

Metal Nanoparticles as Free-Floating Electrodes

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Colloidal metal nanoparticles in an electrolyte environment are not only electrically charged but also electrochemically active objects. They have the typical character of metal electrodes with ongoing charge transfer processes on the metal/liquid interface. This picture is valid for the equilibrium state and also during the formation, growth, aggregation or dissolution of nanoparticles. This behavior can be understood in analogy to macroscopic mixed-electrode systems with a free-floating potential, which is determined by the competition between anodic and cathodic partial processes. In contrast to macroscopic electrodes, the small size of nanoparticles is responsible for significant effects of low numbers of elementary charges and for self-polarization effects as they are known from molecular systems, for example. The electrical properties of nanoparticles can be estimated by basic electrochemical equations. Reconsidering these fundamentals, the assembly behavior, the formation of nonspherical assemblies of nanoparticles and the growth and the corrosion behavior of metal nanoparticles, as well as the formation of core/shell particles, branched structures and particle networks, can be understood. The consequences of electrochemical behavior, charging and self-polarization for particle growth, shape formation and particle/particle interaction are discussed.

Keywords: nanoparticles ; colloidal solutions ; electrical charging ; self-polarization ; mixed-electrode ; particle growth ; particle interaction

Metal nanoparticles have attracted a lot of scientific interest in recent years. The most important practical motivations come from their interesting electronic and optical properties ^{[1][2][3][4]}, their applicability for nanolabeling ^{[5][6]} and sensing ^{[7][8][9][10]} and their catalytic properties ^{[11][12]}. In addition, they are fascinating targets for basic research for understanding the nature of nano-objects and the interaction with biomolecules and living cells ^{[13][14][15][16]} and for designing new materials, as well as micro- and nanosized tools ^{[17][18]}.

An important field of nanoparticle generation and handling is liquid-phase synthesis resulting in colloidal solutions of metal nanoparticles ^{[19][20]}. The existence of nanoparticles in the form of a thermodynamically stable dispersion in a liquid was firstly explained by Michael Faraday about one and a half centuries ago. Already at this time, the importance of the electrical properties of colloidal particles was recognized.

In addition to the presence of an electrical charge on metal nanoparticles, the exchange of charges and the interaction with ions are important for the generation and behavior of metal nanoparticles. Charge transfer processes can include the release of ions from the metal or the conversion of adsorbed metal cations into metal atoms. These processes, as well as oxidation and reduction reactions of other species, can be regarded as local electrochemical processes ^[21]. In the following, important examples of such processes will be regarded and discussed from the point of view of the electrode character of colloidal metal nanoparticles.

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