

# The Electric Soul of Metal Nanoparticles – What Experiments with Microfluidically Prepared Colloids Tell Us

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## Abstract

Metal nanoparticles are of interest for different biomedical and technical applications, for example by conjugation with DNA, enzymes or other biomolecules, for on-chip-labeling, for SERS-analytics, for heterogeneous catalysis and as antibacterial additives. Non-spherical metal nanoparticles are in the focus of developments due to their size- and shape-dependent optical properties. Recent results on the synthesis and behavior of noble metal nanoparticles are discussed from the point of view of the electric behaviour. The particle growth by a metal-catalyzed reductive metal deposition in liquid phase is regarded as an open-circuit mixed electrode system. Potential formation and the related electric charging of metal nanoparticles lead to self-polarization effects. These effects enforce spontaneous symmetry breaking effects during the formation of metal nanoparticles and explain the growth of non-spherical particles with high aspect ratios.

**Keywords:** Nanoparticles, Colloids, Self-polarization, Electrostatic interaction, Symmetry break, Microfluidics, Droplet-based Flow, Micro-segmented Flow

## 1. Introduction

Metal nanoparticles are known since the ancient times. The colorizing of glass by colloidal gold was already used in the Roman Empire [1] and for designing of church windows in the middle age [2]. The colloidal character was later recognized by Michael Faraday, who had also found the high stability of dispersed noble metal particles in liquid environments [3]. Due to Faradays discoveries, there can be no doubt about the fundamental function of electrical charges for the formation and stability of colloidal solutions.

Beside electricity, there are a few well-known other factors of importance for the formation and properties of colloidal systems. At first, the interatomic or intermolecular forces inside the particles are important. They determine the construction of the solid material. They are decisive for an amorphous arrangement of atoms

or molecules as it is found in many polymer particles [4, 5] or a regular crystalline arrangement as it is found in single crystal metal nanoparticles [6, 7]. At second, the environment is important, because it can stabilize or destabilize colloids by solvation. Chemical effects can be controlled by non-ionic as wells as by ionic interactions. Namely, a discharging of colloids by enhancement of ion strength in the solvent is a frequently observed phenomenon [8, 9].

At third, the chemical state of the interface between the particle and the liquid is important. In current literature, the specific adsorption of solution components on the particles surface is often discussed as a reason for a certain particle behaviour or growth. Such an effect of adsorption is in particular considered as the main reason for the formation of non-spherical particles by specific inhibition of the growth of single crystalline planes. This model of (non-spherical)

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particle growth is based on an assumed complete coverage of the particle surfaces by the adsorbing species from solution. The result is an inhibition of the crystal growth in certain directions [10-12]. This model concept might be applicable for some special particles, but it seems to be less suited for explaining the formation of colloidal solutions of non-spherical nanoparticles with high aspect ratios.

Observations from recent microfluidic syntheses and experiments with microfluidically prepared metal nanoparticles suggest that electrical effects play a crucial role and are more important than a growth inhibition by complete coverage of selected crystallographic planes [13]. The new sight on colloidal solutions of noble metal nanoparticles was only possible through the high yield and homogeneity of nanoparticle syntheses under microfluidic conditions [14] and by the possibility of time-resolved analyses of particle formation [15]. In the following, electrical and electrochemical aspects in the formation and behaviour of such metal nanoparticles in colloidal solutions are discussed in order to understand the role of particle charge not only for colloidal stability but in particular for the complete character of individual colloidal particles.

## 2. Principles and advantages of nanoparticle synthesis in micro flow systems

The shape and size of nanoparticles can either be controlled by thermodynamic stability or by kinetic control. In the first case, a high homogeneity of nanoparticles can be achieved if a narrow distribution of sizes and shapes is the most stable state and the activation energy for particle dissolution and growth are low enough for a complete equilibration. In the second case, time-critical steps decide upon the quality of

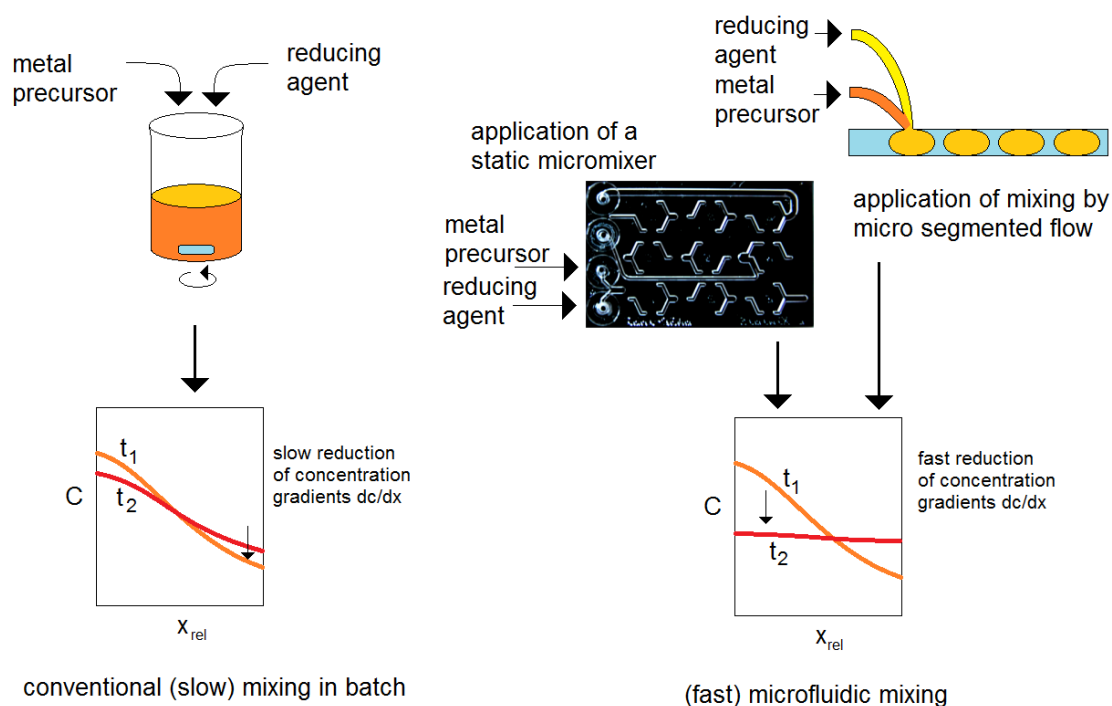
particles. In these steps, homogeneous nanoparticle ensembles can only be achieved if the reaction conditions are homogeneous as well. This requires very fast mixing of reactants and fast heat transfer. A high local homogeneity is important for the nucleation phase, for the first growth phases, and for all in-situ assembling processes.

The challenge of rapid mixing has been overcome by microfluidics. Microreactors are suited for fast mass and heat transfer [16-18]. It could be shown that high quality nanoparticle products from wet chemical syntheses could be prepared by microfluidic approaches, for example for metal oxide [19], semiconductor [20], polymer [21], as well as for metal nanoparticles [22].

Each mixing process is marked by an intermediate phase with high local concentration gradients. These gradients can cause a high diversity of particles, if the critical reaction steps as nucleation and in-situ assembling are going on during mixing. Microfluidic mixing can reduce these concentration gradients very quickly and overcome inhomogeneities during nucleation and in-situ assembling. Static micro mixers of different types are well suited for these fast processes. Particular high mixing rates can be achieved if the internal volume of the mixer is small and comparatively high volume flow rates can be applied (Figure 1). Thus, in a Dean flow micro mixer, for example, mixing times down to below one millisecond could be realized [23, 24]. This type of mixer is well applicable for reaction mixtures with low tendency to side wall deposition and wall-induced nucleation – for example in case of high surfactant concentrations [23]. Otherwise, the high surface-to-volume ratio of these micro mixers can result into considerable rates of reactor fouling.

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**Figure 1. Fast microfluidic mixing for controlling time critical steps during nanoparticle formation**

Side wall effects can be reduced drastically in case of micro segmented flow. By this method, the reaction mixture within the reactor is subdivided into a sequence of droplets, which are embedded in a non-miscible inert carrier liquid [25]. Syntheses, carried out the by micro segmented flow method can combine an efficient decoupling between the reaction mixture and the channel wall with a fast mixing [26]. The reactant solutions are mixed immediately before the injection into the streaming carrier liquid, whereby droplets of equal size and distance are generated. Regular streaming pattern are formed during their further transport through a micro channel or tube. Mixing times between about 3 and 100 ms can be achieved due to the flow-induced circular convection inside the single fluid segments. The method was applied in the syntheses of different semiconductor [27, 28] and metal nanoparticles and supplied a high product quality [29].

### 3. Experimental results in the light of electronic interpretation

#### 3.1. The crucial insight through microfluidic experiments: Why do spheres form?

A spontaneous formation of spheres is caused by a minimization of interface energy. A liquid typically forms a sphere if only interface forces are acting: in the gas phase in absence of gravitation or in emulsions. If isotropic liquids are solidified—for example by freezing or polymerization – solid spherical particles are formed.

The shape of nanoparticles from crystalline materials is always determined by the crystallization, because the crystalline state represents the thermodynamically stable state. In the thermodynamic equilibrium, a spherical single-crystal can only be expected if the amount of its interface energy is higher than the lattice energy.

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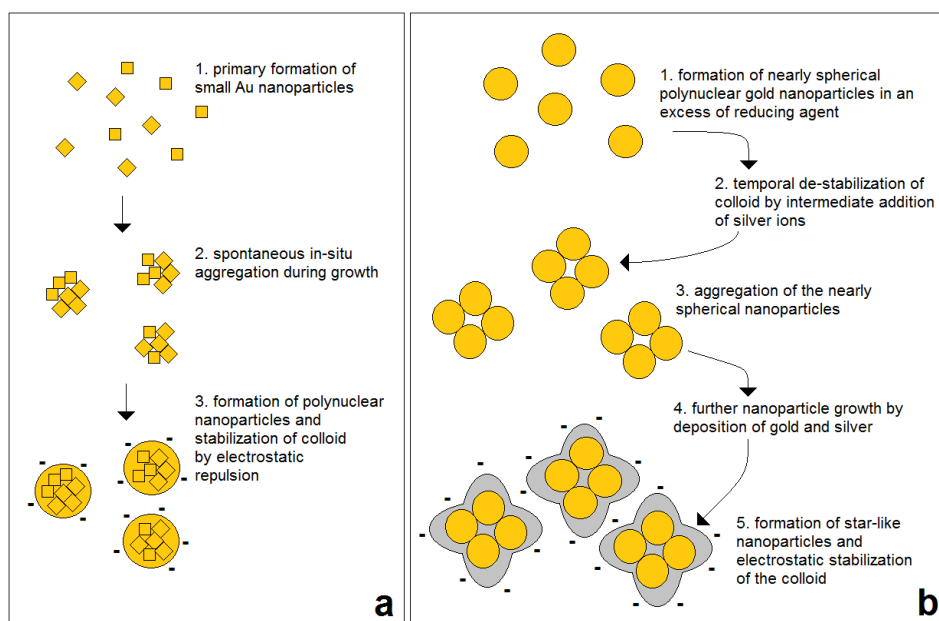
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The typical spherical metal nanoparticles as e.g. in case of gold nanoparticles with sizes above about three nm are not single-crystalline. High resolution transmission electron microscopy has shown that these particles are polynuclear. It means that they are composed of several single crystals, which have formed independently of one another, obviously.

The evolution of these particles was analysed by in situ-SAXS measurements (Small angle X-Ray Scattering) during a flow synthesis of spherical gold nanoparticles [15]. These investigations showed that a nucleation/aggregation mechanism takes place (Figure 2a). Small gold clusters with sizes below 2 nm are formed in the first step. But, the repulsive forces between these particles are not strong enough for formation of a stable colloidal solution. Thus, these small particles aggregate before the particle growth was completed. In result, polynuclear particles with a nearly spherical surface were formed. These subsequently

formed larger gold nanoparticles have a higher ratio of electrostatically repulsive forces to kinetic energy, what means that their colloidal solution is thermodynamically stable.

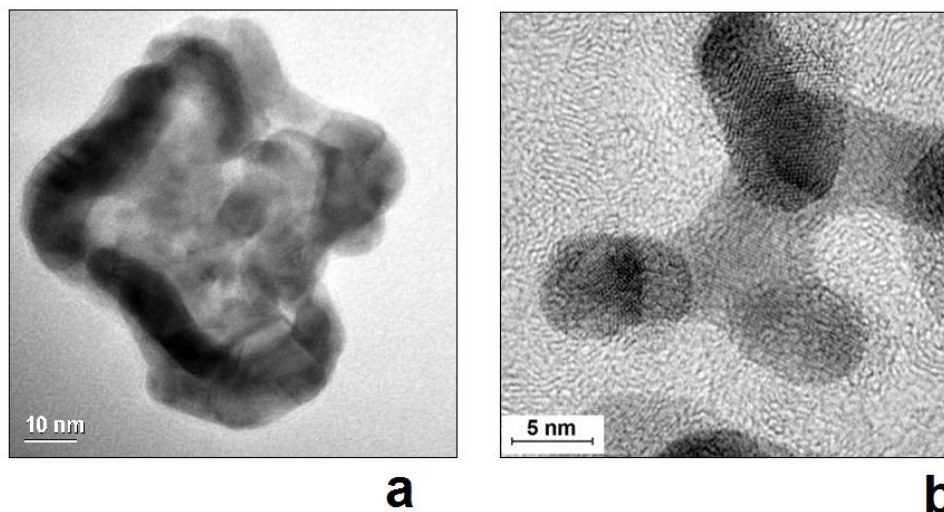
A similar mechanism was already observed during a two-step Au/Ag nanoparticle formation process (Figure 2b). In this case, silver ions were added before the growth of the gold nanoparticles was completed. Also in this case, an in-situ particle assembling was observed resulting in star-like particle structures consisting of several gold cores – the poly-nuclear gold particles formed before. It is assumed that the formation of these particles is initiated by a transient increase of the particle potential due to the addition of the positively charged metal ions, which cause a transient destabilization of the initially formed colloidal state. This assumption is supported by the fact, that under certain concentration conditions larger fractal aggregate structures of small gold cores instead of compact aggregate particles were observed (Figure 3).



**Figure 2. The role of colloidal stability for the formation of metal nanoparticles: a) Nucleation/aggregation mechanism in the formation of spherical gold nanoparticles [15], b) Formation of Au/Ag nanoparticle in-situ assemblies in a two-step synthesis**

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**Figure 3. Formation of dendritic structures of Au/Ag nanoaggregates due to a temporal destabilization of the colloid state**

The electrostatic stabilization of metal colloids results from an excess of reactants of the formation reaction. Normally, these colloidal solutions are generated by reduction of gold (III) in form of tetrachloroaurate by an excess of the reducing agent – for example sodium borohydride or ascorbic acid. The reducing agent is oxidized at the surface of the forming metal nanoparticles releasing electrons into the metal. This results into a negative electrical excess charge after complete consumption of the metal precursor. An addition of negatively charged ligands as citric acid, for example, can further support this negative charging of metal nanoparticles.

An electric excess charge can also be generated by an excess of positive charged particles, which are strongly adsorbing at the particle surface. Thus, positively stabilized colloids can be obtained in an excess of gold-affine cationic surfactants.

### 3.2. Cubes instead of spheres: The role of ligands in gold nanoparticle synthesis

On the first sight, spheres seem to be the

simplest shape for nanoparticles. But, this is not true for metal nanoparticles like gold. The above discussed nucleation/aggregation mechanism and the polynuclear structure of spheres prove that these nanospheres are rather complex objects. The simplest structure for the condensation of metal atoms is their regular arrangement in form of a crystal, simple cubes in the case of a face-centered cubic crystal lattice.

The challenge for realizing this “simplest structure” is to avoid all additional complex processes, which can lead to other structures. At first, the primarily formed nuclei must not aggregate. Thus, the key for getting single crystalline particles is to avoid particle/particle contacts. This can be achieved on the one hand by an enhancement of electrostatic repulsion or the implementation of a steric stabilization by amphiphilic molecules and on the other hand by lowering the contact probability by working in highly diluted systems.

From empirical investigations it was known that an addition of bromide promotes the formation of gold nanocubes [30]. Bromide ions have a high affinity to gold surfaces. In the



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absence of other charged species, the adsorbed bromide ions contribute to particle/particle repulsion by their negative charge. In addition, the coverage of the surface of growing gold nanoparticles reduces the probability of particle fusion in case of a direct contact.

An addition of bromide is also helpful for getting gold nanocubes in an excess of CTAC, a cationic surfactant. The interaction of gold nanoparticles with CTAC leads to a positive charging. But also in this case, bromide prevents particle/particle aggregation and promotes the formation of nanocubes.

Thus, the formation of nanocubes means the appearance of the simplest structure, the simplest single crystalline shape. Overgrown corners of these cubes result into a trisoctahedral structure, which is also single crystalline from its nature (Figure 8).

### 3.3. The mixed electrode character of growing metal nanoparticles in electrolytes

The colloidal state of growing metal nanoparticles remains stable as long as the particles are sufficiently charged. This charge

depends on the electrochemical potential in case of a reductive deposition of metal atoms at the particle surface, which is characteristic for a mechanism with a metal-catalyzed chemical metal deposition:



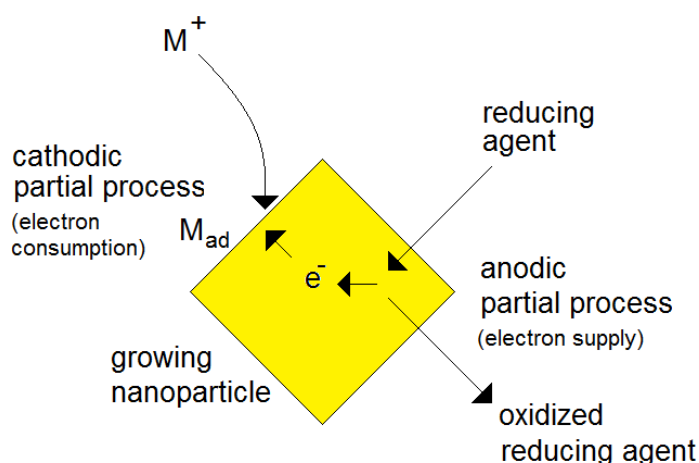
This total reaction is composed of two simultaneous electrochemical partial processes: The cathodic one is the reduction of metal ions to atomically dispersed metal atoms ( $M_{ad}$ ):



The anodic partial process is the oxidation of the reducing agent:



The last reaction supplies the electrons for the reduction of the metal ions. But both processes can proceed on different positions of the growing nanoparticle. They are spatially decoupled and connected only by the electrical current flowing through the metal nanoparticle (Figure 4).



**Figure 4. Growing metal nanoparticles as an open-circuit (outer-currentless) mixed potential electrode: Scheme of the formation of the electrode potential by balancing anodic and cathodic partial current in dependence of the characteristic current-potential-functions of partial processes**

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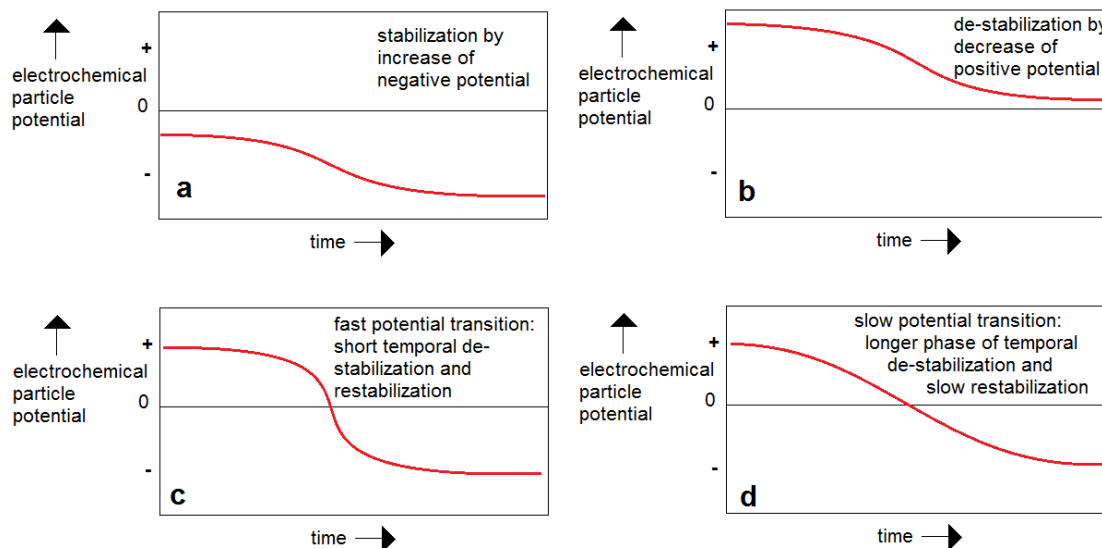
The electrochemical potential of the particle is controlled by the intensities of both partial processes and – vice versa – the intensities of both partial processes depend on the electrochemical potential of the particle. The particle acts as a mixed electrode in an open-circuit state. The formed common electrochemical potential and the intensities of partial processes are adjusted only by the balance of charges, what means the balance of anodic  $I_+$  and cathodic current  $I_-$ :

$$I_+ = I_- \quad (4)$$

The process intensity is controlled by the electrochemical standard potentials of the both partial processes and by the concentrations

(electrochemical activities) of the metal ions and the reducing agent. It can be further modulated by ligands forming complexes with the metal ions or interacting with the reducing agent.

Thus, the charging of the nanoparticle is controlled by the type and concentration of metal ions or their complexes in solutions as well as by the concentration and the redox power of the reducing agent. In addition, ligand concentrations and pH can modulate the partial processes and thus the resulting electrochemical potential of the particle. A high concentration of metal cations or their complexes causes a high particle potential. A high concentration of reducing agent lowers the particle potential.



**Figure 5.** Change of electrochemical potential during the consumption of metal precursors (metal ions or complexes) in case of an excess of reducing agent: a) stabilization of the colloidal state in the case of always negatively charged nanoparticles (for example in the case of a higher concentration of a negatively charged adsorbing ligand), b) partial destabilization in case of always positive nanoparticle charging (for example in the case of higher concentrations of an adsorbing cationic surfactant), c) transitional destabilization and re-stabilization of colloidal state in case of shifting the particle potential from a positive to a negative charge

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An excess of reducing agent is applied in many protocols for wet chemical syntheses of metal nanoparticles. These processes are always marked by a characteristic change in the electrochemical potential of growing particles (Figure 5). In the beginning – at higher metal ion concentrations – a high intensity of the cathodic partial process keeps the particle potential high. In the final phase – the state close to the complete consumption of metal ions – the particle potential is lowering due to the decreasing effect of cathodic partial process and the increasing dominance of the anodic partial process.

The change of the open-circuit electrochemical potential of nanoparticles is always connected with a change in the stability of the colloidal system, which is dependent on the repulsive electrostatic forces of the charged particles. In case of an excess of reducing agent, the exhaustion of metal ions during the particle growth causes a stabilization of the colloidal state if the potential remains always negative, for example if adsorbing negatively charged ligands like citrate ions are present (Figure 5a). This stabilization is caused by the increasing particle-particle repulsion due to increasing negative particle charging.

In contrast, the colloidal state is destabilized if the nanoparticle potential is always in the positive range during the particle growth (Figure 5b). This can be achieved, for example, by a higher concentration of positively charged additives adsorbing on the particle surface, for example by a cationic surfactant as CTAB. In this case, the electrical charging and the forces of particle-particle repulsion are reduced during the consumption of the metal ions. In result, the colloid becomes more and more sensitive during the particle growth. Finally, the repulsion between the colloidal particles can become so low that the particles coagulate and a precipitate is obtained instead of a colloidal solution of

nanoparticles.

It is also possible, that the consumption of metal ions and the increasing dominance of the anodic partial process results in a transition of the electrochemical potential from the positive into the negative state (Figure 5c). In this case, the colloid experiences a destabilization due to the reduction of positive charges in the first phase of particle growth, but can be re-stabilized due to the increasing negative charging during the last phase. The transitional destabilization of the colloidal state might be without effect if the change of the electrochemical potential proceeds very fast. But it leads to particle aggregation and precipitation if the particles have enough time for interaction. A restricted particle aggregation can be expected at a moderate speed of potential transition: The temporal destabilization initiates particle-particle fusion, but these aggregates remain small and the colloid is re-stabilized by a decreasing electrochemical potential before larger coagulates are formed (Figure 5d). In this case, a potential-controlled assembling of nanoparticles is observed.

### 3.4. Self-polarization of conductive nanoparticles

The growing metal nanoparticles are electric conductors. This property is an essential precondition for their function as a mixed electrode for the anodic and the cathodic electrochemical process as discussed in the previous section. The electrical conductivity as well as the electrode function is comparable with the properties of metallic bulk materials, in principle. But, a significant difference between nanoparticles and bulk objects exists in the effect of distribution of excess charges due to the electrochemical potential. The larger extension of conductive bulk objects causes only small electrical fields due to the self-polarization effect, which is caused by the repulsion of excess charges inside the metal. In contrast, a



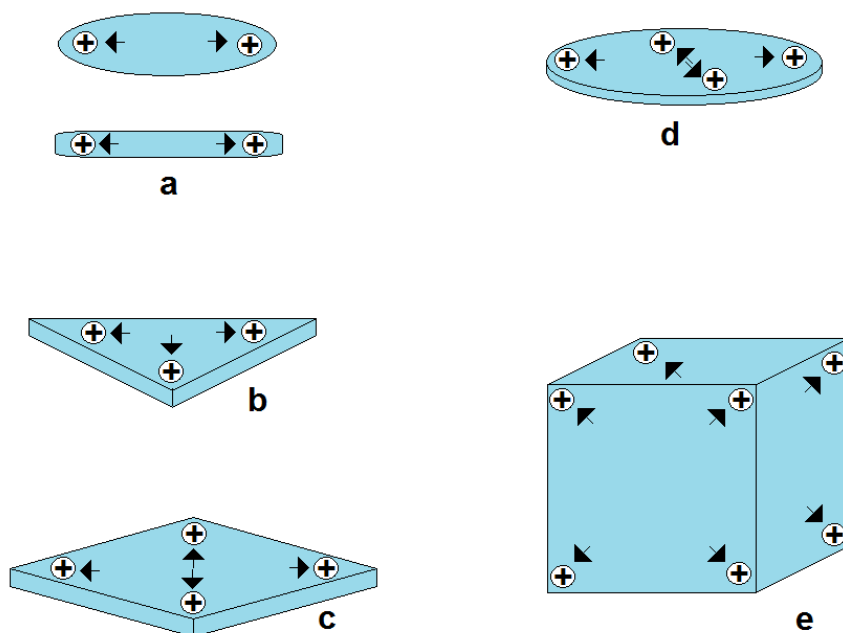
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comparable charging by electrochemical potential leads to a significant repulsion of excess charges over short distances in metal nanoparticles. The resulting self-polarization is in the same order of magnitude as the electrochemical potential itself. An electrical charging by about 0.1 V over a particle length of 10 nm results into an electrical field of  $10^7$  V/m, for example.

The excess charges are localized at the surface of a nanoparticle. Therefore, the repulsion of excess charges leads to homogeneous distribution of charges at the surface of a sphere. Thus, no self-polarization has to be expected on spherical nanoparticles. This symmetric charge distribution gets lost whenever the spherical

symmetry is broken. The repulsion of charges leads to pushing electrical charges towards the poles, edges and corners of non-spherical conductive particles. The charge distribution at the particle surface depends on the particle shape. It reflects the geometry of particles. A symmetric tri-pole structure (Figure 6a) results on ellipsoidal and rod-like particles. Disks possess a higher charged periphery and a lower charged center (Figure 6b). However, the charge is mainly focussed in the corners of flat triangular (Figure 6c), rectangular (Figure 6d) or cubic bodies (Figure 6e). The existence of partial charges at the surface of silver nanoparticles was e.g. also supported by SERS (surface enhanced Raman spectroscopy) measurements [31].



**Figure 6. Self-polarization effect of charged conductive nanoparticles of different shape**

The electric polarizability of metal nanoparticles and the resulting non-symmetric charge distribution must be seen in analogy to the polarizability and charge distribution in molecules. Ionized organic chromophores with

larger conjugated pi-bond systems can be seen as a comparable two-dimensional model for conductive nanoparticles. The charge of these molecule ions is distributed in form of partial charges at two or more peripheral positions of

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the molecules, what is normally described by mesomeric structures in the valence bond model.

In analogy to molecules, the distribution of charges at the surface of non-spherical metal nanoparticles causes also a differentiation of the local reactivity of particles. It modulates the local attraction or repulsion behaviour against charged and polarizable reaction partners and the transfer of electrons by redox reactions, respectively local electrochemical processes: Particle corners and edges with a high excess of negative charge attract positively charged reaction partners. They tend to transfer electrons to these reaction partners and to discharge cations. In contrast, areas with an enhanced positive charge density would attract anions and preferably transfer positive charges to reaction partners.

The asymmetrical charge distribution of growing non-spherical nanoparticles, which act as open-circuit mixed electrode systems, results into a local splitting into particle regions with enhanced anodic partial process activity and particle regions with enhanced cathodic partial process activity. The simplest example for this (mostly partial) separation of electrode activities is given by a charged nanorod (Figure 7): Anionic reaction partners are guided to the poles of positively charged nanorods or positively charged metal ions are released (corrosion), because the anodic partial process preferably takes place at the corners. Cations are repulsed from the corners and have a higher interaction probability at the central region of particle. Here the cathodic partial process preferably proceeds (Figure 7a). The inverse situation has to be expected with nanorods having negative excess charge: Their poles attract positively charged particles and

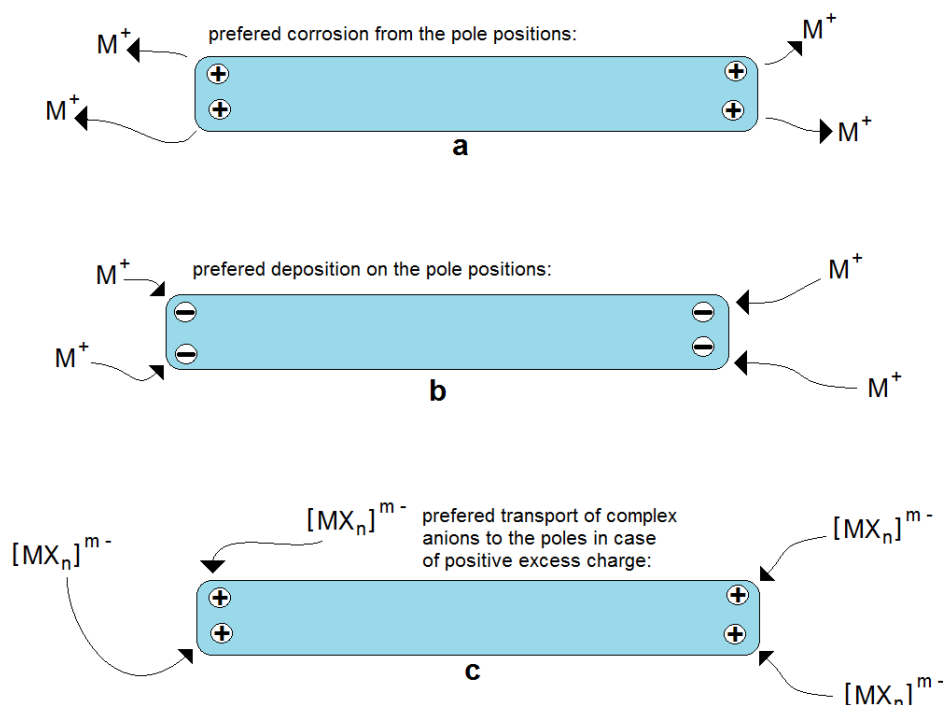
cations from the environment and the poles are regions in which cathodic partial processes are preferred, whereas the anodic partial process proceeds mainly on the central part of the nanorod (Figure 7b).

### 3.5. Control by positive charge: gold nanorods from tetrachloroauric (III) acid in the presence of a cationic surfactant

It is well known from experimental studies, that colloidal solutions of gold nanorods can be achieved, if tetrachloroaurate is chemically reduced in the presence of high concentrations of Cetyltriethylammoniumbromide (CTAB) [32, 33]. Beside effects of micellar structures formed by the surfactant, mainly a selective binding of CTAB and bromide ions on specific crystallographic planes is discussed in literature, which should inhibit the particle growth in certain directions [7, 8, 10-12]. It seems to be obvious that a high excess of the positively charged surfactant, which can be adsorbed at the surface of the growing gold nanorods causes a positive particle charging. The resulting positive excess charge is lowered by the co-adsorption of bromide ions, which have a high affinity to gold surfaces. Zeta potential measurements of colloidal solutions of gold nanorods in the presence of CTAB indicate, that the resulting particle charge is positive, what means that the cation adsorption is dominating the charging of particle despite the high affinity of bromide ions. The zeta potential of gold nanorods, which were obtained in the presence of 0,1 M CTAB, was measured under usage of a Malvern Nano ZS instrument and was determined to +70 mV. But, it has to be taken into account that the co-adsorption of both ion types leads to a lowering of anodic as well as of cathodic activity by CTAB.

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**Figure 7. Symmetry breaking of particle-ion interactions and electrochemical partial processes in case of charged nanorods: a) positively charged particles, b) negatively charged nanorods**

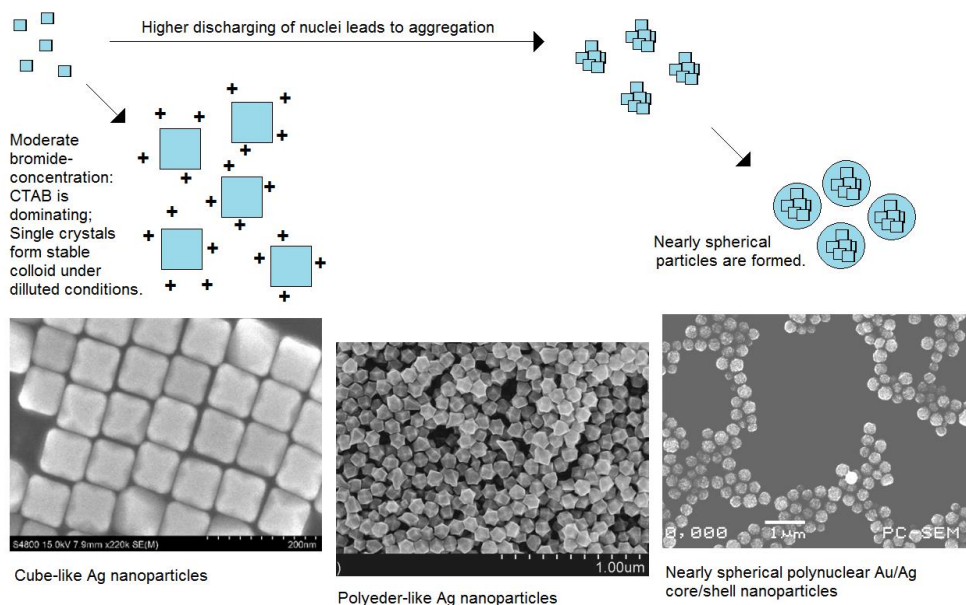
The positive excess charge leads to a high probability for the anodic partial process whenever the reducing agent can get in contact with the gold surface. But, in case of an initial symmetry breaking, the positive charges are pushed into opposite directions. There, they enforce the attraction of the negatively charged tetrachloroaurate complexes. In result, tetrachloroaurate is mainly reduced and decomposed at peripheral positions of a growing nanoparticle, if this particle is positively charged. Here, it is proposed, that the effect of different adsorption and grow inhibition on certain crystallographic planes is restricted mainly to the initial symmetry breaking. This effect is responsible for the formation of rods instead of cubes in case of gold nanoparticles in the presence of CTAB, obviously. The effect of crystallographic planes on the asymmetric growth is more and more reduced after the initial

symmetry break and substituted by the dominating role of the self-polarization of the forming nanorods.

Recent investigations of the role of the bromide concentration on the gold nanoparticle formation and the comparison with the effect of other halide ions showed that the growing behavior can be reliably steered by the bromide concentration, which is due to the particular high affinity of this ion with the gold surface [34]. A moderate enhancement of bromide concentration lowers the positive excess charge of the gold nanoparticles. In result, no symmetry break takes place and cubes or compact polyedric particles can be synthesized (Figure 8). At higher concentrations of bromide, the excess charge is lowered so far that an initial aggregation of nuclei takes place, which results into the formation of compact polynuclear particles with a nearly spherical shape.

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**Figure 8. Explanation of the effect of bromide ion concentration on the formation of differently shaped gold nanoparticles by reduction of tetrachloroaurate in the presence of cetyltriethylammonium ions and bromide ions by the dominance of electrostatic effects**

### 3.6. Control by negative charge: flat silver prisms from silver cations in the presence of polyanionic macromolecules

A very well reproducible synthesis of flat triangular silver prisms with high yield was described by Aherne and coworkers by addition of polystyrene sulfonate in the reaction mixture of silver nitrate and a reducing agent in aqueous solution [35]. They showed that the lateral size and the optical resonance properties can easily be tuned by a variation of the ratio between seed nanoparticles and silver ion concentration in the particle growth step.

The reproducibility and quality of this synthesis and the tunability of optical properties could be further improved by adapting the Aherne-protocol in a microfluidic synthesis [14]. Zeta potential measurements clearly indicate a high negative excess charge of the so-formed nanoparticles. With silver nanoprisms of edge lengths between 20 and 200 nm, the zeta potential was found to be always below -40 mV.

How the symmetry break can be understood in this case?

Polystyrene sulfonate molecules are polyanionic macromolecular chains. In contrast to mostly more or less coiling non-charged macromolecules in solution, polyionic macromolecules are stretched due to the electrostatic repulsion between the charged functional groups. It is assumed, that the nucleation and the first growth phase of silver nanoparticles is connected with an attachment of the silver seed nanoparticles to only one or a few of the negatively charged polymer molecules. Their negative charges push the electrons of the forming metal nanoparticle into peripheral positions. This charge pushing is mainly oriented in perpendicular direction to the main axis of the attached charged macromolecule, what defines a preferred plane for particle growth. The geometry in this plane is given by the crystallographic anisotropy with densely packed atoms (111) causing a hexagonal or even a triangular

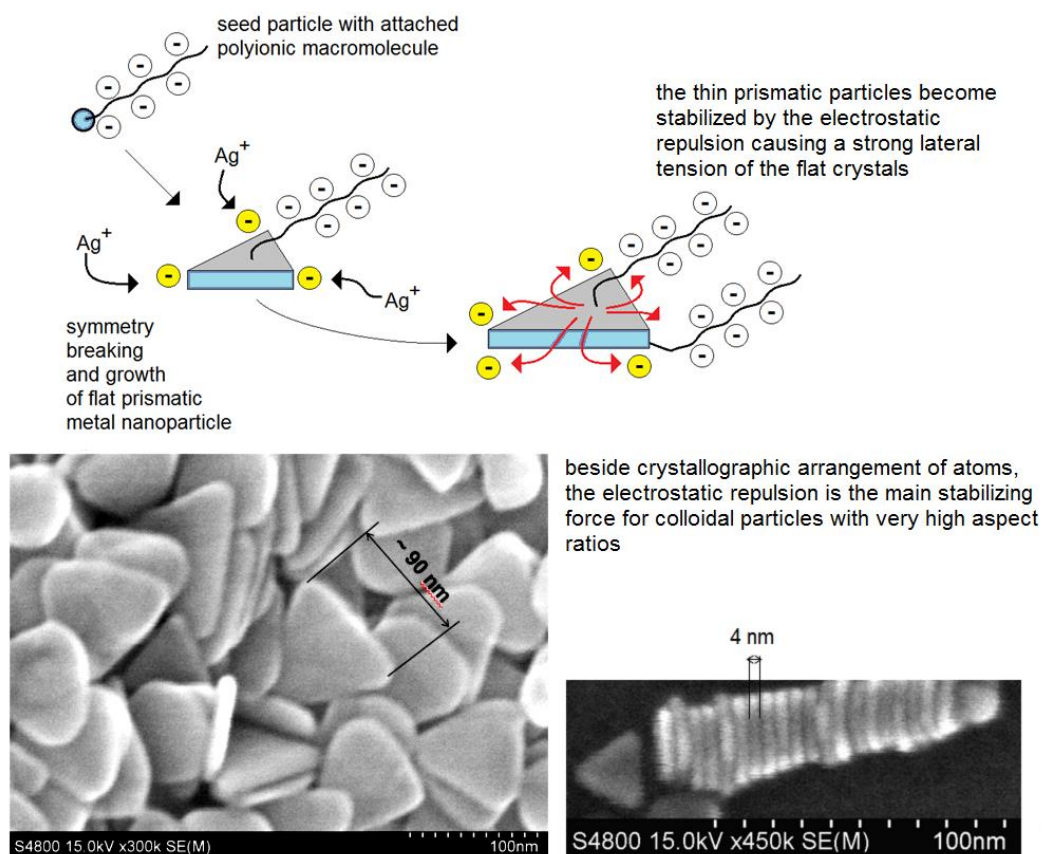
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arrangement of atoms. In result, flat silver nanoprisms are obtained.

The self-polarization model is also suited to explain the preferred formation of triangular instead of hexagonal prisms. In batch preparations, a certain portion of hexagons is found mostly beside the silver nanotriangles. Triangles in a yield of almost 100% have been found in microfluidic preparations with fast mixing of reactants. It is assumed, that a certain stochastic behaviour occurs during nucleation including triangular as well as hexagonal prisms. Some fluctuations during the growth of

nanoparticles lead to temporal spontaneous symmetry breaks, which relates to the side edges of the hexagons. The negative excess charge of the growing nanoparticles is pushed towards the shorter edges and enforces the silver deposition on them. In consequence, the long sides become longer and the short sides become smaller, which enforces the self-polarization effect towards the three short edges. Thus, the further growing is driven by a typical positive feed-back effect. Finally, exclusively nanotriangles are formed.



**Figure 9. Umbrella model for electrostatic stabilization of flat metal nanoprisms due to the self-polarization effect**

There is a further very important aspect of the silver nanotriangle formation, which can be made

plausible by the self-polarization model: the high aspect ratio of the particles. Indeed, very flat

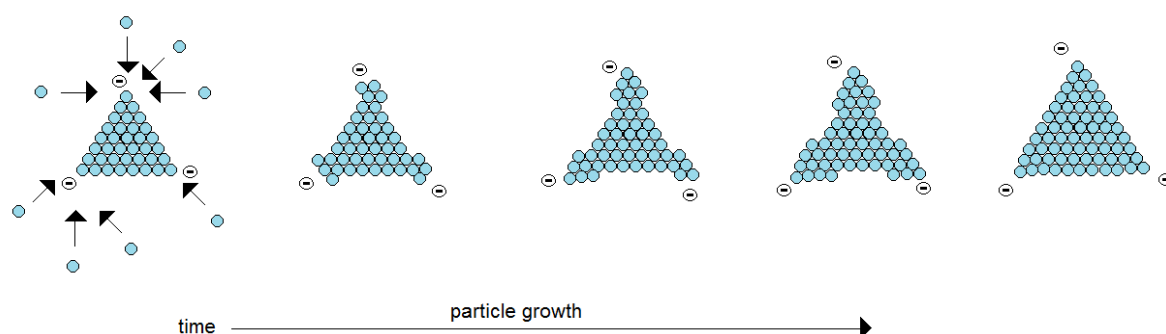


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particles with aspect ratios over 1:50 can be obtained at higher ratios of silver seeds and silver ions during the growth process. However, the most amazing fact is that colloidal solutions of prisms with an edge length of 200 nm or more and a thickness of merely 4 to 5 nm remain stable over several months. A selective protection of the crystallographic top and bottom plane due to a complete coverage by adsorption of the polymer additives cannot supply a convincing explanation for the formation of these

flat particles. But, the formation of these flat nano objects becomes understandable immediately, if an electrostatic stabilization by the repulsion of the excess charges in the corners of the triangles is reconsidered (Figure 9). The fragile shape of flat prisms is stabilized by their internal electric field caused by the self-polarization effect. This potential stretches the particle into a flat geometry in analogy to the fabric of an umbrella, which gets its tension by the force of mechanical springs [13].



**Figure 10. Proposed mechanism for corner-controlled growth during the formation of flat silver triangles at negative excess charge under the influence of polyanionic effectors**

The self-polarization model is also suited to explain how the triangular silver nanoprisms grow. The growth rate on the larger top and bottom planes are very small or negligible. The discharge of silver ions and the deposition of new atomic layers in the growing crystals start always from the negatively charged corners. The new layers grow along the narrow side planes (particle edges) only. This filling process proceeds always from the corners to the central part of the edges (Figure 10). This mechanism explains also, why triangles with sharp corners are formed. The cathodic partial process at the corners is controlling the whole growth process of the particles. In contrast, the charge compensating anodic partial process – the electron supply by oxidation of the reducing agent – can proceed at the large top and bottom

planes.

The key function of electric charge for the stability of silver triangles is reflected impressively by a charge-controlled spontaneous nanoparticle conversion from the flat prismatic into a compact shape. This process can be initiated by a displacement of the polyanionic macromolecules from the nanoparticles surface by a competitive adsorption of an excess of thiocyanate [36]. The release of the multi-charged macromolecules destabilizes the flat prism due to the loss of negative excess charge. In consequence, the “umbrella effect” breaks down and the flat particles collapse. This process could be described well by a “shape isomerization” of nanoparticles, which is going on in analogy to a molecular isomerization reaction. It can easily be monitored in time-cyclic UV-Vis

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measurements by the successive reduction of the intensity of the long-wavelength in-plane absorption mode of the silver nanotriangles and the simultaneous increase of the absorbance corresponding to the short-wavelength electromagnetic resonance of compact silver nanoparticles.

#### 4. Conclusions

The high quality of non-spherical metal nanoparticles obtained by microfluidic syntheses allows new insights into the physical nature of these particles in colloidal solution. These insights are important for the development of new types of metal nanoparticles – in particular non-spherical and composed particles - for applications in labelling, in biomedicine, in bioanalytics, in catalysis and in molecular-based diagnostics. The investigation of optical spectra as well as the measurement of Zeta potentials and the study of the effect of reducing agents, metal ions as well as charged ligands make clear, that the behaviour of colloiddally distributed metal nanoparticles is mainly determined by their electric charge.

During their chemical growth and also during corrosion or other redox reactions, metal nanoparticles have to be considered as an open-

circuit mixed potential system. This point of view illuminates not only the origin and function of electric charge, but also the effects of shifting concentrations and consumption of reactants. The non-spherical and “dimension-reduced” shape of particles like disks, rods and flat prisms is a consequence of a symmetry break. It causes a characteristic distribution of electric charge on the nanoparticles, which leads to a self-polarization and therefore to significant local differences in the intensities of all potential-dependent surface processes. To understand nanoparticle growth processes, shape transformations and nanoparticle assembling, the insight into the “electric soul” of metal nanoparticles is crucial. The insights into the electronic properties and the charge-dependent behaviour of metal nanoparticles will also become very useful for understanding and controlling the interaction of these nanoparticles with each other and with polymers, drugs, biomolecules and cells.

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