

Noble Metal Nanoparticles and Their (Bio) Conjugates. I. Preparation

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Abstract

Noble metal nanoparticles are important subjects in the field of nanotechnology. Various synthetic processes have been summarized and discussed for the preparation of noble metal nanoparticles of different sizes, shapes and solubility. Among them the colloidal fluids are most fascinating. The formation of nanoparticles starts by the reduction of metal salt and continue with the agglomeration of metal atoms to embryos, subnanoparticles and to premature metal nanoparticles. The existence of the microenvironments in the colloidal systems gives nanoparticles unique reactivity towards various molecules and additives. A soft template can be applied to synthesize noble metal nanoparticles in different-shaped biomolecules-based nanoreactors, micelles and liposomes. The size and shape of nanoparticles follows reactant feed composition, reaction conditions, presence or absence of template and type and concentration of reactants.

Keywords: Noble metal (sub) nanoparticles, particle nucleation and preparation, nanostructures

1. Introduction

The gold and silver colloids have fascinated alchemists since ancient times because of their unique colors and environmental stability. Colloidal gold was applied by alchemists in ancient Egypt, India and China for different purposes, for example, in staining glasses. In the ancient China (since 2550 B.C) the red gold colloids were used as a drug of longevity. This colloid was also used in India during the Vedic age in the medicine as a drug for rejuvenation. Later the gold colloids prepared from different gold precursors and natural compounds were used as a drug for vigor of youth and in the treatment of rheumatoid arthritis. The gold fluids that we know today started to be prepared by different chemical procedures from eighteen century.

Nanomaterials generated by conventional (Qin et al., 1998) and electron-beam lithography (Tennant et al., 1995) methods utilizing the top-down approach can lead to nanoparticles around or slightly below 100 nm (≥ 50 nm). To achieve smaller nanoparticles, the synthetic “bottom-up” procedures should be applied. Herein, the atoms formed by reduction of metal salts and molecules included as reduction and stabilizing agents as building units are employed for the construction of various nanoarchitectures. Noble metal colloids noble are mostly synthesized by “wet chemistry” procedures. In the presence of surfactant (a surface-active compound), however, the agglomeration of atoms or their clusters into various nanoparticle sizes and shapes is controlled. The adsorption of surfactant on the particle (aggregate) surface via physisorption and chemisorption prevents particle aggregation into large aggregate (a bulk material) but can regulate the size and shape of nanoparticles.

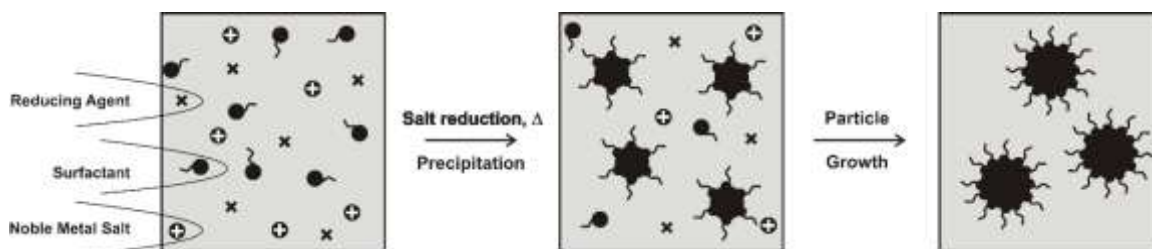
In this first part of the review (Preparation I) we summarize and discuss the preparation of gold and silver nanoparticles including the particle nucleation mechanism.

2. Particle Nucleation

The nanomaterials and nanostructures based on gold colloids can be synthesized by traditional procedures such as vapor phase approaches (Siegel et al., 1998), sol-gel methods (Fegley et al., 1985), sputtering (Fayet & Wöste, 1986), coprecipitation (Tang et al., 1991) chemical reduction (Dumestre et al., 2002) and so on. These nanomaterials have been synthesized by various traditional and nontraditional chemical and (bio) reduction procedures with and without soft (micelles, liposomes,) and hard-templates (CNTs, silica,..) (Jana et al., 2001a; Green 2005). Among them the (co)precipitation is broadly used and it starts with the thermal (or photochemical) (interactions) reactions of precursors leading to the (by) product(s) with decreased solubility in the reaction media (Dumestre et al., 2002; Pileni 2003). In

other words, the precipitation of a new phase (agglomeration of several atoms) results from the supersaturation of solution by reactants. The level and solubility of metal salts in the continuous phase are varied by temperature and solvent quality. Herein, highly soluble chemicals can be converted into less soluble ones and so induce the precipitation events. Under some conditions a certain amount of new fabricated phase (a reaction product) can precipitate from the solution leading to atom clusters or embryos. The creation of a new phase from a metastable state is the generation of new particular entities. This occurs via embryos, which are small, transient clusters of the few metal atoms and/or new precipitated phase. In this embryonic or premicelle stage of the metal nanoparticle nucleation, the nucleated atoms first form clusters such as dimers, trimers, tetramers, etc., and simultaneously formed oligomers may decay in the reaction medium. In this stage the metastable oligomers can disassemble or grow (collide). When the incorporation events dominates over the disaggregation, embryos grow large enough to become stable primary particles (seeds). These oligomers or embryos may disassemble or collide with further metal ions/atoms, finally forming an irreversible colloidal stable seed (sub) nanoparticle. Nucleation ceases when the concentration of growth units falls below the minimum supersaturation level. Once the seed forms, it acts as a convergence point for growth units as long as they are available and grows in dimension (Sau & Rogach, 2010).

Generally, the particle nucleation can proceed by homogeneous and heterogeneous ways: (1) A former proceeds in one step in which precursors are stirred together and then treated by the heat or light. The nucleation and growth events finally result is the appearance of nanoparticles (Scheme 1) (Hyeon et al., 2001). (2) The latter consists of several-steps in the presence of any solid phase (Sun et al., 2000). In the first step the primary (seed) metal particles are generated on different solid structures and then the growth of particles is achieved by the addition of further amounts of precursor(s), stabilizer(s) and additives enable the particle growth and stabilization.

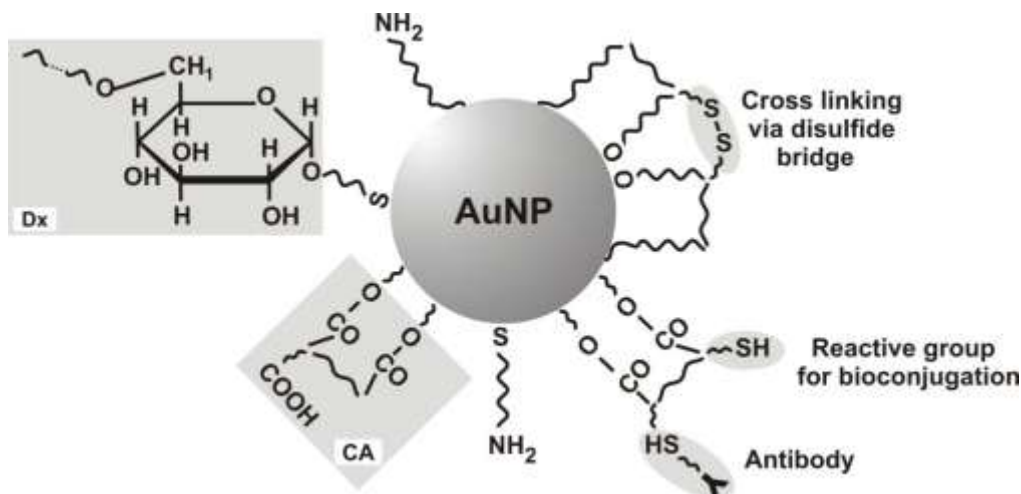


Scheme 1. The particle homogeneous nucleation mechanism (Hyeon et al., 2001)

The particle nucleation is very complex and is accompanied by two opposing factors. One factor is related to the creation of (new) surface at the boundaries of a nucleus that consumes energy. Creation of a new particle phase, on the contrary, is accompanied with the release of energy (De Yoreo & Vekilov, 2003). The high surface particle area (surface-to-volume ratio), thus, creates an energy level barrier for nucleation and the particle growth events. The energy barrier for spontaneous nucleation occurring throughout the solution via homogeneous nucleation is high and therefore requires higher degree of metastability (e.g., supersaturation). The latter occurs on surfaces of pre-existing foreign compounds, hence, some energy is released by the partial elimination of those pre-existing interface by their interaction with embryos and later with primary or (sub) nanoparticles. This energy gain decreases the free energy barrier and favors particle nucleation. Therefore, the heterogeneous nucleation proceeds at the lower (super) saturation level compared to the homogeneous one (Liu 2000). Furthermore the whole energy barrier for the particle nucleation is a complex function of adsorption or/and chemisorption of surface active agents (surfactants) on the particle surface. They influence not only the colloidal stability of (sub) nanoparticles but also their growth. Major benefits of discussed wet chemical procedures are their relatively inexpensive equipment and simple reaction procedure.

3. Preparation of Gold and Silver Nanoparticles

Gold nanoparticles are mostly prepared by reduction of water-soluble gold (III) salts in the presence of capping agent (ligand) able to interact already with the subnanoparticles or their surfaces (chemisorption) blocking its growth beyond the nanometer size range. In the absence of stabilizer formed unstable bare nanoparticles are further aggregate into microparticles or block structures. The particle shell structure is responsible for the stabilization of the nanoparticles in the particular media. The shape and size of the nanoparticles is usually controlled via the careful selection of the capping agent (surfactant, ligand, solvent and additive), reducing agent, reactant concentrations, reaction time, temperature and other conditions. The capping agent interact with the subnanoparticles via physi- and chemisorption due to which they block the particle growth and aggregation as well. They can be modified with compounds carrying functional groups, such as cyano (-CN), thiol (-SH) and amino (-NH₂) groups, known for their high affinity for gold (Scheme 2). Additives having these functional groups can be used as capping agents for gold nanoparticles.



Scheme 2. Schematics of gold nanoparticle modification – adsorption and chemisorption of ligands on the particle surface. AuNP modified with dextran (Dx), citric acid (CA), 2,3-dimercaptosuccinic acid and other capping agents.

Among effective capping agents belong thiol-ended surfactants with different functional groups and high affinities for gold. They can stabilize AuNPs soluble in both polar and in apolar solvents. However, the reduction of water-soluble gold(III) salts usually leads to the generation of water-soluble nanoparticles with broad particle size distribution. On the contrary, the oil-soluble nanoparticles prepared by several procedures lead to nanostructures with narrower particle size distribution. One of them, a high-temperature solution-phase procedure is a reproducible approach for the large-scale synthesis of polymer-decorated gold and silver nanoparticles with diameter below ca. 20 nm (Au) and 30 nm (Ag) and narrow particle size distribution (Hiramatsu & Osterloh, 2004; Jana & Peng, 2003). The simplicity of this procedure is given by three reagents only used: tetrachloroauric acid (or silver nitrate), oleylamine, and a solvent. They can be in additional steps of handling transformed into monodisperse water soluble, for example, by using hydrophilic thiols (Brust et al., 1994). This is provided by the exchange of binding ligands (capping agents). Weak capping agents allow the exchange reactions and make the modification of nanoparticles versatile for biological applications. Among the weak capping agents ranks the citrate salt which acts also as a reducing agent and this approach is important for its simplicity and high reaction yields (Turkevich et al., 1951). The successful utilization of gold or silver nanoparticles (AuNPs or AgNPs) in in vitro and vivo experiments relies on their desired characteristics, namely high water-solubility, biocompatibility, monodispersity and surface functionalities.

The synthesis of silver (sub)nanoparticles (nanoclusters) in aqueous solutions, however, is difficult because silver nanoclusters are unstable and tend to aggregate to larger nanoparticles and even to microstructures: silver oligomers will grow continuously, forming nanoclusters, small and larger nanoparticles and reducing their surface energy, until their growth is stopped by preformed templates or adsorbed capping agents. Various capping agents were used to model the particle growth and to prepare the desired nanoparticles. Decorated silver nanoparticles were prepared by various procedures using biopolymers (DNA, peptides, proteins...), dendrimers, (bio)polymer capsules, polymer microgels, polyelectrolytes, and functional oligopolymers as protecting and stabilizing agents (Petty et al., 2004; Zhang et al., 2005; Shen et al., 2007; Ledo-Suarez et al., 2007). The small water-soluble fluorescent silver nanoparticles can be also prepared by using various radiolytic and photochemical reducing processes for the reduction of silver salts (Zheng et al., 2007; Xu & Suslick, 2010a).

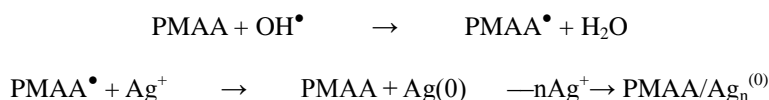
The water-soluble silver nanoparticles can be also prepared by the sonochemical approach. The agglomeration of formed atoms into silver subnanoparticles were regulated by soft templates, for example, as sodium salt of polymethylacrylic acid (PMAA) and other common polyelectrolytes (Xu & Suslick, 2010b). Similar low- and medium-molecular weight polyelectrolytes were used as the capping agent to stabilize and protect the silver nanoclusters in the aqueous solution. The low-molecular weight electrolytes generate the polymer stabilized nanomaterials while the polyelectrolytes fabricate the entrapped nanomaterials. Sonochemistry is also used to prepare various other metal (nano)materials (Bang & Suslick, 2010).

The formation, growth, and implosive collapse bubbles in a liquid irradiated with ultrasound is connected with the high intensity ultrasound derived from primarily acoustic cavitation (Suslick & Flannigan, 2008). Localized hot spots with temperatures of ~5000 K and pressures of hundreds of bars can be generated during ultrasonic irradiation of water (Suslick & Flannigan, 2008). Herein, under these conditions, highly reactive radicals HO_2^\bullet , H^\bullet , OH^\bullet , and other reactive species such as e_{aq}^- , are formed during ultrasonic irradiation of water (Rosenthal et al., 2004; Ciawi et al., 2006). This remembers similar effects of γ -ray or deep-UV irradiation of aqueous solutions. The reduction of noble metal salts to

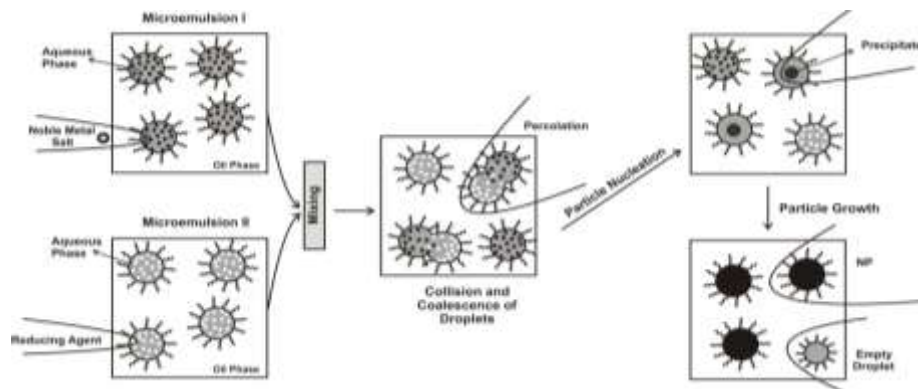
atoms via aqueous sonolysis led to different noble metal nanoparticles in aqueous or alcohol solutions (Guo et al., 2008; Okitsu et al., 2005; Perkas et al., 2008). Sonochemical irradiation of silver salts in aqueous solutions alone leads to the formation of instable particles. However, the template or capping agent helps to depresses the strong aggregation of silver embryos and subnanoparticles and prevents aggregation of these small nanoclusters into large silver nanoparticles or microparticles as reaction advances (Xu & Suslick, 2010b).

Highly reactive radical fragments can be generated under UV irradiation of the aqueous solutions saturated with metal precursors. The photochemical yield of this simple reaction, however, is very low. In order to increase this yield various chromophores, dyes or photosensitizers were used. These photosensible additives absorb UV light and form very unstable excited states. They are transformed to triplet states which then decay to (bi) radicals able to reduce the silver salt. Among photosensible additives or templates belongs low- and medium- molecular weight poly (methacrylic acid) (PMAA) which exhibits both the stabilization and reducing abilities in the preparation of silver nanoparticles (Diez et al., 2009). The charged PMMA (its sodium salt) exhibits a good stabilization efficiency and depresses further growth of nanoclusters to large nanoparticles. The PMAA controls the concentration and activity of OH^\bullet radicals, that is, it acts as OH^\bullet radical scavengers and inhibits the oxidation of silver nanoparticles to silver oxide or its dissolution to the reaction medium (Belloni et al., 1998). The further important activities of PMAA is the formation of radicals via chain-transfer mechanism and their participation in the reduction mechanism of silver salt to silver atoms and their association with the polymer chains ($\text{PMAA}/\text{Ag}_n^{(0)}$):

Highly reactive radicals can be generated under UV irradiation of the metal salt saturated aqueous solutions. Chromophores, dyes or photosensitizer absorbs UV light due to which the excited states are generated. The formed unstable singlet excited states transform to triplet states which then decay to biradicals able to reduce the silver salt. Among templates low-molecular weight poly (methacrylic acid) (PMAA) has been shown to be a versatile phototemplate for preparing stable silver nanoclusters under UV irradiation (Diez et al., 2009). The charged carboxylate groups (sodium salts) provide stability for silver nanoclusters and prevent further growth of nanoclusters to large nanoparticles. PMAA serves as OH^\bullet radical scavengers to prevent oxidation of small silver clusters to form silver oxide (Belloni et al., 1998). The formed (by) products (including radicals) exhibit strong reducing power and produce silver atoms associated with the polymer chains ($\text{PMAA}/\text{Ag}_n^{(0)}$):



The thermally- or photoinitiated inverse (water-in-oil) microemulsion is broadly used to prepare a wide array of noble metal nanoparticles over a relatively narrow particle size distribution (Capek, 2006). Reverse micelles are formed by the association of surfactants in the apolar solvent and form transparent media (Misra et al., 2004; McLeod et al., 2003). They solubilize water, hydrophilic precursors and polar additives within the polar ionic core of the emulsified aqueous microdroplet. By mixing of two microemulsions (first micelles saturated with water, metal salt precursors and second ones with reducing agents and desirable additives) proceeds the desired reduction of metal salt with the reducing agent to metal atoms which aggregate into oligomers, embryos and primary particles and at the end of nucleation to premature nanoparticles (Jain et al., 1996) (Scheme 3). When water is solubilized in the droplet by wetting within the micelles, then the boundary strength increases and the intermicellar exchange among the microemulsion droplets decreases. The reverse is true for the nanodroplets rich in water. Here the chemical reaction and co-precipitation of tiny nanoparticles proceed more easily and large particles appear.



Scheme 3. The schematic view of the synthesis of noble metal nanoparticles by reactions proceeding via microdroplets collisions (Capek, 2004).

Stability of microemulsion is one of the most important parameters that regulates the size and formulate the shape of nanoparticles. The net interparticle attraction and repulsion forces regulate the particle aggregation and the size of final aggregates. The required repulsion forces for the stable nanoparticles favour the narrow particle size distribution (Glomm, 2005). The presence of the ionic groups at the particle surface generates the electrostatic repulsion layer. They together with the counterions form an electric double layer that prevent nanoparticles (colloids) against van der Waals attraction and eliminates the particle agglomeration (Hunter, 2004). The thickness of the electric double layer is a measure of how far the repulsive potential extends from the particle surface. The electrostatic repulsion between nanoparticles can be varied by the bulk ionic strength and temperature. The electrostatic repulsion force diminishes significantly at high salt concentration and low temperature where electric double layer structure is highly suppressed. Under such conditions the degree of dissociation of functional groups decreases as well as the whole surface charge. Steric stabilization achieved mostly by amphiphilic (co)polymers, non-ionic surfactants and/or hydrophilic macromolecules grafted on hydrophobic particle surfaces impart a barrier that prevents colloids from coming close enough such that van der Waals attractive forces can dominate (Glomm, 2005). When the layers of two interacting nanoparticles overlap the concentration of the surface chains increases as well as free energy and osmotic pressure. The molecules of solvent enter the overlap area and separate the interacting particles. Steric stabilization force diminishes significantly at high temperature and does not depend on the salt concentration.

As it was already mentioned the nanoparticles with narrow particle distributions are necessary for successful utilization of gold or silver nanoparticles (AuNPs or AgNPs) in the preparation of hybrid nanoparticles and biological assays. The monodisperse gold nanoparticles can be achieved by using the soft template (inverse micelles) (see above), the seeded procedure (Murphy & Jana, 2002) and/or by varying the ratio of strong and weak reducing agents in co-precipitation approaches (Jana & Peng, 2003). Herein, the secondary nucleation is suppressed and a number of preformed metal nanoparticles is constant during the whole growth interval providing the narrow particle size distribution. Furthermore the selected ratio of strong and weak reducing agents leads to the formation of stable metal nanoparticles with different sizes, shapes and functionalities (Jana & Peng, 2003; Roucoux et al., 2002). This simple approach is applied for the preparation of zero- (0D) and one-dimensional (1D) (anisotropic) nanoparticles by the combination with various capping agents (including (co)surfactants) (Jana & Peng, 2003; Jana, 2004).

Inverse microemulsions of cationic surfactant didodecyldimethylammonium bromide (DDAB) were reported for the preparation of gold nanoparticles of required properties (Lin et al., 2000). Through controlling the amounts of surfactant, water, reducing agent, gold salt and the reaction conditions this approach leads to the production of spherical nanoparticles but with a wide size distribution (1 - 80 nm). This behavior was discussed in terms of the simultaneous contribution of both micelle and precipitation (homogeneous and heterogeneous) nucleation mechanisms. The low DDAB concentration favors more the homogeneous nucleation with the spontaneous formation of large nanoparticles. The small nanoparticles were formed within the nanodroplets (aqueous saturated micelles). After stirring of gold nanoparticles with some (co)surfactants (dodecanethiol), the color of the colloid turned from dark red to slightly purple caused by the association of the nanoparticles (Krebig & Genzel, 1985). The chemisorbed dodecanethiol probably desorbs the surfactant from the particle surface that initiates interparticle attraction and particle aggregation (Dubois & Nuzzo, 1992). When these aggregates were redissolved into toluene with an extra of dodecanethiol added and the solution was heated under reflux the color of the colloid changed back to red due to a deaggregation of the particle associates. The reflux digestion caused a dramatic improvement of particle size distribution. The increased volume of water, on the contrary, increased the particle size distribution.

Silver nanoparticles were prepared using microemulsion droplets of anionic emulsifier AOT (sodium di(2-ethylhexyl) sulphosuccinate) dispersed in dodecane. Emulsified aqueous droplets solubilized silver precursor (silver nitrate) and reducing agent (hydrazine hydrate) (Zhang et al., 2006; Zhang et al., 2007; He et al., 2004). Collision and coalescence of these microemulsion droplets started the reduction of silver precursor and the formation of silver oligomers and primary silver nanoparticles. Aggregation of (sub)nanoparticles led to the formation of silver nanoparticle core decorated by the organic shell and their size varied by a complex way with precursor and water concentrations. Variations of the primary particle formation, particle collisions and particle growth with the precursor concentration regulated the particle size and particle size distribution. Oswald ripening (OR) is a further parameter which can tune the particle size. The collision among nanoparticles is increased with precursor concentration, therefore the protection obtained by chemisorbed AOT molecules on the particles' surface is weakened. The collision is more pronounced among the tiny particles that aggregate into large particles especially at the higher precursor concentration which is supported by the increase in the absorption intensity. At low precursor concentration, the maximum absorption wavelength is blue shifted, meaning a decrease of the particles size. The particle size increased, on the contrary, at higher silver nitrate concentration and therefore the maximum absorption is shifted to a red region. The size of silver nanoparticles increased with higher water level, the ratio () [water]/ [surfactant] and decreased with increasing

amount of surfactant as follows:

$$d(\text{nm})/\omega : 1.52/2.5, 3.39/7.5, 4.98/15.0$$

The particle size distribution was narrower and more spherical nanoparticles were formed at a low water content.

The UV light irradiation was used for the formation of small hybrid silver nanoparticles in microemulsions (Barnickel et al., 1992). These microemulsions with the particle diameter ca. below 10 nm are transparent or semitransparent. Relevant microdroplets (their components) mostly absorb UV light (scattering is slight) and excited reactants can take part in the reduction of metal precursors. The photoinitiation mechanism of particle nucleation is complex because some or all components reaction system absorb light. These molecules such as nonionic surfactant (its terminal hydroxyl groups), reducing agents or additives (dyes) are then transferred to the excited entities and participate in the charge transfer reactions.

Cetyltrimethyl ammonium bromide (CTAB) is part of different procedures for the construction of isotropic and anisotropic micelles (microdroplets, microemulsions) as soft templates used for the preparation and shaping of noble metal nanoparticles (Jana & Pal, 2001b; Törnblom & Henriksson, 1997; Lin et al., 1994). Herein the shaping of microdroplets and nanoparticles can be varied by the surfactant level in the reaction system. For example, spherical micelles appear in a dilute (≤ 1 mM) solution of CTAB surfactant and convert to cylindrical micelles at higher concentrations (≥ 20 mM). The similar behavior can be obtained by the addition of some other organic solubilizers (salicylates) helping more with changing of the spherical micelles to rodlike even to wormlike nanostructures (Törnblom & Henriksson, 1997; Lin et al., 1994). The anisotropic micelles (microdroplets) are formed at high surfactant concentration (and ionic strength) and the aspect ratio increased with increasing CTAB concentration (Murphy et al., 2005). However, there are also papers with different behavior. Perez-Juste et al. have reported that the (nanorod) aspect ratio decreased with increasing surfactant concentration at high CTAB level (Perez-Juste et al., 2004). The template mechanism was also questioned by Pileni and co-workers who have shown that spherical reverse micelles induce not only spheres (0D) but also various other nonspherical particle (1D) (Salzemann et al., 2004). Furthermore, Wei and Zamborini AFM studies did not find any correlation between seed size and nanostructure shape or stabilizer concentration, underscoring the importance of the particle nucleation or initial seed structure, rather than other-shape evolution (Wei & Zamborini, 2004). On the contrary, Gole and Murphy have reported some changes in the dimensions of the nanorods as a function of seed size and stabilizer concentration (Gole & Murphy, 2004).

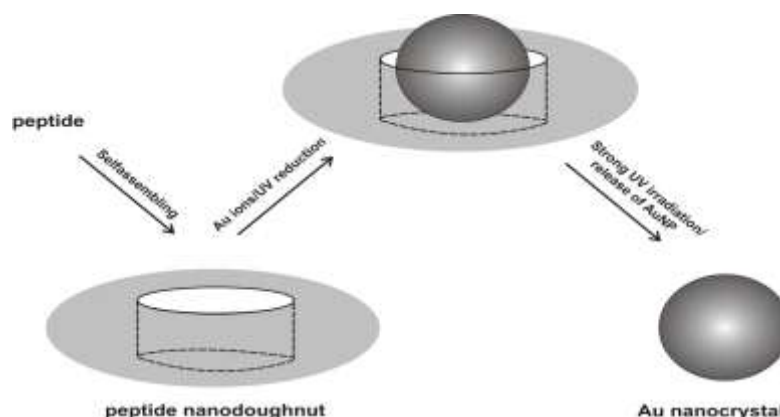
Further studies also showed the complex mechanism particle nucleation and some contradictories in the CTAB/gold salt reaction systems. X-ray absorption spectroscopy studies showed that the particle nucleation proceeds via the complex formation and ligand exchanges in the CTAB- HAuCl_4 - AuBr_4^- ion colloid. The Au^{3+} solution is reduced mostly to Au^0 atoms by the addition of the reducing agent ascorbic acid and formed gold atoms aggregated to gold oligomers (Au_{13} clusters) (Chen et al., 2007). Therein the reaction mechanism is open to discussion while ascorbic acid is known to reduce Au^{3+} ions to only Au^+ state in the presence of a large quantity of CTAB and the fate of formed Au^+ -CTAB complex is unknown (Perez-Juste et al., 2004).

Water soluble silver nanoparticles maintain adequate solution stability at submicromolar levels but not at millimolar ones (Lok et al., 2007). In this scenario, the soft- and hard- templates improves the preparation of water-soluble silver nanoparticles. An artificially-prepared spherical vesicle (liposome) composed of a lamellar phase lipid bilayer was successfully used as a soft template for the preparation of the several water-soluble noble metal nanoparticles. Liposome templates can employ surface ligands for attaching to atoms or metal ions. They encapsulate a region of aqueous solution inside a hydrophobic membrane. Hydrophobic additives can be dissolved into the membrane, and in this way liposome can carry both hydrophobic and hydrophilic entities. This allows liposomes to act as micro- and nanoreactors for the preparation of noble metal nanoparticles (Meyre et al., 2006). Several procedures have been reported in these uni- or multilamellar vesicles. A significant amount of AuNPs but inhomogeneous in shape and size was obtained using classical reducing agent (Chow et al., 1996). However, the gold nanoparticles were also generated in the run without a reducing agent. The reduction of Au(III), thus, took place in the presence of the lipid molecules egg yolk phosphatidylcholine only and the amount of AuNPs per vesicle was very low (Meldrum et al., 1993). The spontaneous, in-situ synthesis of AuNPs without any reducing agent within onion-type multilamellar vesicles was also reported by Regev et al. (Regev et al., 2004). In this case the lipid monoolein acts as a chemical reductant for the gold salt: $\text{RCH}(\text{OH})\text{CH}_2(\text{OH})$ being oxidized to $\text{RCH}(\text{OH})\text{CO}_2\text{H}$ when Au(III) ions are reduced to neutral gold atoms. Isolated AuNPs obtained by this approach are polydisperse both in size and shape, ranging from 8 to ca. 100 nm, and flat epitaxed triangular crystals with truncated corners or sphere-like or even elongated particles appeared.

Touitou et al. have used the lipid bilayers of ethosomes, vesicles composed of phospholipid, ethanol and water, for the preparation of gold nanoparticles (Touitou et al., 2000). The formed biocompatible soft capsules are able to encapsulate and deliver through the skin highly lipophilic molecules (Jain et al., 2007). These malleable vesicles deliver also

cationic or hydrophilic drugs. Significant improvements of the method described for gold-encapsulated ethosomes show that i) the nanoparticles are homogeneous in size and shape, and that the size can be tuned by the temperature synthesis, ii) the ethosomes are mostly unilamellar and the nanoparticles lay inside the lipid bilayer, leaving the surface and the internal volume free for further functionalizations, and iii) the ethosomes are able to encapsulate a large amount of gold nanoparticles.

Three-dimensional self-assemblies of proteins provide ideal templates for deposition of silver or gold atoms to different composite nanostructures (Heddle, 2008). The protein nanoreactor provides the shielding of the nucleation loci from bulk solution where chemical reactions take place (Heddle, 2008; de la Escosura et al., 2009). Importantly, the protein surface is amenable to both genetic and chemical manipulation to impart specific functionalities by design and it is easily achievable due to presence of accessible amino, thiol, and carboxyl groups (Zeng et al., 2007; Kang et al., 2009). The self-assembled peptides nanodoughnuts serve as template nanoreactors for the preparation of gold nanoparticles (Djalali et al., 2003; Keren et al., 2003; Djalali et al., 2004) (Scheme 4). Monodisperse gold nanocrystals grew inside the template by the reduction of gold (III) salt to neutral gold atom (Djalali et al., 2004). Free nanoparticles were isolated by the destruction of protein shell using UV irradiation and heating. The size of nanoparticles was regulated by the choice of protein type and concentration. Furthermore, the type of salt precursor and the reactant concentrations were also connected with the size and shape of nanoparticles. A strong reducing agent, for example, provided large and slightly broader particle size distribution. Some nanodoughnut templates can be also used in the controlled release and/or drug delivery systems.



Scheme 4. Scheme for the peptide nanodoughnut formation (Djalali et al., 2004).

The self-assembled peptides into nanotubes, for example, can serve as template for the preparation of anisotropic (nanorod) gold nanoparticles (Matsui & Gologan, 2000). The peptide templates are known to be generated via intermolecular hydrogen bonds between amide and carboxylic acid groups. The metal salts precursors initiated the formation of complex aggregates with the peptide templates. The complexes between the organic gold salt and polar and ionic groups of the peptide molecules (nanotubes) were confirmed by the UV and IR spectroscopy. The amide peak shifts were observed in amide-containing self-assembled monolayers, after gold salts were bound to their amide groups (Manna et al., 2001). When the peptide/gold ions structures were weakly reduced by UV irradiation and transferred to peptide/gold nanoparticles structures the mechanical strength of the new structures increased. This was not the case for the peptide nanostructures without gold nanoparticles.

4. Conclusion

Various OD and 1D noble metal nanoparticles have been synthesized using different procedures in micellar solutions. The shape and size of the noble metal nanoparticles is usually achieved through the careful selection of reducing agents, reaction temperature, reaction mode (batch, semicontinuous or continuous), different additives and capping agents. Stabilizers, co-stabilizers and different solvents are broadly applied to vary the size and shape of nanoparticles. Mixing of two microemulsions carrying the appropriate reactants where the collisions of droplets start the nucleation generates the nanoparticles with a relatively narrow particle size distribution. The low stability of the metal nanoparticles prepared by the traditional approaches can be increased by using the thiol capped-surfactants. These ligands also help to introduce the functional groups that can't be prepared by other synthetic methods.

Acknowledgements

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Nomenclature

0D	zero-dimensional
1D	one-dimensional
AFM	atomic force microscopy
AgNPs	silver nanoparticles
AOT	sodium bis(2-ethylhexyl)sulfosuccinate
AuNPs	gold nanoparticles
CA	citric acid
C ₁₂ E ₄ (Brij 30), C ₁₂ E ₅ , C ₁₂ E ₆ , C ₁₂ E ₄ (Brij 30)	poly(ethylene glycol)monododecyl ethers
CTAB	cetyltrimethyl ammonium bromide
DB24C8	dibenzo[24]crown-8
DBA	dibenzylammonium
DDAB	didodecyldimethylammonium bromide
Dx	dextran
H ₂ PtCl ₆	hexachloroplatinum acid
HRTEM	high resolution TEM
LNTs	lipid nanotubes
MSNPs	mesoporous silica nanoparticles
NMOFs	nanoscale metal–organic frameworks
NRs	nanorods
OPS	oligopolystyrene
OR	Oswald ripening
PEG	poly(ethylene glycol)
PMAA	poly(methacrylic acid)
PtCl ₆ ²⁻	platinum salt
PVP	polyvinylpyrrolidone
SPIO	superparamagnetic iron oxide
SPIO-DB24C8	crownether-decorated superparamagnetic iron oxide nanoparticles
TEM	transmission electron microscopy
TEOS	tetraethyl orthosilicate
ω	ratio of [water]/[surfactant]

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