Nanocrystals Hot Paper

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Metal Dendrimers: Synthesis of Hierarchically Stellated Nanocrystals by Sequential Seed-Directed Overgrowth**

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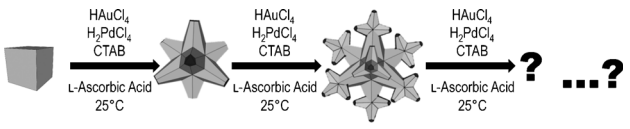
Abstract: *Hierarchically organized structures are prevalent in nature, where such features account for the adhesion properties of gecko feet and the brilliant color variation of butterfly wings. Achieving artificial structures with multiscale features is of interest for metamaterials and biomimetic applications. However, the fabrication of such structures relies heavily on lithographic approaches, although self-assembly routes to superstructures are promising. Sequential seed-directed overgrowth is now demonstrated as a route to metal dendrimers, which are hierarchically branched nanocrystals (NCs) with a three-dimensional order analogous to that of molecular dendrimers. This method was applied to a model Au/Pd NC system; in general, the principle of sequential seed-directed overgrowth should enable the synthesis of new hierarchical inorganic structures with high symmetry.*

Branched metal nanocrystals (NCs) are of interest because of their structure-dependent light-scattering and absorption properties and their utility in plasmon-enhanced surface spectroscopies and catalytic processes.[1–3] The synthesis of symmetrically branched metal NCs was recently achieved with seed-mediated methods, where the symmetry of the seeds directs the symmetry of the final stellated NCs.[4–6] Structures with hierarchical features have also been synthesized.[7–10] However, routes to hierarchically branched NCs are often haphazard or yield structures with inhomogeneous and asymmetric branching patterns.[3,11] Inspired by the uniformity in organic dendrimers where molecular connectivity provides symmetry control,[12] we report a similar level of structural control in an inorganic NC system where the benefits of organic synthesis cannot be exploited. This goal was achieved by using principles of seed-mediated methods.

"Dendrimer-like" branched nanoparticles have been reported,[13–16] but these particles are not characterized with the branching symmetry of organic dendrimers. Our method provides an inorganic analogue by using shape-controlled seeds to determine the branching symmetry, which is preserved in each subsequent generation of branching. There are three primary requirements for the synthesis of organic dendrimers: 1) the selection of a reactive initiator that indicates growth direction, 2) an iterative reaction sequence with branching at specific sites, and 3) reactive chain growth with concentric branching.[12] These requirements are paralleled in our inorganic NC system by 1) the selection of shape-controlled NC seeds to template branch-growth direction, 2) the sequential use of seed-mediated co-reduction to control where branched growth is initiated, and 3) concentric overgrowth of Au/Pd branches onto previously formed branch tips.

Seed-mediated co-reduction is central to the synthesis of metal dendrimers as seed symmetry dictates the final hierarchical structure and symmetry. Furthermore, the co-reduction process functions as a robust route to symmetrically branched NCs. As originally demonstrated in a model Au/Pd system, Au and Pd precursors are simultaneously reduced to deposit metal onto shape-controlled Au or Pd seeds to achieve symmetrically branched Au/Pd NCs.[17] The reactive initiator is the shape-controlled NC seed, where branched growth is initiated at the vertices of the seeds and continues in the ⟨111⟩ directions.[17] For example, NCs with eight branches and O_h symmetry can be produced from nanocubes.[4] Just as with the growth of organic dendrimers from an initiator, the resulting product should have the capability to initiate a subsequent generation (G_n) of growth. That is, the resulting product now serves as a seed to initiate the next generation of metal branches, which grow concentrically from the previously formed structure. In our system, the new branches initiate from the branch tips of the previous generation. Conceptually, this process can be repeated any number of times. This idea is illustrated in Scheme 1 and parallels the synthesis of organic dendrimers.

To demonstrate the possibility to synthesize metal dendrimers, octahedral Au seeds (which adopt cubic shapes prior to branch initiation) were used as the initiator (I). Different generations of metal dendrimers are shown in Figure 1. A scanning electron microscopy (SEM) image of the NC seeds is shown in Figure 1a (top), along with a SEM image of the



Scheme 1. General seed-mediated co-reduction approach to synthesize Au/Pd dendrimers. The ratio of the Au and Pd precursors was held constant at 5:1.

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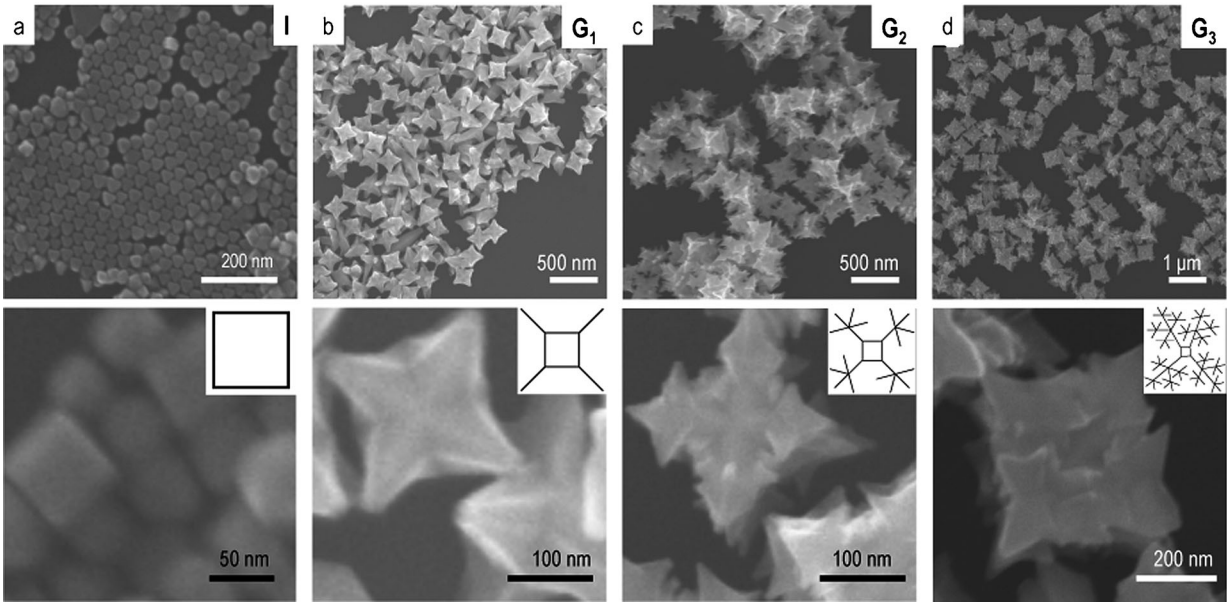

Figure 1. Low- (top) and high-magnification (bottom) SEM images and corresponding two-dimensional stick models of a) initiator seeds, b) G_1 NCs, c) G_2 NCs, and d) G_3 NCs. The bottom part in (a) shows the cubic intermediate that is formed when the seeds adopt a new shape prior to branched overgrowth. The two-dimensional stick models are simplified views down the center of the particle oriented along the (100) plane to further demonstrate the large number of branches from each vertex. Only one half of the branches are shown in the two-dimensional models. Branch lengths and angles are not to scale.

cubic intermediate with a 2D projected stick model of the core (bottom). Co-reduction of the Au and Pd precursors results in NCs with eight branches, so called octopods. These particles (G_1) have O_h symmetry; their SEM images are shown in Figure 1b (please note that many particles are oriented in such a way that only four branches are visible). First, mainly Au is deposited onto the seeds, with a Pd-rich bimetallic phase localized on the exteriors of the particles and at the branch tips.[4] After purification, co-reduction to deposit additional metal onto these branched seeds results in additional branched growth off of the tips of each G_1 branch (Figure 1c). Under kinetic control, branched growth is initiated at the tips owing to the lower coordination numbers at the branch tips, whose sites are thus of higher energy.[17,18] A SEM tilt study revealed that four G_2 branches grow from one G_1 branch of an octopod, which leads to a total of thirty-two branches assuming that four branches grow from each of the eight G_1 branches (Figure 2). One branch continues in the direction of the original G_1 branch, with three new branches in the ⟨111⟩ directions. In these NCs, the O_h symmetry of both the G_1 and I seeds has been conserved, although some minor protrusions from the branches were observed, which can be considered as slight deviations from the ideal dendrimer structure.

Scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDS) of a G_2 dendrimer confirmed that the interior of the particle is Au-rich, with a Pd-rich phase on the exterior and at the branch tips (Figure 3a–d). The distribution of the two metals is similar to that in the G_1 dendrimers.[19] Electron diffraction confirmed that the particles are single-crystalline (Figure 3e,f). When the nanocrystals were oriented along the [100] zone axis, electron diffraction indicated that branches

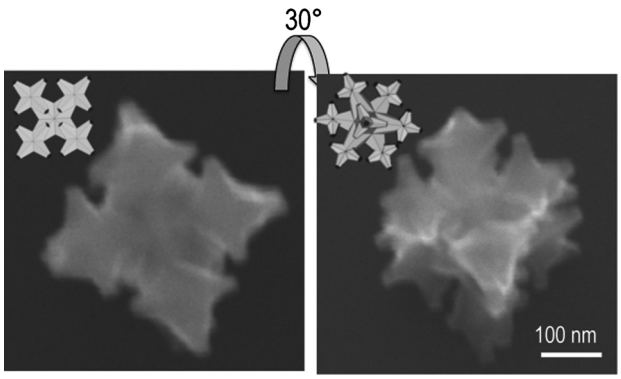

Figure 2. SEM tilt study of G_2 NCs built from octopods.

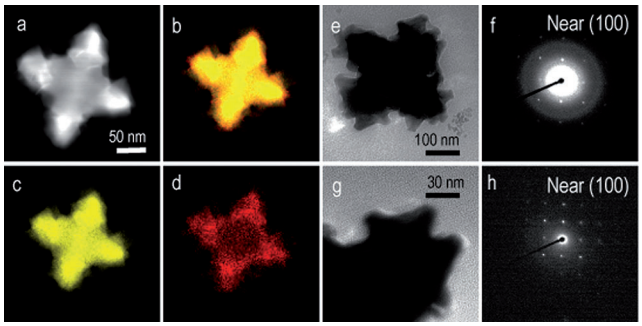

Figure 3. G_2 NCs built from Au/Pd octopods. a) STEM image of an individual G_2 NC. b) STEM-EDX elemental mapping of the G_2 NCs shown as an overlay of the Au and Pd signals, which are shown separately in (c) and (d); gold yellow, palladium red. e) TEM image and f) corresponding electron diffraction pattern through the center of the particle. g) TEM image and h) corresponding electron diffraction pattern through the upper right set of branches.

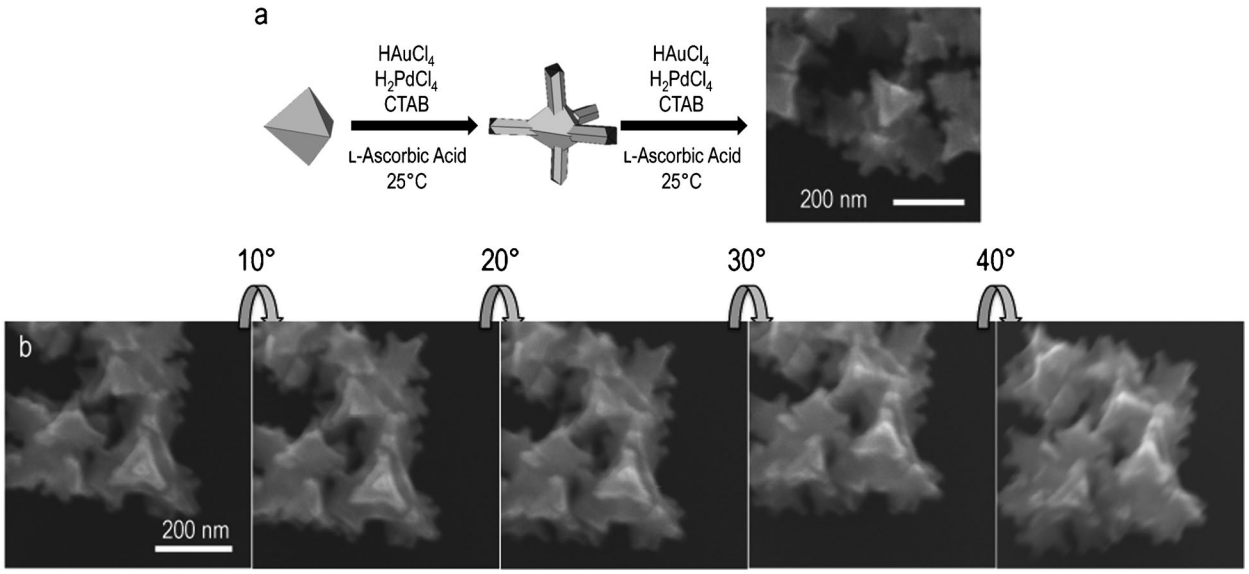

Figure 4. a) Co-reduction of Au and Pd precursors onto Au right bipyramids. A SEM image shows the morphology of the final branched structure. b) SEM tilt study of G_2 NCs built from pentapods.

grow in the ⟨111⟩ directions, which is the same as for the G_1 NCs (Figure 3g,h). As G_1 NCs are single-crystalline as well, this result confirms that both an iterative reaction sequence and reactive chain growth are achieved with this approach.

Interestingly, the characterization of an impurity within this sample highlights the possibility to achieve metal dendrimers with different branching symmetries and the generality of sequential seed-directed overgrowth as a route to hierarchically branched NCs. In particular, Au right bipyramids are a common impurity in the synthesis of Au octahedra.[5] After one round of seed-mediated co-reduction, Au/Pd pentapods (with five branches) with D_{3h} symmetry were obtained by overgrowth from each vertex.[5] These pentapods have two axial and three equatorial branches with the twin plane from the seed extending through the equatorial branches (Figure 4a). Further analysis of this phenomenon was previously provided by DeSantis and Skrabalak.[5] A SEM tilt study of a G_2 dendrimer NC built from a G_1 Au/Pd pentapod seed showed that four branches grow from each axial branch (Figure 4b). These branches grow in similar directions as they did for NCs with octopod G_1 seeds; one branch extends from the original G_1 branch, and three branches grow in the ⟨111⟩ directions. However, owing to the twinned nature of the equatorial branches, symmetry assignment is difficult at those positions although a minimum of six branches ordered around each equatorial vertex is evident. This result highlights that this approach can work for different initiators to achieve hierarchically branched NCs with different symmetries.

After collection of G_2 dendrimers with 32 branches (Figure 1c, see the Experimental Section), excess reagents were removed, and the seed-mediated co-reduction process was repeated again to produce G_3 dendrimers. Structural characterization by SEM indicated that four branches grew from each of the tips of the G_2 branches. Assuming that all of the tips provided similar overgrowth, NCs with 128 branches were obtained (Figure 1d). Overall, the G_3 NCs appeared to be relatively monodisperse; O_h symmetry was maintained although the defined protrusions have led to some reduction in symmetry owing to the larger seed size and a decrease in local branch uniformity with each subsequent generation. In contrast to organic dendrimers, where infinite branches are theoretically possible, in this system, each subsequent generation has smaller branches. Therefore, after the G_3 stage, branches are too small to be characterized. STEM-EDX mapping showed that Au is localized predominately in the interior of the particle (Supporting Information, Figure S1). A Pd-rich phase is dispersed on the outside owing to additional Au/Pd branches growing off the Pd-rich tips of the G_2 NCs. By symmetry arguments and previous growth patterns, branches likely grow in the ⟨111⟩ directions; however, owing to the large size of the NCs, electron diffraction studies were not possible. Thus, this data indicates that the Au and Pd deposition pattern is similar to that of the G_1 and G_2 NCs, with the underlying symmetry being transferred through the concentric branching process.

The number of branches formed during each generation step can be calculated using a variation of the exponential calculation used for predicting the number of terminal groups in an organic dendrimer system [Eq. (1)]:[20]

$$n_g = f_k\,(f_v)^{G-1} \tag{1}$$

where n_g represents the number of branches in the gth generation, f_k is the functionality of the core (number of vertices), and f_v is the functionality of the branching unit (i.e., the number of branches at each nucleation site).[20]

The equation was modified for the metal dendrimer system because at G_1, only one branch grows from each vertex, and subsequently, four additional branches are formed at each vertex during each new generation step. Previously, we found that at the vertices of a Pd octahedral seed, four

branches grow in the ⟨111⟩ directions.[5] During the second generation, four branches grow because the branches are octahedron-like.[19] Thus, the G_2 NCs grow similarly to branches off an octahedral seed. Notably, at G_0/I, no branches exist on the core, even though there are eight vertices (nucleation sites). From Eq. 1, the exponential relationship between the number of branches from each branch can be exploited to predict the number of branches at a given generation. In our system, using a Au octahedron, which is reshaped to a Au cube during overgrowth, as the seed, $f_k = 8$ because of its eight vertices; however, the value of f_v depends on the generation step. In G_1, only one branch grows at each site, therefore $f_v = 1$, whereas further generations yield four branches at each branching site. For right-bipyramidal seeds, this equation does not hold for generations past G_1 on account of the twinned seed.

Implementing the rules of dendrimer growth and design, metallic dendrimer NCs have been obtained by sequential seed-directed overgrowth. By manipulating the seed shape, the number of branches is readily controlled. By repeating the seed-mediated co-reduction process, iterative chain growth with concentric branching is possible. Through the introduction of a twin plane in the seeds, we were able to access hierarchically branched NCs beyond the traditional molecular connectivity of organic dendrimers. Unique branching symmetries are thus accessible. Using these rules and parameters, the design of bimetallic hierarchically stellated NCs with high surface areas and symmetry has been achieved. This approach could be applied to other systems with different seed shapes and compositions.[5]

Experimental Section

Chemicals: L-Ascorbic acid ($C_6H_8O_6$, L-AA, 99%), $PdCl_2$ (99.98%), chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 99.9%), cetyltrimethylammonium bromide (CTAB, 98%, LOT No. BCBK3869V), and trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, ≥99%) were purchased from Sigma. Concentrated hydrochloric acid (HCl, 12.1M) was purchased from Mallinckrodt. Nanopure water (18.2 MΩcm) was used in all experiments. An aqueous H_2PdCl_4 solution (10 mM) was prepared by stirring $PdCl_2$ (44.6 mg) in 25 mL of HCl (pH 1.69) for one hour while heating at approximately 70°C.

The method for the synthesis of octahedral Au seeds was adapted from a literature procedure.[21] CTAB (1.5 mL, 0.1M) was diluted with nanopure water (8.2 mL). Next, $HAuCl_4 \cdot 3H_2O$ (250 μL, 0.01M) and trisodium citrate (50 μL) were added to the vial. The reaction vial was capped and allowed to sit undisturbed in a 110°C oil bath for six hours. Particles were collected by centrifugation for 30 minutes at 3900 rpm and diluted with water to a total volume of 3 mL.

The method for seed-mediated co-reduction was adapted from a literature procedure.[17] For nanocrystal growth, CTAB solution (2 mL, 0.2M) was added to a reaction vial. Next, H_2PdCl_4 solution (0.1 mL, 10 mM) and $HAuCl_4 \cdot 3H_2O$ solution (0.05 mL, 0.1M) were added followed by an L-AA solution (1.5 mL, 0.1M). Then, water (21.4 mL) was added, followed by 1 mL of the seed solution. These reaction vials were gently shaken, then capped, and allowed to sit undisturbed in a 25°C oil bath for two hours. Particles were collected by centrifugation for 30 minutes at 3900 rpm and diluted with water to a total volume of 3 mL. For successive generations, after centrifugation, the process was repeated using 1 mL of the solution containing previously synthesized branched nanocrystals as the seeds. A discussion of the optimization process and details on instrumentation and characterization can be found in the Supporting Information.

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