the sample dried from the solution synthesized with the lack of the reducing agents (curve 4). The reduced value of g corresponds to the following interaction



producing $(AuR)^{\bullet}$ complex where the electron radical delocalizes into the electron shell of Au atoms, with a substantial contribution of the spin-orbital interaction. The similar phenomenon was observed for complex formation of the humate-radical with Pb(II) ions [26].

The spectra of all samples contain signal with $g = 2.062$ regardless of a preparation route. This signal is also reported in a number of papers [13, 15, 27], in particular the EPR spectra measured at low temperatures contain a distinct fine structure observed on the EPR spectra of our samples. We associate the origin of this signal with the paramagnetic state of the reduced $5d^{10}6s^1$ gold in the nanoparticle with an odd number of atoms. The general model of the orbital origin of the paramagnetic properties of the ensemble of gold nanoparticles was considered in [28]. The fine structure is attributed to quantum confinement of the nanoparticle electron structure [15, 29], which is predicted theoretically [30].

The spectra were registered against some wide background signal whose nature remains unclear for us. We can assume that this feature can be attributed to cyclotron resonance which can take place in metal containing nanoparticles provided the anomalous skin effect conditions are met [31].

4 Conclusion

This research proposes practically the radio spectroscopy control for the synthesis of Al/Au nanoparticles. These systems are of both practical and model value (as to understanding of the nature of nanoparticle magnetism). The NMR spectroscopy can control the technological process at various stages.

First, NMR spectra clearly indicate the state of the initial solution $[HAuCl_4]^{-}$ and $[AlCl_4]^{-}$ precursors, while the necessity of keeping the temperature range being argued and explained in detail. The heating of the precursor solutions is shown to be the crucial point for the successful synthesis of the Al/Au nanoparticles, which is associated with formation of the unit line in the NMR ^{35}Cl

spectra with chemical shift of 0.2 – 0.5 ppm as to the reference peak of the free chlorine ion. We relate this line to the formation of Al-Cl-Au complexes as "germs" for the future nanoparticles. Further temperature increase till 350 K causes decomposition of this line into two signals: aquated chlorine ion and chlorine ion outer bound in a nanocluster.

Second, NMR ^{35}Cl spectrum of the final synthesized solution of the nanoparticles reveals 2.5 ppm chemical shift toward downfield, provided stoichiometric, temperature and other procedure requirements are precisely met. This shift is attributed to the reduced electron screening of the chlorine atoms due to stabilization of their spatial localization under hydrogen bonding within the metal containing supporting matrix based on the tannin molecule.

Third, NMR spectra of aluminum demonstrated complete removal of the water molecules from the coordination environment of the aluminum atoms since the line of 6-coordinated aqua-complex of Al is absent at the spectra measured after the synthesis.

Fourth, NMR spectroscopy allows one to implement structural and functional monitoring of the complex ion-molecular system of $HAuCl_4$, $HAuCl_4$, tannin, citrate, bicarbonate.

The existence of the paramagnetic properties of the synthesized structures is evidenced by the available EPR signals. The EPR spectra of the samples prepared by various routes are found to possess the impacts of all possible intermediate charged states of the gold stabilized within the tannin based matrix: Au^{2+} ($g = 2.17$) which is coupled with narrow line of the charged radical ($g = 2.0048$) – for the samples centrifuged from the stoichiometric solution, Au^{+} in complex with tannin ($g < 2$) – for the samples prepared by water vaporization from the solution with reduced content of the reducing agents, as well as completely reduced state of Au^0 ($g = 2.062$) whose paramagnetism is attributed to the gold nanoparticles with odd number of atoms. The latter is revealed for all samples regardless the method of their preparation.

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Victor Kislyuk is Senior Researcher of G. V. Kurdyumov Institute of Metal Physics, National Academy of Sciences of Ukraine. PhD degree awarded in 1999. He has the grade of Associate Professor since 2006. Research interests and expertise: organic conducting materials and composites for electronics, in particular for photovoltaics, characterization of materials by spectroscopic techniques.

Andrii Melnyk was born in Kyiv in 1974. He received his Master degree from the National Technical University of Ukraine “Kiev Politechnical Institute” in 1996. He is Research Assistant at the Institute for Sorption and Endoecology Problems of the NAS of Ukraine since 2009. He is an employee of “EPR Spectroscopy” open access centre based on Bruker Elexsys E580 spectrometer. His professional interests include carbon-based nanomaterials, nanocomposites, spin probes and spin-labeled molecules, magnetic films and nanoparticles, transition metal ions, defects and impurities in crystalline and amorphous solids.

Nikolay Buryak PhD since 1975. Senior Researcher of V. I. Vernadskiy Institute of General and Inorganic Chemistry since 1984. Participated in the state program on Fundamental issues of synthesis for Chemical Industry. Expertise in UV-vis absorption, IR spectroscopy, nanostructured systems, nanomaterials, nanotechnologies.

Volodymyr Trachevskij PhD since 1975. Head of laboratory of Technological center of National Academy of Sciences of Ukraine. Expertise in diagnostics of self organization in condensed matter by spectroscopic techniques including NMR, EPR, IR, UV-vis, XPS. The author of more than 300 articles and 15 books.