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Mediated electrochemical synthesis of metal nanoparticles

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The review integrates and analyzes data of original studies on the mediated electrosynthesis of metal nanoparticles — a new efficient and environmentally attractive process for obtaining these particles in the solution bulk. The general principles and specific features of electrosynthesis of metal nanoparticles by mediated electroreduction of metal ions and complexes are considered. The discussed issues include the role of cyclic voltammetry in the development of this method, the method efficiency, some aspects of selection of mediators, and aggregation, stabilization and catalytic activity of the metal nanoparticles thus obtained. Analysis of the results of mediated electrosynthesis of Pd, Ag, PdAg, Au, Pt and Cu nanoparticles stabilized by various compounds and mediated electrogeneration of highly active metal particles is used as basic data for discussion.
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1. Introduction

In recent years, metal nanoparticles (MNPs) have been among the most actively studied nanoobjects. This interest is due to unique physical and chemical properties of these particles and wide diversity of their potential applications, which include catalysis, biomedicine, optics, electronics, sensorics and so on.[1–15] Metal nanoparticles have been known for a long time, for example, the AuNPs (colloidal gold) were first prepared by Faraday back in 1857 [16] by chemical reduction of a gold salt in an aqueous solution, but they have been actively studied only for the last ~25 years. The MNP preparation methods are conventionally divided into physical, chemical, biochemical and electrochemical. Initially, physical methods based on evaporation of massive metal induced by a particular physical impact and their subsequent condensation as NPs were considered to be most promising.

Currently, chemical reduction of metal ions † in solution using various reducing agents is the most successful and popular method for MNP preparation. Biochemical methods have found limited use for the preparation of MNPs; only a few cases of synthesis of gold, silver, copper and zinc NPs have been reported.[17,18]

Electrochemical processes are normally used to prepare MNPs and nanocomposites based on them supported on a conducting substrate (electrode). A variety of electrochemical procedures have been analyzed in reviews.[19–21] The properties of MNPs synthesized in this way are widely studied in electrocatalytic reactions. However, for more extensive use of MNPs, in particular, as catalysts of chemical reactions, it is necessary that they occur in the solution bulk in some other states, *e.g.*, in a stabilizer shell, on non-

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† Hereinafter, by metal ions are meant not only solvated ions, but also their complexes.

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conducting solid supports, in matrices, nanocapsules and so on. The electrochemical methods for the synthesis of such MNPs are little developed, but they are of obvious interest as they are environmentally benign; this has stimulated us to integrate for the first time the available results on this subject.

First of all, it is noteworthy that dispersion of a massive metal electrode during electrolysis is one of the electrochemical processes for the preparation of colloidal metal in solution. This process was described for the first time by Haber[22] more than 100 years ago and was later discussed in other studies (see, for example, Refs 23–29) as regards corrosion of electrodes and formation of monometallic (Bi, Pb, Sn, Pt, Rh, Au, Cu, Ag, Ni) and bimetallic (Pt–Rh, Pt–Ru, Pt–Ni, Au–Co, Au–Cu, Fe–Co) NPs at high cathode potentials (current densities) in the direct- or alternating-current mode. These results are discussed in the review of Petrii.[19] In recent years, this method was further developed in the studies of Smirnova and co-workers.[30–37] The authors successfully used dispersion under alternating current in alkaline aqueous solutions for targeted generation of platinum and platinum alloy nanoparticles in solutions. They obtained particles with average sizes from 3 to 12 nm on various supports (carbon, graphene, metal oxides, carbon/metal oxide composites), which were of interest as catalysts for low-temperature fuel cells. The presumptive scheme of NP formation[37] includes numerous electrochemical and chemical steps, key steps being the reduction of alkali metal ion, the insertion of the resulting metal atom into platinum, its subsequent chemical and electrochemical oxidation and oxidation of the hydroxide ion. The process occurs at high cathode and anode potentials and is accompanied by hydrogen evolution.

Other methods for MNP preparation under mild conditions based on the electroreduction of metal ions are more attractive. The metal generated in this case is known to be deposited on the electrode surface. This method underlies industrial manufacturing of metals and metal black, as well as metal plating and metal refining processes.[38] In the presence of MNP stabilizers, the proportion of the deposited metal decreases, but still remains high. Indeed, in the preparation of AgNPs in aqueous solution by the electroreduction of silver ions in the presence of poly(*N*-vinylpyrrolidone), up to 80% of the metal is deposited on the cathode, while in the presence of tetraalkylammonium salts and sodium dodecylbenzenesulfonate, the generated metal is deposited at the cathode almost entirely.[39,40] Metals (Na, Li, Ga, Al, Pd, Au, Ag, Zn, *etc.*) and alloys are deposited on the cathode upon the electroreduction of ions in ionic liquids,[19,41–48] which combine the properties of the solvent, supporting electrolyte and MNP stabilizer. Therefore, in all new methods used to generate MNPs, the metal deposition problem is solved in some way. For example, in order to reduce the contribution of this process, the use of pulse sonoelectrochemistry was proposed. The accumulation of MNPs on the electrode upon short-term pulse electrolysis was combined with subsequent transfer of these NPs into solution upon sonication of the electrode (Scheme 1).[49–51] This procedure was employed to obtain Cu, Zn, Co, Ni, Cr and Ag nanoparticles and Co–Ni, Fe–Ni, Fe–Co and Fe–Co–Ni alloy nanoparticles with a typical average size of 10 nm to 1 μm; however, the need for sonication complicates the process.

Scheme 1

$$n M^{z+} + n z e^- \longrightarrow (M^0)_{n,\,dep} \xrightarrow{\text{sonication}} (M^0)_{n,\,sol}$$

where $(M^0)_{n,\,dep}$ are deposited particles and $(M^0)_{n,\,sol}$ are solvated particles.

One more method for electrosynthesis of MNPs in the solution bulk was proposed by Reetz and co-workers.[52–57] The method includes electrolysis in aprotic organic media (tetrahydrofuran, dimethylformamide, acetonitrile or their mixtures) in an undivided cell with a sacrificial anode, a platinum cathode and tetraalkylammonium (R_4N^+) or -phosphonium (R_4P^+) salts with long alkyl substituents R as supporting electrolytes. The proposed scheme of the process (Scheme 2) includes the dissolution of the anode to give metal ions, which diffuse towards the cathode surface and are reduced there to the metal(0). It is believed that the ammonium and phosphonium surfactant cations prevent the metal deposition on the electrode and stabilize MNPs in solution. This method was used to obtain ultrasmall ($\leqslant$10 nm) Pd, Co, Ni and Ti nanoparticles. Subsequently this method was employed to synthesize Ag,[39,58] Cu[59] and Au[60,61] nanoparticles. Using two sacrificial anodes connected to two power sources, bimetallic Ni–Pd, Fe–Co and Fe–Ni nanoparticles were prepared.[57] Although this method is simple, its application is restricted to the use of aprotic media and surfactant cations. Note also that in the beginning of the electrolysis, where no metal ions are present in the solution, the cathodic process evidently involves the electrochemical reduction of the supporting electrolyte cation, and the influence of this reaction on the generation of MNPs remains obscure.

Scheme 2

Anode: $M_{mas} \longrightarrow M^{n+} - n e^-$

Cathode: $M^{n+} + n e^- + Stab \longrightarrow M_{col}/Stab$

Total: $M_{mas} + Stab \longrightarrow M_{col}/Stab$

Here M_{mas} is massive metal, M_{col} is a colloidal particle, Stab is a stabilizer.

In any case, this side reaction proceeds not only in the beginning, but also for some time during the subsequent electrolysis until a sufficient concentration of metal ions is accumulated in the solution to ensure the specified current. Hence, at the end of electrolysis, a certain concentration of metal ions will remain in the solution, with partial metal deposition on the electrode being also unavoidable.[39,40] Probably, the combination of these factors accounts for the fact that the yields of MNPs do not exceed 60% in many cases. Note also that the authors (see, for example, Refs 57–61) often carry out electrolysis in an ultrasonic bath, but do not discuss the role of sonication. The available results of studies on pulse sonoelectrochemistry[49–51] suggest that sonication not only ensures stirring of the solution, but also promotes the transfer of generated MNPs from the cathode surface to the solution bulk and their breaking into smaller particles.

The following designations are used in the review:
AN — acetonitrile,
AFM — atomic force microscopy,
bipy — bipyridine,
CE — current efficiency,
$[Co(sep)]^{3+}$ — cobalt(III) sepulcrate,
CTA — cetyltrimethylammonium ion,
CTAC — cetyltrimethylammonium chloride,
CV — cyclic voltammetry,
DMSO — dimethyl sulfoxide,
DMF — *N*,*N*-dimethylformamide,
DLS — dynamic light scattering,
DCB — *o*-dichlorobenzene,
ER — electroreduction,
GC — glassy carbon,
Med — mediator,
Med_{red} — reduced form of the mediator,
Med_{ox} — oxidized form of mediator,
MNP — metal nanoparticle,
M@Stab — metal nanoparticles encapsulated into a stabilizer shell,
MV^{2+} — methylviologen,
MVCA-C_n^{8+} — tetraviologen calix[4]resorcinarene,
p(MVCA^{8+}–*co*-St) — tetraviologen calix[4]resorcinarene copolymer with styrene,
NP — nanoparticle,
PVP_{10} — poly(*N*-vinylpyrrolidone) with a molecular mass of 10000,
PVP_{40} — poly(*N*-vinylpyrrolidone) with a molecular mass of 40000,
SEM — scanning electron microscopy,
St — styrene,
STEM — scanning transmission electron microscopy,
TEM — transmission electron microscopy,
THF — tetrahydrofuran,
XRPD — X-ray powder diffraction.

2. General principles of mediated electrosynthesis of metal nanoparticles and factors determining the process efficiency

The undesirable deposition of the metal generated upon electroreduction of ions can be markedly suppressed by using the mediated electrosynthesis of MNPs (Fig. 1),[62–85] which has a number of obvious advantages.

2.1. Characteristic features of the mediated electrosynthesis of metal nanoparticles

The key feature is that the metal ions are reduced in the solution bulk rather than on the electrode surface. The main role of the cathodic process is to convert the oxidized form of the mediator (Med_{ox}) to the reduced form (Med_{red}). The latter diffuses from the electrode surface into the solution bulk where it reduces the metal ions. Under conditions of diaphragm electrolysis (see Fig. 1 *a*), the metal ions are usually added to the solution as an appropriate salt or complex, while in the case of an undivided cell, they are generated *in situ* upon anode dissolution during the electrolysis (see Fig. 1 *b*).

In both cases, the cathode potential should correspond to the reduction potential of Med_{ox} and the electric charge passed during electrolysis is strictly equal to that necessary for metal ion reduction. In the case of electrolysis with a sacrificial anode, this is maintained automatically because

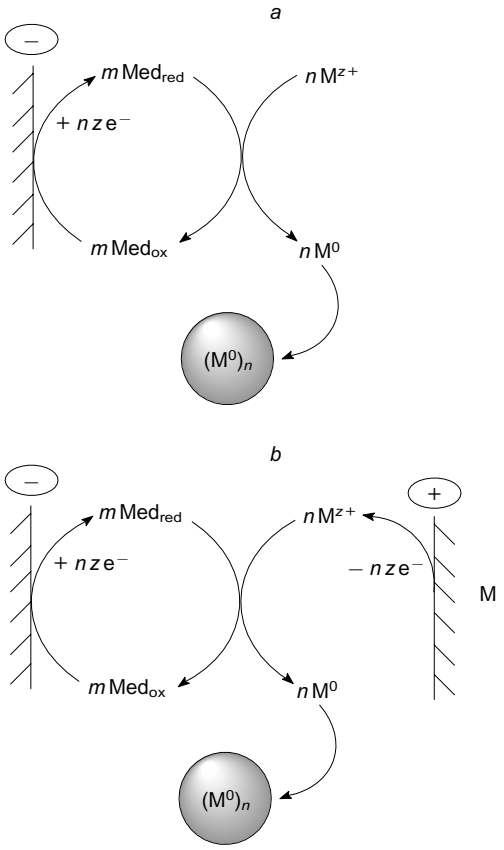


Figure 1. Diagram of the mediated electrosynthesis of nanoparticles $(M^0)_n$ in the solution bulk in a divided (*a*) and undivided (*b*) cell (with a sacrificial anode).[62–85]

the process leads to generation of equivalent amounts of the metal ion and Med_{red}. This process in an undivided cell appears more beneficial, because in the ideal case, the only result of electrolysis is the transfer of the massive metal to the solution as MNPs (Scheme 3), which complies with green chemistry principles.

Scheme 3

Anode: $M_{electrode} - nze^- \longrightarrow nM^{z+}$

Cathode: $mMed_{ox} + nze^- \longrightarrow mMed_{red}$

Solution: $mMed_{red} + nM^{z+} \longrightarrow mMed_{ox} + nM^0$

$nM^0 \longrightarrow (M^0)_n$

Total: $M_{electrode} \pm nze^- \longrightarrow (M^0)_n$

It should be emphasized that mediated electrosynthesis of MNPs (both in a divided and undivided cell) is carried out using usual electrochemical equipment and, furthermore, this method does not involve sonication, which would complicate the equipment and increase the consumption of electricity.

A necessary thermodynamic condition for the mediated electrosynthesis of MNPs, which follows from galvanic cell thermodynamics, is a more negative equilibrium potential

of the Med_{ox}/Med_{red} redox couple with respect to the equilibrium potential of the $M^{z+}/(M^0)_n$ system. The reduction of the mediator on the electrode may occur either more easily or less easily than the reduction of the metal ion.

If Med_{ox} is reduced more easily than the metal ion, the undesirable metal reduction and deposition on the electrode are completely ruled out. Meanwhile, if the mediator is reduced less easily than the metal ion present in the electrolyte, then in the beginning of the electrolysis, both the metal ion and the mediator are reduced on the electrode. The metal thus formed is deposited on the electrode. As the time goes on (a fraction of second or several seconds), a certain concentration of Med_{red} is attained in the near-electrode layer. With appropriate selection of the mediator and the concentration ratio of Med_{ox} and metal ions, the rate of mediated reduction of the latter would be higher than the rate of their diffusion towards the electrode surface. Therefore, a sort of protective layer of Med_{red} is formed in the near-electrode area, which traps and reduces all metal ions arriving from the solution bulk and thus prevents their access to the electrode surface. The thickness of the protective layer increases with time and a part of Med_{red} is distributed throughout the solution bulk as a result of stirring and reduces the metal ions there.

Hence, electrochemistry provides the unique opportunity of virtually selective reduction of the mediator in the presence of the more easily reducible substrate. If metal ions are initially absent and arise only during electrolysis upon the dissolution of the anode material, the protective layer of Med_{red} is formed in the absence of a metal ion, with the latter being reduced only in the solution bulk. Below we show that the mediated process opens up a new, in principle, opportunity for the preparation of MNPs even if the reduction of the metal ion on the electrode is difficult or impossible, for example, if the metal salts (complexes) are insoluble or poorly soluble, if metal ions are encapsulated into micelles, polymer globules or other matrices or immobilized on a non-conducting solid support and, finally, if heterogeneous systems are used in which the cathode and the metal ion are in different phases.

2.2. Factors determining the size and shape of metal nanoparticles and their role

Research directed towards the development of methods for MNP synthesis focuses on the preparation of monodisperse particles of definite size and shape, which determine the properties of these particles. Until recently, this problem has been solved most successfully by chemical reduction of metal ions. Among numerous factors (the natures of reducing agent, metal and stabilizer, their concentration ratio, the medium, temperature, *etc.*) that determine the degree of dispersion, size and shape of the MNPs formed upon reduction, the reducing ability of the reducing agent is among the most important ones. The general trend is as follows: a high reduction rate of metal ions results, most often, in the generation of spherical MNPs of small size, while slow reduction leads to larger MNPs of various shapes (cubes, octahedra, pyramids, wires, films and so on).[1–7]

The natures of reducing agents used for metal ion reduction in the reported chemical[1–7] and electrochemical[62–85] syntheses of noble metal NPs are different. Whereas in the chemical synthesis, chemically stable compounds are used for reduction (such as sodium borohydride, lithium aluminium hydride, hydrogen, hydrazine, alcohols, aldehydes, *etc.*), in the case of mediated electrosynthesis, this role is played by less stable Med_{red} (radical ion species and complexes of metals in low oxidation states). Nevertheless, the general trends established for the chemical preparation of MNPs are also applicable to mediated electrosynthesis. For example, during the mediated electrosynthesis, the metal reduction rate can be controlled by using mediators with different redox properties and, moreover, this opens up a new opportunity for the automatic control over the rate of mediated electrolysis throughout the whole process by varying the concentration of Med_{red} *via* variation of the current (potential) using any specified programme. In turn, when the metal ion reduction rate is controlled, it is possible to obtain MNPs with specified size and shape.

2.3. Effect of the adsorption of Med_{ox} and Med_{red} on the electrosynthesis of metal nanoparticles

So far, while considering the mediated electrosynthesis of MNPs with metal ion reduction in the solution bulk, we assumed that Med_{ox} and Med_{red} are not adsorbed (not deposited) on the electrode. However, in principle, mediated electrosynthesis of MNP may involve the adsorption of Med_{ox} and/or Med_{red} on the electrode.

If Med_{ox} is adsorbed, but Med_{red} is not, the reduction of the metal ion takes place in the solution bulk; in the absence of other complicating factors, the outcome of electrosynthesis would differ little from the results obtained for the case where neither Med_{ox} nor Med_{red} are adsorbed on the electrode. When Med_{red} is adsorbed, the reduction of the metal ion depends on the degree of adsorption and coverage of the electrode surface. If only a part of generated Med_{red} is adsorbed, it will reduce the metal ions in both the solution bulk and the adsorbed Med_{red} surface layer. When all the generated amount of Med_{red} is adsorbed, the reduction of metal ion takes place only in the $(Med_{red})_{ads}$ layer. If the metal ion is reduced more easily than the mediator and the electrode surface coverage with Med_{red} is incomplete, then some of the metal ions will be reduced directly on the electrode, with the metal being deposited on the electrode surface. However, when the electrode surface is completely covered by Med_{red}, a protective (isolating) layer is formed, which rules out the possibility of metal ion reduction directly on the electrode. In this case, the electroreduction is fully mediated and this electrosynthesis of MNPs can be expected to be quite efficient.

2.4. Aggregation of metal nanoparticles

The information given below characterizes the main approaches and methods for suppression of MNP aggregation. The generation of MNPs (irrespective of the process chosen for this purpose) leads to the formation of thermodynamically unstable particles, which are usually prone to aggregation (agglomeration). Suppression of the MNP aggregation is a significant problem. It is addressed using various approaches that include the following:

— decreasing the surface energy of nanoparticles by modifying their surface with neutral or charged ligands (*e.g.*, phosphines,[86–88] amines,[89–91] alkanethiols[92,93]), surfactants (*e.g.*, tetraalkylammonium cations[52–56]);

— separation of MNPs from one another by encapsulation in micelles, *e.g.*, inverse micelles of sodium dodecyl sulfate,[94,95] or by matrix encapsulation.[96–104]

Encapsulation in matrices, especially polymers, is used for MNP stabilization and for the targeted synthesis of hybrid metal–polymer nanocomposites.[1, 5, 20, 21] These MNPs are employed in catalytic reactions[5, 20, 21] and to impart new properties to polymers.[1] A number of methods for the preparation of MNPs inside polymeric shells have been reported. According to the most popular method, MNPs are prepared in the presence of a linear polymer such as PVP,[96] polyaryl ether,[97] polyethyleneimine[98] and so on. This gives rather large metal particles.

One more method is based on the redox reaction between a monomer and a metal salt.[99–101] In this reaction, the metal ion is reduced to metal(0) and the monomer undergoes oxidative polymerization. This gives nano-sized polymeric globules with encapsulated ultrasmall ($\leqslant$10 nm) MNPs. Yet another method for the preparation of MNPs inside the polymer is based on the reduction of metal ions in the presence of polymer nanocapsules,[102–104] the size of the capsule determining the metal particle size.

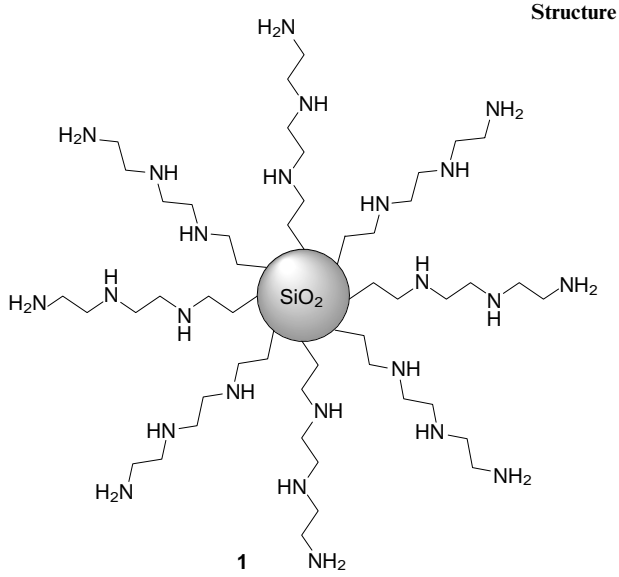
2.5. Stabilization and catalytic activity of metal nanoparticles

An important feature of transition metal NPs that attracts considerable attention of researchers is their high catalytic activity.[1–7,13–15] The considered methods for MNP stabilization prevent their aggregation; however, this also decreases the catalytic activity. This effect is more pronounced in the case of stabilization by ligands rather than by porous polymer matrices or weakly bound surfactants. Therefore, MNPs stabilized by polymers and surfactants are more interesting for catalysis, but unstabilized MNPs on a massive solid support are even more attractive. In the latter case, the immobility of NPs ensures their stability, with a greater part of MNP surface remaining vacant and retaining the catalytic activity.

There are numerous examples[1, 5, 13, 20–22, 31–36, 105–112] of catalytic and electrocatalytic activities exhibited by MNPs deposited on electrodes or other solid supports. However, in these cases, the catalytic reaction zone is limited only to the MNP-coated part of the solid support/solution interface. This drawback can be eliminated by immobilizing MNPs on dispersed or soluble stable nanoparticles of a different nature; for the aggregative stability of MNPs to be retained, the support nanoparticles should be much larger in size. In this case, the whole solution bulk will act as the reaction zone. A collision of nanoparticles may give rise to a bond between the surface metal atoms of two different particles. If the support particles are larger, their thermal fluctuations will cleave the formed bond; therefore, the MNPs attached to the surface of these nanoparticles will be stable against aggregation. If the support nanoparticles are small, the thermal fluctuation energy will be insufficient to cleave the M—M bond formed. As a result, aggregation of the MNPs will take place. The applicable supports include nanoparticles of various nature, in particular, polymers,[113, 114] porous carbon,[30, 32, 33, 115–118] modified carbon nanotubes,[119] graphene,[31] oxidized graphene,[120] silicate NPs (SiO_2),[121, 122] metals,[123] metal oxides,[34, 124–127] carbon — metal oxide composites.[35, 36]

The mediated electrosynthesis allows the preparation of nanocomposites with high catalytic activity in solution. For example, non-modified silica NPs (SiO_2) and alkylamino-modified NPs (SiO_2-NHR) (structure **1**) were used as supports.[65, 70, 73, 75]

Structure 1



1

One more possibility for the preparation of catalytically active particles by mediated electrosynthesis also deserves mention. As has been shown,[128–137] the mediated electroreduction of metal ions can generate, in the solution bulk, metal ions in a low oxidation state, atoms and clusters not stabilized by ligands or stabilizers (bare), *i.e.*, intermediates formed in the initial stages of MNP electrosynthesis. Since they are not stabilized, they exhibit high activity both as catalysts and as reactants; therefore, they have been designated by the notion 'highly active metal particles'. Examples of such reactions will be considered below.

2.6. Choice of mediators and their specific properties

While choosing the mediator, one should adhere to several general principles. First of all, the reduction of Med_{ox} should be chemically reversible (electrochemical reversibility, quasi-reversibility of irreversibility of the reduction make no matter), and the reduced form Med_{red} should efficiently reduce the metal ion to recover the initial Med_{ox}. If the mediator can bind and even stabilize the MNPs, for the preparation of the $(M^0)_n$–$(Med_{ox})_m$ nanocomposite particles generated in the solution, they should not be adsorbed on the electrode or on the walls of the electrolytic cell.[64, 68, 69, 74, 80, 84]

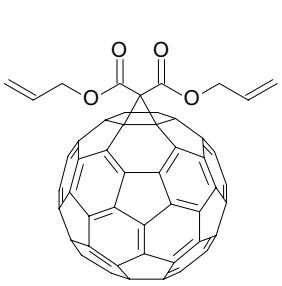
It is noteworthy, however, that in some cases, the ability of Med_{ox} to be adsorbed on the electrode is useful. In recent years, MNPs have been widely studied as the active components of electrochemical sensors,[8, 9, 11, 12] while nanocomposites adsorbed on the electrode may be of interest for the design of this type of sensors.

In aprotic media, many organic, organoelement and inorganic compounds and metal complexes are reversibly reduced both chemically and electrochemically,[138–140] and the range of possible mediators with different reducing abilities is very broad.

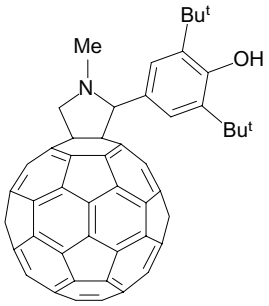
In proton-donor aqueous and aqueous-organic media, the number of possible candidate mediators is smaller, because most of the above-mentioned compounds are reduced irreversibly under these conditions and cannot be used as mediators.

The following compounds have been reported to date as mediators for MNP electrosynthesis in aprotic media:

Structures 2, 3



2 (MF)



3 (FP)

methylviologen,[64, 69, 77] tetraviologen calix[4]resorcinarene,[64, 68, 69] anthracene,[72] molecular oxygen,[76, 79] fullerenes C_{60} [74, 80] and C_{70},[84] 61-bis(allyloxycarbonyl)methano[60]fullerene (structure **2**) and *N*-methyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)fullereno-C_{60}-[1,2-*c*]pyrrolidine (structure **3**).[84]

The mediators used in aqueous and aqueous–organic media include methylviologen [free (Refs 63, 65, 67, 70, 71, 73, 75, 77, 78 and 83), bound to the calix[4]resorcinarene platform,[62, 63] with a polymer nanocapsule *p*(MVCA^{8+}-*co*-St) [66, 82]] or the complexes $[Cr(bipy)_3]^{3+}$, $[Co(bipy)_3]^{3+}$ and $[Co(sep)]^{3+}$ (Ref. 81). All mediators were used at the potentials of the first reversible reduction step (Table 1).

In aprotic solvents, the first reduction steps of anthracene,[139] molecular oxygen,[139] fullerenes C_{60} and C_{70}, MF and FP [141–145] result in the formation of the corresponding radical anions, whereas the reduction of metal complexes in water leads to decreasing oxidation state of the central ion ($M^{3+} \rightarrow M^{2+}$).[146] Each of these mediators transfer one electron, the reduction process is not complicated by the adsorption of components of the redox system, and the current peaks in the cyclic voltammograms are controlled by the mass transfer rate.

Whereas application of metal complexes as catalysts in the chemical and electroreduction of organic compounds is a usual practice, the use of metal complexes as mediators in the electrosynthesis of MNPs is a novel issue.

Anthracene is a well known mediator of electroreduction of organic substrates and metal ions.[128–136] It is used for the same purpose in the chemical synthesis of highly dispersed metals: an alkali metal reduces anthracene to the radical anion, which in turn reduces the metal ions in the solution bulk to give a highly dispersed metal.[147, 148]

The employment of oxygen as a mediator in the reduction processes described below (see Section 4.1) is a new, unusual oxygen application (more commonly, oxygen acts an an oxidant). Oxygen is an environmentally safe gas, soluble in organic liquids under ambient conditions being taken up directly from air up to concentrations quite sufficient for the mediator function.[149] Furthermore, in this case, there is no need to use other mediators and, hence, to separate them from MNPs or to conduct reactions under inert atmosphere.

Table 1. First reduction peak potentials (E_p) of mediators and metal ions.

Substrate	Medium	$-E_{p,\,red}$/V (*vs.* SCE)	Ref.
	Reduction of mediators		
Anthracene	DMF – 0.1 M Bu^n_4NCl	1.92	72
O_2	DMF – 0.1 M Bu^n_4NCl	0.96	76, 79
Fullerene C_{60}	DCB – DMF (2 : 1) – 0.1 M Bu^n_4NCl	70.38	74
Fullerene C_{70}	Toluene – DMF (2 : 1) – 0.1 M Bu^n_4NCl	0.30	84
MF	Toluene – DMF (2 : 1) – 0.1 M Bu^n_4NCl	0.36	84
FP	Toluene – DMF (2 : 1) – 0.1 M Bu^n_4NCl	0.44	84
MV^{2+}	DMF – 0.1 M KPF_6	0.47	77
MV^{2+}	DMSO – 0.1 M Bu^n_4NCl	0.51	64
MV^{2+}	DMF (40 vol.%) – H_2O – 0.1 M KNO_3	0.67	77
MV^{2+}	H_2O – 0.1 M KNO_3	0.72	77
MV^{2+}	H_2O – 0.1 M NaCl	0.70	65
MV^{2+}	H_2O – 0.02 M CTAC	0.80	71
MVCA-C_1^{8+}	DMSO – 0.1 M Bu^n_4NCl	0.41	64
MVCA-C_5^{8+}	DMSO – 0.1 M Bu^n_4NCl	0.42	64
MVCA-C_{10}^{8+}	DMSO – 0.1 M Bu^n_4NCl	0.42	64
p(MVCA^{8+}-*co*-St)	H_2O – 0.1 M NaCl	0.56	66
$[Co(sep)]^{3+}$	H_2O – 0.1 M NaCl	0.60	81
$[Co(bipy)_3]^{3+}$	H_2O – 0.1 M $NaClO_4$	−0.02	81
$[Cr(bipy)_3]^{3+}$	H_2O – 0.1 M $NaClO_4$	0.52	81

Table 1 (continued).

Substrate	Medium	$-E_{p,\ red}$/V (*vs.* SCE)	Ref.
	Reduction of metal ions		
$[PdCl_4]^{2-}$	DMF–H_2O (3 : 2)–0.1 M NaCl	0.91	62
$[PdCl_4]^{2-}$	DMSO–0.1 M Bu^n_4NCl	1.00	64
$[PdCl_4]^{2-}$	H_2O–0.1 M NaCl	~0.15	66
$([PdCl_4]^{2-}\cdot 2CTAC^+)_n$	H_2O–0.02 M CTAC	~0.40	67
$[CoCl_4]^{2-}$	DMF–0.1 M Bu^n_4NCl	2.22	72
Ag^+	H_2O–0.1 M KNO_3	−0.09	77
Ag^+	DMF–0.1 M $Bu^n_4NPF_6$	~ −0.20	79
AgCl	H_2O, 0.1 M $NaBF_4$, SiO_2-NHR	See [a]	70
Au^I	DMF–0.1 M Bu^n_4NCl	0.10	76
Au^I	*o*-DCB–DMF (2 : 1)–0.1 M Bu^n_4NCl	0.03	74
Au^I	H_2O–0.1 M NaCl	~ −0.29	73
$PtCl_2$	DMF–H_2O (2 : 3)–0.1 M KPF_6	See [b]	75
Cu^{2+}	DMF–H_2O (3 : 2)–0.1 M $Bu^n_4NBF_4$	0.10	83

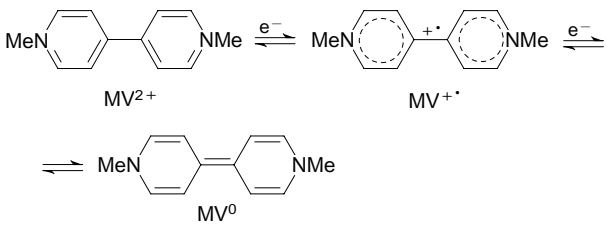
[a] No peak, [b] no clearly defined peak.

Fullerenes are new objects that attracted researchers' attention on the verge of the 21st century. From the electrochemical standpoint, they are of interest, first of all, because they are capable of stepwise and reversible attachment of up to six electrons per molecule to give stable mono- and polyanions.[141–145] The anionic reduction products of numerous fullerene derivatives, in particular, many methanofullerenes and fulleropyrrolidines are also rather stable.[150] The reversibility of the electron transfer steps makes fullerenes and their derivatives applicable as mediators for the transfer of one or several electrons from the electrode to the substrate. The radical anions and dianions generated from fullerenes and their derivatives are not protonated by proton donors such as water and phenol.[150–154] Therefore, fullerenes and their derivatives can act as mediators at the potentials of generation of these anionic species not only in aprotic, but also in moderately proton-donor media, which considerably extends the scope of applicability of these compounds as mediators. It should be emphasized that the potential of fullerenes and fullerene derivatives as mediators is far from being fully disclosed.[74, 80, 84] Only several available publications consider the mediator behaviour of fullerenes C_n at the generation potentials of radical anions $(C_n)^{-\bullet}$, dianions $(C_n)^{2-}$ and tri(radical anions) $(C_n)^{3-\bullet}$ in the electroreduction of organic compounds,[155–169] oxygen [170] and nitrite ions.[171]

While turning to consideration of the electrochemical behaviours of methylviologen, tetraviologen calix[4]resorcinarenes and polymer viologen-containing nanocapsules, we would like to point out that the electroreduction of methylviologen proceeds in two steps at relatively low potentials to give the $MV^{+\bullet}$ radical cation in the first step and neutral diamine MV^0 in the second step (Scheme 4).[172]

The reversibility of the peaks C_1, A_1 and C_2, A_2 in Fig. 2 indicates that both products of methylviologen reduction are stable in both aqueous and non-aqueous media. The electrogenerated $MV^{+\bullet}$ (peak C_1) can potentially transfer

Scheme 4



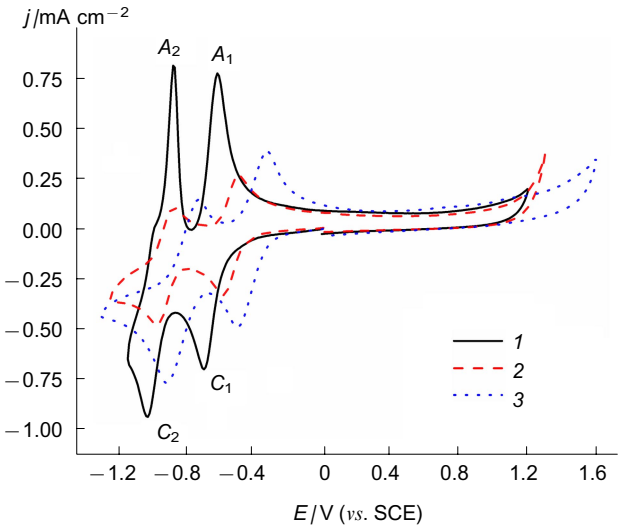


Figure 2. CV curves for MV^{2+} (2.0 mmol litre^{-1}) in H_2O–0.1 mol litre^{-1} NaCl (*1*),[73] 60% aqueous DMF–0.1 mol litre^{-1} NaCl (*2*)[63] and DMF–0.1 mol litre^{-1} $Bu^n_4NPF_6$ (*3*).[69] GC electrode, potential sweep rate v = 100 mV s^{-1}. For peaks A_1, A_2, C_1, C_2, see the text.

one electron, while MV^0 (peak C_2) can transfer two electrons, and each of these species can reduce ions of many metals.

A mediated process involving methylviologen can be conveniently monitored visually. The point is that the $MV^{+\bullet}$ radical cations are intensively blue-coloured [172] and the solution colour appears only after the exhaustive reduction of M^{z+} ions when the $MV^{+\bullet}$ radical cations are no longer consumed and start to be accumulated in the solution bulk. Owing to this fact, together with the ready solubility of methylviologen salts and reduction products in polar media, methylviologen is a promising mediator for MNP electrosynthesis.

The mediators that have been used in a series of experiments include not only methylviologen MV^{2+}, but also tetraviologen calix[4]resorcinarenes in a cone conformation with methyl ($MVCA-C_1^{8+}$), pentyl ($MVCA-C_5^{8+}$) and decyl ($MVCA-C_{10}^{8+}$) substituents attached to the lower rim of the calix[4]resorcinarene platform and four viologen moieties at the upper rim (Scheme 5).[62–64, 68, 69]

In this respect, the previously obtained data on the use of tetraviologen calix[4]resorcinarenes for the design of new molecular devices and supramolecular systems with electrochemically controllable non-covalent interactions proved to be quite useful.[173–181] According to Schemes 4 and 5, the electroreduction of the above mediators is reversible and includes two steps giving stable radical cations and neutral diamines, respectively. Since all four viologen units in calixresorcinarenes are reduced at the same potential, reduction at the first step potential gives the $MVCA-C_n^{4(+\bullet)}$ tetra(radical cation), while that at the second step potential yields neutral $MVCA-C_n^0$ (see Scheme 5).[173–181] All calix[4]resorcinarenes are reduced at the same potential, but somewhat more easily than MV^{2+}.

The $MVCA-C_n^{4(+\bullet)}$ tetra(radical cation) can potentially serve as a donor of four electrons; as the electrons are transferred, the donor ability is retained, *i.e.*, $MVCA-C_n^{4(+\bullet)}$, $MVCA-C_n^{5+3\bullet}$, $MVCA-C_n^{6+2\bullet}$ and $MVCA-C_n^{7+\bullet}$ are equally prone to give off electrons. This is a rather unique case for organic compounds, as their donor ability commonly decreases as electrons are detached (for example, the fullerene radical pentaanion $C_{60}^{5-\bullet}$ is less prone to give off an electron than the hexaanion C_{60}^{6-}; in the case of the C_{60}^{4-} tetraanion, this ability is even lower.)

In principle, the $MVCA-C_n^{4(+\bullet)}$ tetra(radical cation) is capable of reducing four singly charged metal cations M^+ to give $(M^0)_4$ clusters and can stabilize this cluster in the calix[4]resorcinarene cavity by means of donor–acceptor interactions with four viologen electron–acceptor units.

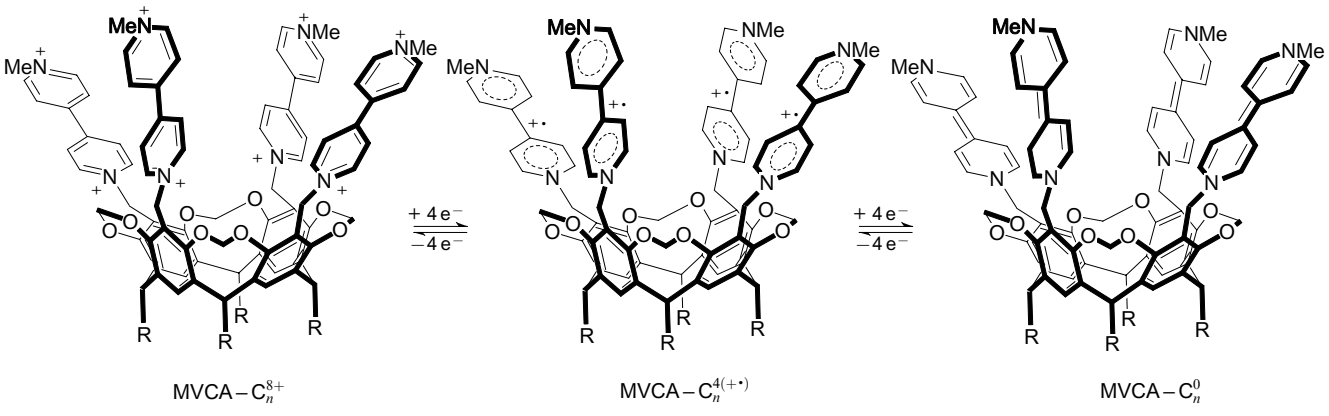
In addition, calix[4]resorcinarenes contain hydrophilic (methylviologens) and hydrophobic (calixarene platform and hydrocarbon groups at the lower rim) moieties. Therefore, similarly to other amphiphiles, they are prone to self-association [182] and are potentially able to stabilize MNPs also by encapsulation into the hydrophobic cavities of the associates.

Thus, at the first step reduction potentials, tetraviologen calix[4]resorcinarenes can simultaneously function as both mediators (multielectron transferring agents) and MNP stabilizers. The attractiveness of $MVCA-C_n^{8+}$ as mediators in the electrosynthesis of MNPs in the solution bulk is somewhat limited by two complicating factors, namely, adsorption of the initial ($MVCA-C_n^{8+}$) and reduced ($MVCA-C_n^{4(+\bullet)}$) species on the electrode and the ability of radical cations of the viologen moieties to form π-dimers.

These factors are virtually absent in organic solvents, in particular, in DMSO, at the $MVCA-C_n^{8+}$ concentration of 0.5 mmol litre^{-1}. Indeed, in DMSO, calixresorcinarenes and their reduced forms (except for $MVCA-C_{10}^{8+}$) are not adsorbed on the electrode and the corresponding radical cations are not π-dimerized. However, on going from non-aqueous to aqueous–organic and aqueous media, the contribution of the adverse factors sharply increases. For example, the proportion of the π-dimer of $MVCA-C_5^{8+}$ is 75% in 90% aqueous DMF, 90% in 30% DMSO and virtually 100% in pure water, although the methylviologen radical cations $MV^{+\bullet}$ do not undergo π-dimerization under similar conditions and at similar concentrations.[168]

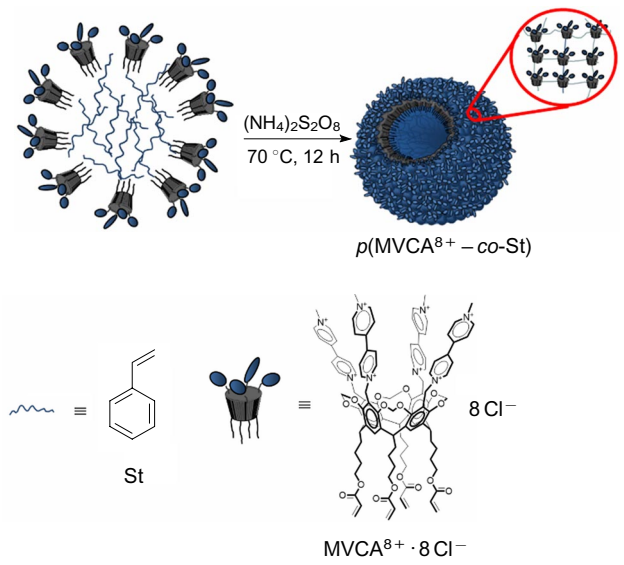
The π-dimerization [178–181] affords difficult-to-oxidize macromolecular associates (π-polymers), which are adsorbed and deposited on the electrode.[180] This is accompanied by partial adsorption of the initial calix[4]resorcinarenes, which increases with increasing water content, length of the hydrocarbon groups at the lower rim and volume of counter-ions.[178–181] As a consequence, the mediated reduction of metal ions occurs not only in the solution bulk, but also on the electrode surface and is accompanied by co-deposition of calix[4]resorcinarenes and electrogenerated MNPs on the electrode.

Scheme 5



$MVCA-C_n^{8+}$ $MVCA-C_n^{4(+\bullet)}$ $MVCA-C_n^0$

Scheme 6



The water-soluble viologen-containing polymeric nanoparticle $p(\mathrm{MVCA}^{8+}-co\text{-St})$ prepared by copolymerization of tetraviologen calix[4]resorcinarene (MVCA^{8+}) with styrene (Scheme 6) has voids, which can be considered as a sort of nanocapsules.[82, 113, 183] The electroreduction of this polymeric NP includes two-step reduction of the methylviologen moiety to the radical cation and neutral diamine.[183] The product of first step reduction $p(\mathrm{MVCA}-\mathrm{C}_n^{4(+\bullet)}-co\text{-St})$ is adsorbed on the electrode.

In addition, larger particles of different size formed upon reversible intermolecular π-dimerization of radical cations of the $\mathrm{MV}^{+\bullet}\cdots\mathrm{MV}^{+\bullet}$ methylviologen subunits both within one polymeric nanoparticle and between the nanoparticles are deposited on the electrode to give the π-polymers $[p(\mathrm{MVCA}_n^{4(+\bullet)}-co\text{-St})]_n$.[66, 82] The reductive ability is much lower for the $\mathrm{MV}^{+\bullet}\cdots\mathrm{MV}^{+\bullet}$ dimers than for the $\mathrm{MV}^{+\bullet}$ monomers. The adsorbed $p(\mathrm{MVCA}_n^{4(+\bullet)}-co\text{-St})$ and deposited $[p(\mathrm{MVCA}_n^{4(+\bullet)}-co\text{-St})]_n$ form a protective layer which prevents the metal ion reduction directly on the electrode. In this case, the mediated reduction of metal ions occurs on the electrode surface bearing the adsorbed and deposited reduced mediator species rather than in the solution bulk (Fig. 3).[82]

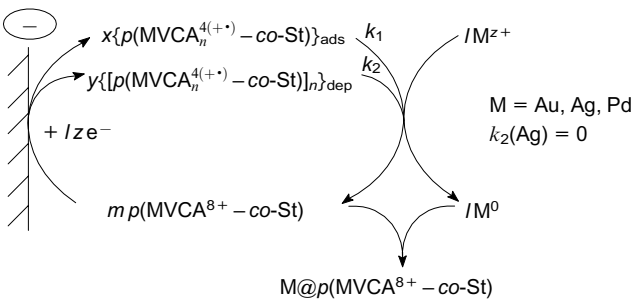


Figure 3. Scheme of $p(\mathrm{MVCA}^{8+}-co\text{-St})$-mediated reduction of metal ions.[82]

3. Cyclic voltammetry in the mediated electrosynthesis of metal nanoparticles

The mediated electrosynthesis of MNPs implies the mediator reduction during electrolysis under controlled potential. Note that implementation of the reaction on a preparative scale requires that the reduction potentials of the mediator and the metal ion be known and data on the stability and adsorption (deposition) of the initial and reduced forms of the mediator and the metal ion on the electrode be available. Of high value is the preliminary information about the theoretical possibility of mediated electroreduction of metal ions.

This information can be gained using various voltammetry techniques, first of all, cyclic voltammetry (CV). In the voltammetric measurements, the electrode is usually made of the same material as employed in preparative electrolysis, because the electrode material affects both the reduction potentials of metal ions and the adsorption of substrates.

It has been noted above that a necessary thermodynamic condition for mediated electrosynthesis of MNPs is a more negative $\mathrm{Med}_{ox}/\mathrm{Med}_{red}$ equilibrium redox potential (E_{eq}^{Med}) than the $\mathrm{M}^{z+}/(\mathrm{M}^0)_n$ equilibrium redox potential (E_{eq}^{M})

$$\Delta E_{eq} = E_{eq}^{Med} - E_{eq}^{M} < 0 \qquad (1)$$

The major contribution to the equilibrium potential is made by the standard potential E_0 in accordance with the Nernst equation

$$E_{eq} = E_0 + \frac{RT}{n\mathrm{F}}\ln\frac{a_{ox}}{a_{red}} \qquad (2)$$

where R is the universal gas constant, T is temperature, n is the number of electrons, F is the Faraday constant, and a_{ox} and a_{red} are the activities of the oxidized and reduced forms, respectively.

The standard potential E_0 is used rather often as a measure of the equilibrium potential. Since the mediator is not consumed during the mediated reduction and the M^{z+} concentration decreases, for the quantitative mediated reduction of M^{z+}, the difference between the standard potentials of the mediator and the metal ion should be sufficiently high ($\Delta E_0 \leqslant -0.30$ V). The standard potentials depend on the medium and for the $\mathrm{M}^{z+}/(\mathrm{M}^0)_n$ redox system they also depend on the nature of M^{z+} (solvated ion, metal complex or metal salt) and the size of the metal species $(\mathrm{M}^0)_n$. Therefore, the standard potentials of both redox systems should be determined for the conditions of the mediated process.

The E_0^{Med} value can be determined rather easily from a CV experiment as a half sum of the Med_{ox} reduction peak (E_C) and Med_{red} reoxidation peak (E_A) potentials.[184]

$$E_0^{Med} \approx E_{1/2} = \frac{E_C + E_A}{2} \qquad (3)$$

The E_0^{M} value can be determined in a similar way. However, in the latter case, only a rough estimate is possible. The reason is that the oxidation potential of metal nanoparticles depends on the particle size: the larger the MNP, the higher the oxidation potential.[185] The sizes of MNPs that are formed in solution and that are deposited on

the electrode during CV measurement will differ in the general case. Thus, the oxidation potential E_A of the deposited metal will not correspond to the oxidation potential of the MNPs synthesized in solution. However, it is obvious that the oxidation potential of MNPs in solution will be more positive than the M^{z+} reduction potential. Hence, the standard potential E_0^M will be intermediate between the M^{z+} reduction and metal oxidation potentials.

Thus, by measuring the potentials of the reduction (see Table 1) and reoxidation peaks of mediators and metal ions, it is possible to select a mediator that would not be subject to thermodynamic restrictions for the mediated electrosynthesis of NPs of a particular metal under selected conditions. In order to prove the occurrence of the mediated electroreduction of a metal ion, a series of CV experiments is necessary.

The voltammetric responses are sensitive to processes that take place in the near-electrode layer. When the rate of mediated electroreduction of a metal ion is very low and the Med_{red} removal from the electrode surface is diffusion-controlled, this process in the near-electrode layer proceeds to a low extent. As a consequence, voltammetric measurements are insensitive to mediated reduction, for example, as in the $[Co(bipy)_3]^{3+}$-mediated reduction of Ag^+ (Ref. 81) and MV^{2+}-mediated reduction of $PtCl_2$.[75] However, when the rate of mediated reduction is relatively high, this process can be efficiently detected by voltammetric methods. Depending on the particular situation, several CV techniques can be utilized to prove the presence of mediated reduction of metal ions.

The case that the mediator is reduced more easily than the metal ion, which is usual for mediated processes, has been described theoretically and quantitatively.[185] The occurrence of mediated reduction of a metal ion is evidenced by the catalytic gain of the mediator reduction current and a decrease in the Med_{red} oxidation current in the presence of a metal ion. For example, these effects were observed in the anthracene-mediated reduction of $[CoCl_4]^{2-}$ in DMF[72] and the methylviologen-mediated reduction of $[PdCl_4]^{2-}$ in DMSO.[64] When the mediated reduction rate is very high, the CV curves may display the mediated reduction as a pre-peak ahead of the mediator reduction peak C_1 rather than as a catalytic current gain. This is the case for the $[PdCl_4]^{2-}$ reduction in 60% aqueous DMF with methylviologen and tetraviologen calix[4]resorcinarene MVCA–C_5^{8+} as mediators.[62, 63]

If the mediator is reduced less readily than the metal ion, the above approach is inapplicable for detecting the mediated reduction of the metal ion. In this case, the current at the mediator reduction potential is composed of the mediator reduction current, the currents of the mediated reduction of the metal ion and the current of metal ion reduction directly on the electrode. The higher the mediated reduction current, the lower the current of the metal ion reduction on the electrode. Due to the mutual compensation of these two effects, no catalytic gain of the mediator reduction current takes place; therefore, it may seem that mediated reduction of the metal ion does not occur at all. In the same way, the decrease in the Med_{red} oxidation current as a result of the mediated process is counterbalanced by the decrease in the metal ion reduction current on the electrode; as a result, the Med_{red} oxidation current 'does not respond' to the occurrence of the mediated process.

However, in these cases, too, there are techniques[68, 69, 73, 74, 76–79, 81, 83] that allow CV detection of the mediated reduction of metal ions. One of such techniques can be demonstrated in relation to the methylviologen-mediated Ag^+ reduction.[69] The mediated process can be easily evaluated qualitatively by comparing the heights of the oxidation peaks of deposited silver (A_1) generated at the reduction potentials of silver ions (−0.20 V) and the mediator (−0.62 V) for different periods of holding the electrode at these potentials (microelectrolysis). The CV curves presented in Fig. 4 show an increase in the amount of deposited

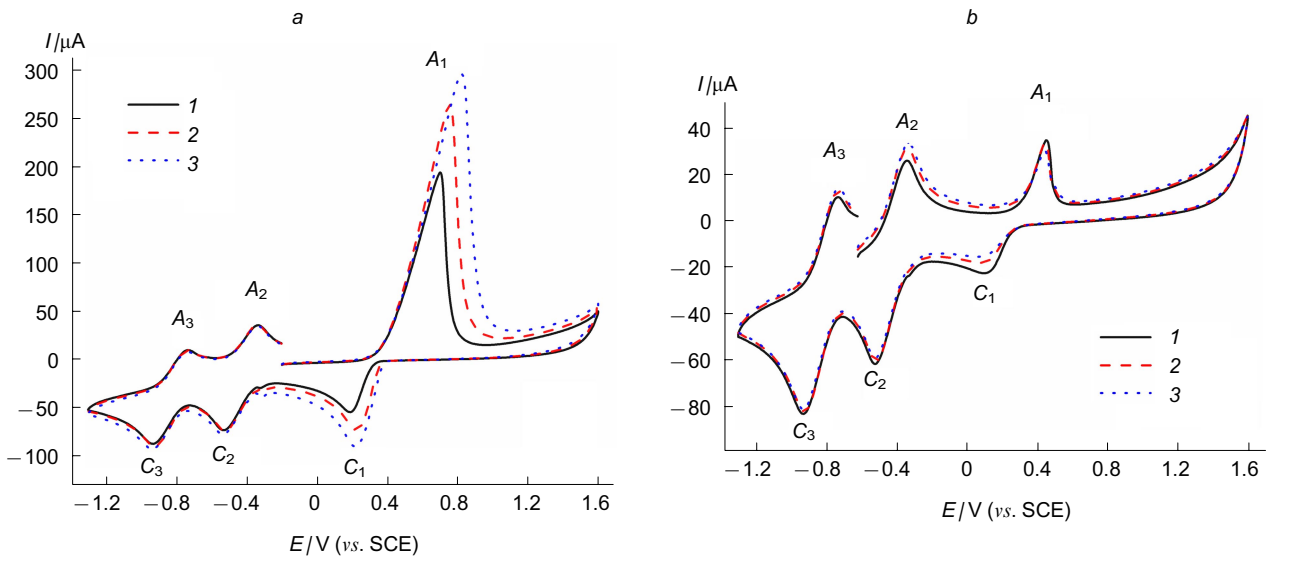


Figure 4. CV curves for the MV^{2+} (2.0 mmol litre^{-1})–Ag^+ (1.5 mmol litre^{-1}) system in DMF–0.1 mol litre^{-1} $Bu^n_4NPF_6$ after holding the electrode at E = −0.20 (*a*) and −0.62 V (*b*) for 1 (*1*), 2 (*2*), 3 min (*3*).
GC electrode, v = 100 mV s^{-1} (Ref. 69). A_1 is the oxidation peak for deposited silver, A_2, A_3 and C_2, C_3 are methylviologen reoxidation and reduction peaks, C_1 is the silver ion reduction peak.

silver with increasing time of keeping the electrode in the solution without stirring at the reduction potential of only silver ions. During similar microelectrolysis at the mediator reduction potential, the amount of deposited silver is much lower and does not increase with increasing time of electrolysis. It is noteworthy that in the latter case, the amount of the generated metal cannot be lower than that in the former case. The observed effect implies that in the latter case, some metal is reduced on the electrode only in the beginning of the electrolysis, while subsequently mediated reduction of silver ions takes place, *i.e.*, the major amount of the metal is generated in the solution.

The occurrence of the mediated reduction of silver ions can also be estimated quantitatively by transforming the CV curves (Figs 4, 5 *a*) to time dependence of the current.[69] This is illustrated in Fig. 5 *b*, which shows the current *vs.* time plot ($I-\tau$) obtained by transformation of the CV curve for the reduction of silver ions in the absence of a mediator in the potential range from the initial value (+0.38 V) to the reverse potential (−0.62 V) and then to +1.27 V. By integrating the dependence $I-\tau$ separately for the reduction and reoxidation, one can determine the quantity of charge (Q_{red} and Q_{ox}) and by using the Faraday law, one can find the amounts of metal generated and deposited on the electrode during recording of the CV curve. The difference between the two last-mentioned values is equal to the amount of the metal in the solution.

The results of this calculation demonstrated (Table 2) that in the absence of a mediator, the generated metal (Ag^0) is almost completely deposited on the electrode and does not migrate to the solution. The metal is also quantitatively deposited if the potential is reversed at −0.20 V.

For the preliminary microelectrolysis, Q_{ox} was calculated in a similar way except that the anodic potential range was extended to +1.50 V, because when the potential reaches +1.27 V, the oxidation currents do not decrease to the background level, that is, the oxidation of the deposited silver still continues at +1.27 V. In this case, Q_{red} can be determined by coulometry or calculated directly from the experimentally measured $I_{red}-\tau$ dependence. However, Q_{red} can be determined more easily by equating it to Q_{ox}, because in the absence of a mediator, the generated metal is quantitatively deposited on the electrode. In our studies, we used the last-mentioned method; therefore, the current efficiency of the deposited metal in the absence of a mediator is always 100%.

The Ag^+ ions are not bound by MV^{2+}; therefore, the Ag^+ reduction peak currents determined by the rate of diffusion of ions towards the electrode are equal in the absence and in the presence of a mediator. Hence, for the presence of a mediator, the values obtained without it were taken as Q_{red}, whereas Q_{ox} was calculated by a method similar to that described above involving the transformation of the experimental CV curve.

It can be seen from the obtained data, which are summarized in Table 2, that in the presence of a mediator when the electrode is kept at the mediator reduction potential, the proportion of the deposited metal is much lower and decreases with time. After 3 min of electrolysis, only 13% of the generated metal is deposited on the electrode and 87% of the metal occur in the solution. The real yields of the metal in the solution are even higher, because the amount of the metal generated in a mediated process is higher than the amount taken in the calculations since the rate of metal ion reduction is determined by the sum of mediator and metal ion diffusion rates.

It is clear that the proof for the mediated reduction of metal ions by the method described above is valid only in the case where the generated metal is deposited on the electrode and is oxidized in the available potential range. This approach was employed for the mediated reduction of Ag^+ ions in organic, aqueous-organic and aqueous

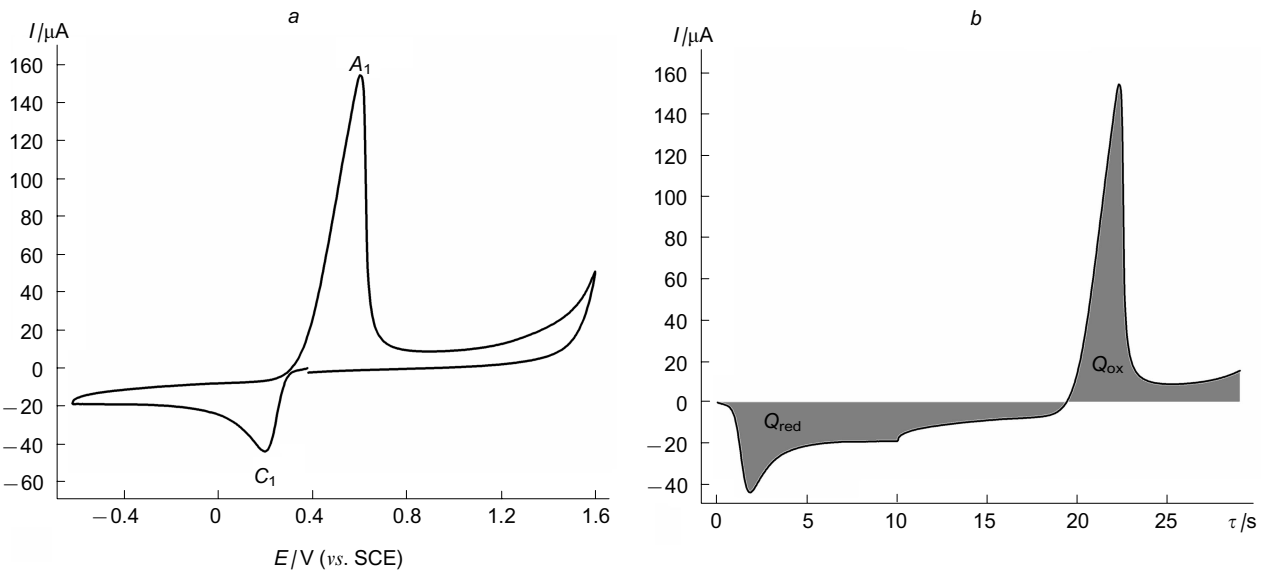


Figure 5. CV curve of Ag^+ (1.5 mmol litre^{-1}) in DMF–0.1 mol litre^{-1} $Bu^n_4NPF_6$, v = 100 mV s^{-1} (*a*) and current *vs.* time dependence (*b*) [obtained by the transformation of the CV curve (*a*)].[69]
(*a*) A_1 is the oxidation peak of deposited silver, C_1 is the reduction peak of silver ions; *b*: Q_{ox} and Q_{red} are the amounts of electric charge consumed for oxidation and reduction of silver ions.

Table 2. Silver ion reduction modes during CV and microelectrolysis and characteristics of the resulting Ag_{dep}.[69]

Reduction of Ag^+			Characteristics of deposited silver			
mode	$-E$/V (see [a])	τ/min (see [b])	E range for the calculation of Q_{ox}/V	Q_{ox}/μA s	m/μg	CE (%)
			No mediator			
CV	0.20	–	0.31–1.27	215	0.24	100
	0.62	–	0.32–1.27	306	0.34	100
Microelectrolysis	0.62	1	0.27–1.50	834	0.93	100
	0.62	2	0.25–1.50	1327	1.48	100
	0.62	3	0.21–1.50	1551	1.74	100
			MV^{2+} *mediator*			
CV	0.20	–	0.31–1.27	211	0.24	100
	0.62	–	0.23–1.27	211	0.24	71
Microelectrolysis	0.20	1	0.26–1.50	569	0.64	68
	0.20	2	0.22–1.50	836	0.94	63
	0.20	3	0.22–1.50	1057	1.18	68
	0.62	1	0.13–1.50	180	0.20	22
	0.62	2	0.13–1.50	192	0.21	14
	0.62	3	0.15–1.50	198	0.22	13

[a] Reverse potential for CV or microelectrolysis potential. [b] Period of holding at a specified potential before recording of the CV curve (microelectrolysis).

media;[68,69,77,79,81] Au^I (Refs 73, 78) and $[PdCl_4]^{2-}$ ions[85] in aqueous media; and Cu^{2+} ions in an aqueous-organic medium.[83] However, the deposited metal is not always oxidized in the available potential range, *e.g.*, gold in DMF or in DCB–DMF and toluene–DMF mixtures.[74,76,79,84] In this case, a different procedure was proposed to prove the mediated reduction of metal ions.[74,84] According to this procedure, the CV curves are also recorded after the electrode was held at the metal ion (−0.10 V) and mediator (−0.40 V) reduction potentials for different periods of time and the reduction peaks of the metal ion (peak C_1) and mediator (peak C_2) are analyzed

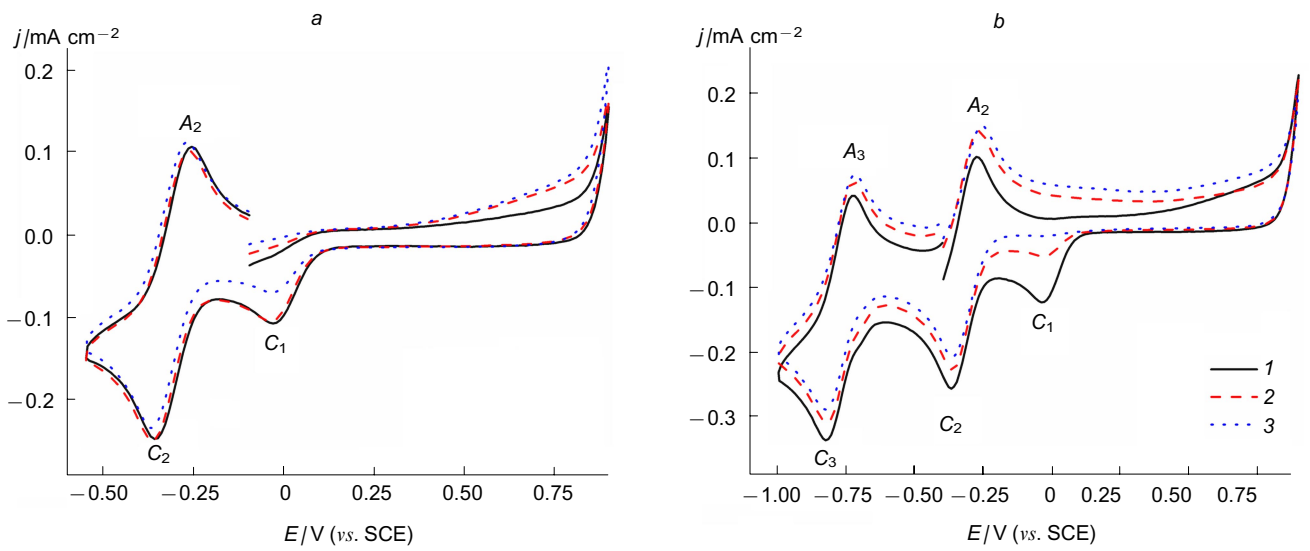


Figure 6. CV curves for the C_{60} (1.5 mmol litre^{-1})–AuCl (1.0 mmol litre^{-1}) system in the DCB–DMF (2 : 1)–0.1 mol litre^{-1} Bu^n_4NCl medium after holding the electrode at potentials E = −0.10 (*a*) and −0.40 V (*b*) for 0 (*1*), 1 (*2*), 3 min (*3*). GC electrode, v = 100 mV s^{-1} (Ref. 74).
C_1 is the reduction peak of gold ions, A_2, A_3 and C_2, C_3 are C_{60} reoxidation and reduction peaks, respectively.

(Fig. 6).[74] During the electrolysis at $E = -0.10$ V, the near-electrode layer is depleted in the metal ions, the diffusion layer becomes thicker with time, and with increasing the process (microelectrolysis) time, the metal ion reduction peak current decreases. At -0.40 V, both the mediator and the metal ion are reduced on the electrode. If no mediated reduction of the metal ion takes place, the metal ion reduction peak current decreases, as in the previous case. If the mediated process does take place, this decrease would be much more pronounced, because the rate of reduction of the metal ion will be determined by the sum of the diffusion rates of the mediator and the metal ion. The mediator reduction peak current remains invariable (see Fig. 6).

Cyclic voltammetry provides quantitative information about the consumption of the mediator and the metal ion in the preparative electrolysis. The information is gained by comparison of the reduction peak currents of the mediator and the metal ion before and after the electrolysis. In addition, in some cases, the MNPs formed in the solution bulk during preparative electrolysis can be detected by CV by observing the peak of their oxidation on the indicator electrode. Metal nanoparticles bearing a stabilizing shell are larger and less mobile than molecules and the currents of their diffusion-controlled oxidation peaks are rather low. Therefore, a necessary condition for reliable experimental detection of the MNP oxidation peaks is adsorption of the stabilized MNPs on the electrode surface. A criterion of adsorption is an increase in the peak current with increasing time of holding the electrode in solution without stirring and without application of the potential.[63]

4. Examples of synthetic applications of the mediated process

In this Section, we consider a number of cases demonstrating the scope of application of the mediated electroreduction of metal ions for the preparation of MNPs and nanocomposites,[62–85] for generation of highly active metal particles[128–137] in the solution bulk and for the use of MNPs obtained in this way as catalysts for organic synthesis.[65, 66, 79, 82, 85]

4.1. Mediated electrosynthesis of metal nanoparticles

The electrolysis conditions at the controlled first step reduction potential of the mediator and characteristics of the obtained MNPs are summarized in Table 3. For comparison, the results of a similar experiment conducted at the metal ion reduction potentials are presented. All electrolyses were carried out at room temperature.

Generally, it can be noted that the mediators chosen on the basis of voltammetric measurements can also function at the preparative level. The mediated electroreduction of metal ions was used to prepare nanoparticles of silver,[68–71, 77, 79–82, 85] gold,[73, 74, 76, 78, 79, 82, 84] cobalt,[72] copper,[83] palladium[62–66, 79, 85] and platinum[75] and bimetallic PdAg nanoparticles[85] in the solution bulk. As can be seen by examining Table 3, the mediated electrosynthesis of MNPs was successfully implemented in aqueous (entries 3, 4, 10, 12–17, 20, 25–39), aqueous–organic ($DMF-H_2O$, entries 1, 2, 8, 9, 21, 45–49) and organic (DMF, DMSO, DMF–DCB, DMF–toluene, entries 11, 18, 19, 22–24, 40–44, 50) solutions; in water–DCB two-phase system (entry 24), using metal salts and complexes, both soluble (Ag^+, Au^I, $[PdCl_4]^{2-}$, entries 1–10, 23, 24, 32–34, 39–44) and poorly soluble {AgCl, $PtCl_2$, $([PdCl_4]^{2-}\cdot 2\,CTA^+)_n$, $AgCl@CTA^+$, entries 12–17, 26–30, 45–48}, and reduced either more readily or less readily than the mediator. In addition, MNPs have been obtained upon generation of metal ions *in situ* (Ag^+, Au^I, $[CoCl_4]^{2-}$, Cu^{2+}) on dissolution of the anode material (Ag, Au, Co, Cu) during the electrolysis (entries 18–22, 25, 31, 35–38, 49, 50).

The composition and structure of MNPs were determined by atomic force and electron (scanning, scanning transmission and transmission) microscopy, microprobe analysis, X-ray powder diffraction. Silver, gold and copper nanoparticles exhibit a characteristic absorption band (λ_{max}, Table 3) in the visible region caused by the surface plasmon resonance of the particles;[1, 3, 4, 6, 186] therefore, UV-Vis spectroscopy was also used to prove their formation.

It is noteworthy that if the metal ion could be reduced on the electrode irrespective of the presence of a mediator, then the generated metal (Ag, Pd, PdAg, Au, Pt, Cu) would always be deposited on the cathode (see, for example, entries 1–3, 18, 26, 31, 45, 46 in Table 3).[62–85] These results emphasize the key role of the mediated electroreduction of metal ions for the preparation of MNPs in the solution bulk.

4.1.1. Stability of metal nanoparticles

Silver, gold, palladium and platinum nanoparticles obtained in solutions proved to be quite stable to oxidation with air oxygen at room temperature. The NPs of these metals isolated and dispersed in ethanol were equally stable. Conversely, CoNPs obtained *via* anthracene-mediated reduction of $[CoCl_4]^{2-}$ in a DMF–0.1 M Bu^n_4NCl mixture were rapidly oxidized with air oxygen to give oxidized cobalt NPs (Ref. 72), and only these particles were characterized. The PVP_{10}-stabilized copper nanoparticles proved to be much more stable; they were completely oxidized only over a period of 12 h.[83] The silver present in CTAC-stabilized ultrasmall AgNPs (< 1.5 nm, amorphous silver) and in the PdAg alloy NPs is oxidized in chloride-containing aqueous media to give AgCl even more slowly.[85]

In the absence of a stabilizer, MNPs are already agglomerated during the electrolysis to give larger particles of different shape that are deposited in the solution and on the electrode (see Table 3, entries 2, 26, 32, 45). Although stabilized MNPs are more durable, they still can agglomerate. Indeed, slow enlargement (Ostwald ripening) was noted for the PVP_{40}-stabilized AgNPs (Ref. 79) and ultrasmall AuNPs.[76]

4.1.2. Composition and structure of nanocomposites

In the absence of stabilizers, MNPs are present as agglomerates in a relatively pure state.‡

‡ The case is that the surface metal atoms have an uncompensated valence irrespective of the metal particle size (clusters, nanoparticles or massive metal). Therefore, the metal particle surface always bears a layer of foreign chemisorbed or adsorbed substances (oxygen, solvent and so on). This is often neglected in the characterization of particles; however, this is always the case in the preparation of MNPs in solutions. It is impossible to obtain MNPs in solutions in the absolutely pure state without chemi(ad)sorbed compounds; therefore, hereinafter, we speak of the preparation of MNPs in a relatively pure state.

Table 3. Conditions of mediated electrosynthesis and characteristics of the obtained NPs [GC electrode, $T = 295$ K, magnetic stirring, inert atmosphere (except for oxygen used as the mediator)].

Entry	Conditions of electrolysis					Characteristics of the obtained particles							Ref.
	mediator	stabilizer	medium	$-E$/V (*vs.* SCE)	procedure of electrolysis	MNP	$E_{p,ox}$/V	λ_{max}/nm	particle size/nm				
									I	II	III	IV	
					Source of metal ion: $[PdCl_4]^{2-}$								
1	–	–	DMF – H_2O (3 : 2), 0.1 M NaCl	1.00	1	Pd [a]	–	–	–	–	–	–	62
2	MV^{2+}	–	DMF – H_2O (3 : 2), 0.1 M NaCl	0.70	1	Pd [b]	–	–	–	–	–	–	63
3	MV^{2+}	SiO_2	H_2O, 0.1 M NaCl	1.00	1	Pd [c]	–	–	–	–	–	–	65
4	MV^{2+}	SiO_2 – NHR	H_2O, 0.1 M NaCl	1.00	1	Pd	–	–	–	250	3 – 6	–	65
5	MVCA – C_1^{8+}	–	DMSO, 0.1 M Bu_4^nNCl	(0.40 – 0.70)	1	Pd	–	–	1280	60 – 180	–	–	64
6	MVCA – C_5^{8+}	–	DMSO, 0.1 M Bu_4^nNCl	(0.40 – 0.70)	1	Pd	0.35	–	255	80 – 260	–	–	64
7	MVCA – C_{10}^{8+}	–	DMSO, 0.1 M Bu_4^nNCl	(0.40 – 0.70)	1	Pd	0.37	–	1000	190 – 300	–	–	64
8	MVCA – C_5^{8+}	–	DMF – H_2O (3 : 2), 0.1 M NaCl	0.60	1	Pd	0.46	–	850	45	–	–	62
9	MVCA – C_{10}^{8+}	–	DMF – H_2O (3 : 2), 0.1 M NaCl	0.60	1	Pd [d]	–	–	–	–	–	–	63
10	*p*(MVCA – *co*-St)	–	H_2O, 0.1 M NaCl	0.90	1	Pd	0.46	–	30 – 500	85	3 – 8	–	66
11	O_2	PVP_{40}	DMF, 0.1 M Bu_4^nNCl	1.00	1	Pd	–	–	8	44 ± 10	< 1 – 2	–	79
					Source of metal ion: $([PdCl_4]^{2-} \cdot 2\,CTA^+)_n$								
12	MV^{2+}	CTAC	H_2O, 0.02 M CTAC	0.90	1	Pd	0.57	–	44	–	5 ± 3	4.66	67
13	MV^{2+}	CTAC	H_2O, 0.1 M NaCl	0.80	1	Pd	0.42	–	51	14 ± 3	5 ± 1	–	85
					Source of metal ion: PdNP + $AgCl@CTA^+$								
14	MV^{2+}	CTAC	H_2O, 0.1 M NaCl	0.80	1	PdAg (76% Pd)	0.17, 0.38	–	51	16 ± 5	8 ± 2	–	85
					Source of metal ion: $AgCl@CTA^+$								
15	MV^{2+}	CTAC	H_2O, 0.1 M NaCl	0.80	1	Ag	0.10	405	8, 17	34 ± 11	18 ± 5	–	85

Table 3 (continued).

Entry	Conditions of electrolysis					Characteristics of the obtained particles							Ref.
	mediator	stabilizer	medium	$-E$/V (*vs.* SCE)	procedure of electrolysis	MNP	$E_{p,ox}$/V	λ_{max}/nm	particle size/nm				
									I	II	III	IV	
					Source of metal ion: AgNP + $([PdCl_4]^{2-} \cdot 2\,CTA^+)_n$								
16	MV^{2+}	CTAC	H_2O, 0.1 M NaCl	0.80	1	PdAg (50% Pd)	0.40	–	22	22 ± 6	6 ± 1	–	85
					Source of metal ion: $([PdCl_4]^{2-} \cdot 2\,CTA^+)_n$ + AgCl@CTA^+								
17	MV^{2+}	CTAC	H_2O, 0.1 M NaCl	0.80	1	PdAg (68% Pd)	–	–	4	14 ± 4	6 ± 1	–	85
					Source of metal ion: Ag^+								
18	MV^{2+}	–	DMF, 0.1 M $Bu^n_4NPF_6$	1.10	2	Ag[e]	–	–	–	–	–	–	69
19	MVCA-C_5^{8+}	–	DMF, 0.1 M $Bu^n_4NPF_6$	1.10	2	Ag	0.46	412	1200–1900	⩾30	–	–	68, 69
20	MV^{2+}	PVP_{40}	H_2O, 0.1 M KNO_3	0.80	2	Ag	–	406	16	35 ± 9	26 ± 6	–	77
21	MV^{2+}	PVP_{40}	DMF–H_2O (2 : 3), 0.1 M KNO_3	0.80	2	Ag	–	416	14	51 ± 7	38 ± 12	–	77
22	MV^{2+}	PVP_{40}	DMF, 0.1 M KPF_6	0.55	2	Ag	–	408	11, 31	39 ± 10	20 ± 7	–	77
23	O_2	PVP_{40}	DMF, 0.1 M Bu^n_4NCl	1.10	1	Ag	0.35	421	22	9 ± 2	5 ± 2	–	79
								428[f]	37[f]	22 ± 6[f]	17 ± 5[f]	7.5[f]	
24	C_{60}	–	Two-phase system DCB–H_2O	0.38	1	Ag	–	–	817	–	36 ± 13	6–19	80
25	$[Co(bipy)_3]^{3+}$	PVP_{40}	H_2O, 0.1 M $NaClO_4$	0.30	2	Ag	–	450	170	156 ± 51	83 ± 53, 1220 × 94	–	81
					Source of metal ion: AgCl								
26	MV^{2+}	–	H_2O–0.02 M NaCl	1.00	1	Ag[c]	–	–	–	–	–	–	71
27	MV^{2+}	SiO_2-NHR	H_2O, 0.1 M $NaBF_4$	0.90	1	Ag	–	383	–	120–160	120–160	–	70
28	*p*(MVCA^{8+}–*co*-St)	–	H_2O, 0.1 M NaCl	0.65	1	Ag	0.20	413	57	–	–	7–11	82
29	$[Co(sep)]^{3+}$	PVP_{40}	H_2O, 0.1 M NaCl	0.85	1	Ag			254, 1100	60 × 42	46 × 27	20–35	81
					Source of metal ion: AgCl@CTA^+								
30	MV^{2+}	CTAC	H_2O, 0.02 M CTAC	1.00	1	Ag	–	423	77	39 ± 15	34 ± 24	8–16	71

Table 3 (continued).

Entry	Conditions of electrolysis					Characteristics of the obtained particles							Ref.
	mediator	stabilizer	medium	$-E$/V (*vs.* SCE)	procedure of electrolysis	MNP	$E_{p,ox}$/V	λ_{max}/nm	particle size/nm				
									I	II	III	IV	
					Source of metal ion: Au^{I}								
31	–	PVP_{40}	H_2O, 0.1 M NaCl, pH 3.0	1.00	2	Au [a]	–	–	–	–	–	–	78
32	MV^{2+}	–	H_2O, 0.1 M NaCl	0.90	1	Au	0.90 – 1.10	–	–	14 – 100	14 – 100	12 – 26	73
33	MV^{2+}	SiO_2-NHR	H_2O, 0.1 M NaCl	0.90	1	Au	–	–	–	120 – 160	⩽20	12 – 26	73
34	MV^{2+}	PVP_{40}	H_2O, 0.1 M NaCl	0.90	1	Au	1.00	523	67	5 – 14	5 – 14	8 – 18	73
35	MV^{2+}	PVP_{40}	H_2O, 0.1 M NaCl, pH 3.0	0.80	2	Au	1.00	535	18, 59	30 ± 8	26 ± 9	–	78
36	MV^{2+}	PVP_{40}	H_2O, 0.1 M NaCl, pH 3.0	0.90	2	Au	0.99	532, 610	25	30 ± 8	27±9	–	78
37	MV^{2+}	PVP_{40}	H_2O, 0.1 M NaCl, pH 5.0	0.85	2	Au	0.96	526	13	20 ± 3	15 ± 6	–	78
38	MV^{2+}	PVP_{40}	H_2O, 0.1 M NaCl, pH 5.0	0.99 – 0.86	2	Au	0.98	530	21, 53	23 ± 5	19 ± 5	–	78
39	*p*($MVCA^{8+}$ -*co*-St)	–	H_2O, 0.1 M NaCl	0.65	1	Au	1.10	543→551	650	72 ± 16	51 ± 8, 19 ± 3	–	82
40	O_2	PVP_{40}	DMF, 0.1 M Bu^n_4NCl	1.10	1	Au	–	–	7	–	<2	–	76, 79
							–	600 [g]	14, 23 [g]	135 × 48 [g]	112 × 58 [g]	20 – 31	76, 79
							–	–	–	70 ± 46 [g]	46 ± 14 [g]	–	76, 79
							–	550 [h]	67 [h]	–	56 ± 25 [h]	24 – 51	76, 79
							–	680 [h]	–	–	105 ± 29 [h]	–	76, 79
							–	540 [i]	46 [i]	–	13 ± 8 [i]	7 – 13	76, 79
							–	610 [i]	99 [i]	–	–	–	76, 79
41	C_{60}	–	DCB – DMF (2 : 1), 0.1 M Bu^n_4NCl	0.40	1	Au	–	–	–	–	27 ± 14	9 – 14	74
42	C_{70}	–	Toluene – DMF (2 : 1), 0.1 M Bu^n_4NCl		1	Au	–	–	–	9 ± 3	10 ± 1	8 – 9	84
43	MF	–	Toluene – DMF (2 : 1), 0.1 M Bu^n_4NCl		1	Au	–	–	–	19 ± 4	18 ± 5	10 – 12	84
44	FP	–	Toluene – DMF (2 : 1), 0.1 M Bu^n_4NCl		1	Au	–	–	–	20 ± 3	19 ± 5	12 – 16	84

Table 3 (continued).

Entry	Conditions of electrolysis					Characteristics of the obtained particles							Ref.
	mediator	stabilizer	medium	$-E$/V (*vs.* SCE)	procedure of electrolysis	MNP	$E_{p,ox}$/V	λ_{max}/nm	particle size/nm				
									I	II	III	IV	
					Source of metal ion: $PtCl_2$								
45	MV^{2+}	–	DMF – H_2O (2 : 3), 0.1 M KPF_6	0.70	1	Pt [c]	–	–	–	–	–	–	75
46	MV^{2+}	SiO_2	DMF – H_2O (2 : 3), 0.1 M KPF_6	0.70	1	Pt [b]	–	–	–	–	–	–	75
47	MV^{2+}	SiO_2-NHR	DMF – H_2O (2 : 3), 0.1 M KPF_6	0.70	1	Pt	–	–	–	157 ± 40	3 ± 2	–	75
48	MV^{2+}	PVP_{40}	DMF – H_2O (2 : 3), 0.1 M KPF_6	0.70	1	Pt	–	–	–	–	18 ± 9	–	75
					Source of metal ion: Cu^{2+}								
49	MV^{2+}	PVP_{10}	DMF – H_2O (3 : 2), 0.1 M $Bu^n_4NBF_4$	0.80	2	Cu	0.10	601	–	20 – 50	2 – 50	7 – 21	83
					Source of metal ion: $[CoCl_4]^{2-}$								
50	Anthracene	–	DMF, 0.1 M Bu^n_4NCl		2	Co [j]	–	–	24	20 – 30	–	–	72

Notes. The following designations are used: 1 is electrolysis in a divided cell with initial addition of the metal ion to the solution, 2 is electrolysis in an undivided cell with metal ion generation in the solution from sacrificial anode during electrolysis; $E_{p,ox}$ is the oxidation peak potential of adsorbed MNPs on the indicator electrode; λ_{max} is the absorption wavelength corresponding to the surface plasmon resonance of MNPs; I is the average hydrodynamic diameter of the largest number of solvated metal particles with a stabilizer (DLS method); II is the size of metal particles with a stabilizer (SEM, AFM); III is the MNP size (TEM, STEM); IV is the size of metal crystallites (XRPD). [a] The generated metal is completely deposited on the cathode. [b] The generated metal is deposited on the cathode and in solution. [c] The generated metal is deposited in the solution. [d] The MVCA-C^{8+}_{10}-bound palladium nanoparticles are deposited on the cathode. [e] Black precipitate, [f] after 60 days; [g] after 15 days; [h] within 48 h after the dispersion of isolated NPs in ethanol; [i] within 8 h after the dispersion of isolated NPs in water. [j] Oxidized cobalt.

The nature of the stabilizer noticeably affects the results of MNP electrosynthesis. The SiO_2 NPs and the same particles modified by alkylamino groups (SiO_2-NHR), PVP_{10}, PVP_{40} and CTAC were used as stabilizers (see Table 3). In some cases, mediators also served as the stabilizers, in particular, calix[4]resorcinarene MVCA–C_n^{8+} (n = 1, 5, 10) (see Table 3, entries 5–9, 19, 28), calix[4]resorcinarene–styrene copolymer p(MVCA^{8+}–co-St) (entries 10, 39) or fullerenes C_{60}, C_{70}, MF (**2**) and FP (**3**) (entries 24, 41–44). In these cases, an additional stabilizer was not added to the solution. It was found that the SiO_2 NPs do not bind or stabilize palladium, gold or platinum

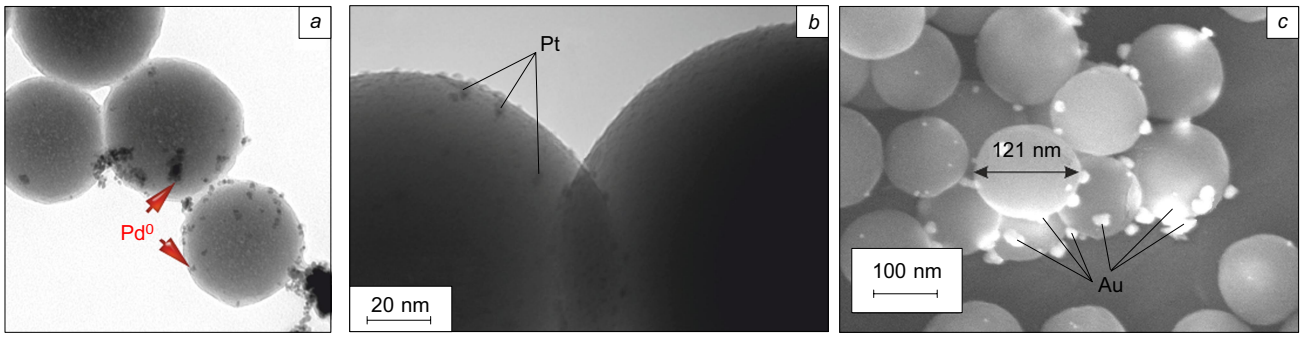


Figure 7. TEM (*a*, *b*) and SEM images (*c*) of the palladium (*a*), platinum (*b*) and gold (*c*) nanoparticles electrochemically deposited on SiO_2-NHR.[65, 73, 75]

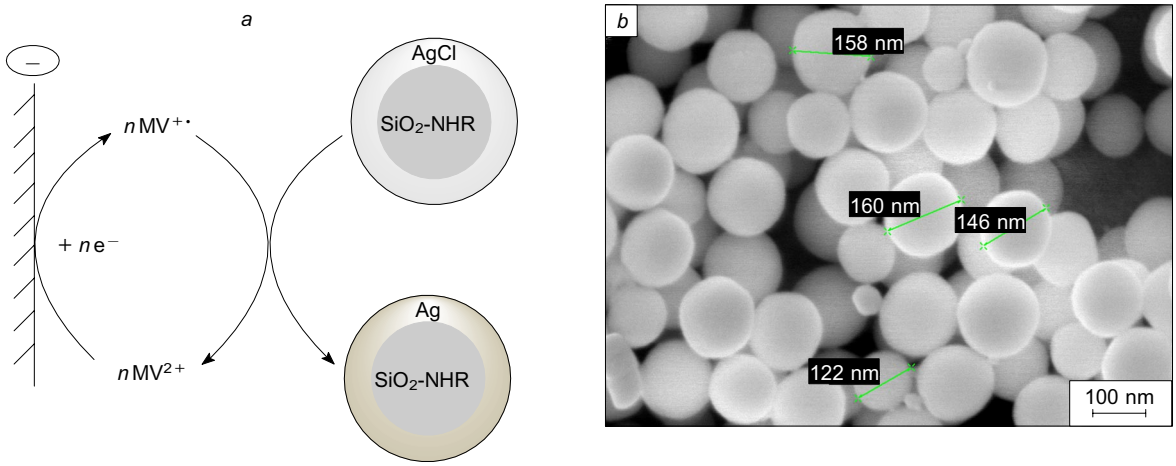


Figure 8. Scheme of the mediated electrosynthesis (*a*) and SEM image (*b*) of the SiO_2-NHR core/silver shell nanocomposite.[70]

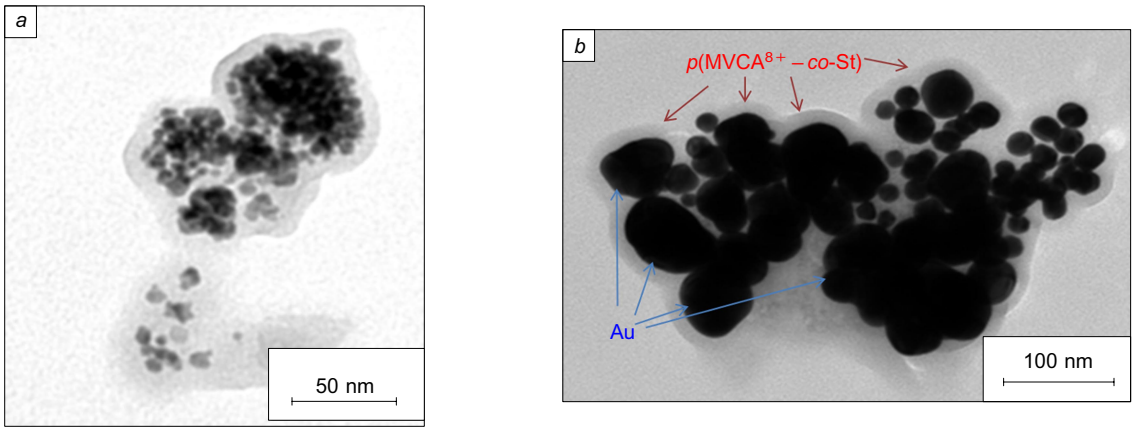


Figure 9. TEM images of the Pd@p(MVCA^{8+}–co-St) (*a*)[66] and Au@p(MVCA^{8+}–co-St) (*b*)[82] nanocomposites.

nanoparticles.[65, 73, 75] The behaviour of MVCA–C_1^{8+} towards PdNPs is similar.[64] In other cases, a MNP nanocomposite with the stabilizer is formed.

Note that in aqueous DMF, tetraviologen calix[4]resorcinarene with decyl substituents at the lower rim of the MVCA–C_{10}^{8+} calixarene platform functions simultaneously as a mediator and a stabilizer and is adsorbed on the GC electrode. As a consequence, the Pd–MVCA–C_{10}^{8+} nanocomposite is quantitatively deposited on the cathode.[63] However, it was shown [64] that this calix[4]resorcinarene is readily soluble in DMSO. It should be borne in mind that in all cases where the stabilizers are readily soluble in the media used, they are not adsorbed on the electrode and nanocomposites are formed only in the solution bulk.

The structure of nanocomposites depends on the nature of the metal and the stabilizer. The silica nanoparticles modified with alkylamino groups (SiO_2-NHR) bind MNPs in the surface layer. This gives rise to M–SiO_2-NHR nanocomposites in which MNPs (M = Pd, Au, Pt) are stabilized in the SiO_2-NHR surface layer (Fig. 7).[65, 73, 75] The poorly soluble AgCl salt is attached to the SiO_2-NHR surface and is reduced (Fig. 8) to give the SiO_2-NHR core/silver shell nanocomposite.[70] The structure of the M–*p*(MVCA^{8+}–*co*-St) nanocomposites also depends on the nature of the metal. The ultrasmall PdNPs (3–8 nm) are mainly encap-

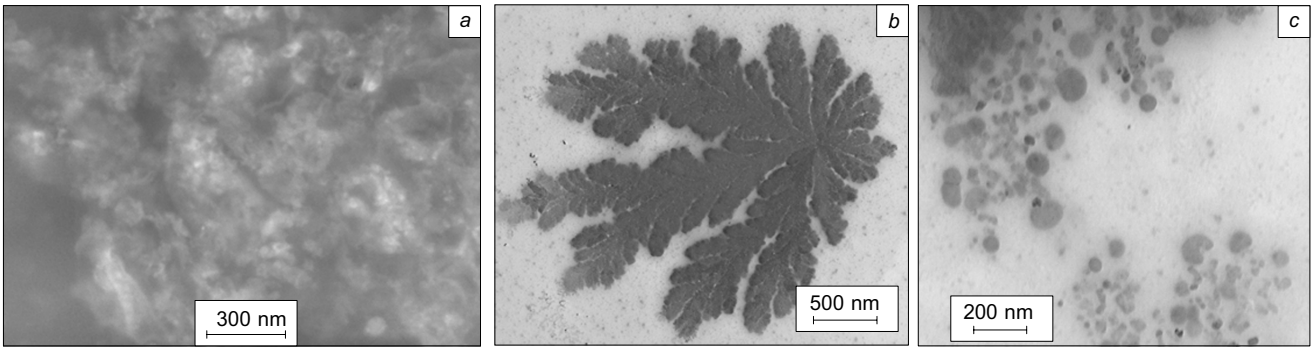


Figure 10. SEM (*a*) and STEM images (*b*, *c*) of the Pt@PVP_{40} nanocomposites of various shapes.[75]

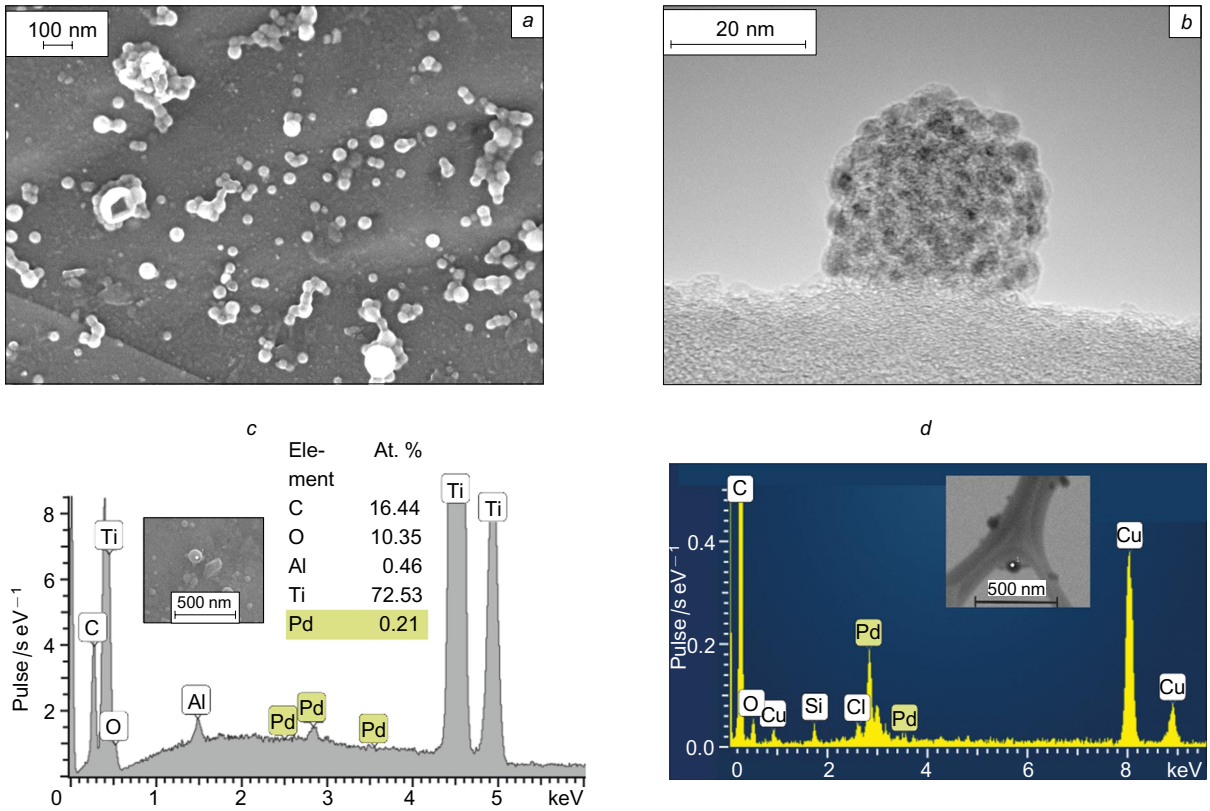


Figure 11. SEM (*a*) and TEM images (*b*) and energy dispersive spectra (Cu, Ti, Al from the support) (*c*, *d*) of the Pd@PVP_{40} nanocomposite.[79]

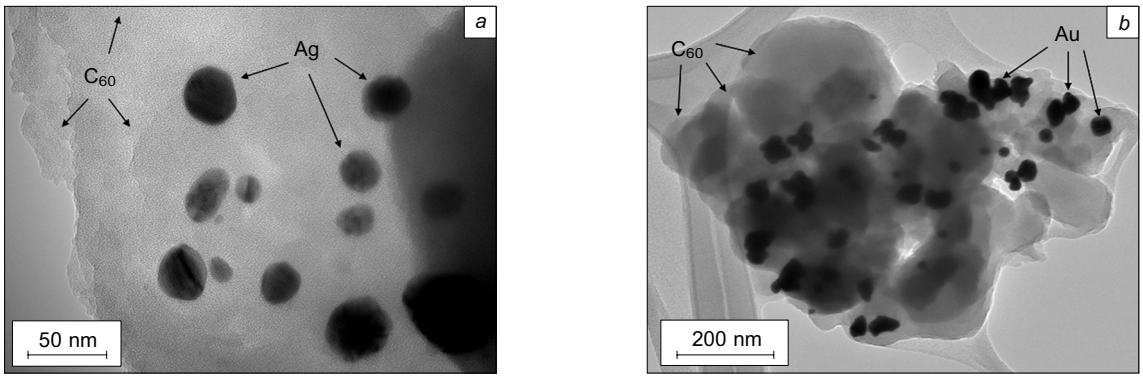


Figure 12. TEM images of Ag (*a*) and Au (*b*) nanoparticles dispersed in a C_{60} matrix.[74, 80]

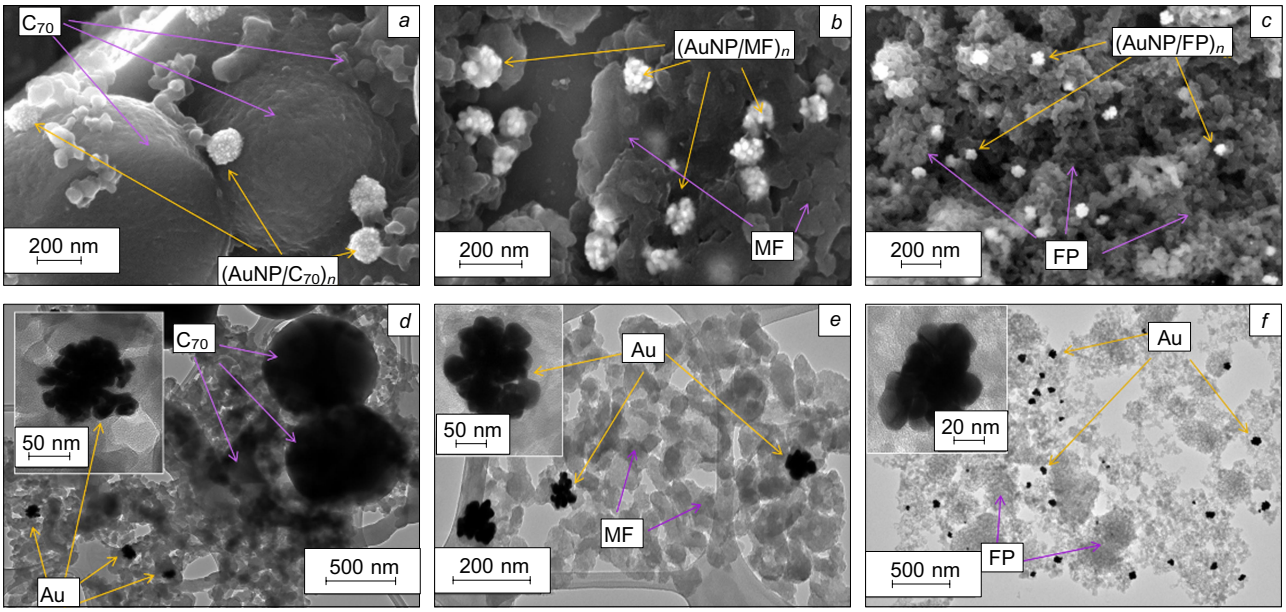


Figure 13. SEM (*a*–*c*) and TEM images (*d*–*f*) of AuNPs in the C_{70} (*a*, *d*), MF (*b*, *e*) and FP (*c*, *f*) matrices.[84]

sulated in polymer nanocapsules (Fig. 9),[66] whereas larger gold and silver nanoparticles are stabilized in a shell composed of several polymer molecules.[82] In the case of other stabilizers, the nanocomposite structure is the same, namely, MNPs stabilized in a shell. These nanocomposites are often designated as M@stabilizer.

The MNP/SiO_2-NHR nanocomposites occur in solution after electrolysis as single particles, their state being retained after deposition on a solid support (Fig. 7, 8).[65, 70, 73, 75] In the case of organic stabilizers, nanocomposites often bind either other nanocomposite particles or excess stabilizer by means of multiple-point interactions of the shell molecules. This gives aggregates of various shape and size.

According to dynamic light scattering data, the average hydrodynamic diameter of most of the aggregates obtained in the electrolysis exceeds the size of single nanocomposite particles by a large factor (see Table 3). The aggregates deposited on the support have relatively large size, different compositions and diverse shapes. For example, aggregates of the Pt@PVP_{40} nanocomposite are spherical or dendritic (Fig. 10),[75] while the Pd@PVP_{40} particles are raspberry-shaped (Fig. 11);[79] aggregates of Au–C_{60} and Ag–C_{60} nanocomposites are individual nanocomposites bound in a fullerene matrix (Fig. 12);[74, 80] and flower-shaped aggregates of Au–C_{70}, Au–MF and Au–FP nanocomposites are bound in the stabilizer matrix (Fig. 13).[84] The conclusions about the particle composition were based on energy dispersive X-ray spectroscopy data. This is exemplified in Fig. 11 *c*,*d*, which presents the experimental EDX spectra of the Pd@PVP_{40} composite.

The bimetallic Pd–Ag nanoparticles were obtained by the methylviologen-mediated reduction in water in the presence of CTAC by three procedures:

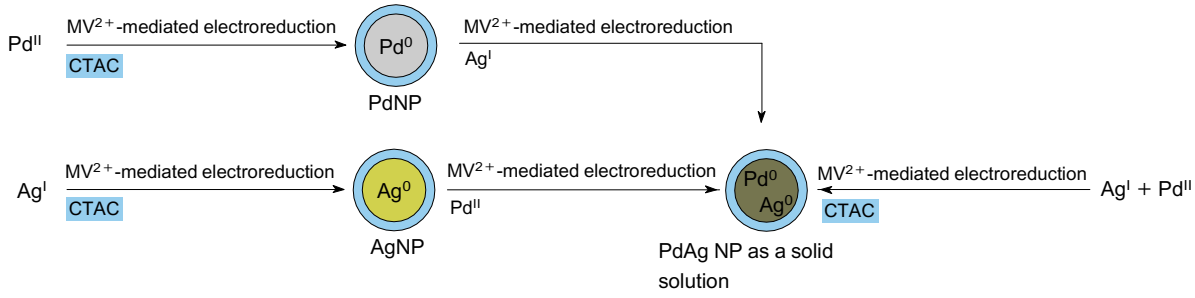
— preliminary synthesis of palladium NPs followed by reduction of an equimolar amount of AgCl in the same medium (see Table 3, entries 13, 14);

— preliminary synthesis of silver NPs followed by reduction of $[PdCl_4]^{2-}$ (entries 15, 16);

— joint reduction of $[PdCl_4]^{2-}$ and AgCl (entry 17).[85]

Any of these procedures affords an alloy of two metals as a solid solution (Scheme 7). The driving force of alloy

Scheme 7



formation is energy release of ~33 kJ mol^{-1}. In the first procedure, the NP size (8 ± 2 nm) and the palladium content of the alloy (76 at.%) are somewhat higher than in the other two procedures (6 ± 1 nm, 50 at.% and 68 at.%, respectively), but the sizes of alloy crystallites in the NPs are equal (2–5 nm). In the case of CTAC stabilization of metallic nanoparticles, the resulting nanocomposites occur as aggregates both in solution and on the support.

4.1.3. Size and shape of metal nanoparticles

Analysis of the data summarized in Table 3 indicates that the size, shape and degree of dispersion of MNPs are dictated by the joint action of quite a few factors — the natures of the metal, mediator and stabilizer; composition of the medium; the method used to introduce the metal ion (the use of metal salts or generation of ions by anode dissolution during electrolysis); and the period of time during which the obtained MNPs are kept in solution. The available data are clearly insufficient for extracting the contribution of a particular factor from their sum; therefore, it is possible only to describe the existing facts.

In most cases, mediated electrosynthesis leads to generation of MNPs of ideal or non-ideal spherical shape. Along with them, methylviologen-mediated reduction of AgCl nanospheres stabilized in a CTAC shell (AgCl@CTA$^+$, ~330 nm) gives a minor amount (4%) of short nanorods (Fig. 14),[71] while the [Co(bipy)$_3$]$^{3+}$-mediated reduction of Ag$^+$ ions gives rather long nanowires (1220 × 94 nm) (Fig. 15);[81] in the [Co(sep)]$^{3+}$-mediated reduction of Ag$^+$ ions and methylviologen-mediated reduction of Cu^{2+}, mainly oval-shaped MNPs are formed.[81,83]

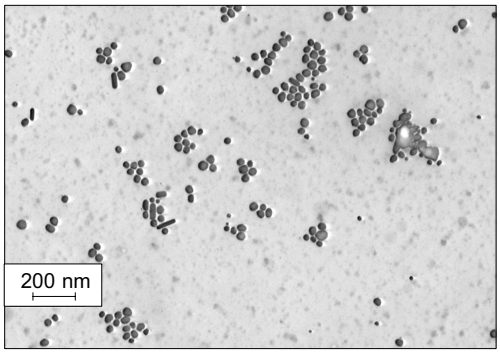


Figure 14. STEM image of the Ag@CTAC nanocomposite obtained by the MV^{2+}-mediated reduction of AgCl@CTAC in H_2O–0.02 M CTAC.[71]

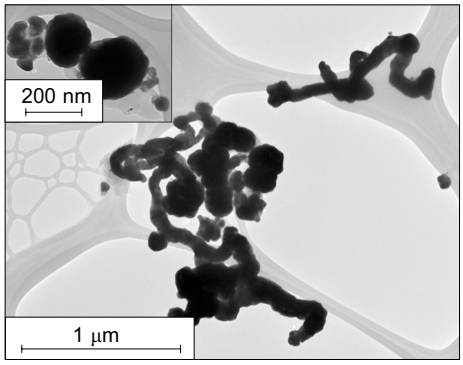


Figure 15. TEM image of the Ag@PVP$_{40}$ nanocomposite obtained by [Co(bipy)$_3$]$^{3+}$-mediated reduction of Ag$^+$ in H_2O–0.1 M $NaClO_4$.[81]

Oxygen-mediated electrosynthesis in DMF was used to prepare PVP$_{40}$-stabilized ultrasmall nanoparticles of gold (< 2 nm),[76] silver (5 ± 2 nm) and palladium (< 1–2 nm).[79] When kept for 60 days in solution after electrolysis, the spherical AgNPs are enlarged to 17 ± 5 nm.[79] During 15 days, AuNPs are converted to V-shaped particles of 112 ± 53 nm length and 58 ± 22 nm width; isolation and dispersion in ethanol with keeping for 48 h afforded hexagonal NPs (105 ± 29 nm) and polygons (56 ± 25 nm); while the dispersion in water with keeping for 8 h resulted in the formation of spherical NPs (13 ± 8 nm, Fig. 16).[79]

Generally, the examples presented in Table 3 attest to the applicability of mediated electroreduction of metal ions for the synthesis of MNPs and nanocomposites based on them in the solution bulk. These studies did not aim at optimizing the processes for the preparation of monodispersed particles of definite size or shape, but only demonstrated the possibility to carry out the mediated electrosynthesis of MNPs under various conditions. Nevertheless, even the available data suggest the possibility to control the size and, to some extent, the shape of metal nanoparticles. Variation of the medium and the natures of the mediator, metal ion and stabilizer resulted in the preparation of spherical NPs of diameters from < 1–2 to 3–8 nm for Pd, from 5 ± 2 to 83 ± 53 nm for Ag, from 5–14 to 51 ± 8nm for Au and from 3 ± 2 to 18 ± 9 nm for Pt. Also, AgNPs were synthesized as ellipsoids, nanorods and nanowires, silica core/silver shell particles; and V-shaped, hexagonal and polyhedral AuNPs were prepared.

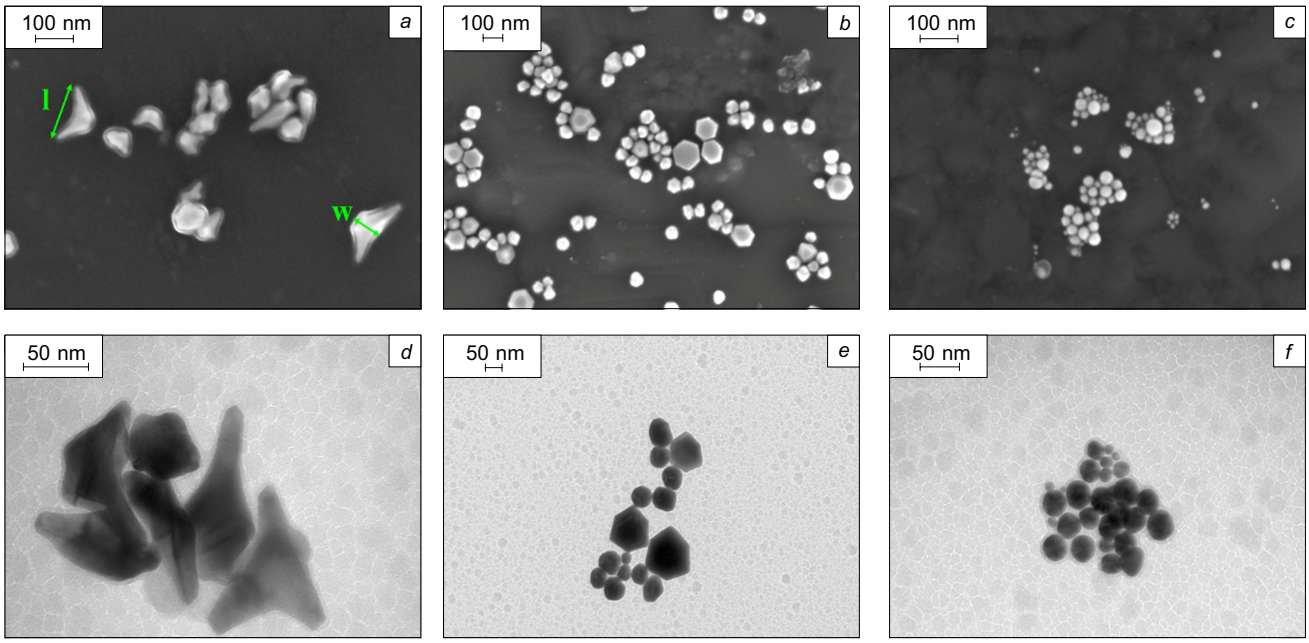


Figure 16. SEM (*a*–*c*) and TEM images (*d*–*f*) of gold nanoparticles.[76] Medium: (*a*, *d*) DMF, (*b*, *e*) EtOH, (*c*, *f*) H_2O.

4.1.4. Efficiency of the synthesis

The mediated electrosynthesis of MNPs is, most often, efficient. Passage of the theoretically required amount of electric charge results in a quantitative conversion of the metal ions to MNPs, *i.e.*, the current efficiency for MNP formation is close to 100%. Electrolysis usually proceeds without complications and the mediator is not consumed. However, some exceptions are possible.

Note, first of all, that only one case of mediator consumption was detected in the $[Cr(bipy)_3]^{3+}$-mediated reduction of Ag^+ ions in an aqueous medium.[81] The process gave some products (probably chromium oxides and/or hydroxides) passivating the electrode, which prevented complete conversion of Ag^+ ions.

In the electrosynthesis of AgNPs in an undivided cell, the anodic dissolution of metallic silver is accompanied by the anode dispersion because of non-uniform dissolution (Fig. 17); therefore, the overall current efficiency for AgNPs

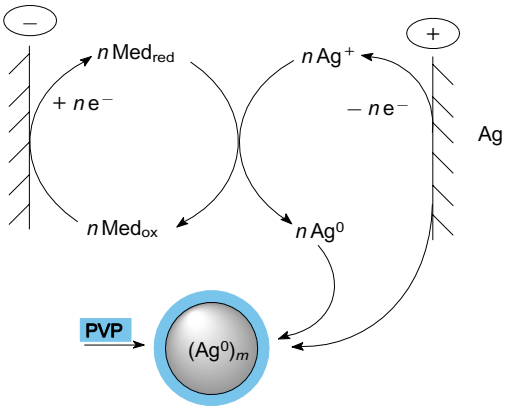


Figure 17. Mediated electrosynthesis of the Ag@PVP nanoparticle in an undivided cell.[69, 77, 81]

in solution is 128%–160%.[69, 77, 81] Conversely, in a similar experiment using an Au anode in a DMF – 0.1 M Bu^n_4NCl system, the current efficiency is lower than 100% (40%–60% depending on the conditions of electrolysis) due to side oxidation of components of the supporting solution.[78] In the *p*(MVCA^{8+}-*co*-St)-mediated reduction of AgCl nanoparticles (~250 nm), they cannot be completely reduced even at a 2.5-fold excess of the electric charge passed. The reason is the isolating effect of the π-polymers [*p*(MVCA $^{4+\bullet}$–*co*-St)]$_n$ deposited on the electrode, which do not reduce the AgCl nanospheres by themselves (see Fig. 3).[82] In the synthesis of PdNPs in aqueous media, reduction of the mediator (MV^{2+}, MVCA-C_n^{8+}) is accompanied by electrocatalytic evolution of hydrogen, which leads to the consumption of an additional amount of electric charge (120%–150%).[63]

The chemical reduction of metal ions in two-phase aqueous organic systems is an efficient method for the synthesis of ultrasmall monodisperse MNPs known as the Brust–Schiffrin method.[93] A distinctive feature of this method is that the reducing agent and the metal ion are initially located in different phases of the liquid system and the MNPs formed are stabilized in one of the phases. Ultrasmall gold,[93, 187–190] silver,[188, 190–193] palladium [193, 194] and copper [188, 190, 195–197] nanoparticles were prepared in this way.

In principle, some procedures of mediated electrosynthesis can be carried out in two-phase systems. As an example, C_{60}-mediated electrosynthesis of AgNPs was carried out in a water–*o*-dichlorobenzene system in a divided electrolytic cell (Fig. 18).[80] The glassy carbon cathode, fullerene and 0.1 M $Bu^n_4NBF_4$ supporting electrolyte were located in the organic phase, while $AgNO_3$ and 0.1 M $NaBF_4$ were in the aqueous phase. In this process, the Ag/C_{60} nanocomposite is formed in the organic phase (see Table 3, entry 24). Note, however, that DCB was not the optimal choice as regards the process efficiency, because reductive dechlorination of DCB takes place as a side

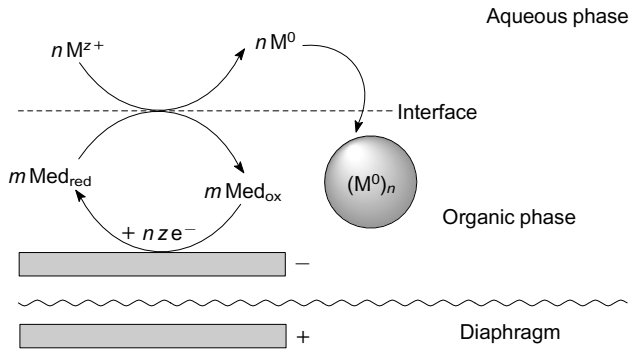


Figure 18. Mediated electrosynthesis of MNPs in an aqueous organic two-phase system in a divided cell.[80]

reaction involving clusters and silver nanoparticles and giving AgCl.

4.2. Catalytic activity of metal nanoparticles

Mono- and bimetallic (polymetallic) NPs are widely studied in the catalytic reactions of various substrates and energy conversion in fuel cells and batteries.[1–7,13–15,20,21,31–37,105,198–205] Palladium and palladium/silver bimetallic nanocatalysts catalyze a broad range of reactions such as hydrogenation, coupling (Suzuki, Sonogashira, Heck and other reactions), selective and complete oxidation of organic compounds, CO oxidation with oxygen and so on.[206–218] These are only some examples out of the broad range of possible transformations. However, as regards this review, it is of interest, first of all, whether the MNPs formed upon the mediated electrosynthesis are efficient co-reagents for these reactions. From this standpoint, the catalytic activities of the synthesized monometallic (Pd, Ag, Au) and bimetallic NPs were tested in relation to two model reactions — reduction of nitroaromatic compounds[65,66,79,82,85] and Suzuki coupling.[79,85]

4.2.1. Reduction of *p*-nitrophenol

Development of new methods for the reduction of nitroarenes to anilines is important due to the wide use of anilines in the industrial production of polymers, dyes and pharmaceuticals.[219] Recent studies demonstrate that metallic nanoparticles are rather promising catalysts for the synthesis of amines.[220] In the presence of metallic nanoparticles, hydrogenation of nitroarenes proceeds under mild conditions without the addition of acids.[221]

The reduction of *p*-nitrophenol with excess sodium borohydride does not proceed in the aqueous medium at room temperature in the absence of a catalyst. The addition of a catalyst in 2 mol.% amount (metal relative to *p*-nitrophenol) leads to a gradual decrease in the absorption band of *p*-nitrophenol at 400 nm and an increase in the absorption band of the *p*-aminophenol product at 300 nm. Figure 19 shows a typical experimentally obtained dependence.

Since sodium borohydride is taken in an excess, the reaction is described by pseudo-first-order kinetics (Fig. 19 *c*). The rate constants of the pseudo-first-order reaction (k_1) and the catalytic activity of MNPs (k_2 was calculated as the ratio of k_1 to the molar concentration of the metal) are given in Table 4. It can be seen that all of the tested MNPs exhibit relatively high catalytic activity; the highest activity was found for PdNPs, while the lowest activity was inherent in AuNPs. This value for the catalytic activity of AuNPs is markedly lower than the values reported in the literature.[222–226] Apparently, this is due to the relatively large size of metal particles in the obtained Au@*p*(MVCA^{8+}–*co*-St) nanocomposite. The palladium nanoparticles encapsulated in the pores of the *p*(MVCA^{8+}–*co*-St) polymer are less active than those encapsulated in the CTAC shell, although they have a much smaller size (see Table 4) and, hence, a higher surface area. The bimetallic PdAg catalysts have approximately equal moderate activities. In other words, upon the addition of catalytically less active silver to PdNPs, the catalytic activity of MNPs towards the reduction of *p*-nitrophenol decreases, irrespective of the silver content and the method of addition.

The activity of some of the MNPs is not manifested immediately as they are added to the solution. In the case of PdAg@CTAC and Pd@*p*(MVCA^{8+}–*co*-St), an induction period ($\sim$600 s) is present. According to publications,[106,227] the induction period is needed for the diffusion

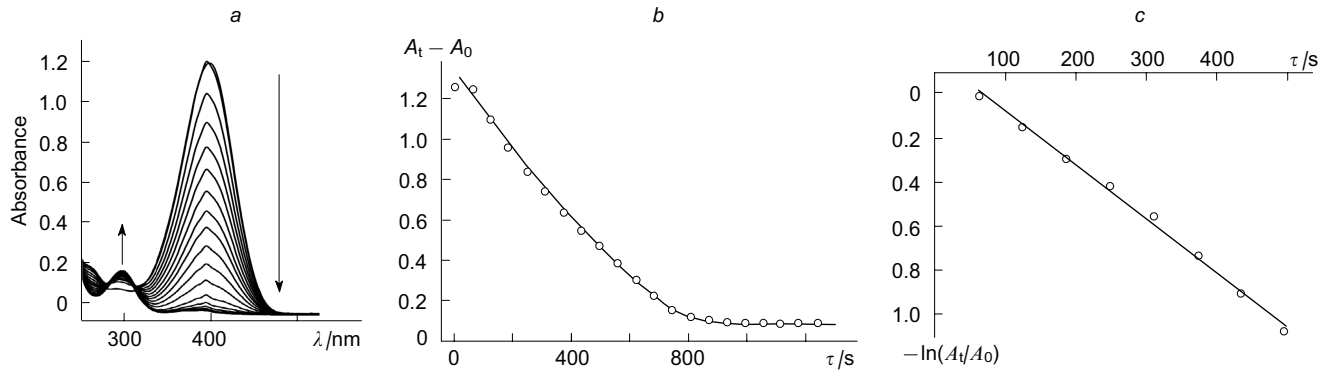


Figure 19. Reduction of *p*-nitrophenol (0.1 mmol litre^{-1}) with sodium borohydride (5 mmol litre^{-1}) in the presence of AgNPs (2 μmol litre^{-1}).[85]
(*a*) Variation of the UV-Vis spectrum of the reaction mixture after the addition of AgNPs; (*b*) variation of the absorbance at 400 nm *vs.* time (A_0 is the absorbance before the addition of AgNPs, A_t is the current absorbance); (*c*) the semilogarithmic kinetic curve. H_2O medium, $T = 22$ °C.

Table 4. Catalytic activity of mono- and bimetallic NPs obtained by mediated electrosynthesis in the reduction of *p*-nitrophenol and the Suzuki coupling, $T = 295$ K.

Entry	Nanoparticle	Stabilizer	MNP size /nm	Reduction of *p*-nitrophenol [a]		Suzuki coupling [b]	Ref.
				k_1 /ms^{-1}	k_2 /s^{-1} mol^{-1} litre	biphenyl yield after 24 h (%)	
1	Pd	CTAC	5 ± 1	6.0	3.0×10^3	91	85
2	PdAg (76% Pd)	CTAC	8 ± 2	4.4	1.1×10^3	100	85
3	PdAg (68% Pd)	CTAC	6 ± 1	3.0	7.4×10^2	72	85
4	PdAg (50% Pd)	CTAC	6 ± 1	4.6	1.2×10^3	50	85
5	Ag	CTAC	18 ± 5	2.5	1.2×10^3	4	85
6	Pd	*p*(MVCA^{8+}–*co*-St)	3–8	1.4	7.0×10^2	–	66
7	Pd	PVP_{40}	<1–2	3.3	1.7×10^3	100	79
8	Au	*p*(MVCA^{8+}–*co*-St)	19 ± 3, 51 ± 8	0.26	–	130	82

[a] C(*p*-nitrophenol) = 0.1 mmol litre^{-1}, $C(NaBH_4)$ = 5 mmol litre^{-1}, C(M) = 2 μmol litre^{-1}, H_2O; [b] C(iodobenzene) = C(phenylboronic acid) = 5 mmol litre^{-1}, C(M) = 0.1 mmol litre^{-1}, $C(K_2CO_3)$ = 15 mmol litre^{-1}, H_2O.

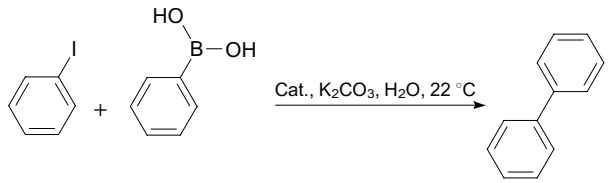
of reactants towards the metal surface or for restructuring of the catalyst surface for adsorption of the reactants. After the induction period, the reaction rate sharply increases and reaches approximately the same value as observed for other MNPs.

4.2.2. Suzuki reaction

The Suzuki reaction is a widely used coupling reaction giving a C–C bond in the arylation of aryl halides catalyzed by palladium complexes. This process is usually carried out in organic solvents at high temperatures. In recent years, the number of publications on the use of water-soluble PdNPs in this reaction has increased,[228–230] although in this case, too, efficient catalyst operation requires elevated temperatures.

The obtained palladium and bimetallic NPs showed high catalytic activities towards the Suzuki reaction (Scheme 8): in the presence of 2 mol.% of MNPs, iodobenzene reacts with phenylboronate under mild conditions (H_2O, $T = 22$ °C).

Scheme 8



In the case of PdNPs, biphenyl is formed in a nearly quantitative yield (91% and 100%) in 24 h (see Table 4). The catalytic activity of the PdAg alloys is generally correlated with the palladium content in the alloy. A low concentration of silver (24 at.%), which is almost inactive in this reaction, enhances the catalytic properties of palladium; however, at higher silver concentrations (⩾32 at.%), the activity of palladium decreases.

Thus, above analysis of test reactions, hydrogenation of nitroaromatic compounds and Suzuki coupling, confirmed the expected high activity of MNPs synthesized by mediated electrosynthesis.

4.3. Electrogeneration of highly active metal particle

A different possibility to obtain catalytically active metal particles by mediated electrosynthesis was described in the 1990s.[128–137, 231] One-step electroreduction of multicharged ions under the action of mediators (that transfer one electron) affords metal ions in low oxidation states, which are unstable (in some cases), but really existing intermediates. Hence, the mediated electroreduction of metal ions can be applied not only to prepare MNPs (see Section 4.1), but also to generate, in the solution bulk, metal ions in low oxidation states or metal atoms and clusters unstabilized by ligands (or other stabilizers) and, in this respect 'bare' (but still solvated, see below). These species are referred to as 'highly active metal particles'.

It should be emphasized that in the course of time (in particular, during the electrolysis), some intermediates are reduced and some other ones are enlarged *via* both attachment of different M^0 atoms and cluster self-assembly. Therefore, for these particles to exhibit activity, they must be generated *in situ* during the target process.

The research into the mediated electrogeneration of unstabilized highly active metal particles *in situ* have been described in a series of publications [128–133, 135–137] and integrated.[134, 231] Below we outline the most important results and conclusions of kinetic studies and give examples of implemented syntheses.

Transition metal complexes are known to catalyze chemical [232] and electrochemical [233–239] reductive homo- and cross-coupling of organic halogen compounds. The catalytically active species are metal complexes in low oxidation states (0 for Ni,[233–236] Pd [238] and Rh [239] complexes or 1 for Co complexes.[237]). Hence, for demonstration of the catalytic activity of metal species generated in a mediated process, Ni^{2+}, Co^{2+}, Pt^{2+}, Pd^{2+} and Rh^{3+} ions were used and aromatic and aliphatic organochlorine and -bromine compounds served as substrates (Table 5). Since the mediated reduction of metal ions was carried out in the presence of organohalogen substrates, one more issue is added to the requirements imposed on mediators used for MNP electrosynthesis (reversible reduction, efficient metal ion reduction with Med_{red}), in particular, the mediator should be reduced more easily than the substrate. All of

Table 5. Half-wave potentials ($E_{1/2}$) of mediators, metal ions and organohalogen compounds measured by polarography with respect to bottom mercury in DMF.[231]

Compound	Supporting electrolyte (C = 0.1 mol litre^{-1})	$-E_{1/2}$ /V
	Mediators	
4-Methoxybenzophenone	Bu^n_4NI	1.35
9,10-Diphenylanthracene	Bu^n_4NI	1.35
9,10-Dimethoxyanthracene	Bu^n_4NI	1.40
Anthracene	Bu^n_4NI	1.44
Dietyhyl phthalate	Bu^n_4NI	1.47
1-Aminoanthracene	Bu^n_4NI	1.55
Pyrene	Bu^n_4NI	1.55
	Metal ions	
$RhCl_3$	$Bu^n_4NBF_4$	−0.21, 0.42
$PdCl_2$	$Bu^n_4NBF_4$	−0.05
$Ni(BF_4)_2$	Bu^n_4NI	0.64
$Co(BF_4)_2$	Bu^n_4NI	0.74
$PtCl_2$	$Bu^n_4NBF_4$	1.25
	Organhalogen compounds	
$PhCH_2Cl$	Bu^n_4NI	1.82
Bu^nBr	Bu^n_4NI	1.93
1-Bromo-2-methoxy-2-methylcarbonylcyclopropane	Bu^n_4NI	1.98
Pr^nBr	Bu^n_4NI	1.98
1,1-Dichloro-2-methoxycarbonyl-2-methylcyclopropane	Bu^n_4NI	2.07
1,1-Dichloro-2,2-diphenylcyclopropane	Bu^n_4NI	2.13
PhBr	Bu^n_4NI	2.13
PhCl	Bu^n_4NI	2.26
Bu^nCl	Bu^n_4NI	2.38

the used mediators (see Table 5) comply with these requirements. In aprotic organic media (DMF, AN, DMSO) with tetraalkylammonium salts as supporting electrolytes in the first stage, these mediators undergo electrochemically reversible reduction to give stable radical anions. This reaction proceeded much less readily than the reduction of metal ions, but considerably more readily than the reduction of substrates.

When the substrate R–Hal is added to the solution of a mediator, the catalytic gain of the current of mediator reduction to the radical anion takes place, which is indicative of R–Hal reduction with this radical anion. The current gain becomes more pronounced upon the subsequent addition of metal ions to the solution and grows even more as the concentration of these ions increases. The catalytic nature of the current gain was indicated by the considerably lower activation energy in comparison with the values obtained in the absence of metal ions. The effective rate constants calculated taking into account the current gain attest to high catalytic activity of both the system consisting of the organic mediator and the metal ion[134] and the metal ion in this system. In terms of this activity, metal ions are arranged in the following sequence:[134]

$$Rh^{3+} > Ni^{2+} = Pt^{2+} > Co^{2+} > Pd^{2+}$$

The metal particles generated on the electrode under similar conditions, in the absence or in the presence of a mediator, did not show catalytic activity.

The set of obtained data made it possible to describe the catalytic reduction of R–Hal by Scheme 9,[134,231] which includes the mediator reduction on the electrode to the radical anion, the subsequent reduction of the metal ion with the radical anion to generate bare ions in low oxidation states, atoms, clusters and ultrasmall metal nanoparticles. These highly active particles altogether efficiently reduce the organohalogen substrates.

Scheme 9

$$Med + e^- \rightleftharpoons Med^{-\bullet}$$

$$Med^{-\bullet} + M^{2+} \rightleftharpoons Med + M^+$$

$$M^+ + M^+ \longrightarrow M^+—M^+$$

$$Med^{-\bullet} + M^+ \longrightarrow Med + M^0$$

$$M^0 \xrightarrow{M^0} M_2^0 \xrightarrow{M^0} M_3^0 \longrightarrow \ldots \longrightarrow M_n^0$$

$$[M^+, M^+—M^+, M^0, M_2^0 \ldots M_n^0] + R–Hal \longrightarrow R–M–Hal \longrightarrow \ldots$$

In the general case, the route from the metal ion to a nanoparticle comprises quite a few electron transfer and nucleation steps. The initial steps of this process are depicted in Scheme 9 in relation to the reduction of a doubly charged M^{2+} ion without ligands or stabilizers, assuming the formation of M^+ ions, their dimers and metal atoms and clusters. The reduction takes place in the solution, and all these particles (precursors), including M^{2+}, are undoubtedly solvated. This is not specially indicated; however, in the case of dissolution of compounds or ions present in solution, it is always implicitly meant that the species are solvated. The above explanation of the term 'bare' (as not bound to a ligand or stabilizer) by no means refers to the absence of a solvation shell.

Apart from the interaction with the solvent, complex formation between the intermediate, the M^{2+} ion, on the one hand, and the mediator, on the other hand, cannot be ruled out in some cases. In the presence of a stabilizer, the precursor can also react with it. This brings about the question of what the state of the metal ion in these particles is. In other words, whether there exists a donor–acceptor complex with a partial or complete charge transfer between the acceptor (metal ion) and the donor (a metal particle — atom, cluster or NP).

The metal particles are oxidized rather easily. Hence, they can be electron donors, while metal ions are reduced rather easily and, therefore, they can be electron acceptors. Thus, the formation of charge transfer complexes is not forbidden; conversely, there are grounds for their formation. If the complex is formed, its surface is positively charged; if no complex is formed, the metal particle will be

neutral. With this presentation, it is clear that charged particles are possible only for intermediate states. For the final state of MNPs where the metal ion is no longer present in the solution, MNPs should be neutral. In the absence of a stabilizer, the M^{z+}/M^0 redox system is in equilibrium and the formation of a complex is determined by the balance of free energies, that is, energy release upon binding of the metal ion to the metal particle and solvation of the resulting complex and energy build-up as a result of metal ion and metal particle desolvation. The ion solvation energy depends appreciably on the ion size (inverse square dependence on the radius); therefore, the formation of the complex will result in a considerable loss in the solvation energy. In the case of MNPs, it is rather unlikely that this loss would be made up for by the energy release upon the bond formation. However, as the metal particle size decreases, the probability of energy release increases, the complex formation being quite likely in the case of clusters and very likely in the case of dimers. In the presence of stabilizers prone to multiple-point donor–acceptor interactions with metal clusters and nanoparticles, the probability of formation of charge transfer complexes is even higher.

Generally, the considered method for the preparation of unstabilized intermediates comprising metal atoms, clusters and ultrasmall nanoparticles is of obvious interest. On the one hand, these particles cannot be prepared by other electrochemical methods due to inevitable reduction of target particles or nucleation to give the metal phase on the electrode surface, while on the other hand, these particles are highly active, which can be conveniently used for various synthetic purposes. In view of the high activity of the generated metal, anthracene- and naphthalene-mediated electrosynthesis of metal (nickel, cobalt, iron) carbonyls was carried out under mild conditions.[135,136] Highly active aluminium was prepared by the mediated electroreduction of aluminium ions in solution and used for deoxygenation of triphenylphosphine oxide.[137] The reduction of aryl bromides using a double mediator system, methylviologen–Pd^{II}, resulted in the electrosynthesis of biaryls.[240]

The significance of the results described in this Section is well summarized in the Conclusion of a Doctoral Thesis:[231] 'high catalytic properties were shown for a binary catalytic system based on an organic mediator for electronstransfer and some transition metal ions for electroreduction of some substrates. This process opens up prospects for not only the catalytic reduction of organohalogen and other compounds, but also for *in situ* preparation of highly dispersed metals and conduction of reactions based on them. In principle, this is a self-contained area of research.' Thus, the idea of mediated electroreduction of metal ions stated more than 25 years ago has been embodied in a series of successful works of mediated electrosynthesis of MNPs, which form the basis of the present review.

5. Conclusion

The review integrates the research and development works on the mediated electrosynthesis of MNPs. During the time elapsed since the first publication, a set of original studies have been performed. As a result, the general principles of the mediated electrosynthesis of MNPs were formulated, the factors determining the efficiency of this method were elucidated, the advantages of the method were evaluated and its position among other methods of MNP synthesis were established. These issues represent the main content of this review.

The considered results provide grounds for concluding that generally the mediated electroreduction of metal ions is an efficient method for the synthesis of MNPs in the solution bulk in different states: in a stabilizer shell, on non-conducting supports, in matrices and nanocapsules. In the vast majority of experiments carried out in the presence of MNP stabilizers and with the theoretical amount of the electric charge being passed, complete conversion of metal ions to MNPs takes place. The mediator is not consumed in this process, the generated metal is not deposited on the cathode, but the nanocomposite of MNPs with the stabilizer is formed. This method is convenient and easy for implementation; it is suitable for the preparation of both mono- and bimetallic NPs. The current somewhat decreases during the electrolysis, but still remains relatively high until the end of the electrolysis, which makes it possible to carry out the quantitative reduction of metal ions over a rather short period of time. The mediated electrosynthesis is also fairly efficient in the case where the metal ion cannot be reduced directly on the electrode due to the formation of a poorly soluble salt (complex) or if the metal ions and the cathode occur in different phases of an aqueous–organic system.

The mono- and bimetallic NPs obtained in this way could find use in catalysis, which is supported by their high catalytic activity in the test reactions of hydrogenation of nitroaromatic compounds and Suzuki coupling. The highly active metal ions in a low oxidation state and metal atoms and clusters generated *in situ* in a mediated process are also attractive for this purpose.

Of special note are fullerenes and their derivatives — compounds promising for wide use as sensors, photovoltaic cells and nanostructured devices in modern electronics.[241,242] Using fullerenes together with MNPs, one may expect not only retention of properties of both components, but also enhancement of their properties. The synergistic effect was clearly demonstrated by enhancement of the chromophore properties of fullerenes and AuNPs in the conversion of visible light energy into the electric energy.[243–245] The syntheses of M/fullerene nanocomposites promising for the use in solar cells are few in number.[243–247] The mediated electrosynthesis may become a convenient method for their manufacturing.

Examples of mediated electrosynthesis of MNPs presented in this review do not exhaust all the possibilities of this method. It is beyond doubt that mediated electrosynthesis opens up the way to the preparation of mono- and bimetallic particles of other metals and nanocomposites and monodispersed MNPs of required size and shape.

The mediated electrosynthesis fundamentally extends the scope of electrochemical methods for MNP synthesis, thus approaching it to the scope of chemical methods. In the longer view, the mediated electrosynthesis may develop to become a universal analogue of chemical methods for MNP synthesis. Here it is pertinent to emphasize that the chemical synthesis of MNPs implies the use of equivalent amounts of the reducing agent and gives its oxidized form as an inevitable product. Meanwhile, the electrochemical process requires catalytic amounts of a non-consumable mediator and the reduction occurs under the action of electric current. From this standpoint, the electrochemical process is more consistent with green chemistry principles. Further-

more, the mediated method provides unique possibility for the control over the reaction rate using any reasonably specified programme during electrolysis by automatic current control and the possibility to stop and reinitiate the reaction at any time by switching electrolysis on and off. Finally, while in the chemical process, metal ions are specially introduced in the solution, it is also possible in the mediated process. However, in the electrolysis in undivided cell, metal ions may be initially absent in the solution, but they are generated during electrolysis *via* dissolution of the anode.

We believe that owing to the use of mediators, electrochemical method may occupy a decent place in the vigorously developing area of preparation of metal nanoparticles in solutions.

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