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Review

Controlled growth of uniform noble metal nanocrystals: Aqueous-based synthesis and some applications in biomedicine

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ABSTRACT

Aqueous-dispersed single and binary noble metal nanocrystals have attracted much attention as key materials in many fields, especially in biomedicine, catalysis, etc. Controlled growth of the metal nuclei allow for the manipulation of uniform morphology of final products. This behavior would tailor their unique physiochemical and electronic properties and follows by their practical applications. This review presents an overall picture of kinetic formation of a particle and then summarizes an overview of recent progress in many research groups concerning aqueous- and/or polyol-based syntheses of many types of aqueous-dispersed single metallic and bimetallic nanocrystals with controlled shape. The main advantages in these synthetic approaches for the shape-controlled metal nanocrystals are simple, versatile, environmentally friendly, low cost, pure and single-crystalline products, and high yield. The formed products can be easily dispersed in water medium and compatible for biotechnological field. Particularly the biomolecule (antibody including protein and/or DNA)-conjugated gold nanocrystals have been utilized as an active agent for a broad range of biomedical applications. We expect that this review will have a high potential towards novel materials fabrication and nanotechnological fields.

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1. Introduction

Single and binary noble metal nanocrystals as a class of novel materials have shown unique physiochemical and electronic properties depending on their size and shape. They are often substantially different from their small molecules, constituents or bulk counterparts and have been extensively investigated due to their fundamental and technological scientific importance [1–3]. The development of the synthetic routes for desired single and binary noble metal nanomaterials has been a great major task for both theoretical studies and practical applications. In the past decades, two broad synthetic strategies "bottom-up" and "top-down" have been devoted to such materials [4]. The nanoscale materials

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synthesized from atomic precursors that aggregate together to form clusters and subsequently nanocrystals are referred to as "bottom-up" synthesis. Conversely, when the nanometer sizes are reached by physically tearing down large building blocks, the process is referred to as "top-down" synthesis. The advantage of the physical top-down method is the production of a large quality of pure nanocrystals, however the synthesis of uniform nanocrystals and their size/shape control are very hard to achieve. "Bottom-up" synthetic route is of primary interest to materials researchers because the fundamental building blocks are atoms; thus colloidal chemical methods can be used to synthesize uniform nanocrystals with controlled particle size and shape. For example, polyol reactions of precursor monomer solution flourished by Xia group are a successful strategy for shape control of a variety of metal nanocrystals [5]. Sau and Rogach [1] provided a review of colloid-chemical synthetic routes and morphology control of nonspherical noble metal nanoparticles. Yang et al. [2] suggested an overall picture of shaped metal nanoparticles in aqueous solution. The author mentioned the key parameters such as crystallographically selective adsorbates and seeding processes that effect on the final shape of products. Niemeyer et al. [6] revealed that the evolutionary optimized biomolecules (e.g., nucleic acid, proteins, etc.) as a capping agent are utilized in the production of metal nanostructures with high potential applications in biomedicine. Accordingly, Jones et al. [7] has carried out the self-assembly of the shape-directed crystallization of DNA-capped metal nanoparticles as building blocks into colloidal ordered superlattices. Wei et al. [8] demonstrated that in the presence of a single lysozyme protein crystal to template the in situ growth of gold nanoparticles slows down the fast kinetics of gold nanoparticle formation. Herein we have focused on the bottom-up strategy including aqueous-based routes often referred to as colloid-chemical approach involving the synthesis of nanoscale particles within a continuous solvent to form a colloidal sol. A wide range of noble single-metallic and bimetallic nanomaterials has been synthesized by these colloid-chemical pathways due to their simple, inexpensive, and versatile means.

Noble metal nanocrystals are probably the most extensively researched nanomaterials and a frequent tool in nanotechnology because of their peculiar electronic and optical properties and useful applications in many fields such as catalysis, optics, sensors, biocompatibility/conjugation with proteins/DNA antibodies, and medical therapy [9–13]. Particularly the Surface Plasmon Resonance features of Au nanocrystals have enabled a wide variety of applications in biomedical researches, such as cancer diagnosis, cancer treatment, drug delivery, and DNA analysis [13]. The antibody-conjugated Au nanoparticles were utilized as "light-activated nanoscopic heaters". In principle, control of the particle shape and size by simply tuning the reaction parameters would allow for the generation of particles with new properties from the same materials. For example, the excellent catalytic performances of 5 nm-sized Au nanoparticles for reduction of nitric oxide and oxidation of carbon monoxide and hydrogen at low temperature were recognized in comparison with bulk gold species [14]. The Pt nanocrystals could selectively catalyze different types of chemical reactions, with {1 0 0} and {2 1 0} facets being most active for reactions involving H_2 and CO, respectively [15]. This behavior is well-established that the catalytic performance of the nanocrystals has a strong correlation with the shape of single-crystalline nanoparticles, depending on the percentage of active facets exposed. In the case of localized Surface Plasmon Resonance (LSPR) and Surface-Enhanced Raman Scattering (SERS), Au and Ag nanocrystals often exhibit unique optical properties in the visible region. Symmetric spherical crystals generally have a single scattering peak, however the rods, triangular prisms, cubes expose more corners/edges as compared with spherical crystals, displayed multiple scattering peaks [16].

Bimetallic (alloy or intermetallic) nanostructures forming from two single components have been drawing much attention because of their superior or tunable properties in comparison with the single-component species [17]. Deciphering the bimetallic structures (core–shell or dumbbell) attributes of these metal–metal interfaces have been proposed to be originated from one or more of three contributions: (i) charge transfer between the metal and support; (ii) presence of low coordinative metal sites; (iii) quantum size effects. These unique combinations of specific properties would make the multi-metal materials to be potentially useful for catalytic, optical, electronic, magnetic, biomedical applications. For example, Pt–Cu alloys displayed composition-dependent electrocatalytic activity for formic acid oxidation [18]. Some reviews mentioning the aqueous-solution approaches for controllable synthesis of uniform bimetallic nanocrystals have been published recently. Wang and Li [19] reviewed the liquid-phase synthesis and catalytic applications of bimetallic nanocrystals. The author indicated that the organic surfactants play several key roles along the course of bimetallic nanocrystal formation. There are mostly three main types of formed bimetallic structures including core/shell, heterostructure, and alloy. In general, two main routes have typically been used for the controlled growth of bimetallic nanocrystals: (i) direct heterogeneous nucleation and growth of the metal precursors onto the surfaces of pre-formed seeds for the generation of core/shell or heterostructures; (ii) alloys are a homogeneous mixture of two metals and generated by formed metal–metal bonds. Xia group also reviewed their published results towards a variety of bimetallic nanocrystals with highly branched morphologies in polyol- and/or aqueous-solution [20]. Such formed branch-shaped nanocrystals definitively based on kinetically controlled overgrowth, aggregation-based growth, heterogeneous seeded growth, selective etching, and template-directed methods. In summary, rational shape-controlled syntheses of single-metallic and bimetallic nanocrystals are of vital importance to understand the growth mechanism and size/shape-dependent properties that are an essential requirement for the practical applications.

In-depth and comprehensive understanding growth behavior and morphology evolution are crucial for efficient synthesis and quality control of inorganic nanocrystals. Among the nanostructures, single-crystalline nanocrystals have received much attention. In principle, the shape of single-crystalline face-centered-cubic metal nanocrystals enclosed completely by equivalent {1 0 0}, {1 1 1}, {1 1 0} facets, corresponding to cube, octahedron, and rhombic dodecahedron, respectively [2]. In bottom-up synthesis, the growth process of nuclei is described by classical Ostwald ripening mechanism, in which the growth of larger particles at the expense of smaller ones is driven by surface energy reduction. This phenomenon is extensively used to explain the formation of thermodynamically stable nanocrystals with nearly spherical morphologies. For the controlled self-assembly of nanoparticles into well-defined anisotropic nanostructures, organic capping reagents usually play critical roles in reducing the activity of the nanocrystal surface to promote or tune the ordered self-assembly. An oriented attachment mechanism could offer as an additional tool to design advanced materials with anisotropic properties and could be used for the controllable synthesis of more complex crystalline one-dimensional structures. In addition, the sterically diffusive kinetics and selective binding or nonbinding of surfactant molecules to different faces of the growing nanocrystal can also control the product's morphology due to the possibility of breaking the limitations of crystal growth dynamically [21–23]. In some cases, the formation of intrinsic anisotropic nanocrystals is found to be a highly kinetics-driven process, which occurs far away from the thermodynamic equilibrium, and must be overdriven by high precursor monomer concentrations [24].