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An Unusual Example of Hyperbranched Metal Nanocrystals and Their Shape Evolution

Xiong Wen Lou, Chongli Yuan, and Lynden A. Archer*

School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853-5201

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Noble metal (Au, Ag, Pt, Pd) nanoparticles have recently attracted intensive research interest because of their important applications in catalysis, biological labeling, optics, and data storage.[1−13] As a result, many methods have been developed for synthesis of metal nanoparticles in a wide range of nonspherical shapes, including wires/rods,[3] disks,[4] sheets/plates,[5] cubes,[6] prisms,[7] hollow structures,[8] and platonic nanocrystals.[9] Most recently, Xia's group reported the first synthesis of silver right bipyramids.[16] Although thousands of papers have been published describing synthesis of noble metal nanocrystals with the aforementioned shapes, synthesis of branched metal nanocrystals still remains very limited. Unlike semiconductor materials (e.g., CdS, CdSe),[10] for which branched nanostructures such as well-defined tetrapods can be synthesized employing intrinsic crystal polymorphisms (e.g., zinc blende and wurtzite type), branched metal nanostructures have only recently been reported for gold,[11] platinum,[12] and rhodium[13a] probably because of the fact that most noble metals have highly symmetric face-centered cubic (fcc) crystal structures. In all syntheses of branched metal nanostructures, a surfactant (e.g., cetyltrimethylammonium bromide) is required as a shape-directing agent by preferential adsorbing on specific crystal planes. The branched metal nanocrystals are, therefore, largely derived from the intrinsic crystal structures.[11,12] Branched metal nanostructures have also been fabricated by employing branched DNA scaffolds.[13b−d] We have previously fabricated single-crystalline four-armed α-MoO_3 nanostructures through artificially manipulating crystal growth directions.[17] In this communication, we report the first example of hyperbranched metal nanocrystals prepared in aqueous solution at room temperature without using surfactant. Remarkably, the branch growth is believed to be kinetically controlled, and the growth directions are nonspecific. These nanocrystals serve as the metastable intermediate species toward final quasi-spherical or disklike nanoparticles.

In a typical synthesis, 0.2 mL of 20 mM $AgNO_3$ is added to 2 mL of deionized water, under vigorous magnetic stirring (∼1500 rpm), followed by 0.05−0.4 mL of freshly prepared trisodium citrate solution (100 mM) and 0.3−1.2 mL of L-ascorbic acid (40 mM), consecutively. The color of the solution progresses from colorless to light gray (within 30 s) to dark gray within a few hours, to yellowish within days after the reaction is initiated.

Figure 1A displays a transmission electron microscopy (TEM) micrograph of the hyperbranched silver nanocrystals. It is apparent that the as-prepared structures have relatively uniform overall size, approximately 400 nm including a 200 nm body and 100 nm arms. The bodies have a very dark contrast, indicating rich three-dimensional (3D) structures,[14] which are likely formed by self-organizing two-dimensional (2D) gearlike nanocrystals via two modes: flat attachment (Figure 1B, inset) and crossover (Figure 1B; more field-emission scanning electron microscopy (FESEM) images in Supporting Information, SI-4). Indeed, many free-standing 2D flat gearlike nanocrystals (Figure 1C) were also observed with a thickness of about 20 nm estimated from high-magnification scanning electron microscopy (SEM) images (e.g., Figure 1B). Figure 1D shows a two-layer gearlike flat nanocrystal, and its corresponding electron diffraction (ED) pattern (Figure 1E) clearly shows superposition of two sets of slightly mismatched spots (the enlarged images are given

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* Corresponding author. E-mail: laa25@cornell.edu.

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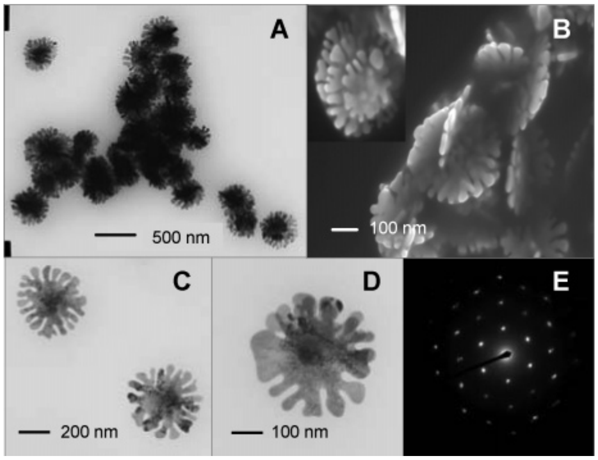

Figure 1. TEM images (A, C, D) and a SEM image (B) of hyperbranched silver nanostructures (0.2 mL of trisodium citrate, 0.6 mL of L-ascorbic acid, 3 h). (C) 2D flat nanocrystals; (D) a two-layer structure; and (E) the corresponding ED pattern (ED was taken focusing the whole crystal).

in Supporting Information, SI-3). From the ED analysis (ED patterns taken by focusing on the whole crystal), it is concluded that the 2D nanostructures are single-crystal and lie flat on their (111) planes and that the arms could grow in any radial direction. This feature is very different from branched Au nanocrystals where the branches only grow along specific directions.[11] High-resolution TEM analysis is clearly the most effective method for evaluating this claim. However, all attempts to obtain suitable lattice images have proven unsuccessful because of the instability of the Ag crystal lattice under the high-energy electron beam irradiation (FEI Tecnai G20, 200 kV). Nevertheless, the crystal structure of these branched Ag nanostructures can also be examined in detail using selected area electron diffraction (SAED). SAED patterns are summarized in Figure 2A. It is apparent from this figure that patterns taken from multiple locations on a branched Ag nanostructure are essentially identical, indicative of its single-crystalline character. The crystal structure was also characterized by X-ray powder diffraction (XRD, see Supporting Information, SI-5). All four peaks can be assigned undisputedly to (111), (200), (220), and (311) planes of fcc silver (JCPDS card no. 04-0783; space group, *Fm*3*m*), respectively.[6] The elemental composition was confirmed by energy-dispersive X-ray (EDX) microanalysis at the single-nanocrystal level, shown in Figure 2B.[18]

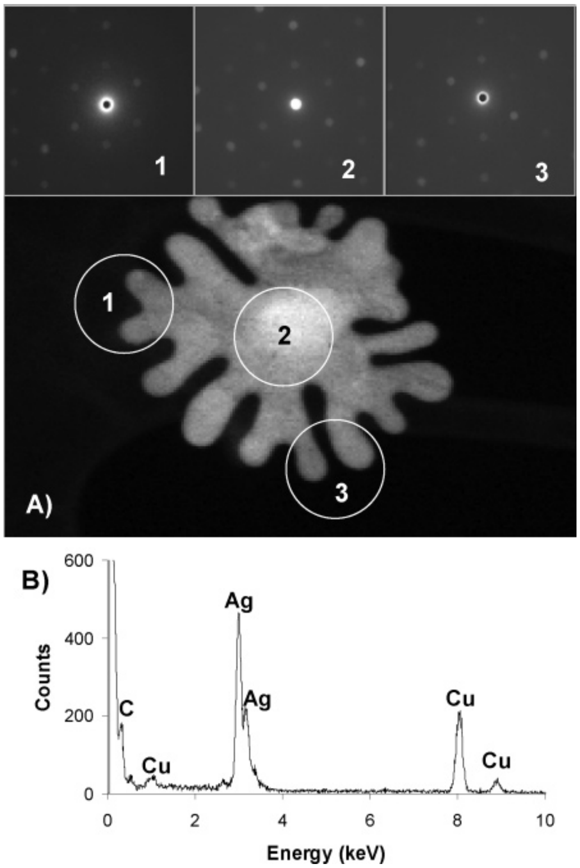

Figure 2. (A) Dark-field TEM image with insets 1−3 being SAED patterns from selected areas indicated by white cycles in the TEM image; (B) EDX spectrum of a single Ag nanocrystal, where the signals of Cu and C are generated from the Cu grid and carbon support film, respectively.

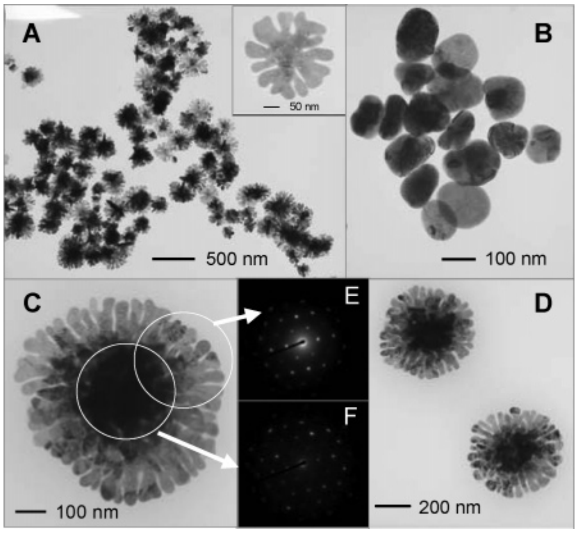

Figure 3. TEM images of silver nanocrystals (0.1 of mL trisodium citrate, 0.3 mL of L-ascorbic acid, 30 min of seeding, and 30 min of reaction; A), where the inset shows a high-magnification 2D structure; (B) nanoparticles corresponding to A with a few days of reaction; (C) same conditions with A but without seeding, where E and F are the corresponding ED patterns for the selected area in C; and (D) same conditions with C but with 0.6 mL of L-ascorbic acid.

The effect of the "seeding" period t_s (i.e., the stirring time after adding trisodium citrate and before adding L-ascorbic acid) was also studied. In general, larger t_s results in smaller size and larger fraction of 2D nanocrystals. As shown in Figure 3A ($t_s \approx 30$ min), the nanocrystals have average sizes of about 300 nm only, and a relatively large fraction of particles have light and uniform contrast corresponding to 2D nanogears (see Figure 3A, inset). In comparison, nonseeded preparations resulted in an average size of about 600−700 nm and densely packed arms (Figure 3C). Even for 3D hyperbranched structures with densely packed arms, the SAED pattern (Figure 3E) indicates that the arms have essentially the same crystal orientation, while the SAED pattern from the dark center region shows less orientation (Figure 3F). The size of the nanocrystals can also be effectively controlled by increasing the concentration of L-ascorbic acid and/or trisodium citrate. As an example, by

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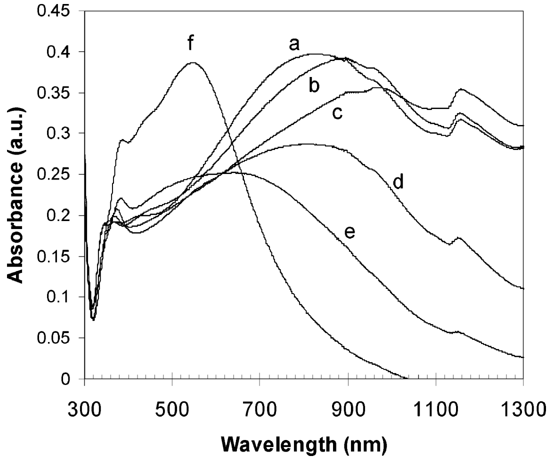

Figure 4. UV−vis−NIR spectra of silver nanostructures corresponding to the same conditions as those in Figure 3A at different times: (a) 2 min; (b) 10 min; (c) 1 h; (d) 6 h; (e) 22 h; and (f) 2 days.

simply increasing the L-ascorbic acid to 0.6 mL, the average size reduces to about 400−500 nm (Figure 3D).

Spontaneous formation of hyperbranched anisotropic silver nanostructures in solution is rather unexpected because silver itself has a highly symmetric fcc crystal structure and the synthesis is carried out in an "isotropic" aqueous medium.[11e] We believe that these structures are most likely the result of kinetically controlled growth.[11a,12] Indeed, these hyperbranched structures are thermodynamically unfavorable and evolve to stable regular shapes via Ostwald ripening. To rule out the possibility of continuous deposition of unreacted silver ions on preformed branched silver nanostructures, we measured the concentration of silver ions in the supernatants by inductively coupled plasma. It is found that virtually all silver ions are reduced after 30 min of reaction ($[Ag^+] \approx 0.4$ ppm vs the original $[Ag^+] \approx 200$ ppm). Figure 3B shows the quasi-spherical or disklike nanoparticles harvested after several days of reaction. Note that the average size of the nanoparticles is similar to that of bodies of hyperbranched nanocrystals (Figure 3A). Interestingly, similar shape evolution was also observed for dry samples kept on the TEM grid, but the latter process is about 10−50 times slower.

The process of shape evolution was further monitored by ultraviolet−visible−near-infrared (UV−vis−NIR) spectra. Interestingly, the UV−vis−NIR spectrum of these hyperbranched silver nanocrystals is similar to the one from silver bipyramids.[16] As shown in Figure 4, all the spectra have two peaks in common located at 330−380 nm and 1160−1170 nm. The peak at short wavelength may be attributed to the out-of-plane quadrupole.[15] The peak in the NIR region (~1165 nm) might arise from the in-plane dipole resonance mode associated with silver nanoplates whose edge lengths exceeded 100 nm.[7] It might also be attributed to the strong coupling of anisotropic arms. The peak at longer wavelength (1190 nm) has been reported for a mixture of silver nanobelts and triangular nanoplates.[7a] The hyperbranched silver nanocrystals also exhibit a broad peak around 800−940 nm attributed to in-plane dipole plasmon resonance.[15] Following the shape evolution, this peak first red-shifts from 800 to 940 nm (Figure 4a−c) within a few hours associated with anisotropic growth, then gradually blue-shifts to around 600 nm (Figure 4d,e) in about 1 day indicating gradual disappearance of the anisotropic shape (see TEM images in Supporting Information, SI-1).[15b] Finally, there arises a strong and narrow peak located around 450−550 nm (Figure 4f) corresponding to quasi-spherical or disklike silver nanoparticles (see Figure 3B).[4]

At present, the precise growth mechanism is not fully understood. Control experiments with citrate or L-ascorbic acid alone do not produce hyperbranched nanocrystals (see Supporting Information, SI-2). We, therefore, suspect that citrate and L-ascorbic acid play complementary roles in the synthesis: the former acting as a shape-directing agent and the latter as a reducing agent. This view is consistent with work by Mirkin and co-workers showing that citrate can be used as a shape-directing agent to prepare Ag nanoprisms.[7b−d] Exactly how and why citrate plays this role is an open question. One possibility is that the slow-reacting citrate adsorbs preferentially on Ag(111) planes, defining preferred directions for further crystal growth. Specifically, during the earliest stages of the reaction we believe L-ascorbic acid rapidly reduces the silver nitrate precursor to yield disklike (or possibly nanoprism) Ag bodies sandwiched between citrate ions, which is then followed by branch growth in the radial directions. Thus, the branch formation process appears to have nothing to do with the intrinsic crystal structure of Ag but seems to originate from competing (dissimilar) reduction reaction kinetics of ascorbic acid and citrate. Clearly more detailed work is needed to evaluate this mechanism and to determine if it can be extended to synthesize hyperbranched nanocrystals for other noble metal systems.

In conclusion, hyperbranched silver nanocrystals have been successfully arrested in aqueous solution at room temperature. These structures are shown to exist either as 2D gearlike or self-organized 3D objects. We propose that even in the absence of an explicit structure-directing agent, dissimilar reaction kinetics of trisodium citrate and L-ascorbic acid leads to formation of hyperbranched metal nanocrystals.

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Supporting Information Available: TEM images, FESEM images, and XRD patterns (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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