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Ignác Capek

# Noble Metal Nanoparticles

Preparation, Composite Nanostructures,  
Biodecoration and Collective Properties

 Springer

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*For my daughters Jana and Martina*

# Preface

This book focuses on the experimental, and to a lesser extent, theoretical, status of research on the preparation and characterization of noble metal nanoparticles and their conjugates, especially those of silver and gold. As such, this book starts with a brief overview of the foundation work concerned with the chapter topics which include nanomaterials, nanoscience, surface-capping molecules, and traditional and nontraditional reduction agents. Although not an exhaustive study, this book examines and summarizes existing achievements in the methods of noble metal nanoparticle synthesis with mainly spherical morphologies, highlighting how their physical and chemical properties are influenced by their change in the size, shape, and morphology.

The book is organized into five chapters. Efforts have been made to develop one-phase, two-phase, and multiphase syntheses in which the reduction of a metal takes place homogeneously or heterogeneously in a selected organic solvent. High-temperature solution-phase synthesis, which is a very reproducible method, can be used for the large-scale synthesis of organoamine-protected gold and silver monodisperse nanoparticles. Most hydrophobic gold nanoparticles (also sometimes called monolayer protected clusters (MPCs)) with diameters below 10 nm are prepared via the Brust–Schiffrin method: a two-phase liquid/liquid system or a suitable single-phase solvent. The Brust–Schiffrin in situ biphasic gold nanoparticle synthesis introduces the use of a quaternary ammonium ion stabilized by a bromide anion—as a stabilizing agent and a phase-transfer catalyst. A new method combining both concepts, the surfactant-free synthesis and the introduction of (functionalized) ligands, controls the particle size well. The resulting, weakly protected nanoparticles can straightforwardly be stabilized and functionalized by the addition of a variety of ligands. The influence of alkylthiol chain lengths on the colloidal and localized surface plasmon resonance (LSPR) properties of AuNPs is summarized. It is concluded that under slow reduction conditions, nanoparticle growth is controlled also by Ostwald ripening. The generation of silver and gold nanoparticles was investigated under various reaction conditions such as with weak and strong reducing and capping agents, low and high temperatures, various additives (ionic

liquid-surfactants, steric surfactants, acids, polysaccharides, polyakrylamides), as well as synthetic approaches.

Templates were used as an effective method for preparing metal nanocrystals with morphologies similar to, or complementary to, those of the template. Both soft and hard templates can be employed for shape-controlled synthesis of metal nanocrystals. Self-assembled, biological, and synthetic structures such as micelles (or reverse micelles), microemulsions, liposomes and vesicles, biological macromolecules, viruses, etc., belong to the soft template group. Multilayered polymer films and block copolymer films were used as nanoreactors or templates for the formulation of noble metal nanoparticles. Microwave irradiation was found to be a new technique for coating AgNPs onto the surface of polymer beads. A new template method for the preparation of flexible silver/cross-linked poly(vinyl alcohol) (PVA) nanocables via a one-step, in situ reduction of  $\text{Ag}^+$  and  $\text{Ag}^+$ -catalyzed cross-linking PVA chains under hydrothermal conditions is discussed. In fact, the formation of such elegant nanocables was controlled by a synergistic growth mechanism called a synergistic soft–hard template mechanism (SSHM). Colorless floccular precipitates formed when commercial polyacrylamide was added to the aqueous solution of silver nitrate at room temperature. This indicated the coordination of silver ions with  $\text{NH}_2$  groups in polyacrylamide (PAAm), with silver ions serving as weak cross-linkers, attaching polymer chains. A thermosensitive water-soluble polymer, poly(*N*-isopropylacrylamide) (PNIPAM) was also used for the immobilization and stabilization of noble metal nanoparticles. The grafting-onto method, to coat gold nanoparticles with PNIPAM chains of end-functionalized SH groups, was used. Poly(*N*-isopropylacrylamide-acrylic acid-2-hydroxyethyl acrylate) microgel particles acted as a scaffold to form fluorescent silver nanoclusters. Nevertheless, linear polyacrylates or polymethacrylates such as poly(methacrylic acid) also act as excellent scaffolds for the preparation of silver nanoclusters in a water solution, by photoreduction with visible light, UV-light, or sonochemically. Microgels of poly(*N*-isopropylacrylamide-co-acrylic acid-co-acrylamide) can be used to template the formation of fluorescent silver nanoparticles. A poly(ethylene glycole) (PEG)-based, non-ionic block copolymer (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO)) templated the synthesis of luminescent silver particles, with a mean diameter of ca. 8 nm. Infinite coordination polymer particles (ICPs) are a class of emerging functional materials that are formed by bridging repeating organic ligands with metallic nodes. Metal-organic frameworks (MOFs) represent another form of mesoporous materials that are thermally robust and in many cases highly porous.

The polymers known as polyelectrolytes (PE) can be used as reducing/stabilizing agents in one single-step syntheses. The building-up of multifunctional core@shell nanostructures is one of the great advantages of using PE assemblies. In this case, the PE forming the multilayers can be functionalized with drugs, organic dyes, contrast agents, radionuclides, catalysts, organic dyes, and proteins—namely antibodies—allowing the application of the ensuing structures in areas such as drug/gene delivery, biosensing, bioimaging, and photodynamic therapy.

Dendrimers are highly branched, nearly size monodisperse polymers with several structural properties. These structural features include the incorporation of metal nanoparticles, with precise control over nanoparticle size and their defined number of terminal groups for each generation with multiple branch ends, which are available for consecutive conjugation reactions. Moreover, they are able to form stable, dense, well-organized, and closely packed arrays on surfaces. The encapsulation of metal ions inside dendrimers involves, variously, electrostatic and complexation interactions—the dendrimer interior includes coordinating groups such as  $-\text{OH}$ ,  $\text{NH}_2$ , or  $-\text{COOH}$ . One unique approach to the preparation of gold nanoparticles is through the use of poly(amidoamine) (PAMAM) dendrimers. The addition of  $\text{HAuCl}_4$  to neutral G4-PAMAM dendrimers resulted in a protonated dendrimer with  $\text{AuCl}_4^-$  counterions, which were then reduced to metallic gold. The stable brown–red solution of the resulting colloidal gold indicated that the metal colloids were stabilized by the dendrimer. The advantage of using dendrimers as templates to prepare gold nanoparticles lies in the fact that the surface of the particles can be modified with various functional moieties (e.g., targeting ligands and dyes) through dendrimer chemistry for practical biomedical applications (e.g., cancer-cell targeting and imaging).

Silica is widely used as an inorganic coating and templates for nanoparticles of different composition (e.g., quantum dots (QDs), magnetic nanoparticles, lanthanide nanoparticles, and noble metal nanoparticles (especially AuNPs), or as a nanoparticle-based carrier of functional molecules. Using the diversity of silane chemistry, a silica shell, coating, or template can be tailored to have functional groups that can include, but are not limited to, amine, aldehyde, carboxyl, epoxy, and thiol groups. In addition to the use of silica as a structural shell on other template materials, nanoparticles composed of silica can be prepared with sizes that typically range between tens and hundreds of nanometers.

The nanoclusters (nanodots) have a discrete electronic state and exhibit strong size-dependent fluorescence over the region from ultraviolet to near-infrared. The excellent fluorescing properties of these clusters means they are suitable for chemical sensing, bioimaging, and single-molecule. Gold clusters have been studied for decades, and many gold clusters with well-defined compositions such as  $\text{Au}_8$ ,  $\text{Au}_{13}$ ,  $\text{Au}_{25}$ , and  $\text{Au}_{38}$  have been prepared. Thus, having spectral properties that distinguish them from their larger nanoparticle counterparts, as well as organic chromophores, noble metal clusters are a new class of small, innocuous, and bright fluorophores whose spectral properties can be tuned. A more sophisticated design of protection groups (ligands) is required to obtain water-soluble luminescent nanodots. Nanodots can be prepared by chemical reduction or photoactivation in the presence of protection groups. Some biological molecules have shown great potential as protection groups. Single-stranded DNA (ssDNA) is also a good scaffold to obtain luminescent silver nanodots with outstanding photophysics, such as large extinction coefficients, high luminescence quantum yields, and excellent photostability. Biomolecules (proteins) are also utilized for luminescent gold nanodot protection. Thiolate-monolayer protected gold (sub) nanoparticles (nanoclusters (NCIs) or QDs) are stable when efficiently passivated by organothiolate monolayers.

Further research in template-based synthetic strategies has led to the preparation of highly fluorescent, water-soluble AuNCIs and AgNCIs when using PAMAM dendrimers, polyglycerol-block-poly(acrylic acid) copolymers, proteins, and DNA as templates. In these hybrid systems the preparation of various nanocomposites by different synthetic routes. The one-pot sonochemical route was taken for the preparation of gold nanocomposites (AuNCos) with near-infrared emission and Au/AgNCos with high quantities of yellow-emission under mild conditions. The obtained Au-AgNCo was yellow under visible light (with 365 nm excitation) and emitted a strong yellow fluorescence. The emitted wavelength of Au-AgNCo blue-shifted to 565 nm compared to that of AuNCos.

Fluorescent silver subnanoparticles can be produced by photogenerated ketyl radicals that reduce  $\text{Ag}^+$  from silver trifluoroacetate in the presence of cyclohexylamine as a stabilizer. AuNPs and AgNPs can act as the quencher of the fluorescence emission of many organic molecules. The quenching of the tryptophan emission, e.g., by AuNPs was analyzed in terms of the Stern–Volmer equation. The AuNPs were synthesized using a direct reduction process (by laser) in sodium citrate. The absorption curve of the citrate-capped AuNPs showed a plasmon resonance at 520 nm. On addition of  $\text{AgNO}_3$ , there was a decrease in absorption. On excitation with a 532-nm laser for 60 minutes, another peak, at 400 nm, was formed which corresponded to the formation of AgNPs. Also, there was an overall increase in the absorbance which suggested the formation of a core@shell structure.

Poly(vinyl alcohol) (PVA) as a matrix component was based, in part, on the ability of this polymer to serve as an electron donor during the reduction of metal ions. In addition, optically transparent films of PVA can be employed to study the optical properties of noble metal nanoparticles. Incorporation of  $\text{Ag}^+$  into polymer templates was found to be more reproducible when poly(acrylic acid) (PAAc) was present, probably owing to the known ability of this polymer to bind silver ions. A very simple method was used to prepare AuNPs with block copolymer shell structures in situ, using a UV irradiation method with the copolymers (polystyrene-block-poly (2-vinyl pyridine) (PSt-b-PVP)) as templates. AuNPs of  $\sim 28$  nm in diameter were covered by PSt-b-PVP copolymer shells. The UV-visible absorption band corresponding to the surface plasmon resonance (SPR) energy of the core-shell nanoparticles is 530 nm, which is larger than that (522 nm) of free AuNPs of the same diameter (20 nm).

In “silica-directed photosynthesis” the metal nanoparticles formed after irradiation of metal ion solutions are nested into mesoporous silica. The silica framework was chosen because of its transparency meaning that the ionizing radiation would penetrate homogeneously within the solid and ensure a homogeneous initial distribution of reducing radiolytic radicals formed by ionization and excitation of the solvent. The silver or gold ions can then interact with the Si–OH groups on the internal pore surfaces of the silica framework. The silver-silica samples irradiated with lower doses displayed a plasmon resonance absorption centered at about 420 nm. In silicas, the plasmon resonance maximum of silver particles is often observed in the 400–440-nm region.

In “reactive species-directed synthesis” the nanoparticles are prepared by reduction of metal ions by gamma irradiation which first induces ionization and excitation of the aqueous solvent, generating radiolytic molecular and radical species—such as solvated electrons ( $e^-$ ), hydroxyl radicals ( $OH^\bullet$ ), and hydrogen atoms ( $H^\bullet$ ). The solvated electrons and hydrogen atoms reduce the metal ions to metal atoms, which eventually coalesce to form nanoparticles. Pulse-radiolysis is another “bottom-up” method that involves gamma-ray irradiation for the reduction of  $Au^{III}$  instead of the traditional addition of a chemical reductant.

“Biomolecule mediated synthesis” covers the preparation of metal nanoparticles in the presence of biomolecules acting both as reducing and capping agents. Photoreduction has been widely used as a route for synthesis of metal NPs either in solution or in polymeric films. The photochemical synthesis used to obtain such nanoparticles in an aqueous medium with biocompatible reducing agents, therefore, has special significance as the NPs can then be readily used in physiological conditions. Additionally, for biolabeling applications, the size of the fluorophore is crucial for an efficient bioconjugation and targeted delivery. Though several methods have demonstrated for the synthesis of metal nanoclusters, the presence of biopolymeric macromolecules on the nanoclusters negates the size advantage. As a result, though the achieved metal core size is very small, the actual hydrodynamic radius including the stabilizing molecules is comparatively large.

Laser ablation synthesis in solution (LASiS) can be an effective technique for obtaining noble metal nanoparticles (NMNPs). In the LASiS method, nanoparticles are produced during the condensation of a plasma plume formed by the laser ablation of a bulk metal plate dipped into a liquid solution. LASiS is usually considered a top-down physical approach, it is free of the usual disadvantages of chemical procedures and can be complementary to the bottom-up chemical methods for production of NMNPs. Moreover, LASiS has the potential of being a unique method for the synthesis of nanoparticles of different metals, with different surface coatings (if any) and in different solvents. Nanoparticles of gold, silver, platinum, copper, and other materials have been obtained by LASiS in water and organic solvents through this one-step, simple procedure. By irradiation of organic microcrystals suspended in water, photothermal or photomechanical ablation mechanisms with nanosecond or femtosecond laser pulses, respectively, were observed. Nanoparticle stability is a crucial aspect of LASiS in pure solvents. Despite the absence of stabilizers, NMNPs obtained in water and in several organic solvents remain stable for days, months, or even longer time periods. If using NMNPs obtained in the absence of stabilizing agents one should always take into consideration the stability time frame for each set of metal nanoparticles and solvent. In general, the presence of electrolytes (surfactants) during LASiS has negative effects on the stability of NMNPs, due to the screening of particle surface charges.

Ionic liquids (ILs) are well-known and intensively explored for their unique properties such as their wide electrochemical windows, good thermal and chemical stability, as well as their good ionic conductivity and non-volatility. Recently, ILs have been used to replace classic organic solvents for the electrodeposition of

metallic nanocrystallines or nanoparticles. Metal-organic frameworks (MOFs), also called coordination polymers or coordination networks, are a class of hybrid materials formed by the self-assembly of metal ions or clusters and polydentate bridging ligands typically under mild conditions. Solvothermal synthesis of MOFs can be achieved with either conventional heating or a microwave. Because high reaction temperatures are involved in the solvothermal method, more extensive transformations of the precursors typically occur before the formation of the MOFs nanoparticles. Temperatures and heating rates provide additional parameters to control MOFs particle nucleation and growth. Surfactant molecules can also be used to template the MOFs synthesis under solvothermal conditions by coating the surfaces of growing MOFs particles. Surfactant molecules play an important role in defining MOFs morphologies. Because of their unique characteristics, microscale plasmas (i.e., microplasmas) offer specific advantages both for nanomaterial synthesis and for interacting with liquids. Microplasma-induced synthesis and the surface engineering of nanomaterials directly in liquids has also been investigated.

Silver nanoparticles with different structures, such as single-crystal cubes with sharp corners, single-crystal cubes with truncated corners, multiply twinned particles, and single-crystal cuboctahedrons, have been used as sacrificial templates. When silver nanocubes with sharp corners are used as templates, the reaction starts pitting on one of its six faces. Through an alloying and dealloying process, pin-hole-free nanoboxes with hollow interiors and porous nanocages can be obtained along the reaction process. If a silver nanocube with truncated corners is used as a template, the reaction starts at all the corners producing cubic nanocages with holes at their corners. Multipodal, spike-radiating, and dendritic shapes are a few examples of the branched morphologies which can be obtained. Branched NMNPs have been prepared under widely different reaction conditions. Starting with seed structure and leading on to factors such as fast-reaction kinetics, preferential binding effects of capping agents and additives, and relative surface growth have all been invoked to explain their branch-formation mechanisms. Submicrometer-sized hollow silver spheres, using PEO-*b*-PMAA (poly(methacrylic acid))-SDS complex micelles as soft templates, can be prepared. The fabrication of two- and three-dimensional ordered structures of hollow silver spheres using colloidal crystal hard templates can also be undertaken. In addition, monodisperse hollow silver spheres have been prepared with phase-transformable emulsions, composed of natural beeswax used as a hard template. Each method has several intrinsic advantages and disadvantages. Templating against hard (solid) templates is arguably the most effective, and certainly the most common, method for synthesizing hollow microstructures/nanostructures, however, the template-removal step not only significantly complicates the process but also diminishes the quality of the product particles. Preparation of non-spherical hollow structures introduces additional challenges, because the synthetic approaches for spherical hollow structures does not generally apply to the synthesis of non-spherical hollow structures. Furthermore, the fabrication of silver nanoshells has proven more difficult than other types, such as gold nanoshells. Cubic NaCl crystals serve as unconventional non-spherical hard templates, easily coated by AgCl particles around the cube

surfaces because of their similar crystalline structures. Polycrystalline silver nanoparticles, synthesized by thermal reduction of silver ions in a glycine matrix, are stable in aqueous solution and exhibit bright luminescence. Solution plasma, a novel technology, has the potential for the advancement of nanomaterial production and the decomposition of organic-based compounds.

The combination of the magnetic and optical properties of nanoparticles into a single platform has gained further attention due to diagnostic, therapeutic uses and immunomagnetic separation (IMS), drug delivery, and sensing. Therefore, the rationale design, synthesis, and surface modification of multifunctional nanoparticles represent the most important steps. One of the examples of a multifunctional nanoparticle results from a core@shell structured  $\text{Fe}_3\text{O}_4$ @Au nanoparticle. Chitosan acts as a soft template in the formation of multibranch magnetic nanoparticles, and the gold-coating process was carried out in the presence of chitosan to give a better particle dispersity and to avoid agglomeration problems. In addition, the main advantage of using a chitosan matrix is that it acts as a stabilizing agent in the formation of nanoparticles due to the presence of hydroxyl and primary amino groups. The addition of silver ions provides an anisotropic-shaped nanostructure. Gold bimetallic nanoparticles are classified by two types of mixing pattern: core@shell NPs and alloy bimetallic NPs. The alloy bimetallic NPs consist of a homogeneous mixture of gold and another metal in the NP. Many Au bimetallic NPs are alloyed with Ag, Pd, Pt, Zn, Cu,  $\text{ZrO}_2$ , CdS,  $\text{Fe}_2\text{O}_3$ , Eu, Ni, and Rh. The core@shell NPs consist of a metal shell surrounding a gold core, or gold shell surrounding another metal core. The Au- $\text{Fe}_3\text{O}_4$  bimetallic NPs are considered as attractive materials for both biological and medical uses, due to their theranostic (therapy + diagnostic) properties involving magnetic resonance imaging (MRI) and hyperthermia. The Au- $\text{Fe}_3\text{O}_4$  bimetallic NPs are attractive materials for biological and medical areas, due to their theranostic (therapy + diagnostic) properties involving magnetic resonance imaging (MRI) and hyperthermia.

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