Watching the Transformation from Au Nanoparticles to Microplates

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The transformation from Au nanoparticles to microplates was observed. Triangular and hexagonal Au microplates with canal-like stripes were finally formed. It was proposed that Au atoms or ions "flowed" along limited path on Au(111) surface toward edge of microplates.

The properties of metal nanoparticles strongly depend on their shapes, such as multipod,[1] cubes,[2] rods,[3] and prisms,[4,5] as much as on their sizes. For this reason, the shape-selective fabrication of metal nanoparticles is an attractive research focus. In recent years, some groups have reported their methods to fabricate triangular or hexagonal Au nano- or micro-plates in the size range from 100 nm to 10 μm.[6–9] Despite of the fundamental and technological importance of these plates, the challenge for the clarification of formation mechanism has been met with limited success.

In this report, we describe a simple procedure for the synthesis of Au microplates with a size up to 10 μm, based on the use of poly(amido amine) (PAMAM) dendrimer as a reducer and as a stabilizer. Compared with previous reports, the novelties in the present work are: (i) A transformation process from Au nanoparticles to single crystal microplates was clearly shown; (ii) It was found that Au atoms or ions "flowed" along limited path on Au(111) surface toward edge of the microplate. As a result, canal-like stripes were formed on the microplates.

Reactions were carried out at 25 °C in an aqueous solution containing 1.5 mM tetrachloroaurate and 0.05 mM NH_2-terminated fourth-generation (G4) PAMAM dendrimer. PAMAM dendrimers can play the roles of both reducer and stabilizer. Transmission electron microscopy (TEM) was used to monitor the time-dependent microplate growth.

As seen in Figure 1a, Au nanoparticles of ca. 8 nm size were observed at the beginning of preparation, indicating that Au ions were reduced by amine groups in PAMAM dendrimers. However, the ratio of PAMAM dendrimer to Au ions was relatively low, namely, not enough as a stabilizer to prevent the obtained Au nanoparticles from aggregating. The lack of sufficient stabilizer caused the particles to aggregate (see Figure 1b). In the next stage, Au microplates slowly grew from aggregates, and, meanwhile, the amount of Au aggregates gradually decreased (see Figures 1c and 1d). The electron diffraction pattern (Figure 1e) shows the polycrystalline feature of the aggregates. On the other hand, as seen in Figure 1f, the diffraction spots from microplates could be indexed based on the face-centered cubic (f.c.c.) structure of Au.[6–9] The hexagonal nature of the spots is a clear indication that the Au plates are highly oriented with the {111} surface normal to the electron beam. Finally, well-defined triangular and hexagonal Au microplates were fabricated, as typified in Figure 2. Note, when the initial solution contains 0.03 mM tetrachloroaurate and 0.05 mM G4 PAMAM dendrimer, where the molar ratio of PAMAM dendrimer to Au ion is relatively high, the obtained dispersion consists only of spherical nanoparticles (see Supporting Information, Figure S1).[10] Similar spherical Au nanoparticles were also reported in earlier works with high ratio of dendrimer to tetrachloroaurate.[11] These results indicate that the amount of stabilizer is an important parameter in the synthesis of Au microplates.

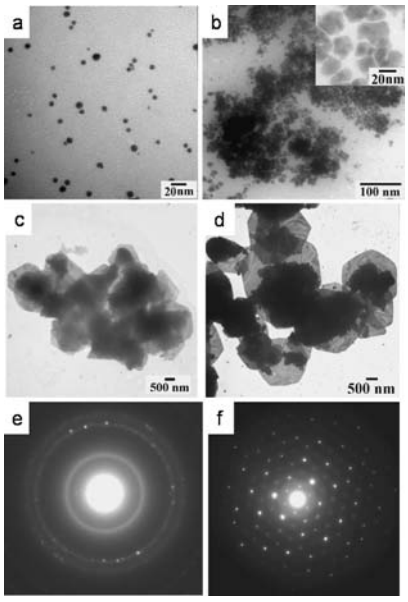

Figure 1. TEM images at different times in the transformation process from Au nanoparticles to microplates. (a) 1 min; (b) 30 min; (c) 8 h; (d) 18 h. (e) and (f) show the electron diffraction patterns from areas of aggregates and thin plates, respectively, in an image (d). Scale bars: (a), (b) inset, 20 nm; (b) 100 nm; (c), (d) 500 nm.

Well-stabilized bulk aggregates of Au nanoparticles usually get a steady state. However, in the present case, aggregates of Au nanoparticles were in an unsteady state and gradually changed to be crystalline. This observation implies that the aggregates in the present work may be constructed by globules of tiny dimension, which are interpositioned by PAMAM dendrimers (See Figure

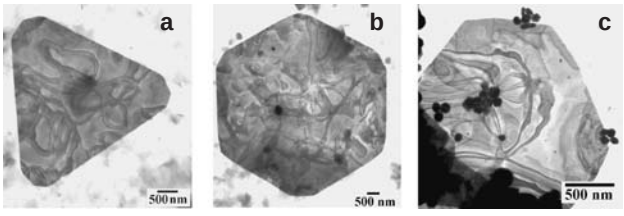

Figure 2. Typical TEM images of triangular (a) and hexagonal (b) Au microplates and (c) a TEM image showing clear flow paths of Au atoms or ions to the edges of a microplate. Scale bars indicate 500 nm.

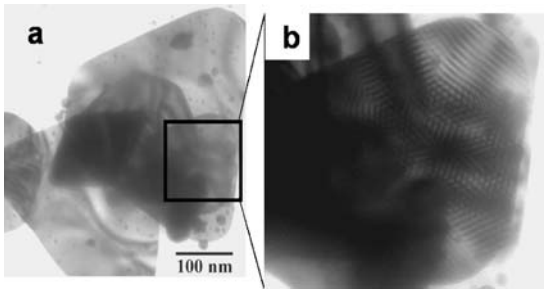

Figure 3. Stacks of two or more Au microplates (a) and Moire' fringe pattern formed by stacking (b). Scale bar indicate 100 nm.

S2).[10] The formation of this architecture can be ascribed to the restricted structure and multi-functional terminal groups of G4 PAMAM dendrimer. The unstability of the composite described above induced the transformation from aggregates to crystalline microplates.

The continuous canal-like stripes, which start from spots, can be seen over the faces of the flat crystals and radiate down to their edges. Figure 2 clearly displayed these stripe lines. This phenomenon has also been observed in earlier reports, and been ascribed to the bending of the thin crystals or the presence of "multiply twinned structures."[5] However, based on our observation, it is reasonable to assume that these strips were the paths, along which Au atoms or ions flow from Au aggregates to the edges of microplates. This assumption was supported by the following two facts. First, all lines started from the aggregates, and ended at the microplate edges. This phenomenon was observed throughout the microplate growth process. Second, the large increase in population and size of Au microplates is accompanied by the loss of aggregates of nanoparticles, suggesting that aggregates of Au nanoparticles continuously provided Au atoms or ions for the growth of microplates. Furthermore, Au atoms or ions flowed on the {111} family of Au crystal facets.

The formation of Au crystal microplates may be due to the special properties of the {111} facets—the fewest number of broken bonds per atom and the lowest surface energy.[5] That is, bringing another gold atoms from the flows to the growing crystal is least energetically favored at the {111} facets, which forced Au atoms or ions continue to flow. Consequently, the crystalline microplates could gradually grow by atoms adding onto more energetically favorable faces other than {111}. This would result in the formation of thin plates with polyhedral shapes. On the other hand, the preferential adsorption of dendrimers on the Au {111} facets can also provide the driving force to form microplates, and this assumption have been used to explain the formation of Au nanorod.[3]

So far, there are two assumptions to explain the formation of Au thin plates. Shankar and co-workers[8] suggested that biomolecules directed association and sinter of the small spherical gold nanoparticles, which were initially formed. A fact that most of the successful methods to prepare microplates were based on biology-relevant molecules seemed to supported this mechanism.[5–8] Very recently, Wang and co-workers[9] proposed that Au nanoparticles orientationally attached each other by using the temple of surfactant and liquid crystal. However, from the present experiment, it is clear that the growth of Au nanoplates is a spontaneous transformation process, in which the unstable aggregates of Au nanoparticles gradually change to the energetically stable state, that is, single crystalline microplates. Importantly, the transportation of Au atoms or ions follows specific paths on a preferential Au crystal facet. This is a probable mechanism, which can explain many experiment phenomena reported previously, such as morphological transformation from spherical shape to nonspherical ones of Au or Ag particles.[12]

The well-resolved interference fringe patterns confirmed the single crystallinity of this Au microplate, as shown in Figure 3. This observation was similar to the results from flat silver crystals.[13] Previous study suggested that flat structures exhibited Moire' patterns on their TEM images. In the present case, Moire' patterns could also be observed, if two or more microplates were stacked with tight contact. The observation of fringe patterns indicates that this kind of microplates will find potential applications as some optical and electronic devices.

In summary, the transformation of Au nanoparticles to microplates was observed. The growth of Au microplates is an energetically favorable process, and the self-transportation of Au atoms or ions follows specific paths on a preferential Au crystal facet {111}.

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