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Nucleation, Growth, and Aggregation of Au Nanocrystals on Liquid Surfaces *

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We report the formation of gold ramified aggregates after deposition of Au on an ionic liquid surface by thermal evaporation method at room temperature. It is observed that the aggregates are composed of both granules and nanocrystals with hexagonal or triangular appearances. The most probable size of the nanocrystals is much larger than that of the granules and it increases with the nominal deposition thickness. The formation mechanism of the granules, nanocrystals and aggregates is presented.

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For many kinds of noble metallic nanocrystals with face-centered cubic structure (gold and silver, for instance), their chemical and physical properties directly correlate with their morphologies and microstructures.[1−4] Synthesizing metallic nanocrystals and understanding their growth mechanism are central for further applications of these nanocrystals.

There are kinds of ways to generate metal nanocrystals in a variety of shapes, including sphere, octahedron, cube, cuboctahedron, and so on. The most popular is the solution-phase method,[5] in which a precursor compound is needed to be decomposed or reduced to generate zero-valent atoms. Poly (vinyl pyrrolidone) is used as dispersant to prevent particle agglomeration. Another way is the solvated metal atom dispersion (SMAD) method, which involves vaporization of a metal under vacuum and co-deposition of the atoms with the vapors of a solvent on the walls of a reactor cooled to liquid nitrogen temperature.[6] Normally, the fabrication of metallic nanocrystals requires rigorous experimental conditions, such as high temperature, catalysis, or electricity.[7−9]

Ye *et al.*[10−13] presented a series of results on the catalyst-free growth of various metallic aggregates on liquid surfaces at room temperature. The formation of the aggregates obeys a two-stage growth model which involves the growth of compact atomic clusters during deposition and the subsequent aggregation of the clusters. The ramified aggregates formed on the liquid surfaces generally exhibit polycrystalline structures.[11] The experimental evidence illuminated that both the microstructure and the growth mechanism of the aggregates are quite different from those on solid-state substrates.[12,13]

Recently, an interesting experimental result about the growth of one-dimensional Zn nanocrystals on silicone oil surfaces was reported.[14] Generally, liquid surfaces can be considered as isotropic and free-standing substrates.[10,11,15] Therefore, deposited atoms and atomic clusters may randomly diffuse on the substrates with large diffusion coefficient at room temperature.[10] The formation of the one-dimensional Zn nanocrystals, which cannot be explained by the two-stage growth model,[10] mainly relies on both the large diffusion coefficient of the deposited Zn atoms on the isotropic liquid substrates and anisotropic characteristics of the hcp microstructure of the Zn nanocrystals.[14]

In this Letter, we present an SEM study on the gold (Au) ramified aggregates grown on ionic liquid surfaces. The experiment was carried out by thermal evaporation without the assistance of catalysts at room temperature. We find that the aggregates are composed of both granules and nanocrystals with hexagonal or triangular shapes. The most probable size of the nanocrystals is about 45.0 nm, which is much larger than that of the granules. Based on the experimental results, we propose that both the morphologies of the seed crystals (seeds) and stacking faults play a crucial role in the growth mechanism of the granules and nanocrystals.

The samples were prepared by thermal evaporation of 99.99% pure Au in a vacuum of about 3×10^{-4} Pa at room temperature. The ionic liquid (99%, $C_8H_{15}BF_4N_2$) with a vapor pressure close to zero at room temperature was chosen as the liquid substrate, which was painted onto a $10 \times 10\,\text{mm}^2$ frosted glass surface with the thickness of about 0.5 mm. The deposition rate f and the nominal deposition thickness d were determined by a quartz-crystal balance located near the substrate. The filament (tungsten) was fixed at 130 mm right above the liquid substrate and quartz-crystal balance. In our experiment, the deposition rate was fixed at $f = 0.006$ nm/s.

After deposition, the samples were kept in the vacuum chamber for time period $\Delta = 30$ min and then removed from the vacuum chamber. The Au atomic aggregates were then transferred from the ionic liquid surface to a polished single crystalline silicon wafer by covering the silicon wafer on the liquid substrate for 10 min and separating it carefully. To remove the ionic liquid from the aggregates completely, the silicon wafer with the aggregates was then washed carefully with acetone and ethanol step by step.[14] Af-

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ter that, the measurements of the scanning electron microscopy (SEM, Zeiss Supra 55) equipped with an energy-dispersive x-ray spectrometer (EDS) were performed for the as-prepared samples. The microstructure of the Au nanocrystals was measured by a transmission electron microscope (TEM, JEM-2010).

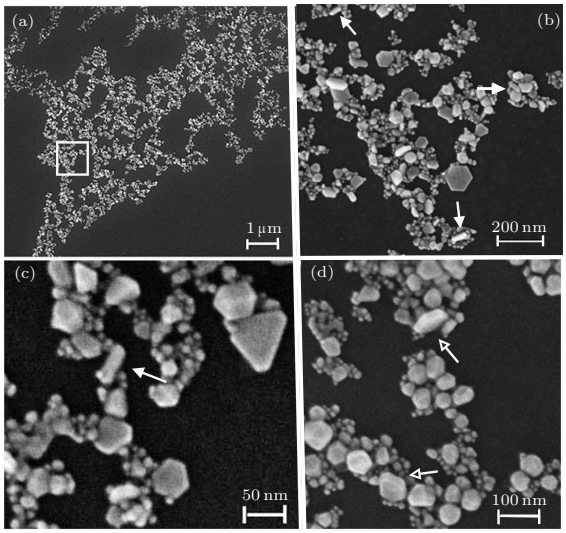

Fig. 1. SEM images of the Au aggregates grown on ionic liquid surfaces (nominal deposition thickness $d = 2.5$ nm): (a) the morphology of the Au ramified aggregates, (b) the enlarged picture of selected area of (a), (c) hexagonal and triangular nanocrystals and some large granules with polyhedral appearances, (d) the side view of two hexagonal nanocrystals pointed by the open arrows. Several suspected "nanobars" are pointed by the solid arrows.

Figure 1 shows the morphologies of the Au ramified aggregates on the ionic liquid surfaces with different magnifications. Figure 1(a) shows the overall overhead view of the ramified aggregates, which is similar to the aggregate morphologies observed before.[10,11] However, it is quite unexpected that both of the granules with relatively small sizes and nanocrystals with hexagonal or triangular appearances appear in the aggregates simultaneously, as shown in Fig. 1(b), which is an enlarged picture of the selected area in Fig. 1(a). Furthermore, from Fig. 1(b), we see that the average size of the nanocrystals is larger than that of the granules. This phenomenon should be related to the formation mechanism of the granules and nanocrystals. The experimental results shown in Fig. 1(b) are different from those of previous experiments.[10,11]

The granules and nanocrystals with the characteristic morphologies can also be seen clearly in Figs. 1(c) and 1(d). From the side view of the hexagonal nanocrystals shown in Fig. 1(d), we can see that the nanocrystals exhibit a plate-like morphology. Our measurement shows that the average thickness of the nanocrystals grown on the liquid surfaces is in order of around 10 nm. From Figs. 1(c) and 1(d), it can be seen that some of the large granules present polyhedral appearances. The regular geometric morphologies indicate that the granules and nanocrystals may exhibit single crystal microstructure.

We propose that all nanocrystals with hexagonal or triangular appearance grow along the liquid surface. In Fig. 1, some hexagonal nanocrystals seem to grow vertically. We believe that this phenomenon results from the aggregate transfer process in the experiment, which may change the positions and orientations of the nanocrystals obviously. Meanwhile, from Fig. 1, some suspected nanobars may be observed, as pointed by the solid arrows in Figs. 1(b) and 1(c). In fact, these nanobars are the side views of the plate-like nanocrystals, since the length of the nanobars is very close to the size of the nanocrystals.

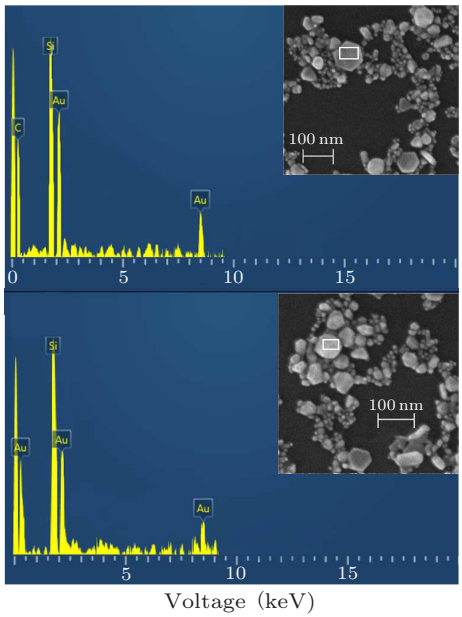

Fig. 2. EDS spectrums of the white rectangle regions shown in the insets (nominal deposition thickness $d = 2.5$ nm). The spectrum is presented with log scale on the y-axis.

To confirm the compositions of the granules and nanocrystals, the EDS spectrum was measured. As shown in Fig. 2, we can see that the nanocrystals are composed of Au and the signal of silicon in the spectrum is attributed to the silicon wafer. No evidence of other impurities has been found in this spectrum.

For further study of the formation mechanism of the hexagonal nanocrystals, statistical measurements on the sizes of hexagonal nanocrystals are performed. Figure 3 shows two size distributions of the Au nanocrystals with different nominal deposition thicknesses, i.e., $d = 1.7$ nm and $d = 2.5$ nm, respectively. We find that the sizes of the hexagonal nanocrystals (i.e., W, the distance between two opposite parallel edges of the Au hexagonal nanocrystals) range from 10 nm to about 120 nm. The most probable sizes in Figs. 3(a) and 3(b) are about 42 ± 2 nm and 48 ± 1 nm, respectively, which indicates that the most probable size of the Au nanocrystals increases with d.

To investigate the microstructure of the Au nanocrystals, the TEM measurement for a hexagonal nanocrystal was performed and the corresponding results are shown in Fig. 4. The morphologies of the Au hexagonal nanocrystals and granules can be seen in Fig. 4(a). A clearer picture of the hexago-

nal nanocrystal, indicated in the rectangular area of Fig. 4(a), is taken and shown in Fig. 4(b). The corresponding fast Fourier transform (FFT) of the selected area in Fig. 4(b) confirms that the Au nanocrystal exhibits the single crystal structure, as shown in Fig. 4(c). An inverse fast Fourier transform (IFFT) image of the selected area in Fig. 4(b) is shown in Fig. 4(d), from which we can obtain that the lattice spacing of the atomic planes is 0.23 nm, corresponding to the {111} plane spacing of the Au crystal.

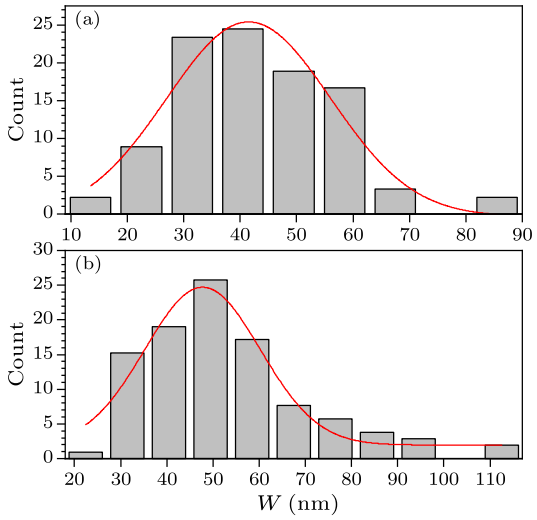

Fig. 3. Statistical distributions of sizes of Au hexagonal nanocrystals for the samples prepared with the nominal deposition thicknesses (a) $d = 1.7$ nm and (b) $d = 2.5$ nm.

Based on these experimental results, we propose that, basically, the formation process of the Au ramified aggregates still follows the traditional two-stage growth model.[10] In the first stage, the deposited atoms diffuse randomly and then nucleate to form Au atomic clusters. The growth of the clusters forms the granules and nanocrystals with the hexagonal and triangular appearances. In the subsequent stage after deposition, the granules and nanocrystals continue to diffuse on the liquid surface by Brownian motion and finally aggregate.

Obviously, there are no new physics in the second stage. However, in the first stage, the phenomenon that the growth of the atomic clusters finally results in both the granules and nanocrystals on the liquid surfaces is quite unusual,[10,11] which indicates a new growth mechanism in such a system. Experimentally, in the first stage, it is very difficult to trace the growth process *in situ* at the moment, therefore the precise formation mechanism of the granules and nanocrystals on the liquid surfaces cannot be obtained directly. However, from these experimental results and the related existing theories, we can present a reasonable proposal in the following.

During deposition, the deposited atoms diffuse randomly on the isotropic and free-standing ionic liquid surface, encounter with each other and form atomic clusters via self-nucleation. Subsequently, the clusters aggregate into small seed crystals (or seeds). The seeds grow in size by aggregation of more clusters and the free deposited atoms. The formation of the seeds shows that they start to have relatively stable crystallinity and well-defined crystallographic facets exposed on their surface.[16]

Since the type of seeds plays a significant role in the final morphologies of the granules and nanocrystals,[17] we propose that there are two different kinds of seeds formed on the liquid surface: the compact seeds (single crystal seeds, singly twinned seeds and multiply twinned seeds, etc.) and the plate-like seeds.[16] The final morphologies of the products are mainly determined by the corresponding seeds.[17] This gives an explanation that both the granules and nanocrystals may exist in the ramified aggregates simultaneously, as shown in Fig. 1.

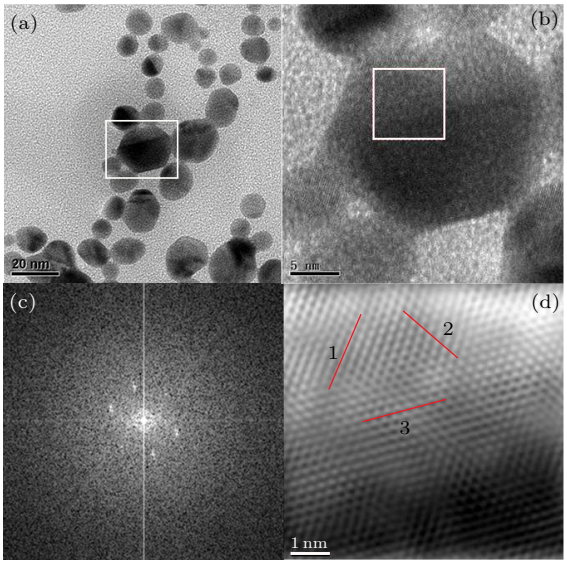

Fig. 4. TEM images of a Au nanocrystal ($d = 2.5$ nm): (a) TEM image of the Au nanocrystals and granules, (b) the enlarged image of the rectangular area of (a), (c) the corresponding FFT of the selected area in (b), (d) the IFFT image of the selected area in (b).

The compact seeds grow into granules by coalescing with other atomic clusters and the later deposited atoms. According to Wulff's theorem, the total surface free energy of a system with a given volume should be minimal.[18] For the metals with fcc microstructures, including Au crystals, the close-packed {111} facets possess the lowest surface free energy.[19] Therefore, we deduce that the granules should grow from the seeds that are mainly enclosed by {111} facets to lower the total surface free energy. As the crystal seeds grow and their sizes increase gradually, crystals with compact shape may appear. This deduction is in agreement with our TEM measurement for the granules (see Fig. 4).

The nanocrystals are supposed to grow from the plate-like seeds. When the atomic clusters and deposited atoms meet each other during diffusion, some of them may coalesce and form the plate-like seeds, instead of the compact seeds. Then, the plate-like seeds grow and form the hexagonal and triangular nanocrystals by coalescing with other atomic clusters and the later deposited atoms. This growth process may be

related to the presence of the stacking faults in the nanocrystals, which is common in the growth process of hexagonal and triangular nanocrystals.[20,21] Furthermore, it can be deduced that the more the plate-like seed coalesce with other atomic clusters and deposited atoms, the greater the possibility of forming the hexagonal and triangular nanocrystals because the average size of the nanocrystals is larger than that of the granules, as shown in Fig. 1.

More than 10 years ago, an experimental result for the microstructure and growth mechanism of the Ag and Au atomic aggregates on silicone oil surfaces was reported by Xie *et al.*[11] Their experimental result indicated clearly that the Au aggregates were composed of the quasi-spherical granules,[11] which seems to contradict with the experimental result shown in Fig. 1. However, it should be mentioned that in Xie's experiments commercial silicone oil (Dow Corning 705 Diffusion Pump Fluid) was used as the liquid substrate and the deposition rate (i.e., $f = 0.01\,\mathrm{nm/s}$) is much larger than that in our experiment. Therefore, we propose that the property of the liquid substrates and the deposition rate are two key experimental conditions for the growth of the plate-like Au seeds and nanocrystals.

If this proposal is correct, then we expect that the plate-like Au nanocrystals with hexagonal or triangular appearances should disappear and the Au aggregates should be composed of only granules if the deposition rate is large enough. In fact, we did not observe any plate-like nanocrystals in the samples prepared at the deposition rate $f = 0.02\,\mathrm{nm/s}$ in our experiment, which indicates that the higher deposition rate is not beneficial for formation of the plate-like seeds and nanocrystals. A similar phenomenon also occurred in the solution-phase method, in which the low reaction rate is an important factor to obtain plate-like metal nanocrystals.[22,23]

Finally, it should be emphasized that in our SEM measurement for all the Au samples only the granules and nanocrystals with hexagonal or triangular appearances were observed. The one-dimensional nanocrystals, such as nanowires, nanobars, nanobands, did not appear in any of the Au samples prepared under different experimental conditions. This result is in good agreement with the previous prediction since the Au crystals possess fcc microstructure and it does not exhibit the growth direction characteristics on the isotropic liquid substrates.[14]

In summary, we have studied the microstructure and the growth mechanism of the Au ramified aggregates on ionic liquid surfaces. The aggregates are composed of both the granules and nanocrystals with hexagonal or triangular appearances. Our experimental result indicates that the most probable size of the nanocrystals increases with the nominal deposition thickness. It is suggested that the formation process of the Au ramified aggregates basically follows the traditional two-stage growth model. However, both granules and hexagonal and triangular nanocrystals may be formed simultaneously on the liquid substrates, and the morphologies of the nanocrystals are mainly determined by the shapes of the corresponding seeds. The experimental results show that the property of the liquid substrate and the deposition rate are two key conditions for the growth of the nanocrystals.

We still face many challenges in this field. For example, the experiment shows that the average thickness of the nanocrystals grown on the liquid surfaces is around 10 nm. However, the physical nature of this phenomenon is unclear at the moment. To find the growth mechanism of the nanocrystals precisely, it is necessary to trace the growth process and the microstructure evolution of the seeds and nanocrystals. Therefore, further theoretical study on this new system is still needed.

The experimental phenomena shown in this letter indicate that more liquid materials may be used as substrates to fabricate various metallic nanocrystals. Since the liquid substrates can be considered as isotropic and free-standing surfaces, the growth characteristics of different crystals may get enough salience. Therefore, we propose that, by using this energy saving, environmental protection and inexpensive method suggested here, more large nanocrystals with plentiful morphologies may be fabricated massively on different liquid surfaces in the near future.

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