Crystal Coalescence

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Preservation of Lattice Orientation in Coalescing Imperfectly Aligned Gold Nanowires by a Zipper Mechanism**

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Long-range order is a common feature in devices and their components. Top-down methods can easily create long-range repeating features in screws, gears, and propellers,[1] but such an apparently simple task is still a great challenge for bottom-up processes. In nanocrystals, the regular shapes and facets are a manifestation of the underlying lattice order.[2] Bridged by such an internal order, it would be feasible, at least in theory, to grow distant crystal domains with spatial alignment.

Herein, we synthesize solid gold rings (Figure 1 c) in a colloidal solution by low-temperature coalescence of coils of Au nanowires (NWs). Surprisingly, after the coalescence, the axial lattice orientation of the original AuNWs is roughly maintained. We are able to grow spatially aligned Ag blocks from the rings (Figure 1 d), thus confirming the preservation of the Au lattice. Thus, this system provides a unique platform for studying the mechanism of crystal coalescence, with a large number of similar structures in well-defined states.

Lattice order in nanocrystals can arise from the growth of single crystals during direct deposition or Ostwald ripening, or from the oriented attachment (OA) of primary nanocrystals. The former theories have been well-established.[3] Notably, the latter is also gaining popularity because of an increasing body of evidences.[2b,4]

For many (us included), the theory of OA is hard to comprehend, particularly regarding to the detailed steps in the mysterious alignment of colloidal nanocrystals by random collision. There is no question that such a process can eventually occur, but there is a lack of discussion on how it occurs. There are many questions to be answered: Even if a vectorial force (for example, dipole interactions) is guiding the face-to-face alignment (defined as the z direction) of two nanocrystals, how can the lattice orientations be aligned also in the x and y directions (Supporting Information, Figure S1)?[5] What keeps the nanocrystals together during their "dancing" of lattice alignment? After the attachment of two nanocrystals and with ligands trapped in between, how does the underlying lattice "feel" the orientation of the opposing lattice? How do the ligands eventually escape and how is the resulting gap filled? These questions highlight the large gap from nanocrystal collision to coalesced supercrystals.

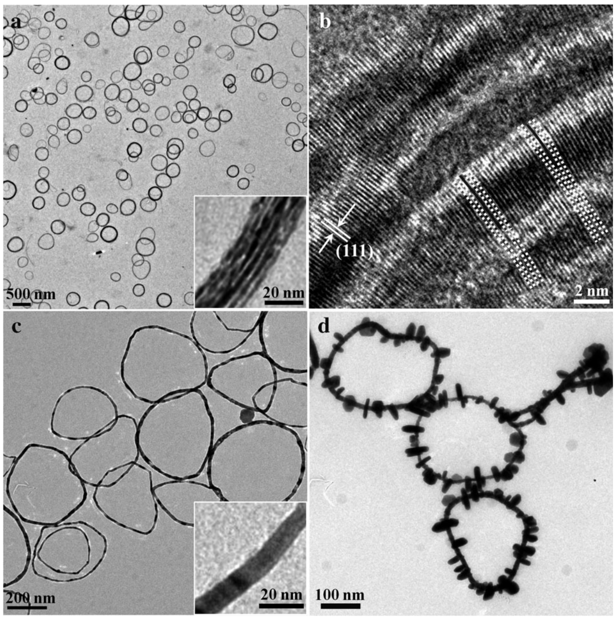

Figure 1. TEM images of a) as-synthesized Au nanorings. b) HRTEM image of a typical ring section, showing the imperfectly aligned (111) planes; the lines mark the extra length an outer NW must traverse. c) Solid rings after coalescence. d) Perpendicular Ag blocks grown on the coalesced rings. For large-view images, see the Supporting Information.

It is tempting to propose that the attachment of nanocrystals may occur after all of the ligands are lost from the two colliding faces. But in previous reports, ligands were typically present in the solution. It takes about 175 ligands to fully cover a 5×5 nm^2 area of a Au(111) facet.[5,6] Given the large junction area during the typical assembly, it is statistically improbable for all of the ligands to be cleared before a successful collision event.[5] The dissociation of surface ligands must be sequential. With ligands present, lattice alignment is difficult, but premature coalescence may lock in the ligands and freeze the crystals in a wrong alignment. Thus, a sound theory would demand logical steps that can resolve the interlocking of three major events: ligand loss, lattice alignment, and coalescence.

The key evidence in the literature supporting OA can be roughly categorized into two groups: The first group of studies considered both the primary nanocrystals and the final unified supercrystals.[4e,f] The critical starting state at the instant of successful collision, that is, the exact configuration

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of two colloidal nanocrystals, cannot be known. The second group of studies investigated the in situ coalescence of nanocrystals during TEM characterization.[3a,4j,7] Typically, the studied nanocrystals are case-specific, with nearly rounded shape and small facets. Under high-energy electron irradiation, the coalescing nanocrystals were rotating and moving, making it difficult to define the original lattice orientation.

In comparison to such systems, bundling single-crystalline AuNWs in a colloidal solution provides an ideal platform for revealing the detailed steps of crystal coalescence.

In our system, the single-crystalline AuNWs were coiled into rings by emulsion droplets; this method was modified from our recent report:[8] The initial AuNWs were synthesized using oleylamine as the ligand.[9] After purification, they were dispersed in a mixture of 250 μL of THF and 0.3 μL of oleylamine. Then, 1 mL of aqueous SDS solution (8 mM) was added to induce emulsification, where the solvent-shifting method caused the dissolved oleylamine in THF to be excluded as fine droplets. The sample was then heated at 60°C for 2 h. With the removal of the residue THF, the oil phase contracted further, causing the embedded AuNW bundles to coil into rings.[8] Most of the product was circular rings, which can be easily isolated by centrifugation (96% in purity, Figure 1a). These rings have an average diameter of 476 ± 85 nm and bundle width of 27 ± 8 nm. Closer inspection showed that the rings were composed of close-packed AuNWs with roughly parallel alignment. Figure 1b shows the HRTEM image of a typical ring section. The NWs were all single-crystalline with the Au(111) planes perpendicular to the wire axis, as was previously known in the initial syntheses.[9b,10] The inter-wire separation was overall quite uniform within the bundles (inset of Figure 1a), indicating the presence of surface ligands.

After purification, the rings with parallel AuNWs were coalesced into solid rings. Briefly, the Au rings were dispersed in 500 μL of aqueous SDS solution (4 mM), followed by addition of 5 μL of H_2O_2 (35% w/w). After heating the mixture at 100°C for 2 h, solid rings were obtained. As shown in Figure 1c, the coalesced rings often deviated from smooth circles, probably because the hardening Au wires forced some local sections to straighten. Furthermore, the rings have a slightly wavy outline and obvious kinks. Their average diameter remained roughly unchanged at 474 ± 93 nm, but the average width of the solid rim decreased to 15 ± 4 nm.[5]

The coalescence appeared to be promoted by ligand deficiency and the reduction of surface Au ions.[10c] Control experiments with replenished oleylamine (0.3 mM) did not give coalesced rings. Although H_2O_2 can act as both oxidant and reductant,[11] other reductants such as ascorbic acid and formaldehyde can also be used to promote coalescence; oxidants such as $(NH_4)_2S_2O_8$ cannot be used (Supporting Information, Figure S13).[5] Direct heating without additives have no obvious effects. The reduction of surface Au ions was further supported by X-ray photoelectron spectroscopy (XPS) results (Supporting Information, Figure S17).[5]

To our great interest, HRTEM analysis of the coalesced rings showed that most of the non-kinked sections were single-crystalline (Figure 2), with Au(111) planes perpendicular to the wire axis. In other words, it appeared that the lattice orientation of the original AuNWs was preserved. Given the size of the rings, the coalescence was unprecedented in terms of structural preservation (the wire shape in overall ring conformation) and the total coalesced volume. The AuNWs cannot move away or rotate outward because they were restricted in the bundles. Most importantly, the facile solution process allowed us to trap intermediates for mechanistic study.

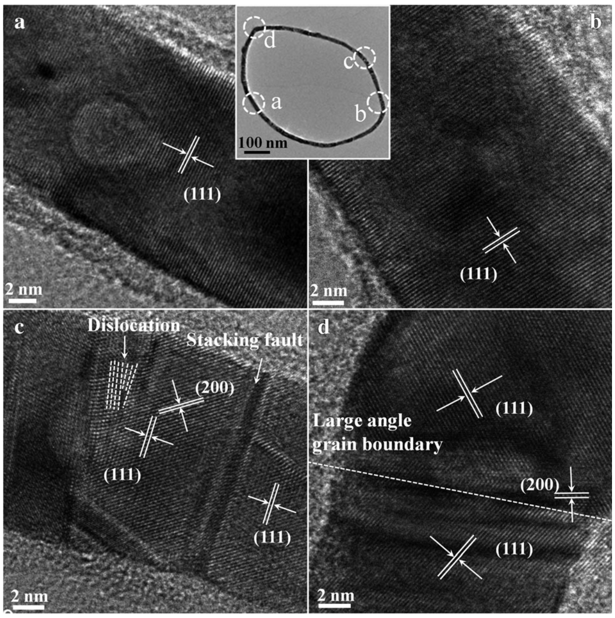

Figure 2. a)–d) HRTEM images of magnified sections of a typical coalesced Au ring.

The coalescence results cannot be explained by ripening or Au deposition: After purifying the rings, the residue Au ions in the solution were negligible. On the other hand, ripening is expected to cause thick wires to grow thicker at the cost of thin ones or certain ring sections. On the contrary, the coalesced rings were highly uniform in width without thinned NWs or broken sections.[5]

At the initial state before coalescence (Figure 1b), by geometric requirement an outer NW in the ring must traverse a longer distance than an inner NW. Although all of the NWs were roughly aligned in the $\langle 111 \rangle$ directions, the alignment cannot be perfect. Considering the random twisting of different NWs and the multiple loops in a bundle, it is highly improbably that the neighboring NWs can always align in the x and y directions (see the cross-section in Figure 5). Thus, a great amount of structural reorganization will be needed to align the nanocrystals and remove the imperfections.

After the coalescence, there were occasional dislocation defects near the outer rim of the fused wires (Figure 2c), which is consistent with their longer outer periphery. Furthermore, stacking faults can often be observed, particularly near the kinks. Given the near circular shape of the rings, the sharp turning angles at the kink sites probably resulted from the squeezing of nearby straightened sections. At such sites, usually the (111) planes on the two sides were misaligned, and grain boundaries can be identified (Figure 2 d).

To study the crystallinity in a large number of rings, we tried to grow Ag blocks on them: The coalesced rings were first mixed with the reductant ascorbic acid and the ligand 2-mercaptopyridine in a THF/H_2O mixture (1:1 v/v). Then, $AgNO_3$ was added and the sample was incubated at room temperature for 20 minutes. Owing to the strong ligand, Ag growth was not uniform, forming blocks (Figure 1 d; Supporting Information, Figure S6).[5] HRTEM confirmed that the Ag blocks were epitaxially aligned with the underlying Au lattice (Figure 3). Regardless of their position, the Ag blocks were always aligned perpendicular to the wire axis (Figure 3 b; Supporting Information, Figure S7).[5] Although ordering of nanocrystals in terms of uniform spacing has been reported,[12] the ordering of the Ag blocks with consistent alignment was highly unusual. There is no reason for a Ag block to "feel" the alignment of a distant Ag block, except that all of them must have aligned with the orderly Au lattice over the entire ring. This is unambiguous evidence for the preservation of lattice orientation in a large number of the coalesced rings.

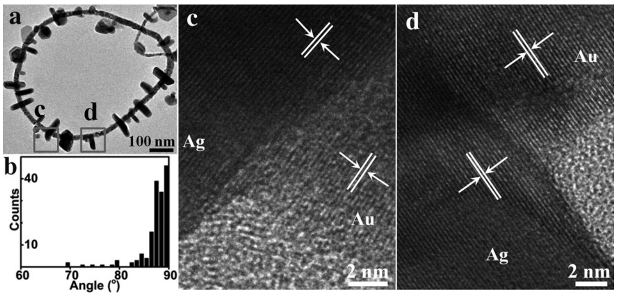

Figure 3. a) TEM image showing a typical coalesced ring with grown Ag blocks. b) Histogram of the angles between a Ag block and the Au wire. c),d) HRTEM images corresponding to the marked areas in (a).

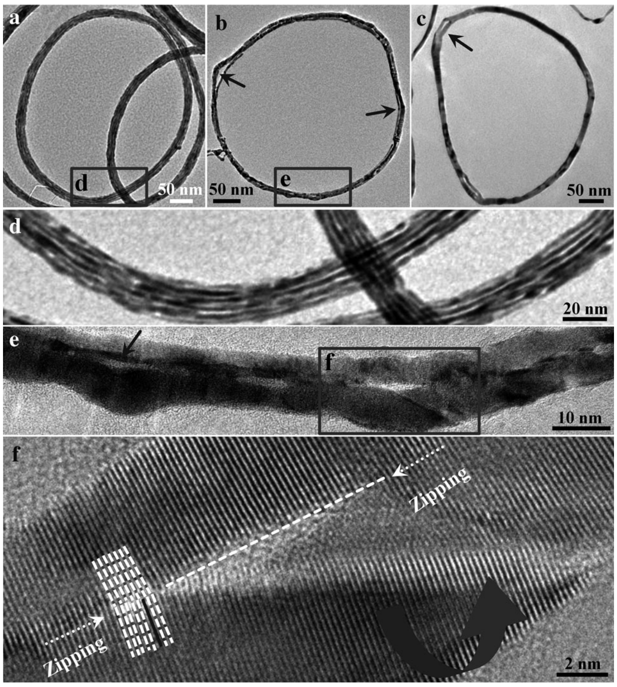

Figure 4. TEM images of coalescence intermediates isolated after heating with H_2O_2 for a) 30, b) 45, and c) 90 min. d)–f) Magnified ring sections as indicated in a)–c).

To trap the coalescing intermediates, we reduced the time of the heating step with H_2O_2 from 2 h to 30, 45, and 90 min (Figure 4). At $t = 30$ min, coalescence between neighboring AuNW sections can be observed. The coalesced NWs became thicker, but the rings did not deviate obviously from the overall smooth circular shape. At $t = 45$ and 90 min, the rings were no longer smooth. Most of the AuNWs were fused together, but large gaps were frequently observed between thick strands. It appeared that the initial coalescence occurred rapidly, whereas the removal of twisted sections and bulges took longer. Selected images are shown in Figure 4 b,c to illustrate the "squeezed" ring sections (see larger views in the Supporting Information, Figures S9, S10):[5] In a number of cases, a few strands of AuNW were forced to bulge out from the main strands, probably as a result of their different initial perimeters. The extra length of the strands near the outer rim can no longer be accommodated in the coalesced wire. Though this length difference was distributed in the initial ring, the sequential coalescence of the AuNWs can accumulate the difference onto a few spots, causing significant bulges.

In Figure 4 e,f, a bulged section was found to have a twisted configuration. Such a high-energy strain cannot be explained by crystal growth or simple OA.[9b,10d] Apparently, the coalescing AuNWs from both sides of this bulge has accumulated sufficient twist in the "squeezed" section. Should such a section eventually coalesce into a solid block, it is conceivable that defects (for example, a grain boundary) will be generated. The small gap shown in Figure 4 f was narrower than the gaps in Figure 1 d and thus most of the ligands at its inner surface should have dissociated by this time.

Given the extensive coalescence in our system, it is obvious that the ligand loss, lattice alignment, and coalescence must all have occurred in a progressive manner. On the basis of our observations, we propose a "zipper" mechanism (Figure 5) to resolve the inter-dependence of these events: coalescence should initiate at a small active site with no ligand,[13] forming a coalesced junction; in the small junction, the lattices can align by tilting and rotating the NWs; such an active site can then zip along the NWs causing sequential loss of ligands; with a number of zipping active sites, the NWs in a bundle can be eventually coalesced together.

We hypothesize that the reduction of surface Au ions may promote ligand dissociation. This can initiate the active sites by two possible scenarios: a) The reduced Au atoms may preferentially nucleate at a random ligand-deficient site, forming a fresh island (without ligand). Considering the Brownian motions of the NWs, such an island can exert steric influence on the ligands of a neighboring AuNW, facilitating their dissociation and thus causing a coalesced junction to form. (It would be less probable for two ligand-deficient sections at neighboring NWs to occur right opposite to each other.) b) During the structural vibration of the rings (part of

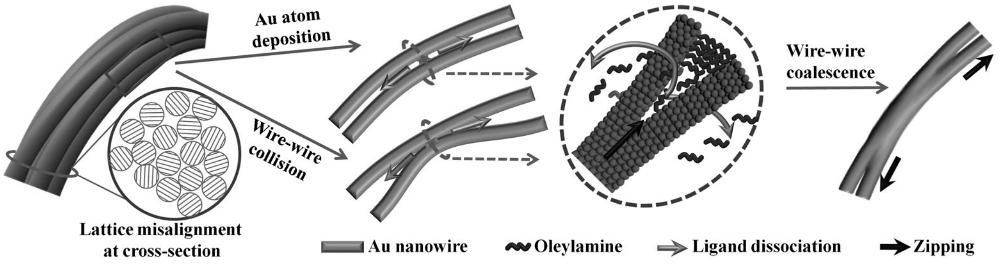

Figure 5. Representation of the coalescence of Au NWs by the zipper mechanism.

its Brownian motion), the constituent NWs may collide with each other, ejecting the surface ligands on the contact point. Directly coalescing two NWs without an island is potentially problematic because the ligands surrounding the active site would demand a gap in between. But as the Au NWs in our systems were ultrathin and highly flexible, we are actually more inclined towards scenario (b).

Once a coalesced junction is formed, matching its lattice with the neighboring NWs can lower its energy. This may be assisted by local wire vibration that tilts or rotates the NWs. In the literature, it is known that small junctions[3a,4j,7] ($d < 5$ nm) or thin NWs[2e] ($d = 2$ nm) can rotate and reorganize their lattices. The wedge space near the coalesced junction (for example, Figure 4 f) should be strained, and this may promote ligand dissociation. Filling the high-curvature tip of a wedge is more favorable than depositing Au atoms on a surface facet. Such selective deposition or coalescence pushes the wedge along the NWs and causes the "zipping" of the active site.

As the coalesced wires grow thicker, they become mechanically stronger and harder to bend. Confined by the overall circular shape, the inability to curve a crystalline wire induces strain, which can be occasionally relaxed by the insertion of dislocations near the outer rim (Figure 2 c). As the coalescing sites zipping around the ring, the accumulated twist or strain can eventually become too large to be reconciled, particularly when a section is being squeezed from both sides. As a consequence, strands are forced to twist or bulge out (Figure 4). Eventually, with prolonged coalescence, most of the Au NWs/strands are coalesced together, except a few rings with bulged sections (Supporting Information, Figure S5).[5]

At the initial state, the ligand-deficient ultrathin Au NWs have a high surface energy. The zipping process is driven by the reduction in the overall surface to volume ratio of the Au domains (that is, reduction of the gold–solvent interfacial energy). Zipping provides a low-energy pathway to minimize the extent of atomic reorganization by tilting and twisting the NWs. Because the initial Au NWs were roughly aligned in the $\langle 111 \rangle$ directions, their inability to rotate out of the ring plane caused their axial lattice orientation to be preserved.

In summary, we have presented a case study on the coalescence of nanocrystals: single-crystalline Au nanowires were used; they were pre-arranged in parallel to give an unambiguous initial state for their coalescence; the reaction was carried out in solution, so that the key intermediates were trapped and characterized; and finally, the preserved lattice orientation was proved in a large number of rings. A zipper mechanism is proposed to reconcile the interlocked events of ligand loss, lattice alignment and coalescence, with logical steps that are consistent with the experimental observations. By showing how the lattice alignment was achieved and how the many imperfections were removed during the coalescence, our new data helps the theory of oriented attachment by shortening the gap between the collision of colloidal nanocrystals and the coalesced supercrystals.

Crystal coalescence is an important process in the synthesis of nanocrystals. Understanding it is a first step towards rational synthetic designs. As shown in this work, the ability to control lattice alignment is essential for creating spatially-aligned Ag blocks at the nanoscale and by facile self-assembly.

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