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Chapter

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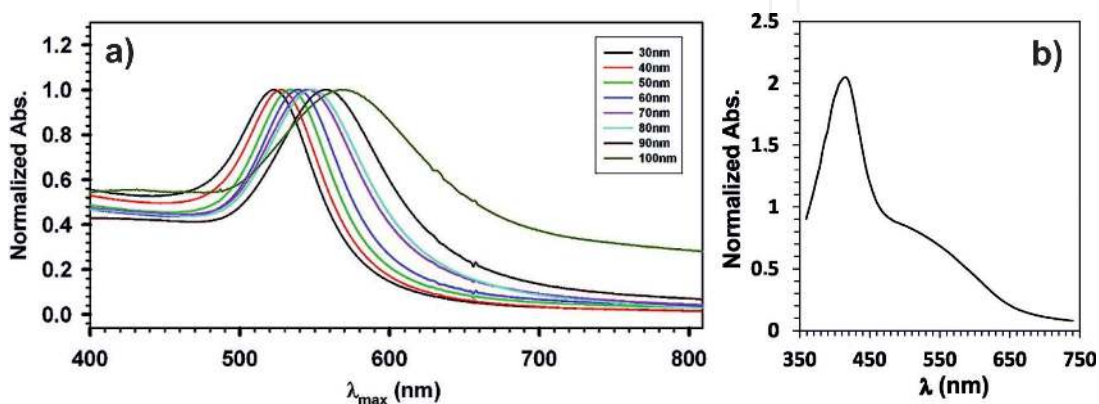
Figure 1.
(a) Dependence of the absorbance of the localized surface plasmon resonance (LSPR) of gold nanoparticles on their size. Reproduced with permission from [33]. (b) Broadening of the LSPR absorbance peak due to the aggregation of 30 nm-sized silver nanoparticles.

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 nonreduced 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):

$$\Delta G = -zF \, \Delta E \tag{1}$$

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):

$$\Delta E = E_R - E_L = E_{Mez+/Me} - E_{ox/red} \tag{2}$$

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

$$E_{ox/red} = E^o_{ox/red} + (RT/zF) \ln (a_{ox}/a_{red}) \tag{3}$$

where $E^o_{ox/red}$ 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 $E^o_{Mez+/Me}$ 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^o instead of ΔE. It is relatively a rational consideration because if the ΔE^o 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^o [V]	Redox system	Half-reaction	E^o [V]
Iron	$Fe^{2+} + 2e^- \rightleftharpoons Fe^o$	−0.447	Ruthenium	$Ru^{2+} + 2e^- \rightleftharpoons Ru^o$	+0.455
Cobalt	$Co^{2+} + 2e^- \rightleftharpoons Co^o$	−0.28	Rhodium	$Rh^{3+} + 3e^- \rightleftharpoons Rh^o$	+0.758
Nickel	$Ni^{2+} + 2e^- \rightleftharpoons Ni^o$	−0.257	Palladium	$Pd^{2+} + 2e^- \rightleftharpoons Pd^o$	+0.951
Copper	$Cu^{2+} + 2e^- \rightleftharpoons Cu^o$	+0.3419	Osmium	$Os^{2+} + 2e^- \rightleftharpoons Os^o$ Ref. [140]	+0.7
Silver	$Ag^+ + e^- \rightleftharpoons Ag^o$	+0.7996	Iridium	$Ir^{3+} + 3e^- \rightleftharpoons Ir^o$	+1.156
Gold	$Au^{3+} + 3e^- \rightleftharpoons Au^o$	+1.498	Platinum	$Pt^{2+} + 2e^- \rightleftharpoons Pt^o$	+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^o [V]	Cit.
Hypophosphorous acid	$HPO_3^{2-} + 2H_2O + 2e^- \rightleftharpoons H_2PO_2^- + 3OH^-$	−1.65	[139]
Borohydride	$H_2BO_3^- + 5H_2O + 8e^- \rightleftharpoons BH_4^- + 8OH^-$	−1.24	[139]
Hydrazine	$N_2 + 4H_2O + 4e^- \rightleftharpoons N_2H_4 + 4OH^-$	−1.15	[140]
Hydroxylamine	$N_2O_2^- + 6H_2O + 4e^- \rightleftharpoons 2NH_2OH + 6OH^-$	−0.73	[140]
Formic acid	$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH$	−0.14	[140]
Hydrogen peroxide	$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	−0.076	[140]
Ascorbic acid	$C_6H_6O_6 + 2H^+ + 2e^- \rightleftharpoons C_6H_8O_6$	−0.054 (pH = 7)	[140]
Formaldehyde	$HCOOH + 2H^+ + 2e^- \rightleftharpoons HCHO + H_2O$	−0.02	[140]
Hydrogen	$2H^+ + 2e^- \rightleftharpoons H_2$	0.000	[140]
Stannum(II)	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15	[140]
p-Aminophenol	$OC_6H_4NH + 2H^+ + 2e^- \rightleftharpoons HOC_6H_4NH_2$	+0.599	[149]
Hydroquinone	$C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_4(OH)_2$	+0.699	[140]
Citric acid	$CH_3COCH_3 + 3CO_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_8O_7$	+1.1	[150]
Glucose	$C_6H_{12}O_7 + H_2O + 2e^- \rightleftharpoons C_6H_{12}O_6 + 2OH^-$	$\approx +0.65$ (pH = 12.8)	[151]
Galactose	$C_6H_{12}O_7 + H_2O + 2e^- \rightleftharpoons C_6H_{12}O_6 + 2OH^-$	$\approx +0.7$ (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
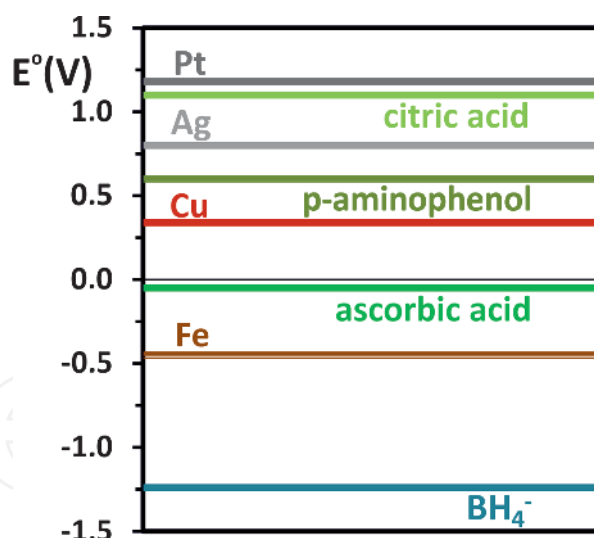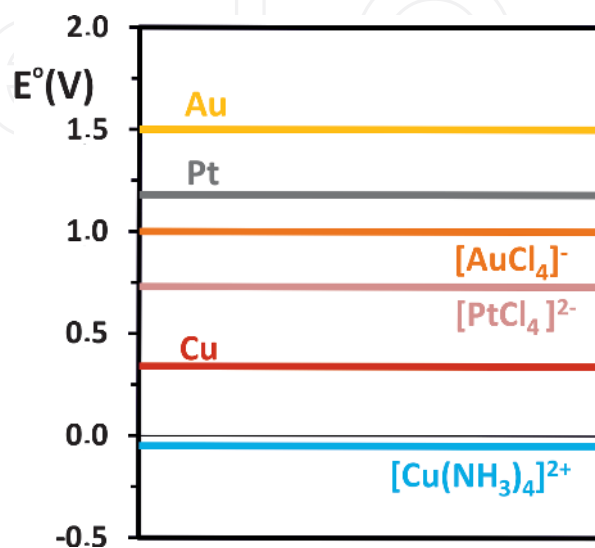
Figure 2.
*Comparison of the standard redox potentials of the metals and reductants selected from **Tables 1** and **2** as representative of the typical reaction systems for the preparation of the metal nanoparticles.*

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 $E_{red/ox}$ 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].
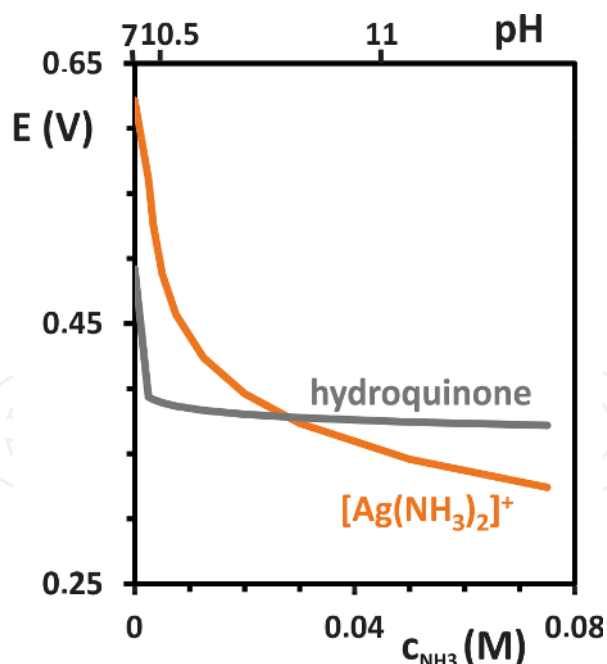
Figure 4.
Comparison of the redox potential dependence for the complex metal ion [Ag(NH₃)₂]⁺ and hydroquinone reductant on the concentration of ammonia. The change of the ammonia concentration in the reaction system is connected with the change of pH. It is clearly visible that at pH ≈ 10.8 (concentration of ammonia about 0.0275 Mol/dm³), the potentials of both redox systems are identical. Values of redox potentials were calculated using Eq. (10) for system Q/H₂Q and Eq. (4) for the system [Ag(NH₃)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):

$$E_{[Ag(NH3)2]+/Ag} = E^o_{Ag+/Ag} + (RT/F) \ln\{(a_{[Ag(NH3)2]+})(a_{NH3})^{-2}\beta_2^{-1}\} \qquad (4)$$

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:

$$E_{H+/H2} = (RT/F) \ln (a_{H30+}) = -(2303RT/F) \, pH \tag{5}$$

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]:

$$BH_4^- + 8OH^- \rightleftharpoons BO_2^- + 6H_2O + 8e^- \quad E^o = -1.24 \text{ V} \tag{6}$$
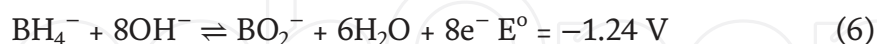
However, if the pH is shifted into a slightly acidic region, the reaction mechanism is significantly changed, and the oxidation of the borohydride anion can be simply written as follows:

$$BH_4^- + 3H_2O \rightleftharpoons B(OH)_3 + 7H^+ + 8e^- \quad E^o = -0.48 \text{ V} \tag{7}$$
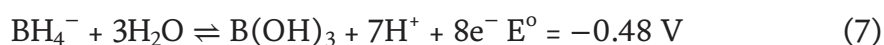
Additionally, the environment enables also a side reaction—direct hydrolysis of the borohydride anion accompanied by the hydrogen release:

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \tag{8}$$
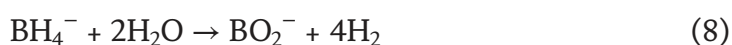
In this situation, hydrogen, generated according to Eq. (8), can become the main reducing agent. However, such a complicated reaction of the tailored nanoparticle synthesis and the reproducibility of such synthetic experiment are rather poor. The dependence of oxidation mechanism and redox potential 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 H_2Q) 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):

$$C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_4(OH)_2 \text{ resp. } Q + 2H^+ + 2e^- \rightleftharpoons H_2Q \qquad (9)$$

As H_2Q is a weak acid ($pK_1 = 9.85$ a $pK_2 = 11.4$), the concentration (resp. activity) of the Q^{2-} ion is dependent on pH, which is then reflected in the equation for potential of the Q/Q^{2-} redox system:

$$
\begin{aligned}
E &= E^o{}_{Q/Q2-} + (RT/2F) \ln (a_Q/a_{Q2-}) \\
&= E^{o'}{}_{Q/Q2-} + (RT/2F) \ln ([H^+]^2 + K_1[H^+] + K_1K_2)
\end{aligned}
\qquad (10)
$$

where $E^{o'}{}_{Q/Q2-}$ is a formal redox potential of the Q/Q^{2-} redox system and K_1 and K_2 are partial dissociation constants of H_2Q [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 H_2Q 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/Q^{2-} 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 H_2Q was used as the reducing agent for Ag^+ ions, resp. $[Ag(NH_3)_2]^+$ 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 H_2Q can be observed also with ascorbic acid (AA). As it is a stronger acid than H_2Q, 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 $AuCl_4^-$ 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 Ag_2O/Ag is significantly lower (E^o = 0.342 V) than of the system Ag^+/Ag (E^o = 0.799 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 $AuCl_3(OH)^-$ 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 $AuCl_{4-x}(OH)_x^{x-}$ 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., ±1 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

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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