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Structural Control of Three-dimensional Assemblies of Anisotropic Gold Nanoparticles Based on Their Different Shapes

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We have observed novel formation of differently shaped three-dimensional aggregates among hydrophobic gold nanospheres, nanorods, and nanobones. Gold nanobones preferentially formed spherical assemblies of 100-nm scale. In the case of gold nanorods, the shapes of assemblies were profoundly affected by the aspect ratios, changing from spherical to bundle-like structure.

Noble metal nanoparticles have become more and more important to electronics, photonics, biotechnology, and so on, because they have unique optical and electronic properties depending on size and shape.[1,2] In particular, anisotropic gold nanoparticles such as gold nanorods (AuNRs: rod-like gold nanoparticles) exhibit a couple of plasmon bands corresponding to localized surface plasmon resonance along the vertical and the longitudinal directions.[3] Using this unique optical property, some fascinating applications have been proposed. For example, Kawata et al. proposed a super-resolution imaging device utilizing side-to-side assembling gold (or silver) nanorods.[4] Niidome and Yamada applied the polarized laser-induced shape change of AuNRs that were doped in a polymer film intended for application to spectral encoding.[5] For such applications, the development of tailor-made assembly of such anisotropic nanoparticles is of fundamental importance.

Until now, there have been a number of reports for assembling and aggregation of AuNRs in side-to-side[6–9] or end-to-end[6,7,10–13] alignment. Studies on one-, two-, and three-dimensional assembling of AuNRs have also been reported.[6,9] However, the previous assembling has been achieved only in sophisticated decoration of AuNRs or substrates for deposition.

We demonstrate here a novel method for three-dimensional assembling of anisotropic gold nanoparticles as well as gold nanospheres, by two-phase transfer. In this study, we used AuNRs and gold nanobones (AuNBs: bone-like gold nanoparticles) (see TEM image of Figure S1 in Electronic Supporting Information (ESI)),[14] and gold nanospheres (AuNSs) for comparison. AuNRs and AuNBs were prepared by slight modification of our previous method,[15] in the presence of a large excess of hexadecyltrimethylammonium bromide (CTAB); thus they are hydrophilic and are capped with CTAB. We have prepared five kinds of AuNRs with different aspect ratios: AuNR-1 (aspect ratio (AR): 2.1 ± 1.0), AuNR-2 (2.4 ± 0.7), AuNR-3 (3.9 ± 0.7), AuNR-4 (5.8 ± 1.7), and AuNR-5 (7.3 ± 2.4). In order to fabricate their assemblies, they were first made hydrophobic by capping with dodecanethiol (DT). On the other hand, DT-capped AuNSs were directly prepared according to a previous method.[16]

The three-dimensional assemblies of Au nanoparticles were prepared as follows (Figure S2, ESI):[14] A hexane solution of an appropriate amount of DT-capped hydrophobic Au nanoparticles was mixed with an aqueous solution containing a surfactant 2R10enQ (Figure S3, 100 mM),[14,17] and then the mixture was sonicated for 20 s. After leaving overnight, the aqueous phase turned reddish purple. The sample solution was centrifuged to remove unwanted surfactant, and then absorption and TEM measurements were made.

Figure 1 shows TEM images of the three kinds of assemblies consisting of AuNSs (diameter: 6.6 ± 0.7 nm), AuNBs (AR: 3.3 ± 0.5) and AuNR-3s (AR: 3.9 ± 0.7). Clearly, AuNSs form nearly spherical assemblies with roughly 50-nm diameters (Figure 1a). It is noteworthy that in the case of AuNBs, roughly spherical assemblies with ca. 100-nm diameters are exclusively generated (Figure 1b). In contrast, AuNR-3s build up well-aligned bundle-like structures of ca. 100-nm diameters as shown in Figure 1c. In order to clarify the number of assembling AuNR-3s, we took the TEM and SEM images of the bundle-like assemblies of AuNR-3s, as shown in Figure 2; a part of the TEM image of Figure 1c is shown as Figure 2a to clarify the top-view of the bundle-like structure. Figures 2b and 2c show the SEM images with low and high resolutions. A bird's-eye image (tilt angle 40°) of SEM was also measured, as shown in Figure 2d. These SEM observations verify the well-

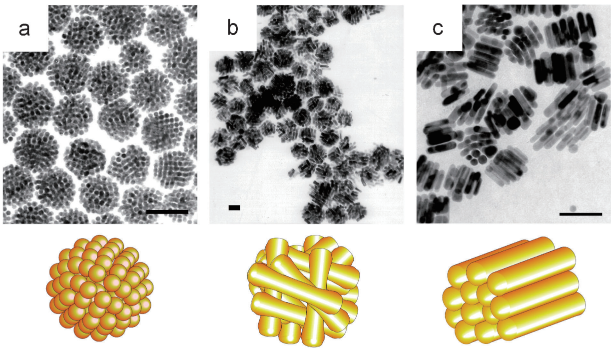

Figure 1. TEM images of nanoparticle assemblies when 2R10enQ is used as the surfactant: (a) AuNS, (b) AuNB, (c) AuNR-3 (AR: 3.9 ± 0.7). Scale bar is 50 nm. The bottom figures show schematic images of the corresponding assemblies.

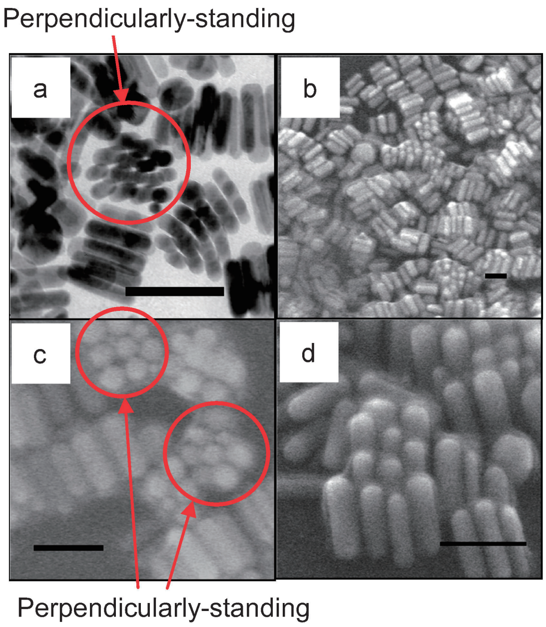

Figure 2. TEM images of assemblies of AuNR-3 (a) (a part of Figure 1c is shown), and the SEM images on the TEM grid taken with low resolution (b) and high resolution (c), and with a bird's-eye view (tilt angle 40°) (d). Scale bar is 50 nm.

aligned structures of AuNR-3s. It is also clear that the assemblies form well-aligned bundle-like structures mostly consisting of 8–20 particles.

These results are interpreted as follows. AuNBs with both edges swollen compared to the middle region, are a disadvantage for snug and parallel (side-to-side) packing for steric reasons as well as from the van der Waals interactions among alkyl chains of capping DT molecules. Therefore, AuNBs preferably constitute spherical assemblies with some twisted aggregation, apart from parallel packing. As a result, the assemblies of AuNBs take thermodynamically stable and roughly spherical structures. The sizes of all assemblies were evaluated to be roughly 100 nm from the TEM observations. The ζ potential of resultant assemblies of AuNR-5s, using 2R10enQ was +40 mV. This implies that the assemblies of AuNR-5s are surrounded by surfactants.

In order to investigate the AR dependence of AuNRs on the shape of assembled structures, various kinds of AuNRs with different ARs were examined. Figure 3 shows TEM images of five kinds of AuNRs: AuNR-1, AuNR-2, AuNR-3, AuNR-4, and AuNR-5. Clearly, AuNR-1 (AR: 2.1 ± 1.0) and AuNR-2 (2.4 ± 0.7) formed spherical assemblies with 50–100-nm sizes. On the contrary, bundle-like assemblies were generated for AuNR-3 (3.9 ± 0.7), AuNR-4 (5.8 ± 1.7), and AuNR-5 (7.3 ± 2.4). From these results, it is suggested that AuNRs with AR of larger than 3 favorably take well-aligned bundle-like structures with parallel packing, while spherical structures are formed by AR of less than 3.

The average distance between AuNR-3 in the bundle-like assembly is roughly evaluated to be 1.8 ± 1.0 nm, from the TEM image. Taking into consideration the ca. 1.8 nm length of an extended dodecyl group of DT,[18] surfactant molecules among the nanorods seem to take at least some extent interdigitated configurations. Therefore, it is suggested that the formation of the bundle-like structures depends on the van der Waals interactions among the dodecyl groups of capping DT molecules. For AuNR-3, AuNR-4, and AuNR-5, with relatively larger ARs, the van der Waals interactions among the dodecyl groups of capping DT molecules must induce the formation of bundle-like structure. However, as to AuNR-1 and AuNR-2, with relatively smaller ARs, bundle-like structures may be unfavorable because of decreased van der Waals interactions and uncomfortable parallel alignments.

These observations imply the following mechanism for the formation of assemblies. By sonication of a mixed solution of a hexane solution of DT-capped Au nanoparticles and an aqueous solution of 2R10enQ, microdroplets of the hexane solution including the assemblies are generated in the aqueous phase. Then, the assemblies are gradually extracted to the aqueous phase through being capped with 2R10enQ.

Figure 4 shows UV–vis–NIR extinction spectra of the aqueous solutions of the AuNR-2, AuNR-5, and the corresponding assemblies generated. In the colloidal solution of AuNR-2, a couple of plasmon bands due to transverse and longitudinal oscillation were observed around 520 and 630 nm, respectively, while they collapsed into one broad plasmon band around 580 nm in the assemblies (Figure 4a). These absorption spectral changes by the formation of bundle-like assemblies, are consistent with the theoretical calculations reported by Foss et al.[19] or El-Sayed et al.[20] Thus, it is suggested that AuNR-2s take spherical assemblies. In the colloidal solution of AuNR-5, on the other hand, plasmon bands appeared around 530 and 1300 nm, respectively (a broad band around 850 nm may be due to some shorter rods). The longitudinal plasmon band around 1300 nm substantially showed blue shift to 750 nm, while the

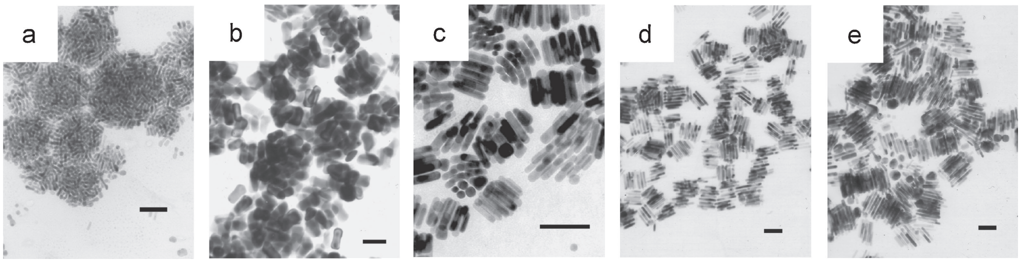

Figure 3. TEM images of assemblies formed from AuNRs with different aspect ratios, when 2R10enQ is used as the surfactant. Aspect ratios are: (a) 2.1 ± 1.0 (AuNR-1), (b) 2.4 ± 0.7 (AuNR-2), (c) 3.9 ± 0.7 (AuNR-3), (d) 5.8 ± 1.7 (AuNR-4), and (e) 7.3 ± 2.4 (AuNR-5). Scale bar is 50 nm.

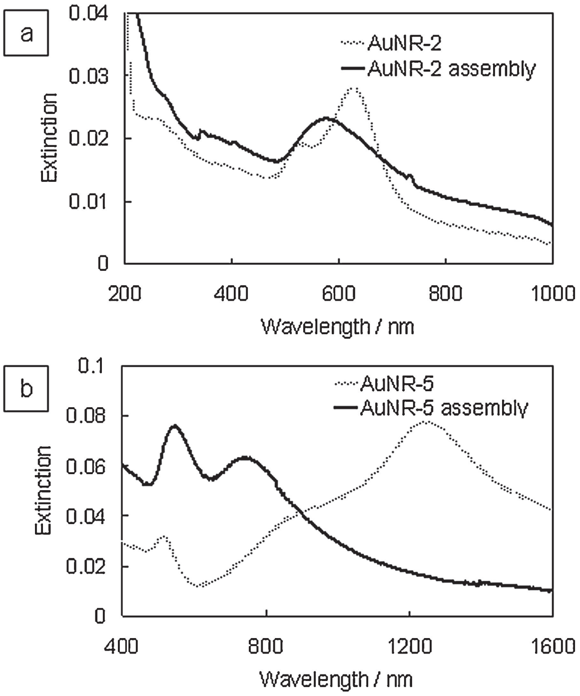

Figure 4. UV–vis–NIR extinction spectra of the aqueous colloidal solution (solid line) and the assemblies (dotted line) of AuNR-2 (a) and AuNR-5 (b), when 2R10enQ is used as the surfactant.

transverse plasmon band around 520 nm showed somewhat red shift to 550 nm. These results are quite consistent with the fact that AuNR-5s take the bundle-like structures in the assemblies, as has been theoretically simulated for the change in the AR value of Au nanorods.[3,19]

In conclusion, the present study demonstrated that the shape of aggregates of gold nanoparticles was profoundly affected by the shapes of original nanoparticle structures. Especially, the shape of the edges as well as AR of rod-shaped (bone and rod) nanoparticle can control the shape of their aggregates. These aspects are important for further precise control of the shape of nanoparticle aggregates. We are investigating the effects of surfactants on the formation and shape of three-dimensional assemblies.

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