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Electric Discharge in Liquids as Technique to Obtain High-Dispersed Materials Based on Metals of IB Group

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Abstract—Nowadays, there is an intensive development of the electric arc discharge method, first proposed in 1922 by T. Svedberg. That method is an effective tool for the synthesis of nanomaterials such as metals, oxides, binary compounds and, in some cases, has undoubted advantages compared to the other methods. In particular, the formation of silver and gold nanoparticles is possible in the absence of any reductants and surfactants. The copper nanostructures synthesis is based on the more cost effective and productive technology compared to the other physical methods. In this article, the main achievements and prospects for the application of the electric discharge method in liquid for the synthesis of the silver, gold and copper nanostructures are presented.

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INTRODUCTION

The past two decades have been characterized by a sharp increase in a number of works dedicated to the synthesis and research of materials in the nano-state. The interest to such objects is related to their special physical and physicochemical properties [1–3]. The activity of works in this area has been also encouraged by the development of informative instrumental methods applicable for characterization of nanomaterials.

Among methods to synthesize high-dispersion particles a special place is given to the method using an electrical discharge in a liquid offered by a Swedish scientist Theodor Svedberg in 1922 [4]. In his works Svedberg used an arc discharge, which was formed between metal electrodes immersed in liquid and contacting with metal powder when high-frequency alternating current was passed through the electrodes. In this case rapid melting and evaporation of the metal is observed and followed by subsequent condensation of its vapors in vapors of the liquid medium. Thus, it is an electrical condensation method, which, according to Richard Feynman's classification, is a “bottom-up” method. The main advantage of this method is its universal character. Its only fundamental limitation is the necessity for the dispersed material to be electrically conductive. For 90 years since the moment the electrical condensation method was discovered, it has been applied to synthesize sols of a great number of metals [5], binary compounds [6], carbon materials, and core-shell structures. The electrical condensation method itself has also been further developed; methodologies to synthesize nanoparticles from the material of the electrodes by erosion of the electrodes under electrical discharge conditions have been proposed.

At present, there is a surge of interest to the arc discharge method. This method was successfully used to synthesize carbon nanostructures from nanotubes [7] to complex structures with embedded metals [8]. Syntheses of carbon nanoparticles of various shapes are carried out in vacuum, organic solvents, and liquid nitrogen. Obtainment of carbon “bulbs” in water [9] served as a starting point to study the possibilities of electrical discharge in liquid to synthesize non-carbon structures, including metals [10–13], silicon [14], oxides [15–17], and carbides [18].

The method using an electrical discharge in a liquid is characterized by high productivity, relatively low costs, and a possibility of scaling and performing one-stage synthesis of nanomaterials. The disadvantage of this method is obtainment of nanoparticles with a broad size distribution. Moreover, under electrical discharge conditions interaction of the forming high-dispersion particles with the medium is inevitable; therefore, it is impossible to obtain absolutely pure metals by using the electrical condensation method. At the same time, it is possible to carry out directed synthesis of a variety of nanomaterials by regulating the process of interaction between the medium and the particles formed under the influence of the arc discharge.

The present article provides an overview of the current state of research works, as well as the main achievements and prospects for application of the electrical condensation method to produce nanoparticles of copper and its oxides, silver, and gold.

Physicochemical Aspects of the Electrical Condensation Process

The most common approach to obtainment of nanoparticles using the method of an electrical discharge in a liquid is based on erosion of the electrodes, the material of which is the target metal, under electrical discharge conditions when the electrodes are immersed in a liquid medium. The formation of the arc discharge between the electrodes causes a high rise in the temperature (~10000 K); under such conditions the material of the electrodes melts and evaporates. There is simultaneous evaporation of the liquid in the electrode gap. Metal vapors transform into nanoparticles, condensing in a liquid medium and forming a dispersion.

The process of transformation of metal vapors to suspended nanoparticles can be described in three stages, including nucleation, growth of clusters, and condensation in a liquid medium. The nucleation rate of the unit volume of the new phase is described by the following equation [19]:

$$I = N_\upsilon \frac{kT}{h} \exp\left[\frac{-(\Delta G + \Delta g)}{kT}\right],$$

where N_υ is the number of atoms in the raw material; ΔG is the change in free energy in the formation of the new phase; Δg is the activation energy required by “new” atoms in order to overcome the surface forces of the already formed crystal; T is the absolute temperature; h is the Planck constant; and k is the Boltzmann constant.

At a constant temperature the nucleation rate is determined primarily by the value of ΔG, which also influences the vapor saturation rate of the solid material. It is evident that a high saturation rate can be achieved if the metal, vaporized at a high temperature, rapidly condenses at a low temperature. Therefore, the temperature difference in the electrical discharge zone and in the liquid medium is a critical parameter, determining the properties of the resulting nanoparticles.

Introduction of surfactants in the liquid medium contributes to stabilization of nanoparticles. Moreover, the appearance of ions resulting from dissociation of molecules of ionogenic surfactants in the solution facilitates the discharge ignition. The temperature of the discharge arc is determined by the characteristics of the electric current applied to the electrodes.

Thus, the decisive influence on the properties of nanoparticles formed as the result of the discharge is made the parameters of the electric current (current intensity, voltage, and pulse duration in the pulsed mode of power supply), temperature, and the composition of the liquid medium.

The processes leading to the production of nanoparticle dispersions are complicated by degradation of the liquid medium molecules and oxidation of the metal particles. The solvent decomposition products contaminate the surface of nanoparticles. Therefore, obtainment of metal nanoparticles requires special conditions in order to prevent oxidation processes. At the same time, the method of electrical discharge in liquid can be applied to obtain particles of such materials as oxides, carbides etc.

Production of Nanoparticles of Copper and Its Oxides

Nanoparticles of copper and its oxides are promising for use in catalysis [20–24], gas sensors [25], magnetic materials with memory effects [26], semiconductor equipment [27–28], high-temperature superconductors [29], and inorganic composites [30]. As compared to palladium, platinum, and gold, copper nanostructures are relatively cheap, it encourages the performance of works on improvement of the existing methods for their formation. Moreover, the use of the method of an electrical discharge in a liquid for production of noble metal nanoparticles is a good alternative to traditional chemical methods that often involve the use of expensive chemicals harmful to the environment.

Experimental studies [31–36] demonstrated that erosion of copper electrodes under discharge conditions in distilled water resulted in the formation of nanoparticles of copper oxides: a mixture of

CuO/Cu_2O oxides with an average particle size of ~100 nm [31], needle-like nanoparticles of CuO, 20 nm in diameter and 80 nm in length [33], spherical nanoparticles of CuO with the average diameter of 50 nm [34], and spherical nanoparticles of Cu, reaching 58 nm in size [32]. The formation of copper oxides is explained by oxidation of the originally formed copper nanoclusters by oxygen atoms of water molecules.

Oxidation processes can be prevented by introducing additional components (reducing agents) into the liquid medium. Thus, in work [31] ascorbic acid was used to prevent oxidation of copper nanoparticles in the solution. Partially dispersed red-colored copper nanoparticles, 10–15 nm in size, are formed in the boiling solution of ascorbic acid, which is confirmed by the methods of X-ray phase analysis and transmission electron microscopy. The particles tend to aggregate and are slowly oxidized in air. It is also noted that the content of carbon-containing products formed as a result of decomposition of ascorbic acid under discharge conditions cannot be quantified by using the the methods mentioned above.

When a cationic surfactant (cetyltrimethylammonium bromide) is added into a solution of ascorbic acid under discharge conditions, the formation of sufficiently stable spherical copper structures, ranging from 700 nm to 1 μm in diameter, composed of individual particles 5–35 nm in size, is observed. The role of this surfactant in the synthesis of copper nanoparticles is different from the examples described in various works [37, 38], where this surfactant, in particular, efficiently forms micelles, facilitating the growth of anisotropic structures. Copper nanoclusters, formed under discharge conditions as a result of the electrode erosion, become covered by a monolayer of cetyltrimethylammonium bromide molecules, bound to the surface of copper clusters by $CH_3–N^+$ groups, and, therefore, become stabilized as the hydrophobic residues of the surfactant molecules are directed outwards, efficiently preventing the aggregation of nanoparticles.

Ignition of a discharge between copper electrodes immersed in a sodium nitrate solution results in the formation of polycrystalline nanorods of CuO, 10–16 nm in size [39]. In order to obtain nanoparticles of Cu_2O and Cu it is necessary to introduce ascorbic acid and hydrazine hydrate, respectively, into the solution of $NaNO_3$. The introduction of ascorbic acid leads to the formation of stable nanoparticles of Cu_2O with the initial size of 4–10 nm, that can grow up to 300–500 nm and have high crystallinity. With time, the resulting nanoparticles of copper grow in size to reach 30–50 nm.

Thus, there is some discrepancy between experimental data [31], according to which the presence of ascorbic acid in the solution prevents oxidation of copper particles, and work [39], in which ascorbic acid only partially prevents oxidative processes in the solution. This fact can be explained by different discharge ignition conditions, in particular, by presence of sodium nitrate in the aqueous solution [39].

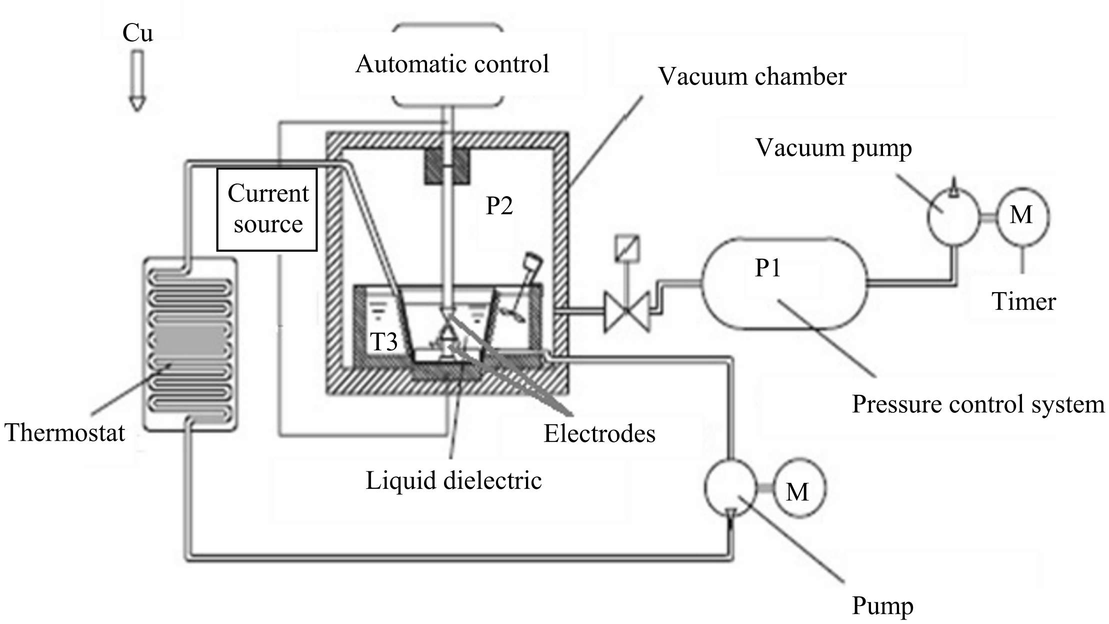
Addition of ethylene glycol into distilled water partially prevents oxidation of copper particles [33]; in mixtures, containing water and ethylene glycol, the formation of Cu_2O nanoparticles, 20–40 nm in size, is observed. Under discharge conditions in a pure ethylene glycol medium spherical nanoparticles of copper, ~10 nm in diameter, are formed.

Ethylene glycol was also selected in work [40] to be used as a solvent due to its low polarity, which is important for application of the suspension, and its low vapor pressure, which is a condition necessary for the use of the solvent in the reaction system proposed in work [41] and elaborated in detail in work [36]. The average diameter of the obtained individual particles was 2.7 nm; such particles were also present in larger agglomerates reaching 20–30 nm in size. The plasmon peak at 260 nm, observed in the optical spectra of the obtained suspensions, corresponds to copper nanoparticles. Apart from that, in the absorption spectra there are no oscillations at 550–600 nm, corresponding to copper in the oxidized state.

Small amounts of such products of ethylene glycol decomposition under electrical discharge conditions as 2-methyl-1,3-dioxolane and 1,3-dioxolane are found in the suspensions.

Thus, the bulk material of the electrodes can be effectively transformed into nanostructures at room temperature. The presented experimental data were obtained under electrical discharge conditions in polar media, ensuring the required level of the solution conductivity. Nonpolar solvents were used only in original works [4, 5]; however, these works provide only a qualitative description of the occurring processes.

The method using an electrical discharge in a liquid makes it possible to obtain nanoparticles with good



Scheme of nanoparticle synthesis system based on the method of an electrical discharge in a liquid [33].

crystallinity, which is confirmed by the X-ray and electron diffraction methods. Thus, at the amplitude values of the current intensity of 15–50 A the electrical discharge in distilled water leads to the formation of face-centered copper crystals with an average size of ~20 nm [32].

The key parameters affecting the nanoparticles production process are characteristics of the discharge. With an increase in the power of the electric current applied to the electrodes there is a temperature rise in the discharge zone; therefore, evaporation of the metal from the surface of the electrodes is accelerated. Moreover, it should be expected that with a rise in the intensity of the discharge current the size of the forming nanoparticles will increase. The electric current power also affects the size distribution of the particles, as the discharge causes simultaneous release of a great number of atoms from the surface of the electrodes, which then form clusters of different size. Condensing in the liquid medium, the clusters form nanoparticles of different size. With a decrease in the temperature of the solvent, smaller nanostructures are obtained. These patterns were confirmed by work [32] as follows: the size of particles formed as a result of the electrode erosion increased with a rise in the electric current power from 58 ± 9 nm at 50 A and 74 ± 12 nm at 70 A to 131 ± 20 nm at 100 A.

In works [33–36] a system called SANSS (Submerged Arc Nanoparticle Synthesis System) was used to obtain copper nanoparticles. The main distinctive feature of the synthesis of nanoparticles in this system is that the process is carried out at low pressures (several tens of torr). A vessel with a liquid dielectric is placed into the vacuum chamber; copper electrodes are put into the vessel (see figure). The system is equipped with devices maintaining a low pressure level. The Submerged Arc Nanoparticle Synthesis System ensures ample opportunities for flexible control of the key parameters of the electrical discharge process, including the composition and temperature of the dielectric medium, amplitude values of the current intensity and voltage of the discharge, and duration of the current pulses in case of the pulsed discharge mode.

The average size of nanoparticles formed in the SANSS grows with an increase in the duration of the current pulse and the temperature of the liquid medium [34]. The size of nanoparticles nonlinearly depends on the intensity of the applied electric current. It is established that the minimum particle size (~68 nm) is achieved at an amperage of 8 A, whereas particles, obtained at the threshold current intensity values of 2 A (average size of 231 nm) and 15 A (average size of 278 nm), tend to aggregate and precipitate. An increase in the voltage applied to the electrodes results in a decrease in the size of nanoparticles. Keeping pressure at a low level also contributes to the formation of smaller particles [35, 36].

Nanoparticles synthesized in the SANSS are characterized by a narrow size distribution [33, 36].

The method using an electrical discharge in a liquid makes it possible to obtain nanoparticles of various shapes. In a pure solvent, in particular, in distilled water, spindle-like [31], needle-like [33, 34], and plate particles [35, 36] are formed, whereas in ethylene glycol spherical particles are obtained [32, 33, 40]. While the formation of spherical structures in homogeneous solutions is in line with the thermodynamic theory of heterogeneous nucleation, the formation of irregularly-shaped nanoparticles can be attributed to the influence of low pressures, which is a condition implemented in the SANSS [33–36].

The morphology of nanoparticles is affected by changes in the composition of the liquid medium. Thus, particles change into a spherical shape if the electrical discharge takes place in an aqueous solution of ascorbic acid [31]. The stability of small-sized spherical nanoparticles increases with addition of cetyltrimethylammonium bromide into the solution of ascorbic acid [31]. An electrical discharge in the solution of sodium nitrate leads to the formation of polycrystalline nanorods of CuO, 10–16 nm in size [39]. Researchers divide the process of the formation of CuO nanorods into the following stages: (a) formation of copper nanoclusters under electrical discharge conditions; (b) rapid oxidation of clusters into CuO particles; (c) anisotropic growth of the particles with the formation of nanorods; and (d) formation of CuO similar shaped particles as a result of Ostwald maturation.

The formation of CuO nanorods is confirmed by the methods of X-ray photoelectron spectroscopy and Raman spectroscopy [39].

Nanoparticles of a polygonal and plate shape are formed under electrical discharge conditions in mixtures of water and ethylene glycol [33].

One of the approaches aimed to increase the stability of nanoparticles is to create a protective polymer shell. A method has been developed to combine the effect of an electrical discharge, generated between copper electrodes at low pressures, and additional functionalization of the forming nanoparticles by organic molecules [40–43]. Under electrical discharge conditions a vapor consisting of copper atoms is formed between the electrodes. This vapor is then directed to radio frequency discharge plasma, containing argon and organic molecules (fragments). Thus, the process of the nanoparticle synthesis is interconnected with polymerization in plasma. Depending on which organic molecules are used as a protective shell, nanoparticles can be obtained in the hydrophilic [40, 43] or hydrophobic state [42, 43]. In work [43] ethylene glycol and ethane were used. The thickness of the organic layer on the surface of copper nanoparticles, 1–2 nm in size, is 4–5 nm for ethane and 2–3 nm for ethylene glycol. This layer is formed by $CH_3^{\bullet}$, $C_2^{\bullet}$, $CH_2^{\bullet}$, and $CH^{\bullet}$ radicals in the first case and $HO{-}CH_2{-}CH_2^{\bullet}$, $HO{-}CH_2^{\bullet}$, and HO in the second case. The layer based on ethylene glycol is better structured.

The Submerged Arc Nanoparticle Synthesis System makes it possible to control the composition of nanoparticles. Thus, applying pulse voltage, ultralow pressures (<10 torr), and a high inert gas flow rate it is possible to obtain particles consisting of a copper core, 50 nm in diameter, on which a thin (~8 nm) layer of ethane molecules is chemisorbed [42].

In work [44] an electrical discharge was used to synthesize CuO/Ta_2O_5 core–shell nanoparticles. The discharge (the electric current amplitude of 35 A, the voltage at breakdown is reduced from 83 to 30 V) is ignited between a carbon cathode and a steel anode with embedded micrograins of Ta/Cu, immersed in deionized water. The resulting nanoparticles are represented by single crystals with semiconducting properties, which include nuclei with the elemental composition of copper–oxygen (~20 nm in diameter) and tantalum–oxygen (~5 nm) with an insignificant admixture of carbon forms.

Long-term aggregative stability of particles, including stability at elevated temperatures, is a crucial factor ensuring their successful application. Thus, copper nanoparticles, obtained in the boiling solution of ascorbic acid [31], tend to aggregate and are slowly oxidized in air. Addition of cetyltrimethylammonium bromide into the solution of ascorbic acid results in an increase in the stability of nanostructures.

In case the synthesis process is carried out in a sodium nitrate solution with addition of ascorbic acid stable nanoparticles are formed [39] (the work does not give any data on the aggregative stability of particles obtained without a stabilizer).

The authors of work [40] studied the influence of the applied temperature on the stability of particles synthesized under plasma polymerization conditions. The suspensions displayed aggregative stability at room temperature. In experiments, studying aggregative stability at elevated temperatures, the samples were heated to 100°C and 197°C (boiling point of ethylene glycol) and exposed to these temperatures for 20 min. After 10 min. it was possible to observe small agglomerates in the suspensions heated to 100°C. When heated to the boiling point of ethylene glycol, large porous aggregates were formed at temperatures above 150°C. In this case, the aggregation cannot be the result of degradation of the stabilizing layer on the surface of nanoparticles, formed in the presence of the surfactant in the suspension of particles, but most likely it is the result of activated Brownian motion, when a high collision rate of suspended particles is achieved. In this case the aggregates can be redispersed using a gentle ultrasonic treatment. The absorption spectra in the UV and visible regions, made after the ultrasonic treatment, are completely consistent in both cases; there are no statistically significant differences, which proves the reversibility of the agglomeration process.

The reversibility of the agglomeration process was used to redisperse functionalized nanoparticles in water and a phosphate buffer solution. It is demonstrated that in both aqueous solutions there is formation of agglomerates which can be redispersed using an ultrasonic treatment. The ability of nanoparticles to agglomerate in aqueous media is significantly influenced by the ionic strength of the solution; in particular, the degradation of aggregates by an ultrasonic treatment in the phosphate buffer solution occurs at a much slower rate.

Production of Silver Nanoparticles

Silver nanoparticles possess valuable optical, electronic, antiseptic, and catalytic properties [3]. Silver particles serve as a material for manufacturing of electronic, optical, and sensor devices. A cheap and environmentally-friendly method to synthesize silver nanoparticles is based on the effect of an electrical discharge in a liquid medium containing silver-bearing material.

In this case it is not always necessary to introduce surfactants or stabilizers, preventing particles from aggregating, into the aqueous medium. Moreover, the possibility to vary the characteristics of the discharge and the properties of the aqueous medium makes it possible to control the size and shape of the forming nanoparticles [45], which are the parameters that have a decisive influence on the application of nanoparticles in different areas.

In the overwhelming majority of research works on the production of silver nanoparticles using the method of an electrical discharge in a liquid the synthesis of nanoparticles was carried out in aqueous media. When a discharge is applied to silver electrodes immersed in distilled or deionized water [46–51], it is possible to obtain spherical silver nanoparticles of different size: 20–30 nm [47, 48], 6–25 nm [49], 5–35 nm [51], and exceeding 30 nm [50]. According to the data from works [46, 50], such particles maintained aggregative stability for, at least, three weeks. In work [47] the synthesized nanostructures remained stable for several months at room temperature.

The aggregative stability of nanoparticles in an aqueous medium without the presence of stabilizers can be explained by an extremely thin oxide layer formed through chemisorption of oxygen atoms, generated as a result of water electrolysis in the discharge process, on the surface of nanoparticles [51]. While hydrogen, which is the second product of decomposition of water molecules, does not interact with the silver surface at room temperature and is removed in a molecular form, oxygen is adsorbed creating a negative charge on the surface of silver nanoparticles and forming a system of hydrogen bonds with the water molecules of the surrounding liquid medium. Correspondingly, electrostatic repulsion forces between negatively charged particles prevent them from agglomerating and precipitating. The maximum value of ζ-potential for silver suspensions is –45 mV [51].

Disadvantages of such an approach to the synthesis of silver nanoparticles include a wide size distribution of particles as compared to solution methods and a necessity to use solid silver as an electrode material. Addition of surfactants makes it possible to narrow the nanoparticle size distribution. Thus, microscopic methods show the formation of almost monodispersed silver nanostructures (average particle size of ~14 nm) under discharge conditions in the solution of cetyltrimethylammonium bromide [46, 50]. A similar effect is made by sodium citrate; silver particles stabilized by citrate ions are ~30 nm in size. As the stabilizing effect of cetyltrimethylammonium bromide molecules and sodium citrate is caused, apart from electrostatic effects, by steric interactions, nanostructures obtained in their presence remain stable for more than six months.

The size of particles forming under discharge conditions in a liquid medium in the presence of surfactants depends on their concentration. Thus, with an increase in the concentration of sodium citrate [52] the particles become smaller and their size distribution is narrowed. A high content of citrate in the solution results in an increase in the average size and size distribution of nanostructures due to the electric arc instability; therefore, their aggregative stability is disturbed.

Under discharge conditions in an aqueous solution of sodium nitrate cooled to 2°C [53] it is possible to obtain anisotropic nanoparticles represented by elongated particles (average size of 15 × 5 nm), which eventually become larger to form filaments, 15 nm in diameter and more than 100 nm in length, and then aggregate. Cooling in the electrical discharge process prevents the initially formed anisotropic particles from changing shape. Such an influence of sodium nitrate was previously noted in work [39]; under conditions of an electrical discharge between copper electrodes, immersed in a solution of $NaNO_3$, the formation of polycrystalline nanorods of CuO was observed. It should be noted that the role of sodium nitrate in processes leading to the formation of anisotropic structures in the solution has not been studied.

In the above-described works silver nanoparticles are formed as a result of electrode erosion. In work [54] nanosilver was for the first time obtained under conditions of an electrical discharge between titanium electrodes, immersed in a solution of $AgNO_3$. According to this approach, nanoparticles are formed through direct reduction of Ag^+ cations by electrons from the discharge zone; in this case the resulting particles are smaller in size and have a narrower size distribution. Titanium is selected as an electrode material due to its high melting point and low chemical activity. Erosion of titanium atoms from the surface of the electrodes under discharge conditions is negligible.

Nanoparticles obtained in the absence of stabilizers are sedimented in the course of two weeks. Suspensions formed in the presence of sodium citrate remain stable for several months; the average size of particles in the citrate solution is 27 ± 14 nm.

The process of formation of silver nanoparticles under electrical discharge conditions is described by the same pattern as the process of formation of copper nanoparticles. The decisive influence is exerted by the power of the electric arc and, correspondingly, its temperature. These parameters largely define the size of the forming nanoparticles, their size distribution and shape, as well as the process efficiency.

With a rise in the intensity of the discharge current there is an increase in the size of particles [46, 49, 50, 54], which is evidenced by a shift in the position of the plasmon peak in the optical absorption spectra [55, 56]. Thus, works [46, 50] describe a red shift in the optical spectra: the plasmon peak at 392 nm (10 A) moves to 394 nm (15 A) and 398 nm (20 A). The average size of nanoparticles is 8, 10, and 13 nm, respectively [46].

In case an electric arc is burning in the direct current mode an increase in the current intensity above a certain limit leads to the widening of the nanoparticles size distribution, followed by the loss of aggregative stability of nanostructures. Moreover, the stability of the arc is disturbed as well. Thus, in works [46, 50] the current intensity of 10 A was a threshold value for efficient evaporation of silver. When this value was exceeded, there was an uncontrolled growth of nanoparticle aggregates in the solution, resulting in their precipitation.

The dimensional characteristics of silver nanoparticles are affected by the duration of the electric current application. The same power of the arc is achieved in case of a medium intensity current and long periods of the electric current application and short-time pulses of a large amplitude. Thus, the completeness of reduction of silver cations by electrons from the discharge zone, which can be evaluated on the basis of the plasmon peak intensity, reaches its maximum at the following parameters of the current pulse: 15 A, 6–7 min and 35 A, 1 min [54]. However, a rise in the intensity of the current leads to an increase in the rate of erosion of titanium electrodes [54], which contaminates silver nanoparticles in the solution. Moreover, it is noted that the intensity of the electric current, applied to the electrodes, also affects the aggregative stability of silver aqueous suspensions and the character of the particle size distribution. Therefore, it is more preferable to apply a medium-amplitude current.

The above described pattern is also characteristic for the process of production of silver nanoparticles carried out in a mode implemented in the SANSS [49].

While the shape of copper nanoparticles obtained using the method of an electrical discharge is quite diverse and varies depending on the composition of the liquid medium and the discharge conditions (pressure), in case of silver nanoparticles spherical nanostructures are formed with few exceptions [46–52, 54]. This fact is confirmed by the methods of optical spectroscopy (in the absorption spectra it is possible to observe a plasmon peak at ~400 nm, which is characteristic for spherical nanoparticles of silver) and transmission electron microscopy.

As mentioned above, the formation of anisotropic silver particles is possible under discharge conditions in a sodium nitrate solution [53]. There is a plasmon peak at 302 nm in the absorption spectra of the sol, which corresponds to silver clusters. Polycrystalline filaments are formed in the solution and eventually grow is size. According to the electron diffraction data, particles with a face-centered cubic lattice are surrounded by an amorphous phase, which is, probably, represented by silver clusters, aggregated in the solution, which have failed to crystallize. Coarsening of the filaments can be associated with crystallization of the amorphous phase. As a result of ageing the nanofilaments get aggregated and sedimented.

It should be noted that, unlike copper-based nanostructures, anisotropic silver particles cannot be synthesized in the SANSS [49].

An interesting example, illustrating application of the method of an electrical discharge in a liquid, is the production of Ag/Pt bimetallic nanocomposites [57]. A discharge between a silver cathode and a platinum anode, immersed in an aqueous solution containing sodium dodecyl sulfate and sodium chloride, causes the formation of high-dispersion spherical nanoparticles (average size of 4.6 ± 0.9 nm). Unlike CuO/Ta_2O_5 structures described above [44], there is no interaction between the metals of the core and the shell in such nanoparticles. According to the data of photoelectron spectroscopy, silver is in an unoxidized state, whereas platinum nanoparticles are partially oxidized. With an increase in the duration of the discharge the relative content of silver rises and reaches an average of 96 wt %. The size of platinum nanoparticles, forming the core of the nanostructures, lies within a range of 0.4–0.82 nm.

Production of Gold Nanoparticles

Due to their chemical inertness and relative ease of preparation, gold nanoparticles are more widely used as compared to silver. Potential application areas of such particles include catalysis [13], biosensors [58], and electronic engineering [59]. This fact, in particular, explains the development of works aimed to create and improve methods for production of gold nanoparticles.

In connection with the fact that gold is an expensive material only few researchers use it as an electrode material [13, 51, and 60] under electrical discharge conditions. The most widely applied electrode materials are tungsten [61–69] and titanium [52, 70, and 71], which are chemically inert and resistant to erosion at high temperatures.

Using the electrical discharge method it is possible to obtain gold nanoparticles as a result of the reduction of $AuCl_4^-$ ions, contained in the liquid medium, by electrons from the plasma channel [62, 66, 70]:

$$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-,$$

$$AuCl_4^- + 2e^- \rightarrow AuCl_2^- + 2Cl^-,$$

$$3AuCl_2^- \rightarrow AuCl_4^- + 2Au^0 + 2Cl^-,$$

$$AuCl_2^- + e^- \rightarrow Au^0 + 2Cl^-.$$

Apart from electrons, other reactive particles, generated under discharge conditions, in particular, hydrogen atoms can also serve as reducing agents [64, 65, 67].

It was proposed for the first time to apply the method using an electrical discharge in a liquid to synthesize gold nanoparticles in work [13]. Gold electrodes were placed in deionized water and subjected to erosion under the effect of a discharge occurring when a high-intensity direct current was applied to the electrodes [13, 51]. Under such conditions it was possible to obtain spherical nanoparticles of gold, 7–40 nm in size. The stability of particles obtained in water without stabilizers is related to the adsorption of oxygen atoms, formed as a result of decomposition of water molecules under discharge conditions, on their surface [72, 73]. These atoms establish a network of hydrogen bonds with the surrounding water molecules, thus forming negatively charged micelles of nanostructures, which is confirmed by the value of ζ-potential ($\zeta = -35$ mV). Repulsive forces between gold nanoparticles protect them from aggregation and sedimentation in aqueous suspensions (analogy with silver particles).

Nanoparticles obtained in deionized water [13, 51] have a wider particle size distribution as compared to particles synthesized using chemical reduction methods.

It was possible to reduce the size of gold nanoparticles by using titanium electrodes immersed in a solution of chloroauric acid ($HAuCl_4$) in deionized water [50, 70, and 71]. At a concentration of $HAuCl_4$ of ~10 μM the content of nanostructures in the resulting sol is small, which is associated with the low concentration of tetrachloroaurate ion and is reflected in an insufficiently clear plasmon absorption peak, corresponding to colloidal gold. At high concentrations (~1 mM) the content of nanoparticles formed as a result of the reduction of $AuCl_4^-$ ions by electrons from the discharge zone, is much greater. There is also a symbatic increase in the intensity of the plasmon absorption peak at 520 nm.

In the absence of stabilizers spherical particles, 3–12 nm is size, that are quick to aggregate and sediment, are formed in such a solution [50]. Apart from that, as noted in work [69], when water alone is used as a solvent, electrons from the plasma zone, participating in the reduction of gold-containing ions, are captured by water molecules.

The presence of citrate ions in the reaction medium leads to a reduction in the average size of nanoparticles and ensures their aggregative stability for several months. Such an effect is also made by polyvinylpyrrolidone and sodium dodecyl sulfate [65, 67, 69]. With an increase in the concentration of the surfactant the size of particles is reduced. Apart from that, molecules of sodium dodecyl sulfate present in the solution of $HAuCl_4$ contribute to the formation of structures of various shapes, including anisotropic (triangular, pentagonal, hexagonal, and dendritic) and spherical particles, in the reaction medium [65, 67]. The nanoparticles have a polycrystalline structure. At high concentrations of gold ions in the initial solution it was possible to obtain spherical nanoparticles, 25–50 nm in size, which corresponds to the complete reduction of $AuCl_4^-$ ions. A decrease in the concentration of $AuCl_4^-$ leads to the formation of anisotropic structures (average size of 10–20 nm).

It is proved that atomic hydrogen is the principal reducing agent in the process of production of gold nanoparticles from tetrachloroaurate ions [65, 67]. Thus, in a medium containing *N-tret*-butyl-α-phenylnitrone, a spin trap for $H^•$ and $OH^•$, other things being equal, no formation of gold particles was observed.

An electrical discharge between tungsten electrodes immersed in a micellar solution, a mixture of the solution of bis(2-ethylhexyl) sodium sulfosuccinate (surfactant) in dodecane and a solution of $HAuCl_4$ in distilled water, leads to the formation of spherical nanoparticles of gold, 6.3 ± 1.4 nm in diameter [61, 64]. In this case the size of particles can be adjusted by changing the size of reverse micelles, varying the molar ratio of water and the surfactant. Thus, with an increase in the distilled water/surfactant molar ratio the peak of plasmon absorption of gold nanoparticles is shifted towards shorter wavelengths as follows: the water/surfactant molar ratio of 4 is corresponded by the most intensive peak at 522 nm, the molar ratios of 7.5 and 11 – by peaks at 525 and 533 nm, respectively; this pattern is observed within an average nanoparticle diameter range of 3–11 nm.

According to the data of high-resolution transmission electron microscopy, gold nanoparticles in the form of micelles have a face-centered cubic lattice and different morphology. Spherical nanoparticles are monocrystalline; multiple twinning particles in the form of icosahedra having axes of the 5th order are also found in the solution and their content reaches ~94%. Such crystals usually have particles of metals with face-centered cubic packing, as well as particles of silicon and germanium at early stages of the particle growth and thin film formation [74]. According to one of the models describing the formation of such particles, they can be obtained by successive twinning of tetrahedral nanoparticles. Another model suggests that these crystalline structures can be obtained at the initial nucleation of crystals, which will later grow maintaining their shape.

In order to study microstructural characteristics of gold nanoparticles nanostructures below 10 nm in size were synthesized on the basis of the chemical reduction method. The content of non-spherical particles, obtained using the solution method, is 63% against 94% in case of the discharge method. This difference can be explained by the fact that the key particle, contributing to the reduction of $AuCl_4^-$ ion to Au^0, is atomic hydrogen, migrating from the plasma zone to the liquid phase, which is confirmed by a reduction in the solution pH. After the reduction of tetrachloroaurate ion the atoms of gold form nanoparticles of different microstructure without the participation of reducing agents. Twinning nanocrystals of icosahedral symmetry are the most stable forms of particles below 10 nm in size.

In an aqueous solution of $HAuCl_4$, containing KOH, spherical nanostructures, 11–100 nm in size, were obtained using the method of an electrical discharge [62, 66, and 68]. High-resolution electron microscopy demonstrates that the majority of the particles are polycrystalline structures with a face-centered cubic lattice.

It was possible to synthesize particles of a smaller size (10.5 ± 3.6 nm) using an aqueous solution of $HAuCl_4$, containing potassium chloride and gelatin [63]. Potassium chloride was added to increase conductivity of the solution, whereas gelatin was used as a stabilizer. It is established that potassium chloride does not only influence the solution conductivity, but it also promotes the formation of spherical nanoparticles [69]. Thus, with an increase in the concentration of KCl the plasmon absorption peak in the resulting suspensions of colloidal gold moves from 542 to 528 nm, which is an evidence of a reduction in the size of gold particles. At the same time, the absorption spectra of suspensions, containing no potassium ions, exhibit an additional intensive band between 600 and 650 nm, which corresponds to non-spherical particles. According to the data of transmission electron microscopy, in the absence of potassium chloride in the liquid medium it is possible to observe the formation of gold nanostructures of various shapes, including triangular, square, and close-to-spherical nanoparticles with a diameter of 20.85 ± 2.78 nm, as well as nanorods, 10 nm in diameter and 40–45 nm in length. In a medium, containing potassium chloride, the overwhelming majority of particles are spherical structures, 16.38 ± 0.48 nm in size. The change in the nanoparticle shape can be explained by acceleration of the reaction in plasma in the presence of potassium ions. Gold particles below 10 nm in size are represented by single crystals, whereas nanoparticles more than 15 nm in diameter are polycrystalline.

Under conditions of an electrical discharge between gold electrodes immersed in absolute ethanol spherical particles, ranging from 2 to 20 nm in size, are formed [60]. The zeta potential of the suspension of gold nanoparticles in ethanol is –50 mV, which is sufficient to keep gold nanoparticles in a stable colloidal form. This suspension is aggregately stable and negatively charged on the particle surface [72, 73]. It should be noted that the application of a discharge between gold electrodes in absolute ethanol leads to the formation of smaller nanoparticles as compared to the process carried out in deionized water.

The rate of release of gold atoms from the surface of gold electrodes is proportionate to the electric power of the arc. Under conditions of high electric power in the plasma zone a high rate of generation of electrons and radicals, participating in the formation of gold nanoparticles from $AuCl_4^-$ ions, is achieved.

As shown above, the dimensional characteristics of nanoparticles depend on the mode of the electric current applied to the electrodes, i.e. direct current at relatively low average values of current and voltage and, correspondingly, a prolonged discharge [50, 62, 70] or alternating current with short pulses (duration of microseconds) of a great amplitude [13, 61, 63–69]. In the latter case the amplitude values of current and voltage are limited by the values at which erosion of the electrodes takes place [59].

Studies of the influence of the discharge duration demonstrated that the complete reduction of tetrachloroaurate ions by electrons and radicals from the discharge zone takes three [60], four [50, 70, 71], ten [64, 68], fifteen [62], or forty-five minutes depending on the discharge mode [65, 67]. The distinctive feature of the method of an electrical discharge in a liquid as compared to other techniques, using a solution of $HAuCl_4$, is the "dissolution" of gold nanoparticles in the solution in the course of the discharge, which is reflected in the nanoparticle size reduction. The complete reduction of tetrachloroaurate ions to gold nanoparticles is corresponded by the plasmon absorption peak of the maximum intensity [63]. With a reduction in the size of particles the maximum absorption peak in the optical spectra is shifted from 580–600 nm to 520–540 nm [62, 64, and 68].

The rates of formation and dissolution of gold nanoparticles are proportionate to the applied voltage. The number of hydrogen atoms and electrons generated by the discharge grows exponentially with an increase in the applied voltage. An increase in the voltage leads to a reduction in the size of particles [65, 67]. With an increase in the current intensity the size of nanoparticles in the reaction medium grows; large-size clusters are prone to aggregation [65–67].

The size of particles grows with an increase in the inter-electrode distance [68]. The most narrow nanoparticle size distribution can be achieved at a minimum distance of 1 mm. Under such conditions gold nanoparticles have ζ-potential of –45.4 ± 1.3 mV, ensuring perfect stability of nanoparticles in a liquid [68].

CONCLUSIONS

The method using an electrical discharge in a liquid is a powerful tool for the synthesis of nanostructures. A wide range of variables makes it possible to control the particle formation process. In particular, it is possible to obtain nanoparticles with a size distribution comparable to the one that is characteristic for particles synthesized using solution methods. In a number of cases the method of an electrical discharge in a liquid has a distinct advantage over other methods. Thus, the formation of silver and gold nanoparticles often does not require the presence of reducing agents or surfactants in the reaction medium. Moreover, using the method of an electrical discharge in a liquid it is possible to efficiently synthesize anisotropic particles of these metals, which are applied in electronic engineering, medicine, and sensors [75]. The synthesis of copper nanostructures can be carried out with a use of an installation ensuring economic feasibility and sufficiently high productivity of the process. The accumulated experimental data make it possible to predict successful application of this method for the production of sols and nanoparticles of noble metals.

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