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Magnetic field controlled particle-mediated growth inducing icker-like silver architectures

Yunxia Zhang, Shaodong Sun, Xiaozhe Zhang, Linli Tang, Xiaoping Song, Bingjun Ding, Zhimao Yang *

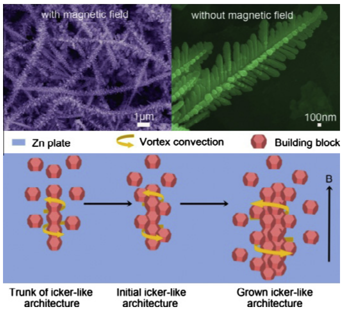
State Key Laboratory for Mechanical Behavior of Materials, MOE Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, People's Republic of China

HIGHLIGHTS

- Silver icker-like architectures were grown via a modified replacement reaction.
- The products occupied long trunks and short branches rather than dendrites.
- Magnetic field effects were extremely crucial to silver crystal growth.
- Silver crystals were grown by a multistep particle-mediated growth process.
- A proposed formation mechanism reasonably explained the unusual growth.

GRAPHICAL ABSTRACT

Long silver icker-like architectures have been artificially and successfully achieved through a simple and economical electroless deposition process assisted by an external magnetic field. The morphologies and crystal growth habits of the silver products could be controllably tuned through altering the reaction time and solution concentration under the external magnetic field. A credible formation mechanism has been proposed on the basis of the diffusion-limited aggregation (DLA) model, shape magnetic anisotropy and fast complex micro-magnetohydrodynamic (MHD) convection effects induced by the external magnetic field for the nanoparticles possessing a truncated octahedron structure. The results indicate that metal crystals are grown by a multistep particle-mediated growth process with the nanoparticles as basic building blocks, which is absolutely different from the previous researches generally involving the ion-mediated growth process or the aggregations of numerous nanoparticles along the magnetic field directions because of dipolar interactions. Moreover, such silver icker-like architectures may be promising candidates for a broad range of applications related to optics, catalysis and biomedicine.



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ABSTRACT

An unusually anisotropic growth or quasi-one-dimension growth of silver architectures can be achieved when an external magnetic field is applied to a simple replacement reaction. The external magnetic field greatly promotes the growth of trunks along ⟨1 1 1⟩ directions but weakens the growth of branches along ⟨3 1 1⟩ directions, resulting in a silver icker-like architectures. The influences of the external magnetic field, solution concentration and reaction time have been investigated in detail. The formation of silver icker-like architectures could be attributed to shape magnetic anisotropy and fast complex micro-magnetohydrodynamic (MHD) convection effects induced by the external magnetic field of the nanoparticles possessing a truncated octahedron structure. Moreover, the magnetic field effect on the crystal growth of nanostructures generally involves the ion-mediated growth process or the aggregations of numerous nanoparticles along the magnetic field directions because of dipolar interactions. Our experiments and

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* Corresponding author. Address: Xi'an Jiaotong University, No. 28, Xianning West Road, Xi'an, Shaanxi 710049, People's Republic of China. Tel./fax: +86 2982665995.
E-mail address: zmyang@mail.xjtu.edu.cn (Z. Yang).

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discussions, however, indicate that metal crystals are grown through a multistep particle-mediated growth process with the nanoparticles as basic building blocks.

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1. Introduction

Crystal growth is at the heart of various research fields ranging from collochemistry, materials, semiconductor device and surface chemical physics to quantitative analysis of molecular-level DNA [1–6]. It is fundamentally significant to understand the original processes of crystal formation for precisely controlling the crystal growth activities. Classically, growth of crystals has been regarded as an ion-mediated growth via atom-by-atom or monomer-by-monomer addition to an inorganic or organic template or by dissolution of unstable phases (small particles or metastable polymorphs) and reprecipitation of the more stable phase [7]. While, the non-classically particle-mediated growth involves the mesoscopic transformation of self-assembled, metastable or amorphous precursor particles into nanoparticulate architectures [8,9]. The primary nanoparticles can assemble to an iso-oriented crystal via oriented attachment (OA) forming a single crystal upon fusion of the nanoparticles, or a mesocrystal via mesoscale assembly [9]. Those above two crystal growth models have worked particularly well in materials science for the anisotropic growth of diverse nanocrystals [10].

The size, shape, structure and crystal growth of a material can be considerably manipulated in a controllable fashion by external stimuli, such as stress, temperature, pH, electric or magnetic field [11–15]. Among the above external stimuli, the external magnetic field has attracted tremendous attention because of its remarkable role in the anisotropic growth of metal nanostructured materials such as nickel dendritic crystals [16], magnetic chains of cobalt spheres [17], dense vortex of silver dendrites [18] and protein crystals [19,20] and so forth. In fact, the magnetic field has been introduced as an efficient tool to influence the crystal growths of materials in past decades [21–24], for example, an external magnetic field could act on the growth and assembly behavior of magnetic cobalt nanocrystallites [25] and $\langle 110 \rangle$-oriented Fe_3O_4 [26] nanowires, respectively. The magnetic-field-induced nucleation and growth self-assembly process could also produce large maghemite nanocube superlattices with a high degree of crystallographic orientational order [27]. Moreover, the magnetic field effect on crystal growth is one of the current topics in basic and applied chemistry [28–30]. Recently, the crystal lattice of Co_3O_4 nanocubes has been influenced by the alignment of spins in the Co_3O_4 particles induced by an external magnetic field [31]. The external magnetic field is not only important for the oriented aggregations of silver-embedded magnetic nanoparticles [32] but also significant for the growth and assembly of Ni nanoparticles [33]. Additionally, Numoto et al. [34] have achieved the observation of the orientation of membrane protein crystals grown in high magnetic force fields. However, most of those previous researches into the magnetic field effect on crystal growth of nanostructures only involve the ion-mediated growth process by atom/molecular addition where soluble species deposit on the solid surface [7] or the nanoparticles just assemble to form linear chains by dipolar interaction along the magnetic line of force under the attraction of an external magnetic field. So far, little attention has been paid to the particle-mediated growth process dominated by an external magnetic field during the chemical reactions in solution. Furthermore, most of the ingredients used in previous protocols have involved magnetic materials (Ni, Co and Fe), thus a small external magnetic field could be effective to the chemical reaction processes. Although a relative higher (>1 T) magnetic field has been further confirmed to also work for nonmagnetic materials or feeble magnetic materials (for example silver) [18,21,35], it is still a large challenge to gain the underlying growth mechanism and effects of an external magnetic field during the reaction process.

Herein, we find that magnetic field also has exceedingly important effect on the non-classically particle-mediated growth of silver icker-like architectures during the replacement reactions. The growth process of the silver icker-like architectures is composed of three steps: (1) individual atoms aggregate locally to form nanoparticles through a fast process; (2) magnetic field induce the self-assembly of nanoparticles along the magnetic field directions to form the silver trunk; (3) simultaneously, induced magnetic vortex convections around the silver trunk will promote spiral growth of the silver icker-like architectures. Combining the results of experimental observations and discussions of the magnetic field effect, we propose a detailed mechanism which could reasonably explain the self-organization of nanoparticles during the particle-mediated growth of silver icker-like architectures in this reaction system. Furthermore, the formation of silver icker-like architectures demonstrates that the external magnetic field effect can greatly promote the growth rate of trunks but weaken the growth rate of branches of silver dendrites, resulting in the extremely long $\langle 111 \rangle$-oriented trunks and quite short $\langle 311 \rangle$-oriented branches. This unusual anisotropic growth or quasi-one-dimension growth of silver architectures induced by the external magnetic field is absolutely different from the $\langle 211 \rangle$-oriented silver dendrites obtained in the absence of an external magnetic field under otherwise the same conditions. Thus, an external magnetic field has not only changed the growth habit of the silver products, but also made the purposive design of spatial arrangement possible. Moreover, such silver icker-like architectures may be promising candidates for a broad range of applications related to optics, catalysis and biomedicine.

2. Experimental section

2.1. Synthesis

All the chemicals were of analytical grade and used as purchased without further purification. Only three ingredients were required in this protocol: commercial zinc plates (99.99%), silver nitrate and deionized water. Specifically, all Zn plates were first treated with the deionized water and dilute hydrochloric acid to remove the surface contamination, and then rinsed with deionized water and alcohol. The $AgNO_3$ (aq.) with a certain Ag^+ concentration was prepared using an analytically pure $AgNO_3$ reagent. The Zn plate was immersed in the container with some $AgNO_3$ solution. The external magnetic field was applied by an electromagnet field control platform (Fig. S1(a) provided in Supplementary materials, EMP-7, available at East Changing Technologies (ECT) in Beijing). The crucial components were the two parallel truncated cone-shape electromagnets whose top diameter was 76 mm (Fig. S1(b)). When the distance between the two electromagnets was 20 mm, the magnetic field in the center could be up to 2.3 T, and the magnetic field would practically decrease along the z axis at a pace of 2.3×10^{-4} T/mm from the center to the two sides. Meanwhile, the experimental unit with a horizontal width of about 10 mm was put in the center of the two electromagnets. Then, the external magnetic field on either boundary of the experimental unit could still be 2.29885 T. Therefore, the applied external

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