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Physicochemical Aspects of Metal Nanoparticle Preparation

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Abstract

Physicochemical properties, including optical properties or catalytic activity, and biological properties of metal nanoparticles are considerably influenced by their diameter. Therefore, a tailored synthesis of metal nanoparticles represents a key topic in the field of nanotechnology, and the number of research papers, concerning this topic, has been annually growing with an arithmetic progression. Metal nanoparticles are most frequently prepared via chemical reduction of metals in ionic form from their solutions. Using this synthetic approach, tailored parameters of the particles can be achieved via the adjustment of numerous factors: difference of potentials of the metal redox system and the reducing agent redox system, pH of the reaction mixture, and its temperature. The influence of these three factors on the diameter of the prepared metal nanoparticles will be discussed in the following chapter with respect to general laws and based on numerous examples from research practice.

Keywords: metal nanoparticles, tailored preparation, size distribution, chemical reduction, redox potential, pH, temperature

1. Introduction

Metal nanoparticles can be classified among the most studied nanomaterials due to their numerous potential applications [1–3]. Silver and gold nanoparticles have found their targeted applications in the enhancement of Raman scattering due to the optical properties that are associated with the existence of localized surface plasmon resonance (LSPR) [4–8] with the absorption maximum in visible part of the electromagnetic part of the spectra. Thanks to this fact the particles provide a significant enhancement of the Raman signal used in the highly sensitive analytical method of surface-enhanced Raman spectroscopy (SERS) [9–12] used in biology and medicine [13–17]. Transitional metals are commonly known for their high catalytic activity, which is even amplified by the nanodimension of the metal nanoparticles with high ratio between the surface area and the volume of the particle because the catalytic process is located on the surface [18–20]. From the application point of view, even the magnetic behavior of the metal nanoparticles must be taken into account [21, 22]. Last, but not least, the biological activity of the metal nanoparticles must be mentioned, especially in the case of the silver nanoparticles [23–25]. These particles became one of the phenomena of nanotechnology. Recently, more and more products of everyday usage involve

these particles, which are applied with respect to their high antibacterial activity against most of the pathogenic bacteria, fungi, and candida [26–28]. As the metal nanoparticles represent a material, which is of high importance, from the research and application point of view, this chapter will be devoted to the methods of their tailored preparation via wet chemical reduction methods. The attention will be paid to the influence of the physicochemical conditions of the particular chemical reaction, to the influence of redox potentials and pH, and to the influence of temperature on the reduction process.

Nanoparticles are generally defined as 3D objects, where at least one of the dimensions is in the range from 1 to 100 nm [29], which is reflected in an abrupt change of the properties and behavior of the materials in the macroscopic range of diameter. Silver nanoparticles represent a typical example of such a material, which biological activity (i.e., antibacterial activity and toxicity against higher organisms) is significantly increased with the decreasing particle diameter [30–32]. Similarly, optical properties of the metal nanoparticles also significantly depend on the diameter range of the particles. The position of the absorption maximum is shifted to the red part of the spectrum with the growing silver or gold nanoparticle size (**Figure 1a**) [33–36].

The catalytic activity of metal nanoparticles is dependent on their diameter because the smaller the particles are, the greater the specific surface area (SSA) is, and the SSA represents the key parameter in heterogeneous catalysis [37–42]. Aside from all of these dependencies, size dependency is monitored also for magnetic properties [43, 44], electrochemical behavior based on dependency of Fermi level on the nanoparticle diameter [45, 46], and also for physical properties, which are considered constant for macroscopic objects—e.g., melting point [47–49] or heat capacity [50–52]. However, dramatic change in the nanomaterial properties happens when the diameter is below 3 nm (note: some of the authors state 5 nm or even 10 nm), which corresponds to approx. 1000 silver atoms [53–55]. Concerning such tiny particles, the organization of valence electrons is changed, and there is a shift from a band structure typical for metals to the organization HOMO-LUMO typical for molecular mass organization. However, a complete shift from one layout structure to the other one happens at the dimension below 1 nm when the particles contain maximally tens of atoms, and their behavior is strongly influenced by quantum effects, which is not commonly observed in the case of nanomaterials [5, 46, 55–57]. These particles are usually named as clusters, and their abnormal optical properties (i.e., fluorescence) are nowadays in the center of the interest of the studies focused on optical properties of nanomaterials [58–63]. Such tiny particles

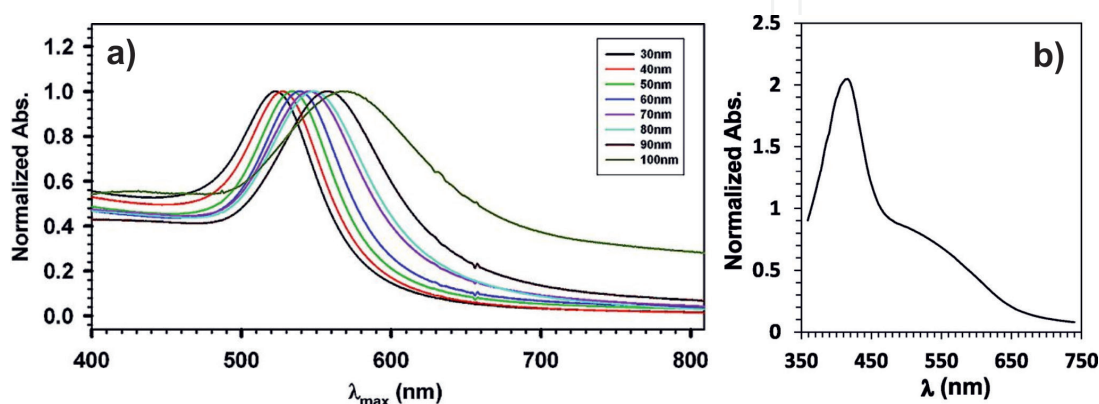


Figure 1. (a) Dependence of the absorbance of the localized surface plasmon resonance (LSPR) of gold nanoparticles on their size. Reproduced with permission from [33]. (b) Broadening of the LSPR absorbance peak due to the aggregation of 30 nm-sized silver nanoparticles.

represent a unique part of the nanotechnology field, and they will not be discussed any further in the follow-up parts of this chapter.

Aside from the preparation of the nanomaterials, characterization of such a material represents an issue, which will be discussed in considerable detail. Fundamental information about the nanomaterials can be obtained via the measurement of diameter of the particles and their size distribution (also called polydispersity). The characterization methods are either direct or indirect. The direct methods are almost exclusively represented by microscopic methods—electron microscopy and scanning probe microscopy [64, 65]. Intensive development of electron microscopy in the last decade enabled to spread this technique and price availability of scanning electron microscopes (SEM). This characterization method has a limitation of its resolution, which is approx. 10 nm. It disables characterization of smaller particles and does not offer the size distributions of groups of tiny particles. However, one of the greatest advantages of this technique is an easy implementation of energy dispersive spectroscopy (EDS) method [66], which enables qualitative evaluation of chemical composition of the particles. Significantly greater resolution (usually approx. 0.1 nm) can be achieved with the technique of transmission electron microscopy (TEM) [67]. Recently, another technique has become more popular—scanning transmission electron microscopy (STEM). It is a technique, which combines advantages of both electron microscopy techniques, and this way brings new viewpoints into the field of nanomaterial characterization [68].

Electron microscopy represents a method, which requires a good preparation of the characterized sample as it is inserted into a chamber under a high vacuum. It exhibits a problem for metal nanoparticles as they have a strong tendency to aggregation. SEM, with a suitable module even for the metal nanoparticles (i.e., environmental SEM), enables to characterize even wet samples. Similar modules for wet samples are also available for TEM. However, both of the modifications represent economy and technology demanding adjustments, which disables their widespread usage. Another problem with the characterization of metal samples dwells in high electron adsorption by the metal nanoparticles which evokes heating up of the sample and its possible thermal transformation or destruction of the carrying layer of the microscopy grid (carbon, Formvar, etc.). The sample can also involve non-reduced metal ions, which are due to the stream of electrons immediately reduced, and then the observed objects are not truly corresponding with the state of the sample deposited onto the microscopy grid. For example, it is impossible to use electron microscopy for characterization of silver halogenide nanoparticles. The above-listed drawbacks cannot be commonly connected with the second microscopy technique—with the microscopy with scanning probe. The most common adjustment of such a microscopy is in the adjustment of atomic force microscopy (AFM), and it does not require any sophisticated pretreatment of the sample because the characterization does not require vacuum [69]. Due to the specificity of this method (mechanical motion of the scanning probe in a close connection with the surface), this method is more suitable for a study of layers of nanoparticles. If a resolution comparable with TEM is required, the time for gathering sufficiently great amount of data is significantly prolonged [70]. All of the electron microscopy methods are time demanding and require an experienced operator, and therefore they do not prevail over the indirect methods of the nanoparticle characterization. In the case of the metals from the I. B group from the periodic system (Cu, Ag, Au—coinage metals), the nanoscopic characteristics of the prepared particles can be confirmed using a simply qualitative indirect method of UV-vis spectroscopy. Thanks to the size-dependent position and shape of the absorption maximum of LSPR in the visible part of the spectra, it is relatively easy to evaluate qualitatively the size of the prepared nanoparticles and their polydispersity. A typical dependency of the

absorption maximum of LSPR on the diameter of spherical particles can be seen in **Figure 1a** [33]. The evaluation of polydispersity of the system can be obtained from the width of the absorption band—the wider the band is, the more polydisperse the system is. UV-vis spectroscopy is such a sensitive technique that there can be observed even more separated absorption maxima corresponding with a highly polydisperse system involving more diameter fractions (multimodal system) [71]. Often it can happen in the case of the aggregated particles, when the larger aggregates can be seen in the spectrum as a flat maximum, which is significantly shifted into the red part of the spectrum compared with the original maximum corresponding with the LSPR of the non-aggregated particles (**Figure 1b**) [72, 73]. The spectrum can be complicated due to the presence of nonspherical particles—e.g., particles with plate morphology will have three absorption maxima in the spectrum, each of them corresponding with the particular diameter of the plate [74].

Quantitative information concerning particle diameter and polydispersity can be obtained from dynamic light scattering method (DLS). This indirect characterization method is based on the diameter determination based on the time-dependent change of the light scattered intensity (using coherent light source) in the system involving particles moving under Brownian motion in the dispersion [75–77]. This method enables quick evaluation of the particle diameter and polydispersity of the system based on enormous number of particles (note: the measurement is realized from tens of seconds up to minutes). This method works in a great diameter range—from 0.3 nm to 3 μm . Unfortunately, DLS is an indirect characterization method based on model behavior of spherical particles, which represent a serious disadvantage for measuring nonspherical particles. Another complication represents a polydisperse system, where the resulting average diameter (Z -average d_z) is highly influenced by the largest particles present in the system [78, 79]. The problem of differently weighted particles based on their different diameters is neglected in numerous papers, and the difference between the diameter obtained from electron microscopy and DLS is explained as the difference between the real and hydrodynamic diameter. The influence of nanoparticle solvation (or the presence of adsorbed molecules including stabilizers of macromolecular character) on the resulting particle diameter can be in couple of percents, but the presence of large particles in the system is responsible for the difference in tens of percents. In the case of the electron microscopy, all the particles are considered with the same weight, while in the case of DLS, the weight of each particle in the average d_z is given by the power of five of its diameter [80–83]. The instruments working on the DLS principle are equipped with software, which enables different modes according to which the particles can be weighted (incl. the weighting identical with electron microscopy), but it is necessary to keep in mind that the recalculation is based again on the approximation model and its accuracy, which unfortunately decreases with growing polydispersity of the system [84]. The DLS method is therefore more suitable for monitoring of the processes in the dispersed systems (e.g., processes of particle aggregation) than for the determination of absolute values of diameters of the particles in the system. On the other hand, DLS represents one of the fundamental methods defined in ISO 22412:2017 for the determination of diameter of colloidal particles. From the other commonly used indirect methods of determination of the particle diameter, it is necessary to mention Scherrer method of determination of crystal domains using powder RTG diffraction (XRD). The calculation is based on the dependency of line broadening at half the maximum intensity (FWHM) on the diameter of the nanoparticles [85]. This method does not evaluate a full particle diameter. It determines the size of coherent domains, which the resulting particle is formed of. It is a method, which is highly suitable for the study of aggregates, where the independent particles (grains) joined one another into a large aggregated object.

Metal nanoparticles can be prepared using both physical and chemical methods. Physical methods of the nanoparticle preparations are based on the use of macroscopic objects, which are disintegrated onto the nanoobject using different kinds of mechanical milling procedures, dispergators, or sonicators. Generally, these methods are labeled as “top-down methods.” Unfortunately, these methods are not suitable for metal nanoparticle preparation due to the typical mechanical properties of the material (malleability, ductility). Therefore, different kinds of energy, such as the application of laser beam on macroscopic material, are preferred for the preparation of metal nanoparticles. The method is called a laser ablation [86–89]. The nanoparticles are formed due to a local overheating of the metal material, its evaporation, and consequential condensation of the vapors. This process does not need to be initiated by any other substances and as such is able to produce highly clean nanoparticles. The diameter of the generated particles can be tailored due to the energy applied, wavelength, and the laser pulses [90–93]. The diameter of the generated particles and polydispersity of the system can be modified by further application of laser [94, 95]. As the generated dispersions are usually highly diluted, it is not necessary to add any stabilizers into the system. However, stabilizers are usually added into the system as they can prolong temporal stability of the dispersed system, and their presence in the system from the very beginning can significantly influence the particle characteristics [96–98]. The application of laser ablation in practice is limited as the number of produced particles is relatively low; their production is barely enough for research purposes. Comparable transition of macroscopic material to vapors and consequential condensation can be also realized in tube furnace, where the energy flow is directly in a form of heat [99, 100]. The disadvantage of this method is related to possible contamination of the furnace. Moreover, this process is highly energy demanding. Recently, a new method, ranged into the top-down methods, has been introduced. It is a method of vacuum sputtering. This method is based on the bombardment of a target with energetic gas ions generated via the collision of electrons and carrier gas in vacuum using direct current (DC), radio frequency (RF), or magnetron sputtering [101–104]. This method is primarily designed for the generation of nanoparticle layers on the surface of a solid substrate. However, a modification of the process, when the solid substrate is replaced by the surface of a liquid, enables preparation of liquid dispersion of nanoparticles [105–107]. The enumeration of physical methods of nanomaterial preparation cannot be completed without the lithographical techniques. These techniques enable only fabrication of nanostructural layers [108].

Chemical methods of nanoparticle preparations, compared to the physical ones, are based on the reduction of analytical solutions containing the corresponding metal ions to atoms using the appropriate reducing agent. The first neutral atoms form nuclei of the emerging nanoparticles which can quickly grow due to the proceeding reduction of the ions until the diameter of the nanoparticles is reached—LaMer mechanism of the nanoparticle growth [109]. The reduction of the metal ions can be achieved using a variety of reducing agents. Aside from suitable reducing agents, the reduction can be also done using photochemical, radiochemical, or electrochemical approaches. Photochemical approach is usually based on the application of UV or vis irradiation, which generates in the solution, at the presence of suitable organic sensibilizers, radicals that fulfill the role of a reducing agent and reduce the metal ions to neutral metal atoms in the solution [110, 111]. Direct photochemical reduction is possible for some photosensitive materials (e.g., silver halogenides). Free electrons are generated by absorption of photons by these substances, and therefore direct reduction of the metal ions from crystal lattice can proceed in this way [112]. However, in this special case, it is necessary to highlight that the ions are not reduced directly from the solution because the photosensitive

compounds have limited solubility. Photoreduction therefore proceeds in solid state [113]. Radiochemical reduction uses highly energetic gamma irradiation, X-ray irradiation, or accelerated electrons and does not need additional organic molecules, which would produce radicals. These kinds of irradiations enable to produce radicals from the solvent molecules [114–116]; eventually the applied accelerated electrons can be responsible for the reduction of the metal ions [117, 118]. Therefore the generated particles are really clean although it is highly recommended to add suitable stabilizers into the systems in order to prevent unwanted aggregation of the primarily generated particles. The reduction of metal ions in solutions can be also achieved using electrochemical methods. In this case, the electrons, needed for completion of the reduction, are supplied by the electrode. The surface of the electrode is then covered by a film consisting of the generated particles [119–121]. One of the biggest advantages of this method is its variability thanks to the possibility of the reducing potential adjustment or possibility to adjust the passing current [122–124]. This method of nanoparticle generation is commonly used for layers of nanoparticles generated on glass with conductive layer of indium tin oxide (ITO) glass [125]. In the case of the liquid dispersion of nanoparticles, prepared via the electrochemical approach, it is necessary to prevent firm attachment of the generated particles on the surface of the electrode. For this purpose the combination of electrochemical reduction with ultrasound is generally used [126]. However, the commonly used approach to electrochemical preparation of nanoparticles is based on the use of a mediator molecule, which is reduced on the cathode, and then the reduced form of the mediator diffuses into the solution where it is used for reduction of the metal ion. Methylviologen is the most commonly used mediator [127–130].

2. Preparation of metal nanoparticles by chemical reduction: role of the redox potentials

Preparation of nanoparticles of transition metals via wet route chemical reduction method is probably the most frequently used one. It is widely used both in research and in technological practice [131–133]. The reasons why this kind of preparation method is used are simple—from the economic and technological point of view, it represents the most convenient approach. The preparation of nanomaterials following the wet chemical reduction method does not have any specific demands for complicated technological equipment or installation, in most of the case just a suitable vessel equipped with stirring mechanism and a possible adjustment of temperature (note: for elevated temperature, heating is needed; for lower than room temperature, simple cooling bath is usually sufficient) is needed. Moreover, the productivity of chemical reduction methods is significantly higher than other methods of metal nanoparticle preparations. The whole synthetic process is easy to scale up from a preparation of a couple of milliliters of the reaction mixture up to tens of liters. Another advantage is also a wide range of available reducing agents. The reducing agents are commonly inexpensive substances, and therefore the economic balance of the whole process is not anyhow weighted down in this aspect. Also the energy balance of the whole process is in favor of the wet chemical reduction method, compared to the physical methods of metal nanoparticle preparation. However, a certain disadvantage can be found in the limited possibility to design the particle diameter. This handicap has been almost erased thanks to the intensive research of this aspect in the last 20 years. Additionally, the research brought also a possibility to adjust other fundamental properties like morphology, which is highly problematic to achieve even via physical approach to metal nanoparticle synthesis [134, 135].

From the thermodynamic point of view, the synthesis of metal nanoparticles via wet chemical reduction method can spontaneously proceed only under the condition of negative value of the difference of Gibbs energy (ΔG). To achieve such negative ΔG values, the difference of redox (reduction-oxidative) potentials of the redox systems metal ions and oxidized and reduced form of the reducing substance must be positive. As the primary process of the electron transfer between the redox forms of the redox system is reversible in its principle, the description of the proceeding processes can be done thanks to the analogy to the processes proceeding on the electrodes in a galvanic cell. The difference in Gibbs energy (ΔG) for the reaction in a galvanic cell is given by the difference of equilibrium potentials of the electrodes (ΔE) according to Eq. (1):

$$\Delta G = -zF \Delta E \quad (1)$$

where F is Faraday constant and z represents the number of electrons exchanged among the reactants in cell reaction [136]. The ΔG has to be negative for spontaneous course of the reaction, and therefore the ΔE —i.e., the difference of the potentials of the reacting redox systems—has to be positive. According to the convention, this difference of the electrode potentials is defined as the difference between the right and the left electrode, whereas the oxidation proceeds on the left and the reduction on the right electrode. If the metal ion reduces and the molecule of the reducing agent is being oxidized, the ΔE can be defined by Eq. (2):

$$\Delta E = E_R - E_L = E_{\text{Mez}^+/\text{Me}} - E_{\text{ox/red}} \quad (2)$$

The potentials of both redox systems $E_{\text{Mez}^+/\text{Me}}$ and $E_{\text{ox/red}}$ depend on the ratio of the activity (concentration) of the oxidized and reduced form according to the Nernst equation in Eq. (3):

$$E_{\text{ox/red}} = E_{\text{ox/red}}^{\circ} + (RT/zF) \ln (a_{\text{ox}}/a_{\text{red}}) \quad (3)$$

where $E_{\text{ox/red}}^{\circ}$ represents the value of standard redox potential for the particular redox system in the hydrogen scale (standard redox potential of the hydrogen electrode was determined to the value of 0) and a_{ox} and a_{red} represent activities of the oxidized and the reduced forms of the given redox system in the solution. The activity of a solid metal is unitary, and although the real value of $E_{\text{Mez}^+/\text{Me}}^{\circ}$ is dependent on the particle diameter for little nanoparticles [137], this dependency would not be taken into account in these considerations. More complicated situation is the estimation of the redox potential of the reducing agent. Although the primary process of electron transfer can be considered reversible, the oxidized form of the molecule of the reducing agent is usually unstable and undergoes consequential chemical reactions with the substances available in the solution. Therefore, the process becomes irreversible, and it is almost impossible to determine the concentration of the oxidized form. Thus, the fundamental decision if the redox process can be realized is based on the value of ΔE° instead of ΔE . It is relatively a rational consideration because if the ΔE° has a negative value, then positive value of ΔE of both redox systems cannot be achieved. Such a large difference would be necessary for a quick course of the redox procedure [138]. The values of redox potentials of the discussed metal systems are listed in **Table 1**.

It is obvious that noble metals like silver, gold, palladium, or platinum can be reduced from their salts using even relatively weak reducing agents. However, for the reduction of less noble metals like copper and especially iron, cobalt, and nickel, only stronger reducing agents, e.g., sodium borohydride, must be used. It is

Redox system	Half-reaction	E° [V]	Redox system	Half-reaction	E° [V]
Iron	$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}^0$	−0.447	Ruthenium	$\text{Ru}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ru}^0$	+0.455
Cobalt	$\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}^0$	−0.28	Rhodium	$\text{Rh}^{3+} + 3\text{e}^- \rightleftharpoons \text{Rh}^0$	+0.758
Nickel	$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}^0$	−0.257	Palladium	$\text{Pd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pd}^0$	+0.951
Copper	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}^0$	+0.3419	Osmium	$\text{Os}^{2+} + 2\text{e}^- \rightleftharpoons \text{Os}^0$ Ref. [140]	+0.7
Silver	$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}^0$	+0.7996	Iridium	$\text{Ir}^{3+} + 3\text{e}^- \rightleftharpoons \text{Ir}^0$	+1.156
Gold	$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}^0$	+1.498	Platinum	$\text{Pt}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pt}^0$	+1.18

Table 1. Standard electrochemical potentials of noble metals and triad Fe, Co, and Ni [139]. All potentials are referred vs. standard hydrogen electrode (SHE) using IUPAC recommendation.

Redox system	Half-reaction	E° [V]	Cit.
Hypophosphorous acid	$\text{HPO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2\text{PO}_2^- + 3\text{OH}^-$	−1.65	[139]
Borohydride	$\text{H}_2\text{BO}_3^- + 5\text{H}_2\text{O} + 8\text{e}^- \rightleftharpoons \text{BH}_4^- + 8\text{OH}^-$	−1.24	[139]
Hydrazine	$\text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons \text{N}_2\text{H}_4 + 4\text{OH}^-$	−1.15	[140]
Hydroxylamine	$\text{N}_2\text{O}_2^- + 6\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 2\text{NH}_2\text{OH} + 6\text{OH}^-$	−0.73	[140]
Formic acid	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCOOH}$	−0.14	[140]
Hydrogen peroxide	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{HO}_2^- + \text{OH}^-$	−0.076	[140]
Ascorbic acid	$\text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{C}_6\text{H}_8\text{O}_6$	−0.054 (pH = 7)	[140]
Formaldehyde	$\text{HCOOH} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCHO} + \text{H}_2\text{O}$	−0.02	[140]
Hydrogen	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.000	[140]
Stannum(II)	$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$	+0.15	[140]
p-Aminophenol	$\text{OC}_6\text{H}_4\text{NH} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HOC}_6\text{H}_4\text{NH}_2$	+0.599	[149]
Hydroquinone	$\text{C}_6\text{H}_4\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{C}_6\text{H}_4(\text{OH})_2$	+0.699	[140]
Citric acid	$\text{CH}_3\text{COCH}_3 + 3\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{C}_6\text{H}_8\text{O}_7$	+1.1	[150]
Glucose	$\text{C}_6\text{H}_{12}\text{O}_7 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{OH}^-$	$\approx + 0.65$ (pH = 12.8)	[151]
Galactose	$\text{C}_6\text{H}_{12}\text{O}_7 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{OH}^-$	$\approx + 0.7$ (pH = 12.8)	[151]

Table 2. Standard electrochemical potentials of various reductants commonly used in the synthesis of metal nanoparticles. All potentials are referred vs. standard hydrogen electrode (SHE) using IUPAC recommendation.

not realistic to think that the nanoparticles of less noble metals can be prepared via green reducing methods using reducing substances of biological origin [141–147], in this case, substances of a type of polyphenols, the redox potential is insufficient with respect to the highly negative values of standard redox potentials of the metal systems [148]. The values of redox potentials of the commonly used reduction agents are listed in **Table 2**.

Figure 2 shows graphically comparison of redox potentials of some reducing agents and metals. The reducing agent can be effective, in the process of the metal ion reduction, only if the redox potential is under the redox potential of the metal

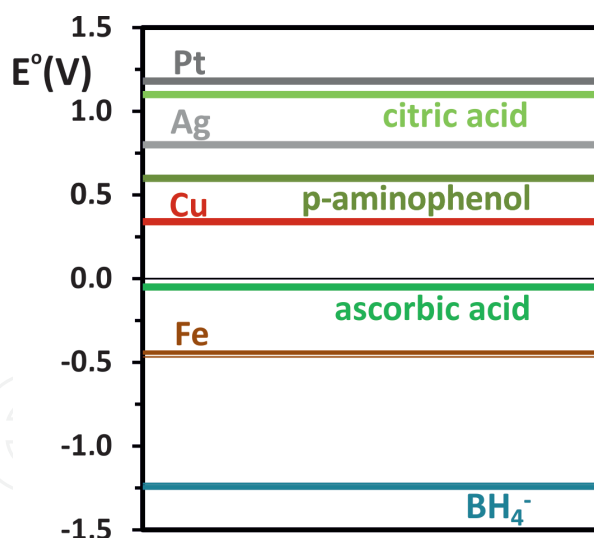


Figure 2.
 Comparison of the standard redox potentials of the metals and reductants selected from **Tables 1 and 2** as representative of the typical reaction systems for the preparation of the metal nanoparticles.

redox system on the hydrogen scale. However, any positive value of ΔE is not sufficient for real and effective course of the reduction leading to the formation of metal nanoparticles under room temperature. The value of ΔE from approx. 0.15–0.3 V is commonly agreed to ensure sufficiently quick course of the reaction. Based on all of the stated facts, it can be concluded that the impact of the ΔE value is crucial. The higher the value of ΔE is (i.e., the stronger the reducing substance is), the quicker the reduction of the metal ions is, and the generated nanoparticles are smaller [152]. Due to a quick reduction, steep growth of oversaturation proceeds. According to the theory of new phase formation, a great number of nucleation centers are generated under such conditions. The nuclei grow quickly, thanks to the aggregation mechanism in majority, up to the final particle diameter within a couple of seconds. The result of such a process is a formation of tiny nanoparticles, which is a typical example of the use of sodium borohydride as the reducing agent, which enables the synthesis of silver nanoparticles, gold nanoparticles, and nanoparticles of other metals that have the diameter smaller than 10 nm. The first usage of sodium borohydride, as the reducing agent for the synthesis of silver nanoparticles, was described by Creighton, Blatchford, and Albrecht in the 1980s. This collective of authors used sodium borohydride for the preparation of SERS substrate [153]. Unfortunately, a quick reduction of available metal ions has negative consequences such as poor reproducibility of the synthesis and high polydispersity of the generated particles in the system. Therefore, the synthesis is likely to proceed under lowered temperature (note: the system is placed into a cooling bath) and with the addition of stabilizing substances. In the borohydride reduced systems, citrate molecules are frequently used as stabilizing agent as it prevents aggregation of the generated particles. The citrate ions can be, in the next step, easily removed from the surface layers due to the addition of different molecules in the process of nanoparticle functionalization [154–156]. Strong reducing agents cannot, however, guarantee synthesis of nanoparticle systems with minimal polydispersity of the generated particles as the two phases of the nanoparticle formation—nucleation and particle growth—are not well differentiated. Not even the usage of weak reducing agents, requiring elevated temperature for its effective function, can solve this problem. The process of silver nanoparticle preparation introduced by Lee and Meisel is based on the reduction of silver ions with citrate, boiling the reaction mixture [157]. Thanks to high kinetic energy (boiling water), new nuclei can be generated even in further stages of the reduction process, and the resulting system is then highly polydisperse.

The average diameter of the generated particles is due to the slower course of the reaction, significantly bigger (40–50 nm) than for the borohydride method [158, 159]. However, when the citrate anion is used as the reducing agent of Au^{3+} cations (Turkevich method [160–162]), the greater difference in redox potentials of both of the systems predetermines significantly quicker reduction of the particles and generation of smaller particles (approx. 15 nm) with even better polydispersity of the system. Therefore, it is necessary to compare the results achieved with different reducing agents only for one metal redox system where the growing diameter of the generated particles can be unambiguously put into context with the decreasing reducing strength of the reducing agent. This behavior was observed also for the silver nanoparticles prepared via the modified Tollens process using different reducing saccharides with different reducing ability [30, 163, 164].

The above-listed examples proved that the course of the metal ion reduction, leading to the production of metal nanoparticles, is given by the ΔE more than the value of $E_{\text{red/ox}}$ of the used reducing agent. However, the estimation of the ΔE value (note: accurate calculation is rather complicated or even impossible) is complicated by the dependency of redox potential of the reducing agent and very frequently also of the metal redox system on pH, which will be discussed in the independent part. It is also necessary to take into account the interaction of metal ions with other substances available in the reaction system as they can form complex substances with these ions. Such substances—ligands—can be added into the reaction system on purpose. However, sometimes they can be also counterparts of a complicated, not well-defined biological system of the reducing system (in the case of the green methods) [165–167]. In other case, the reducing substance can play the role of a reducing agent and a ligand, which forms a complex compound with the available metal ion. It is typical for reducing polymers including a nitrogen atom as heteroatom, e.g., poly(vinylpyrrolidone) (PVP), polyethylenimine (PEI), or polyaniline (PANI) [168–174]. Such a formation of a complex compound is widely applied in practice for the tailored preparation of metal nanoparticles. Complexing agent can influence reduction rate of the metal ion due to the change of redox potentials via complexation of metal ions (see some examples of potential change on **Figure 3**). This way it significantly influences the nuclei formation and their consequential growth. The synthesis of silver nanoparticles, using the reduction of diammonium silver complex cation with reducing sugars (already mentioned modified Tollens

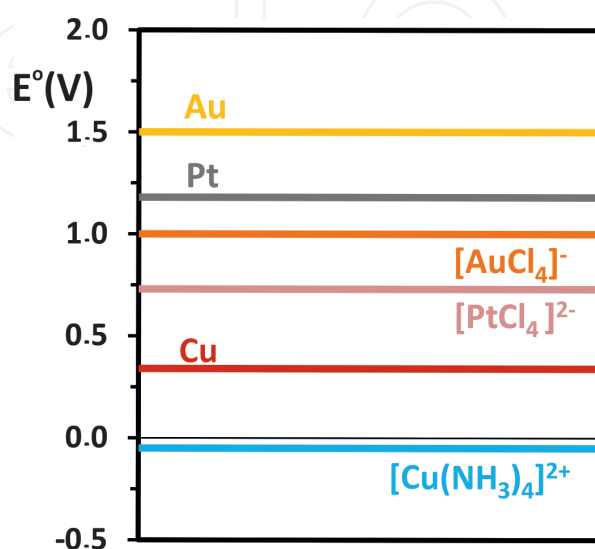


Figure 3. Comparison of the standard redox potentials of the free metal ions and their typical complex ions, which are employed in the reaction systems for the preparation of the metal nanoparticles. Values of standard redox potentials of the complex ions are taken from tables by Dobos [140].

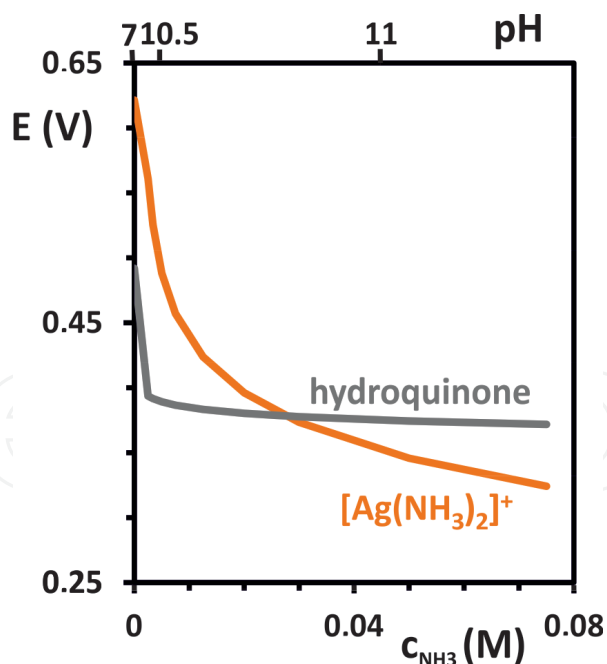


Figure 4.

Comparison of the redox potential dependence for the complex metal ion $[Ag(NH_3)_2]^+$ and hydroquinone reductant on the concentration of ammonia. The change of the ammonia concentration in the reaction system is connected with the change of pH. It is clearly visible that at $pH \approx 10.8$ (concentration of ammonia about 0.0275 Mol/dm^3), the potentials of both redox systems are identical. Values of redox potentials were calculated using Eq. (10) for system Q/H_2Q and Eq. (4) for the system $[Ag(NH_3)_2]^+/Ag$. The needed values of constants were taken from tables by Dobos [140].

reaction), represents a suitable example of such a tailored metal nanoparticle preparation. The diameter of the generated silver nanoparticles can be adjusted by means of the ammonia concentration throughout the change of the redox potential of the silver redox system due to the bond of majority of the Ag^+ cations into a stable complex compound $[Ag(NH_3)_2]^+$ according to Eq. (4):

$$E_{[Ag(NH_3)_2]^+/Ag} = E^{\circ}_{Ag^+/Ag} + (RT/F) \ln\{(a_{[Ag(NH_3)_2]^+}) (a_{NH_3})^{-2} \beta_2^{-1}\} \quad (4)$$

where β_2 represents a stability constant of the complex cation $[Ag(NH_3)_2]^+$ [175]. **Figure 4** shows how is such a difference reflected in the course of the potential of silver redox system side by side with the course of the difference of the potential of the used reducing agent with the changing pH value (with the growing ammonia concentration in the reaction system). The growing ligand concentration in the reaction system is reflected in a decrease of ΔE , decrease in the rate of the reaction, and growth of the particle diameter [163, 176–179]. Also ligand exchange for any other, which would form a stronger complex with the metal ion, will lead to a decrease of ΔE and consequential decrease of the reaction rate, which will lead to the growth in the diameter of the finally generated particles. This behavior was observed in the case of silver nanoparticles, prepared with the assistance of sulfite ligand as the complexing agent. This ligand has six order higher stability constants than the values for ammonia complex with this metal [175]. Therefore, the growth of the size of the prepared particles was more than significant. The generated particles had several hundreds of nanometers in diameter [180].

3. Preparation of metal nanoparticles by chemical reduction: role of the pH

The tailored preparation of metal nanoparticles using the method of chemical reduction not be done without the control of pH of the system. The adjustment

of pH helps to manage the diameter of the prepared particles and reproducibility of the reducing process. The influence of pH is connected with the fundamental principles:

1. pH usually influences redox potential of the used reducing agent and can significantly change even the mechanism of its oxidation.
2. pH influences redox potential of the metal, which is usually based on the formation of a new compound, where the reduced metal ion is bound.
3. pH significantly influences stability of the generated metal nanoparticle dispersion by means of the change of their zeta potential, or via the electric properties of the stabilizing molecules, e.g., via a change in the dissociation of the function groups in the polymer electrolytes.

The first two mentioned principles are the most important. As the diameter of the generated particles can be tailored due to the strength of the reducing agent, this aspect will be devoted more attention. The simplest description of the change of redox potential with pH is for the system where gaseous hydrogen is used as the reducing agent. If the solution, containing ionic metal, is saturated with gaseous hydrogen under the atmospheric pressure, the equation for the redox potential H^+/H_2 is significantly simplified:

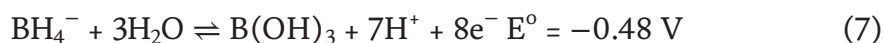
$$E_{H^+/H_2} = (RT/F) \ln (a_{H_3O^+}) = -(2303RT/F) \text{ pH} \quad (5)$$

If pH increases from deep acidic value 1 to neutral value of 7, the original redox potential is shifted from 0.0 to -0.414 V. As the reduction potential of hydrogen is significantly increased, the reduction will proceed quicker, and the average particle diameter will be smaller [181].

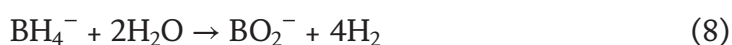
In the case of one of the strongest inorganic reducing substances, used for the metal nanoparticle generation, the change of pH from acidic region to alkali one does not mean just the change in redox potential but also a change in the oxidation mechanism of this substance. The oxidation of the borohydride anion proceeds as follows in the alkali environment [139]:



However, if the pH is shifted into a slightly acidic region, the reaction mechanism is significantly changed, and the oxidation of the borohydride anion can be simply written as follows:



Additionally, the environment enables also a side reaction—direct hydrolysis of the borohydride anion accompanied by the hydrogen release:



In this situation, hydrogen, generated according to Eq. (8), can become the main reducing agent. However, such a complicated reaction of the tailored nanoparticle synthesis and the reproducibility of such synthetic experiment are rather poor. The dependence of oxidation mechanism and redox potential on pH

can be observed for the system of hydrazine and hydroxylamine [182]. Both of these substances are commonly used as the reducing agents in the processes of nanoparticle preparation [183–189].

Organic reducing substances, used in the preparation of metal nanoparticles, exhibit more predictable behavior than the inorganic ones. These substances are weak electrolytes, in majority, and as such their dissociation is influenced by pH. Generally, the substances, which behave as weak acids, have stronger reducing ability in alkali region of pH, and those that behave like weak bases have stronger reducing ability in acidic pH range. It is connected with higher degree of dissociation of these reducing substances in the particular pH region. In literature, *p*-dihydroxybenzene (also labeled as hydroquinone or H₂Q) is usually stated as a typical representative of such a substance [190]. Its dissociated form is oxidized, in two one-electron steps, across semiquinone, to *p*-benzoquinone (often labeled as quinone or Q):



As H₂Q is a weak acid ($\text{pK}_1 = 9.85$ a $\text{pK}_2 = 11.4$), the concentration (resp. activity) of the Q²⁻ ion is dependent on pH, which is then reflected in the equation for potential of the Q/Q²⁻ redox system:

$$\begin{aligned} E &= E^\circ_{\text{Q/Q}^{2-}} + (RT/2F) \ln (a_{\text{Q}}/a_{\text{Q}^{2-}}) \\ &= E^\circ_{\text{Q/Q}^{2-}} + (RT/2F) \ln ([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2) \end{aligned} \quad (10)$$

where $E^\circ_{\text{Q/Q}^{2-}}$ is a formal redox potential of the Q/Q²⁻ redox system and K_1 and K_2 are partial dissociation constants of H₂Q [139]. Quinone is not an electrolyte, and therefore its dissociation is not a part of the equation of the influence of redox potential on pH. In the case of other organic substances, both redox forms can be electrolytes, and therefore the equation of the dependency of redox potential on pH is significantly more complicated as both of the dissociations must be involved. However, the real mechanism of the H₂Q oxidation is more complicated due to the formation of semiquinone, but the pH dependence of the redox potential is not influenced [191–193]. The dependency of the redox system of Q/Q²⁻ on pH side by side with the dependency of the potential of the redox system Ag⁺/Ag on the ammonia concentration is shown in **Figure 4**. It is obvious that the pH and the concentration of the complexing agent for ions influence ΔE of the reaction, its reaction rate, and also the diameter of the generated metal nanoparticles. In this case, when H₂Q was used as the reducing agent for Ag⁺ ions, resp. [Ag(NH₃)₂]⁺ at pH lower than 7, the value of ΔE is low and the reduction of silver ions does not proceed [194, 195]. Similar dependency of redox potential on pH as H₂Q can be observed also with ascorbic acid (AA). As it is a stronger acid than H₂Q, a certain reducing ability can be observed already at pH lower than 7 (approximately pH = 6), but it does not behave as an effective reducing agent until pH 9 is reached. In such a case, the reduction is completed within several minutes, and the generated silver nanoparticles (AgNPs) have the diameter smaller than 50 nm [11, 196, 197]. Weak reducing agents, e.g., reducing saccharides, are able to reduce silver ions only under pH higher than 7. However, truly defined particles can be generated under much higher pH, i.e., under pH around 12 [30, 163, 198–200]. Also polymers are typical representatives of substances with a weak reducing ability which can be achieved only under specific conditions as, e.g., optimal pH for the reduction [201–208]. Pluronic P123 (a copolymer of PPO and PEO) has a slight reducing ability due to the polyethylene oxide blocks (PEO). The reducing ability grows with the growing pH. This polymer is not able to perform reduction of AuCl₄⁻ ions in acidic region. However,

with the growing pH, it is possible to generate gold nanoparticle dispersion with the average particle diameter of 10 nm and the SPR in the region of approx. 550 nm when the final pH of the dispersion is higher than 10 [209].

In the case of the metal redox systems, the influence of the pH is related to the reaction of the OH^- ions with the metal ions. Hydroxides, oxidehydroxides, oxides, or stable complex substances are commonly formed by this reaction. A typical example represents formation of poorly soluble Ag_2O in Ag^+ solution at pH higher than 9. The redox potential of the system $\text{Ag}_2\text{O}/\text{Ag}$ is significantly lower ($E^\circ = 0.342 \text{ V}$) than of the system Ag^+/Ag ($E^\circ = 0.799 \text{ V}$). This change of redox potential is reflected in a lower rate of reduction and a formation of big particles. In the case when glucose is used as the reducing agent, the generated particles are even larger than 100 nm [181, 194, 195, 210, 211].

On the contrary, in the case of gold chloride, respectively complex anion AuCl_4^- , it is possible to exchange coordinated Cl^- ions for OH^- anions in aqueous environment, according to the adjusted pH. The complex anion of the composition of $\text{AuCl}_3(\text{OH})^-$ is formed under the pH lower than 6. All the Cl^- anions are replaced by the OH^- anions when the pH becomes higher than 12. The newly formed complex anions are more stable than the original ones, and therefore the reaction rate is significantly reduced due to the decrease of the redox potential of the system Au^{3+}/Au . It is then reflected in the growth of the AuNPs' diameter [212]. In the case of the Turkevich method of AuNPs' preparation, the situation is complicated with the way the pH changed. It proceeds with a growing concentration of citrate, which is added as reducing agent. Therefore, although the newly generated anion $\text{AuCl}_{4-x}(\text{OH})_x^{x-}$ is more stable, the reduction rate can grow with the growth of the reducing agent concentration. This factor together with the positive dependence of the reduction power citrate on the pH can prevail, and then the diameter of the generated AuNPs decreases with the growing pH [213]. It must be taken into account that the pH value can influence both redox pairs in return. Therefore, the prediction of the diameter dependence of the prepared nanoparticles on pH represents a highly complicated task in some cases.

4. Preparation of metal nanoparticles by chemical reduction: role of the temperature

The temperature is the last physicochemical parameter, which can have an impact on the course of the metal nanoparticle synthesis and which is therefore worth discussing in this chapter. It is generally known that temperature influences both chemical balance and rate of chemical reaction. The first case cannot be, however, used as the one, which has a major influence on the metal nanoparticle preparation via a reducing process. This fact is caused by the minimal changes of the potential values, i.e., $\pm 1 \text{ mV/K}$ [214]. This difference in ΔE , in favor of the products of the reduction process, is too minor to have any significant impact. The change in temperature, however, significantly influences the rate of the chemical reaction. The increase in temperature leads to the increase in the reduction rate according to the Arrhenius equation. As it was already mentioned before, the mechanism of the nanoparticle formation fundamentally consists of two steps: (1) generation of nuclei and (2) growth of the nuclei up to the size of a final nanoparticle [215, 216]. Both of the stages of the nanoparticle formation require different activation energies, and therefore their dependency on temperature differs [212, 217]. The nuclei formation is more energy demanding, and therefore the increase of temperature in this step is reflected in steeper increase of its rate than the rate of the nanoparticle growth. The increase in temperature is then reflected in the increase of

the polydispersity of the system because new nuclei will be generated for the whole reaction time side by side with the growing particles. This effect can be especially well observed in the case of the weaker reducing agents as, e.g., for the preparation of silver nanoparticles according to Lee and Meisel [157]. This effect is even more significant concerning very weak reducing agents of polymer character [204, 205]. Contrariwise, the average particle diameter decreases with the increased rate of the nuclei formation [218, 219].

Higher temperature is used especially with weaker reducing agents with the aim to increase the rate of chemical reaction and eventually to increase the salt conversion. On the contrary, the use of stronger reducing agents requires a decrease in this parameter—i.e., cooling of the reaction mixture can positively influence also polydispersity of the generated particles in the system. The improvement of the system polydispersity is predetermined by two contributions: first, by a limited generation of the future nanoparticle nuclei, and second, by a limited Brownian motion of the generated particles. Lowered temperature is used commonly especially in cases when borohydride is used as the reducing agent. The original procedure suggested by Creighton, Blatchford, and Albrecht used ice-cold bath [153]. However, cooling with ice is insufficient for suppression of the quick generation of the nuclei in the course of the whole reaction time. Therefore, neither polydispersity nor reproducibility of the resulting nanoparticles are not satisfactory. Both parameters were further improved when the addition of citrate anion was introducing into this already established synthesis. The citrate does not play the role of reducing agent at this temperature, but it prevents the unwanted aggregation of generated particles. As such, it fulfills the role of a stabilizing agent [156]. To reach lower temperatures than 0°C, it is necessary to use other solvents but just water. The temperature of −25°C can be achieved when water is replaced by mixed solvent—water-ethanol (1:1 v/v). However, the particles generated in this mixed solvent exhibit even worse aggregation stability than the particles prepared in a pure aqueous environment. Therefore, it is necessary to use a stabilizer—in this case, sodium polyacrylate was introduced. Under such a low temperature, the ability of the nuclei formation is significantly limited, which is then reflected in the increased diameter of the generated nanoparticles—3.4 nm for −5°C and 7.2 nm for −25°C. The polydispersity of the system, however, follows the already discussed trend, i.e., it is decreased with the decreasing temperature [220].

5. Conclusion

Metal nanoparticles represent one of the key pillars of nanotechnology. Their physicochemical properties are unique and different to other types of nanomaterials that they have abruptly found their way to numerous commercial applications. However, the applications are strongly dependent on the efficiency of their production—especially respecting primarily defined diameter and morphology. Nowadays available methods of metal nanoparticle production do not fully fulfill the needs given by the research and practice. In order to design preparation of tailored nanoparticles, it is highly important to be aware of the impact of the different physicochemical parameters predetermining the diameter and morphology of the generated nanoparticles. Let us name at least a couple of them—the influence of the difference of redox potentials of the reaction components, pH of the reaction mixture, and its temperature. These three parameters have been discussed in this chapter with respect to the current state of knowledge. However, aside from the three discussed parameters, there are several other parameters with key influence. One is molar ratio among the reactants, which was already effectively used by Turkevich

for a tailored preparation of gold nanoparticles [154, 160, 212, 221, 222]. The whole reduction process can be also influenced by other substances present in the reaction system—e.g., molecules of surfactants, polymers, and other low-molecular organic substances with O, N, and S heteroatoms, which significantly influence the process of nucleation and growth of the nanoparticles [223–226] and also the aggregation stability of the final system [227–229]. The process of “seed-mediated” preparation of nanoparticles is based on the preparation of seeds, in diameter of nanometers, using strong reducing agents. The nuclei are, in the next step, let to grow into their required diameter, thanks to the addition of new portion of the metal ions reduced by using weaker reducing agent [11, 230, 231]. Reasonable adjustment of both steps, nanoparticles in a wide range of diameters, can be prepared. Additionally, this approach also provides dispersions of nanoparticles with reasonably good values of polydispersity [31, 232, 233].

Acknowledgements

The work was supported by ERDF project “Development of Pre-applied Research in Nanotechnology and Biotechnology” (No. CZ.02.1.01/0.0/0.0/17_048/0007323).

Conflict of interest


The authors certify that there is no actual or potential conflict of interest in relation to this article.

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References

- [1] Tadros TF. Industrial applications of dispersions. *Advances in Colloid and Interface Science*. 1993;**46**:1-47
- [2] Rusk P, editor. *Metal Nanoparticles: Concepts and Applications*. New York: Willford Press; 2016
- [3] Harish KK, Venkatesh N, Bhowmik H, Kuila A. Metallic nanoparticle: A review. *Biomedical Journal of Scientific & Technical Research*. 2018;**4**(2):3765-3775
- [4] Creighton JA, Eadon DG. Ultraviolet visible absorption-spectra of the colloidal metallic elements. *Journal of the Chemical Society, Faraday Transactions*. 1991;**87**(24):3881-3891
- [5] Scholl JA, Koh AL, Dionne JA. Quantum plasmon resonances of individual metallic nanoparticles. *Nature*. 2012;**483**(7390):421-468
- [6] Ringe E, Sharma B, Henry AI, Marks LD, Van Duyne RP. Single nanoparticle plasmonics. *Physical Chemistry Chemical Physics*. 2013;**15**(12):4110-4129
- [7] Marhaba S. Effect of size, shape and environment on the optical response of metallic nanoparticles. In: Seehra M, Bristow A, editors. *Noble and Precious Metals*. London: IntechOpen; 2017. pp. 215-238
- [8] Araujo TP, Quiroz J, Barbosa ECM, Camargo PHC. Understanding plasmonic catalysis with controlled nanomaterials based on catalytic and plasmonic metals. *Current Opinion in Colloid & Interface Science*. 2019;**39**:110-122
- [9] Ujihara M. Solution-phase synthesis of branched metallic nanoparticles for plasmonic applications. *Journal of Oleo Science*. 2018;**67**(6):689-696
- [10] Eremina OE, Semenova AA, Sergeeva EA, Brazhe NA, Maksimov GV, Shekhovtsova TN, et al. Surface-enhanced Raman spectroscopy in modern chemical analysis: Advances and prospects. *Russian Chemical Reviews*. 2018;**87**(8):741-770
- [11] Xing LX, Xiahou YJ, Zhang PN, Du W, Xia HB. Size control synthesis of monodisperse, quasi-spherical silver nanoparticles to realize surface-enhanced Raman scattering uniformity and reproducibility. *ACS Applied Materials & Interfaces*. 2019;**11**(19):17637-17646
- [12] Sarfo DK, Izake EL, O'Mullane AP, Ayoko GA. Fabrication of nanostructured SERS substrates on conductive solid platforms for environmental application. *Critical Reviews in Environmental Science and Technology*. 2019;**49**(14):1294-1329
- [13] Turzhitsky V, Qiu L, Itzkan I, Novikov AA, Kotelev MS, Getmanskiy M, et al. Spectroscopy of scattered light for the characterization of micro and nanoscale objects in biology and medicine. *Applied Spectroscopy*. 2014;**68**(2):133-154
- [14] Sarycheva AS, Brazhe NA, Baizhumanov AA, Nikelshparg EI, Semenova AA, Garshev AV, et al. New nanocomposites for SERS studies of living cells and mitochondria. *Journal of Materials Chemistry B*. 2016;**4**(3):539-546
- [15] Gong LS, Wang YP, Liu JB. Bioapplications of renal-clearable luminescent metal nanoparticles. *Biomaterials Science*. 2017;**5**(8):1393-1406
- [16] Klebowski B, Depciuch J, Parlinska-Wojtan M, Baran J. Applications of noble metal-based nanoparticles in medicine. *International Journal of Molecular Sciences*. 2018;**19**(12):4031

- [17] Elahi N, Kamali M, Baghersad MH. Recent biomedical applications of gold nanoparticles: A review. *Talanta*. 2018;**184**:537-556
- [18] Astruc D. Nanoparticles and Catalysis. Weinheim: Wiley-VCH; 2008
- [19] Chaturvedi S, Dave PN, Shah NK. Applications of nano-catalyst in new era. *Journal of Saudi Chemical Society*. 2012;**16**(3):307-325
- [20] Zhao PX, Feng XW, Huang DS, Yang GY, Astruc D. Basic concepts and recent advances in nitrophenol reduction by gold- and other transition metal nanoparticles. *Coordination Chemistry Reviews*. 2015;**287**:114-136
- [21] Gubin SP. Magnetic nanoparticles. Wiley-VCH: Weinheim; 2009
- [22] Kudr J, Haddad Y, Richtera L, Heger Z, Cernak M, Adam V, et al. Magnetic nanoparticles: From design and synthesis to real world applications. *Nanomaterials*. 2017;**7**(9):243
- [23] Kvitek L, Panacek A, Soukupova J, Kolar M, Vecerova R, Pucek R, et al. Effect of surfactants and polymers on stability and antibacterial activity of silver nanoparticles (NPs). *Journal of Physical Chemistry C*. 2008;**112**(15):5825-5834
- [24] Duran N, Duran M, de Jesus MB, Seabra AB, Favaro WJ, Nakazato G. Silver nanoparticles: A new view on mechanistic aspects on antimicrobial activity. *Nanomedicine: Nanotechnology, Biology and Medicine*. 2016;**12**(3):789-799
- [25] Prasher P, Singh M, Mudila H. Silver nanoparticles as antimicrobial therapeutics: Current perspectives and future challenges. *3. Biotech*. 2018;**14**:8(10)
- [26] Panacek A, Kolar M, Vecerova R, Pucek R, Soukupova J, Krystof V, et al. Antifungal activity of silver nanoparticles against *Candida* spp. *Biomaterials*. 2009;**30**(31):6333-6340
- [27] Kumar SSD, Rajendran NK, Hourel NN, Abrahamse H. Recent advances on silver nanoparticle and biopolymer-based biomaterials for wound healing applications. *International Journal of Biological Macromolecules*. 2018;**115**:165-175
- [28] Deshmukh SP, Patil SM, Mullani SB, Delekar SD. Silver nanoparticles as an effective disinfectant: A review. *Materials Science & Engineering, C: Materials for Biological Applications*. 2019;**97**:954-965
- [29] Auffan M, Rose J, Bottero JY, Lowry GV, Jolivet JP, Wiesner MR. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nature Nanotechnology*. 2009;**4**(10):634-641
- [30] Panacek A, Kvitek L, Pucek R, Kolar M, Vecerova R, Pizurova N, et al. Silver colloid nanoparticles: Synthesis, characterization, and their antibacterial activity. *The Journal of Physical Chemistry. B*. 2006;**110**(33):16248-16253
- [31] Agnihotri S, Mukherji S, Mukherji S. Size-controlled silver nanoparticles synthesized over the range 5-100 nm using the same protocol and their antibacterial efficacy. *RSC Advances*. 2014;**4**(8):3974-3983
- [32] Ginjupalli K, Shaw T, Tellapragada C, Alla R, Gupta L, Perampalli NU. Does the size matter? Evaluation of effect of incorporation of silver nanoparticles of varying particle size on the antimicrobial activity and properties of irreversible hydrocolloid impression material. *Dental Materials*. 2018;**34**(7):E158-E165
- [33] Njoki PN, Lim S, Mott D, Park HY, Khan B, Mishra S, et al. Size correlation of optical and spectroscopic

properties for gold nanoparticles. *Journal of Physical Chemistry C*. 2007;**111**(40):14664-14669

[34] Schneider S, Halbig P, Grau H, Nickel U. Reproducible preparation of silver sols with uniform particle-size for application in surface-enhanced Raman-spectroscopy. *Photochemistry and Photobiology*. 1994;**60**(6):605-610

[35] Emory SR, Haskins WE, Nie SM. Direct observation of size-dependent optical enhancement in single metal nanoparticles. *Journal of the American Chemical Society*. 1998;**120**(31):8009-8010

[36] Mogensen KB, Kneipp K. Size-dependent shifts of Plasmon resonance in silver nanoparticle films using controlled dissolution: Monitoring the onset of surface screening effects. *Journal of Physical Chemistry C*. 2014;**118**(48):28075-28083

[37] Sharma RK, Sharma P, Maitra A. Size-dependent catalytic behavior of platinum nanoparticles on the hexacyanoferrate(III)/thiosulfate redox reaction. *Journal of Colloid and Interface Science*. 2003;**265**(1):134-140

[38] Panigrahi S, Basu S, Praharaj S, Pande S, Jana S, Pal A, et al. Synthesis and size-selective catalysis by supported gold nanoparticles: Study on heterogeneous and homogeneous catalytic process. *Journal of Physical Chemistry C*. 2007;**111**(12):4596-4605

[39] Roldan CB. Synthesis and catalytic properties of metal nanoparticles: Size, shape, support, composition, and oxidation state effects. *Thin Solid Films*. 2010;**518**(12):3127-3150

[40] Panacek A, Prucek R, Hrbac J, Nevecna T, Steffkova J, Zboril R, et al. Polyacrylate-assisted size control of silver nanoparticles and their catalytic activity. *Chemistry of Materials*. 2014;**26**(3):1332-1339

[41] Roldan Cuenya B, Behafarid F. Nanocatalysis: Size- and shape-dependent chemisorption and catalytic reactivity. *Surface Science Reports*. 2015;**70**(2):135-187

[42] Suchomel P, Kvitek L, Prucek R, Panacek A, Halder A, Vajda S, et al. Simple size-controlled synthesis of Au nanoparticles and their size-dependent catalytic activity. *Scientific Reports*. 2018;**15**:8

[43] Carpenter EE, Seip CT, O'Connor CJ. Magnetism of nanophase metal and metal alloy particles formed in ordered phases. *Journal of Applied Physics*. 1999;**85**(8):5184-5186

[44] Rudakov GA, Tsiberkin KB, Ponomarev RS, Henner VK, Ziolkowska DA, Jasinski JB, et al. Magnetic properties of transition metal nanoparticles enclosed in carbon nanocages. *Journal of Magnetism and Magnetic Materials*. 2019;**472**:34-39

[45] Ivanova OS, Zamborini FP. Electrochemical size discrimination of gold nanoparticles attached to glass/indium-tin-oxide electrodes by oxidation in bromide-containing electrolyte. *Analytical Chemistry*. 2010;**82**(13):5844-5850

[46] Scanlon MD, Peljo P, Mendez MA, Smirnov E, Girault HH. Charging and discharging at the nanoscale: Fermi level equilibration of metallic nanoparticles. *Chemical Science*. 2015;**6**(5):2705-2720

[47] Letellier P, Mayaffre A, Turmine M. Melting point depression of nanosolids: Nonextensive thermodynamics approach. *Physical Review B*. 2007;**76**(4):045428

[48] Goswami GK, Nanda KK. Thermodynamic models for the size-dependent melting of nanoparticles: Different hypotheses. *Current Nanoscience*. 2012;**8**(2):305-311

- [49] Gao F, Gu Z. Melting temperature of metallic nanoparticles. In: Aliofkhazraei M, editor. Handbook of Nanoparticles. Cham: Springer; 2016. pp. 661-690
- [50] Wang BX, Zhou LP, Peng XF. Surface and size effects on the specific heat capacity of nanoparticles. International Journal of Thermophysics. 2006;27(1):139-151
- [51] Likhachev VN, Vinogradov GA, Alymov MI. Anomalous heat capacity of nanoparticles. Physics Letters A. 2006;357(3):236-239
- [52] Singh M, Lara S, Tlali S. Effects of size and shape on the specific heat, melting entropy and enthalpy of nanomaterials. Journal of Taibah University for Science. 2017;11(6):922-929
- [53] Aiken JD, Finke RG. A review of modern transition-metal nanoclusters: Their synthesis, characterization, and applications in catalysis. Journal of Molecular Catalysis a-Chemical. 1999;145(1-2):1-44
- [54] Mathew A, Pradeep T. Noble metal clusters: Applications in energy, environment, and biology. Particle and Particle Systems Characterization. 2014;31(10):1017-1053
- [55] Campos A, Troc N, Cottancin E, Pellarin M, Weissker HC, Lerme J, et al. Plasmonic quantum size effects in silver nanoparticles are dominated by interfaces and local environments. Nature Physics. 2019;15(3):275
- [56] Scholl JA, Garcia-Etxarri A, Koh AL, Dionne JA. Observation of quantum tunneling between two plasmonic nanoparticles. Nano Letters. 2013;13(2):564-569
- [57] Scholl JA, Garcia-Etxarri A, Aguirregabiria G, Esteban R, Narayan TC, Koh AL, et al. Evolution of plasmonic metamolecule modes in the quantum tunneling regime. ACS Nano. 2016;10(1):1346-1354
- [58] Zhang LB, Wang EK. Metal nanoclusters: New fluorescent probes for sensors and bioimaging. Nano Today. 2014;9(1):132-157
- [59] Khandelwal P, Poddar P. Fluorescent metal quantum clusters: An updated overview of the synthesis, properties, and biological applications. Journal of Materials Chemistry B. 2017;5(46):9055-9084
- [60] Jeseentharani V, Pugazhentiran N, Mathew A, Chakraborty I, Baksi A, Ghosh J, et al. Atomically precise noble metal clusters harvest visible light to produce energy. ChemistrySelect. 2017;2(4):1454-1463
- [61] Crawford SE, Hartmann MJ, Millstone JE. Surface chemistry-mediated near-infrared emission of small coinage metal nanoparticles. Accounts of Chemical Research. 2019;52(3):695-703
- [62] Yu HZ, Rao B, Jiang W, Yang S, Zhu MZ. The photoluminescent metal nanoclusters with atomic precision. Coordination Chemistry Reviews. 2019;378:595-617
- [63] Wang QY, Wang SY, Hu X, Li FY, Ling DS. Controlled synthesis and assembly of ultra-small nanoclusters for biomedical applications. Biomaterials Science. 2019;7(2):480-489
- [64] Mittemeijer EJ. Fundamentals of Materials Science : The Microstructure-Property Relationship Using Metals as Model Systems. Heidelberg; New York: Springer; 2010
- [65] Lin PC, Lin S, Wang PC, Sridhar R. Techniques for physicochemical characterization of nanomaterials. Biotechnology Advances. 2014;32(4):711-726

- [66] Joy DC, Romig AD, Goldstein J. Principles of Analytical Electron Microscopy. New York: Plenum Press; 1986
- [67] Fultz B, Howe JM. Transmission Electron Microscopy and Diffractometry of Materials. Heidelberg; New York: Springer; 2013
- [68] Tanaka N. Scanning Transmission Electron Microscopy of Nanomaterials : Basics of Imaging and Analysis. London: Imperial College Press; 2014
- [69] Giessibl FJ. Advances in atomic force microscopy. Reviews of Modern Physics. 2003;**75**(3):949-983
- [70] Humphris ADL, Miles MJ, Hobbs JK. A mechanical microscope: High-speed atomic force microscopy. Applied Physics Letters. 2005;**86**(3):34106
- [71] Gentry ST, Kendra SF, Bezpalko MW. Ostwald ripening in metallic nanoparticles: Stochastic kinetics. Journal of Physical Chemistry C. 2011;**115**(26):12736-12741
- [72] Prucek R, Panacek A, Fargasova A, Ranc V, Masek V, Kvitek L, et al. Re-crystallization of silver nanoparticles in a highly concentrated NaCl environment-a new substrate for surface enhanced IR-visible Raman spectroscopy. CrystEngComm. 2011;**13**(7):2242-2248
- [73] Panacek A, Kvitek L, Smekalova M, Vecerova R, Kolar M, Roderova M, et al. Bacterial resistance to silver nanoparticles and how to overcome it. Nature Nanotechnology. 2018;**13**(1):65-71
- [74] Roh J, Yi J, Kim Y. Rapid, reversible preparation of size-controllable silver nanoplates by chemical redox. Langmuir. 2010;**26**(14):11621-11623
- [75] Berne BJ, Pecora R. Dynamic Light Scattering : With Applications to Chemistry, Biology, and Physics. Dover ed. Mineola, NY: Dover Publications; 2000
- [76] Bhattacharjee S. DLS and zeta potential-What they are and what they are not? Journal of Controlled Release. 2016;**235**:337-351
- [77] Maguire CM, Rosslein M, Wick P, Prina-Mello A. Characterisation of particles in solution-A perspective on light scattering and comparative technologies. Science and Technology of Advanced Materials. 2018;**19**(1):732-745
- [78] Allen T. Powder Sampling and Particle Size Determination. 1st ed. Amsterdam; Boston: Elsevier; 2003
- [79] Hagendorfer H, Kaegi R, Parlinska M, Sinnet B, Ludwig C, Ulrich A. Characterization of silver nanoparticle products using asymmetric flow field flow fractionation with a multidetector approach-A comparison to transmission electron microscopy and batch dynamic light scattering. Analytical Chemistry. 2012;**84**(6):2678-2685
- [80] Bootz A, Vogel V, Schubert D, Kreuter J. Comparison of scanning electron microscopy, dynamic light scattering and analytical ultracentrifugation for the sizing of poly(butyl cyanoacrylate) nanoparticles. European Journal of Pharmaceutics and Biopharmaceutics. 2004;**57**(2):369-375
- [81] Mahl D, Diendorf J, Meyer-Zaika W, Epple M. Possibilities and limitations of different analytical methods for the size determination of a bimodal dispersion of metallic nanoparticles. Colloids and Surfaces A-Physicochemical and Engineering Aspects. 2011;**377**(1-3):386-392
- [82] Boyd RD, Pichaimuthu SK, Cuenat A. New approach to inter-technique comparisons for nanoparticle size measurements; using atomic

force microscopy, nanoparticle tracking analysis and dynamic light scattering. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*. 2011;**387**(1-3):35-42

[83] Souza TGF, Ciminelli VST, Mohallem NDS. A comparison of TEM and DLS methods to characterize size distribution of ceramic nanoparticles. In: 8th Brazilian Congress on Metrology (Metrologia 2015). 2016. p. 733

[84] Hallett FR, Watton J, Krygsman P. Vesicle sizing-Number distributions by dynamic light-scattering. *Biophysical Journal*. 1991;**59**(2):357-362

[85] Vorokh AS. Rrer formula: Estimation of error in determining small nanoparticle size. *Nanosystems: Physics, Chemistry, Mathematics*. 2018;**9**(3):364-369

[86] Bubb DM, O'Malley SM, Schoeffling J, Jimenez R, Zinderman B, Yi SY. Size control of gold nanoparticles produced by laser ablation of thin films in an aqueous environment. *Chemical Physics Letters*. 2013;**565**:65-68

[87] Zhang JM, Claverie J, Chaker M, Ma DL. Colloidal metal nanoparticles prepared by laser ablation and their applications. *ChemPhysChem*. 2017;**18**(9):986-1006

[88] Zhang JM, Chaker M, Ma DL. Pulsed laser ablation based synthesis of colloidal metal nanoparticles for catalytic applications. *Journal of Colloid and Interface Science*. 2017;**489**:138-149

[89] Sportelli MC, Izzi M, Volpe A, Clemente M, Picca RA, Ancona A, et al. The pros and cons of the use of laser ablation synthesis for the production of silver nano-antimicrobials. *Antibiotics-Basel*. 2018;**7**(3):E67

[90] Yan ZJ, Chrisey DB. Pulsed laser ablation in liquid for micro-/ nanostructure generation. *Journal of*

Photochemistry and Photobiology, C: *Photochemistry Reviews*. 2012;**13**(3):204-223

[91] Baruah PK, Sharma AK, Khare A. Effective control of particle size, surface plasmon resonance and stoichiometry of Cu@Cu_xO nanoparticles synthesized by laser ablation of Cu in distilled water. *Optics and Laser Technology*. 2018;**108**:574-582

[92] Baruah PK, Singh A, Rangan L, Sharma AK, Khare A. Optimization of copper nanoparticles synthesized by pulsed laser ablation in distilled water as a viable SERS substrate for karanjin. *Materials Chemistry and Physics*. 2018;**220**:111-117

[93] Wang ZY, Zhou R, Wen F, Zhang RK, Ren L, Teoh SH, et al. Reliable laser fabrication: The quest for responsive biomaterials surface. *Journal of Materials Chemistry B*. 2018;**6**(22):3612-3631

[94] Zeng HB, Du XW, Singh SC, Kulinich SA, Yang SK, He JP, et al. Nanomaterials via laser ablation/ irradiation in liquid: A review. *Advanced Functional Materials*. 2012;**22**(7):1333-1353

[95] Gonzalez-Rubio G, Guerrero-Martinez A, Liz-Marzan LM. Reshaping, fragmentation, and assembly of gold nanoparticles assisted by pulse lasers. *Accounts of Chemical Research*. 2016;**49**(4): 678-686

[96] Mafune F, Kohno J, Takeda Y, Kondow T, Sawabe H. Formation and size control of silver nanoparticles by laser ablation in aqueous solution. *The Journal of Physical Chemistry. B*. 2000;**104**(39):9111-9117

[97] Mafune F, Kohno J, Takeda Y, Kondow T, Sawabe H. Formation of gold nanoparticles by laser ablation in aqueous solution of surfactant.

The Journal of Physical Chemistry. B. 2001;**105**(22):5114-5120

[98] Fan GH, Ren ST, Qu SL, Wang Q, Gao RX, Han M. Stability and nonlinear optical properties of Cu nanoparticles prepared by femtosecond laser ablation of Cu target in alcohol and water. Optics Communication. 2014;**330**:122-130

[99] Magnusson MH, Deppert K, Malm JO, Bovin JO, Samuelson L. Gold nanoparticles: Production, reshaping, and thermal charging. Journal of Nanoparticle Research. 1999;**1**(2): 243-251

[100] Kruis FE, Fissan H, Rellinghaus B. Sintering and evaporation characteristics of gas-phase synthesis of size-selected PbS nanoparticles. Materials Science & Engineering, B: Solid-State Materials for Advanced Technology. 2000;**69**: 329-334

[101] Rahman MM, Hattori N, Nakagawa Y, Lin X, Yagai S, Sakai M, et al. Preparation and characterization of silver nanoparticles on localized surface plasmon-enhanced optical absorption. Japanese Journal of Applied Physics. 2014;**53**(11):11S

[102] Kim HR, Sahu BB, Xiang PJ, Han JG. Direct synthesis of magnetron sputtered nanostructured Cu films with desired properties via plasma chemistry for their efficient antibacterial application. Plasma Processes and Polymers. 2018;**15**(9):1800009

[103] Hirsch UM, Teuscher N, Ruhl M, Heilmann A. Plasma-enhanced magnetron sputtering of silver nanoparticles on reverse osmosis membranes for improved antifouling properties. Surfaces and Interfaces. 2019;**16**:1-7

[104] Yin GL, Bai SH, Tu XL, Li Z, Zhang YP, Wang WM, et al. Highly sensitive and stable SERS substrate fabricated by co-sputtering and atomic

layer deposition. Nanoscale Research Letters. 2019;**18**:14

[105] Siegel J, Kvitek O, Ulbrich P, Kolska Z, Slepicka P, Svorcik V. Progressive approach for metal nanoparticle synthesis. Materials Letters. 2012;**89**:47-50

[106] Wender H, Migowski P, Feil AF, Teixeira SR, Dupont J. Sputtering deposition of nanoparticles onto liquid substrates: Recent advances and future trends. Coordination Chemistry Reviews. 2013;**257**(17-18):2468-2483

[107] Nguyen MT, Yonezawa T. Sputtering onto a liquid: Interesting physical preparation method for multi-metallic nanoparticles. Science and Technology of Advanced Materials. 2018;**19**(1):883-898

[108] Varadan VK. Nanoscience and Nanotechnology in Engineering. Singapore; Hackensack, NJ: World Scientific; 2010

[109] Lamer VK, Dinegar RH. Theory, production and mechanism of formation of monodispersed hydrosols. Journal of the American Chemical Society. 1950;**72**(11):4847-4854

[110] Mandal M, Ghosh SK, Kundu S, Esumi K, Pal T. UV photoactivation for size and shape controlled synthesis and coalescence of gold nanoparticles in micelles. Langmuir. 2002;**18**(21):7792-7797

[111] Murshid N, Smith DS, Kitaev V. Photochemical formation of tunable gold nanostructures using versatile water-soluble thiolate Au(I) precursor. Particle & Particle Systems Characterization. 2018;**35**(11):1800285

[112] Bartlett TR, Sokolov SV, Compton RG. Nanoparticle photochemistry via nano-impacts. Russian Journal of Electrochemistry. 2016;**52**(12):1131-1136

- [113] Stampelcoskie KG, Scaiano JC. Silver as an example of the applications of photochemistry to the synthesis and uses of nanomaterials. *Photochemistry and Photobiology*. 2012;**88**(4):762-768
- [114] Abedini A, Daud AR, Hamid MAA, Othman NK, Saion E. A review on radiation-induced nucleation and growth of colloidal metallic nanoparticles. *Nanoscale Research Letters*. 2013;**13**:8
- [115] Abedini A, Bakar AAA, Larki F, Menon PS, Islam MS, Shaari S. Recent advances in shape-controlled synthesis of noble metal nanoparticles by radiolysis route. *Nanoscale Research Letters*. 2016;**11**:1-13
- [116] El-Batal AI, Mosallam FM, El-Sayyad GS. Synthesis of metallic silver nanoparticles by fluconazole drug and gamma rays to inhibit the growth of multidrug-resistant microbes. *Journal of Cluster Science*. 2018;**29**(6):1003-1015
- [117] Wang M, Park C, Woehl TJ. Quantifying the nucleation and growth kinetics of electron beam nanochemistry with liquid cell scanning transmission electron microscopy. *Chemistry of Materials*. 2018;**30**(21):7727-7736
- [118] ThiteAG, KrishnanandK, SharmaDK, Mukhopadhyay AK. Multifunctional finishing of cotton fabric by electron beam radiation synthesized silver nanoparticles. *Radiation Physics and Chemistry*. 2018;**153**:173-179
- [119] Vais RD, Sattarahmady N, Heli H. Green electrodeposition of gold nanostructures by diverse size, shape, and electrochemical activity. *Gold Bulletin*. 2016;**49**(3-4):95-102
- [120] Yang SM, Paranthaman MP, Noh TW, Kalinin SV, Strelcov E. Nanoparticle shape evolution and proximity effects during tip-induced electrochemical processes. *ACS Nano*. 2016;**10**(1):663-671
- [121] Brasiliense V, Clausmeyer J, Dauphin AL, Noel JM, Berto P, Tessier G, et al. Opto-electrochemical in situ monitoring of the cathodic formation of single cobalt nanoparticles. *Angewandte Chemie, International Edition*. 2017;**56**(35):10598-10601
- [122] Mandke MV, Pathan HM. Electrochemical growth of copper nanoparticles: Structural and optical properties. *Journal of Electroanalytical Chemistry*. 2012;**686**:19-24
- [123] Nishimura T, Nakade T, Morikawa T, Inoue H. Effect of current density on electrochemical shape control of Pt nanoparticles. *Electrochimica Acta*. 2014;**129**:152-159
- [124] Zayer MQ, Alwan AM, Ahmed AS, Dheyab AB. Accurate controlled deposition of silver nanoparticles on porous silicon by drifted ions in electrolytic solution. *Current Applied Physics*. 2019;**19**(9):1024-1030
- [125] Bian JC, Li Z, Chen ZD, He HY, Zhang XW, Li X, et al. Electrodeposition of silver nanoparticle arrays on ITO coated glass and their application as reproducible surface-enhanced Raman scattering substrate. *Applied Surface Science*. 2011;**258**(5):1831-1835
- [126] Grez P, Rojas C, Segura I, Heyser C, Ballesteros L, Celedon C, et al. Photoelectrochemical properties of nanostructured copper oxides formed sonoelectrochemically. *International Journal of Electrochemical Science*. 2017;**12**(8):7240-7248
- [127] Yanilkin VV, Nastapova NV, NasretdinovaGR, FedorenkoSV, JilkinME, Mustafina AR, et al. Methylviologen mediated electrosynthesis of gold nanoparticles in the solution bulk. *RSC Advances*. 2016;**6**(3):1851-1859

- [128] Nasretdinova GR, Osin YN, Gubaidullin AT, Yanilkin VV. Methylviologen mediated electrosynthesis of palladium nanoparticles stabilized with CTAC. *Journal of the Electrochemical Society*. 2016;**163**(8):G99-G106
- [129] Kokorekin VA, Gamayunova AV, Yanilkin VV, Petrosyan VA. Mediated electrochemical synthesis of copper nanoparticles in solution. *Russian Chemical Bulletin*. 2017;**66**(11):2035-2043
- [130] Yanilkin VV, Nastapova NV, Nasretdinova GR, Osin YN, Evtjugin VG, Ziganshina AY, et al. Structure and catalytic activity of ultrasmall Rh, Pd and (Rh plus Pd) nanoparticles obtained by mediated electrosynthesis. *New Journal of Chemistry*. 2019;**43**(9):3931-3945
- [131] Abou El-Nour KMM, Eftaiha A, Al-Warthan A, Ammar RAA. Synthesis and applications of silver nanoparticles. *Arabian Journal of Chemistry*. 2010;**3**(3):135-140
- [132] Guo SJ, Wang EK. Noble metal nanomaterials: Controllable synthesis and application in fuel cells and analytical sensors. *Nano Today*. 2011;**6**(3):240-264
- [133] Khan M, Shaik MR, Adil SF, Khan ST, Al-Warthan A, Siddiqui MRH, et al. Plant extracts as green reductants for the synthesis of silver nanoparticles: Lessons from chemical synthesis. *Dalton Transactions*. 2018;**47**(35):11988-12010
- [134] Zhang Z, Shen WF, Xue J, Liu YM, Liu YW, Yan PP, et al. Recent advances in synthetic methods and applications of silver nanostructures. *Nanoscale Research Letters*. 2018;**18**:13
- [135] Fievet F, Ammar-Merah S, Brayner R, Chau F, Giraud M, Mammeri F, et al. The polyol process: A unique method for easy access to metal nanoparticles with tailored sizes, shapes and compositions. *Chemical Society Reviews*. 2018;**47**(14):5187-5233
- [136] Atkins PW, De Paula J. *Elements of Physical Chemistry*. 6th ed. Oxford: Oxford University Press; 2013
- [137] Masitas RA, Zamborini FP. Oxidation of highly unstable < 4 nm diameter gold nanoparticles 850 mV negative of the bulk oxidation potential. *Journal of the American Chemical Society*. 2012;**134**(11):5014-5017
- [138] Troupis A, Triantis T, Hiskia A, Papaconstantinou E. Rate-redox-controlled size-selective synthesis of silver nanoparticles using polyoxometalates. *European Journal of Inorganic Chemistry*. 2008;**36**:5579-5586
- [139] Haynes WM, Lide DR, Bruno TJ. *CRC Handbook of Chemistry and Physics : A Ready-Reference Book of Chemical and Physical Data*. 96th ed. Boca Raton, FL; London: CRC Press; 2015
- [140] Do D. *Electrochemical Data : A Handbook for Electrochemists in Industry and Universities*. Amsterdam; New York: Elsevier Scientific Pub. Co.; 1975
- [141] Quester K, Avalos-Borja M, Castro-Longoria E. Biosynthesis and microscopic study of metallic nanoparticles. *Micron*. 2013;**54-55**:1-27
- [142] Adil SF, Assal ME, Khan M, Al-Warthan A, Siddiqui MRH, Liz-Marzan LM. Biogenic synthesis of metallic nanoparticles and prospects toward green chemistry. *Dalton Transactions*. 2015;**44**(21):9709-9717
- [143] Beyene HD, Werkneh AA, Bezabh HK, Ambaye TG. Synthesis paradigm and applications of silver nanoparticles (AgNPs), a review. *Sustainable Materials and Technologies*. 2017;**13**:18-23

- [144] Khandel P, Yadaw RK, Soni DK, Kanwar L, Shahi SK. Biogenesis of metal nanoparticles and their pharmacological applications: Present status and application prospects. *Journal of Nanostructure in Chemistry*. 2018;**8**(3):217-254
- [145] Ali J, Ali N, Wang L, Waseem H, Pan G. Revisiting the mechanistic pathways for bacterial mediated synthesis of noble metal nanoparticles. *Journal of Microbiological Methods*. 2019;**159**:18-25
- [146] Gunarani GI, Raman AB, Kumar JD, Natarajan S, Jegadeesan GB. Biogenic synthesis of Fe and NiFe nanoparticles using *Terminalia bellirica* extracts for water treatment applications. *Materials Letters*. 2019;**247**:90-94
- [147] Ravikumar KVG, Sudakaran SV, Ravichandran K, Pulimi M, Natarajan C, Mukherjee A. Green synthesis of NiFe nano particles using *Punica granatum* peel extract for tetracycline removal. *Journal of Cleaner Production*. 2019;**210**:767-776
- [148] Costentin C, Louault C, Robert M, Saveant JM. The electrochemical approach to concerted proton-electron transfers in the oxidation of phenols in water. *Proceedings of the National Academy of Sciences of the United States of America*. 2009;**106**(43):18143-18148
- [149] Polak J. Structure/redox potential relationship of simple organic compounds as potential precursors of dyes for laccase-mediated transformation. *Biotechnology Progress*. 2012;**28**(1):93-102
- [150] Rodrigues TS, Zhao M, Yang TH, Gilroy KD, da Silva AGM, Camargo PHC, et al. Synthesis of colloidal metal nanocrystals: A comprehensive review on the reductants. *Chemistry—A European Journal*. 2018;**24**(64):16944-16963
- [151] Holade Y, Engel AB, Servat K, Napporn TW, Morais C, Tingry S, et al. Electrocatalytic and electroanalytic investigation of carbohydrates oxidation on gold-based nanocatalysts in alkaline and neutral pHs. *Journal of the Electrochemical Society*. 2018;**165**(9):H425-H436
- [152] Roto R, Rasydta HP, Suratman A, Aprilita NH. Effect of reducing agents on physical and chemical properties of silver nanoparticles. *Indonesian Journal of Chemistry*. 2018;**18**(4):614-620
- [153] Creighton JA, Blatchford CG, Albrecht MG. Plasma resonance enhancement of Raman-scattering by pyridine adsorbed on silver or gold sol particles of size comparable to the excitation wavelength. *Journal of the Chemical Society-Faraday Transactions*. 1979;**75**:790-798
- [154] Philip D. Synthesis and spectroscopic characterization of gold nanoparticles. *Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy*. 2008;**71**(1):80-85
- [155] Jiang XC, Chen CY, Chen WM, Yu AB. Role of citric acid in the formation of silver nanoplates through a synergistic reduction approach. *Langmuir*. 2010;**26**(6):4400-4408
- [156] Pinto VV, Ferreira MJ, Silva R, Santos HA, Silva F, Pereira CM. Long time effect on the stability of silver nanoparticles in aqueous medium: Effect of the synthesis and storage conditions. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*. 2010;**364**(1-3):19-25
- [157] Lee PC, Meisel D. Adsorption and surface-enhanced Raman of dyes on silver and gold sols. *The Journal of Physical Chemistry*. 1982;**86**(17):3391-3395
- [158] Larmour IA, Faulds K, Graham D. SERS activity and stability of the

most frequently used silver colloids. *Journal of Raman Spectroscopy*. 2012;**43**(2):202-206

[159] Mikac L, Ivanda M, Gotic M, Mihelj T, Horvat L. Synthesis and characterization of silver colloidal nanoparticles with different coatings for SERS application. *Journal of Nanoparticle Research*. 2014;**16**(12):2748-1

[160] Turkevich J, Stevenson PC, Hillier J. A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discussions of the Faraday Society*. 1951;**11**:55

[161] Turkevich J, Stevenson PC, Hillier J. The formation of colloidal gold. *The Journal of Physical Chemistry*. 1953;**57**(7):670-673

[162] Enustun BV, Turkevich J. Coagulation of colloidal gold. *Journal of the American Chemical Society*. 1963;**85**(21):3317-3328

[163] Kvitek L, Prucek R, Panacek A, Novotny R, Hrbac J, Zboril R. The influence of complexing agent concentration on particle size in the process of SERS active silver colloid synthesis. *Journal of Materials Chemistry*. 2005;**15**(10):1099-1105

[164] Michalcova A, Machado L, Marek I, Martinec M, Slukova M, Vojtech D. Properties of Ag nanoparticles prepared by modified Tollens' process with the use of different saccharide types. *Journal of Physics and Chemistry of Solids*. 2018;**113**:125-133

[165] Afshinnia K, Marrone B, Baalousha M. Potential impact of natural organic ligands on the colloidal stability of silver nanoparticles. *The Science of the Total Environment*. 2018;**625**:1518-1526

[166] Bhattarai B, Zaker Y, Bigioni TP. Green synthesis of gold and silver

nanoparticles: Challenges and opportunities. *Current Opinion in Green and Sustainable Chemistry*. 2018;**12**:91-100

[167] Amin ZR, Khashyarmansh Z, Bazzaz BSF, Noghabi ZS. Does biosynthetic silver nanoparticles are more stable with lower toxicity than their synthetic counterparts? *Iranian Journal of Pharmaceutical Research*. 2019;**18**(1):210-221

[168] Han J, Li LY, Guo R. Novel approach to controllable synthesis of gold nanoparticles supported on polyaniline nanofibers. *Macromolecules*. 2010;**43**(24):10636-10644

[169] Signori AM, Santos KD, Eising R, Albuquerque BL, Giacomelli FC, Domingos JB. Formation of catalytic silver nanoparticles supported on branched polyethyleneimine derivatives. *Langmuir*. 2010;**26**(22):17772-17779

[170] Han J, Wang MG, Hu YM, Zhou CQ, Guo R. Conducting polymer-noble metal nanoparticle hybrids: Synthesis mechanism application. *Progress in Polymer Science*. 2017;**70**:52-91

[171] Gregor L, Reilly AK, Dickstein TA, Mazhar S, Bram S, Morgan DG, et al. Facile synthesis of magnetically recoverable Pd and Ru catalysts for 4-nitrophenol reduction: Identifying key factors. *Acs Omega*. 2018;**3**(11):14717-14725

[172] Bouche M, Fournel S, Kichler A, Selvam T, Gallani JL, Bellemin-Laponnaz S. Straightforward synthesis of L-PEI-coated gold nanoparticles and their biological evaluation. *European Journal of Inorganic Chemistry*. 2018;**6**(25):2972-2975

[173] Batista CCS, Albuquerque LJC, de Araujo I, Albuquerque BL, da Silva FD, Giacomelli FC. Antimicrobial activity of nano-sized silver colloids stabilized by nitrogen-containing polymers: The key

influence of the polymer capping. RSC Advances. 2018;**8**(20):10873-10882

[174] Sarkar R, Kumar CA, Kumbhakar P, Mandal T. Aqueous synthesis and antibacterial activity of silver nanoparticles against pseudomonas putida. Materials Today-Proceedings. 2019;**11**:686-694

[175] Kotrlý S, Šůcha L. Handbook of Chemical Equilibria in Analytical Chemistry. Chichester; New York: Horwood; Halsted Press; 1985

[176] Yin YD, Li ZY, Zhong ZY, Gates B, Xia YN, Venkateswaran S. Synthesis and characterization of stable aqueous dispersions of silver nanoparticles through the Tollens process. Journal of Materials Chemistry. 2002;**12**(3):522-527

[177] Hussain JI, Talib A, Kumar S, Al-Thabaiti SA, Hashmi AA, Khan Z. Time dependence of nucleation and growth of silver nanoparticles. Colloids and Surfaces A-Physicochemical and Engineering Aspects. 2011;**381**(1-3):23-30

[178] Dondi R, Su W, Griffith GA, Clark G, Burley GA. Highly size- and shape-controlled synthesis of silver nanoparticles via a templated tollens reaction. Small. 2012;**8**(5):770-776

[179] Panneerselvam R, Xiao L, Waites KB, Atkinson TP, Dluhy RA. A rapid and simple chemical method for the preparation of Ag colloids for surface-enhanced Raman spectroscopy using the Ag mirror reaction. Vibrational Spectroscopy. 2018;**98**:1-7

[180] Pruček R, Panacek A, Soukupova J, Novotny R, Kvitek L. Reproducible synthesis of silver colloidal particles tailored for application in near-infrared surface-enhanced Raman spectroscopy. Journal of Materials Chemistry. 2011;**21**(17):6416-6420

[181] Evanoff DD, Chumanov G. Size-controlled synthesis of nanoparticles.

1. "silver-only" aqueous suspensions via hydrogen reduction. The Journal of Physical Chemistry. B. 2004;**108**(37):13948-13956

[182] Wiberg E, Wiberg N, Holleman AF. Inorganic Chemistry. 1st ed. San Diego; Berlin; New York: Academic Press; De Gruyter; 2001

[183] Leopold N, Lendl B. A new method for fast preparation of highly surface-enhanced Raman scattering (SERS) active silver colloids at room temperature by reduction of silver nitrate with hydroxylamine hydrochloride. The Journal of Physical Chemistry. B. 2003;**107**(24):5723-5727

[184] Nickel U, Mansyreff K, Schneider S. Production of monodisperse silver colloids by reduction with hydrazine: The effect of chloride and aggregation on SER(R) S signal intensity. Journal of Raman Spectroscopy. 2004;**35**(2):101-110

[185] Pal A, Shah S, Devi S. Synthesis of Au, Ag and Au-Ag alloy nanoparticles in aqueous polymer solution. Colloids and Surfaces A-Physicochemical and Engineering Aspects. 2007;**302**(1-3):51-57

[186] Puranik SS, Joshi HM, Ogale SB, Paknikar KM. Hydrazine based facile synthesis and ordered assembly of metal nanoparticles (Au, Ag) on a bacterial surface layer protein template. Journal of Nanoscience and Nanotechnology. 2008;**8**(7):3565-3569

[187] Minati L, Benetti F, Chiappini A, Speranza G. One-step synthesis of star-shaped gold nanoparticles. Colloids and Surfaces A-Physicochemical and Engineering Aspects. 2014;**441**:623-628

[188] Todor IS, Szabo L, Marisca OT, Chis V, Leopold N. Gold nanoparticle assemblies of controllable size obtained by hydroxylamine reduction at room

temperature. *Journal of Nanoparticle Research*. 2014;**16**(12):2740

and Engineering Aspects. 2010;
372(1-3):172-176

[189] Cheng ZP, Chu XZ, Wu XQ, Xu JM, Zhong H, Yin JZ. Controlled synthesis of silver nanoplates and nanoparticles by reducing silver nitrate with hydroxylamine hydrochloride. *Rare Metals*. 2017;**36**(10):799-805

[197] Chen B, Jiao XL, Chen DR. Size-controlled and size-designed synthesis of nano/submicrometer Ag particles. *Crystal Growth & Design*. 2010;**10**(8):3378-3386

[190] Sucha L, Kotrly S. *Solution Equilibria in Analytical Chemistry*. London, New York: Van Nostrand Reinhold Co.; 1972

[198] Kozlova ES, Nikiforova TE. Incorporation of silver nanoparticles into a cellulose matrix for preparing package materials for foodstuffs. *Russian Journal of Applied Chemistry*. 2015;**88**(4):638-646

[191] Uchimiya M, Stone AT. Reversible redox chemistry of quinones: Impact on biogeochemical cycles. *Chemosphere*. 2009;**77**(4):451-458

[199] Tang JQ, Fu XW, Ou QH, Gao KP, Man SQ, Guo J, et al. Hydroxide assisted synthesis of monodisperse and biocompatible gold nanoparticles with dextran. *Materials Science & Engineering, C: Materials for Biological Applications*. 2018;**93**:759-767

[192] Huynh MT, Anson CW, Cavell AC, Stahl SS, Hammes-Schiffer S. Quinone 1 e(−) and 2 e(−)/2 H⁺ reduction potentials: Identification and analysis of deviations from systematic scaling relationships. *Journal of the American Chemical Society*. 2016;**138**(49):15903-15910

[200] Aguilar NM, Arteaga-Cardona F, Estevez JO, Silva-Gonzalez NR, Benitez-Serrano JC, Salazar-Kuri U. Controlled biosynthesis of silver nanoparticles using sugar industry waste, and its antimicrobial activity. *Journal of Environmental Chemical Engineering*. 2018;**6**(5):6275-6281

[193] Martinez-Cifuentes M, Salazar R, Ramirez-Rodriguez O, Weiss-Lopez B, Araya-Maturana R. Experimental and theoretical reduction potentials of some biologically active ortho-carbonyl Para-quinones. *Molecules*. 2017;**22**(4):E557

[201] Si S, Bhattacharjee RR, Banerjee A, Mandal TK. A mechanistic and kinetic study of the formation of metal nanoparticles by using synthetic tyrosine-based oligopeptides. *Chemistry—A European Journal*. 2006;**12**(4):1256-1265

[194] Jacob JA, Mahal HS, Biswas N, Mukherjee T, Kapoor S. Role of phenol derivatives in the formation of silver nanoparticles. *Langmuir*. 2008;**24**(2):528-533

[202] Palui G, Ray S, Banerjee A. Synthesis of multiple shaped gold nanoparticles using wet chemical method by different dendritic peptides at room temperature. *Journal of Materials Chemistry*. 2009;**19**(21):3457-3468

[195] Xie T, Jing C, Li M, Ma W, Ding ZF, Long YT. pH-response mechanism of a redox reaction between silver ions and hydroquinone. *Journal of Physical Chemistry C*. 2016;**120**(40):23104-23110

[196] Qin YQ, Ji XH, Jing J, Liu H, Wu HL, Yang WS. Size control over spherical silver nanoparticles by ascorbic acid reduction. *Colloids and Surfaces A-Physicochemical*

[203] Lah NAC, Johan MR. Facile shape control synthesis and optical properties of silver nanoparticles stabilized by Daxad 19 surfactant. *Applied Surface Science*. 2011;**257**(17):7494-7500

- [204] Zhang AQ, Cai LJ, Sui L, Qian DJ, Chen M. Reducing properties of polymers in the synthesis of noble metal nanoparticles. *Polymer Reviews*. 2013;**53**(2):240-276
- [205] Li YF, Gan WP, Zhou J, Lu ZQ, Yang C, Ge TT. Hydrothermal synthesis of silver nanoparticles in Arabic gum aqueous solutions. *Transactions of Nonferrous Metals Society of China*. 2015;**25**(6):2081-2086
- [206] Biao LH, Tan SN, Wang YL, Guo XM, Fu YJ, Xu FJ, et al. Synthesis, characterization and antibacterial study on the chitosan-functionalized Ag nanoparticles. *Materials Science & Engineering, C: Materials for Biological Applications*. 2017;**76**:73-80
- [207] Kora AJ, Sashidhar RB. Biogenic silver nanoparticles synthesized with rhamnogalacturonan gum: Antibacterial activity, cytotoxicity and its mode of action. *Arabian Journal of Chemistry*. 2018;**11**(3):313-323
- [208] Zhang XW, Sun HY, Tan SN, Gao J, Fu YJ, Liu ZG. Hydrothermal synthesis of Ag nanoparticles on the nanocellulose and their antibacterial study. *Inorganic Chemistry Communications*. 2019;**100**:44-50
- [209] Shou QH, Guo C, Yang LR, Jia LW, Liu CZ, Liu HZ. Effect of pH on the single-step synthesis of gold nanoparticles using PEO-PPO-PEO triblock copolymers in aqueous media. *Journal of Colloid and Interface Science*. 2011;**363**(2):481-489
- [210] Merga G, Wilson R, Lynn G, Milosavljevic BH, Meisel D. Redox catalysis on “naked” silver nanoparticles. *Journal of Physical Chemistry C*. 2007;**111**(33):12220-12226
- [211] Pucek R, Ranc V, Balzerova O, Panacek A, Zboril R, Kvitek L. Preparation of silver particles and its application for surface enhanced Raman scattering with near-infrared excitation. *Materials Research Bulletin*. 2014;**50**:63-67
- [212] Agunloye E, Panariello L, Gavriilidis A, Mazzei L. A model for the formation of gold nanoparticles in the citrate synthesis method. *Chemical Engineering Science*. 2018;**191**:318-331
- [213] Kettemann F, Birnbaum A, Witte S, Wuithschick M, Pinna N, Kraehnert R, et al. Missing piece of the mechanism of the Turkevich method: The critical role of citrate protonation. *Chemistry of Materials*. 2016;**28**(11):4072-4081
- [214] Peckham GD, McNaught IJ. The variation of electrochemical cell potentials with temperature. *Journal of Chemical Education*. 2011;**88**(6):782-783
- [215] Vekilov PG. The two-step mechanism of nucleation of crystals in solution. *Nanoscale*. 2010;**2**(11):2346-2357
- [216] You HJ, Fang JX. Particle-mediated nucleation and growth of solution-synthesized metal nanocrystals: A new story beyond the LaMer curve. *Nano Today*. 2016;**11**(2):145-167
- [217] Zhou Y, Wang HX, Lin WS, Lin LQ, Gao YX, Yang F, et al. Quantitative nucleation and growth kinetics of gold nanoparticles via model-assisted dynamic spectroscopic approach. *Journal of Colloid and Interface Science*. 2013;**407**:8-16
- [218] Si S, Dinda E, Mandal TK. In situ synthesis of shape-selective gold nanocrystals using oligopeptide template: Effect of various reaction parameters. *Journal of Nanoscience and Nanotechnology*. 2008;**8**(11):5934-5941
- [219] Nishimoto M, Abe S, Yonezawa T. Preparation of Ag nanoparticles using hydrogen peroxide as a reducing agent. *New Journal of Chemistry*. 2018;**42**(17):14493-14501

- [220] Kvitek L, Bartova A, Prucek R, Panacek A, Soukupova J, Zboril R, editors. *Low Temperature Synthesis of Silver Nanoparticles 10th Anniversary International Conference on Nanomaterials–Research and Application, NANOCON 2018*; 2018; Brno, Czech Republic. Ostrava, Czech Republic: Tanger Ltd.; 2018
- [221] Agunloye E, Gavriilidis A, Mazzei L. A mathematical investigation of the Turkevich organizer theory in the citrate method for the synthesis of gold nanoparticles. *Chemical Engineering Science*. 2017;**173**:275-286
- [222] Shi L, Buhler E, Boue F, Carn F. How does the size of gold nanoparticles depend on citrate to gold ratio in Turkevich synthesis? Final answer to a debated question. *Journal of Colloid and Interface Science*. 2017;**492**:191-198
- [223] Sardar R, Funston AM, Mulvaney P, Murray RW. Gold nanoparticles: Past, present, and future. *Langmuir*. 2009;**25**(24):13840-13851
- [224] Mourdikoudis S, Liz-Marzan LM. Oleylamine in nanoparticle synthesis. *Chemistry of Materials*. 2013;**25**(9):1465-1476
- [225] Ling DS. Surface ligands in synthesis, modification and assembly of nanoparticles for biomedical applications. *Nanomedicine: Nanotechnology, Biology and Medicine*. 2016;**12**(2):461-461
- [226] Larm NE, Essner JB, Pokpas K, Canon JA, Jahed N, Iwuoha EI, et al. Room-temperature Turkevich method: Formation of gold nanoparticles at the speed of mixing using cyclic oxocarbon reducing agents. *Journal of Physical Chemistry C*. 2018;**122**(9):5105-5118
- [227] Soukupova J, Kvitek L, Panacek A, Nevecna T, Zboril R. Comprehensive study on surfactant role on silver nanoparticles (NPs) prepared via modified Tollens process. *Materials Chemistry and Physics*. 2008;**111**(1):77-81
- [228] Heinz H, Pramanik C, Heinz O, Ding YF, Mishra RK, Marchon D, et al. Nanoparticle decoration with surfactants: Molecular intercalations, assembly, and applications. *Surface Science Reports*. 2017;**72**(1):1-58
- [229] Kang H, Buchman JT, Rodriguez RS, Ring HL, He JY, Bantz KC, et al. Stabilization of silver and gold nanoparticles: Preservation and improvement of plasmonic functionalities. *Chemical Reviews*. 2019;**119**(1):664-699
- [230] Zhang T, Song YJ, Zhang XY, Wu JY. Synthesis of silver nanostructures by multistep methods. *Sensors*. 2014;**14**(4):5860-5889
- [231] Chen MJ, He YR, Liu X, Zhu JQ, Liu R. Synthesis and optical properties of size-controlled gold nanoparticles. *Powder Technology*. 2017;**311**:25-33
- [232] Bastus NG, Comenge J, Puntès V. Kinetically controlled seeded growth synthesis of citrate-stabilized gold nanoparticles of up to 200 nm: Size focusing versus Ostwald ripening. *Langmuir*. 2011;**27**(17):11098-11105
- [233] Wu KJ, Torrente-Murciano L. Continuous synthesis of tuneable sized silver nanoparticles via a tandem seed-mediated method in coiled flow inverter reactors. *Reaction Chemistry & Engineering*. 2018;**3**(3):267-276