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Centrifugal Shape Sorting of Faceted Gold Nanoparticles Using an Atomic Plane-Selective Surfactant

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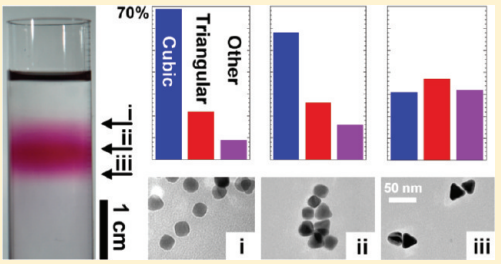
Supporting Information

ABSTRACT: Highly refined shape populations of gold nanoparticles (AuNPs) are important for emerging applications in catalysis, plasmonics, and nanomaterials growth. To date, research efforts have focused on achieving monodisperse shape by synthetic control or postsynthetic processing that relies on centrifugal sedimentation-based sorting schemes where differences in the particle mass and aspect ratios (e.g., rods and spheres) provide a driving force for separation. Here, we present a technique to reversibly modify the sedimentation coefficients of AuNPs possessing different shapes that would otherwise be virtually indistinguishable during centrifugal sedimentation due to their similar densities, masses, and aspect ratios by exploiting the preferential affinity of the surfactant cetyltrimethylammonium bromide (CTAB) for the Au(100) facet. The resulting tailored sedimentation coefficients enable AuNP shape sorting via density gradient centrifugation (DGC). DGC-refined populations of faceted AuNPs are shown to significantly enhance the growth rate of InAs nanowires when used as seed particles, emphasizing the importance of shape control for nanomaterials growth applications.



SECTION: Physical Processes in Nanomaterials and Nanostructures

Faceted metal nanoparticles (NPs) are central to numerous research efforts in the fields of catalysis,[1,2] plasmonics,[3,4] and nanomaterials growth.[5,6] Due to the strong dependence of chemical and physical properties on NP shape,[7] much effort has been devoted to producing homogeneous NP shape populations using both synthetic and postsynthetic methods. While progress has been made toward controlling the shape of metal NPs during synthesis,[8−11] the residual presence of spurious shapes still remains a challenge. Centrifugal sorting schemes to further refine as-produced NP shape distributions have shown great promise among NPs with starkly different aspect ratios or masses, particularly for separating rod-shaped NPs from spherical NPs or sorting NPs of different aggregation states.[12−14] However, the goal of sorting polyhedral NPs possessing similar sizes and aspect ratios has remained elusive due to their comparable sedimentation coefficients. Here, we demonstrate the ability to centrifugally sort AuNPs by shape using the surfactant cetyltrimethylammonium bromide (CTAB) that preferentially binds to Au(100) facets, thereby providing differences in the sedimentation coefficient as a function of AuNP shape.

The fabrication of faceted AuNPs used in this study has been reported previously.[6] Briefly, the gold precursor, $HAuCl_4$, is reduced in the presence of a surfactant, CTAB, which influences the AuNPs' growth kinetics along specific crystallographic planes due to its affinity for the Au(100) facet[15] (see Supporting Information). Although the size (mean diameter) of the as-synthesized AuNPs is well-controlled, this synthesis procedure produces a range of shapes including faceted NPs, spheres, and additional ill-defined shapes that are difficult to categorize. Because the nonfaceted byproducts are undesirable for applications such as nanowire growth, we focused our efforts on reducing the proportion of spherical and "other" (i.e., ill-defined) shapes of AuNPs by sorting via density gradient centrifugation (DGC). Because the relatively high buoyant density of these structures precludes an equilibrium isopycnic centrifugal sorting strategy like that used for carbon nanomaterials,[16,17] the AuNPs must be sorted transiently by sedimentation coefficient.

While most transient DGC sorting schemes rely on structurally inherent differences between sedimentation coefficients of the constituent species, the AuNPs studied here

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possess similar masses, densities, and frictional coefficients,[18] yielding essentially indistinguishable sedimentation coefficients, as defined by the following equation

$$s = \frac{m(1 - \rho_s/\rho_p)}{f}$$

where m is the total particle mass, ρ_s and ρ_p are the densities of the solvent and particle, respectively, and f is the frictional coefficient, which depends most heavily on the nanoparticle aspect ratio and the viscosity of the solvent.

As previously noted, the atomic plane selectivity of the cationic surfactant CTAB is exploited to grow shaped AuNPs. It follows that the most well-defined shapes synthesized via this method (i.e., those with ⟨100⟩ surface facets) are likely to host the highest amount of surfactant and affiliated hydration layers, thereby reducing the overall density and increasing the frictional coefficient of the encapsulated AuNP. Consequently, the differences in surfactant encapsulation between shapes provide differential sedimentation, thus potentially enabling sorting via DGC.

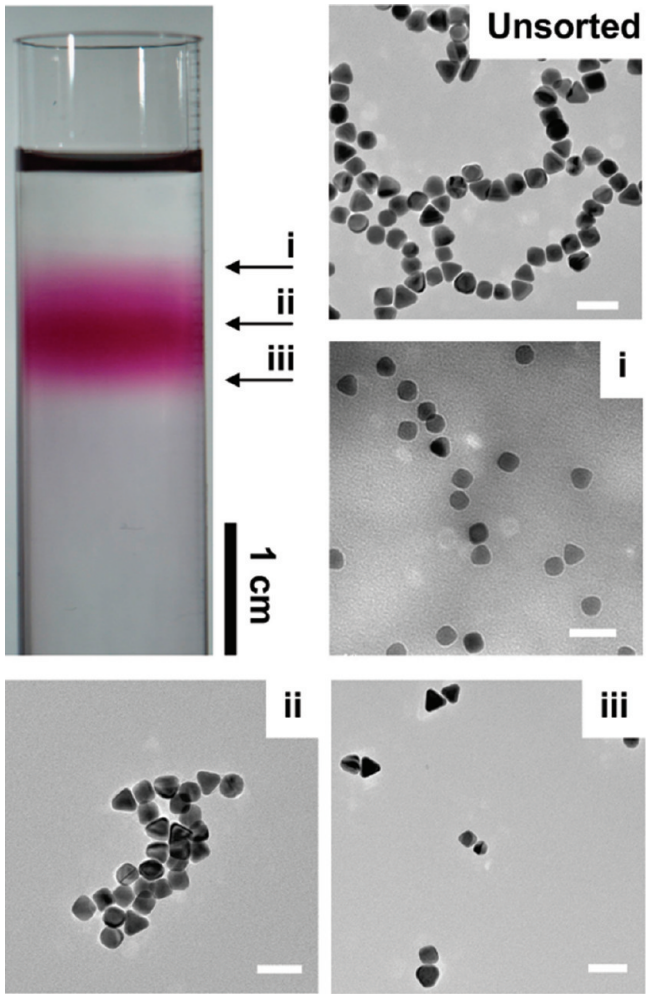

Figure 1. Photograph of a centrifuge tube after sorting AuNPs by shape in a density gradient. TEM images of the AuNPs before centrifugal sorting as well as the collected fractions indicated in the centrifuge tube photograph. TEM scale bars are 50 nm.

The as-produced AuNPs were first concentrated 40× by briefly centrifuging the solution to fully sediment the sample to the bottom of the centrifuge tube followed by decanting of the supernatant. The supernatant was then replaced with an aqueous 0.016 M CTAB solution and bath sonicated, which separates aggregates to provide a well-dispersed solution of individually CTAB-encapsulated AuNPs and concurrently provides differences in sedimentation coefficient due to the surface selectivity of the CTAB.

The density gradient medium iodixanol was selected due to its high viscosity[19] in an effort to slow the AuNPs to the point where subtle differences in sedimentation could be exploited for sorting. A 1 mL underlayer of 60% w/v iodixanol (1.32 g cm^{-3}) was added to a 13.2 mL Ultra Clear centrifuge tube (Beckman), on top of which a 10 mL linear density gradient of 30−40% w/v iodixanol (1.16−1.21 g cm^{-3}) was formed. All solutions included 0.016 M CTAB to inhibit AuNP aggregation during sorting. Finally, 200 μL of the concentrated AuNP solution was layered on top, and the tube was centrifuged at 4000 rpm (2000 × g) for 70 min using a Beckman SW41Ti rotor.

After centrifugation, a wide band of AuNPs was observed within the density gradient, as shown in Figure 1a. Quarter-millimeter fractions were collected from the tube using a piston gradient fractionator (Biocomp Instruments) and used to prepare transmission electron microscopy (TEM) samples for analysis. Representative TEM images from three selected fractions are shown in Figure 1b−d, and the accompanying distributions of shapes obtained via analysis of numerous additional TEM images are presented in Table 1 (see Supporting Information).

Table 1. Distribution of Shapes in Unsorted AuNPs and Sorted Fractions i−iii (Figure 1) Obtained via TEM Image Analysis

fraction	cubic (%)	triangular (%)	spherical (%)	other (%)
unsorted	36	39	2	23
i	69	22	6	3
ii	58	26	6	10
iii	31	37	12	20

Fractions near the top of the AuNP band are heavily enriched in faceted particles (>90% are cubic or triangular), while spherical and other shapes are minimized. Conversely, the lower fractions in the centrifuge tube are enriched in these nonfaceted species. This trend is consistent with the hypothesis that the surface selectivity of the adsorbed CTAB provides adequate sedimentation coefficient differentiation for sorting. Shapes with few or poorly defined Au(100) surface planes are expected to host fewer surfactant molecules on the surface, thus providing a higher buoyant density relative to the faceted NPs. Because higher NP buoyant density leads to a larger sedimentation coefficient, the nonfaceted NPs reach a lower point in the centrifuge tube following centrifugation. This concept can be extended to well-defined polyhedrons of different shapes to explain the observed enrichment of cubic AuNPs relative to triangular particles at the top of the band, where the greater Au(100) surface area present on cubic structures compared to pyramidal particles dominated by (111) planes[20] hosts more surfactant and thus leads to reduced sedimentation (see Supporting Information).

Faceted AuNPs have recently been shown to possess superior growth characteristics for semiconductor nanowires

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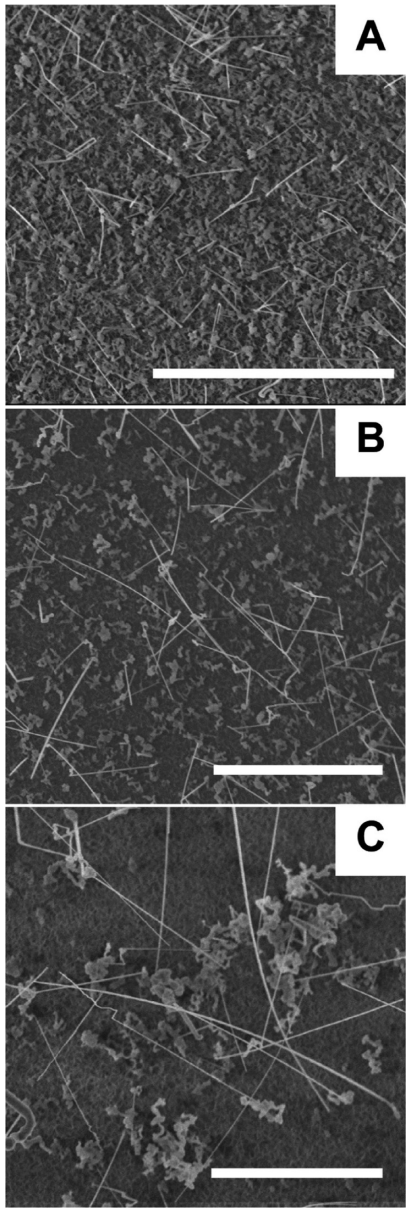

Figure 2. SEM images of NWs grown from each set of AuNPs: (A) spherical AuNPs; (B) unsorted polydisperse faceted AuNPs; (C) DGC-enriched faceted AuNPs. Scale bars are 5 μm.

(NWs) compared to spherical AuNPs.[6] In particular, a notable enhancement in the NW growth rate was demonstrated for faceted AuNPs. However, this earlier study used mixtures of faceted and spherical AuNPs similar to the aforementioned unsorted sample (see unsorted fraction in Table 1). Consequently, by employing enriched populations of faceted AuNPs, further enhancements in NW growth rates should be achievable.

To test this hypothesis, InAs NWs were grown by an established physical vapor transport method using AuNP seeds.[6] We compared the following three AuNP samples: commercially available spherical AuNPs (Ted Pella, Inc.), unsorted polydisperse faceted AuNPs (see unsorted fraction in Table 1), and DGC-enriched faceted AuNPs (fraction i in Table 1). Each of these AuNP samples was deposited onto Si(100) substrates after thoroughly rinsing the particles of the surfactant and iodixanol via repeated centrifugation and

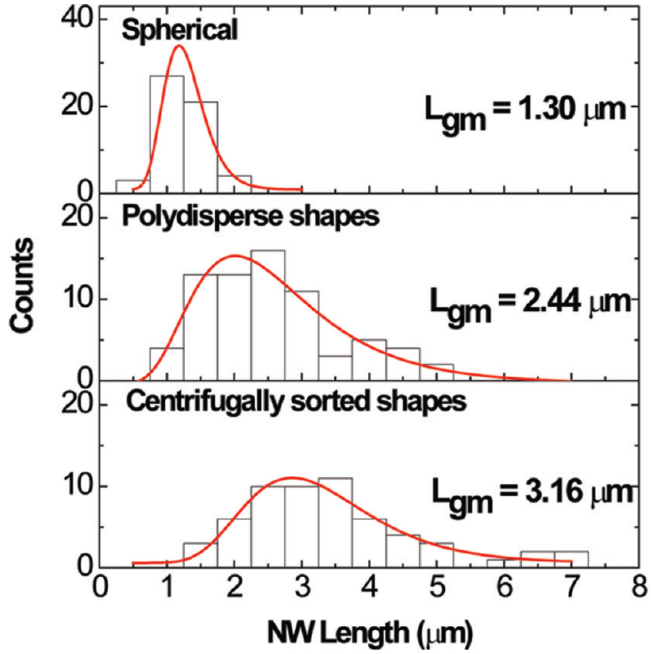

Figure 3. Histograms of NW lengths fabricated using spherical AuNPs, unsorted polydisperse faceted AuNPs, and DGC-enriched faceted AuNPs. Log-normal distribution fits and geometric mean NW lengths, L_{gm}, are shown.

resonication in deionized water. The NWs were grown on all substrates simultaneously in a tube furnace by flowing 10% H_2 in Ar over a sublimed InAs solid source toward the AuNP samples for 1 h.

Scanning electron microscopy (SEM) images of the resulting InAs NWs grown from each of the three AuNP samples are presented in Figure 2, and the corresponding length histograms obtained from an analysis of several SEM images are shown in Figure 3. The observed length distributions reveal a clear dependence on the degree of faceting in the initial AuNP seed material. The geometric mean of the NW lengths, L_{gm}, for the DGC-enriched faceted AuNPs is nearly 30% greater than that for the unsorted polydisperse faceted AuNPs and 140% greater than the spherical AuNPs. This growth rate enhancement is consistent with previous studies where it was found that flat surfaces on a faceted seed particle can enhance wetting,[21] which directly impacts the NW growth kinetics.[6]

In conclusion, we have introduced a DGC strategy for isolating faceted AuNPs from nonfaceted AuNPs with similar aspect ratios. By using an atomic plane-selective surfactant, CTAB, the structurally similar sedimentation coefficients of faceted and nonfaceted AuNPs are differentially modified, thus allowing sedimentation-based DGC to sort by AuNP shape. This approach provides substantial enrichment of cubic and triangular AuNPs over spherical and ill-defined AuNPs, thus enabling direct enhancement of InAs NW growth rates. The additional observed enrichment between cubic and triangular faceted shapes suggests that this approach can be further tuned to yield monodisperse shapes of a variety of NP materials by selecting appropriate surface-selective surfactants. In addition to NW growth, the ability to isolate monodisperse populations of shape-selected NPs is expected to impact plasmonics, catalysis, and related fields that require precise control over NP faceting.

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■ ASSOCIATED CONTENT

Supporting Information

Additional experimental details and TEM images of unsorted and sorted AuNP samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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