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Fundamental Growth Principles of Colloidal Metal Nanoparticles – a new Perspective

Jörg Polte[1,*]

[1]Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany

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ABSTRACT: In the last decades, much effort was put into the development of synthetic strategies to produce nanoparticles of different sizes and morphologies and a large number of scientific contributions are dedicated to the characterization and application of metal nanoparticles. In contrast, only few studies deal with particle formation mechanisms. As a consequence, theoretical concepts to describe particle growth processes are very rare and the few existing models are hardly able to explain how synthesis parameters influence the final particle. This contribution discusses recent experimental results from which a novel growth concept based on colloidal stability is deduced. The growth concept is in contrast to nucleation models and allows a description of colloidal growth processes from a different perspective. It states that for most syntheses the minimal particle size is rather determined by colloidal than thermodynamic stability making a nucleation model irrelevant. .

1 Introduction

In the last 50 years, the development of colloidal nanoparticle syntheses has been pursued intensively due to theenormous technological applications and fundamental scientific interest. Colloidal nanoparticles exhibit interesting electrical, optical, magnetic, and chemical properties different to their bulk counterparts. These properties are determined by parameters such as size, shape, composition or crystalline structure. Their unique properties qualify them for a wide range of potential applications in fields such as medicine, biotechnology and catalysis, placing colloidal nanoparticles among the most intensely studied nanoscale materials. In principle, it is possible to adjust their properties in the desired manner by controlling one of the above listed parameters which essentially requires the understanding of the formation processes. The foundations of metal colloid science were laid by Michael Faraday in the 19th century with his ground-breaking experiments on gold sols. Faraday attributed the red color of a solution to the presence of colloidal gold, obtained by reduction of dissolved chloroaurate using white phosphorus.[2] Further important progress in the description of nanoparticle behavior was achieved by Wilhelm Ostwald at the end of 19th century, in particular by his theory of particle growth via Ostwald ripening.[3] His son Wolfgang Ostwald became one of the most influential scientists in the field of colloidal chemistry in the beginning of the 20th century and is the founder of the german colloid society. In 1925, Richard Zsigmondy received a Nobel Prize for his work on colloids and the invention of the ultra microscope, which enabled the direct observation of particles contained in colloidal solutions. Since Faraday's ground breaking work in 1857 numerous experimental methods for the synthesis of metal, metal oxide and semiconductor nanoparticles have been developed,[1] such as the classical reduction of chloroauric acid in aqueous solution by trisodium citrate.[4] This synthetic procedure became popular upon the work by John Turkevich in the 1950s, a professor of chemistry in Princeton and a pioneer in the field of catalysis. To explain the underlying processes of colloidal formation of such syntheses, the classical nucleation theory (developed by Becker and Döring in the 1930s)[5] with its transformation to nanoparticles by LaMer and co-workers in the 1950s[6,7] is still seen as the basic model. Nevertheless, several studies demonstrated that the classical nucleation theory (CNT) fails to describe nanoparticle growth.[8] Accordingly, Oxtoby noted that "nucleation theory is one of the few areas of science in which agreement of predicted and measured rates to within several orders of magnitude is considered as major success".[9] As a result, even after more than 150 years of research in the field of metal colloids, formation mechanisms of nanoparticles are still discussed controversially. No theory or theoretical model exists so far that is able to describe or predict the evolution of the particle size or size distribution comprehensively. Moreover, only limited information of the different underlying physico-chemical processes like the reduction process or the stability of the colloids are available.[8] Xia et al. described this situation very appropriate by stating that "at the current stage of development, it is not an exaggeration to say that the chemical synthesis of metal nanocrystals (as well as for other solid materials) remains an art rather than a science".[20] Exemplarily, different and also contradictory mechanisms are derived for the classical citrate synthesis of gold nanoparticles (Turkevich method).[4,10–19] In fact, it is impressive what kind of nanostructure can be synthesized without having a deep understanding of the underlying principles but it does not need much imagination what would be possible with a profound mechanistic knowledge.

In my opinion, the main reason for that lack of knowledge was the absence of reliable experimental information about the particle growth process, in particular of the particle size and concentration during the growth process. Thus, the development of experimental setups for time resolved in-situ measurements which allow the determination of that demanded information represents the most capable approach to reveal the key steps of nanoparticle formation. In the last 5-6 years, colleagues and I could show that setups applying small angle X-ray scattering (SAXS) can exactly deliver the required information.[18,19,21–23] In these publications several metal nanoparticle (mainly Au- and Ag-NP) syntheses were investigated applying these novel techniques and setups. For

each investigated synthetic procedure a detailed growth mechanism could be deduced.
The aim of this paper is to elucidate a major issue in colloidal science by analyzing and comparing the different growth mechanisms: the identification of fundamental principles of colloidal nanoparticle growth.

The structure of this paper is as follows: (i) a brief description of nanoparticles, their properties and theoretical approaches to describe particle growth (section 2); (ii) a short introduction to the concepts of colloidal stability necessary to understand the herein proposed concepts of particle growth (section 3); (iii) a summary of the important results and findings from the recent studies comprising the mechanistic interpretations (section 4.1); (iv) a discussion of growth mechanisms for syntheses with a monomer supplying chemical reaction faster than the actual particle growth (section 4.2.1); (v) an introduction of new concept of colloidal growth (section 4.2.2 and 4.2.3); (vi) a discussion of Ostwald ripening processes (section 4.3); (vii) a discussion of growth mechanisms of syntheses for which the monomer supplying reaction governs the growth kinetic using the Turkevich method as an example (section 4.4); and (viii) critical discussion of the suitability of nucleation models and the herein introduced growth concept with focus on metal colloids (section 5). The following two sections (i.e. 2 and 3) are a summary of common approaches to synthesize (metal) colloids, describe colloidal growth and a brief introduction of colloidal stability which can be skipped by the proficient reader. However, these briefly summarized subjects need to be understood to follow the discussion of this contribution.

2 Brief description of colloidal nanoparticles, their properties and theoretical approaches to describe nanoparticle growth

The preparation of NPs can be realized by numerous physical and chemical methods. For nanoparticles physical methods often rely on a “top-down” approach by subdividing some bulk (precursor) material into smaller units. In contrast, chemical procedures are in mainly “bottom-up” approaches that start with a chemical reaction delivering the metal atoms, followed or accompanied by controlled aggregation of atoms into particles. In general, chemical routines (i.e. reduction, thermal decomposition or sol-gel syntheses) are more suitable to obtain small and uniform particles. This publication focuses on metal NPs prepared via wet chemical reduction processes - the probably most common synthetic procedure for metal nanoparticles.

For these syntheses, metal NPs (Au, Ag, Pd, Pt, Cu ...) are often prepared in aqueous or non-aqueous solutions by the reduction of a dissolved metal precursor (typically a metal salt) with a reducing agent such as sodium borohydride, ascorbic acid, trisodium citrate or alcohols.[26] This procedure is often carried out in the presence of a stabilizing agent, whereby the stabilizer influences the aggregation behavior of atoms, clusters and NPs. Stabilizing agents adsorb on a NP surface and provide via repulsive forces an electrostatic stabilization (like citrate ions) or a steric stabilization (as for polymers such as PVA (poly (vinyl alcohol) and PVP (polyvinylpyrrolidone)). Furthermore, organic ligands with a strong affinity to metal surfaces via phosphine or thiol functionality can suppress NP aggregation. Thiols used as capping agents include disulfides, polymers with mercapto groups and dendrimers.[1,27,28] Micelles or droplets in emulsion can be employed as nano-reactors which confine the precursor solution locally; hence, spatial separation precedes nanoparticle formation.[29]

Size control of nanoparticles can be obtained via thermodynamic, kinetic or stoichiometric means. Strategies can rely on strongly adsorbed stabilizer on the NP surface, arresting a limited amount of reactants in micelles (i.e. stoichiometric control), suppressing further “nucleation events” (e.g. seeded- growth), or subsequent treatments that increase NP size homogeneity (digestive ripening). A common approach for size control is the use of capping agents that typically adsorb on the nanocrystal surface, creating a nanoparticle-stabilizer entity which then represents a thermodynamically very stable nanoparticle configuration. As reported for several metal nanoparticle syntheses, a variation of the capping agent type or concentration (i.e. stoichiometry) enables a size variation of the derived NPs. In case of thiol-stabilized Au-NP this results in a size variation between 1 and 4 nm in diameter, but fails often for larger particles since significantly wider size distributions are obtained.[1] In general, the thermodynamic approach of NP size control, i.e. forming stable bondings between protective agents and nanoparticles can generate problems in application such as catalysis, where e.g. sulfur originating from the capping agents thiol groups is difficult to remove and acts detrimental by blocking catalytically active sites. Access to larger NPs with narrow size distribution is usually gained via “seeded-growth".[28,30] In case of noble metal NPs, typically small seeds are generated by fast reduction (e.g. $HAuCl_4$ + $NaBH_4$) in presence of a stabilizing agent (e.g. sodium citrate), succeeded by addition of a weak reducing agent (e.g. ascorbic acid) and a second stabilizer (e.g. CTAB).[27,28,30–37] The particle growth is induced by adding repeatedly small amounts of precursor. To avoid further generation of new (small) particles, the reduction of added precursor is often relatively slow because of the use of a “mild reducing agent".[28,30] In practice, size control is rather based on extensive experimental trial-and-error strategies than on a directed design of a synthesis process.

2.1 Nucleation

Nucleation is a purely thermodynamic model which describes the process of the first step in a first order phase transition. It describes the appearance of a new phase - the nucleus- in the metastable primary phase.

The vast majority of the available theoretical work of nucleation applying equilibrium thermodynamics and are based on the classical nucleation theory (CNT) developed by Becker and Döring more than 70 years ago.[5] The CNT utilizes that a thermodynamic system tend to minimize its Gibbs free energy (i.e. to maximize the entropy of the whole system). Originally, a thermodynamic approach describing the condensation of liquid from the vapor phase,[9] it was extended to other types of phase transitions.[38,39] Thus, making it an apparent ideal candidate for precipitation processes as well as crystallization of solids. This thermodynamic theory was also transferred to growth processes of nanoparticles such as LaMer's theory.[6] The CNT only describes the nucleation, particle growth is separated as a subsequent process. The further growth can be explained via different growth processes such as diffusion limited growth, aggregation or Oswald ripening. Further approaches to characterize the particle growth are models using rate equations that are able to describe the size evolution of nanoparticles via the use of rates for certain changes such as a rate of monomer attachment. Formulating and solving (in general numerically) these expressions evolve a size distribution of the particles with respect to time.[40]

The concept of CNT is based on the macroscopic Gibbs capillary effect, meaning that macroscopic entities such as the surface energy are taken to develop expressions for the nucleation rate.[5] In this context it has to be distinguished between homogeneous and heterogeneous nucleation. Nucleation which occurs at nucleation sites on solid surfaces contacting the liquid or vapor are referred to as heterogeneous nucleation. Exemplarily, a heterogeneous nucleation in the field of nanoparticle growth occurs at the surface of particles in solution providing nucleation sites, used in seeded-growth syntheses. In contrast, homogeneous nucleation occurs spontaneously and randomly, but requires a supercritical state such as a supersaturation.

2.1.1 Homogeneous Nucleation

The Gibbs free energy of a nucleus is in general expressed as the sum of a negative and a positive term. The negative term represents an energy favorable bonding between a monomer and a cluster or theoretically also between two monomers leading to a lowering of the bulk energy. The positive term describes how unfavorable such a bonding is due to an increase in the free surface energy. In its simplest form with spherical symmetry, the free energy of a cluster (ΔG) is given as:

$$\Delta G = -\frac{4}{3}\pi r^3 |\Delta G_V| + 4\pi r^2 \gamma \tag{1}$$

with the radius r, the difference in bulk free energy per unit volume $|G_V|$ and the surface energy per unit area γ. Due to the negative (bond making) and positive (surface energy) terms, the curve of the cluster free energy displayed in Figure 1a has a maximum at a radius r_c called the critical radius, whereby the corresponding energy barrier is called the activation energy ΔG_c. For clusters smaller than r_c growth is unfavorable and dissolution more probable. For clusters with a radius larger than r_c, growth is favored. The critical radius can easily be determined by solving Eq. (1) for $dG/dr = 0$ leading to:

$$r_c = \frac{2\gamma}{|\Delta G_V|}. \tag{2}$$

Substituting r in Eq. (1) by r_c from Eq. (2) yields the expression for the critical free energy ΔG_c:

$$\Delta G_c = \frac{16\pi\gamma^3}{|\Delta G_V|^2} \tag{3}$$

The nucleation rate $J(T, \Delta G_c)$ can be expressed using the Arrhenius equation since the energy barrier is an activation energy and thus nucleation a statistical process:

$$J(T, \Delta G_c) = A exp\left(\frac{-\Delta G_c}{k_B T}\right). \tag{4}$$

2.1.2 Heterogeneous Nucleation

Heterogeneous nucleation is referred to as nucleation at preferential sites of surfaces. The basic assumption is that at preferential sites such as phase boundaries or impurities, the effective surface energy is lower which decreases the activation energy. This makes nucleation at these preferential sites more probable. As a result, heterogeneous nucleation occurs more often than homogeneous nucleation. In the field of nanoparticle syntheses, heterogeneous nucleation is seen as the driving force for a successful seed-mediated growth. Nevertheless, in a nanoparticle synthesis it is assumed that both kind of nucleation occur, both consecutively and parallel.

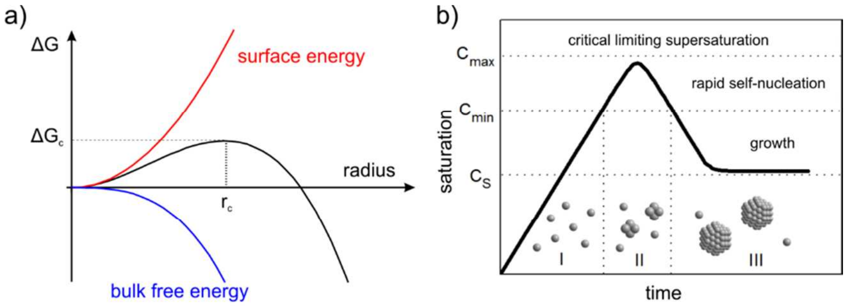

Figure 1 (a) The dependence of the cluster free energy, ΔG, on the cluster radius, r according to the classical nucleation theory (CNT). The curve has a maximum free energy ΔG at a critical cluster size, r_c, which defines the first stable particles - the nuclei. (b) The principle of nanoparticle nucleation due to LaMer's mechanism of (sulfur) nucleation derived from CNT. The (theoretical) qualitative curve describes the monomer concentration as a function of time.

2.2 LaMer's Nucleation Theory

The concept of CNT was transferred to nanoparticle syntheses by LaMer and his colleagues back in the 1950s proposing the concept of burst nucleation.[6,7] The pioneering concept was developed from their research on various oil aerosols and sulfur hydrosols. In the burst nucleation process, nuclei are generated at the same time due to homogeneous nucleation and subsequently grow without additional nucleation. The basic idea of that nanoparticle formation concept is to separate nucleation and growth. Consequently, it is a separation of a homogeneous from a heterogeneous phase. Such a process enables control of the particle size distribution during growth. The mechanism, displayed in Figure 1b, is as follows: (I) the concentration of monomers is increasing (in the case of metallic nanoparticles most likely due to reduction) and reaches at a certain time a certain critical supersaturation level (C_S) at which homogeneous nucleation is possible but ``effectively infinite",[6] (II) the saturation increases and reaches a level (C_{min}) at which the energy barrier (activation energy) for nucleation can be overcome leading to a rapid self-nucleation - the burst nucleation, (III) due to the burst nucleation, the supersaturation level lowers immediately below this self-nucleation level ending the nucleation period; growth then occurs by diffusion of further monomers in solution towards particle surfaces which can be interpreted as heterogeneous nucleation/growth. The expected corresponding particle concentration with respect to time would be a fast increase at the self-nucleation stage (II) and a more or less constant value during the final growth stage (III).

The LaMer model and its modifications are still the only commonly accepted models describing the general mechanism of the nanoparticle formation process. In principle, the model rationalizes also conventional strategies for size adjustment of colloidal NPs, i.e. fast reduction to induce a rapid build-up of supersaturation. As a consequence, many nucleation events lead to many small NPs, and few events to less and bigger particles. Moreover, the principles of “seeded-growth” are derived from the concept of classical nucleation, i.e. suppressing further nucleation by slow reduction to use reduced monomers exclusively for growth of already formed particles. However, the LaMer model is not able to predict or characterize the evolution of nanoparticle size distributions. It only describes the process of nucleation followed by a growth of the stable nuclei, but the characteristics of the growth remain more or less unspecific. Accordingly, LaMer stated:”...the process of growth of stable nuclei to form discrete particles can proceed by diffusion of molecularly dissolved sulfur to the nuclei”.[6]

2.3 Theoretical Approaches Describing Particle Growth

The model of LaMer interpreted for the synthesis of monodisperse particles is a concept of separating nucleation and growth. Thus, theoretical models for the actual growth of the nuclei forming the nanoparticles are needed to predict the final size distribution. Soon after LaMer proposed his mechanism, Reiss developed a growth model known as “growth by diffusion” in which the growth rate of spherical particles depends solely on the monomer flux supplied to the particles.[41]

Reiss deduced that if the diffusional growth is only dependent on the monomer flux, smaller particles will then grow faster in presence of larger particles, leading to a size focusing (narrowing of size distribution). However, this is a very simplified mechanism since it does not include other effects such as aggregation, coalescence or dissolution (Ostwald ripening). Sugimoto et al. extended Reiss's model qualitatively by including dissolution effects obtaining a size dependent growth rate by considering the Gibbs-Thomson equation.[42] As a consequence, broadening of the size distribution due to nanoparticle dissolution is also possible (dependent on the monomer concentration). Experimentally, Alivisatos and co-workers deduced such a focusing and defocusing behavior of the size distribution for the hot-injection synthesis of CdSe nanoparticles.[43]

Alternative approaches to characterize particle growth are models using rate equations that are able to describe the size evolution of nanoparticles by means of rates for certain changes, such as a rate for a monomer attachment. Formulating and solving (in general numerically) these mathematical expressions evolves the size distribution of the particles with respect to the time. Several publication developed kinetic models using only rate equations to describe the nucleation and growth of nanoparticles.[40,44] Additionally, it was theoretically shown that diffusion limitation is not necessarily required for the size focusing effect. A further approach was introduced by Privman et al. who developed a model consisting of two steps: a burst nucleation step, followed by an aggregation of the primary particles into micron sized colloidal agglomerates.[45] The model incorporated the CNT for the first step and rate equations for the second step.

In summary, several approaches including CNT, single particle growth laws or rate equations are typically used to characterize particle growth. Numerous other studies exist that extend, improve or combine these models (as Privman did).[45]

The common problem of all theoretical models is the severely limited availability of experimental time-resolved in-situ data for rates of nanoparticle formation and growth. Such data enables the determination of particle growth mechanisms and kinetics and thus would allow verifying theoretical models.

Moreover, the chemical aspect of creating monomers (e.g. due to reduction) which are able to grow onto the NP surface is often strongly simplified or neglected. Hence, models that can describe quantitatively the formation, growth and coalescence of colloidal metal or metal oxide nanocrystals and are able to reproduce the changes induced by variation of the synthesis conditions, i.e. concentrations, pH, temperature and stabilizers, do not exist. In a nutshell, the lack of profound experimental data is one of the major obstacles [8] to change the current state of colloidal synthesis “from “alchemy” to chemistry”.[46]

3 Brief Introduction to the concepts of colloidal stability

One of the most important aspects in colloid science is the mechanism of (metal) nanoparticle stabilization in the dispersing medium. In general, particles at the nanoscale are unstable and tend to agglomerate because at short interparticle distances they are attracted to each other by van der Waals, electrostatic or magnetic forces. Without any counteractive repulsive forces nanoparticles aggregate, agglomerate or undergo coalescent processes. In the theory of colloidal chemistry such repulsive forces can be achieved by electrostatic or steric stabilization.[47]

Electrostatic stabilized nanoparticles are described to have at least one electrical double layer due to a surface charging. The resulting Coulomb repulsion forces between the particles decays exponentially with particle to particle distance. If the electrostatic repulsion is sufficiently high, it prevents the particles from any kind of coagulation.

In the following section, important particle interactions are discussed briefly (a more detailed description can be found in the supporting information S1).

3.1 Van der Waals Interaction - Nanoparticle Attraction Force

The common way to describe intermolecular forces is to use the so called Lennard-Jones potential which is an expression for the interaction energy of the pair potential $W(r)$ of two molecules at a distance r:

$$\mathrm{W(D)} = -\frac{C}{\mathrm{r}^6} + \frac{B}{r^{12}} \tag{5}$$

with the constants C and B for the attractive Van der Waals and repulsive Born repulsion, respectively.[48,49] At first, the second term (Born repulsion) will be neglected.

The Van der Waals interaction energy $W_a(D)$ between two particles with radius R_1 and R_2 can be theoretically obtained by integrating over all intermolecular forces between all constituent molecules of the particles, which finally yields for two spherical particles:

$$W_a(D) = -\frac{\pi^2\rho_1\rho_2}{6}C\left[\frac{2R_1R_2}{c^2-(R_1+R_2)^2} + \frac{2R_1R_2}{c^2-(R_1-R_2)^2} + ln\left(\frac{c^2-(R_1+R_2)^2}{c^2-(R_1-R_2)^2}\right)\right] \tag{6}$$

with the electron density ρ, the center to center distance between the two particles c and the distance between the two particle surfaces D ($D = c - (R_1 + R_2)$). For two identical particles with $R = R_1 = R_2$ and $D \ll R$ (particles in close proximity) the equation reduces to approx.:

$$W_a(D) = -\frac{\pi^2\rho_1\rho_2 CR}{12D} = -\frac{AR}{12D} \tag{7}$$

with the Hamaker constant A. The findings from Eq. (6) and (7) show that the surface interaction potential (thus the surface forces) decays less with respect to distance D than the interaction potential between two molecules ($1/D$ compared to $1/r^6$) and that the potential is proportional to the particle size ($W_a(D) \sim R$).

3.2 Electrostatic Interaction - Nanoparticle Repulsion Force

The attractive Van der Waals interactions discussed beforehand can promote reversible agglomeration or even irreversible aggregation of suspended particles. The preparation of stable nanoparticles demands forces opposing the Van der Waals attraction. This can be provided by the particle surface charge resulting in a repulsive interparticle forces.

In solution, solvated ions surround the particles and shield their surface charge. This can be described using the Stern-Gouy-Chapman theory in which the surface potential decreases within two layers known as the electric double layer (EDL) - a compact inner and a diffuse outer layer. The thickness of this double layer is called Debye length λ (κ^{-1}) and can be quantified using simple electrostatics. Obviously, the distribution of the electric surface potential $\psi(x)$ is required for the description of the double layer. The Poisson equation states:

$$\varepsilon\varepsilon_0\frac{d^2\psi(x)}{dx^2} = -\rho(x) \tag{8}$$

with x as the distance from the particle surface, the electrical potential $\psi(x)$, the permittivity of vacuum ε ($8.854e^{-12}\ CJ^{-1}m^{-1}$), dielectric constant of the solution ε_0 and the charge density ρ.

Applying the known as the Debye-Hückel linearization of exponential functions ($\exp(\pm x) = 1 \pm x + ..$) the Poisson equation can be approximated as:

$$\varepsilon\varepsilon_0\frac{d^2\psi(x)}{dx^2} = \sum_i \frac{z_i^2 e^2 n_{i\infty}^2 \Psi(x)}{k_B T} = \kappa^2\Psi(x) \tag{9}$$

with $n_{i\infty}$ as the concentration of ion i (co- or counter-ions) at $x = \infty$ and the Debye constant κ

$$\kappa = \left[\sum_i \frac{z_i^2 e^2 n_{i\infty}^2}{k_B T}\right]^2. \tag{10}$$

The Debye screening length λ_D which measures the diffuse layer thickness is defined as $\lambda_D = \kappa^{-1}$. The simple solution for the differential equation (Eq. (8)) is:

$$\psi(x) = \psi_o(x)\exp(-\kappa x) \tag{11}$$

with the surface potential ψ_0 at $x = 0$. This equation describes the decrease of the electric surface potential in the EDL, but actually the interaction between at least two EDLs are of interest to describe colloidal stability. The forces due to the EDL are caused by the overlap of the electric potential distribution and the overlap of the ion concentration (osmotic pressure). These forces need to be determined for different systems (i.e. particle geometries, EDL properties). Exemplarily, for the EDL interparticle force between two spherical particles with radius R and surface to surface distance D using the Derjaguin approximation the following expression is found to be a good approach (constant surface potential and particle radii much larger than the thickness of the EDL are assumed)[48]:

$$F\,(D) = -2\pi\varepsilon\varepsilon_0\kappa R\psi_\delta^2\exp(-\kappa D) \qquad (12)$$

with the interparticle energy $W_R = \int_D^\infty F(D)dD$:

$$W_R(D) = 2\pi\varepsilon\varepsilon_0 R\psi_\delta^2\exp(-\kappa D) \qquad (13)$$

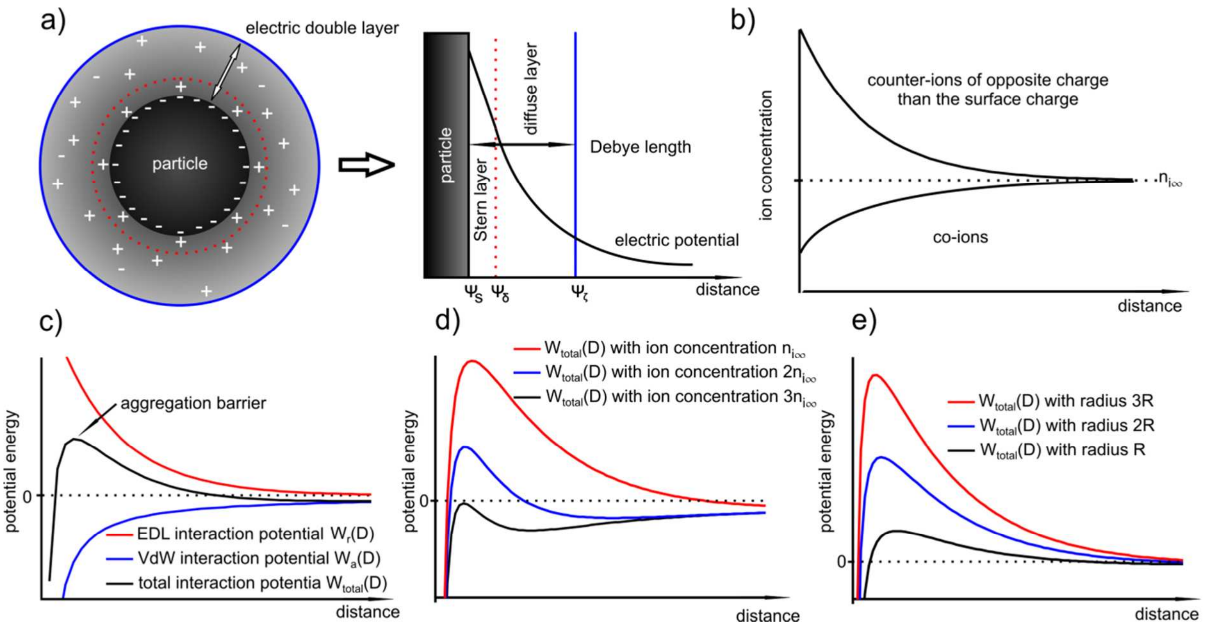

Figure 2 (a) Formed electric double layer (EDL) around a nanoparticle due to the Gouy-Chapman model which consists of the inner Stern layer and the outer diffuse layer (b) corresponding decrease of the counter- and co-ion concentration with respect to the distance from the particle surface; (c) schematic of the EDL, Van der Waals and total interaction potential (TIP) of two nanoparticles; (d) and (e) influence of the ion concentration and the particle size on the TIP.

3.3 DLVO Theory

More than 70 years ago, two Russian (Derjaguin and Landau) and two Dutch (Verwey and Overbeek) scientists developed a theory of colloidal stability which is still seen as one of the groundbreaking characterization models in the physics and chemistry of colloids - the DLVO theory.[50] The basic assumption is that the total force between colloidal particles is the addition of the Van der Waals (attractive) and the EDL (repulsive) forces. In the DLVO theory the effect of Van der Waals and double layer forces are combined, so that the potential interaction energy between two particles or two surfaces in a liquid is assumed to be the sum of the Van der Waals and EDL interaction energy:

$$W_{total}(D) = W_a(D) + W_r(D) \qquad (14)$$

which can be rewritten with Eq. (7) and (13) for two identical particles with radius R in close proximity to:

$$W_{total}(D) = W_a(D) + W_r(D) = -\frac{AR}{12D} + 2\pi\varepsilon\varepsilon_0 R\psi_\delta^2\exp(-\kappa D) \qquad (15)$$

Note that in particular the second term changes with different assumptions (constant surface potential or surface charge, thin EDL compared to the particle size and vice versa etc.)

A representative resulting total interaction potential (TIP) is displayed in Figure 2c. The TIP demonstrates some fundamental features that become important in the explanation of particle growth processes. The shape of the curve is the consequence of the exponential and steep decay of the repulsive and attractive term, respectively. The resulting maximum of the curve represents the aggregation barrier and determines the colloidal stability. The barrier creates effectively an activation energy for aggregation that two particles have to overcome when they collide.

In this picture several parameters affect the stability of the system (i.e. the barrier): (i) the ion type and concentration, (ii) the value of the surface potential and (iii) the particle size. Although, Eq. (12) is limited to two identical particles, it describes the properties of the whole system quite well since expressions for spherical particles with different sizes show in general similar dependencies with respect to size, surface charge, and ion concentration. The Van der Waals attraction is relatively independent of the ion concentration, but the repulsive term strongly depends on it since the counter-ions are the dominant ions in the Stern and diffuse layer. The ion concentration is directly proportional to κ and thus to the exponential decrease of the surface potential. This means that the higher the ion concentration (in particular the counter-ion concentration) the smaller is the EDL. In Figure 2d it is shown how the ion concentration in principle affects the TIP.

Moreover, Eq. (15) (i.e. with the assumption of a constant surface potential and a thin EDL), reveals that in close proximity the particle size is proportional to both the attractive and repulsive terms. Consequently, the TIP is directly proportional to the radius which means that with increasing size the shape of the curve and the position of the maximum does not shift to another distance whereas the aggregation barrier increases. As a more general rule, one can state that in almost all cases of charge stabilized particles the aggregation barrier increases with increasing size and therefore also the colloidal stability. In other words, larger particles are in general colloidally more stable than smaller particles. This is illustrated in Figure 2e.

3.4 Steric Stabilization

Steric stabilization is a process in which colloidal particles are prevented from aggregating by adsorption of large molecules at the particle surface, such as polymers or surfactants, providing a protective layer. The prevention of coagulation of these large molecules can be explained via simple mechanisms. The density of the adsorbed molecules in the interparticle space would increase tremendously, if the interparticle distance would become smaller and smaller. This would cause a decrease in entropy, thus an increase of the free energy which is energetically less favorable. Due to the increased density, osmotic repulsive forces would also increase. Furthermore, a higher solubility of the stabilizing molecule counteracts agglomeration.[51]

As an approximation, the interaction potential described in the DLVO theory can be extended by a further term describing the repulsive forces due to the steric stabilization W_{steric}:

$$W_{total}(D) = W_a(D) + W_r(D) + W_{steric} \quad (16)$$

The repulsive interaction potential W_{steric} is not a long range interaction and does not significantly depend on the particle size since the stability is mainly determined by parameters such as polymer concentration, temperature, average chain length and the solubility of the polymer.[48,52]

4 Principles of metal colloidal growth

In some of my recent contributions two main topics and scientific issues were addressed: (1) the development of techniques and experimental setups that enable the investigation of nanoparticle growth processes; and (2) the study of different nanoparticle syntheses (in parts with these novel techniques and setups) to reveal their corresponding growth mechanisms.[19,53,21,23,22,54–58] Several metal nanoparticle syntheses were investigated time-resolved and in-situ. For each of these systems a growth mechanism could be deduced. In the following, the findings and mechanistic interpretations of Au-NP and Ag-NP syntheses with sodium borohydride (relatively strong reducing agent) and sodium citrate (relatively mild reducing agent) are briefly summarized. Comparing the results, similarities can be identified that allows evaluating the governing principles of the particle growth. Moreover, a general mechanism and growth concept for syntheses of colloidal metal nanoparticles in which the monomer-supplying chemical reaction is faster than the actual growth can be derived. It is shown, that this concept of colloidal nanoparticle growth allows a more sophisticated interpretation of syntheses with mild reducing agents such as the reduction of tetrachloroauric acid with sodium citrate - known as the Turkevich method.

4.1 Summary of the findings from recent studies of the growth mechanisms of colloidal metal nanoparticles

The growth process of Au-NPs obtained via the reduction of tetrachloroauric acid ($HAuCl_4$) with sodium borohydride ($NaBH_4$)which is following denoted as Au-System 1 proceeds in two steps (see Figure 7 in [21]). The first step is the reduction of the ionic gold to Au monomers within less than 200 ms accompanied by the formation of primary particles. In a second step, these primary particles grow due to coalescence along with a corresponding decrease in the number of particles. In consequence, particle growth in Au-System 1 is driven only by coalescence in the experimentally accessible time.

The growth mechanism of Ag-NPs obtained via the reduction of silver perchlorate ($AgClO_4$) with $NaBH_4$ (following denoted as Ag-System) is actually the same but consist of two well separated steps of coalescence. The growth mechanism can be divided into four steps as illustrated in Figure 6 in [23]. The first two steps are the same as in the growth mechanism of the beforehand described growth mechanism of Au-System 1. The third step is a metastable state which is related to the hydrolysis of BH_4^- to $B(OH)_4^-$. At a certain point of the hydrolysis (when most of the BH_4^- is converted) the colloidal stability of the particles decreases initiating a further coalescent process which is the final step of the synthesis.[22] Furthermore, it is shown that the addition of a steric stabilizing agent (in that case PVP) affects the particle size at each step, the long term stability of the silver colloids and the duration of the metastable state, but not the growth mechanism itself.

The Turkevich method refers to the reduction of $HAuCl_4$ with sodium citrate (Na_3Ct) at elevated temperature and is the most common synthesis to produce monodisperse gold colloids in aqueous solution,[59,60] in the following denoted as Au-System 2. In contrast to $NaBH_4$, sodium citrate is a mild reducing agent. As a consequence, the monomer supplying chemical process in the Turkevich method is not separated from the nanoparticle growth as it is the case for Au-System 1 and Ag-System. The growth mechanism of Au-System 2 was investigated with a novel coupling of analytical methods - a combination of SAXS and X-ray absorbtion near-edge structure (XANES) which allowed a simultaneous determination of the mean oxidation state of the gold precursor (XANES) as well as the size, number and polydispersity of formed particles (SAXS).[53] The measurements were conducted using a levitated droplet with samples being extracted from a batch mix at different reaction times. In addition, a SAXS setup applying a free liquid jet was developed to be able to measure containerless the particle growth with a high time resolution.[19] From the investigations, a growth mechanism which consists of four steps could be deduced as illustrated in Fig. 4 in [53]. The first step incorporates a fast reduction of a small amount of gold precursor and the formation of first small clusters (step 1). Resulting clusters undergo coalescent processes (step 2) forming particles with radii larger than 1.5 nm. This is followed by a diffusional growth to a mean radius of about 4-5 nm (step 3). Finally, particles grow rapidly until the gold precursor is consumed (step 4). The rate of chemical reduction changes and is coupled to the four physical steps of particle formation and *vice versa*.

4.2 Category 1 syntheses: Monomer supplying chemical reaction faster than the actual particle growth

For the investigated systems the use of $NaBH_4$ as reducing agent results in a reduction much faster than the actual growth (few milliseconds or less vs. several seconds). Consequently, the monomer supplying chemical reaction, i.e. the reduction, is separated from the actual particle growth. In the following, syntheses with this characteristic are denoted as Category 1 syntheses.

The mechanistic studies of Category 1 syntheses (Au-System 1 and Ag-System) revealed growth mechanisms which are always governed by coalescence, even after the addition of a steric stabilizing agent. A process of coalescence (merging of particles) is followed by a process of aggregation which is the result of insufficient colloidal stability. As a result, it is found that the particle growth and thus the final size distribution is primarily governed by colloidal stability and thus independent from any kind of classical or non-classical nucleation process.[23] The following discussion is separated in three subsections. The first subsection discusses the general growth mechanism of Category 1 syntheses. In the second, a general concept of nanoparticle formation for idealized syntheses is deduced. In the last subsection, the validity of that idealized growth concept for “real” syntheses is discussed.

4.2.1 General Growth Mechanism of Category 1 syntheses

As a thought experiment one can assume to have an infinitely fast mixing and precursor reduction. In this idealized image, the reduction would lead to the existence of a high amount of single metal atoms in solution that tend to bind with other metal atoms forming dimers. These dimers tend to bind again with further metal atoms and/or dimers and so on. This results in coalescent processes and without an emerging colloidal stabilization of small clusters and particles it would lead to a continuous growth and a complete precipitation of the metal in solution. In case of nanoparticle syntheses (i.e. in the case of no precipitation), the colloidal stability determines which particles undergo agglomeration and aggregation and finally coalesce. In this microscopic image of the thought experiment, only the colloidal stability governs the particle growth and determines the final nanoparticle size distribution of Category 1 syntheses. In a macroscopic image this idealized growth can be described with a low solubility of metal atoms in water. It can also be explained with the probability of collisions of metal atoms with each other (or of metal atoms with small metal clusters) due to diffusion and their Van der Waals interaction (an attraction force) together with the strong binding forces between metal atoms in molecular metal clusters as well as in metal nanoparticles. In fact, these physical processes are directly correlated with the solubility. The solubility results from simultaneous and opposing processes of dissolution and precipitation of solids. It describes effectively the rate of the metal bonding formation probability (due their diffusion and attraction forces) and the probability that the bonding between metal atoms breaks (dissolution).

In the case of metal clusters, the probability of metal bonding breaking at room temperature is very low. Melting points of small metallic clusters in the gas phase are in general above 500 K.[61–64] As a result, Ostwald ripening processes are very unlikely to occur during the commonly used syntheses of metal colloids (most are conducted below 400 K) but are often claimed without a conclusive explanation or any profound experiment. This issue is discussed in section 4.3.

The electrostatic and steric stabilization of the investigated systems also explains the slower particle growth kinetic known from precipitation kinetics of systems without a significant colloidal stability.[65] Without a significant aggregation barrier between particles (e.g. due to electrostatic or steric stabilization) the probability that two particles aggregate in each collision process (which occurs due to their Brownian movement and their Van der Waals attraction) is very high and decreases with an increasing repulsive potential. Time-resolved precipitation studies using SAXS show for selected systems in which a significant barrier does not evolve that within few milliseconds the particle size is already around 20-30 nm in radius.[65,66] The results of these publications are also of great importance to understand nanoparticle growth. In contrast to precipitation, the investigated nanoparticle growth processes with $NaBH_4$ as reducing agent (Au-System 1 and Ag-System) have final particle sizes in a range of 2-8 nm in radius and proceed on a time-scale of few seconds. Furthermore, the particles have a size distribution with mean radii below 1 nm at around 200 ms (also in the absence of any stabilizing agent!).[21,23] This indicates that even very small clusters with radii below 1 nm have already a substantial colloidal electrostatic stabilization that decelerates the growth. Actually, it is completely unclear at which size an electrostatic stabilization evolves that affects the growth. It might already be the metal dimer or probably correlated with the size of the metal transition.

In this idealized thought experiment the growth of nanoparticles is only due to aggregation and coalescence if the reduction is much faster than the actual growth, i.e. reduction is well separated from particle growth. This finding is supported by our experimental results and appears to be a fundamental principle of nanoparticle formation.[23]

So far in this thought experiment, it is assumed that the duration for mixing the reactants and the reduction process is infinitely small which is obviously not the case for any real synthetic system. It is known that mixing conditions can have an influence on the final size. In case of Au-System 1, a significant change of the final particle size distribution was not observed if mixing the solutions with a micro-structured mixer (mixing time in the range of 50 µs) or mixing the solutions 1:1 with two Eppendorf Tips (mixing time in the range of a second). In contrast, for Ag-System mixing conditions clearly have an influence on the growth and therefore on the final size.[22] However, for the investigated systems the mixing conditions might change the final particle size but not the growth mechanism itself. Thus, the beforehand findings of the thought experiment are also valid without the assumption of an infinitely fast mixing. In contrast, the reduction rate is not negligible with respect to the mechanism. This is obvious when comparing the deduced growth mechanisms of Au-System 1 and Au-System 2. The influence of the reduction and in particular of the reduction rate (i.e the monomer supplying rate) will be discussed later in this contribution.

As pointed out in the thought experiment and deduced in recent publications, the growth mechanisms of syntheses with fast reduction (Au-System 1 and Ag System) is primarily correlated with colloidal stabilization (the relation of attractive and repulsive forces between clusters/nanoparticles). Thus, a generalized particle growth model demands a description of colloidal stability such as the commonly used DLVO theory derived in the 1940s.[50,67] As already stated, the basic assumption of the DLVO theory is that the total force between colloidal particles is the sum of attractive Van der Waals and repulsive EDL forces. The steric stabilization is not considered in the classical DLVO approach. In the case of spherical symmetry, the total interaction potential between two identical particles with radius R in close proximity can be written as in Eq.(15) (note that the DLVO approach as well as the derivation of the equation consists of idealizations and approximations). The resulting total potential and the influence of the radius and the ion concentration are shown in Figure 2.

For simplification purposes, it can be assumed that in the case of the syntheses with strong reducing agents the total ion concentration is constant after mixing the solutions. The metal precursors are immediately reduced and the chemical conversion of residual BH_4^- into $B(OH)_4^-$ occurs on a time-scale of several minutes to hours (for details see experiment SI-4 of the supporting information in Wuithschick et al.[22]). Moreover, a size dependence of the surface potential is at first also neglected. The constant ion concentrations appear to be reasonable but the constant surface potential might be too rigorous (one could also keep the surface charge density constant). However, it will be shown that this simplification does not affect the general interpretation of the growth processes.

In this above described simplified DLVO model, the interaction energy between two identical spherical particles is directly proportional to their size (see Eq. (15)) which means that with increasing size also the aggregation barrier increases (see Figure 2e). As a consequence, the probability of aggregation between two particles decreases with increasing size. In other words, the probability of a coalescent process between two smaller particles is higher than between two larger particles. At a certain particle size the aggregation barrier has increased so that the thermal energy of these particles is too low to overcome the barrier which makes a process of aggregation or coalescence very unlikely. This particle size in turn corresponds to the minimum stable particle size and primarily determines the final size distribution.

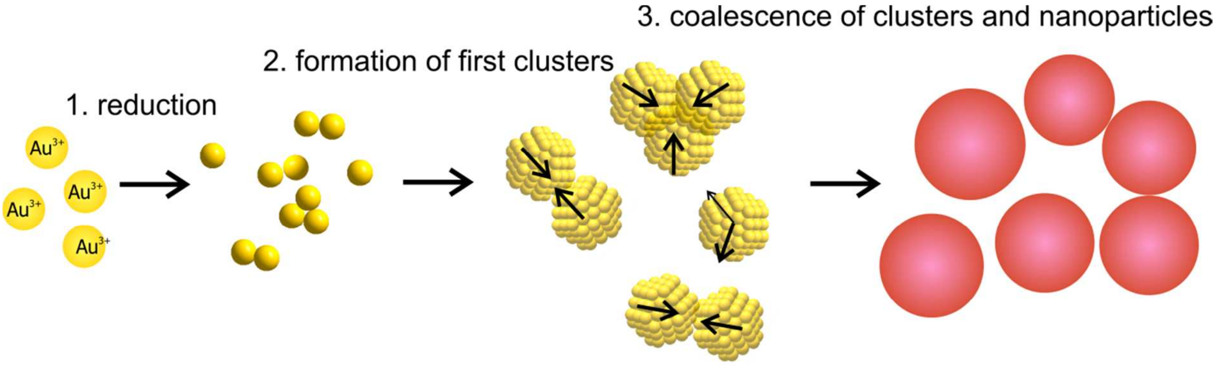

Figure 3 Scheme of the generalized 3-step mechanism of nanoparticle growth due to coalescence.

Summarizing, the beforehand discussion lead to two major conclusions concerning the metal nanoparticle growth of syntheses with fast reducing agents (Category 1 syntheses):

1. The actual nanoparticle growth is only due to aggregation and coalescence.

2. The final size distribution strongly depends on the increase of the aggregation barrier with increasing particle size.

The consequential general mechanism for the growth of metal nanoparticles with fast reducing agents can be expressed with three steps displayed in Figure 3. The first step is a fast reduction of the metal ions. The metal atoms will form dimers and small clusters which marks the second step. In the final and third step the clusters grow due to aggregation and coalescence until reaching a final particle size at which the particles are sufficiently stabilized. It must be noted, that the second step is consciously not referred to as nucleation whereby the reason for this is discussed below.

4.2.2 Generalized concept of colloidal nanoparticle formation for Category 1 syntheses

The discussed mechanisms of nanoparticle growth for Au-System 1 and the Ag-System are based on aggregation and subsequent coalescence. In the following, a simple theoretical concept for nanoparticle formation of Category 1 syntheses is proposed which contradicts nucleation and growth models (in particular the classical nucleation theory[5] and its transfer to nanoparticles by LaMer and co-workers).[6,7] Only the basic concepts of colloidal stability such as the classical DLVO theory are used.[50,67]

Based on the experimental results with the fast reducing agent $NaBH_4$, two fundamental aspects (see the two enumerated statements above) and a generalized mechanism of nanoparticle growth (see Figure 3) are deduced in the previous section.

This leads to a picture of nanoparticle growth, for which a concept of nucleation is nonessential because the final particle size distribution is determined by the increase of colloidal stability (i.e. the increase of the size depending interaction potential between the particles). The formation of any primary cluster that overcome a certain critical radius is irrelevant. With focus on metal nanoparticle syntheses, the concept of nucleation and in particular the classical nucleation theory is discussed below. The general principle of the growth mechanism due to coalescence is displayed in Figure 4a. Typical interaction potentials between two identical spherical particles with their dependence on the particle size due to the concept of electrostatic stabilization are displayed in Figure 4b and c.

For a simplified picture of growth it is at first assumed that coalescence occurs only between particles with similar size although this is not the case in reality. Subsequently, this model is extended to real systems. However, at least for the Au-System 1 the probability that only particles with similar size undergo a coalescent process is much higher than between particles of different size. This can be deduced from the constantly low polydispersity of 10-15% during the growth.

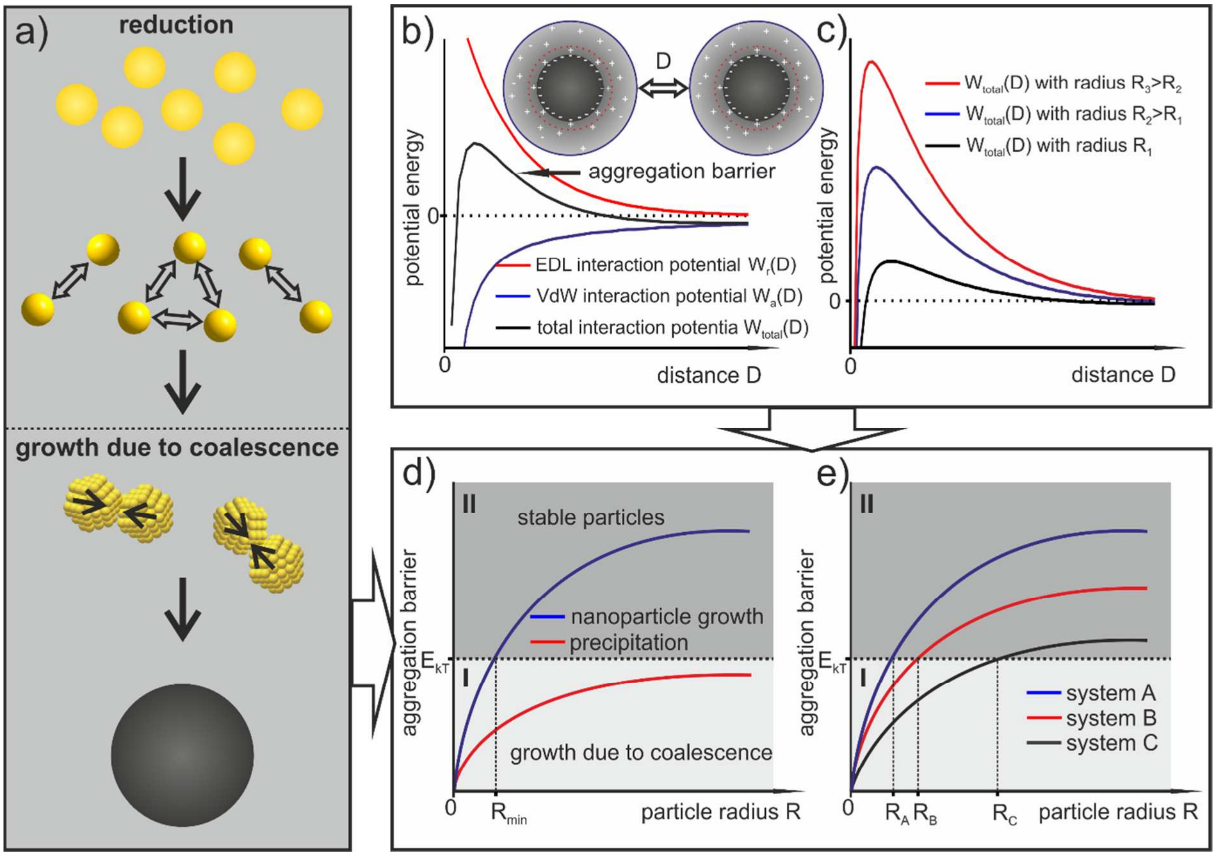

Figure 4 (a) The general principle of the growth mechanism due to coalescence is displayed. (b) and (c) The interaction potential between two identical spherical particles with their dependence on the particle size due to the concept of electrostatic stabilization (EDL) is displayed. (d) The deduced novel theoretical concept of nanoparticle growth is illustrated

In this simplified model, the increase of the aggregation barrier with increasing particle size (as shown in

Figure 4c) indicates that at a certain particle size the thermal energy is not sufficient to overcome the increasing barrier of aggregation. The criteria for stability can be assumed to be the primary maximum of the aggregation barrier curve since the corresponding distance represents the highest interaction energy. This situation is displayed in

Figure 4d. It shows an anticipated increase of the primary maximum of the total interaction potential between identical particles with respect to particle size. In the following this curve will be denoted as “stability curve”. Note, that the stability curves displayed in Figure 4d and e are only qualitative.

The diagram in Figure 4d is separated in two sections by the thermal energy of the particles E_{kT}. If the aggregation barrier is below that energy (section I) the particles can aggregate and subsequently coalesce. If the barrier is above that energy (section II), the colloidal stability is sufficient to prevent further growth. Thus, section I represents the area in which aggregation and coalescence (therefore growth) is possible and section II represents the area of colloidally stable particles. The blue curve in Figure 4d displays nanoparticle growth since the stability curve reaches section II at which aggregation and coalescence stops. In contrast, the red curve represents a process of precipitation as the stability curve remains in section I. As a consequence, the radius at which the aggregation barrier curve crosses the boundary between the two sections (denoted as R_{kT}) is the particle size at which a further growth becomes energetically unfavored and therefore very unlikely. In this idealized image, the critical radius R_{kT} represents the smallest particles of the final size distribution since same sized particles slightly smaller than R_{kT} still coalesce and reach the stability region at radii larger than R_{kT}. In Figure 4e three stability curves with different slopes are displayed leading to three different final average radii.

The stability curve can also be transferred to a size dependent probability function for particle coalescence. The probability of coalescence decreases the closer the aggregation barrier curve comes to the boundary between section I and II. In this simplified image, the particle formation process of Au-System 1 can be described with system A of Figure 4e. It is a growth process only due to coalescence producing monodisperse stable particles.

The corresponding Ag-NP synthesis without PVP as steric stabilizer- (Ag-System 1) can be represented by systems B and C. In the beginning of the synthesis, particle growth can be described with system B because the particles formed in the first step are slightly bigger than for the Au-NPs of system 1. The BH_4^- conversion during the metastable phase and its influence on the surface chemistry leads to rapid change of colloidal stability (end of metastable phase). The aggregation barrier decreases which can be depicted by a change of the aggregation barrier curve from system B to C. This represents further growth due to coalescence. Accordingly, the Ag-NP synthesis with PVP as additional steric stabilizer can be described with system A to C.

So far, the proposed growth model is limited to a growth in which only particles with same or similar size undergo coalescent processes as it is roughly the case for Au-System 1. It also demands an instant coalescence subsequent to an aggregation since only interaction of spherical particles are considered. In the following, several idealizations are discussed and the more general validity of this idealized growth concept is demonstrated.

4.2.3 Validity of the idealized growth concept

The beforehand paragraph discusses a special colloidal synthesis -a synthetic system in which the monomer supply is much faster than the actual growth. Growth is solely determined by aggregation and coalescence. As a consequence, a description of such a particle formation demands a description of colloidal stability.

The simplified image of nanoparticle growth as depicted in Figure 4 demands several idealizations: (i) instant coalescence subsequently to aggregation; (ii) coalescence limited to same sized spherical particles; and (iii) primary maximum as criterion for stability. In addition, the equations used for the qualitative description presuppose several idealizations common in colloidal science. In the following, for each of the mentioned idealization it is discussed why the picture of growth can still be transferred to real synthetic systems.

(i) Influence of Coalescence Kinetic on Particle Size

In the simplified image described beforehand only coalescence of spherical particles is assumed. Thus, the merging of two aggregated particles into one larger spherical particle needs to be almost infinitely fast. Otherwise, the subsequent coalescent process of this entity is obviously not between spherical particles. The second coalescent step in the Ag-NP synthesis (Ag-System 1) is not infinitely fast. It is in the range of several seconds which can be deduced from UV-vis and SEM experiments. The UV-vis spectra during the second coalescent step reveal a broadening of the plasmon resonance band and an increased absorption at higher wavelengths characteristic for non-spherical particles and aggregates (see Figure 2c in [23]). In addition, SEM images showed aggregated particles for that growth stage (see Figure 4c in [23]). Actually, a simple eye-experiment also indicates the existence of aggregates for 30-60 s during the metastable state (see photographs in Figure 2a in [23]). Thus, also non-spherical particles are existent and probably also merge with each other during the second coalescence step in the Ag-System. Consequently, merging of only spherical particles cannot be assured even for syntheses with spherical final particles. Although, it does not change the general picture of growth it remains an opened question if it has an influence of the final particle size distribution. For a purely electrostatic stabilization, it is hard to predict if a non-spherical aggregate has a higher colloidal stability than a spherical particle with the same volume. Concerning only the (geometric) Derjaguin approximation (i.e. assuming a constant surface potential or surface charge density) the aggregation barrier would be dependent on the geometric arrangement of the two particles (i.e. their relative orientation and position).[69] Depending on the geometric arrangements, the colloidal stability of a non-spherical aggregate might be higher or lower compared to a spherical particle with same volume. Hence, the kinetic of coalescence, merging or crystal reorganization (i.e. the kinetic of free energy minimization of the particle) does not change the picture of growth but might influence the final particle size. Indeed, it was shown that the second coalescent step in which non-spherical aggregates are present causes the lack of size control in the Ag-NP synthesis. Eliminating the second coalescent step reveals a size-controlled Ag-NP synthesis.[22]

(ii) Primary Maximum as Criterion for Particle Stability

A common scientific approach to describe a certain process is an argumentation via an energy barrier. In this publication the interaction energy was discussed for particle growth processes. The value of the primary maximum was taken as criterion for stability which simplifies the issue, but provide a useful approximation. The average thermal (or kinetic) energy of a colloidal particle in Brownian motion is $E_{kT} = (3/2)k_BT$ whereas a particle can have a kinetic energy E_{kin} below or above this value. The higher the difference between E_{kin} and E_{kT}, the lower the probability for a particle with such a E_{kin}. The Brownian motion results from arbitrary collision with molecules of the surrounding medium or other particles. In general, colloidal solutions of metal nanoparticles are very diluted and particles are large and heavy compared to the solvent molecules. Therefore, the kinetic energy of the particles will not differ much from E_{kT} and for the herein described systems it is very unlikely (though not impossible) that a particle will have a thermal energy of $10k_BT$ or more. As a consequence, the particles should be colloidally stable if the aggregation barrier (V_{max}) is approximately the average thermal energy. In this contribution $V_{max} = E_{kT}$ as criterion for a sufficient colloidal stability is assumed to be reasonable (i.e. ratio of 1). Even if the ratio is higher, it would not change the principle growth concept.

(iii) Coalescence limited to same-sized Nanoparticles

So far, the proposed growth concept is limited to a growth in which only particles with same or similar size can undergo coalescent processes as it was roughly the case for Au-System 1. The assumption of similarity is necessary to illustrate the simplified image of growth (see Figure 4). Following, it is discussed why that principal idea of particle growth does not change if aggregation or coalescence can occur between particles of different sizes.

In real systems particles of different sizes undergo aggregation or coalescent processes. Thus, in addition to the interparticle energy barrier between two dissimilar particles one needs to consider the probability that two colloidal particles of arbitrary size collide. In the beforehand simplified image the particle concentration does not need to be considered since only same sized particles undergo coalescence.

A broad range of publications deal with theoretical descriptions of coagulation of dissimilar sized particles. To the best of my knowledge, the principle theoretical approaches always comprise population balanced equations. Each equation concerns the concentration of a single entity (particles of specific size) which can increase or decrease due to aggregation or decomposition. Depending on the described system, the mathematical incorporation of physical effects such as particle diffusion, thermodynamic stability or particle interactions is required. In most publications about coagulation, decomposition is not considered since in general it is intended to describe the coagulation of larger particles for which decomposition due to non-sufficient thermodynamic stability is very unlikely. Actually, the ground breaking work was done by Smoluchowski almost 100 years ago which describes the kinetic of particle coagulation caused by binary aggregation but without decomposition or fragmentation. Smoluchowski derived a set of non-linear differential equations:

$$\frac{dc_i(t)}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} K_{i-j,j}c_{i-j}(t)c_j(t) - c_i(t)\sum_{j=1}^{\infty} K_{i,j}c_j(t). \tag{17}$$

With c_i as the concentration of a particle with i times the mass of a defined monomer (e.g. the atom). K_{ij} is the coagulation Kernel (sometimes also coagulation rate or frequency) and is a function which describes the coagulation probability between particle i and j. The first term in Eq. (17) describes the gain and the second the loss of particles with mass m_i due to coagulation. Thus, the number of new clusters with mass $m_i + m_j$ formed by aggregation per unit time and unit volume ($N_{i+j}/\Delta V \Delta t$) corresponds to the respective cluster concentration (c_i and c_j) and the coagulation kernel:

$$\frac{N_{i+j}}{\Delta V \Delta t} = K_{i,j}c_i(t)c_j(t). \tag{18}$$

Several years after Smoluchowski, Müller extended this theory for continuous cluster mass distributions by introducing a particle mass density $c(x,t)$ whereby $c(x,t)dx$ represents the average number of particles with a mass between x and $x + dx$.[70] Thus, the term $c(x,t)c(y,t)K(x,y)dxdy$ represents the average numbers of coagulation processes between particles of mass x to $x + dx$ with particles of mass y to $y + dy$ during the time interval dt. This converts the discrete Smoluchowksi model into integro-differential equations:[70]

$$\frac{\partial c(x,t)}{\partial t} = \frac{1}{2}\int_0^x K(x-y,y)c(x-y,t)c(y,t)dy - c(x,t)\int_0^x K(x,y)c(y,t)dy. \tag{19}$$

In general, the set of the differential equations (Eq. (17) or (19)) cannot be solved analytically and demand numerical approaches. For simulations of nanoparticle growth a stochastic Monte-Carlo method is commonly applied. Anyway, the scope of this contribution is to deduce general growth characteristics and not to provide a further mathematical approach using the Smoluchowski equation. For this purpose the Smoluchowski approach is at first discussed for non-interacting particles and subsequently extended for particle interaction.

In any Smoluchowski approach the type of particle interaction is specified with the coagulation Kernel. Therefore, a broad range of different kernels were described in literature in the past 100 years. The simplest case are non-interacting spherical particles (i.e. without attractive or repulsive forces) with Brownian movement. For such particle coagulation, Smoluchowski deduced the kernel as

$$K_{i,j} = const.\cdot (r_i + r_j)(1/r_i + 1/r_j). \tag{20}$$

Since $x{\sim}r^3$, Eq. (20) can be rewritten in terms of masses to:

$$K(x,y) = const.\cdot (x^{1/3} + y^{1/3})(1/x^{-1/3} + 1/y^{-1/3}). \tag{21}$$

As a consequence of Eq. (20) and (21), this purely Brownian Kernel has a parabolic shape. It means that the Kernel is higher for particles with different size than for particles of same size. For example, the Kernel value of a coalescent process between particles with a size ratio of 10 (i.e. r_2=10r_1 or vice versa) is approx. three times larger than the Kernel value for coalescence of same sized particles. For Au-System 1 and the Ag-System a size ratio of 10 is approx. also the size range of their particle growth (in the first coalescent step) since the size after the first coalescent step is approx. 1.5 nm (in radius) and the hydrodynamic radius of a single gold atom is around 0.15 nm. Thus, the probability for a single atom to coalesce with a 1.5 nm particle is around 3 times higher than with another atom but only if (I) the concentrations of both species are the same and (II) no interaction between the particles exist (see Eq. (18)). These both limitations are not the case for the growth of charged nanoparticles and therefore following discussed.

(I) For the $NaBH_4$ syntheses, the metal precursor is completely reduced within the mixing time of the solutions leading to high concentrations of metal atoms and molecular-like metal clusters in the beginning of the synthesis. The concentrations of these small entities will be much higher than the concentrations of the larger particles because larger particles in this synthesis consist of around 500-1000 atoms. Consequently, the particle concentration decreases during the synthesis due to the increasing particle size which has been investigated with time-resolved SAXS experiments. The coalescence probability is proportional to the Kernel and the respective particle concentrations (see Eq. (18)). Consequently, the probability of metal atoms or molecular like metal clusters to coalesce with larger particles can decrease by 2-3 orders of magnitude (as the concentration does).

(II) As for any synthesis, the final nanoparticles are colloidal stable due to the particle interaction forces whereby the repulsive forces becoming dominant with increasing particle size (otherwise one would not have a stable colloidal solution). In 1934, Nicolai Fuchs described that phenomenon for the coagulation of aerosol particles[71] and introduced a ratio W (later known as the Fuchs stability ratio) as a correction factor which describes the coagulation probability of two charged particles if the coagulation probability of uncharged particles is 1. Applying the Fuchs stability ratio the Kernel can be modified to:[71]

$$K_{i,j} = const.\cdot \frac{1}{W_{ij}}(r_i + r_j)\left(\frac{1}{r_i} + \frac{1}{r_j}\right). \tag{22}$$

The general form of the Fuchs stability ratio is given by:

$$W_{i,j} = 2\int_2^{\infty} \frac{\left(\exp\left(\frac{W_{total}(x)}{kT}\right) - 1\right)}{x^2}dx \tag{23}$$

with the interaction potential between the two particles $W_{total}(x)$ and the dimensionless center to center distance x that was normalized with the arithmetic mean of the radii of the two interacting particles i and j.[71] Several mathematical expression of the interaction potential of particles with different sizes are described in literature whereby different assumption were made. Hogg, Healy and Fuerstenau presented in the 1960s a general expression for charged particles applying the Derjaguin and Debye-Hückel approximation in which the attractive and the repulsive potentials are dependent on the radii R_1 and R_2 of two interacting particles:[72]

$$W_{total}(D) = W_a(D) + W_r(D) = \quad (24)$$
$$-\frac{AR_1R_2}{6(R_1+R_2)D} + \frac{\epsilon\epsilon_0 R_1R_2(\psi_{\delta 1}^2+\psi_{\delta 2}^2)}{R_1+R_2}\left(\frac{2\psi_{\delta 1}\psi_{\delta 2}}{\psi_{\delta 1}^2+\psi_{\delta 2}^2} ln\left(\frac{1+\exp(-\kappa D)}{1-\exp(-\kappa D)}\right) + \ln(1-\exp(2\kappa D))\right).$$

With D as the surface to surface distance D ($W_{total}(D)$ can easily be written as $W_{total}(x)$ with $D = \frac{(r_i+r_j)(x-2)}{2}$). For Eq. (24) a constant surface potential (Eq. (24) can also be rewritten for a constant surface charge) and particle radii much larger than the thickness of the EDL (i.e. assumption of a thin electric double layer ($\kappa \cdot r > 10$)) are assumed. For particles which are governed by the increasing Coulomb repulsion forces, Reerink and Overbeek pointed out that the primary maximum of the interaction potential (W_{max}) is the dominant factor in restricting aggregation.[73] They described a reasonable approximation for the stability ratio W_{ij} using the primary maximum:

$$W_{ij} \approx \frac{1}{2\kappa a}\exp(W_{max}/k_BT) \quad (25)$$

with the Debye constant κ and a as the arithmetic mean of the particle radii.

The integral in Eq. (23) or W_{max} in Eq. (25) can be positive or negative depending on the forces between the two particles. Simplifying, if the integral or W_{max} is positive, the repulsive forces dominate the particle interaction which leads to a decrease of the coagulation probability (the Kernel) over the probability of the purely Brownian coagulation (vice versa if the attractive forces dominate). As a rule of thumb for particle syntheses, the particle interaction decreases the probability of particle coalescence during the particle growth since the aggregation barrier increases with increasing size of the interacting particles. For the herein discussed $NaBH_4$ syntheses, the repulsive forces dominate the growth at least for the larger particles (with radii between 1-2 nm). Three cases of particle interactions need to be considered: (1) between two "large" particles (with radii of 1.5 - 2nm); (2) between a "large" and a "small" particle (below 1 nm in radius) and (3) between two "small" particles. Obviously, the repulsion forces will be the highest for case 1 and the smallest for case 3. Thus, the coagulation probability will very likely decrease most for case 1 and least for case 3.

Summarizing the discussion of the limitations (I) and (II), it can be concluded that both - the particle concentration and the particle interaction - tremendously increase the probability of coalescence between particles of similar size. As a consequence, the particle coalescence of charged nanoparticles lead to final particles with relatively low polydispersity which is in contrast to the often referred publication of Sugimoto.[42] For the skeptical reader: exactly this growth characteristic could be measured with time-resolved SAXS experiments for syntheses with growth due to coalescence.[21,23] For aerosol particle (which are typically in the µm size range), Friedlander and co-workers have already described a similar growth characteristic in the 1960s with their theory of the *self-preserving* size distribution. [74,75]

A simple experiment which illustrates the influence of particle concentration and interaction on the nanoparticle size distribution is the separation of the Au-System 1 synthesis in several growth steps. A detailed description of that experiment can be found in the supporting information (SI-1). The experiment comprises three different mixing conditions of precursor and reducing agent solution whereby all three colloidal solutions have the same final gold concentration. The first mixing condition is the standard synthesis with a 1:1 mixing of the two reactants to obtain 10 ml of colloidal solution with a final gold concentration of 0.25 mM (e.g. mixing with Eppendorf pipettes 0.5 mM $HAuCl_4$ with 3 mM $NaBH_4$ solution in the range of a second). The particles grow due to coalescence to a size of approx. 1.5 nm in radius and are colloidally stable for minutes (i.e. within further 60 min they grow to a size of approx. 1.8 nm in radius).[21] To prevent further growth to 1.8 nm, PVP as stabilizing agent is added to the "final" colloids (i.e. after approx. 5 min). The second mixing comprises a synthesis in two steps. At first 5 ml of a colloidal gold solution with the standard synthesis (with 1:1 mixing) is prepared (leading to 1.5 nm particles) and subsequently, at first 2.5 ml of 3 mM $NaBH_4$ and then 2.5 ml of a 0.5 mM $HAuCl_4$ solution is added. For the third order, at first 2.5 ml of 3 mM $NaBH_4$ is added to 5 ml colloidal gold solution (also prepared with the standard procedure). Subsequently, the 2.5 ml $HAuCl_4$ solution is added in 30 steps with additions of around 40 µl every 5-10 s (note that every growth step comprises around 3-4 s). The final particles of the first mixing condition (standard 1:1 mixing) have a mean radius of 1.44 nm at a polydispersity of 10%. For the second mixing condition in which $HAuCl_4$ is reduced in the presence of existing particles (with a mean radius of 1.44 nm) the final mean radius increased to 1.64 nm. The experiment reveals that around 50 % of the added $HAuCl_4$ grow on existing particles and with the remaining 50 % new particles are formed. Therefore, the final particle concentration in the second procedure equates to approx. 75 % of the concentration in the first procedure. The growth mechanism of the second mixing procedure can be deduced from known mechanistic knowledge of the standard synthesis. The existing particles with a mean radius of 1.44 nm are colloidally stable. The addition of $HAuCl_4$ (to the colloidal solution with sufficiently BH_4^- ions) leads to an almost immediate reduction. The gold atoms can either grow on existing particles or form small metal clusters (dimers etc.) which are not colloidally stable. The probability for the growth on existing particles is much lower than the formation of small clusters which is caused by the higher aggregation barrier but mainly due to the relatively low concentration of the existing particles. With the same argumentation the formed small molecular like metal clusters grow further due to coalescence with themselves whereby the corresponding aggregation probability decreases with increasing size caused by the increasing aggregation barrier and decreasing concentration. According to this argumentation, the probability for an aggregation process between colloidally unstable particles decreases more with increasing size than the probability between unstable and existing particle. Consequently, with the second mixing condition less and larger particles are created than with the standard synthesis. This effect is reinforced with the increase of the subsequent addition. For each of the subsequent growth steps the concentration of the unstable particles is decreased and the concentration is directly proportional to the aggregation probability. This concentration influence can be observed for the third mixing condition (i.e. 30 additions of around 40 µl) in which the final mean radius is 1.75 nm and around 90 % of the added gold salt grow onto the existing particles.

(iv) Commonly used idealization

As common in science, theoretical descriptions of certain processes or states are made by using idealizations, approximations or measurements of experimental quantities. For the theoretical description of charged colloidal particles this includes typically idealizations or approximations of the charged surface, the resulting electrical potential, the double layer dimensions, the adsorption behavior of ions or the interaction of charged surfaces. In addition, the measurements of certain experimental quantities are often necessary for the description of colloidal stability such as the zeta potential.

For particles during the growth, any of the beforehand mentioned idealization can hardly be made which makes a theoretical description very difficult. Exemplarily, the surface charge density of small metal clusters is very likely to be different than of larger metal nanoparticles nor will the surface potential be the same. The dimensions of the double layer with respect to the particle size also differ during growth (i.e. the final metal nanoparticle might have a thin double layer with respect to the nanoparticle size but for small clusters this is very unlikely the case). Also a time-resolved zeta potential measurement of particles during growth is experimentally not possible. Consequently, the herein used mathematical equations for particle interactions are only used to support the qualitative explanation of the experimental results and should be seen as those.

4.3 Ostwald ripening of metal clusters – an unlikely process?

Experimentally, it is very difficult to distinguish between a growth due to coalescence and a growth due to Ostwald ripening. In both cases the particle concentration decreases with increasing particle size. Although the growth kinetic can indicate that one or the other process is more likely, it remains in most cases rather speculative. In this and some of my former contribution, it is stated that a growth due to Ostwald ripening is very unlikely since it can be assumed that at room temperature small nanoparticles are thermodynamically stable. However, a broad range of publications make a contrary assumption. In a recent study, colleagues and I tried to investigate the thermodynamic stability of metal clusters with a rather uncommon approach – a growth study of nanoparticles in standard soda lime glasses. The idea was that in a solid glass matrix, particle movement is inhibited even for extremely small clusters. Actually, only atoms can diffuse in the glass matrix. As a result, growth can only occur via monomer addition (i.e. atoms). In that growth study, it could be shown that molecular silver clusters in a glass matrix which are predominantly silver dimers are stable up to about 410 °C.[54] These results revealed that small molecular-like metal clusters (in a glass matrix) are thermodynamically stable even at elevated temperatures. Indeed, the surrounding matrix has an influence on the thermal stability of a metal cluster but one would not expect a dissolution of metal clusters in aqueous and non-aqueous solutions in the temperature range of most synthetic procedures (<150 °C). Obviously, this is not true if the solution contains chemical additives such as corrosive acids (e.g. HNO_3) or ligands that can etch the particle surface. A consequence of the metallic glass experiments for the herein described colloidal syntheses is that aggregation or coalescence caused by non-sufficient colloidal stability is a much more likely process than Ostwald ripening due to non-sufficient thermodynamic stability. Nevertheless, Ostwald ripening is an often claimed growth mechanism for (metal) nanoparticles but to the best of my knowledge not a single publication exists which provides convincing experimental indications of an Ostwald ripening growth for syntheses in common temperature ranges (<200 °C). This includes colloidal metal, metal-oxide and semiconductor nanoparticle syntheses.

4.4 Category 2 Syntheses – kinetic of monomer supplying reaction determines growth kinetic

So far, the discussion is limited to synthetic systems with a monomer supplying chemical reaction much faster than the actual growth. For almost all synthetic procedures this is not the case. The borohydride reduction represents an exception. In general, the kinetics of the chemical reaction governs the particle growth kinetics. As a consequence, one could assume for the majority of syntheses that a nucleation and growth model to describe the particle formation can be a promising approach. However, the following discussion demonstrates that a nucleation and growth approach might not be as helpful as often assumed. It rather reveals that the beforehand discussed growth model which is governed by colloidal stability can be extended to a broad range of colloidal syntheses. In this contribution, this is exemplarily discussed for the most common Au-NP synthesis – the classical Turkevich method.

4.4.1 Refinement of the Growth Mechanism

For the Turkevich method (Au-System 2), a four-step model of Au-NP formation was proposed in 2010.[19,53] In these two publications, the Turkevich synthesis was investigated with SAXS, XANES, UV-vis, SEM and TEM. The growth mechanism could be derived directly from the experimental data. It revealed a precise image of the particle formation whereas the growth mechanism was not incorporated into a superordinate concept of growth as done beforehand for the $NaBH_4$ syntheses. Note that these experiments were done at 75 or 85 °C for which the reduction kinetic is much slower than at 100°C used for the standard Turkevich method. In a future publication, it will be shown that at higher temperature the growth mechanism is the same. The knowledge gained from the $NaBH_4$ syntheses enable a more precise interpretation of the growth mechanism and a superordinate growth concept for Au-System 2.

In particular the SAXS experiments applying a free-liquid jet revealed that the four steps occur concomitant to four different steps of the reduction kinetic.[19] In the first step the reduction rate is rather high, the number of particles increases and initial particles of about 1-2 nm in radius are rapidly formed. In the second step reduction continues, but at a much lower rate, and the freshly formed particles that are likely to have a weak stabilization undergo coalescent processes leading to a decrease of the number of particles. When the particle size reaches a mean radius of about 2.5 nm, the number of particles remains constant, but particles keep growing in size. Taking the polydispersity into account, the smaller particles in that size distribution have radii of around 1.5 nm. One can deduce that at this particle size the electrostatic stabilization of the citrate capped colloids is sufficient to prevent further coalescence. Subsequently, the Au-NPs grow due to the diffusion of gold atoms reduced in solution (as stated in the mechanism). Hence, a diffusional growth comprises the third step of the growth process which further decreases the polydispersity. When the particles reach a radius of around 4-5 nm, the growth rate increases drastically and the remaining 70-80 % of the gold salt is reduced rapidly. In this fourth step, particle size increases to the final radius.

The first two steps correspond in first place to a growth due to coalescence whereby a fast reduction occurs in the first minutes after mixing the solutions. The amount of particles formed in the first two steps remains constant in the following two steps of growth. Indeed, the first two steps can also be described by a nucleation process with subsequent growth due to aggregation. However, this nucleation model would describe a quite unimportant process concerning the evolution of the final particle size. The formation of the gold dimer or probably slightly larger clusters (which are thermodynamically stable) does not affect the outcome of the first two steps and therefore also of the final particles. The particle size distribution and concentration at the end of the first two steps is determined by the amount of reduced gold and the colloidal stability since this will define the particle size and concentration. Actually, from the time-resolved SAXS experiments it appears that the amount of gold is defined already in the first 2-3 minutes whereby the coalescence kinetic is slightly slower.

The third step of the growth mechanism is interpreted as a growth by diffusion, meaning that gold ions are reduced anywhere in solution and grow onto the existing particles. In the fourth step the reduction rate increases tremendously leading to a fast reduction of the remaining gold salt (interpreted as autocatalytic surface reduction) and the reduced gold grows onto the existing particles. Again, no further particles form. For both steps, it might be possible that as an intermediate step some gold atoms form small gold clusters which subsequently coalesce with the particles. The probability for such a process is dependent on size and concentration of the existing particles as well as on the formed clusters. This issue is discussed in this contribution for the $NaBH_4$ syntheses. Consequently, if or if not new particles are formed is mainly determined by the reduction rate which is relatively low during the third step. However, the difference of reduction rate between the first step in which the primary particles are formed and the third step is not as big as further particle formation can be excluded. In the fourth step the reduction rate increases tremendously leading to a fast reduction of the remaining gold salt and is even higher than in the first step. Actually, in each of the last two steps a small amount of newly formed particles could be expected, in particular in the final step. This becomes evident when comparing these two final steps with the first two steps or with the Au-System 1. For Au-System 1 the experiment with the different mixing conditions (see 4.2.3 (iv) or SI-1) reveal that even very slow additions of the gold precursor lead to a further particle formation although the existing particles in Au-System 1 are much smaller and their concentration much higher (both decrease the probability that further particles are created).

In fact, the particle growth without further particle formation in the last two steps could be explained with four different processes:

I The existence of an energy or concentration barrier to the formation of small nanoparticles as it is predicted in the CNT

II The diffusional growth as presumed in the existing growth mechanism.

III The formation of gold clusters that subsequently undergo coalescent processes with the particles formed in the first two steps

IV The reduction in proximity or directly at the particle surface with subsequent growth onto the particle.

The first process (I) of an energy barrier is very unlikely since in the first two steps such an energy barrier would not allow the fast formation of particles. In addition, it is previously discussed that dissolution of small gold clusters/nanoparticles is very improbable. The second and third process (II and III) appear to be very reasonable especially in the third step of the synthesis in which they could occur, both consecutively and parallel. However, these two processes can hardly explain the fourth step of the growth mechanisms. In the fourth step, the reduction rate increases tremendously (higher than in the first step) and even for such a relatively high reduction rate (see Fig. 2c in [19]) no further particles are formed. Consequently, the most probable explanation for the final two growth steps is a reduction of gold ions which are attached in the proximity of the particle surfaces (i.e. as co-ions in the EDL). Hence, the reduction in the third and fourth step is most likely a catalytic reaction at the NP surface making process IV the most probable explanation for particle growth without further particle formation.

The enrichment of gold ions in the EDL can also be deduced from a subsequent addition of $HAuCl_4$ solution to final Au-NP. The plasmon band slightly shifts towards higher wavelengths leading to a color change (in standard UV-vis cuvettes) from red to violet. As shown in previous publications the color change is neither caused by any aggregation[56] nor by the absorption of the gold ions themselves.[55] Consequently, the red-shift is most likely due to the adsorption of $HAuCl_4$ on the NP surface influencing the surface chemistry or the dielectric constant of the surrounding medium. The same argumentation explains the grey and later purple color of the colloidal solution in the course of the reaction. The ruby red color of the final colloids represents the state without any gold ions in solution.

The tremendous change of the reduction rate between step 3 and step 4 (although it has no impact on the final particle size since the particle concentration remains constant) remains unclear. It appears that the fourth step occurred for all investigated citrate reduced Au-NP systems (at different concentration and temperature) if the average radius is about 4 nm. However, such a size dependent effect would lead to an increase of the polydispersity or even to a bimodal size distribution because particles that reach this size at first (sufficient for such a fast surface reduction) would grow much faster than the existing smaller particles. In contrast, the polydispersity remains low or even decreases further which makes a size dependent effect very unlikely. Thus, the change of the reduction rate seems to relate to the changing chemical composition of the solution during the reaction (probably caused by product(s) of the reduction).

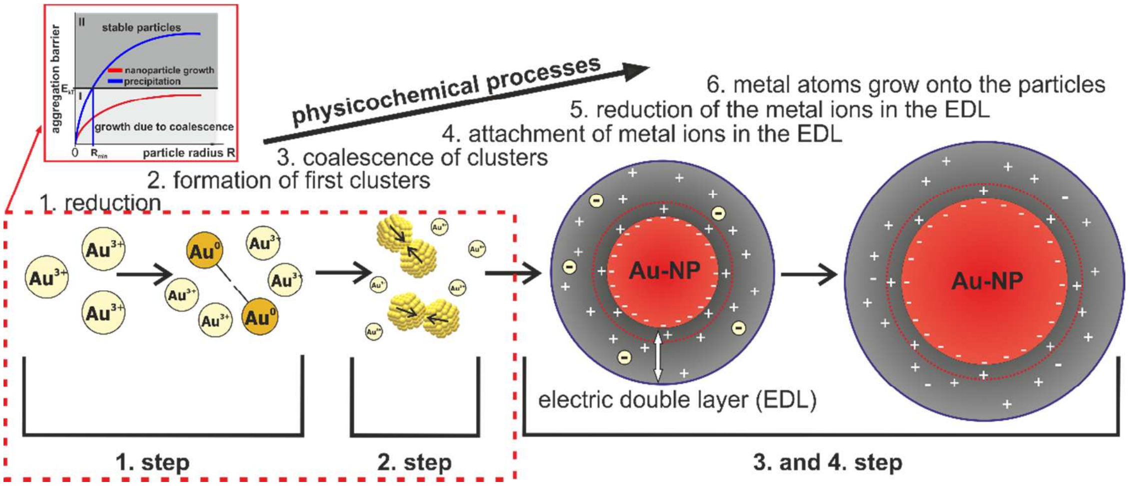

Figure 5 Scheme of the refined 4-step nanoparticle growth mechanism of the Turkevich method

The preceding discussion leads to a refinement of the four-step growth mechanism described in Polte et al.[19,53] Actually, six different sequential physico-chemical processes occur during the growth of a particle which are displayed in Figure 5. The first process is a reduction of gold salt. Subsequently, the metal atoms form small clusters (second process) which undergo coalescent processes to form NPs (third process). As a consequence, gold ions are attached near the surface in the EDL as co-ions (fourth process), get reduced (fifth process) and grow onto the particles (sixth process). Step 1 of the growth mechanism consists of the first two processes (reduction and formation of first clusters) and the third process (coalescence of clusters) represents step 2. The last three processes (gold ion attachment, reduction and growth) occur in step 3 and 4 whereby the two steps are only separated by a slow and fast reduction in the fifth process.

4.4.2 General Aspects of the Refined Growth Mechanism

The growth mechanism of the Turkevich method extends the growth due to coalescence (deduced for synthetic systems of fast reducing agents - see Figure 3) by a process of attachment of gold ions and their reduction in the EDL followed by the growth of the metal atoms onto the particle. The underlying growth principle of that synthesis is a seed mediated growth. It is a matter of opinion if the growth mechanism is separated in four steps. It also possible to describe it with three (e.g. merging step 3 and 4), five (e.g. separating step 1) or even more steps. It is a personal perception that the growth mechanism is described at best with a 4-step mechanism whereby the particle growth proceeds via 6 sequential physico-chemical processes. The steps 1 and 2 in the four-step mechanism define the final size distribution because the remaining gold salt is subsequently growing onto the existing and stable "seed" particles. The seed particles (which comprises less than 3 % of the amount of gold) have a much higher polydispersity but due to the following seeded growth process (in step 3 and 4), the polydispersity decreases from around 50 % to about 10 %. This growth characteristic is in accordance with the so-called "focusing effect" or "growth by diffusion model" described by Reiss in the 1950s.[41]

For the Turkevich method, the resulting final monodisperse Au-NP in a one-pot synthesis are basically determined by two factors. The first factor is the change of reduction chemistry and kinetic between the seed particle formation and the actual seeded growth. The reduction chemistry in the beginning of the reaction enables the seed formation and a change of the reduction chemistry terminates it. Subsequently, reduction occurs in the vicinity of the particle surface. Thus, less than 3% of the gold amount is available for the seed particle formation. The SAXS experiments applying a free-liquid jet even revealed that the four steps of growth occur concomitant to four different steps of the reduction kinetic.[19] However, the kinetic changes between step 3 and 4 seem to have no influence on the final size. The second factor is the colloidal stability of the seed particles. At any time during the synthesis the colloidal stability determines the minimum particle size. Thus, the lower the colloidal stability the larger the seed particles which leads to a lower seed particle concentration and therefore larger final particles. Without a sufficient colloidal stability to few seed particles are formed leading to relatively large final particles or even precipitation. Indeed, the colloidal stability can change during the growth. The minimum particle size in the beginning of the Turkevich synthesis is about 1.5 nm in radius (i.e. smaller particles are not detected) which corresponds approx. to the particle size of the $NaBH_4$ systems.

Summarizing, for the Turkevich method the interplay of several physico-chemical processes leads to an almost ideal seeded growth process in a one-pot synthesis with a seed particle formation in the beginning and a subsequent seeded growth most likely driven by a surface enhanced reduction.

5 Nanoparticle Growth: Thermodynamic Stability vs. Colloidal Stability

As stated in the beginning, nucleation is a thermodynamic model which describes the first step in a first order phase transition with the appearance of a new phase - the nucleus- in the metastable primary phase. In general, most nucleation models are described with the classical nucleation theory (CNT) which applies equilibrium thermodynamics and was originally developed for vapor condensation.[68]

In the following, the previous mechanistic findings for metal nanoparticle syntheses are discussed concerning the classical nucleation approach and subsequently extended for the general case of nucleation and nanoparticle growth.

The CNT and its transfer to NP syntheses from LaMer predicts a certain degree of saturation (supersaturation) of monomers necessary for the formation of first stable particles (nuclei) that are larger than a minimum critical size. Below that critical size the particles or clusters are thermodynamically not stable. Due to the particle formation this saturation decreases below that certain saturation degree. Subsequently, the formed and stable particles (nuclei) are in the growth stage (for instance due to a monomer supply) until reaching their final size. Following this theoretical paradigm, an ideal nucleation and growth process (i.e. growth without aggregation) leads to an increase of the number of particles in the beginning, which remains constant in the growth stage. If such a growth behavior is measured, it is often concluded that the formation process is described at best with a nucleation model. However, this is in general not as straight forward as usually assumed since if A implies B it does not follow that B implies A. Again, the underlying basic concept of CNT is the process of nucleation. What does this effectively mean for the herein discussed metal NP syntheses?

The CNT and its transfer to NP syntheses from LaMer[6] presumes the need of a certain concentration of reduced metal atoms in solution which allows the formation of first small clusters/nanoparticles - the nuclei. The solubility of metal atoms in a solvent such as water is not exactly known, but should be extremely small (effectively 0). So, it can be assumed that such a supersaturation effectively occurs as long as metal atoms are in solution (i.e. as long as all the reduced metal atoms are not part of a cluster or particle). Furthermore, it was discussed that a dissolution of small clusters ($r < 0.5$ nm) for common synthesis temperatures is very unlikely. Therefore, a supersaturation already exists at extremely low concentrations since very small metal clusters consisting of few atoms are already thermodynamically stable. For common synthesis temperatures (< 200°C) even the metal dimer is very likely to be thermodynamically stable. In this case the critical cluster size would be the metal atom. In contrast, the size at which a cluster or particle is colloidally stable is in general in the range of nanometers (i.e. clusters/particles consisting of several hundred or thousand atoms).

For the herein described syntheses, aggregation and coalescence steps are the first size determining steps. For the syntheses with $NaBH_4$ as reducing agent, the growth is solely due to aggregation and coalescence and consequently the increasing colloidal stability determines the final size distribution. For the Turkevich synthesis, a fast reduction and coalescence growth step (steps 1 and 2) determines the size of the seed particles. The concentration of the formed seed particles determines the number of particles on which the gold salt is distributed and therefore the final size.

Even if a nucleation like process in these syntheses really occurs as the first step of the phase transition, it has no impact on the growth process and therefore the final size. It would probably only describe the formation of a metal dimer or another very small metal cluster. These small metal clusters might be thermodynamically stable but they are not colloidally stable. Thus, the clusters grow further by aggregation and coalescence until they reach a colloidally stable size. In this case it is irrelevant if the first thermodynamic stable cluster is the dimer or another slightly larger cluster. From a physical point of view, the concept of NP growth with a minimum particle size governed by colloidal stability as proposed herein are hardly to connect with the CNT, the model of LaMer or any other nucleation model since these theories have a contrary concept of energy barrier. The basic idea behind any nucleation model is that clusters/nanoparticles have to overcome an energy barrier due to a certain particle size (particles with a critical radius) to be able to grow in size. In contrast, the growth governed by colloidal stability states that clusters/nanoparticles always grow at least to a size, at which they cannot overcome an energy barrier of aggregation. In other words, a nucleation model deals with something like an activation energy to form first thermodynamically stable particles, whereas the growth governed by colloidal stability deals with a deactivation energy (an energy barrier at which aggregation or coalescence stops) - hence, two theoretical approaches with two contrary basic assumptions.

For a broad range of nanoparticle syntheses (i.e. also for metal-oxide and semiconductor NPs) the colloidal stability and not the thermodynamic stability determine the minimum particle size. For these syntheses a theoretical model describing the first relevant particle formation step demands the description of the colloidal stability and also of the monomer supplying reaction if this reaction is not faster than the actual growth. The two herein discussed synthetic systems which are classified in two categories can be seen as model systems for this broad range of colloidal syntheses. The almost ideal separation between monomer supply and actual growth of Category 1 syntheses leads to a particle growth which is only due to aggregation and coalescence. Even for very low concentrations particles grow at least to the minimal particle size by aggregation and coalescence. As a consequence for Category 2 syntheses in which the monomer supplying reaction is governing the growth kinetic, the first stable particles are also growing to or slightly above the minimal particle size by aggregation and coalescence. The Turkevich method as an almost perfect seeded growth in a one-pot synthesis represents a model system for Category 2 synthesis. The first particles are formed by a fast coalescence step whereby the largest proportion of the gold monomers is evenly distributed on the previously formed (seed) particles. As discussed, this must result from a change of the reduction chemistry during the synthesis. Indeed, most syntheses will not have a perfect separation between monomer supply and growth nor will they consist of an ideal seeded growth. However, they can be described by a combination of the herein discussed synthetic model systems since (i) the first relevant growth step will be a growth due to aggregation and coalescence and (ii) the following growth is either due to a monomer supply or a further growth due to aggregation and coalescence. The growth due to aggregation or coalescence in (ii) is either between colloidal unstable particles or between a colloidal unstable and a colloidal stable particle. The particle growth due to the subsequent additions of $HAuCl_4$ and $NaBH_4$ to colloidal gold (see 4.2.3 (iv)) illustrates these possible growth processes. The subsequent additions lead to the formation of new particles formed solely by coalescence and to the growth of preformed (colloidally stable) NPs either due to monomer addition or due to the coalescence with colloidally unstable metal clusters.

Hence, theoretical growth descriptions of most colloidal nanoparticle syntheses demand basic knowledge of the underlying growth mechanism, the minimal particle size (determined by the colloidal stability) and the chemical reactions occurring during the syntheses but not a description of a nucleation event.

6 Conclusion

This contribution provides a detailed discussion of growth principles for colloidal metal nanoparticles which is based on time-resolved experimental investigations of several gold and silver nanoparticle syntheses. The syntheses are classified in two categories. The first category comprises colloidal syntheses for which the monomer supplying reaction is faster than the actual growth. This category is mainly covered by syntheses with BH_4^- as reducing agent. It is deduced that the growth mechanism of Category 1 syntheses is only due to aggregation and coalescence and therefore governed by colloidal stability. For theses syntheses an idealized concept of nanoparticle growth is presented which is in contrast to the commonly applied LaMer model.

For most syntheses, the monomer supplying reaction is much slower and governs the kinetic of particle growth. These syntheses are classified as Category 2 syntheses and discussed using the most popular gold nanoparticle synthesis as an example – the Turkevich method. For the Turkevich method, an interplay of several physico-chemical processes leads to an almost ideal seeded growth process in a one-pot synthesis. The seed particles are formed in the beginning of the synthesis with a subsequent seeded growth which is most likely driven by a surface reduction. The seeded growth mechanism with the resulting final monodisperse gold nanoparticles is caused by two factors: a change of the reduction chemistry and the colloidal stability.

For both synthetic classes the minimal particle size is in general determined by the colloidal and not by the thermodynamic stability making a nucleation model irrelevant. For Category 1 syntheses the minimal particle size corresponds to the smallest final size and for Category 2 syntheses to the smallest seed particle size. Furthermore, it is discussed why Ostwald ripening is a very unlikely growth process for most metal colloid syntheses.

The herein discussed growth mechanisms can be seen as model cases of synthetic systems. Other synthetic system might not have a distinct separation of the monomer supplying reaction and particle growth as it is the case with Category 1 syntheses or might not comprise a perfect seed mediated growth as Category 2 syntheses. Nevertheless, the growth of most syntheses can be described by a combination of the herein discussed synthetic model systems and the growth concept based on colloidal stability.

AUTHOR INFORMATION

Corresponding Author

* Joerg Polte, joerg.polte@hu-berlin.de

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ABBREVIATIONS

CNT, classical nucleation theory;

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