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Metal nanoparticles in condensed media: preparation and the bulk and surface structural dynamics

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Contents

I.	Introduction	605
II.	Methods of preparation of metal nanoparticles in condensed media, based on the action of physical factors	605
III.	Chemical synthesis of metal nanoparticles in condensed media	611
IV.	Biosynthesis of metal nanoparticles	617
V.	Regularities of growth of metal nanoparticles in condensed media	621
VI.	The structure of the surface layer of metal nanoparticles and the dynamics of changes in it	623
VII.	Conclusion	625

Abstract. The results of studies on the chemical synthesis and biosynthesis of metal nanoparticles in condensed media published after 2000 are analyzed and described systematically. The growth and transformations of the metallic core of nanoparticles as well as the composition and structure of the surface layer are considered and their effects on the nanoparticle size and shape are analyzed. The bibliography includes 302 references.

I. Introduction

Systems called metal nanoparticles have long been knows as colloidal metals. Supported metal catalysts,[1] magnetic liquids,[2] nonfading thermally stable pigments for glass[3] represent metal nanoparticles. Owing to a vast variety of applications of metal nanoparticles, methods of preparative synthesis of such objects have been well developed. They are based on the interactions of different nature including physical, chemical, biochemical ones, *etc*. Nevertheless, the recent 10 – 15 years have been characterized by a considerable increase in the number of publications concerning the synthesis of metal nanoparticles, especially noble metal nanoparticles (Fig. 1). This is mainly due to two reasons:

— development of novel physical methods of investigation, which allow one to obtain previously unobtainable information; and

— search for new fields of application of nanoparticles in optics, biochemistry, biology and medicine.

Reviews and monographs[4 – 15] provide vast and detailed information on the methods of synthesis and on the properties of metal nanoparticles. Nevertheless, there is a great body of recently reported data that somewhat changes the classical concepts of metal nanoparticles. This review has been written in a continuation of our analysis of trends in the development of preparative methods for the synthesis of metal nanoparticles (see Ref. 11). The aim of this work is to generalize, systematize and analyze the results of research on the synthesis and properties of metal nanoparticles reported since 2000.

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II. Methods of preparation of metal nanoparticles in condensed media, based on the action of physical factors

There is a lot of methods for preparation of metal nanoparticles in condensed media, based on the action of physical factors, such as vaporization of metals, laser ablation, photolysis, radiolysis, *etc*. Some methods can

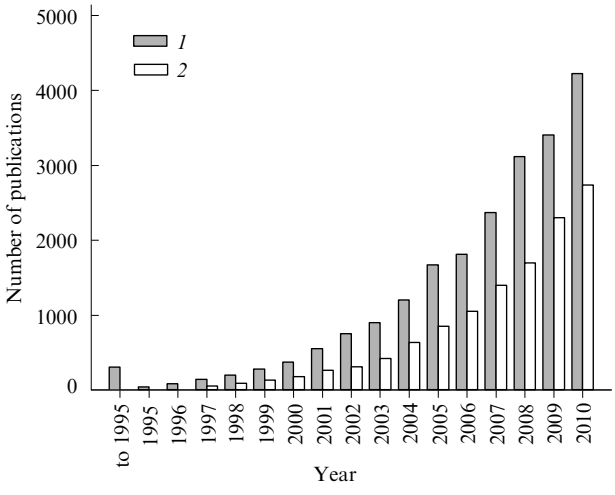


Figure 1. Number of publications from ACS Publishing (*1*) and Springer (*2*) containing the term 'metal nanoparticles'.

only conditionally be treated as physical ones because the action of a physical factor on the system under study may induce chemical reactions leading to formation of nanoparticles. For instance, photolysis, sonication or radiolysis may produce solvated electrons or free radicals that are possible initiators of subsequent transformations. Low-temperature co-condensation of vapours of the iron triad metals and aromatic compounds affords metastable bisarene organometallic compounds. Nevertheless, the growth of particles is initiated by the action of the physical factor on the initial system. Main techniques of preparation of metal nanoparticles using physical methods are listed in Table 1.

Physical methods can be ordered as follows with respect to the number of original publications describing methods of preparation of metal nanoparticles: photolysis, laser ablation, sonochemical methods, radiolysis, low-temperature vapour co-condensation and spark discharge in liquids. This distribution can be explained with ease. Indeed, photolysis is the simplest method both methodologically and from the standpoint of equipment; laser ablation is relatively simple methodologically but requires expensive laser equipment; radiolysis is impossible without highly active sources of radiation (this imposes specific limitations); cryochemical synthesis is characterized by sophisticated experimental design and should be carried out under high vacuum and high consumption of liquid nitrogen.

The reactivity of metal nanoparticles with respect to oxygen and/or water can significantly change the character of processes occurring in systems containing such species. Under normal conditions, non-noble transition metals contain an oxide layer a few nanometres thick. As the particle size decreases from the submicrometre to nanometre range, this becomes critically important because the volumes of the metallic core and the oxide surface layer appear to be comparable. As the surface-area-to-volume ratio increases, the contribution of surface processes unavoidably increases; note that the characteristic chemical reactions of the metal and its oxide are significantly different. This strongly complicates the synthetic procedures and the understanding of the nature of the interactions occurring in the formation of metal nanoparticles.

The amounts of information on the growth mechanisms of the noble and non-noble transition metal nanoparticles are incomparable (this especially concerns the early stages of growth). In studies of the growth and transformations of the metallic core, noble metals can be treated as convenient models because the processes in them should be universal in character. However, the noble metal-based models have a strong limitation because bulk noble metals show no co-

Table 1. Physical methods for preparation of metal nanoparticles in condensed media.

Reaction medium	Particle size /nm		Ref.
	range	average	
Photoreduction			
Silver nanoparticles			
Ethanol solutions of $AgNO_3$ and photopolymerizable rubber	1 – 10	4	16
Aqueous solutions of fatty acid salts	20 – 130	30 – 70	17
Aqueous solutions of silver acetate	1 – 50	3 – 40	18
Aqueous solutions containing a polyethyleneoxyl-polypropylene oxide-polyethylene oxide triblock copolymer and silica	1 – 10	–	19
Aqueous solutions of silver acetyl acetonate	10 – 60	15 – 30	20
Aqueous solution of polyvinylpyrrolidone	3 – 15	5 – 7	21
Aqueous surfactant solutions	2 – 20	4 – 7	22
Aqueous – organic emulsion containing AOT and benzoin	6 – 30	10	23
Water – ionic liquid microemulsion at elevated CO_2 pressure	1 – 9	3 – 4	24
Solutions of $AgNO_3$ and heteropolycyclic aromatic hydrocarbons	1 – 25	10	25
	1 – 12	5	25
Aqueous sodium citrate solution	–	–	26
Hydrolysis of methacryloxypropyl(trimethoxy)silane in the presence of $AgNO_3$ and AgCl	1.5 – 6	3	27
Gold nanoparticles			
Aqueous sodium citrate solution	–	3 – 40	28
Aqueous solution of polyvinylpyrrolidone	20 – 500	70	29
Aqueous and aqueous – organic solutions of surfactants and polymers	5 – 20	6 – 7	30
Copper nanoparticles			
Alcohol solution of copper acetylacetonate and polyvinylpyrrolidone	3 – 5	4	31
	10 – 35	15	
Silver and platinum nanoparticles			
Aqueous solution of sodium dodecyl sulfate	1 – 10	2 – 4	32
Platinum nanoparticles			
Aqueous solutions of cationic and anionic surfactants, polyethylene glycol	1 – 10	3 – 4	33

Table 1 (continued).

Reaction medium	Particle size /nm		Ref.
	range	average	
Rhodium nanoparticles			
Aqueous solution of polyvinylpyrrolidone	1 – 5	1.5	34
Laser ablation			
Silver nanoparticles			
Water	10 – 25	18	35
	1 – 8	4	36
	10 – 100	20 – 25	37
	50 – 1300	200 – 400	38
Aqueous NaCl solutions	10 – 50	10	39
Aqueous NaCl and NaI solutions	1 – 50 (NaI)	16	40
	1 – 25 (NaCl)	8	40
Aqueous solutions of sodium dodecyl sulfate	4 – 30	10 – 18	41
Aqueous solutions of anionic surfactants	–	–	42
Aqueous solution of polyvinylpyrrolidone	1 – 40	11 – 18	43
Ethanol, ethylene glycol	4 – 200	80	44
Primary alcohols	10 – 100	20 – 40	45
Acetonitrile, DMF, DMSO, THF	0.5 – 10	1 – 3	46
Silver – gold nanoparticles			
Water	1 – 20 (Ag)	5	47
	1 – 30 (Au)	12	
Aqueous solutions of $AgNO_3$ or $HAuCl_4$	2 – 20 (Ag)	12	48
Aqueous solutions of G-5 dendrimeric ethylenediamine/amidoamine copolymers	1 – 15 (Au)	3 – 5	49
	1 – 20 (Au)	6	
Gold nanoparticles			
Liquid alkanes	3 – 15	8	50
Platinum nanoparticles			
Aqueous solutions of sodium dodecyl sulfate	1 – 10	4	51
Silver, gold, titanium nanoparticles			
Water, ethanol, dichloroethane, acetone	20 – 200 (Ag – water)	60	52
	3 – 30 (Ag – Au – ethanol)	8	52
Sonication			
Silver nanoparticles			
Aqueous solution of $AgNO_3$ and polymethacrylic acid	1 – 10	2	53
Gold nanoparticles			
Aqueous solution of $NaAuCl_4$ and sodium citrate	20 – 200	40	54
Aqueous solution of $HAuCl_4$ and chitosan	–	22	55
Platinum – ruthenium nanoparticles			
Aqueous solutions of K_2PtCl_4, $RuCl_3$, polyvinylpyrrolidone or sodium dodecylsulfate	1 – 15	2	56
Gold – palladium nanoparticles			
Aqueous solutions of $NaAuCl_4$, $PdCl_2$, NaCl and sodium dodecylsulfate	2 – 20	12	57
Aqueous solutions of $HAuCl_4$, $PdCl_2$ and sodium dodecylsulfate	6 – 10	8	58
Gold – ruthenium nanoparticles			
Aqueous solutions of $HAuCl_4$, $RuCl_3$, polyethylene glycol	15 – 40	20	59
Silver, gold, palladium and platinum nanoparticles			
Aqueous solutions containing $AgNO_3$, $HAuCl_4$, $Pd(NO_3)_2$, H_2PtCl_6 and polysterene beads	–	6 – 10	60

Table 1 (continued).

Reaction medium	Particle size /nm		Ref.
	range	average	
Radiolysis			
Silver nanoparticles			
Aqueous solution of $AgNO_3$, *tert*-butyl or isopropyl alcohol	10 – 100	40	61
Aqueous solution of $AgClO_4$, formate and sodium polyphoshate	–		62
Solution of silver nitrate and poly(4-vinylpyridine) in ethylene glycol	2 – 20	8	63
Silver and gold nanoparticles			
Solutions of $AgNO_3$ or $HAuCl_4$ in isopropyl alcohol – cyclohexane mixture	5 – 50	15	64
Gold nanoparticles			
Aqueous solution of $HAuCl_4$ and ionic liquid	10 – 50	20	65
Nickel nanoparticles			
Aqueous solution of nickel sulfate and sodium hydrophosphate	40 – 100	50	66
Aqueous solution of $Ni(ClO_4)_2$, formate and sodium polyacrylate	–	–	67
Gold – palladium nanoparticles			
Aqueous solutions of salts and polyethylene glycol	2 – 30	10	68
Low-temperature co-condensation of vapours			
Gold and bismuth nanoparticles			
Isopropyl alcohol	5 – 15 (Au)	7 – 10	69
	3 – 10 (Bi)	5 – 6	69
Gold nanoparticles			
Acetone	5 – 15 (Au)	7	70
Gold – copper nanoparticles			
Acetone, 2-butanone, isopropyl alcohol, 2-methoxyethanol, 2-ethoxyethanol, diglyme, THF, DMF	–	2 – 4	71
Nickel – copper nanoparticles			
2-methoxyethanol, isopropyl alcohol, acetone	–	6	72
Cobalt nanoparticles			
Toluene	–	4 – 15	73, 74
Spark discharge in liquid			
Copper, cadmium, zinc, platinum, nickel, silver nanoparticles			
Methanol, propanol, ethyl acetate, amyl acetate, acetone, cyclohexanone	–	1 – 29	75

Note. Notations used are as follows: AOT is sodium bis(2-ethylhexyl)sulfosuccinate, DMF is *N*,*N*-dimethylformamide, DMSO is dimethyl sulfoxide and THF is tetrahydrofuran.

operative interactions typical of many non-noble metals (*e.g.*, formation of a domain structure in ferromagnets).

1. Reactions initiated by free radicals

a. Photochemical reactions

Electromagnetic radiation can produce reactive intermediates leading to formation of metal nanoparticles.[76] At present, there are two experimental designs, *viz.*, a continuous irradiation of samples by UV or visible light or the use of pulsed lasers. A solvated electron produced as a result of a photochemical reaction is a highly reactive species capable of inducing atomic metal which is the source of nanoparticles:[77]

$$H_2O + h\nu \longrightarrow e^- + H_2O^+ \longrightarrow e^-_{solv} + H^+ + {}^{\bullet}OH,$$

$$Ag^+ + e^-_{solv} \longrightarrow Ag^0,$$

$$n\,Ag^0 \longrightarrow Ag^0_n.$$

Photochemical redox reactions resulting in the formation of metal nanoparticles can also proceed without solvated electron (e_{solv}):[28]

$$AuCl_4^- + h\nu \longrightarrow AuCl_3^- + Cl^{\bullet},$$

$$2\,AuCl_3^- \longrightarrow AuCl_4^- + AuCl_2^-,$$

$$AuCl_2^- + h\nu \longrightarrow Au^0 + Cl^- + Cl^{\bullet},$$

$$n\,Au^0 \longrightarrow Au^0_n.$$

The energy of electromagnetic radiation in the short-wavelength segment of visible region and in the UV region

is high enough for homolytic dissociation of O–H bonds in water molecule and production of free radicals. If the reaction medium contains organic compounds, organic radicals (reducing agents for metal ions) can be produced in a secondary process, *e.g.*,[28]

$$H_2O + h\nu \longrightarrow H^{\bullet} + {}^{\bullet}OH,$$

$${}^{\bullet}OH\,(H^{\bullet}) + Me_2CHOH \longrightarrow H_2O\,(H_2) + Me_2C^{\bullet}(OH),$$

$$Ag^{+} + Me_2C^{\bullet}OH \longrightarrow Ag^{0} + Me_2CO + H^{+}.$$

b. Sonochemical reactions

Free-radical reactions resulting in the formation of metal nanoparticles can be induced by intense low-frequency sonication.[53–60] Collapse of a cavitation bubble can be accompanied by homolytic dissociation of chemical bonds in the condensed medium

$$H_2O +))) \longrightarrow H^{\bullet} + {}^{\bullet}OH.$$

If the reaction medium contains cations of those metals that are below hydrogen in the electrochemical series, further steps of free-radical reactions are possible, which result in the formation of nanoparticles,[54, 55, 60]

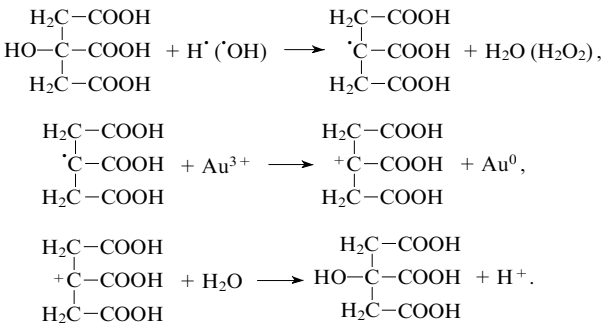
$$AuCl_4^{-} + 3H^{\bullet} \longrightarrow Au^{0} + 3H^{+} + 4Cl^{-},$$

$$n\,Au^{0} \longrightarrow Au_n^{0};$$

$$Ag^{+} + H^{\bullet} \longrightarrow Ag^{0} + H^{+},$$

$$n\,Ag^{0} \longrightarrow Ag_n^{0}.$$

This method is inapplicable to the metals that are above hydrogen in the electrochemical series because the reaction products include a proton. Usually, the reaction medium contains not only the metal compound, but also a stabilizer which can also undergo chemical transformations. For instance, tricitric acid can react with both trivalent gold compounds and free radicals [54]



Sonochemical reactions are used rather often for the preparation of monometallic and bimetallic nanoparticles with both randomly distributed metals and the 'core–shell' structure.

c. Radiolytic reactions

Exposure of the system under study to high-energy radiation (usually, γ-rays) can be followed by initiation of reduction processes leading to formation of stable metal colloids.[61–68] The accompanying processes [61] are similar to those described earlier for the photochemical [28, 77] and sonochemical [54, 55] reduction. Often, the compositions of systems and the concentrations of components are similar for these two methods. At the same time, γ-radiation favours production of not only radicals, but also radical anions owing to the reactions with the components present in the aqueous medium:[62]

$$H_2O + \gamma\text{-quantum} \longrightarrow e_{aq}^{-} + H^{+} + {}^{\bullet}OH,$$

$$CO_2 + e_{aq}^{-} \longrightarrow CO_2^{-\bullet},$$

$$Ag^{+} + e_{aq}^{-} \longrightarrow Ag^{0},$$

$$Ag^{+} + CO_2^{-\bullet} \longrightarrow Ag^{0}.$$

A detailed description of synthetic aspects of radiolytic production of metal nanoparticles can be found in a review.[11]

2. Laser ablation of metals

Initially, laser ablation was developed as a method for cleaning the surface of samples in mass spectroscopic studies.[78, 79] A small surface area of a sample is exposed to high-fluence laser pulses. Under the action of laser radiation, a local area on the surface can be vaporized. The first pulse breaks the surface layer while the action of subsequent pulses causes vaporization of the sample in the bulk. This allows one to obtain information on the chemical composition of the sample at the surface and in the bulk. Using a vessel containing a condensed medium instead of the vacuum chamber of a mass spectrometer, one gets a reactor for the preparation of sols (Fig. 2); this is undoubtfully of interest for preparative-scale purposes in studies of refractory metals.[35–47, 49–52, 80–82]

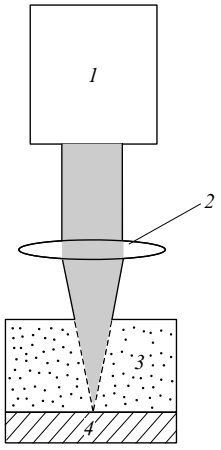


Figure 2. Scheme of a unit for preparation of metal sols by laser ablation. Laser radiation source (*1*), focusing lens (*2*), reaction medium (*3*) and sample (*4*).

The interaction of high-density energy flux produced by the laser pulse with the surface of the sample causes almost instantaneous vaporization of a local area of the sample surface and the formation of a local plasma region containing a vapour of metal atoms.[41] The maximum temperature in the vapour is of the order of 2×10^4 K, being attained about 10^{-8} s after the pulse is applied. Then, the system is cooled in such a manner that the temperature decreases exponentially, *viz.*, by a factor of about ten upon each tenfold increase in the time interval passed after the laser pulse.[83] The amount of vaporized metal depends on the radiation wavelength, on the laser pulse energy and on the heat of vaporization of the metal. It was reported that a pulse of an excimer laser (λ = 308 nm, pulse energy 120 mJ) produces 7.69×10^{-8} g of gold (2.35×10^{14} atoms).[83] If

there is no condensed medium in the immediate vicinity of the vaporization zone, fast irreversible coagulation followed by coalescence of metal particles occurs. These processes are completed by the formation of micrometre-size fractal aggregates during the first millisecond after application of the laser pulse.[83–86]

In the presence of a condensed reaction medium, the situation is basically different. Even low-reactive compounds, such as alkanes, can react with metal atoms and with the surface of the growing nanoparticle, thus stabilizing it. Although metal sols in liquid alkanes are very unstable, their lifetimes are long enough to carry out experiments. Gold sols in liquid alkanes synthesized by laser ablation were reported.[50] The average particle size of the fresh sol is about 8 nm. Laser ablation of metals in water produces unstable metal aquasols with the average size of fresh particles in the range from 4 to 400 nm.[35–38,47] The introduction of electrolytes into the reaction medium stabilizes such colloids.[39,40] This can most probably be explained by adsorption of ions on the surface, which leads to cessation of the growth of particles due to electrostatic stabilization. A more efficient way of stabilizing the particle size is to introduce ionic surfactants into the system.[41,42,51] In this case, not only electrostatic, but also steric stabilization is possible. For instance, the effect of the length of the hydrocarbon chain of anionic surfactant n-$C_nH_{2n+1}SO_3Na$ was reported.[42] A trend to enhancement of the stability of silver aquasols was observed with an increase in n from 8 to 16 (n = 8, 10, 12, 16). Steric stabilization may provide an explanation for the preparation of stable metal aquasols upon introduction of polymers, such as polyvinylpyrrolidone or fifth-generation (G-5) dendrimeric ethylenediamine/amidoamine copolymer into water.[43,49] Not only water, but also polar organic solvents including ethanol[44,45,52] (and other primary alcohols[45]), ethylene glycol,[44] dichloroethane, acetone,[52] acetonitrile, THF, DMF and DMSO[46] can be used as reaction media for the preparation of stable colloidal systems. Usually, the higher the dielectric constant of the reaction medium the more stable the metal colloid sols. Owing to high reactivity of metal atoms and clusters formed under the synthesis conditions this method is of limited use from the standpoint of the nature of the compounds used as reaction medium. Non-noble metals react with halogen-containing compounds, alcohols, *etc*., resulting in stable inorganic and organometallic products.

3. Low-temperature vapour co-condensation

Yet another group of methods for the preparation of metal colloids is based on low-temperature vapour co-condensation. Metal atom vapours produced by vaporization *in vacuo* are co-condensed with an excess amount of a matrix compound onto a surface cooled with liquid nitrogen (Fig. 3). As co-condensation of vapours is completed, the system is no more cooled, the matrix melts and spontaneous growth of metal particles begins in it, resulting in the formation of a metal sol. This and related techniques allow one to obtain a variety of metal organosols.[8,86,87] The undoubtful advantage of this method is its versatility. However, there are also two essential limitations. First, low volatility of refractory metals (molybdenum, tungsten, tantalum) in vacuum makes it impossible to produce preparative-scale amounts of corresponding metal nanoparticles. Second, high reactivity of the metal–cryomatrix pair leads

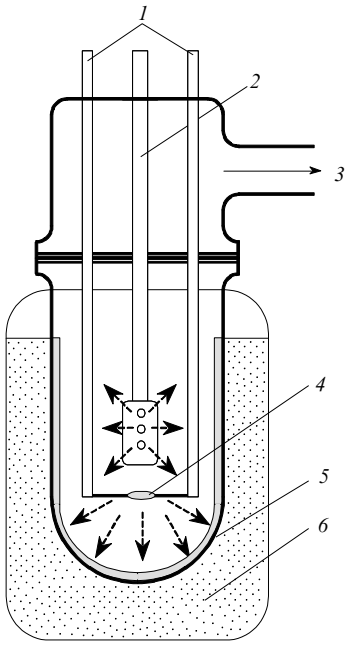


Figure 3. Scheme of a unit for low-temperature co-condensation of the metal and organic reactant vapours.
Metal vaporizer electrodes (*1*), organic reactant feed (*2*), vacuum line (*3*), metal vaporizer (*4*), low-temperature co-condensate matrix (*5*) and liquid nitrogen (*6*).

to formation of stable compounds (metal halides, compounds similar to Grignard reagent, organometallic compounds, *etc*.). Because of this, water, alcohols and haloalkanes are not used as cryomatrices.

If there is no strong interaction between metal atoms and the cryomatrix, dimers and trimers are formed in the solid state even at temperatures that are as low as 20 K.[88] In the case of alkane cryomatrices, switching the cooling off is followed by avalanche-like irreversible growth of particles, which leads to formation of micrometre-size metal aggregates in a rather short time. This can be avoided by thoroughly choosing the substance for the cryomatrix. Stable intermediates (organometallic compounds, metal complexes) can form in the cryomatrix and retain their stability at least below the melting point of the matrix.[73,89,90] Researchers working in this field often use low-melting arenes capable of forming bisarene organometallic compounds and lower aliphatic amines that form metal complexes. Controllable slow decomposition of such intermediates in the presence of stabilizers enables reproducible preparation of stable colloids of metal nanoparticles with an average particle size of a few nanometres.

4. Spark discharge in liquids

Preparation of metal colloids in liquid media is based on the Svedberg method involving pulsed high-frequency spark discharge between metal powder particles in an organic medium. Dispersion of metal under these conditions is a condensation process, *viz*., vaporization of the metal under the action of discharge is followed by condensation of vapours thus produced in the bulk of the solvent. The nanoparticle size is stabilized as a result of the interaction between the surface metal atoms and components contained in the liquid medium. The method was intensively devel-

oped in the 1960s and various techniques were elaborated to obtain preparative-scale amounts of highly disperse metals in polar and nonpolar organic media.[75] More detailed information on the method can be found in a review.[11]

III. Chemical synthesis of metal nanoparticles in condensed media

The action of physical factors can initiate chemical reactions in condensed media, leading to formation of metal nanoparticles. However, the main process has a chemical nature. In the general form, the fundamental redox reaction of formation of nanoparticles can be written as follows:

$$M^{n+} + [Red] \longrightarrow M^0 + [Ox],$$

where M^{n+} is the cationic (oxidized) form of the metal, [Red] is the reducing agent, M^0 is the zero-valence (reduced) metal and [Ox] is the oxidation product of the reducing agent. The closer the metal to the right end of the electrochemical series the more easily the reaction proceeds. A fundamental limitation for this reaction is the nature of the condensed medium in which the reaction proceeds. For instance, nanoparticles of aluminium and metals located above it in the electrochemical series cannot be produced in water and other protic solvents owing to a competing reaction of the reduced metal with proton. Experimental studies on the synthesis of metal nanoparticle sols using chemical reactions are reviewed in Table 2.

Both inorganic and organic compounds are used as reducing agents in the synthesis of nanoparticles. Among inorganic reducing agents, sodium borohydride is most often used. This reaction can be performed in aqueous,[91–97, 150–152, 166, 173–176, 191–197] organic,[98] homogeneous[99, 198, 199] and heterogeneous (Refs 101, 103, 109, 114, 161, 162, 181, 182, 199–211) aqueous–organic media. The most widely used organic reducing agents include sodium citrate,[26, 54, 104–109, 153–156, 177, 178] amines and hydrazine,[110, 114, 126, 161, 163, 164, 167–169, 182, 187] aldehydes and sugars,[111–121, 157] *p*-diphenols.[122–124] Many high-molecular-mass organic compounds also can reduce metal cations under mild conditions.[158, 159, 179] In addition, reduction of cations is possible due to the oxidation of organic reaction media.[127–149, 160, 165, 170–172, 180, 183, 185, 186, 188–190]

To enhance the stability of the nano-sized state, an additional component called stabilizer is introduced into the reaction medium. The role of the stabilizer is to interact with the surface atoms and thus to decrease the excess

Table 2. Methods of chemical synthesis of metal nanoparticles in condensed media.

Reaction medium	Reducing agent	Stabilizer	Average particle size /nm	Ref.
Monometallic systems				
Silver nanoparticles				
Water	$NaBH_4$	sodium citrate	70 (rings)	91
	$NaBH_4$	the same	5 (freshly prepared solution)	92
			10–22 (long-standing solution)	92
	$NaBH_4$	"	8–15	93
	$NaBH_4$	laponite	10	94
	$NaBH_4$	sodium citrate, sodium dodecylsulfate	9.6	95
	$NaBH_4$	polyethyleneimine, polyacrylic acid	4	96
	$NaBH_4$	cellulose	5.5–11.3	97
Ethanol	$NaBH_4$	$NaBH_4$	5	98
Water–acetone (1 : 40)	$NaBH_4$	sodium citrate, styrene/acrylic acid copolymer (9 : 1)	15	99
Water–cyclohexane	$NaBH_4$	oleic acid	9 (pH 2)	100
			6 (pH 7)	100
			8 (pH 11)	100
Water–heptane	$NaBH_4$	rhamnolipid	6	101
Water–chloroform	$NaBH_4$	thiols	2	102
Water–heptane	$NaBH_4$	2-hydroxy-1,3-bis(octadecyldimethylammonium) dibromide	7.1	103
Water	sodium citrate	sodium citrate	–	26
	the same	the same	30–50, 120	104
	"	"	30–75	105
	"	"	30–100	106
	"	sodium dodecyl sulfate	20 × 250 (rods)	107
	"	SiO_2	3–5	108
Water–n-decane	"	AOT	–	109
Water	hydrazine, $NaBH_4$	biomass	15–30	110
	formaldehyde	polyvinylpyrrolidone	10–30	111
	"	"	30–70	112
Ethylene glycol	glycolaldehyde	glycolaldehyde	50	113
Water–cyclohexane	hydrazine, benzaldehyde	oleic acid	3–5	114

Table 2 (continued).

Reaction medium	Reducing agent	Stabilizer	Average particle size /nm	Ref.
Water	formaldehyde	polyvinyl alcohol, polyvinylpyrrolidone	4	115
	glucose	oleic acid	6 – 10	116
	formaldehyde, sorbitol	formaldehyde, sorbitol	20 – 50	117
	sugars	sugars	50 – 200	118
	glucose	glucose	< 1000	119
	D-maltose	D-maltose	25	120
Ethanol	glucose	glucose	2 – 5	121
Water	hydroquinone	hydroquinone	> 200	122
	"	sodium citrate, polyvinyl alcohol, polyvinylpyrrolidone	2 – 15	123
	"	sodium citrate	2.6 – 7.8	124
	$NaBH_4$, hydroquinone	hydroquinone	10 – 25	125
	hydrazine	tetrabutylammonium bromide decanoic acid, dodecylamine	5 – 9 (seeds, rods 50 – 80 nm in diameter)	126
Ethylene glycol	ethylene glycol	polyvinylpyrrolidone	30 – 100 (beads) 30 – 50 × 300 – 10000 (rods)	127 – 135, 136 – 142
	"	polyvinyl alcohol	10 – 30	134
N,*N*-Dimethylformamide	*N*,*N*-dimethylformamide	*N*,*N*-dimethylformamide	~ 100	143
	"	acetylacetone	20	144
N,*N*-Dimethylformamide, dimethyl sulfoxide	"	β-cyclodextrin	4.4	145
N,*N*-Dimethylformamide	"	3-aminopropyltriethoxysilane	6.5 – 19.7	146
	"	*N*,*N*-dimethylformamide	~ 50 (primary solution)	147
	"	polyvinylpyrrolidone	~ 40 (primary solution)	148
	"	"	~ 10 (primary solution)	149
Gold nanoparticles				
Water	$NaBH_4$	dodecyltrimethylammonium bromide	6 [a] 8 [b]	150
	$NaBH_4$	cetyltrimethylammonium bromide	5 × 30 (rods)	151
	$NaBH_4$	lysozyme	2 – 3	152
	sodium citrate	sodium citrate	17	153
	the same	the same	20	154
	"	sodium 3-mercaptopropionate	3 – 4	154
	"	sodium citrate	–	155
	"	the same	–	156
	polyaldehyde dextran	polyaldehyde dextran	21.7	157
	polyvinylpyrrolidone	polyvinylpyrrolidone	6.0	158
	sodium polyacrylate, polyacrylamide	sodium polyacrylate, polyacrylamide	–	159
Ethylene glycol	ethylene glycol	polyvinylpyrrolidone	–	160
Water – toluene	primary amines	primary amines	2.5 – 7	161
	$NaBH_4$	thiols, amines	2 – 7.5	162
Toluene	primary amines	tetrahydrothiophene	10	163
Copper nanoparticles				
Water	Hydrazine	Polyvinyl alcohol, polyvinylpyrrolidone, starch	14 – 34 [c]	164
Ethylene glycol	ethylene glycol	Polyvinylpyrrolidone	45	165
Iron nanoparticles				
Water	$NaBH_4$	bacterial suspension	20 – 30	166
Nickel nanoparticles				
Water	hydrazine	cetyltrimethylammonium bromide, tetradodecylammonium bromide	10	167
	"	polyvinylpyrrolidone, polyacrylic acid	25 [a] 21 [d]	168 168
	"	cetyltrimethylammonium bromide	34	169
Ethylene glycol	$NaBH_4$, ethylene glycol	polyvinylpyrrolidone	3.8	170

Table 2 (continued).

Reaction medium	Reducing agent	Stabilizer	Average particle size /nm	Ref.
Platinum nanoparticles				
Water	polyvinylpyrrolidone	polyvinylpyrrolidone	7	171
Ethylene glycol	ethylene glycol	"	3 – 5	172
Ruthenium nanoparticles				
Water	$NaBH_4$	sodium acetate	2.2	173
Polymetallic systems				
Silver – gold nanoparticles				
Water	$NaBH_4$	$H_2N(CH_2)_3SiO/SiO_2$	3.3 – 7.6	174
	$NaBH_4$	polyvinylpyrrolidone	5.6 (Ag)	175
			6.8 (Au)	175
	$NaBH_4$	horse spleen apoferritin	5.6 – 6.3	176
	sodium citrate	sodium dodecyl sulfate, dodecylamine	15 (Au)	177
			38 (Ag)	177
	the same	sodium citrate	17 – 25	178
	sodium acrylate, sodium polyacrylate	sodium acrylate, sodium polyacrylate	11 – 17	179
Ethylene glycol, *N*,*N*-dimethylformamide	ethylene glycol, *N*,*N*-dimethylformamide	polyvinylpyrrolidone	~10 – 15 (primary solution)	180
Water – cyclohexane	$NaBH_4$	Triton X-100	23 – 260	181
Water – isooctane	hydrazine	AOT	4 – 22	182
Silver – palladium nanoparticles				
Ethylene glycol	ethylene glycol	ethylene glycol	5.5 [c]	183
Silver – platinum nanoparticles				
Ethylene glycol	$NaBH_4$	polyvinylpyrrolidone	3 – 4	184
Gold – copper nanoparticles				
Tetraethylene glycol	tetraethylene glycol	polyvinylpyrrolidone	8 – 10	185
Cobalt – nickel nanoparticles				
Propane-1,2-diol	propane-1,2-diol	propane-1,2-diol	25 – 100	186
Iron – cobalt nanoparticles				
Water	hydrazine	polyethylene glycol	68 (cubes)	187
Platinum – bismuth nanoparticles				
Ethylene glycol	ethylene glycol	ethylene glycol	~19 [c]	188
Platinum – ruthenium nanoparticles				
Ethylene glycol	ethylene glycol	ethylene glycol	2.5 [c]	189
Water – ethylene glycol	"	"	2.3 – 2.6	190
Silver, gold and platinum – palladium nanoparticles				
Water	$NaBH_4$	chitosan	15 – 200	191

[a] Determined by TEM. [b] Determined by dynamic laser light scattering. [c] Determined from the line broadening in power X-ray diffraction patterns. [d] Calculated from the specific surface area determined by the Brunauera – Emmett – Teller method.

surface energy. Various compounds are used as stabilizers; those most often used include sulfur-containing organic compounds (thiols, disulfides, sulfur-containing heterocyclic compounds),[102, 154, 162, 198 – 206, 212 – 223] surfactants (Refs 32, 95, 109, 114, 116, 163, 177, 181, 182, 199, 207 – 209, 220, 224 – 227), and organic compounds containing polar functional groups.[210, 228] Quite often, the reducing agent or a product of its oxidation act as stabilizers.

1. Reduction of metal cations in aqueous medium

Reduction of metal cations is widely used for the preparation of aqueous nanoparticle sols. The closer the metal to bottom of the electrochemical series and the higher the electrochemical potential of the reducing agent the faster and easier the reaction.

Metal nanoparticles can most easily be obtained using sodium borohydride, a traditional inorganic reducing agent.

Most researchers introduce this compound into the solution of a metal salt rather than *vice versa*. This is probably due to simultaneous occurrence of the reduction of the metal cation, the growth of metallic core and stabilization of the nanoparticle surface. It seems likely that the introduction of the reducing agent into the reaction medium leads to an optimum ratio of these processes which gives reproducible results.

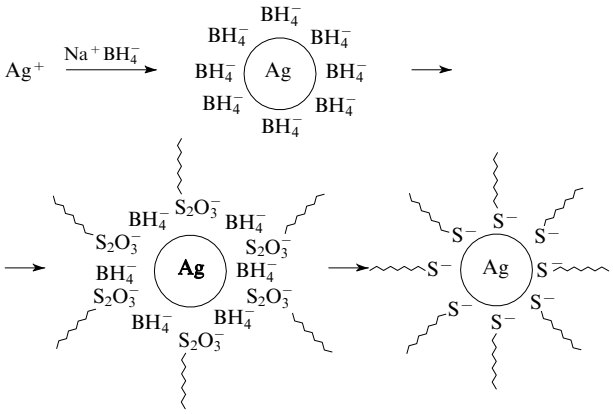
A typical product of synthesis is a metal sol containing nanoparticles with an average size from 1 to 10 nm. Interestingly, different methods of size determination give similar results for samples thus produced. In particular, the particle sizes of a silver sol prepared by reduction with sodium borohydride, determined by different physical methods are as follows.[98] According to powder X-ray diffraction data, crystallites are about 3 nm in size; the particle size distribution plotted based on analysis of TEM micrographs show a maximum at nearly 5 nm, while the particle size distribution obtained by dynamic laser scattering has a maximum in the region 5–7 nm.

Almost all researchers who used sodium borohydride as reducing agent took it in excess with respect to the stoichiometric amount. This is due to two reasons. First, in protic solvents one deals with dissociation of both the proton-donating solvent and the borohydride ion, which forms a hydride; therefore, processes in such reaction media are accompanied by slow formation of hydrogen. Second, if the system contains no particles with high affinity towards the metal surface, the BH_4^- anion can play the role of a stabilizer, namely,[98,219] it forms the negatively charged inner layer of the electrical double layer. However, the borohydride anion is not an efficient stabilizer owing to secondary interactions with the environment. Therefore, in most cases, stabilizers are introduced into the starting reaction medium as an additional component. Nevertheless, secondary processes involving the borohydride anion can be used for stabilization of nanoparticles *in situ*.

Thiols are the most efficient stabilizers of metal nanoparticles because of the high affinity of the thiol group to metals. However, thiols with rather long-chain hydrocarbon fragments are almost insoluble in water and therefore cannot be used directly in the synthesis. At the same time, a thiol group can be formed *in situ* on the surface of particles. A method was developed which allows one to prepare thiol-stabilized gold and silver nanoparticles.[219] It involves reduction of the starting compounds with sodium borohydride in the presence of sodium dodecyl thiosulfate, which is better dissolved in water than dodecylthiol. During the synthesis the surface layer undergoes some transformations. Initially, nanoparticles are stabilized by borohydride anions, then borohydride is partially replaced by thiosulfate which is subsequently reduced to thiol (Scheme 1).

The reducing agents used more rarely than sodium borohydride include sodium citrate (Refs 26, 54, 104–109, 153–156, 177, 178), amines and hydrazine (Refs 110, 114, 126, 161, 163, 164, 167–169, 182, 187). Good solubility of sodium tricitrate in water is due to three carboxyl groups in its molecule while the stability of this compound makes it a more efficient surface stabilizer than the borohydride anion. The redox potential of sodium citrate is much lower than that of sodium borohydride. Taking into account this fact, reactions should be carried out under relatively more severe conditions.

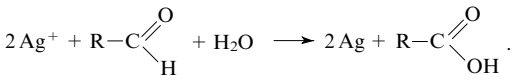
Scheme 1



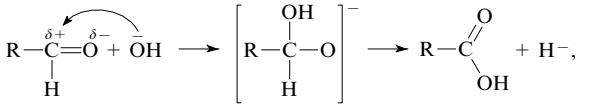
Reduction of metal salts with sodium citrate in aqueous medium usually requires heating, whereas the reaction with sodium borohydride proceeds at room temperature (sometimes, ice-cold solution is used).[54,92,93,151,152,224] Preparation of citrate-stabilized silver nanoparticles using sodium borohydride as reducing agent and sodium tricitrate as stabilizer was reported.[91–93,95,99]

Stabilized metal nanoparticles can be synthesized using nitrogen-containing compounds, *e.g.*, aliphatic amines,[161–163,182,187] hydrazine[110,126,164,167–169] as both reducing agents and stabilizers.

Metal nanoparticles with a positive standard electrochemical potential (E°) can be obtained using the Tollens reaction also known as Silver Mirror Test for aldehydes.



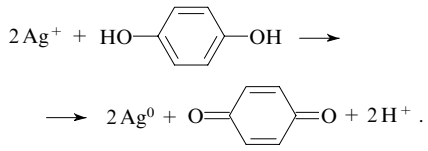
In this reaction, the role of reducing agents is played by the compounds containing an aldehyde group,[111–115,157] or by sugars capable of forming the aldehyde group.[116–119,147,157] The reaction is completed within a few minutes at room temperature[111] and can be used to obtain considerable amounts of nanoparticles necessary for practical applications.[112] A mechanism of reduction of silver ions under the action of formaldehyde in an alkaline medium was proposed.[115] The reaction of formaldehyde with HO^- ion obeys a nucleophilic addition pattern and produces hydride ions. The hydride ion reacts with silver ions and the proton liberated in the alkaline medium reacts with hydroxyl ion to give water.



$$2Ag^+ + H^- \longrightarrow 2Ag^0 + H^+,$$

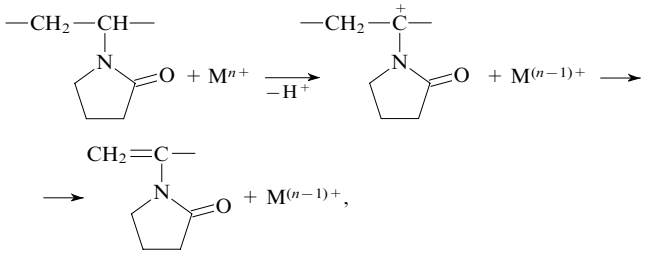
$$H^+ + HO^- \longrightarrow H_2O.$$

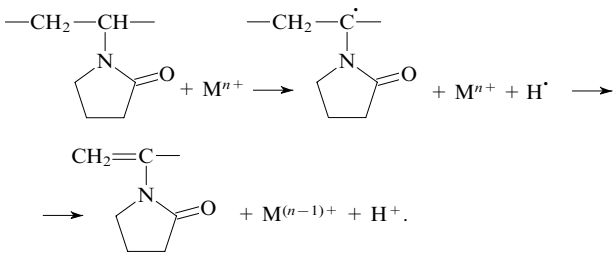
Metal nanoparticles can be synthesized in aqueous media using organic reducing agents well-studied in the redox reactions, such as *p*-diphenols, *e.g.*, hydroquinone and related compounds. The synthesis is based on the interaction between the metal ion and hydroquinone resulting in the formation of a metal nanoparticle and quinone.[122–124]



Changes in the spectral properties of the medium related to the quinone–hydroquinone transformation and the absorption band intensities of the surface plasmon resonance of metal nanoparticles may serve as criteria for reaction completion. In addition, this transformation can be used in studies on the mechanisms of formation of nanoparticles.[229] Oxidation of the quinone leads to formation of stable particles bearing an unpaired electron, which can be detected with ease by EPR.

In addition to low-molecular-mass organic compounds, polymers can also act as reducing agents for metal ions. Polymeric reducing agents can conditionally be divided into two groups. One group comprises high-molecular-mass analogues of the organic reducing agents mentioned above. For instance, the use of polyaldehyde dextran as reducing agent for tetrachloroauric acid was reported.[157] The redox reaction involving such polymers does not affect the backbone. The other group includes those polymers for which not only functional groups, but also the backbone participates in the reaction. Such reactions affect both the chemical composition of the polymer and its molecular-mass characteristics. Reduction of tetrachloroauric acid and silver nitrate with poly(*N*-vinyl-2-pyrrolidone) (PVP) in an aqueous medium was studied.[158] It was shown that the shape, size and optical properties of nanoparticles thus produced exhibit gradual variations depending on the PVP-to-metal (M) ratio and on the reaction temperature. Kinetic studies revealed autocatalytic nature of the reaction with the limiting stage consisting in the formation of a radical or carbocation containing the tertiary carbon atom of the backbone. Two possible reaction mechanisms were proposed, namely, with the formation of free-radical or carbocationic macromolecular intermediates:





The redox reactions involving the backbone atoms result in degradation of the polymer and in shift of the molecular-mass characteristics towards lower molecular masses.

2. Reduction of metal cations in nonaqueous media

Reduction of a metal cation to zero valence should not necessarily be carried out in an aqueous medium. There are numerous methods of production of metal particles in nonaqueous media. They can be divided into two groups.

One group includes methods in which the nonaqueous medium is used only as a solvent.[98,121] The use of nonaqueous solvents is due to the low solubility of the reaction components in water or chemical reactions between substances and water. Organic solvents of lower polarity compared to water show almost no Brønsted acidity and provide a higher solubility of nonpolar compounds and an admissible solubility of polar compounds. A method of preparation of thiol-stabilized gold nanoparticles was reported.[223] Nanoparticles are preliminarily synthesized in methanol by reduction of tetrachloroauric acid with sodium borohydride in the presence of thiol. Then, alcohol is removed *in vacuo* and nanoparticles are re-dispersed in diethyl ether. A comparative study[230] of the reduction of Fe^{II}, Fe^{III}, Co^{II}, Ni^{II} and Cu^{II} compounds with sodium borohydride in water and diglyme showed that, depending on the nature of the reaction medium and on the presence of oxygen in it, the final products may include not only metal particles, but also metal oxides and borides (Table 3).

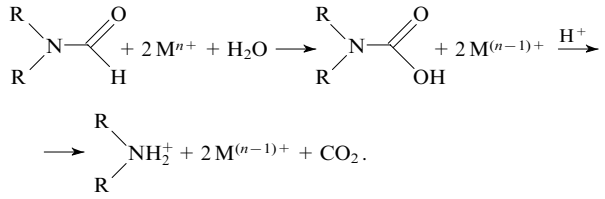
If reduction of iron ions is better conducted in deoxygenated aqueous medium, in the case of cobalt and nickel ions it is more appropriate to carry out the reaction in diglyme instead of water. For copper ions, the lack of oxygen in the reaction medium is more important. Yet another advantage of the nonaqueous media can be a lower partial pressure of vapours; this is of crucial importance for preparative-scale methods involving sonication.[231] Sonication of a solution of tris-μ-(dibenzilideneacetonate)-dipalladium in mesitylene at room temperature is accompanied by intramolecular redox reaction producing palladium nanoparticles.

Table 3. Main routes of borohydride reduction reactions of some transition metal ions.[230]

Metal ion	Standard reduction potential /V	Metal-containing product of borohydride reduction		
		in water under argon atmosphere	in diglyme under argon atmosphere	in water in air
Fe^{3+}	−0.036 [a]	Fe	FeB	Fe, FeO_x
Fe^{2+}	−0.41	Fe	Fe_2B	Fe, FeO_x
Co^{2+}	−0.28	Co_2B	Co	$Co_3(BO_3)_2$, Co
Ni^{2+}	−0.23	Ni_2B	Ni, Ni_2B, Ni_3B	Ni, NiO
Cu^{2+}	+0.34	Cu	Cu	Cu, Cu_2O

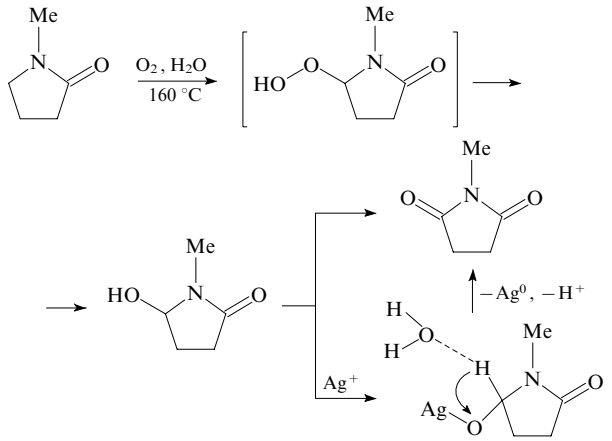
[a] $Fe^{3+} + 3e^- \longrightarrow Fe_{surf}$.

The second group comprises methods in which the reaction medium is involved in the redox reaction (Refs 127–149, 160, 165, 170–172, 180, 183, 185, 186, 188–190, 232). The most often used reaction media include lower acid amides (formamide, dimethylformamide) and short-chain (up to 6 atoms long) polyalcohols, mainly α,ω-diols. A technique for the preparation of colloids of gold nanoparticles in formamide in the presence of PVP was proposed.[233] Both formamide and PVP can act as reducing agents. At room temperature in a deoxygenated medium, tetrachloroauric acid mainly reacts with formamide rather than with PVP. By analogy with the scheme of oxidation of formamides by silver ions [143] one can propose the following scheme of redox reactions resulting in metal nanoparticles:



Under the action of metal ions, the carbonyl group of formamide is oxidized to a carboxyl group. Carbamic acid just formed is unstable and decomposes to amine and carbon dioxide. The concentration of metal ions in the starting reaction mass is low and the amount of water present in the solvent is enough for the reaction to proceed.

The reducing properties of PVP are due to the pyrrolidone heterocyclic moiety that can be oxidized to give 1,5-dioxopyrroles. The oxidation of low-molecular-mass compounds with the pyrrolidone heterocyclic fragment containing a tertiary nitrogen atom has been studied in detail.[234] *N*-Methyl-2-pyrrolidone containing some amount of water is slowly oxidized in air at elevated temperature. The reaction involves the formation of an unstable peroxide intermediate and, subsequently, 5-hydroxy-1-methyl-2-pyrrolidone in which the alcohol group is readily oxidized to the carbonyl group. After *N*-methylpyrrolidone was kept at 160 °C in air for 12 h, the yield of *N*-methyl-1,5-dioxopyrrolidine was 9.1%. This reaction proceeds much more readily in the presence of silver ions; moreover, if silver ions are introduced into the oxidized *N*-methylpyrrolidone containing *N*-methyl-1,5-dioxopyrrolidine, no additional heating is required because the reaction proceeds at room temperature.[234]



A somewhat different situation occurs when using alcohols as reaction media. For the metals that are above hydrogen in the electrochemical series, dissolution of corresponding salts at room temperature causes no visible changes in the system. The colour of the medium (if exists) is due to the solvated ion only. If metals are below hydrogen in the electrochemical series, dissolution of metal compounds at room temperature is followed by the appearance of a weak yellow colour indicating the beginning of a redox reaction. However, the colour of the system does not change to red-brown with time, as is characteristic of concentrated sols of metal nanoparticles. High rate of the reaction as well as high yield of the target product require heating of the system up to the boiling point of the solvent. The reaction is quite often conducted under solvothermal synthesis conditions (at elevated temperature and pressure in an autoclave)[98] or under the action of microwave radiation.[127, 128, 132]

The use of diols as reaction media changes the character of the redox reactions in a specific manner. Two alcohol groups can be oxidized independently. If the oxidation is carried out in air at elevated temperatures, ethylene glycol can produce a number of oxidation products that also may play the role of reducing agents for metal ions. An investigation of the reduction of silver nitrate in ethylene glycol in air [113] showed that under certain conditions ethylene glycol can form acetaldehyde and glycolaldehyde as intermediates. Introduction of acetaldehyde and glycolaldehyde into the reaction significantly changes the spectral properties of the final silver sol. In particular, the maximum of sol absorption in the presence of acetaldehyde is in the region 420 nm, whereas replacement of acetaldehyde by glycolaldehyde leads to shift of this maximum to nearly 560 nm. However, carrying out the reaction in argon instead of atmospheric air strongly affects the intensity of the absorption peak of the surface plasmon resonance of silver nanoparticles. It is believed that the effects observed are due to preferred reduction of silver ions with glycolaldehyde formed from ethylene glycol on heating in air. Most probably, glycolaldehyde is formed *in situ* on the metal surface in the reaction with chemisorbed oxygen. An indirect confirmation is provided by the effect of the introduction of Fe^{III} compounds into the reaction mass on the characteristics of the final silver sol.[129, 136, 137] The introduc-

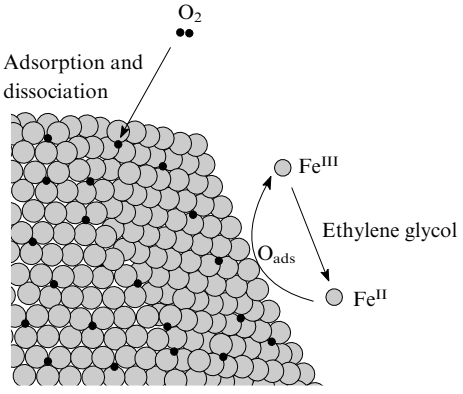


Figure 4. Scheme illustrating a possible mechanism of removal of oxygen atoms adsorbed on silver surface. Oxidation of ethylene glycol by oxygen atoms is impossible.[129]

tion of Fe^{III} salts into the reaction mass causes an increase in the yield of cubic nanoparticles and nanowires.[129] If the oxidation of ethylene glycol and Fe^{II} compounds compete with each other, chemisorbed oxygen atoms are mainly involved in the oxidation of Fe^{II} to Fe^{III} (Fig. 4). At the same time, Fe^{III} compounds in the liquid phase can oxidize ethylene glycol in the absence of oxygen atoms.

3. Reduction of metal cations in mixed aqueous–organic media

Mixed aqueous–organic media can be successfully used for the synthesis of metal nanoparticles. Depending on the solubility of the organic component, two types of systems, homogeneous and heterogeneous, are formed in water. If organic solvents are miscible with water, processes occurring in the course of synthesis of metal nanoparticles are very similar to corresponding processes in homogeneous aqueous or organic media. The organic substance is only needed to provide the solubility of components. The synthesis of silver sols in a mixed water–acetone solvent was reported.[99] This reaction medium was chosen because the solubility of a styrene/acrylic acid copolymer used as stabilizer of silver nanoparticles in water is too low. For the same reason, an aqueous–organic reaction medium was used for the preparation of gold[235] and silver nanoparticles[236] stabilized by 4-aminothiophenol.

Methods for the synthesis of metal sols in one solvent, separation of stabilized nanoparticles and their re-dispersion in another solvent were developed. An example is provided by the technique for the preparation of a sol of hydrophobic silver nanoparticles in cyclohexane.[100] The first step involves reduction of silver nitrate with sodium borohydride in the presence of oleic acid in water. After formation of nanoparticles, a nonpolar phase (cyclohexane) is introduced into the system for complete extraction of the nanoparticles.

A basically different situation is observed for organic solvents immiscible with water. In this case, a direct[114, 161, 162, 181, 199–203, 205–208] or reverse (Refs 101, 103, 109, 182, 209, 210) emulsion is formed in which the synthesis is conducted. Usually, the metal salt and the reducing agent are in the aqueous phase while the stabilizer is in the organic phase. The emulsion is formed by introducing a surfactant into the initial reaction mass; the products of synthesis are transferred to the organic phase with a phase transfer agent. When using quaternary ammonium salts, all these functions are performed by the same compound.

Mixing of aqueous solution of tetrachloroauric acid and a toluene solution of alkylamine in the presence of tetraoctylammonium bromide leads to a redox reaction resulting in amine-stabilized gold nanoparticles with the average sizes in the range from 2.5 to 7 nm.[161] Silver nanoparticles with average sizes 3–5 nm and a narrow particle size distribution were obtained by reduction of silver nitrate in a two-phase system water–cyclohexane.[114] Prior to reduction, benzaldehyde is dissolved in cyclohexane and condensed with hydrazine. After completion of the condensation, oleic acid is introduced into the system and the organic phase is mixed with aqueous solution of silver nitrate. The final product is a silver nanoparticle sol stabilized by oleic acid in cyclohexane. Silver nanoparticles stabilized by 2,2′-dithiopyridine (2,2′-DTP) were prepared.[237] The method is based on reduction of silver nitrate with sodium borohydride in the presence of 2,2′-DTP in a water–methanol–toluene mixture. Dissolution of silver nitrate and 2,2′-DTP in the aqueous–methanol mixture causes the formation of a complex $[Ag(2,2'\text{-DTP})]NO_3$ which is then reduced with sodium borohydride in the two-phase aqueous–organic emulsion.

Colloidal silver particles stabilized by high-molecular-mass compounds, such as polyvinyl alcohol, polyvinylpyrrolidone and starch, can be prepared using an original synthetic procedure.[238] The technique is based on the reduction of complex compounds of monovalent silver (cycloocta-1,5-diene)(1,1,1,5,5,5-hexafluoroacetylacetonate)Ag^{I} in two-phase aqueous–organic medium with hydrogen gas at elevated temperature ($\sim$80 °C). The starting silver compound is dissolved in the organic phase while the stabilizer is dissolved in the aqueous phase. The reaction involves reduction of monovalent silver, formation of metal nanoparticles and their transfer to the aqueous phase. Eventually, one gets a heterogeneous aqueous–organic system containing stabilized silver nanoparticles in the aqueous phase.

IV. Biosynthesis of metal nanoparticles

Various methods of synthesis of nanoparticles using living organisms or enzymes secreted by them were developed for the metals located below hydrogen in the electrochemical series. Biosynthesis of nanoparticles follows two routes. One of them involves the use of low- and high-molecular-mass bioorganic compounds as reducing agents and/or surface stabilizers in the synthesis of metal nanoparticles.[11, 77, 239] In this case, no specific biochemical reactions related to vital activity of living organisms occur. Despite the use of specific bioorganic reducing agents, this route can be treated as traditional. The other route involves reduction of starting compounds in a medium containing living microorganisms (bacteria, fungi, *etc*.) or enzymes secreted by them.[240–242]

1. Reduction with plant extracts

Examples of successful use of plant extracts as reaction media for the synthesis of nanoparticles have been documented. Aloin extracted from *Aloe Vera* leaves can act as both the reducing agent and stabilizer in the synthesis of gold and silver nanoparticles.[243] A similar effect was observed for extracts from *Brassica juncea*[244] and *Pelargonium graveolens*.[245] Specific features of biosynthesis of metal nanoparticles can be used in bioorganic analysis. Although bioorganic compounds have similar reducing abilities, their stabilizing properties can be significantly different. This was used[246] for separation of different bacteriophages. The cultures containing particular bacteriophages form stable coloured colloids of silver nanoparticles, whereas the cultures containing other bacteriophages form no such colloids.

2. Reduction in media containing microorganisms

The introduction of living microorganisms into the reaction medium has its specific features related to involvement of the reduction of metal salts in corresponding metabolic chains. A short list of experimental studies in the field is presented in Table 4. In some cases, nanoparticles produced using certain microorganisms exhibit antibiotic action against some other microorganisms. To reveal the antibiotic effect of nanoparticles prepared by

Table 4. Biosynthesis of nanoparticles using bacteria and fungi.

Bacteria used in biosynthesis	Particle size /nm	Ref.
Gram-positive bacteria		
Bacillus cereus	4 – 5	247
Bacillus licheniformis	50	248
Bacillus sp.	5 – 15	249
Brevibacterium casei	10 – 50	250
Enterococcus faecium	11.2 – 19.7	251
Lactobacilli	10 – 25	252
Lactobacillus spp	11.2 – 19.7	251
Lactococcus garvieae	11.2 – 19.7	251
Pediococcus pentosaceus	11.2 – 19.7	251
Gram-negative bacteria		
Cyanobacteria (*Plectonema boryanum*)	< 10 (intracellular) 1 – 200 (solution)	253
Enterobacter cloacae	28.2 – 122 (52.5 average)	254
Escherichia coli	50	254 – 256
Klebsiella pneumoniae	282 – 122 (52.5 average)	254
Morganella sp.	20 ± 5	257
Pseudomonas stutzeri	to 200	258 – 260
Fungi		
Alternaria alternata	20 – 60 [a]	261
Aspergillus clavatus	550 – 650 [b] (agglomerates)	262
Aspergillus clavatus	10 – 25	263
Aspergillus flavus	8.92 ± 1.61	264
Aspergillus fumigatus	5 – 25 7 – 19	265, 266
Aspergillus Niger	20 [c]	267
Fusarium oxysporum	5 – 50	268, 269
Fusarium solani	54 [c]	270
Trichoderma viride	5 – 90	271, 272
Verticillium	20 ± 12	273

Note. The colloid shows antimicrobial activity against: [a] *Phoma glomerata*, *Phoma herbarum*, *Fusarium semitectum*, *Trichoderma sp.*, *Candida albicans*; [b] *Aspergillus clavatus*; [c] *Staphylococcus aureus*, *Escherichia coli*.

biosynthesis, specific requirements are imposed on the microorganisms. On the one hand, they should be highly producing resistant to heavy-metal ions and nanoparticles to make the synthesis possible. On the other hand, they should not inhibit growth of the 'probe' microorganisms used to study the antibiotic effect.

Since the standard electrode potentials for reduction of the metals standing below hydrogen in the electrochemical series are high ($E^{\circ}_{Cu^{2+}/Cu} = 0.345$ V, $E^{\circ}_{Ag^{+}/Ag} = 0.799$ V, $E^{\circ}_{Au^{3+}/Au} = 1.50$ V), the reduction reactions should proceed under relatively mild conditions of biosynthesis. Almost all compounds that can be oxidized are efficient reducing agents. Numerous examples of synthesis of metal nanoparticles using various bioorganic compounds as reducing agents are available.[240 – 242] Usually, the role of bioorganic reducing agents is played by individual monomeric amino acids or sugars or by their oligomers and polymers.

Generally, the mechanism of biosynthesis of metal nanoparticles is as follows: electron-donating functional groups of bioorganic compounds are coordinated to the M^{n+} ions through donor – acceptor interactions between their own oxygen or nitrogen electron pairs and the unfilled orbitals of the metal. In addition to donor – acceptor interactions, covalent bonds can be formed between thiol groups of sulfur-containing amino acids (*e.g.*, methionine and cysteine) and the metal atom.[267] These covalent bonds play a dual role. On the one hand, they stabilize the colloid being formed. On the other hand, they exclude the chemically bound surface atoms of the metal particle from subsequent interactions.

High resistance of microbial strains to silver is sometimes related to the formation of silver sulfide nanoparticles in reactions of thiols with Ag^{+} ions.[259, 260, 274] Complexation of a thiol with the metal ion is followed by the redox reaction producing zero-valence metal.

Most researchers work with relatively low concentrations of the starting compounds (*e.g.*, the concentration of silver nitrate is usually at most 10^{-3} mol litre^{-1}) because of their intrinsic antibiotic action against bacteria and fungi. As a rule, biosynthetic studies are carried out using cultures harvested after 24 or 72 h of growth. The introduction of a metal salt into the culture is followed by an incubation period preceding visible changes. The duration of the incubation period (from a few minutes to tens of hours[262, 265, 267]) is determined by the rate of reduction of the metal ions, *viz.*, the higher the rate of reduction the shorter the incubation period. Usually, non-enzymatic processes proceed at higher concentrations of the starting compounds.[251] High reduction rate is due to the involvement of reductases secreted by bacteria or fungi to the environment.[254] Completion of the reduction reaction is usually determined visually from cessation of the changes in the colour of the reaction medium. The role of an objective indicator can be played by the intensity of the surface plasmon resonance band of nanoparticles (Refs 245, 246, 250, 254, 264, 273). Even in the absence of visible changes in the colour of the medium (long incubation period; about tens hours) the plasmon resonance band appears in the visible absorption spectra nearly 1 h after beginning of the reaction; a constant intensity of this band indicates completion of the reaction. Depending on the culture and reaction conditions, the reduction takes from ten minutes to 72 h to complete.

The surface plasmon resonance band has a maximum in the same region as in the case of reduction of metal salts with classical reducing agents, such as sodium borohydride[275] or sodium tricitrate.[77] The intensity and (which is most important) width of the absorption band points that the reaction products contain larger and more polydisperse particles with a lower bulk concentration compared to the particles synthesized using the classical reducing agents. This is confirmed by the results of a transmission electron microscopy (TEM) study.

The kinetics of the growth of metal particles under the biosynthesis conditions also shows some characteristic features. The classical synthesis of nanoparticles usually involves more concentrated solutions of salts and reducing agents (*e.g.*, sodium borohydride). This leads to fast intense nucleation in the bulk, which is the reason for rapid consumption of metal ions and cessation of the growth of particles with the formation of a sol containing a large

number of smaller particles characterized by a more narrow particle size distribution. The absorption spectrum of the sol shows a narrow strong symmetric band.[244] For weaker bioorganic reducing agents (compared to sodium borohydride) even at the same initial concentration of ions the bulk concentration of seeds is much lower and the growth of particles takes much longer time. This immediately influences the average particle size, the particle size distribution and the bulk concentration of particles. As a result, the spectrum now exhibits a broad, usually asymmetric absorption band shifted towards the long-wavelength region.

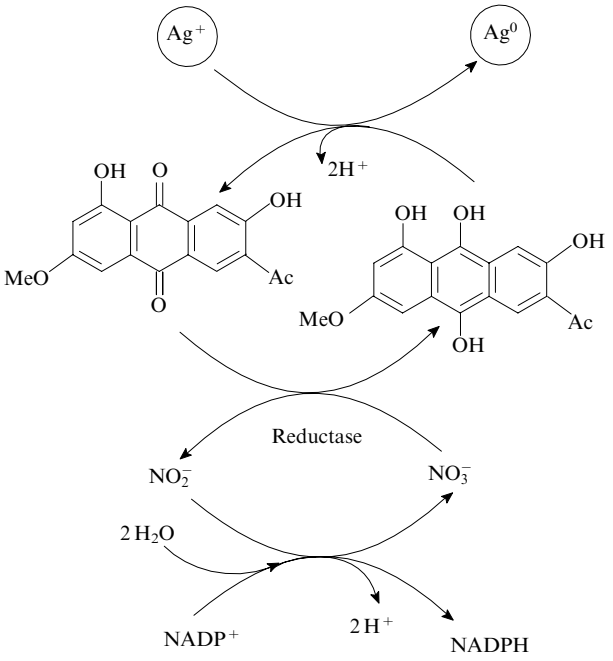
Usually, the spectra of colloids prepared by biosynthesis exhibit not only the absorption band of nanoparticles, but also two bands in the UV region with maxima at 220 and 280 nm. The first band characterizes the absorption of the amide bond in proteins while the second band is attributed to the specific absorption of tyrosine and tryptophan molecules.[247, 264, 265, 268, 269, 272] The IR spectra of colloids prepared by biosynthesis show bands corresponding to products of interaction between the surface metal atoms and functional groups of chemisorbed proteins.[247, 253, 256, 259, 270–272]

Usually, FT-IR spectra of products of biosynthesis of silver nanoparticles exhibit four bands at 1650, 1540, 1423 and 1060 cm^{-1}. The band at 1650 cm^{-1} corresponds to longitudinal vibrations of the N–H bond of the primary amine, the bands at 1540 and 1060 cm^{-1} characterize the secondary amine conjugated with the carbonyl group and the band at 1423 cm^{-1} corresponds the scissoring vibrations of methylene unit of the α-amino acid fragments of the protein.[268]

The UV spectra of the products of biochemical reduction of silver ions show a band in the region 265–270 nm corresponding to the absorption of tryptophan and tyrosine. The luminescence spectra of the same products exhibit an emission band at 340 nm. Its position indicates that the peptide bonds of proteins stabilizing the surface of nanoparticles are in the native state.[268, 276] According to X-ray photoelectron spectroscopy data, the surface of metal particles is covered by a considerable number of nitrogen, sulfur and phosphorus atoms, which points to efficient stabilization of nanoparticles by protein fragments.[253] TEM studies revealed a variety of nanoparticle morphologies. In most cases, relatively symmetric, spherical particles of size in the range from 5 to 50 nm are formed;[120, 250–253, 255, 269–273] often, they are aggregated. Nevertheless, particles in the aggregates do not contact one another; this points to good stabilizing properties of proteins.[268] Under particular conditions, the percentage of triangular prismatic particles (edge length in the range 200–500 nm) can be rather high.[258, 268]

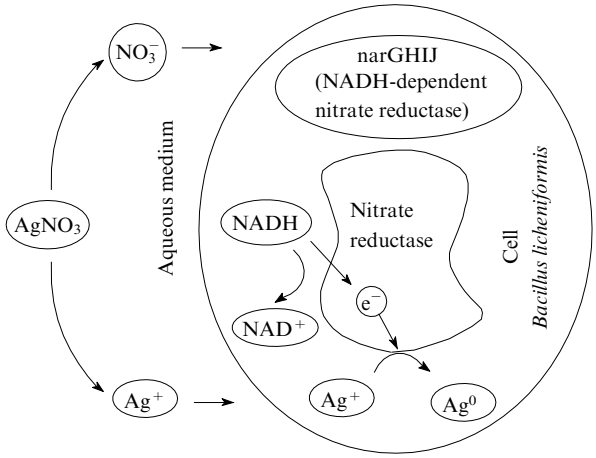
If the role of a nanoparticle surface stabilizer is played by the enzyme of redox reactions (oxidase, reductase), the reduction of metal ions and nitrate ions (if nitrates are used as the starting compounds) may be involved in specific biochemical cycles[248, 268] that can occur both extra- and intracellularly. Possible mechanisms of extracellular biosynthesis of silver nanoparticles by the fungus *Fusarium oxysporum*[268] and intracellular biosynthesis of silver particles by the bacterium *Bacillus licheniformis*[248] are shown in Schemes 2 and 3, respectively.

Scheme 2



NADP is nicotinamide adenine dinucleotide phosphate.

Scheme 3



Such specific cycles (*e.g.*, the Krebs cycle) play a decisive role in aerobic cell metabolism in living organisms. Aerobic biochemical reactions constituting the Krebs cycle represent a catabolic pathway of key bioorganic semiproducts to the simplest inorganic compounds, such as water and carbon dioxide. The biochemical cycles related to the vital activity of microorganisms (*e.g.*, catabolism of phenylacetic acid in *Escherichia coli*[277]) can change the pathways of aerobic processes. A scheme of biosynthesis of silver nanoparticles based on reduction of silver ions with the substances involved in the Krebs cycle was proposed.[252]

Under anaerobic conditions, anaerobic catabolism based on chains of biochemical transformations using Fe^{3+}, NO_3^- and SO_4^{2-} ions is also possible in bacteria. For instance, cyanobacteria can completely utilize nitrate under anaerobic conditions in the course of the following reactions:[253]

$$NO_3^- + 2H^+ + 2e^- \rightleftharpoons NO_2^- + H_2O,$$

$$NO_2^- + 8H^+ + 6e^- \rightleftharpoons NH_4^+ + 2H_2O.$$

The pathways of catabolic processes in anaerobic bacteria, occurring upon introduction of silver nitrate into the medium containing living microorganisms cannot be predicted *a priori*.

3. Extracellular reduction

For chemists and biochemists, it is of no concern how (intra- or extracellularly) does the reduction of silver ions and subsequent stabilization of nanoparticles occur and what (a prokaryote or an eukaryote) is the microorganism. However, this is of paramount importance for researchers working in biology and physiology of microorganisms. The reaction sites are localized using centrifugation and separate analyses of the precipitate and supernatant.[265, 269, 273] If the process is extracellular, no differences between the results obtained for the starting reaction mass and supernatant are observed in the presence of secretions from bacteria and fungi in the reaction medium. If the process is intracellular or involves the outer cell wall, the results obtained are different. Nanoparticles can be irreversibly adsorbed on the cell wall or on eukaryotic organelles. In this case, the role of indicator is played by the colour of precipitate. An additional factor indicating localization of the process is the particle size. It can be of the order of a few nanometres [251, 253, 268, 270, 271] or tens of nanometres in other cases; bimodal particle size distributions were also reported. Smaller particles are formed intracellularly, whereas larger ones are formed extracellularly.

Extracellular reduction of silver nitrate (Refs 249, 251, 257, 265, 269, 273) with, *e.g.*, secretion of the fungi *Verticillium* sectered to the environment [272] is accompanied by the formation and stabilization of relatively large silver nanoparticles with a broad particle size distribution. Similar processes involving *Alternaria alternate*,[261] *Aspergillus clavatus*,[262, 263] *Fusarium solani*,[270] *Klebsiella pneumonia*,[254] *Lactobacilli*,[252] *Pseudomonas stutzeri* [258–260] and *Trichoderma viride* [271, 272] can also be treated as extracellular reduction.

A different situation occurs if the redox reaction proceeds extracellularly with localization on the cell wall.[249] In some cases, proteins (reducing agents) are localized on the outer cell wall instead of going to the environment. This effect was observed for *Fusarium oxysporum* [268] and *Bacillus sp*.[249] The reductase contained in the cell wall of *Fusarium oxysporum* is involved in the reduction [268] in contrast to the reductase contained in *Fusarium moniliforme*. In the case of *Fusarium oxysporum*, the reduction reaction is almost completed within 24 h; however, the reaction with *Fusarium moniliforme* does not proceed at all.[269] Nanoparticles produced in the presence of *Bacillus sp*., are mainly localized on cell walls.[249] When using cultures of living microorganisms, one should take into account the fact that metal ions and metal nanoparticles coordinated to functional groups of bioorganic compounds (constituents of the cell wall) can directly influence the intracellular metabolism. Localization of heavy metals on the cell walls can be used in the preparation of cell samples for electron microscopy studies in order to stain microorganisms that can locally reduce silver ions. A similar technique is used for localization of cells, organelles, specific molecules or their fragments. Highly selective biochemical interactions of the body–antibody, gene–antigene, biotin–streptavidin types, *etc*. are known. By modifying the surface of metal nanoparticles with such molecules one can determine the position and visualize the regions of specific binding to them. For instance, modification of the surface of gold or silver nanoparticles with aptamers [278] allows bioorganic compounds to be determined qualitatively and quantitatively with high selectivity even in so complex systems as native biological liquids.

Fixation of metal ions on the outer bacterial cell walls can be used for applied purposes, *e.g.*, extraction or determination of heavy metals in dilute aqueous solutions.[279] The appropriate bacteria are called metallophiles (by analogy with thermophiles, halophiles, acidophiles, *etc*.). Metallophiles should be metal-resistant, which imposes severe restrictions when choosing the strain. Classical representatives of metallophiles include thiobacteria. Preconcentration of metals by biomass is based on two types of processes, *viz*., 'passive' accumulation due to electrostatic and/or coordination interactions of the cell wall constituents with metal ions and the interactions immediately related to the metabolism of microorganisms. Both types of interaction can be used in the development of biotechnological methods for the determination or preconcentration of metals.

4. Intracellular reduction

Intracellular localization of the reduction of metal compounds can be due to the fact that all necessary conditions are met only after silver ions have penetrated the cytoplasmic membrane or to higher rate of intracellular reduction compared to that of the extracellular process. Biosynthesis of nanoparticles using *Bacillus cereus*,[247] *Enterococcus faecium* [251] and *Lactococcus garvieae* [251] proceeds intracellularly. To produce an admissible amount of the final product of biosynthesis, the stabilized nanoparticle should leave the cell. Usually, the diameter of pores in the cell wall is at most 10 nm. In Gram-positive bacteria, the cell wall is much thinner than 10 nm; as a consequence, they are mainly used for the synthesis of smaller nanoparticles.

A severe obstacle to progress in biosynthesis of nanoparticles is the cytoxicity of ions and nanoparticles.[280] Silver nanoparticles stabilized by sodium dodecyl sulfate can penetrate the cell walls and block enzymes involved in the ATP synthesis.[120] This effect should be more pronounced for prokaryotes rather than eukaryotes. If nanoparticles can not only penetrate the cell wall, but also reach mytochondria, cessation of ATP synthesis due to blockage of the Krebs cycle enzymes (*e.g.*, lactate dehydrogenase) becomes fatal and leads to cell loss.[281]

A layer of a stabilizer of nanoparticles prepared by both classical synthesis (*e.g.*, citrate reduction with tricitrate [77] or according to Tollens [120]) and biosynthesis is comprised of molecules that can be used by microorganisms as components of nutrient solution; therefore, a related secondary process is possible. Receptors on the cell wall surface of microorganisms can recognize functional groups or molecular fragments of bioorganic stabilizers. Then, the microorganism can secrete a secretion containing enzymes favouring digestion of these compounds. As a result of chains of transformations, the stabilizing layer can be 'eaten' and the 'naked' surface metal atoms can be recoordinated to the functional groups contained in the bioorganic molecules localized on the cell wall. Thus, a natural response of microorganisms to surface-functionalized nanoparticles causes their loss. This antimicrobial effect of heavy-metal nanoparticles is called the 'Troyan horse' effect.[282]

Our analysis and comparison of trends in the development of chemical and biochemical methods of synthesis of noble-metal nanoparticles suggests that these processes occur concurrently and almost independently. Progress is being made in those research avenues which are of interest for both chemists and biologists, *e.g.*, molecular biochemistry *in vitro* and *in vivo*, studies on the metabolism of living organisms and how it is influenced by the reduction of metal ions (especially, heavy metal ions), formation of nanoparticles immediately in the biological medium. At present, biosynthesis of nanoparticles cannot be considered as a practically valuable alternative to classical chemical synthesis. This is due to the following factors:

— solution of a particular synthetic task usually requires elaboration of a unique, almost non-transferable technique;

— there are objective limitations imposed by the reaction conditions (temperature, pH of the medium, *etc.*).

The development of high-performance and highly selective methods of biosynthesis of metal nanoparticles in the nearest future is hardly probable. At the same time, there is a clearly seen trend towards application of metal nanoparticles in biology. Targeted formation of the surface layer of nanoparticles (*i.e.*, chemical modification with highly specific compounds) is suitable for obtaining new-generation biomarkers. Their operation is based on highly selective processes of the body–antibody type and on the specific properties of nanoparticles, *e.g.*, the plasmon resonance. It is this avenue of research that attracts the main efforts of specialists working in this field of science.

V. Regularities of growth of metal nanoparticles in condensed media

The development of new methods of synthesis of metal nanoparticles with controllable size and shape is impossible without understanding the mechanisms and driving forces of the processes occurring in the reaction medium. These key problems are touched upon in almost all publications in the field. Despite the simplicity of the scheme of key transformations:

$$M^{n+} \longrightarrow M^0 \longrightarrow M_n^0 \longrightarrow M \text{ (bulk metal)},$$

particular reaction pathways and reproducibility of the final results depend strongly on the reaction conditions.

1. Theoretical foundations of the growth of metal particles in condensed media

There are two types of processes used for the preparation of metal nanoparticles in condensed media, *viz.*, bulk (core formation) and surface ones (interaction with the medium). Both types of processes represent different forms of relaxation of the excess energy typical of metal nanoparticles. The trajectory of the motion of the system in the course of such a relaxation can be different, which immediately affects the final distribution of products. Generally, the mechanism of synthesis of metal nanoparticles can be described by the sequence of a few key transformations (see above).

The first step is the reduction of the metal ion; subsequent stages describe the growth of a metal particle from an atom to bulk metal. Each object in this general scheme is characterized by its own thermodynamic and kinetic parameters. Among the four objects, two are stable, namely, the metal cation (starting point) and bulk metal (final point). Metal atoms have the highest excess energy. The effective concentration of metal atoms is a key parameter determining the thermodynamic and kinetic characteristics of the process. Original publications including the description of methods of synthesis of metal nanoparticles in condensed media present almost no numerical values (even estimates) for the effective concentration of metal atoms. The excess energy of metal atoms relative to the bulk phase can be evaluated from the thermodynamic characteristics of vaporization of the metal in vacuum, which includes two phase transitions, namely, melting and vaporization. The numerical values of the enthalpies of these transformations are listed in Table 5.

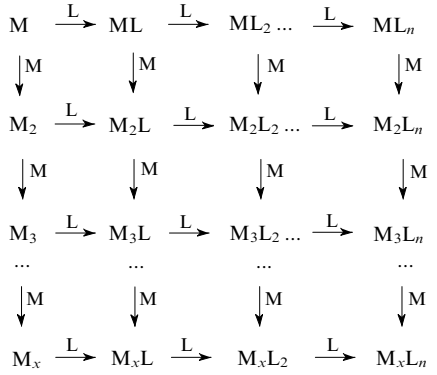
Table 5. Enthalpies of phase transitions and dimerization reactions for some metals.[283]

Metal	Enthalpy /kJ mol^{-1}			Thermal effect of reaction /kJ mol^{-1}
	melting	vaporization	dimerization	$M + M \longrightarrow M_2$
Fe	13.81	416.3	–	–
Co	16.06	424.7	–	–
Ni	17.04	429.7	–	–
Cr	21.03	96.6	–	–
Cu	12.93	337.4	484.2	−190.6
Ag	11.28	289.44	10.0	−168.8
Au	12.72	366.65	15.1	−218.1
Pt	22.17	565.3	–	–
Pd	16.74	378.2	–	–

The enthalpy of dimerization of metal atoms is comparable in absolute value with the enthalpy of chemical reaction. In addition, the formation of small metal clusters from atoms is a barrierless process and proceeds even at about 10 K under the matrix isolation conditions.[284] 'Naked' small metal clusters can exist only in the gas phase in inert atmosphere or in vacuum. If the dimensions of the reactor for vaporization of the metal in vacuum are larger than the free path of the metal atom, the probability of gas-phase dimerization considerably increases. If there are no interactions with the environment, the growth of a particle continues until the formation of a bulk phase. In the text below, this process is conditionally called clusterization.

The second type of interactions possible in condensed media involves chemical reactions activated by atoms and small clusters. In the text below, this type of interactions is conditionally called complexation. A comparison of the energy parameters of the clusterization and complexation reactions showed that the former are energetically more favourable, especially for clusters comprising at most 10 atoms.[285–287]

In the general form, the interaction of a metal atom (M) with components of a condensed medium (L) can be represented as follows:[288]



Complexation can dominate over clusterization if the thermal effect of the chemical reaction of the metal atom with the organic compound. This complexation results in σ- or π-organometallic, metal complex compounds under the conditions of low-temperature co-condensation of vapours of the metal and organic compound, *e.g.*, nickel and bromobenzene,[289] chromium and aromatic compounds,[290] nickel and 1,1′,2,2′-tetracyanoethylene.[291] This type of interactions causes no immediate formation of metal nanoparticles and can only be considered as a channel of relaxation of the excess energy of metal atoms.

Clusterization dominates over complexation until the energies of the processes mentioned above become equal. On the one hand, the interaction of the metal with the components of the condensed medium should be sufficiently strong to provide a decrease in the energy of surface atoms and thus inhibit the growth of particles. On the other hand, it should be weak enough to avoid the formation of stable individual compounds.

The formation of a final metal nanoparticle can conditionally be divided into two stages, the primary (nucleation) and the secondary (formation of the final nanoparticle).[292] As the seeding conditions are met, a nonequilibrium, avalanche-like formation of primary particles usually begins in the reaction medium. This transformation is controlled thermodynamically. The larger the contribution of the chemical component to the nature of this surface interaction the shorter the duration of the growth.

Clusters containing individual metal atoms can be either electrically neutral or charged. Vaporization of silver in vacuum followed by matrix isolation causes the formation of electrically neutral clusters Ag_2 and Ag_3.[284] For reduction of silver ions in a liquid reaction medium, the formation of Ag_2^+, Ag_4^{2+} and similar clusters through incorporation of a metal ion rather than metal atom into the metallic core is more probable.[62, 293] The lifetime of a charged cluster in the condensed medium should be longer than that of the electrically neutral cluster. The reasons are as follows:

— repulsive forces that act between likely charged particles make growth of the cluster less probable;

— surface reduction of the metal ions incorporated into the cluster core by components of the environment is possible; this makes the interactions leading to stabilization of nanoparticles more probable.

2. Isotropic particle growth

If factors that favour or prevent the particle growth along particular directions are absent, spherical particles with the minimum surface area per unit mass (volume) are usually formed. According to calculations, a 1000-fold decrease in the size of a spherical particle (from 1 μm to 1 nm) causes its specific surface area to increase also by three orders of magnitude (from 0.5 to 500 $m^2\ g^{-1}$) and the percentage of surface atoms may be as high as tens of percent (Table 6). At a particle size of about 1 nm, atoms on the surface and in the bulk of the particle become indistinguishable because the particle size corresponds to the doubled lattice constant. Now, the surface-to-bulk atom ratio is determined by the crystal system to which the crystal lattice belongs because the lattice can be significantly distorted if the particle comprises from a few to a few hundreds of metal atoms. Therefore, the values listed above should be considered as numerical estimates only.

Table 6. Size sensitivity of parameters of metal nanoparticles including the number of atoms per particle (A), percentage of surface atoms (B) and the specific surface area (s).

Particle size /nm	A	B (%) (see [a])	s/ $m^2\ g^{-1}$ (see [b])
1	35	~70	508
2	285	~10	254
5	4450	3.5	102
10	3.56×10^4	1.7	50.8
20	2.85×10^5	0.87	25.4
50	4.45×10^6	0.35	10.2
100	3.56×10^7	0.17	5.1
200	2.85×10^8	0.09	2.5
500	4.45×10^9	0.04	1.0
1000	3.56×10^{10}	0.02	0.5

[a] Calculated for layer-by-layer growth with an interlayer spacing of 0.4 nm. [b] Calculated for spherical silver particles with a density of 11.8 $g\ cm^{-3}$.

Often, the initial steps of formation of metal nanoparticles occur under strongly nonequilibrium conditions. Even if there exist physicochemical methods for control of the process, the kinetic characteristics of fast nonequilibrium growth of nanoparticles are such that modern high-speed methods of investigation are too slow. Therefore, the authors of original publications present the qualitative and quantitative characteristics of the final product, which serve as a basis for various hypotheses of the character and mechanisms of fast processes. In the case of metal nanoparticles, the characteristic parameter is the particle size distribution. Solving an inverse problem based on the characteristic particle size distribution, one can reconstruct the growth mechanism. Such a solution can be based on a mathematical model which uses two growth patterns, namely, the step-by-step growth and the concerted growth. In the former case, the growth mechanism involves a layer-by-layer (atom-by-atom) buildup of the particle core. The concerted growth mechanism involves coalescence followed by coagulation of cluster fragments. Both mechanisms lead to formation of spherical metal nanoparticles with a certain particle size distribution.[294, 295] In the case of the atom-by-atom growth of the particle the particle size distribution function $f(d)$ of the final product has the form of a normal (Gaussian) distribution

$$f(d) = a\exp\left[-\frac{1}{2}\left(\frac{d-d_a}{\sigma}\right)^2\right],$$

where a and σ are the characteristic parameters of the distribution and d_a is the average particle size. Considering the particle growth by coagulation and coalescence of cluster fragments, one deals with the lognormal distribution [295]

$$f(d) = a\exp\left\{-\frac{1}{2}\left[\frac{\ln(d/d_a)}{\sigma}\right]^2\right\}.$$

To determine the character of the particle size distribution, the percentages of the particles whose size is at most d ($N < d$) are plotted *vs*. particle size (d) using histograms. Linear dependences are obtained in the coordinates $\log(N < d) - d$ for the normal distribution and in the coordinates $\log(N < d) - \log d$ for the lognormal distribution.[295] Practically, almost all studies on the nanoparticle growth in the liquid or gas phases reveal lognormal particle size distributions.

3. Anisotropic particle growth

Despite the fact that isotropic spherical particles have the lowest energy and are thermodynamically the most stable, their formation can in some cases be accompanied by the formation of non-spherical metal particles. By varying the chemical composition and the structure of the reaction medium or the synthesis conditions one can change the situation in such a manner that non-spherical products will be the major ones.[296] Unlike the primary 'fast' isotropic growth, especially in the initial steps, anisotropic growth is the secondary ('slow') process. It originates from processes similar to Ostwald ripening. The classical Ostwald ripening theory is based on electrolytic dissociation which implies transfer of matter from one particle to another through escape of free ions in the bulk of the solvent. For metal particles, this type of processes is impossible. Even solvated metal atoms cannot be transferred through the bulk of the solvent owing to the excess energy. At the same time, the authors of almost all publications concerning the synthesis of non-spherical metal nanoparticles point that it is based on slow, kinetically controlled transformations. In most cases, non-spherical particles are formed in the two-step synthesis, *viz*., rapid formation of 'primary' particles (seeds) is followed by their transformation to larger, geometrically anisotropic structures. The factors favouring anisotropic growth have been considered in detail in the review.[11]

Based on the results of analysis of numerous experimental data, one can formulate a hypothesis describing the secondary processes of nanoparticle growth and structuring. The early stages of growth in a condensed medium are characterized by the formation of highly reactive small metal clusters. Rapid growth continues until its energy and kinetic characteristics become comparable with the corresponding characteristics of a competitive process (interaction between the surface atoms and components of the environment). The fast growth process leads to formation of a sol of seeds containing both incompletely formed metallic cores and loose surface layers. The metallic core has a highly defect structure capable of self-assembling through crystallization of the inner volume and segregation of the surface layers. In the course of such a crystallization – segregation process, cluster fragments can break away from a less structured nanoparticle and their through-space transfer to another structured nanoparticle is possible.

VI. The structure of the surface layer of metal nanoparticles and the dynamics of changes in it

Some characteristics of metal nanoparticles, *e.g*., hydrophilicity – hydrophobicity, sorption capacity, position of absorption maximum of the surface plasmon resonance and the giant Raman scattering of electromagnetic radiation depend on the chemical composition and structure of the surface. There are no 'naked' nanoparticles in condensed media. The surface of nanoparticles is covered with a layer comprised of adsorbed components of the environment. The composition and structure of this layer directly influence the average particle size. The stronger the interaction between the surface atoms and the adsorbed (chemisorbed) components of the condensed phase surrounding the nanoparticle or the higher the activation barrier to the interactions that break the structure of the surface layer the smaller the particle size corresponding to the formation of a stable colloidal system.

The surface layer comprises not only the atomic layer on the nanoparticle surface, but also the adsorbed (chemisorbed) layer of the condensed medium. Components of the surface layer should not be considered individually; the surface layer is a qualitatively new system whose structure and properties differ from those of the metallic core and the condensed medium.

1. Changes in the surface layer of metal nanoparticles during the synthesis

Nanoscale metal particles coated with an adsorbed layer are metastable systems. They correspond to local rather than global energy minima; the energy of thermal vibrations at a given temperature is insufficient to overcome the barrier. There are two, electrostatic and steric, stabilization mechanisms of this type of colloidal systems. Coagulation of two particles requires the overcoming of a corresponding barrier. Practically, the two mechanisms are rare to occur in pure form. They are based on physisorption of the components that prevent coagulation. The energy is of the order of the energy of van der Waals interactions. In a real system, components of the adsorbed layer can form covalent and coordination bonds with the surface atoms. The contribution of chemisorption is rather large even if, formally, no such bonds are formed. The adsorbate molecule can be electrically neutral under particular conditions and charged under some other conditions. The lone electron pair of the functional group can go to vacant orbitals of the metal atom, thus forming a complex. As a result, one deals with a mixed stabilization mechanism of the final system and the particular components become indistinguishable.

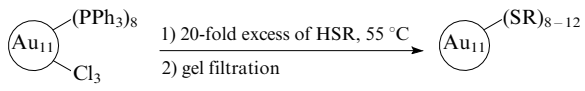
Strictly speaking, a metal nanoparticle at most 1 nm in size has no surface layer at all. The particle size is of the order of the size of 2 – 3 unit cells. On this length scale, interactions of surface atoms with components of the environment are similar to the interactions of individual organometallic and metal complex cluster compounds. Preparation of stable systems with the metallic core in this range of linear dimensions requires a rather strong interaction between metal atoms and the molecules of the environment. The authors of most studies of such objects introduced compounds characterized by sufficiently high

affinity to metals into the starting reaction medium. Most often, these were phosphines (among them, triphenylphosphine was most widely used) and ω-thiol derivatives of various classes of organic compounds.

The stoichiometric compositions of the clusters containing from 7 to 923 metal atoms were also reported.[13, 205, 206, 216, 218, 235, 297–299] However, it should be noted that the corresponding numerical values should be considered as tentative ones if the compositions of the metallic cores were not proved by high-precision methods such as X-ray diffraction analysis or mass spectroscopy. Nevertheless, this information includes experimental data on the dependence of the particle size on the number of atoms in the core rather than the predicted values and can therefore be in some sense valuable.

The surface atoms of 1.5-nm Au_{11} nanoparticles can form the surface donor–acceptor bonds and participate in ligand exchange.[205, 299] The ligand exchange reaction of $Au_{11}(PPh_3)_8Cl_3$ with ω-functionalized thiols is shown in Scheme 4. At the same time, these systems exhibit the properties characteristic of traditional colloid particles having a surface layer with typical hydrophilic–hydrophobic properties.

Scheme 4



Hydrophobic: R = n-C_nH_{2n+1} (n = 3, 6, 8, 12, 16, 18), 4-HOC_6H_4, 4-MeC_6H_4, 4-PhC_6H_4;

hydrophilic: R = $(CH_2)_nCOOH$ (n = 1, 2, 6, 11), $(CH_2CH_2O)_nH$ (n = 2, 3), $(CH_2)_2N^+Me_3Cl^-$, $CH_2CH_2O)_nN^+Me_3Cl^-$ (n = 2, 3), $(CH_2)_2SO_3^-Na^+$.

Electrically neutral and charged gold clusters $Au_{25}SR_{18}$ were reported.[299] Laser desorption ionization mass spectra of the same systems are also available.[300] They exhibit peaks corresponding to clusters containing not only 25, but also 22, 23, 27 and 29 gold atoms. Even if the metallic core becomes destroyed upon desorption under the action of laser radiation, its growth is hardly probable. Most likely, the authors of Refs 299 and 300 synthesized a number of metal clusters with the mass distribution centred at Au_{25}.

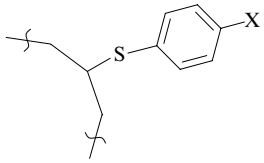
2. Competing processes on the surface of nanoparticles

If competing processes are possible in a real system, the process leading to the maximum decrease in the surface energy dominates. With respect to the energy difference due to stabilization, the processes can be ordered as follows: classical covalent interaction > donor–acceptor interaction > electrostatic interaction.

Covalent bonding between the surface atoms and functional groups of the modifier results in the formation of stable systems characterized by the smallest average particle size. Donor–acceptor interactions of the electron pair of the functional group of the modifier with the vacant orbitals of the surface atoms can lead to formation of stable colloids containing larger particles than in the case of covalent bondng. Competition between electrostatic and donor–acceptor stabilization under comparable conditions gives the smaller particle size in the latter case. Having prepared a colloidal system using a modifier that provides a smaller (in absolute value) decrease in the surface energy, one can then replace the surface layer by a compound which is a better stabilizer. However, one should keep in mind that this is an irreversible process.

3. Chemical modification of nanoparticle surface

By introducing a stabilizer bearing a functional group with high affinity to metals ('anchor' group) into the starting reaction mixture one can obtain functionalized metal nanoparticles in one step. Most often, the role of the 'anchor' group is played by the thiol group. In addition, the stabilizer molecule bears a target functional group, which subsequently determines the nature of the nanoparticle surface. A fragment of the surface of a gold nanoparticle modified with short-chain aromatic thiols[223] can schematically be represented as follows:

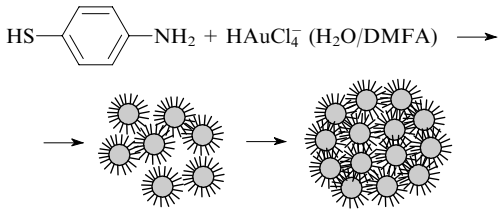


X = OH, COOH, NH_2, Me.

Gold nanoparticles functionalized with thiophenols were synthesized.[223] The use of the thiophenol 'anchor' group determines the average particle size, which appeared to be almost the same in all experiments.

The nature of the outer functional group can influence the agglomeration or self-organization of nanoparticles. An increase in the concentration of *p*-aminothiophenol in the starting reaction mixture leads to a more dense grafting of modifier to the surface. This makes coordnation of metal nanoparticles to the outer amino groups more probable. As a result, particles with higher grafting density form three-dimensional agglomerates (Scheme 5).[235]

Scheme 5



A monolayer of a sufficiently long-chain stabilizer represents a weakly ordered system with labile terminal functional groups (Fig. 5).[217] Unlike the short-chain, *p*-aminothiophenol-type modifiers in which the position of the terminal functional group is almost fixed by the phenyl fragments, the arrangement of terminal hydroxyl groups resembles the situation for a polymer molecule in solution with no rigid fixation to the nanoparticle surface.

The composition and structure of the surface layer also may influence the slow restructuring processes occurring in the metal. The effect of the surface layer on the shape of silver particles was described.[95] The starting colloid containing sodium citrate-stabilized silver nanoparticles can undergo a secondary transformation to both spherical and triangular nanoplates. A proposed model for the converson of silver nanospheres to nanoprisms is shown in Scheme 6.[95]

The modifier molecules containing rather long-chain hydrocarbon substituents, can form micelle-like structures. Coordnation of poly(3-hexylthiophene) to hexadecylamine-stabilized silver nanoparticles was reported.[301] Nonpolar

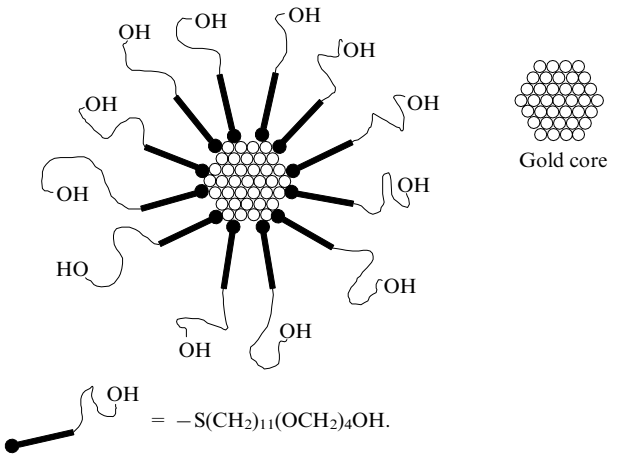
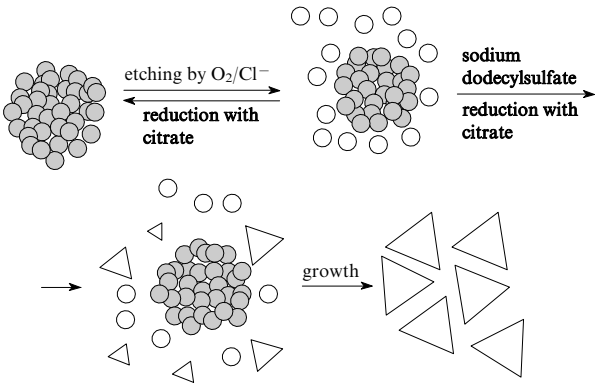


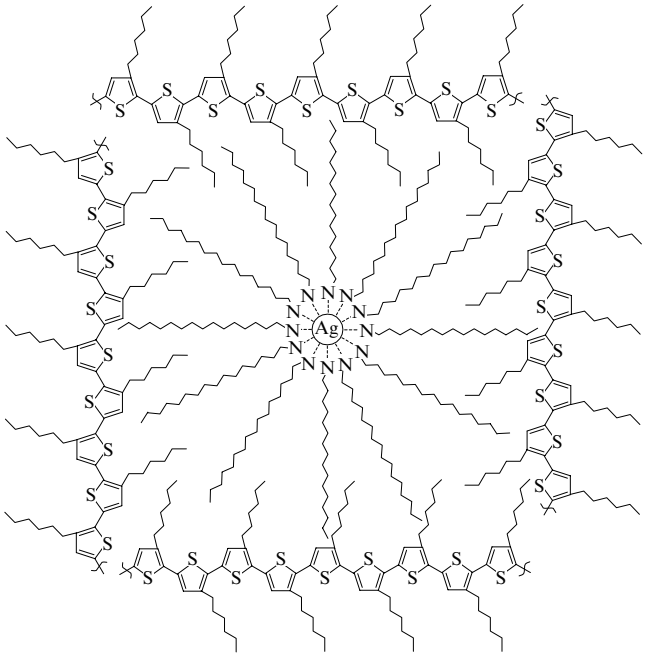
Figure 5. Schematic representation of a gold nanoparticle stabilized by a monolayer of 1-mercapto-1,1-(ω-hydroxytetraethylene glycol).[217]

Scheme 6



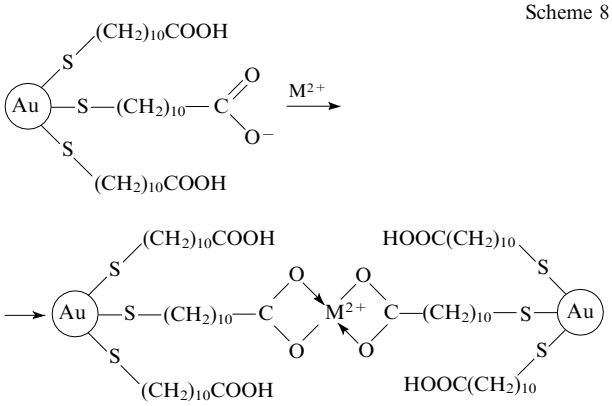
fragments of the hexyl chains of polythiophene are packed with the hexadecyl substituents of the amine (Scheme 7).

Scheme 7



Outer functional groups of modifiers can form complexes with transition metal cations to produce clusters based on other metal nanoparticles. Dimerization of gold nanoparticles through complexation of functional groups of the surface modifier with metal ions is illustrated in Scheme 8.[302]

Scheme 8



M = Pb, Cd, Hg.

A key role in obtaining such clusters[302] is played by the density of grafting of the modifier. At a sufficiently high degree of grafting, aggregation of nanoparticles is possible due to multicentre complexation which leads to chains or even three-dimensional aggregates of nanoparticles, as is observed in micrographs.[302] At the same time, by changing the concentratons and component ratios one can control the clusterization of nanoparticles and form or destroy associates when necessary.

VII. Conclusion

Rapid increase in the number of studies on the synthesis and practical applications of metal nanoparticles observed in the recent decade is due to two main reasons:

— emergence of new methods of investigation, which allow one to control processes and formulate the mechanisms of growth of the nanoparticle core and successive transformation of the surface layer; and

— extension of the field of practical applications of metal nanoparticles as a results of social interest in nanotechnologies.

At present, metal nanoparticles are considered as promising for a number of applications. In medicine and pharmacology, they are of interest as supports (matrices) for immobilization of pharmaceuticals including targeted delivery of pharmaceuticals. The possibility of practical implementation of synergistic biological action of nanoparticles and the pharmaceutical grafted to their surface has been intensively studied. Here, the main problems include studies on the mechanism of the interaction of nanoparticles with cells and penetration of nanoparticles through the blood–brain barrier and other barriers in organism. A new field of scientific research called nanotoxicology emerges.

Yet another avenue of medicine-related applied research on nanoparticles is the laboratory express analysis of biological liquids. Here, application of nanoparticles allows one to improve the selectivity of the analyte determination and to reduce the detection limit. Nanoparticles can be stabilized by various highly selective and highly specific traps used in biochemical analysis, in particular, DNA

sequencing. We believe these systems are promising for such practical applications as the design of biosensors. Seemingly, the use of aptamers, *i.e.*, oligomucleotides characterized by extremely high specificity to biomolecules and many organic compounds is also a topical avenue of research in the title field.

In some cases, nanoparticles allow one to give up on enzymes; this seems to be promising for clinical analysis. Wide use of the new methods in biomedical diagnostics is hampered by the lack of commercially available nanoparticle kits and by the psychological barrier due to the lack of experience on operation with nanoparticles. Both these obstacles are not insurmountable and the 'nanoparticle' methods may appear to be a good supplement to classical biochemical methods.

Metal nanoparticles attract considerable attention of materials scientists. Filling metallic and non-metallic matrices with nanoparticles enables fabrication of composite materials with unique properties. Nanoparticle clusters are promising for the synthesis of metamaterials, for practical applications of nonlinear optical materials and as supports for the giant Raman scattering.

The authors of some publications use metal nanoparticles as supports for immobilized metal complex catalysts. On the one hand, this simplifies the removal of the catalyst from the reaction product. On the other hand, it allows one to achieve synergistic effect in the catalytic action of the grafted complex and the nanoparticle supports for the giant Raman scattering.

However, successful solution to all problems listed above (and omitted ones) requires experience on the preparation of stable concentrated metal sols in both aqueous and organic media, control of the hydrophilic–lipophilic balance and targeted synthesis of nanoparticles with a particle size distribution as narrow as possible and nonspherical particles.

An analysis of the available literature made in this review showed that all synthetic methods do not allow one to obtain 'naked' metal nanoparticles in condensed media. The surface layer, which is unavoidably formed during the synthesis, has strong and in some cases crucial impact on the properties of materials.

Therefore, the development of efficient methods of synthesis of metal nanoparticles with controllable size and shape and showing the necessary sorption, optical, antibacterial and other properties is impossible without understanding the nature of the interactions within the surface layer and its transformations.

Our analysis of the published data also showed that the processes immediately related to the formation of nanoparticle dispersions in condensed media can be accompanied by the secondary processes including the growth, structural ordering and changes in the shape of particles. The understanding of their nature and knowledge of the thermodynamic and kinetic characteristics makes it possible to predict some parameters of the surface layer, *e.g.*, its shape, size, structure and stability.

At present, there is a number of well-recognized avenues of progress in the field of preparative-scale synthesis of metal nanoparticles:

— classical synthesis of nanoparticles involving reduction of metal ions in confined media; the method enables the synthesis of nanoparticles with shape anisotropy;

— reduction of metal ions with organic and bioorganic reducing agents; a combination of mild reduction with organic compounds with the possibility of formation of supramolecular structures due to the presence of polymeric coordinating agents in the reaction medium allows one to synthesize a number of biocompatible materials which cannot be obtained by the classical methods;

— the use of biotechnological methods (reduction *in vitro*) for targeted synthesis of metal nanoparticles; the advances in genetic engineering allow one to produce and grow strains capable of reducing metal ions (including heavy metal ions) under mild conditions with a sufficiently high performance;

— the development of synthetic methods involving chemical modification of the surface of metal nanoparticles.

The last-mentioned avenue sometimes requires much greater efforts than the synthesis itself. In practice, nanoparticles just synthesized are rarely used as is; usually, they are chemically modified in the layer-by-layer fashion. As a result, the final product represents a system of high complexity comprising the metallic core and a system of grafted layers of the modifier.

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