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Synthetic Approaches to Metallic Nanomaterials

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1.1

Introduction

In recent years research involving nanoparticles and nanoscale materials has generated a great deal of interest from scientists and engineers of nearly all disciplines. This interest has been generated in large part by reports that a number of physical properties including optical and magnetic properties, specific heats, melting points, and surface reactivities are size-dependent. These size-dependent properties are widely believed to be a result of the high ratio of surface to bulk atoms as well as the bridging state they represent between atomic and bulk materials. In the nanoscale regime, materials (especially metals and metal oxides) can be thought of as neither atomic species which can be represented by well defined molecular orbitals, nor as standard bulk materials which are represented by electronic band structures, but rather by size-dependent broadened energy states. Because metallic particles are of great importance industrially, an understanding of their properties from small clusters to bulk materials is essential. Although these nanoscale colloidal metals are of interest to scientists of many disciplines, methods for their preparation and chemical applications are primarily the focus of chemists.

Originally called gold sols, colloidal metals first generated interest because of their intensive colors, which enabled them to be used as pigments for glass or ceramics. Nanoparticulate metal colloids are generally defined as isolable particles between 1 and 50 nm in size that are prevented from agglomerating by protecting shells. Depending on the protection shell used they can be redispersed in water ("hydrosols") or organic solvents ("organosols"). The number of potential applications for these colloidal particles is growing rapidly because of the unique electronic structure of the nano-sized metal particles and their extremely large surface areas. A considerable body of knowledge has been gained about these materials throughout the last few decades, and the reader is directed to the numerous books and review articles in the literature which cover these subjects in detail [1–12, 19–26]. This contribution will be focused towards presenting an overview of the synthetic methods used to prepare metallic nanomaterials, factors influencing size and shape, and a survey of potential applications in materials science and biology. Although not covered here, the area of biodirected syntheses is an emerging area of extreme interest [13–18].

1.2

Wet Chemical Preparations

Nanostructured metal colloids have been obtained by both the so-called “top down” and “bottom up” methods. A typical “top down” method for example involves the mechanical grinding of bulk metals and subsequent stabilization of the resulting nanosized metal particles by the addition of colloidal protecting agents [27, 28]. Metal vapor techniques have also provided chemists with a very versatile route for the production of a wide range of nanostructured metal colloids on a preparative laboratory scale [29–34]. Use of metal vapor techniques is limited because the operation of the apparatus is demanding and it is difficult to obtain a narrow particle size distribution. The “bottom up” methods of wet chemical nanoparticle preparation rely on the chemical reduction of metal salts, electrochemical pathways, or the

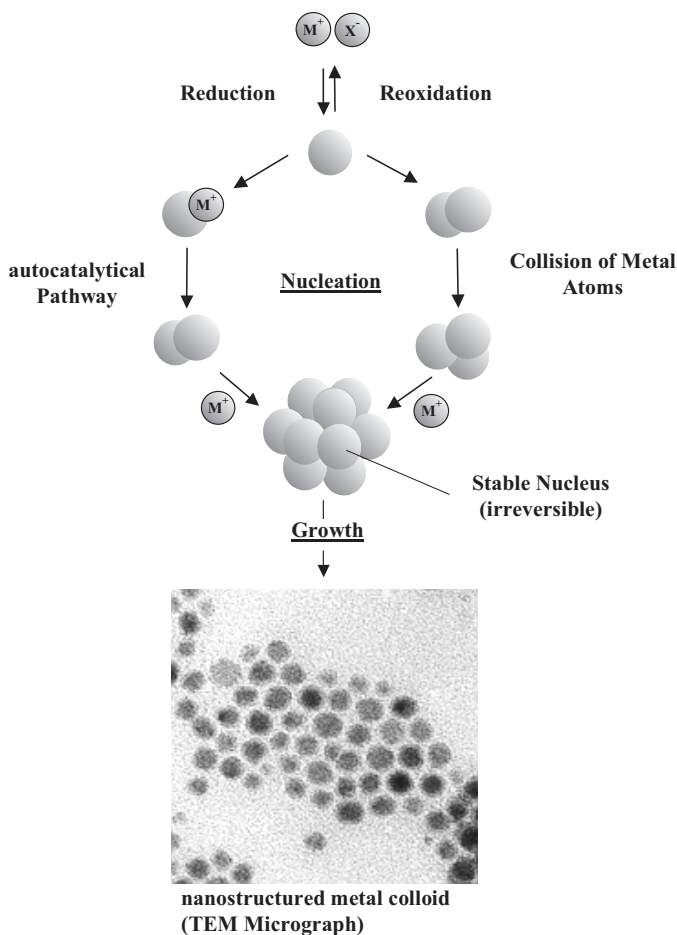


Figure 1.1. Formation of nanostructured metal colloids via the “salt reduction” method. (Adapted from Ref. [4].)

controlled decomposition of metastable organometallic compounds. A large variety of stabilizers, e.g., donor ligands, polymers, and surfactants, are used to control the growth of the primarily formed nanoclusters and to prevent them from agglomerating. The chemical reduction of transition metal salts in the presence of stabilizing agents to generate zerovalent metal colloids in aqueous or organic media was first published in 1857 by Faraday [35], and this approach has become one of the most common and powerful synthetic methods in this field [10, 11, 36]. The first reproducible standard recipes for the preparation of metal colloids (e.g., for 20 nm gold by reduction of $[\text{AuCl}_4^-]$ with sodium citrate) were established by Turkevich [1–3]. Based on nucleation, growth, and agglomeration he also proposed a mechanism for the stepwise formation of nanoclusters which in essence is still valid. Data from modern analytical techniques and more recent thermodynamic and kinetic results have been used to refine this model as illustrated in Fig. 1.1 [31–38].

The metal salt is reduced to give zerovalent metal atoms in the embryonic stage of nucleation [37]. These can collide in solution with further metal ions, metal atoms, or clusters to form an irreversible “seed” of stable metal nuclei. Depending on the difference of the redox potentials between the metal salt and the reducing agent applied, and the strength of the metal–metal bonds, the diameter of the “seed” nuclei can be well below 1 nm.

Nanostructured colloidal metals require protective agents for stabilization and to prevent agglomeration. The two basic modes of stabilization which have been distinguished are electrostatic and steric (Fig. 1.2) [36]. Electrostatic stabilization [see Fig. 1.2(a)] involves the coulombic repulsion between the particles caused by the electrical double layer formed by ions adsorbed at the particle surface (e.g., sodium citrate) and the corresponding counterions. As an example, gold sols are prepared by the reduction of $[\text{AuCl}_4^-]$ with sodium citrate [1–3]. By coordinating sterically demanding organic molecules that act as protective shields on the metallic surface, steric stabilization [Fig. 1.2(b)] is achieved. In this way nanometallic cores are separated

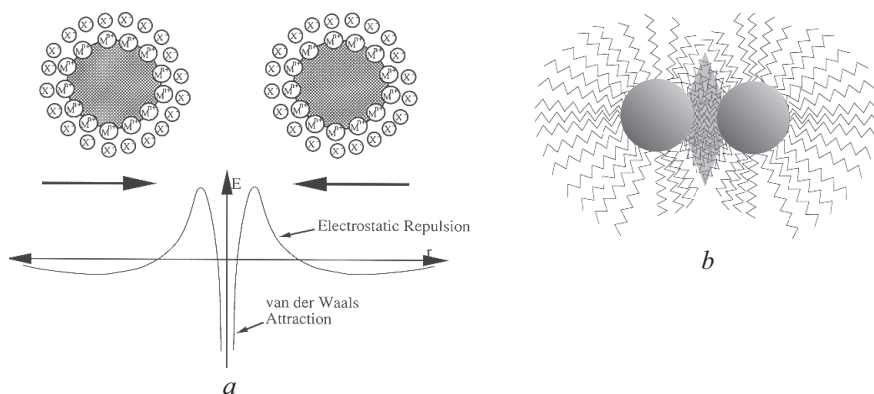


Figure 1.2. (a) Electrostatic stabilization of nanostructured metal colloids. (Scheme adapted from Ref. [36].) (b) Steric stabilization of nanostructured metal colloids. (Scheme adapted from Ref. [36].)

from each other, and agglomeration is prevented. The main classes of protective groups selected from the literature are: polymers and block copolymers [45–48]; P, N, S donors (e.g., phosphines, amines, thioethers) [6, 65–90]; solvents such as THF [6, 91], THF/MeOH [92], or propylene carbonate [93]; long chain alcohols [49–64, 94]; surfactants [6, 7, 9, 21, 22, 93, 95–106]; and organometallics [107–110]. In general, lipophilic protective agents give metal colloids that are soluble in organic media (“organosols”) while hydrophilic agents yield water-soluble colloids (“hydrosols”). In Pd organosols stabilized by tetraalkylammonium halides the metal core is protected by a monolayer of the surfactant coat (Fig. 1.3) [111].

Metal hydrosols, in contrast, are stabilized by zwitterionic surfactants which are able to self-aggregate, and are enclosed in organic double layers. After the application of uranylacetate as a contrasting agent, the transmission electron micrographs show that the colloidal Pt particles (average size = 2.8 nm) are surrounded by a double layer zone of the zwitterionic carboxybetaine (3–5 nm). The hydrophilic head group of the betaine interacts with the charged metal surface and the lipophilic tail is associated with the tail of a second surfactant molecule, resulting in the formation a hydrophilic outer sphere (see Fig. 1.4) [112]. Pt or Pt/Au particles can be hosted in the hydrophobic holes of nonionic surfactants, e.g., polyethylene monolaurate [113, 114].

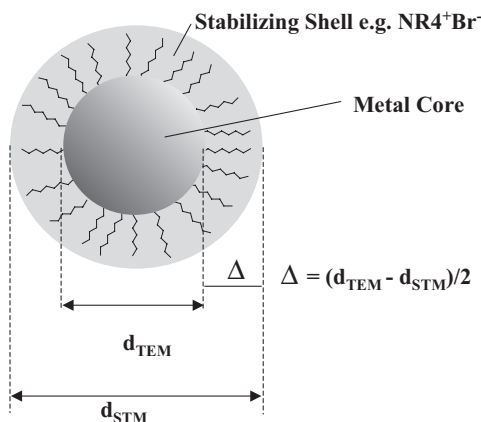


Figure 1.3. Differential transmission electron microscopy/scanning transmission electron microscopy (TEM/STEM) study of a Pd organosol showing that the metal core (size = d_{TEM}) is surrounded by a monolayer of the surfactant (thickness $\Delta = (d_{\text{TEM}} - d_{\text{STM}})/2$). (Adapted from Ref. [9].)

1.3 Reducing Agents

The type of reducing agent employed has been found to greatly affect the resulting particles. It has been experimentally verified in the case of silver that stronger reducing agents produce smaller nuclei in the “seed” [37]. During the so-called “ripening”

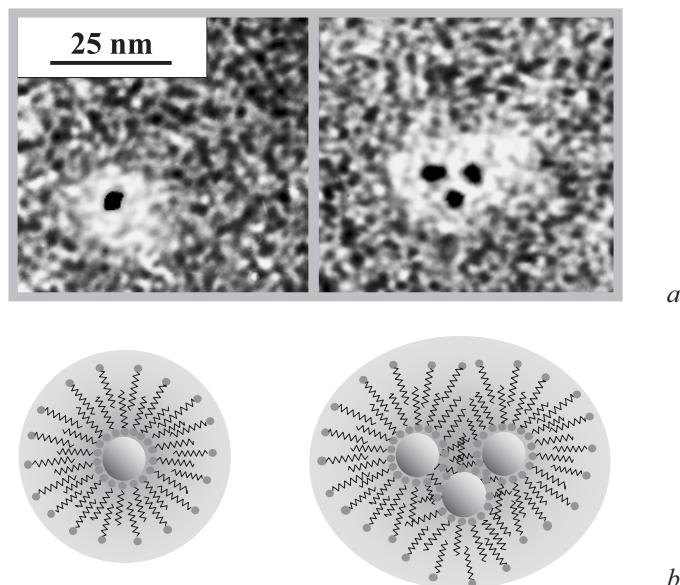


Figure 1.4. (a) TEM micrographs of colloidal Pt particles (single and aggregated, average core size = 2.8 nm) stabilized by carboxybetaine 12 (3–5 nm, contrasted with uranylacetate against the carbon substrate). (b) Schematic

model of the hydrosol stabilization by a double layer of the zwitterionic carboxybetaine 12 (= lipophilic alkyl chain; \bullet = hydrophilic, zwitterionic head group). (Adapted from Ref. [4].)

process these nuclei grow to yield colloidal metal particles in the size range of 1–50 nm which have a narrow size distribution. It was assumed that the mechanism for the particle formation is an agglomeration of zerovalent nuclei in the “seed” or – alternatively – collisions of already formed nuclei with reduced metal atoms. The stepwise reductive formation of Ag_3^+ and Ag_4^+ clusters by spectroscopic methods has been followed by Henglein’s group [38]. Their results strongly suggest that an autocatalytic pathway is involved in which metal ions are adsorbed and successively reduced at the zerovalent cluster surface. The formation of colloidal Cu protected by cationic surfactants (NR_4^+) has been investigated by in situ X-ray absorption spectroscopy which demonstrated the formation of an intermediate Cu^+ state prior to the nucleation of the particles [41]. It is now generally accepted that the size of the resulting metal colloid is determined by the relative rates of nucleation and particle growth, although the processes taking place during nucleation and particle growth cannot be analyzed separately.

The salt reduction method has the main advantage that in the liquid phase it is reproducible and it allows colloidal nanoparticles with a narrow size distribution to be prepared on the multigram scale. The classical Faraday route via the reduction of $[\text{AuCl}_4]^-$ with sodium citrate for example, is still used to prepare standard 20-nm gold sols for histological staining applications [1, 115]. Wet chemical reduction procedures have been applied in the last 20 years or so to combine practically all transi-

tion metals with different types of stabilizers, and the whole range of chemical reducing agents has successfully been applied. In 1981, Schmid et al. established the “diborane-as-reductant route” for the synthesis of $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ (1.4 nm), a full shell (“magic number”) nanocluster stabilized by phosphine ligands [57–72]. Clusters of Au_{55} were uniformly formed when a stream of B_2H_6 was carefully introduced into a Au^{III} ion solution. The “diborane route” for $\text{M}_{55}\text{L}_{12}\text{Cl}_n$ nanoclusters was recently reviewed by Finke et al. [11]. Bimetallic nanoclusters that were made accessible by this method have been thoroughly characterized [65–80]. The phosphane ligands may be exchanged in the Au_{55} nanoclusters quantitatively using silsesquioxanes, which causes important changes in the physical and chemical behavior of the gold clusters [80]. The synthesis and general chemistry of nanosized silica-coated metal particles has been elaborated by Mulvaney et al. [80]. The “alcohol reduction process” described by Hirai and Toshima et al. [10, 45–48] is widely applicable to the preparation of colloidal precious metals stabilized by organic polymers such as poly(vinylpyrrolidone) (PVP), poly(vinyl alcohol) (PVA), and poly(methylvinyl ether). Alcohols containing α -hydrogen atoms are oxidized to the corresponding carbonyl compound (e.g., methanol to formaldehyde) during the salt reduction. The method for preparing bimetallic nanoparticles via the coreduction of mixed ions has been evaluated in a recent review [10]. Recently, it has been demonstrated that through the appropriate choice of reduction temperature and acetate ion concentration, ruthenium nanoparticles prepared by the reduction of RuCl_3 in a liquid polyol could be monodispersely prepared with sizes in the 1–6 nm range [116]. Hydrogen has been used as an efficient reducing agent for the preparation of electrostatically stabilized metal sols and of polymer-stabilized hydrosols of Pd, Pt, Rh, and Ir [117–121]. Moiseev’s giant Pd cluster [Fig. 1.5(a)] [81–86], Finke’s polyoxoanion, and tetrabutylammonium-stabilized transition-metal nanoclusters [Fig. 1.5(b)] [11, 40, 122–126] were also prepared by the hydrogen reduction pathway.

Finke et al. have recently reviewed the characterization of Moiseev’s “giant” cationic Pd clusters [81–86] [Fig. 1.5(a)] [idealized formula $\text{Pd}_{-561}\text{L}_{-60}(\text{OAc})_{-180}$ (L= phenanthroline, bipyridine)] and their catalytic properties [11]. The results of a combination of modern instrumental analysis methods applied to Finke’s nanoclusters have also recently been carefully discussed [11].

Using CO, formic acid or sodium formate, formaldehyde, and benzaldehyde as reductants, colloidal Pt in water [2, 127] was obtained [128]. Silanes have been found to be effective for the reductive preparation of Pt sols [129, 130]. Duff, Johnson, and Baiker et al. have successfully introduced tetrakis(hydroxymethyl)phosphoniumchloride (THPC) as a reducing agent, which allows the size- and morphology-selective synthesis of Ag, Cu, Pt, and Au nanoparticles from their corresponding metal salts [131–136]. Further, hydrazine [137], hydroxylamine [138], and electrons trapped in, for example, $\text{K}^+[(\text{crown})_2\text{K}]^-$ [139], have also been successfully applied as reductants. In addition, BH_4^- has been found to be a powerful and valuable reagent for the salt reduction method. A disadvantage, however, is that transition metal borides are often found along with the nanometallic particles [140, 141]. Tetraalkylammonium hydrotriorganoborates [6, 7, 9, 21, 95–97] offer a wide range of applications in the wet chemical reduction of transition metal salts. The reductant $[\text{BEt}_3\text{H}]$ is

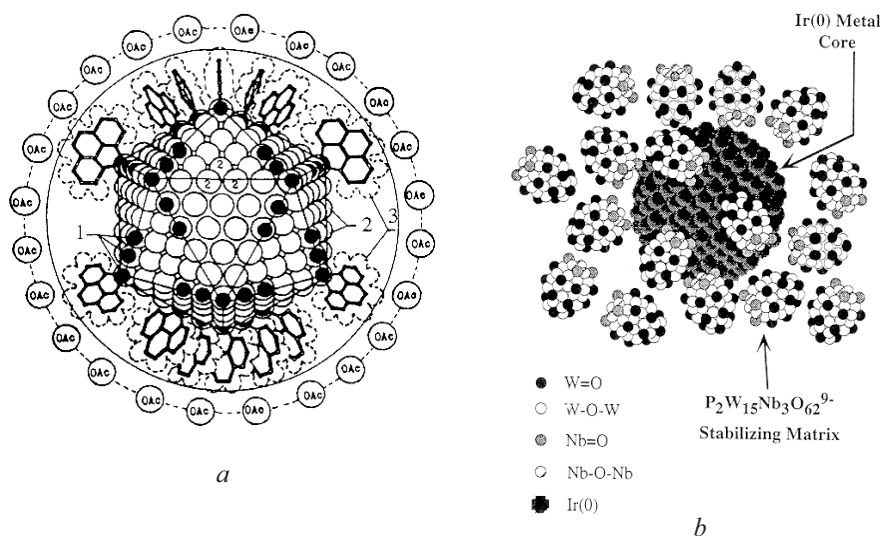
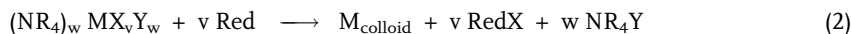


Figure 1.5. (a) Idealized model of Moiseev's "giant palladium cluster" $\text{Pd}_{561}\text{Phen}_{60}(\text{OAc})_{180}$ (Phen = phenanthroline) (adapted from Ref. [4]). (b) Idealized model of a Finke type $\text{Ir}(0)$ nanocluster $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ and Bu_4N^+ -stabilized $\text{Ir}(0)_{300}$. (Adapted from Ref. [4].)

combined with the stabilizing agent (e.g. NR_4^+) in this case. The surface-active NR_4^+ salts are formed immediately at the reduction center at high local concentration and prevent particle aggregation. Trialkylboron is recovered unchanged from the reaction and there are no borides contaminating the products. Most recently it has been demonstrated that the chain length of the alkyl group in the tetraalkylammonium plays a critical role in the stabilization of various metal colloids [142].

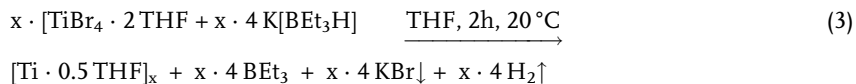


where M = metals of groups 6–11; $\text{X} = \text{Cl}, \text{Br}$; $v = 1, 2, 3$; and R = alkyl, $\text{C}_6\text{--C}_{20}$. The NR_4^+ -stabilized metal "raw" colloids as synthesized typically contain 6–12 wt% of metal. "Purified" transition metal colloids containing ca. 70–85 wt% of metal are obtained by work-up with ethanol or ether and subsequent reprecipitation by a solvent of different polarity (see Tab. 9 in Ref. [6]). When NR_4X is coupled to the metal salt prior to the reduction step the pre-preparation of $[\text{NR}_4^+ \text{BEt}_3\text{H}^-]$ can be avoided. Transition metal nanoparticles stabilized by NR_4^+X^- can also be obtained from NR_4X -transition metal double salts. A number of conventional reducing agents may be applied since the local concentration of the protecting group is sufficiently high to give Eq. (2) [7, 21].



where M = metals; $\text{Red} = \text{H}_2, \text{HCOOH}, \text{K}, \text{Zn}, \text{LiH}, \text{LiBEt}_3\text{H}, \text{NaBEt}_3\text{H}, \text{KBEt}_3\text{H}$; $\text{X}, \text{Y} = \text{Cl}, \text{Br}$; $v, w = 1\text{--}3$ and R = alkyl, $\text{C}_6\text{--C}_{12}$.

The scope and limitations of this method have been evaluated in a recent review [11]. Isolable metal colloids of the zerovalent early transition metals which are stabilized only with THF, have been prepared via the $[\text{BEt}_3\text{H}^-]$ reduction of the preformed THF adducts of TiBr_4 , [Eq. (3)] ZrBr_4 , VBr_3 , NbCl_4 , and MnBr_2 [Eq. (3)].



The results are summarized in Tab. 1.1.

Table 1.1. THF-stabilized organosols of early transition metals.

Product	Starting material	Reducing agent	T (°C)	T (h)	Metal content (%)	Size (nm)
$[\text{Ti} \cdot 0.5\text{THF}]$	$\text{TiBr}_4 \cdot 2\text{THF}$	$\text{K}[\text{BEt}_3\text{H}]$	rt	6	43.5	(<0.8)
$[\text{Zr} \cdot 0.4\text{THF}]$	$\text{ZrBr}_4 \cdot 2\text{THF}$	$\text{K}[\text{BEt}_3\text{H}]$	rt	6	42	–
$[\text{V} \cdot 0.3\text{THF}]$	$\text{VBr}_3 \cdot 3\text{THF}$	$\text{K}[\text{BEt}_3\text{H}]$	rt	2	51	–
$[\text{Nb} \cdot 0.3\text{THF}]$	$\text{NbCl}_4 \cdot 2\text{THF}$	$\text{K}[\text{BEt}_3\text{H}]$	rt	4	48	–
$[\text{Mn} \cdot 0.3\text{THF}]$	$\text{MnBr}_2 \cdot 2\text{THF}$	$\text{K}[\text{BEt}_3\text{H}]$	50	3	70	1–2.5

Detailed studies of $[\text{Ti} \cdot 0.5 \text{THF}]$ [91] show that it consists of Ti_{13} clusters in the zerovalent state, stabilized by six intact THF molecules (Fig. 1.6).

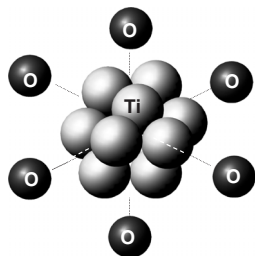


Figure 1.6. Ti_{13} cluster stabilized by six THF-O atoms in an octahedral configuration [7].

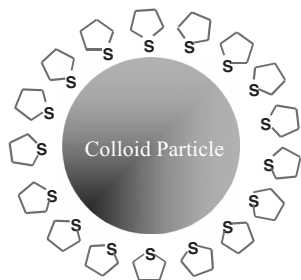


Figure 1.7. Organosols stabilized by tetrahydrothiophene. For $\text{M}=\text{Ti}$, V : decomposition. For $\text{M}=\text{Mn}$, Pd , Pt : stable colloids.

By analogy, $[\text{Mn} \cdot 0.3 \text{ THF}]$ particles (1–2.5 nm) were prepared [143] and the physical properties studied [144]. In the case of Mn, Pd, and Pt organosols the THF in Eq. (3) was successfully replaced by tetrahydrothiophene (THT); but attempts to stabilize Ti and V this way led to decomposition (Fig. 1.7) [7].

Figure 1.8 gives an overview of the $[\text{BEt}_3\text{H}^-]$ method. The advantages of this method may be summarized as follows:

Ti <0.8	V	Cr 3.0	Mn 1-2.5	Fe 3.0	Co 2.8	Ni 2.8	Cu 8.3
Zr	Nb	Mo 2-3		Ru 1.3	Rh 2.1	Pd 2.5	Ag 2-13
			Re	Os	Ir 1.5	Pt 2.8	Au 10




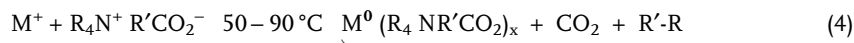
-  Nanometal powders
-  THF-stabilized nanometals
-  NR_4^+ -stabilized nanometals

Figure 1.8. Nanopowders and nanostructured metal colloids accessible via the $[\text{BEt}_3\text{H}^-]$ reduction method (including the mean particle sizes obtained). (Adapted from Ref. [7].)

- The method is generally applicable to salts of metals in groups 4–11 in the periodic table.
- It yields extraordinarily stable metal colloids that are easy to isolate as dry powders.
- The particle size distribution is nearly monodisperse.
- Bimetallic colloids are easily accessible by coreduction of different metal salts.
- The synthesis is suitable for multigram preparations and easy to scale up.

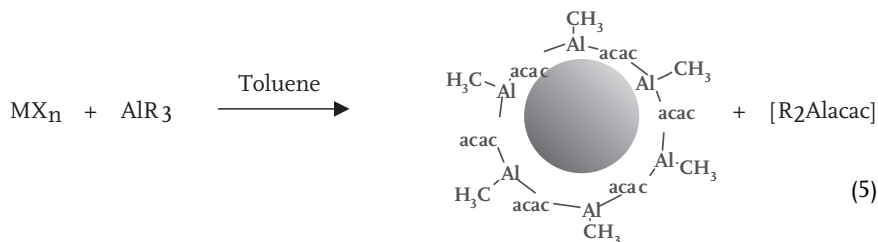
One of the drawbacks of this method, however, is that the particle size of the resulting sols cannot be varied by altering the reaction conditions. Using betaines instead of NR_4^+ salts as the protecting group in Eq. (1), highly water-soluble hydrosols, particularly those of zerovalent precious metals, were made accessible. A wide variety of hydrophilic surfactants may be used in Eq. (2) [7, 21, 96]. Reetz and Maase et al. have reported a new method for the size- and morphology-selective preparation of metal colloids using tetraalkylammonium carboxylates of the type $\text{NR}_4^+\text{R}'\text{CO}_2^-$ (R = octyl, R' = alkyl, aryl, H) both as the reducing agent and the stabilizer [Eq. (4)] [145–147].



where R = octyl, R' = alkyl, aryl, H. The resulting particle sizes were found to correlate with the electronic nature of the R' group in the carboxylate. Electron donors produce small nanoclusters while electron-withdrawing substituents R', in contrast, yield larger particles. For example, Pd particles of 2.2 nm size were found when Pd(NO₃)₂ was treated with an excess of tetra(*n*-octyl)ammonium-carboxylate bearing R' = (CH₃)₃CCO₂⁻ as the substituent. The particle size was found to be 5.4 nm with R' = Cl₂CHCO₂⁻ (an electron-withdrawing substituent). Bimetallic colloids of the following were obtained with tetra(*n*-octyl) ammonium formate as the reductant: Pd/Pt (2.2 nm), Pd/Sn (4.4 nm), Pd/Au (3.3 nm), Pd/Rh (1.8 nm), Pt/Ru (1.7 nm), and Pd/Cu (2.2 nm). The shape of the particles was also found to depend on the reductant: with tetra(*n*-octyl) ammonium glycolate reduction of Pd(NO₃)₂ a significant amount of trigonal particles were detected in the resulting Pd colloid. Recent work in our group has shown that organoaluminum compounds can be used for the "reductive stabilization" of mono- and bimetallic nanoparticles [see Eq. (5) and Tab. 1.2] [107–108].

Table 1.2. Mono- and bimetallic nanocolloids prepared via the organo-aluminum route.

Metal salt	Reducing agent		Solvent Toluene		Conditions		Product m [g]	Metal content wt.%	Particle size F [nm]
	g/mmol	g/mmol	ml	t [°C]	t [h]				
Ni(acac) ₂	0.275/1	Al(<i>i</i> -but) ₃	0.594/3	100	20	10	0.85	Ni: 13.8	2–4
Fe(acac) ₂	2.54/10	Al(me) ₃	2.1/30	100	20	3	2.4	n.d.	
RhCl ₃	0.77/3.1	Al(oct) ₃	4.1/11.1	150	40	18	4.5	Rh: 8.5 Al: 6.7	2–3
Ag-decanoate	9.3/21.5	Al(oct) ₃	8.0/21.8	1000	20	36	17.1	Ag: 11.8 Al: 2.7	8–12
Pt(acac) ₂	1.15/3	Al(me) ₃	0.86/7.6	150	20	24	1.45	Pt: 35.8 Al: 15.4	2.5
PtCl ₂	0.27/1	Al(me) ₃	0.34/3	125	40	16	0.47	Pt: 41.1 Al: 15.2	2.0
Pd(acac) ₂ Pt(acac) ₂	0.54/1.8 0.09/0.24	Al(et) ₃	0.46/4	500	20	2	0.85	Pd: 22 Pt: 5.5 Al: 12.7	3.2
Pt(acac) ₂ Ru(acac) ₃	7.86/20 7.96/20	Al(me) ₃	8.64/120	400	60	21	17.1	Pt: 20.6 Ru: 10.5 Al: 19.6	1.3
Pt(acac) ₂ SnCl ₂	1.15/2.9 0.19/1	Al(me) ₃	0.86/12	100	60	2	1.1	Pt: 27.1 Sn: 5.2 Al: 14.4	n.d.



M = Metals of Groups 6-11 PSE

X = Halogen, Acetylacetonate $n = 2-4$

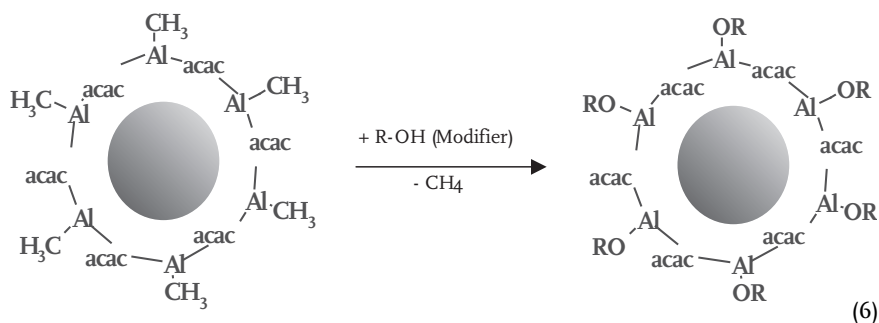
R = C_1-C_8 -Alkyl

Particle sizes 1-12nm

where M = metals of groups 6–11; X = halogen, acetylacetonate, $n = 2-4$; R = C_1-C_8 -alkyl; particle sizes 1–12 nm.

Colloids of zerovalent elements of groups 6–11 of the periodic table (and also of tin) may be prepared according to Eq. (5), in the form of stable, isolable organosols. The analytical data available suggest that a layer of condensed organoaluminum species protects the transition metal core against aggregation as visualized in Eq. (5). The exact nature of the “backbone” of the colloidal organoaluminum protecting agent has not yet been completely established.

Quantitative protonolysis experiments have detected the presence of unreacted organoaluminum groups (e.g., $Al-CH_3$, $Al-C_2H_5$) from the starting material which are still present in the stabilizer. These active $Al-C$ bonds have been used for controlled protonolysis by long-chain alcohols or organic acids (“modifiers”) to give alkoxide groups in the stabilizer [Eq. (6)].



Modifiers: alcohols, carbonic acids, silanols, sugars, polyalcohols, polyvinylpyrrolidone, surfactants, silica, alumina, etc.

The dispersion characteristics of the original sol can be tailored by this “modification” [Eq. (6)] of the organoaluminum protecting shell. A wide variety of dissolubilities of the colloidal metals in hydrophobic and hydrophilic media (including water) has been achieved this way. The active $Al-C$ bonds in the colloidal protecting shell

can react with inorganic surfaces bearing -OH , which opens new ways for the heterogeneous catalyst preparation. The particle size of the metal core is not altered during this modification process (Fig. 1.9) [109].

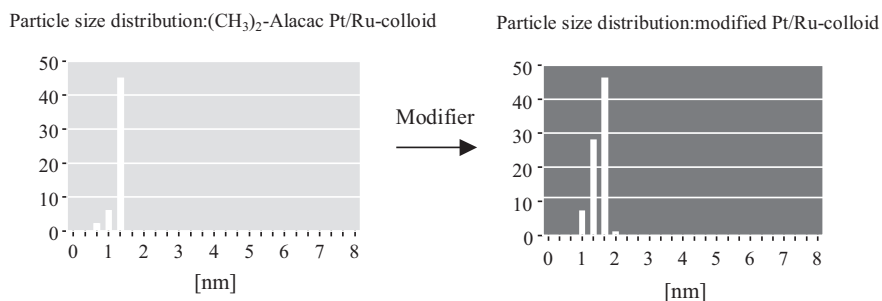
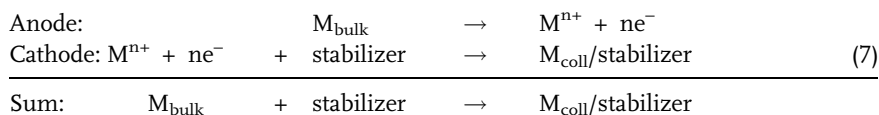


Figure 1.9. Size conservation of colloidal Pt/Ru particles under the hydrophilic modification of the $(\text{CH}_3)_n\text{-Alacac}$ protecting shell using polyethyleneglycol-dodecylether.

1.4 Electrochemical Synthesis

Since 1994 this very versatile preparation route for nanostructured mono- and bimetallic colloids has been further developed by Reetz and his research group [8, 98, 99]. The overall process of electrochemical synthesis [Eq. (7)] can be divided into six elementary steps (see Fig. 1.10).



1. Oxidative dissolution of the sacrificial Met_{bulk} anode
2. Migration of $\text{Met}^{\text{n}+}$ ions to the cathode
3. Reductive formation of zerovalent metal atoms at the cathode
4. Formation of metal particles by nucleation and growth
5. Arrest of the growth process and stabilization of the particles by colloidal protecting agents, e.g., tetraalkylammonium ions
6. Precipitation of the nanostructured metal colloids.

Advantages of the electrochemical pathway are that contamination with byproducts resulting from chemical reduction agents is avoided, and that the products are easily isolated from the precipitate. The electrochemical preparation also provides size-selective particle formation. Experiments using Pd as the sacrificial anode in the electrochemical cell to give $(\text{C}_8\text{H}_{17})_4\text{N}^+\text{Br}^-$ -stabilized $\text{Pd}^{(0)}$ particles indicate that the particle size depends on the current density applied: high current densities led to small Pd particles (1.4 nm); low current densities, in contrast, gave larger particles (4.8 nm) [98]. As was seen in a careful analysis of tetraalkylammonium-stabilized Pd

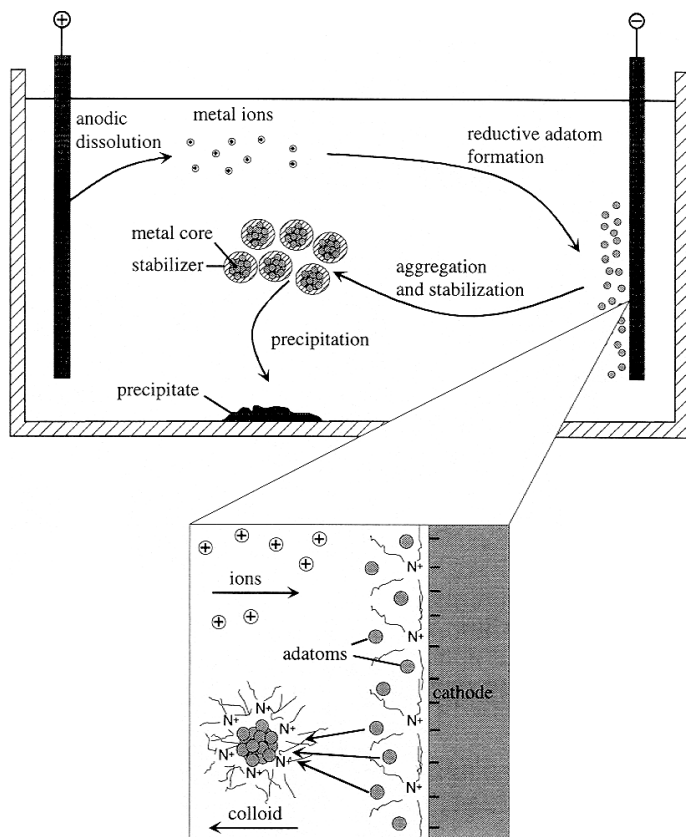


Figure 1.10. Electrochemical formation of NR_4^+Cl^- -stabilized nanometal. (Adapted from Ref. [9].)

and Ni with a combination of transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS), particle size is not controlled by a single cause but rather can be adjusted by varying the following parameters:

- The distance between the electrodes
- The reaction time and temperature
- The polarity of the solvent.

Through the use of electrochemical synthesis nearly monodisperse $\text{Pd}^{(0)}$ particles with sizes between 1 and 6 nm can be obtained. It was also shown that the size of NR_4^+ -stabilized $\text{Ni}^{(0)}$ particles [100] can be adjusted at will. The electrochemical method [98–105] [Eq. (7)] has been successfully applied to prepare a number of monometallic organosols and hydrosols, e.g., of Pd, Ni, Co, Fe, Ti, Ag, and Au on a scale of several hundred milligrams (yields >95%). Using the electrochemical pathway, solvent-stabilized (propylene carbonate) Pd particles (8–10 nm) have also been obtained [93]. If two sacrificial Met_{bulk} anodes are used in a single electrolysis cell,

bimetallic nanocolloids (Pd/Ni, Fe/Co, Fe/Ni) are accessible [103]. In the cases of Pt, Rh, Ru, and Mo, which are anodically less readily soluble, the corresponding metal salts were electrochemically reduced at the cathode (see lower part of Fig. 1.10 and Tab. 1.3).

Table 1.3. Electrochemically prepared metallic colloids

Metal salt	<i>d</i> (nm)	Element analysis
PtCl ₂	2.5 ^b	51.21% Pt
PtCl ₂	5.0 ^c	59.71% Pt
RhCl ₃ · x H ₂ O	2.5	26.35% Rh
RuCl ₃ · x H ₂ O	3.5	38.55% Ru
OsCl ₃	2.0	37.88% Os
Pd(OAc) ₂	2.5	54.40% Pd
Mo ₂ (OAc) ₄	5.0	36.97% Mo
PtCl ₂ + RuCl ₃ · xH ₂ O	2.5	41.79% Pt + 23.63% Rh ^d

^a Based on stabilizer-containing material.

^b Current density: 5.00 mA cm⁻².

^c Current density: 0.05 mA cm⁻².

^d Pt-Ru dimetallic cluster.

Tetraalkylammonium-acetate was used both as the supporting electrolyte and the stabilizer in a Kolbe electrolysis at the anode [see Eq. (8)] [104].



Bimetallic nanocolloids can be prepared by combining the electrochemical methods described in Eqs. (7) and (8) (see Tab. 1.4) [104].

Table 1.4. Bimetallic colloids prepared electrochemically

Anode	Metal salt	<i>d</i> (nm)	Stoich. Energy disperse X-ray analysis
Sn	PtCl ₂	3.0	Pt ₅₀ Sn ₅₀
Cu	Pd(OAc) ₂ ^a	2.5	Cu ₄₄ Pd ₅₆
Pd	PtCl ₂	3.5	Pd ₅₀ Pt ₅₀

^a Electrolyte: 0.1M [(*n*-octyl)₄N]OAc/THF.

By modifying the electrochemical method, the synthesis of layered bimetallic nanocolloids (e.g., Pt/Pd) was achieved [100, 105]. A preformed (Oct)₄NBr-stabilized Pt colloid core (size: 3.8 nm) was electrolyzed in 0.1 M (Oct)₄NBr/THF solution with Pd as the sacrificial anode (Fig. 1.11).

The preformed Pt core may be regarded as a “living metal polymer” on which the Pd atoms are deposited to give “onion-type” bimetallic nanoparticles (5 nm).

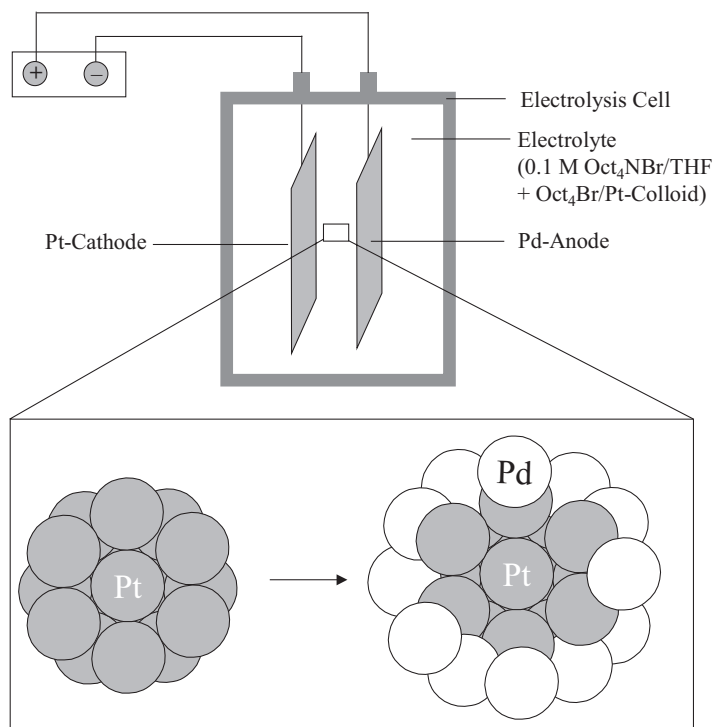


Figure 1.11. Modified electrolysis cell for the preparation of layered bimetallic Pt/Pd nanocolloids. (Adapted from Ref. [100].)

1.5 Decomposition of Low-Valency Transition Metal Complexes

Short-lived nucleation particles of zerovalent metals in solution which may be stabilized by colloidal protecting agents are formed by decomposition of low-valency organometallic complexes and several organic derivatives of the transition metals under the action of heat, light, or ultrasound. Thermolysis [148–153], for example, leads to the rapid decomposition of Co carbonyls to give colloidal Co in organic solutions [148, 149]. Thermolysis of labile precious metal salts in the absence of stabilizers yields colloidal Pd, Pt, and bimetallic Pd/Cu nanoparticles [150] with a broad size distribution. In the presence of stabilizing polymers, such as PVP, these results were greatly improved [151]. Recently, heating in a simple household microwave oven was proposed to prepare nanosized metal particles and colloids [152, 153]. The electromagnetic waves heat the substrate uniformly, leading to more homogeneous nucleation and a shorter aggregation time.

Sonochemical decomposition methods have been successfully developed by Suslick et al. [154] and Gedanken et al. [155–157] and have yielded Fe, Mo₂C, Ni, Pd, and Ag nanoparticles in various stabilizing environments.

By the controlled chemical decomposition of zerovalent transition metal complexes on the addition of CO or H₂ in the presence of appropriate stabilizers, isolable yields of colloidal product in multigram amounts can be prepared [87–90, 158–168]. Bradley and Chaudret et al. [87–90, 159–165] have demonstrated the use of low-valency transition metal olefin complexes as a very clean source for the preparation of nanostructured mono- and bimetallic colloids. Micelles, inverse micelles, and encapsulation methods have also been successfully employed for the preparation of nanoparticulate colloids [38, 39, 94]. It is also worth mentioning that, although beyond the focus of this article, a number of nanoparticulate metal oxide systems have been successfully developed [7, 167–172].

The radiolytic synthesis of mixed Au(III)/Pd(II) solutions has been studied at different dose rates [173]. It was found that at low dose rates, a bilayered cluster with an Au core/Pd shell predominates due to intermetal electron transfer from Pd atoms to Au ions, resulting first in the reduction of the latter to form the core of the particle and then in Pd ion reduction to form the shell. However, at high dose rates when the ion reduction is faster than a possible intermetal electron transfer, genuine alloyed clusters are formed.

1.6

Particle Size Separations

When the particle size deviates less than 15% from the average value, metal colloids are generally addressed as “monodisperse.” Histograms with a standard deviation σ from the mean particle size of approximately 20% are described as showing a “narrow size distribution.” The kinetics of the particle nucleation from atomic units and of the subsequent growth process cannot be observed directly by physical methods. The two primary tools available to the preparative chemist to control the particle size in practice are size-selective separation [51, 174, 175] and size-selective synthesis [41–56, 90, 135–137, 165–181].

So-called *size-selective precipitation* (SPP) was predominantly developed by Pileni [50]. Monodisperse silver particles (2.3 nm, $\sigma = 15\%$) were precipitated from a polydisperse silver colloid solution in hexane by the addition of pyridine in three iterative steps. Recently the two-dimensional “crystallization” of truly monodisperse Au₅₅ clusters has been reported by Schmid et al. [174]. Chromatographic separation methods have thus far proven unsuccessful because the colloid was decomposed after the colloidal protecting shell had been stripped off [145]. Cölfen and Pauck have developed size-selective ultracentrifuge separation of Pt colloids [175]. However, although this elegant separation method gives true monodisperse metal colloids, it still provides only milligram-scale samples. Turkevich et al. were the first to describe size-selective colloid synthesis [1, 2]. They were able to vary the particle size of colloidal Pd between 0.55 and 4.5 nm using the salt reduction method. The crucial parameters were the amount of the reducing agent applied, and the pH value. According to the literature on the process of nucleation and particle growth, the essential factors which control the particle size are the strength of the metal–metal

bond [48], the molar ratio of metal salt, colloidal stabilizer, reduction agent [1, 128, 135, 176–193], the extent of conversion or the reaction time [128], the temperature applied [1, 177, 189], and the pressure [177]. The preparation of nearly monodisperse nanostructured metal colloids using the salt reduction pathway is well documented in the literature. The “control,” i.e., the variation of particle sizes (and shapes), in wet chemical colloid synthesis in practice is left to the intuition of the chemist. At present the most rational method for selecting the particle size is offered by the electrochemical synthesis of Reetz and coworkers. The authors have obtained at will almost monodisperse samples of colloidal Pd and Ni between 1 and 6 nm using variable current densities and suitable adjustment of further essential parameters [98–105]. The resulting particle size in the thermal decomposition method depends on the heat source (see Tab. 1.5) [154]. Size control has also been reported for the sonochemical decomposition method and γ -radiolysis [173, 194, 195].

Table 1.5. Platinum colloids prepared by thermal decomposition methods. (From Ref. [153]).

No. ^a	PVP ^b	NaOH ^b	Average diameter (nm)	Standard deviation (nm)	Relative standard deviation
1	10	0	3.8	0.57	0.15
2	20	0	3.4	0.56	0.16
3	50	0	3.0	0.50	0.17
4	100	0	2.9	0.47	0.16
5	50	2	3.0	0.49	0.16
6	50	4	2.6	0.48	0.18
7	50	6	1.9	0.33	0.17
8	50	8	2.0	0.32	0.16
9	50	10	2.1	0.40	0.19
10	50	0	3.1	1.08	0.35
11	50	8	1.8	0.55	0.31
12	50	0	2.7	0.74	0.27
13	50	8	1.1	0.31	0.28

^a Nos. 1–9 were prepared by microwave dielectric heating without stirring; nos. 10 and 11 were prepared without stirring, and nos. 12 and 13 were prepared with stirring by oil bath heating.

^b Data refer to the molar ratios of PVP (as a monomeric unit) and NaOH to Pt respectively.

The domain of preparation methods using constrained environments affords control of the metal particle shape via the preformation of size and the morphology of the products in nano-reaction chambers [49–64]. Recently, the controlled temperature-induced size and shape manipulation of 2- to 6-nm Au particles encapsulated in alkanethiolate monolayers has been reported [62]. The use of near-infrared laser light has induced an enormous increase in the size of thiol-passivated Au particles up to ca. 200 nm [62]. A new medium-energy ion scattering (MEIS) simulation pro-

gram has successfully been applied to the composition and average particle size analysis of Pt-Rh/ α -Al₂O₃ [63].

1.7

Potential Applications in Materials Science

It is expected that metal nanoparticles and their assemblies will have numerous applications in materials science. It has been demonstrated that physical properties including magnetic and optical properties, melting points, specific heats, and surface reactivity are size-dependent. Quantum size effects are related to the “dimensionality” of a system in the nanometer range. “Zero-dimensional” metal particles might still comprise hundreds of atoms. One-dimensional nanoparticle arrangements (cluster wires) are of potential practical interest as semiconducting nanopaths for applications in nanoelectronics. One-dimensional particle arrangements may be induced through host templates. Using vacuum or electrophoretic methods Schmid et al. [196–198] were able to fill the parallel channels of nanoporous alumina membranes with chains/rows of 1.4-nm Au particles giving one-dimensional “quantum wires” consisting of insulated 20- to 100-Au₅₅ clusters in a helical array. The diameter of the nanowire could be controlled by varying the pore size.

Interestingly, 1.4-nm Au particles were found to arrange themselves into a linear row when attached to single-stranded DNA oligonucleotides [199, 200]. Driven by the technological significance associated with such architectures, the fabrication of ordered two-dimensional nanoparticle arrays has been successfully achieved by several research groups whose work has recently been reviewed [201]. Planar arrays of uniform metal nanoparticles would allow the design of new “supercomputers” with a superior data storage capacity. Langmuir–Blodgett films of nanometal systems have frequently been studied in this respect. Starting with nanoparticles of defined nuclearity, two-dimensional lattices of thiolized Au₅₅, Pd₅₆₁, and Pd₁₄₁₅ have been made [202]. Recently, the first successful preparation of two-dimensional hexagonal and cubic lattices of Au₅₅ nanoparticles by self-assembly on polymer films was reported [174]. Simply dipping polyethylenimine-modified surfaces into aqueous solutions of acid-functionalized Au₅₅ cluster generates the Au₅₅ monolayers shown in Fig. 1.12.

The interactions between the nanoparticles and the surface are obviously strong enough to prevent mechanical removal. Whereas the hexagonal form shown in Fig. 12 (a) is normal for an ordered monolayer, the cubic orientation seen in Fig. 12 (b) is unprecedented. Most of the work published on organized nanometal structures is focused on gold particles and sulfur-containing groups in the various ligands [203–208]. Schiffrin et al. have achieved the self-organization of nanosized gold particles using NR₄⁺X surfactants [209]. Ramos et al. have recently reported the surfactant-mediated two-dimensional crystallization of colloidal crystals [210]. A potential new route to self-assembly of ordered colloidal structures is through the use of attractive Coulomb interactions between colloidal structures and surfactant structures. Nanostructured palladium clusters, stabilized by a monomolecular coat of tetraalkylam-

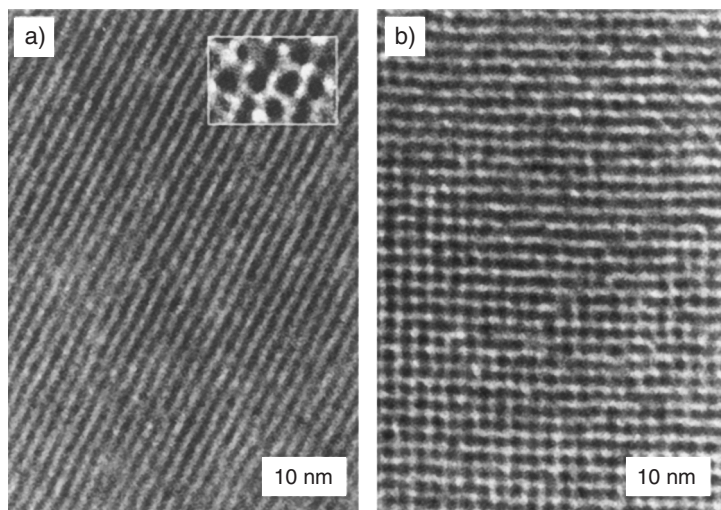


Figure 1.12. Au_{55} monolayers showing a hexagonal (a) and a cubic (b) structure. The insert in (a) shows single clusters in the hexagonal form. (Adapted from Ref. [174].)

monium halide surfactants, self-assemble on carbon surfaces in an ordered manner with the formation of hexagonal close packed (hcp) structures [211–215].

The self-organization of magnetic nanosized cobalt particles was studied by Pileni's group [216, 217]. A comparison of the magnetic properties of deposited cobalt nanoparticles with those dispersed in a solvent indicates a collective flip of magnetization of adjacent particles when they are self-assembled. Mulvaney et al. have described two-dimensional and three-dimensional assemblies of metal core–silica shell nanoparticles in a recent review article [218]. A feature article by Balazs et al. [219] outlines how solid additives can be used to tailor the morphology of binary mixtures containing nanoscopic particles and thereby control the macroscopic properties (e.g., the mechanical integrity) of composites. In addition, computer-aided design has been employed to establish how self-assembled nanostructures can be induced to form arbitrary functional designs on surfaces [220]. Bifunctional spacer molecules such as diamines have been used in attempts to link nanoparticles three-dimensionally [221]. The multilayer deposition of particle arrays on gold has been successfully achieved via the sequential adsorption of dithiol and near-monodisperse nanometal or CdS particles.

Several monometal, bimetal, and metal-semiconductor superlattices have been prepared by dipping a gold substrate into the respective solutions with intermediate steps involving washing and drying [222]. The stepwise three-dimensional assembly of layered gold nanoparticles in porous silica matrices has also been reported [223].

A different field of technological interest stems from the high spin density of nanostructured magnetic metals of the Fe, Co, Ni series [224–225]. THF-stabilized $\text{Mn}^{(0)}$ particles which exhibit superparamagnetism below 20K were described as the first example of an antiferromagnetic metal colloid [226].

New strategies utilizing DNA as a construction material for the generation of bio-metallic nanostructures have made it possible to develop larger “nanotechnology devices” (<100 nm) for microelectronic photolithographic applications. DNA is regarded as a promising construction material for the selective positioning of molecular devices because of its recognition capabilities, physicochemical stability, and mechanical rigidity. Seeman was the first to propose DNA for the precise spatial arrangement of three-dimensional networks [227]. Assemblies of DNA-derivatized gold colloids were recently prepared via the DNA hybridization-based self-organization pathway and the resulting defined arrangements of nanometal particles have real applications in laser technology [228–231]. For example, Alivisatos et al. [199] have obtained defined mono-adducts from commercially available 1.4-nm gold clusters where one reactive maleimido group is attached to every particle. These were coupled with thiolated 18-mer oligonucleotides in order to add an individual “codon” sequence. When a single-stranded DNA template containing complementary codons is added, a self-assembly of nanocrystal molecules is observed (Fig. 1.13) [199, 232]. This work has been the subject of recent reviews [232–234].

Niemeyer et al. [233] have recently reported the coupling of metal particles bearing a biotin substituent with the DNA–streptavidin hybrid. The growth of a 12- μm -long, 100-nm wide conductive silver wire has been achieved using a DNA molecule stretched between two gold electrodes as a template [235].

It remains to be seen how the practical applications of these materials will develop over the next few years.

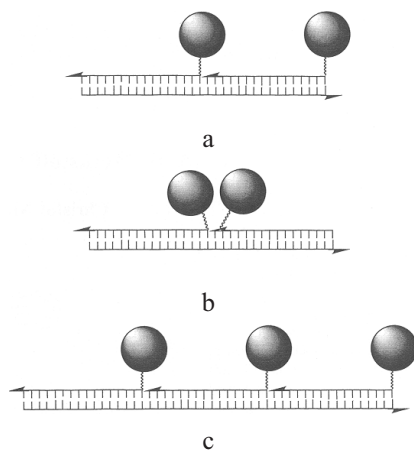


Figure 1.13. Self-organization of conjugates from gold particles (*shaded spheres*) and oligonucleotide codons to supramolecular assemblies by the addition of a template strand. The derivatization of the oligonucleotides in 3' or 5'

position allows control of the mode: head-to-head (a) or head-to-tail (b) homodimers. The trimer (c) is formed using the complementary sequence in triplicate. (Adapted from Ref. [232].)

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