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REVIEW

Particle-mediated nucleation and growth of solution-synthesized metal nanocrystals: A new story beyond the LaMer curve

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Summary A controlled synthesis of colloidal metal nanocrystals is fundamental in order to optimize the properties of these crystalline materials for a given application. However, there is no systematic review on the mechanisms for controlling the morphology of nanoparticles during the particle-mediated growth, a non-classical growth of colloid nanocrystals. Hence, in this review, we summarize and compare recent studies on the particle-mediated nucleation, growth and overgrowth of colloidal metal nanocrystals synthesized via the non-classical particle-mediated route. The kinetic factors influencing the non-classical growth have been widely studied both experimentally and utilizing theoretical simulations. With the rapid development of in situ characterization techniques, the new crystal growth mechanisms of colloidal metal nanocrystals beyond the LaMer curve have been well uncovered. Up to now, a variety of metal nanostructures with different well-controlled 0-dimensional (0D), 1D, 2D, and 3D morphologies have been prepared via particle-mediated growth, which are highlighted in this review.

Introduction

Metallic materials have continuously attracted the attention of researchers in their ongoing endeavor of improving the performance of materials and to develop new functional applications. Today, however, the exploration of novel properties and the invention of new technological

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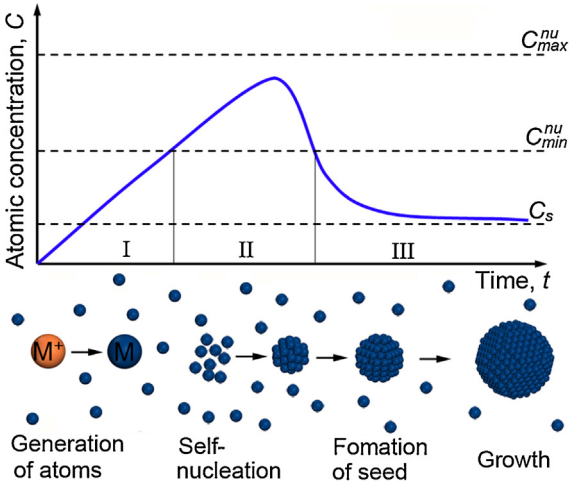

Figure 1 LaMer curve describing three stages of metal nanocrystal formation in solution system. Stage I: atom producing, stage II: nucleation, and stage III: seed formation and growth.
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applications require the construction of metallic materials at the nanometer scale or even on an atomic level with precisely controlled chemical composition, morphology (size and shape), topography and atomic structure (e.g., crystallinity). Among the different methods for a controlled preparation of metal nanoparticles, the chemical synthesis in a solution system is the most intensely studied approach because of its intrinsic advantages, e.g., the easy control, low cost, high yield, narrow size distribution, and the possibility to easily assemble the synthesized nanoparticle into superlattices. In the last 20 years, with the growing ability of scientists to more precisely control the morphology and uniformity of metal nanocrystals, solution synthesis methods have emerged as a powerful approach for the reliable preparation of high-quality metal nanocrystals in quantities suitable for a meaningful study of their shape—property relationships.

For many years, the control of the morphology of colloidal metal nanocrystals has been mainly understood by adopting atom-mediated nucleation and growth theory, in which atoms are the basic building blocks for the nucleation and growth. Such nucleation and growth processes can therefore be described by referring to the evolution of the atomic concentration over time, as illustrated by the so-called LaMer curve, which was firstly established by LaMer and Dinegar [1]. The nucleation and growth process of colloidal metal nanocrystals described by the LaMer curve can be divided into three stages: atom production, nucleation from atoms aggregation, and nanocrystal growth from atoms addition, as illustrated in Fig. 1. In the first stage, metallic atoms are produced either through a reduction of metallic ions with reducing reagents or the thermal decomposition of organometallic compounds. Once the atomic concentration exceeds the point of supersaturation (C_{min}^{nu}), in the second stage, the atoms start to aggregate to form stable small clusters (i.e., nuclei) via self- (or homogeneous) nucleation. Afterwards, the concentration of atoms quickly drops below the minimum supersaturation level (C_{min}^{nu}) and no additional nucleation events will occur. Then, in the third stage, the size of the nuclei gradually increases due to the continuous addition of metal atoms. In this stage, once a cluster has grown past a certain critical size, the activation energy for structural fluctuation will become so high that the cluster eventually becomes locked into a well-defined structure. This critical point marks the birth of a seed [2]. This seed further grows to form the final nanocrystal through the addition of metal atoms until the concentration decreases to C_s (solubility concentration of nanocrystals).

In the past decades, a series of theories have been developed to describe the nucleation and growth of colloidal metal nanocrystals beyond the different stages of the LaMer curve. Because atoms are considered the basic building blocks for the nucleation and growth of nanoparticles in these models, these theories can be classified as atom-mediated nucleation and growth models. For the nucleation stage, several theories such as burst (or homogeneous) nucleation, heterogeneous nucleation, and second nucleation theories have been proposed [3—5]. A variety of processes, e.g., reaction-limited growth, diffusion-limited growth, Ostwald ripening, digestive ripening, Finke—Watzky-type two-step growth, size focusing and defocusing, have been observed to occur during the growth stage [6—12].

Based on these nucleation and growth theories, some mechanisms for controlling the morphology of solution-synthesized metal nanocrystals have been developed. The proposed mechanisms focused on different thermodynamic or kinetic parameters which may change the atomic behavior during the nucleation or growth stages [13]. For example, the shape or morphology of metallic nanocrystals is often related to the intrinsic structure of the nuclei, which can be tuned by changing the thermodynamic or kinetic parameters in the nucleation stage (such as the atomic supersaturation concentration) [2,4,12,13]. In addition, other parameters, e.g., the energy barrier for atom diffusion on the crystal surface, the diffusion route of the atoms in the vicinity of the reaction interface, as well as the surface energy, all significantly affect the growth process of colloidal metal nanocrystals [2,10,12—15].

However, beyond the LaMer curve, many new phenomena have been observed associated with the formation of colloidal metal nanocrystals, which cannot be explained by the theories based on atom-mediated growth. For example, in the nucleation and seed formation stage, the number of small nanoclusters may abruptly decrease with a sudden increase in size [16,17]. In situ observations have shown that small nanoclusters may merge and reshape to form single-crystalline nanoparticles [18,19]. During the growth stage, the nanoparticles may also agglomerate and then grow to form polycrystalline or mesocrystalline mesoparticles [20—23]. Thus, a new nucleation and growth model, in which nanoparticle or cluster is considered as building units for the nanocrystals, has been developed to describe these new phenomena. In order to make a distinction, in this review, the atom-mediated nucleation and growth described by typical LaMer curve is defined as ''classical'' model, and the nucleation and growth considered nanoparticle or cluster as basic building blocks are defined as a ''non-classical''