

Direct Synthesis of Branched Gold Nanocrystals and Their Transformation into Spherical Nanoparticles

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We report a facile synthesis of branched gold nanocrystals by the addition of a suitable amount of NaOH to an aqueous solution of cetyltrimethylammonium bromide (CTAB), HAuCl_4 , and ascorbic acid. The branched nanocrystals were formed within minutes of reaction and showed monopod, bipod, tripod, and tetrapod structures. They are crystalline and have smooth surfaces. These gold multipods are kinetically controlled products and are thermodynamically unstable. The branched nanocrystals quickly transformed into spherical nanoparticles within 1 h of reaction, and the process was essentially complete after 2 days. The morphological transformation has been monitored by both UV–vis absorption spectroscopy and electron microscopy. The appearance of two major absorption bands for the branched gold nanocrystals eventually became only a single band at 529 nm for the spherical nanoparticles. The resulting nanoparticles are single crystals with diameters of 20–50 nm and do not show a faceted structure. When the freshly prepared branched nanocrystals are kept in a refrigerator at 4 °C, their multipod structure can be preserved for over a month without significant spectral shifts.

Introduction

Recently, anisotropic growth of metal nanostructures has become a major focus of nanomaterials research. Among the various different anisotropic morphologies of metal nanostructures, synthesis of branched metal nanocrystals has just begun to receive a greater attention, and only few reports are available. Gold,^{1–7} platinum,^{8–10} and rhodium^{11,12} nanoparticles with multipod morphology have been studied. Interestingly, while branched gold nanocrystals have been exclusively prepared in aqueous solution, platinum and rhodium multipods were mainly synthesized in organic solvents. Chen et al. presented the first example of the branched gold nanocrystals with monopod, bipod, tripod, and tetrapod structures.¹ CTAB, HAuCl_4 , concentrated silver plates, and ascorbic acid were mixed, and then NaOH was added to this solution without shaking to induce the branched gold nanoparticle formation within 1 day. Hao et al. subsequently reported the synthesis of three-tipped gold nanoparticles from a solution of bis-(*p*-sulfonatophenyl) phenylphosphine dihydrate dipotassium, H_2O_2 , sodium citrate, and HAuCl_4 .² The branched nanocrystals were formed within several minutes, as indicated by a change in solution color from colorless to blue. We have previously described a seeding growth approach for the preparation of branched gold nanocrystals.⁴ Sodium dodecyl sulfate (SDS)-capped highly faceted gold particles serving as seeds were allowed to grow into branched nanocrystals by a further addition of HAuCl_4 , SDS, and ascorbic acid. The branched nanocrystals contained twinned boundaries and were fully developed within 2 h. More recently, branched gold nanoparticles grown following biocatalytic processes⁵ and star-shaped gold nanoplates produced through poly(*N*-vinyl-2-pyrrolidone) protection have also been reported.⁶ With the exception of our previous examination of the morphological transformation of the branched gold nanocrystals into

highly faceted nanoparticles with a well-defined decahedron structure, most of the other studies have not observed or addressed the structural stability of these branched gold nanocrystals.⁴

In this study, we report a rapid synthesis of branched gold nanocrystals by mixing an aqueous solution of HAuCl_4 , CTAB, and ascorbic acid, followed by the addition of a suitable amount of NaOH to induce the branch formation. Despite a similar growth approach used to the first branched gold nanocrystal report at first glance, there are several key features and insights presented here for a greater understanding of the nature of branched gold nanocrystals.¹ The gold multipods produced can readily undergo a morphological transformation into spherical nanoparticles. We have followed this structural change with both microscopy and spectroscopy characterization. The single-crystalline structure of the roughly spherical nanoparticles was also carefully examined. To preserve the unique structures of the unstable branched gold nanocrystals synthesized, we have also stored the samples in a refrigerator for a period of time. The resulting particle morphology and the corresponding UV–vis absorption spectra were recorded to assess the feasibility of this particle storage approach.

Experimental Section

Forty-five milliliters of 2.5×10^{-4} M HAuCl_4 (Aldrich, $\geq 99.9\%$) was prepared as an aqueous solution. CTAB (4.5×10^{-3} mol, Aldrich, $>99.0\%$) was added with stirring to this solution until the CTAB powder was completely dissolved. The CTAB concentration in this solution is 0.1 M. The solution was light yellow. Then 250 μL of 0.1 M L(+)-ascorbic acid (Riedel-de-Haën, 99.7%) was added, and the solution became colorless indicating the reduction of Au^{3+} to Au^+ . Finally 300 μL of 0.5 M NaOH (Mallinckrodt) was added to induce the formation of branched gold nanocrystals. The solution turned blue within 3 min of the addition of NaOH, and then it became purplish blue

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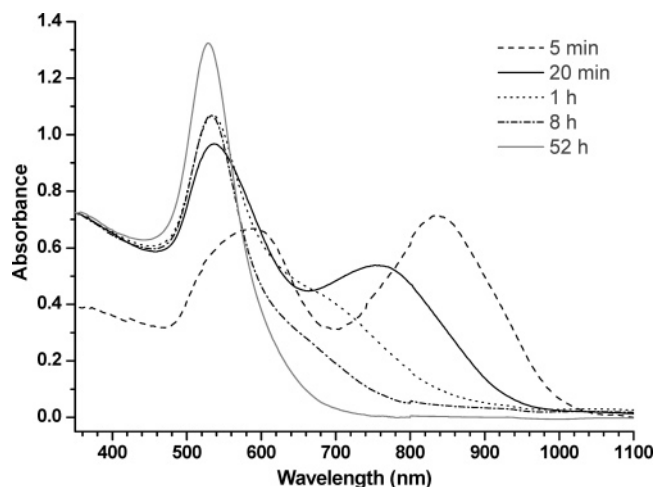


Figure 1. UV-vis absorption spectra of the branched gold nanocrystals taken at different times after the addition of NaOH to start the branch formation process. Each spectral scan takes about 2 min to complete.

between 5 and 20 min after the addition. Finally, it changed to purplish red after 30 min. The solution pH only changed slightly from 3.67 to 3.23 after the addition of ascorbic acid, but it increased drastically to 11.46 with the addition of NaOH and remained steady despite changes in the solution color. To collect the branched gold nanocrystals, after 3–5 min of reaction, the solution was centrifuged at 4500 rpm for 20 min. The supernatant was removed, and the nanocrystal precipitate was transferred to a copper grid for the transmission electron microscopy (TEM) analysis. To preserve the branched morphology of the products, the nanocrystals formed after 3–5 min of reaction were first centrifuged at 4500 rpm for 20 min, followed by supernatant removal and redispersion of the precipitate in 10 mL of ice-cold water in a flask. The sealed flask was quickly placed in a refrigerator and stored at 4 °C for 7 days or more. TEM characterization of the samples was performed on a JEOL JEM-1200CXII electron microscope operating at 120 kV. High-resolution TEM analysis was carried out on a JEOL JEM-3010 electron microscope operating at 300 kV. The UV-vis absorption spectra were taken using a JASCO V-570 spectrophotometer.

Results and Discussion

The recipe for the formation of branched gold nanocrystals is similar to our preparation condition for the seed-mediated synthesis of gold nanorods.¹³ The concentrations of HAuCl₄ and CTAB used are the same as those of the growth solution prepared for nanorod formation. In an attempt to synthesize gold nanorods in a basic condition without the use of gold seed particles, we have discovered a route to make branched gold nanocrystals. The amount of NaOH added was selected to induce a reasonably fast growth of branched nanocrystals; the addition of a larger amount of NaOH can result in a very fast reaction that is unfavorable for the formation of branched nanocrystals. When a much smaller amount of NaOH was added, such that the solution was not sufficiently basic, the reduction of Au⁺ species to metallic gold was found to be quite slow.

The unstable nature of the nanoparticle product can be easily observed by a gradual change in the solution color from deep blue to purplish blue and then to purplish red within the first hour of reaction. Figure 1 gives the UV-vis absorption spectra of the branched gold nanocrystals as a function of time to illustrate the spectral changes. The rapid growth of nucleation particles and the subsequent development of multipods occurred

within the first few minutes of reaction. After 5 min of reaction, the spectrum showed two broad absorption bands centered at 580 and 835 nm. Note that the band centered at 835 nm has a slightly higher absorbance value than that of the 580 nm band. These two bands then blue-shifted rapidly and appeared at 535 and 760 nm after 20 min of reaction with the band at 535 nm having a much higher absorbance. The spectral changes continued after this point with a distinct band at 532 nm and a shoulder band centered at ~690 nm appearing after 1 h of reaction. The 532 nm band also increased its absorbance compared to the 535 nm band, while the long-wavelength band showed a substantial decrease in its absorbance and a pronounced blue shift. After 8 h of reaction, the 532 nm band stayed at the same position, and the weak shoulder band has shifted to ~650 nm. The changes in the spectral profile became very slow and gradual after 8 h of reaction. A single absorption band at 529 nm was recorded after 52 h of reaction, and no more changes to the spectrum were found. The results indicate that the most significant spectral evolution occurs within the first hour of reaction.

The spectral data suggest that there is a big difference in the morphology of the gold nanostructures formed at the very early stage and after storage of the products for 2 days. In fact, the spectrum obtained after 5 min of reaction has an appearance resembling that of short gold nanorods.¹⁴ The morphology of the gold nanostructures formed after 5 min of reaction and 20 min of centrifugation is displayed in Figure 2a. Monopod, V-shaped bipod, and T- and Y-shaped tripod nanoparticles with sizes of a few tens of nanometers are observed. The branches taper off at the ends to give a tipped structure. The TEM image shows that these nanoparticles are not flat, but are rounded in appearance. Most of the nanoparticles exhibit branched structures, which are relatively long and well-developed. High-resolution TEM images of a single tetrapod nanoparticle reveal that the entire particle is crystalline (see Supporting Information). Furthermore, twinning is generally not found in these branched nanocrystals. Figure 2b is a TEM image of the gold nanoparticles synthesized after 20 min of reaction. A mixture of branched nanocrystals and spherical and ellipsoidal nanoparticles are present. The branched nanocrystals also have reduced pod lengths. Clearly, a major morphological transformation to the initially formed branched nanocrystals has taken place. This leads to a large blue shift for the two absorption bands.

This dramatic morphological transformation of the branched gold nanocrystals to spherical nanoparticles then continues more slowly and is essentially complete after 52 h of reaction. Figure 3 provides a TEM image of the final spherical shape of the gold nanoparticles formed after 52 h of storage of the branched nanocrystals at room temperature. Branched nanocrystals are no longer present. These nanoparticles have fairly smooth surfaces, and the particle size is in the range of 20–50 nm. These spherical gold nanoparticles give rise to the single absorption band at 529 nm. To further examine the crystal structure of these spherical nanoparticles, the high-resolution TEM image of a single egg-shaped nanoparticle was taken and is shown in Figure 4a. The nanoparticle has a rounded shape and facets are not present. This smooth particle morphology is unusual for gold nanoparticles of this size range; more frequently, gold nanoparticles should have a faceted structure in this size range.¹⁵ As can be seen, this nanoparticle is single crystalline with clear lattice fringes observable over the entire particle. A selected-area electron-diffraction (SAED) pattern of this nanoparticle is given in Figure 4b. Three diffraction spots with indices of (111), ($\bar{1}\bar{1}\bar{1}$), and (200) are labeled. The lattice

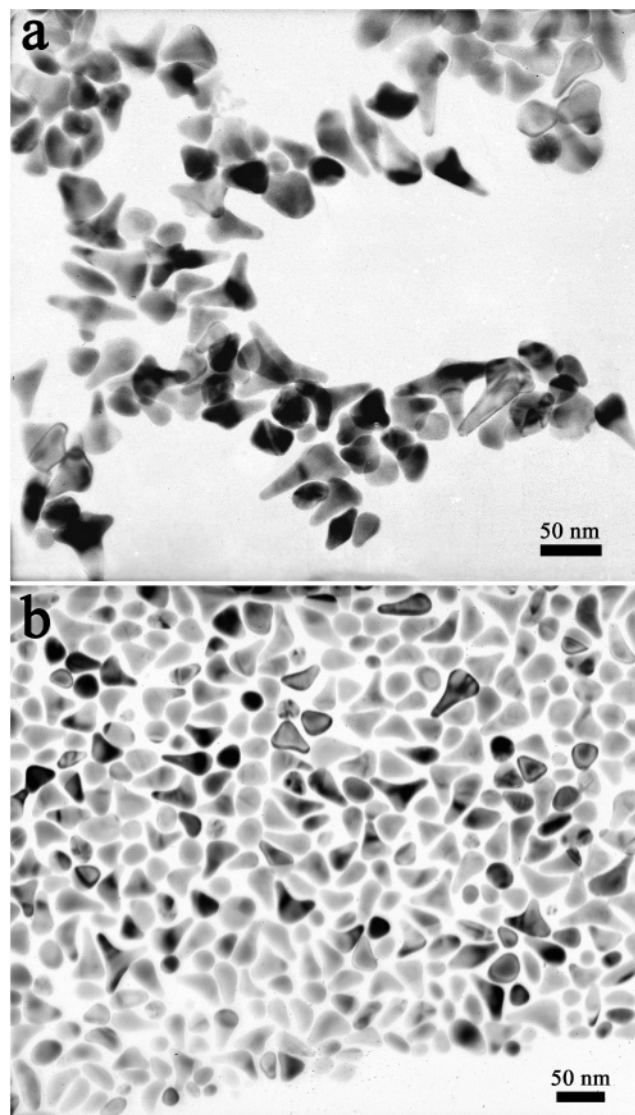


Figure 2. (a) TEM image of the branched gold nanocrystals formed after 5 min of reaction, followed by 20 min of centrifugation and precipitate transfer to a copper grid. A majority of the nanoparticles have developed a branched morphology. (b) TEM image of a mixture of branched and spherical gold nanoparticles observed after 20 min of reaction and 20 min of centrifugation.

fringe image of a small portion of this nanoparticle is provided in Figure 4c. Three sets of lattice planes with d spacings of 2.35, 2.35, and 2.03 Å can be clearly identified and should correspond to the (111), ($\bar{1}\bar{1}\bar{1}$), and (200) lattice planes of the face-centered cubic gold. The relative positions of the diffraction spots match the lattice fringe image obtained well. The SAED pattern with a single set of diffraction spots further indicates that the entire nanoparticle is single crystalline with the same lattice orientation running across the whole nanoparticle.

This fast morphological transformation from a branched structure to a spherical shape is noteworthy, but this type of structural change is not limited to just the branched gold nanocrystals. Multipod-to-sphere transitions have also been observed for platinum multipods.⁹ The unstable nature of the branched gold nanocrystals suggests that they are the kinetically controlled products. AuCl_2^- ions form via the reduction of AuCl_4^- by ascorbic acid.¹⁶ Ascorbic acid is a mild reducing agent and is ineffective in reducing the Au^+ species to metallic gold without the presence of gold seed particles. Upon the addition of NaOH and at a high solution pH, ascorbic acid, with

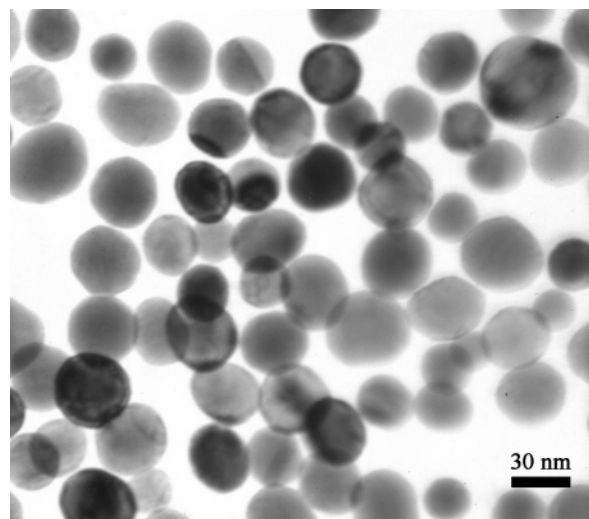


Figure 3. TEM image of the spherical gold nanoparticles formed after 52 h of storage of the branched nanocrystals at room temperature.

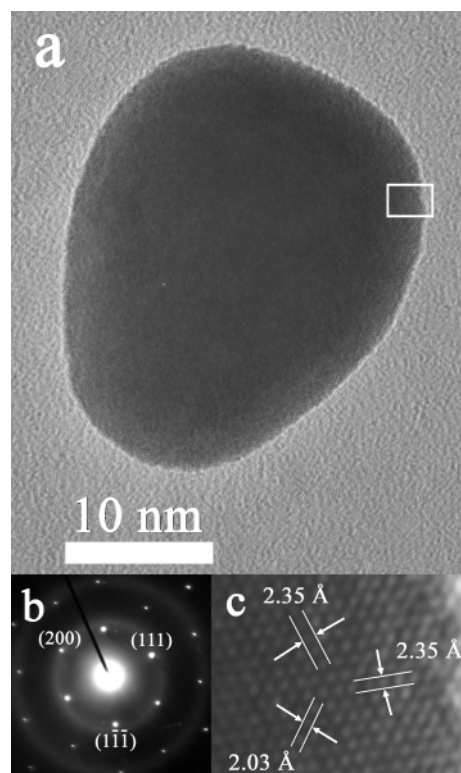


Figure 4. (a) High-resolution TEM image of a single egg-shaped nanoparticle formed after 52 h of storage of the branched nanocrystal at room temperature. Lattice fringes can be clearly seen over the entire nanoparticle. (b) SAED of the single nanoparticle. (c) Lattice fringe image of the rectangular region in panel a.

its $\text{p}K_{\text{a}1} = 4.1$ and $\text{p}K_{\text{a}2} = 11.8$, should deprotonate to ascorbate. $[\text{Au}(\text{OH})_2]^-$ can form under such a high solution pH condition from the AuCl_2^- ions. Ascorbate has been found to be an effective reductant for the formation of branched gold nanocrystals.⁴ $[\text{Au}(\text{OH})_2]^-$ and AuCl_2^- ions are then reduced to metallic gold by ascorbate, while ascorbate ions undergo a two-electron oxidation to form dehydroascorbic acid.¹⁷ The reduction of AuCl_2^- ions to metallic gold is more favored since this reaction has a large positive reduction potential; the reduction potential of $[\text{Au}(\text{OH})_2]^-$ ions to gold is negative. A very fast reaction occurs, and it results in more unregulated particle growth leading to the formation of branched gold nanocrystals. However, this multipod structure is thermodynamically unstable,

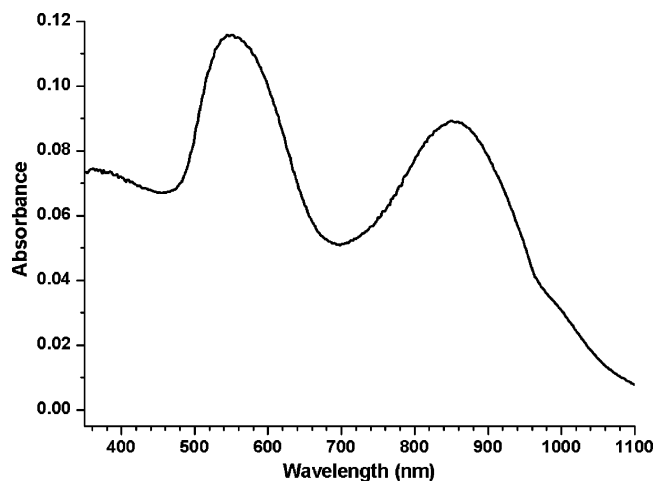


Figure 5. UV-vis absorption spectrum of the branched gold nanocrystals after storage at 4 °C in a refrigerator for 7 days.

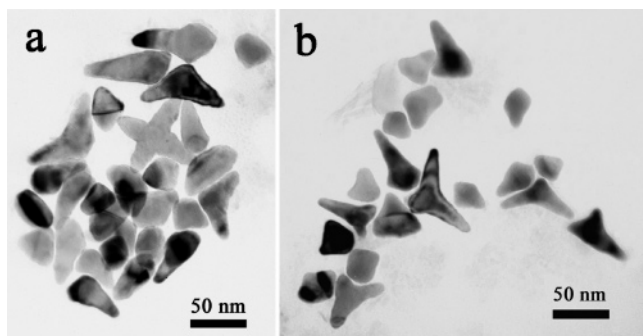


Figure 6. (a and b) TEM images of the branched gold nanocrystals after storage at 4 °C in a refrigerator for 7 days.

and the gold atoms on the branched nanocrystals rearrange quickly to evolve into a more thermodynamically favorable spherical shape. We also found that the replacement of ascorbic acid with sodium ascorbate is not effective in reducing HAuCl_4 to metallic gold without the addition of NaOH. Furthermore, the addition of NaOH without ascorbic acid in the solution also would not form gold nanoparticles. Since the branched gold nanocrystals do not possess facets, the resulting spherical nanoparticles also do not show facets. On the other hand, branched nanocrystals with twinned boundaries were found to be more stable and reverted back to a highly symmetrical decahedral shape after 10 days of storage in a 30 °C water bath.⁴ The unstable nature of the branched gold nanocrystals have also been observed in other reports with the same spectral shift to the blue.^{1,2a}

Even though the branched gold nanocrystals are unstable at room temperature, their multipod structure can be well preserved at low temperatures soon after their synthesis. Figure 5 is a UV-vis absorption spectrum of the branched gold nanocrystals after storage at 4 °C in a refrigerator for 7 days. The spectrum shows two well-resolved bands at ~ 560 and 850 nm. The spectral profile is similar to that obtained for the freshly prepared branched nanocrystal sample after a few minutes of reaction, suggesting that the multipod structure was maintained. The TEM images of this aged sample are given in Figure 6. A large fraction of the particles still retain their branched morphology with monopod, bipod, tripod, and tetrapod structures present. The results demonstrate the feasibility of preserving these

unstable branched gold nanocrystals at 4 °C for an extended period of time. In fact, similar UV-vis absorption spectra were recorded even after the branched gold nanocrystal samples have been stored for over a month.

Conclusion

We have demonstrated a simple method for the rapid formation of branched gold nanocrystals. These kinetically driven branched nanocrystals are very unstable and can quickly transform into thermodynamically more-stable spherical nanoparticles after 1 h of reaction. All the branched nanocrystals have essentially transformed into spherical nanoparticles after 52 h of reaction. The resulting spherical nanoparticles are single crystalline and have a smooth surface structure. The branched gold nanocrystals can be preserved for a long time by keeping the initially formed multipods in water at 4 °C. The results of this study and those of several other previous studies on the branched gold nanocrystals have pointed to the fact that these gold multipods are generally thermally unstable even at room temperature and can only survive at lower temperatures. This dynamic nature of the branched gold nanocrystals may limit their potential application as nanoscale interconnects, as previously proposed.

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Supporting Information Available: Figures showing TEM images of a single branched gold nanocrystal. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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