Faceted Gold Nanorods: Nanocuboids, Convex Nanocuboids, and Concave Nanocuboids

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Supporting Information

ABSTRACT: Au nanorods are optically tunable anisotropic nanoparticles with built-in catalytic activities. The state-of-the-art seed-mediated nanorod synthesis offers excellent control over the aspect ratios of cylindrical Au nanorods, which enables fine-tuning of plasmon resonances over a broad spectral range. However, facet control of Au nanorods with atomic-level precision remains significantly more challenging. The coexistence of various types of low-index and high-index facets on the highly curved nanorod surfaces makes it extremely challenging to quantitatively elucidate the atomic-level structure–property relationships that underpin the catalytic competence of Au nanorods. Here we demonstrate that cylindrical Au nanorods undergo controlled facet evolution during their overgrowth in the presence of Cu2+ and cationic surfactants, resulting in the formation of anisotropic nanostructures enclosed by well-defined facets, such as low-index faceting nanocuboids and high-index faceting convex nanocuboids and concave nanocuboids. These faceted Au nanorods exhibit enriched optical extinction spectral features, broader plasmonic tuning range, and enhanced catalytic tunability in comparison to the conventional cylindrical Au nanorods. The capabilities to both fine-tailor the facets and fine-tune the plasmon resonances of anisotropic Au nanoparticles open up unique opportunities for us to study, in great detail, the facet-dependent interfacial molecular transformations on Au nanocatalysts using surface-enhanced Raman scattering as a time-resolved spectroscopic tool.

KEYWORDS: Localized plasmon resonances, nanocatalysis, surface-enhanced Raman scattering, Au nanorods, low-index facets, high-index facets

Development of detailed, quantitative understanding of the intriguing geometry-dependent optical, electronic, and catalytic characteristics of metallic nanoparticles requires precise control over the particle shapes and facets. One of the most impactful breakthroughs in shape-controlled nanoparticle synthesis has been the seed-mediated anisotropic growth of single-crystalline Au nanorods (NRs) guided by a structure-directing ion, Ag+, and halide-containing cationic surfactants. The quantitative assignments of the crystallographic facets on Au NRs, nevertheless, are still under intense debate, and subtle modification of the NR synthesis protocols may drastically change the local curvatures.

Our enthusiasm for Au NRs stems from the unique combination of their tunable plasmon resonances with exceptional catalytic activities. The state-of-the-art NR synthesis allows one to fine-tune the plasmon resonances of Au NRs over a broad spectral range spanning the entire visible and near-infrared regions through tight control over the NR aspect ratios. It remains significantly more challenging to fine-tailor, at the atomic level, the crystallographic facets exposed on NR surfaces, which determine the site-specific catalytic performance of Au NRs. While Au NRs typically exhibit a cylindrical morphology with two rounded, quasihemispherical ends, they should be more accurately described as reconstructed anisotropic nanocrystals enclosed by various types of facets. The quantitative assignments of the crystallographic facets on Au NRs, nevertheless, are still under intense debate, and subtle modification of the NR synthesis protocols may drastically change the local curvatures.

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and exposed facets on the NR surfaces. Recent high-resolution electron microscopic studies elucidate that each single-crystalline Au NR is essentially enclosed by coexisting high-index and low-index facets with comparable dimensions and thermodynamic stabilities. The structural complexity of the NR surfaces, however, remains a substantial obstacle to the quantitative assessment of the facet-dependent intrinsic catalytic activities of Au NRs.

Here we demonstrate that controlled overgrowth of Au NRs guided by Cu$^{2+}$ and cationic surfactants leads to the formation of various anisotropic Au nanostructures, each of which is enclosed exclusively by one specific type of low-index or high-index facet. This NR overgrowth approach allows us to precisely tailor the facets of anisotropic Au nanoparticles while still retaining the capability to fine-tune the particle aspect ratios, advancing the NR synthesis toward an unprecedented level of geometry control. As demonstrated in this work, creation of well-defined facets on plasmonically tunable Au NRs provides unique opportunities for us to gain quantitative insights into the facet-dependent molecular transformations on Au nanocatalysts using surface-enhanced Raman scattering (SERS) as an ultrasensitive in situ spectroscopic tool.

Our success in facet control of anisotropic nanostructures essentially relies on the utilization of Cu$^{2+}$ ions and surface capping surfactants to guide the facet evolution during NR overgrowth. For face-centered cubic (fcc) noble metals, such as Au, Ag, and Pd, the high-index facets have surface energies significantly higher than those of the low-index $\{111\}$ and $\{100\}$ facets and thus are typically eliminated during nanocrystal growth. However, interactions of foreign ions and

Figure 1. Synthesis and structural characterizations of Au NCBs, CVNCBs, and CCNCBs. (A) Schematic illustration of the selective formation of Au NCBs, CVNCBs, and CCNCBs under appropriate conditions. (B,C) SEM and (D) TEM images of Au NCBs. (E) TEM image of one individual Au NCB viewed along the [001] projection. The insets of panel E show the geometric model and SAED pattern of the Au NCB particle. (F,G) SEM and (H) TEM images of Au CVNCBs. (I) TEM image of one individual Au CVNCB viewed along the [001] projection. The bottom insets of panel I show the geometric model and SAED pattern of the Au CVNCB particle. (J,K) TEM images and the corresponding geometric models of individual Au CVNCBs with various orientations on the TEM grid. (L,M) SEM and (N) TEM images of Au CCNCBs. (O) TEM image of one individual Au CCNCB viewed along the [001] projection. The insets of panel O show the geometric model and SAED pattern of the Au CCNCB particle. (P,Q) TEM images and the corresponding geometric models of individual Au CCNCBs with various orientations on the TEM grid.
surfactants with nanocrystal surfaces may shift the relative energies of various facets and consequently guide the nanocrystals to evolve into thermodynamically unexpected morphologies.\(^3\) In addition, structure-directing ions and surfactants may also fine-regulate, either independently or synergistically, the reaction rates, which determine the degree of supersaturation of the crystal growth units, another important factor governing the facet evolution during nanocrystal overgrowth.\(^3\) As schematically illustrated in Figure 1A, we used the conventional cylindrical Au NRs with rounded ends (Figure S1 in Supporting Information) as the starting materials, which evolved into Au nanocuboids (NCBs) upon overgrowth in the presence of Cu\(^{2+}\) and cetyltrimethylammonium chloride (CTAC). Strikingly different shape evolution was observed in the presence of Cu\(^{2+}\) and binary surfactant systems. Overgrowth of Au NRs in the benzyldimethylhexa-decylammonium chloride (BDAC)/CTAC binary surfactant system resulted in Au convex nanocuboids (CVNCBs), while Au concave nanocuboids (CCNCBs) were obtained in the presence of CTAB/CTAC binary surfactants.

We used a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy-dispersive spectroscopy (EDS) to fully characterize the crystalline structures and bulk compositions of the Au NCBs, CVNCBs, and CCNCBs. As shown in Figure 1B–D, each Au NCB exhibited well-defined cuboidal morphology enclosed by 6 low-index {100} facets. The SAED pattern of an individual Au NCB projected along the [001] zone axis (Figure 1E) further verified the single-crystalline fcc structure of the particle. A CVNCB can be geometrically derived from a NCB upon introduction of surface indentation to the {100} facet (Figure 1L–Q). When a single-crystalline CCNCB particle was projected along the [001] zone axis, 8 out of the 24 facets became parallel to the projection direction and the average dihedral angles were measured to be 23.2° on average, indicating that each CVNCB was enclosed by 24 high-index \{730\} facets.\(^3\) In striking contrast to CVNCBs, a CCNCB is geometrically derived from a NCB upon introduction of surface indentation to the \{100\} facet (Figure 1L–Q). While none of the Cu, N, Cl, or Br elements from the surface adsorbates was detectable using EDS (Figure S2 in Supporting Information), X-ray photoelectron spectroscopy (XPS) results clearly showed the presence of both Cu species and surfactants on the surfaces of NCBs, CVNCBs, and CCNCBs (Figure S3 in Supporting Information), X-ray photoelectron spectroscopy (XPS) results also verified the presence of Ag and CTAB on the surfaces of the cylindrical Au NRs (Figure S4 in Supporting Information). While the atomic ratios of Cu/Au on the surfaces of NCBs, CVNCBs, and CCNCBs were almost the same, the packing densities of the surfactants on the high-index faceting CVNCBs and CCNCBs were significantly higher than those on the low-index faceting NCBs as reflected by the atomic ratios of Cl/Au and Br/Au (Figure 2A), suggesting that stabilization of high-index facets requires relatively high surfactant packing densities. Au NRs exhibited an intermediate surfactant packing density most likely due to the coexistence of high-index and low-index facets on their surfaces. It has been reported that halide-containing cationic surfactants, such as CTAB, CTAC, and BDAC, form positively charged, self-assembled bilayers on Au nanoparticle surfaces.\(^8\) As shown in Figure 2B, the surfaces of Au NCBs, CVNCBs, CCNCBs, and NRs were all positively charged, and the \(\zeta\)-potential values correlated very well with the
relative surface packing densities of the surfactants. High-resolution XPS spectra of the Cu 2p region (Figure 2C) revealed that Cu$^{2+}$ was mostly reduced to Cu(I) species on the surfaces of Au NCBs, CVNCBs, and CCNCBs. Interestingly, we also identified a trace amount of Cu(II) species on the surfaces of CVNCBs and CCNCBs, while only Cu(I) signals were detectable on the NCB surfaces. The XPS results indicate that the coexistence of Cu(I) and Cu(II) species may play a crucial role in stabilizing the high-index \{hk0\} facets, though the detailed mechanism still remains unclear at this stage. The surface adsorption of Cu(I) and surfactants did not modify the lattices or the electronic band structures of Au surface atoms to any detectable extent because no peak shift or split was observed in the high-resolution XPS spectra of the Au 4f region (Figure 2D) in comparison to the spectrum of bulk Au.

The formation of well-defined \{100\} facets on Au NCBs upon NR overgrowth was observed in the presence of Cu$^{2+}$ when CTAC was used as the sole surfactant. If BDAC was used as the surfactant, faceted Au NRs with irregular convex surfaces were obtained while the use of CTAB as the surfactant resulted in faceted NRs with concave surfaces and truncated corners (Figure S5A,B in Supporting Information). In BDAC/CTAB binary surfactants, irregularly shaped Au NRs were obtained (Figure S5C in Supporting Information) as the development of surface convexity and concavity canceled out. These interesting observations imply that BDAC facilitated the formation of convex surfaces while CTAB favored surface concavity. Therefore, the combination of CTAC with BDAC or CTAB provided a unique pathway to generate well-defined high-index \{hk0\} facets upon selective creation of surface convexity and concavity. In addition to the surfactants, Cu$^{2+}$ ions have also been exploited as a shape-directing reagent for the facet-controlled synthesis of various monometallic or bimetallic nanoparticles. Under our experimental conditions, we found that only within narrow Cu$^{2+}$ concentration windows could Au NCBs, CVNCBs, and CCNCBs with well-defined...
The faceted anisotropic Au nanoparticles exhibited greatly enriched extinction spectral features and enhanced plasmonic tunability in comparison to the conventional cylindrical Au NRs. The aspect ratios of the Au NCBs, CVNCBs, and CCNCBs could be fine-tuned either by changing the aspect ratio of the starting Au NR seeds or by adjusting the amount of HAuCl₄ added. The Au CVNCBs and CCNCBs shown in Figure 1 were both derived from NCBs with the same dimensions, which allowed us to study the modifications of plasmonic features caused by surface convexity and concavity. The top panel of Figure 3A shows the optical extinction spectra of aqueous colloidal suspensions of Au NRs, NCBs, CVNCBs, and CCNCBs at nominally the same particle concentration of 2.0 × 10¹⁰ particles mL⁻¹. Although Au NCBs (length = 115 ± 3.8 nm; transverse width = 46 ± 1.8 nm; aspect ratio = ∼2.5) had an aspect ratio lower than that of the cylindrical Au NRs (length = 98 ± 4.2 nm; transverse width = 32 ± 2.1 nm; aspect ratio = ∼3), their transverse and longitudinal plasmon resonances both red-shifted due to their cuboidal morphology. Similar plasmon red shifts were also observed when Au or Ag nanospheres were converted into nanocubes of similar sizes. Interestingly, introduction of surface convexity to the NCBs caused spectral blue shifts of the plasmon resonances, whereas surface concavity significantly red-shifted both the transverse and longitudinal plasmon resonances. All the faceted anisotropic nanostructures, especially the CVNCBs and CCNCBs, exhibited significantly enhanced transverse plasmon peak intensities in comparison to that in the cylindrical NRs. To more quantitatively understand the geometry-dependent plasmonic characteristics of the particles, we used the discrete dipole approximation (DDA) method to calculate the extinction spectra of a Au NR, NCB, CVNCB, and CCNCB with geometric parameters directly extracted from the SEM and TEM images. Both the plasmon resonance frequencies and spectral line shapes calculated by DDA were in excellent agreement with the experimental results (the bottom panel of Figure 3A). The calculated extinction spectrum of CCNCB exhibited multiple transverse plasmon peaks, while in the experimental extinction spectrum of colloidal CCNCBs, the multiple extinction peaks merged into one asymmetrically broadened transverse plasmon band due to the ensemble averaging of the particle orientations and nonuniformity of the surface concavity of the particles.

Because the plasmonic features were sensitively dependent on both the aspect ratios and surface convexity/concavity of the particles, we were able to use extinction spectroscopy in combination with electron microscopies to gain detailed insights into the nanoparticle structural evolution as the amount of HAuCl₄ varied. In the presence of Cu²⁺ and CTAC, the NR overgrowth resulted in the formation of Au NCBs whose aspect ratios progressively decreased as the amount of HAuCl₄ increased until reaching a threshold point where irregularly shaped nanoparticles started to form (Figure S7A–D in Supporting Information). Both the longitudinal and transverse plasmon resonances slightly blue-shifted and became progressively more intense as the aspect ratios of NCBs decreased (Figure S7E in Supporting Information). Au CVNCBs underwent a unique geometric evolution as the amount of HAuCl₄ varied. The surface convexity was initiated at discrete locations, then gradually propagated along the longitudinal axis of the particles, and eventually merged into continuous {730} facets as an increasing amount of Au was grown on the nanoparticle surfaces (Figure S7F–I in Supporting Information). The longitudinal plasmon resonance blue-shifted, and a double-peak transverse plasmon feature emerged (Figure S7J in Supporting Information) upon the formation of discontinuous surface convexity. The extinction peak at ∼570 nm completely disappeared when fully developed CVNCBs with well-defined {730} facets formed. For Au CCNCBs, both the degree of surface indentation and transverse widths increased with the amount of HAuCl₄ (Figure S7K–N in Supporting Information). Both the longitudinal and transverse plasmon peaks of Au CCNCBs progressively red-shifted and became more intense as the amount of HAuCl₄ increased (Figure S7O in Supporting Information).

The facet Au NRs exhibited enhanced plasmonic refractometric sensitivities in comparison to the conventional cylindrical Au NRs. As shown in Figure S8 in Supporting Information, the shift of plasmon resonance wavelengths exhibited a linear dependence on the refractive index of the surrounding medium. For all the anisotropic nanostructures, their longitudinal plasmon resonances displayed higher refractometric sensitivities than transverse plasmon resonances. The longitudinal plasmon resonance of CCNCBs exhibited a refractometric sensitivity of 650 nm RIU⁻¹, significantly higher than those of NRs, NCBs, and CVNCBs (Figure 3B). While the transverse plasmon resonance of Au NRs was essentially insensitive to the refractive index of the surrounding medium, the transverse plasmon resonances of Au NCBs, CVNCBs, and CCNCBs all exhibited greatly enhanced refractometric sensitivities compared to Au NRs. The calculated refractometric sensitivities of various plasmon modes were in excellent agreement with the experimental results (Figure 3B and Figure S8 in Supporting Information). The faceted Au NRs, especially CCNCBs, hold great promise for multiplex refractometric molecular sensing because of the high refractometric sensitivities of both the longitudinal and transverse plasmon modes.

The surface convexity and concavity also introduced interesting modifications to the near-field plasmonic properties of the nanoparticles. Figure 3C shows the cross-sectional views of calculated near-field enhancements (E/E₀) plotted in a logarithm scale) of a Au NR, NCB, CVNCB, and CCNCB at resonance excitations. Much higher local-field enhancements were generated upon excitation of the longitudinal plasmons than the transverse plasmons due to the stronger coupling of light with the plasmons along the longitudinal direction. The NCB, CVNCB, and CCNCB all exhibited significantly more intense local-field enhancements than the cylindrical NR upon excitation of their transverse plasmon resonances. The maximum plasmonic field enhancements were located in close proximity to the particle corners and edges, providing hot spots for SERS on individual nanoparticles. Figure 3D shows the SERS spectra collected on colloidal Au NRs, NCBs, CVNCBs, and CCNCBs (∼1.0 × 10¹¹ particles mL⁻¹) coated...
with 4-nitrothiophenol (4-NTP) self-assembled monolayers (SAMs) at 785 nm excitations. After displacements of CTAC, CTAB, or BDAC with 4-NTP on the nanoparticle surfaces, both the facets and particle geometries were well-preserved (Figure S9 in Supporting Information). We estimated the enhancement factors (EFs) by comparing SERS signals to normal Raman signals from pure 4-NTP based on three Raman modes at 1076, 1338, and 1570 cm\(^{-1}\), respectively (see details in Supporting Information). Among the four nanostructures, Au NCBs exhibited the highest EFs on the order of \(10^7\) because of the presence of hot spots at the particle corners/edges and the resonance excitation of their longitudinal plasmon. Although the plasmons of Au CVNCBs and CCNCBs were off-resonance with the excitation laser, EFs on the order of \(10^6\) were still achieved on individual colloidal nanoparticles. These empirical EFs represented the enhancements averaged over the entire nanoparticle surfaces. The localized EFs in the hot spots were estimated to be at least 1 order of magnitude higher than

![Figure 4](image_url)

Figure 4. Facet-dependent catalytic activities of Au NCBs, CVNCBs, and CCNCBs. (A) Schematic illustration of the catalytic hydrogenation of surface-adsorbed 4-NTP by AB. The reaction is illustrated as a two-step consecutive process (4-NTP is the reactant, DMAB is the intermediate, and 4-ATP is the final product). Two-dimensional color-coded intensity maps of time-resolved SERS spectra collected from 4-NTP molecules adsorbed on the surfaces of Au (B) CVNCB, (D) CCNCB, and (E) NCB at different reaction times after exposure to 2 mM AB. (C) Representative SERS spectra collected from 4-NTP molecules adsorbed on the surfaces of Au CVNCBs at reaction times of 0, 70, and 116 s. (F) \(\theta_{4\text{-NTP}}\) and (G) \(\theta_{4\text{-ATP}}\) as a function of reaction time \(t\) during the reactions catalyzed by Au CVNCBs, CCNCBs, and NCBs. The error bars show the standard deviations obtained from five experimental runs under identical reaction conditions. The results of the least-squares curve fitting are shown as solid curves for the reactants and products. (H) Comparison of \(k_1\) and \(k_2\) on Au CVNCBs, CCNCBs, and NCBs. (I) \(k_1\) and (J) \(k_2\) as a function of AB concentrations \(C_{AB}\) on Au CVNCBs, CCNCBs, and NCBs. The results of the least-squares fitting using the Langmuir adsorption isotherms are shown as solid curves. Comparison of (K) \(K_{EQ1}\) and \(K_{EQ2}\) and (L) \(\alpha_1\) and \(\alpha_2\) of the two-step surface reactions on Au CVNCBs, CCNCBs, and NCBs.
the average EFs. We also used the DDA method to calculate the surface-averaged field enhancements at both the excitation wavelength (785 nm) and the Raman scattering wavelengths. The calculated average field enhancements (Figure 3F) correlated extremely well with the experimental SERS results. The experimentally estimated EFs were ∼100 times higher than the calculated \( \frac{E_0}{E_{\text{Raman}}} \) values because the DDA method only calculated the electromagnetic enhancements without considering the chemical enhancements in SERS.

The well-defined facets of Au NCBs, CVNCBs, and CCNCBs enabled us to quantitatively correlate the atomic-level surface structures with the catalytic activities of the nanoparticles. We used room temperature catalytic hydrogenation of 4-nitrophenol (4-NP) by ammonia borane (AB) as a model reaction to assess the catalytic activities of various facets. AB is a stable hydrogen storage material in aqueous environments with hydrogen storage capacity as high as 19.5 wt \%\(^{47}\). When AB and 4-NP were mixed in aqueous K\textsubscript{2}CO\textsubscript{3} solution (pH ∼10), no hydrogenation reaction was observed at room temperature over extended time periods up to a few days. Hydrogen release from AB can be catalyzed by metallic nanoparticles, and the released hydrogen may be further used to drive hydrogenation of organic molecules.\(^{48}\) Rapid hydrogenation of 4-NP was observed when AB and 4-NP were mixed in aqueous K\textsubscript{2}CO\textsubscript{3} solution in the presence of colloidal Au nanoparticles, and the reaction kinetics could be monitored, in real time, using UV–vis spectroscopy. As shown in Figure S10 in Supporting Information, the high-index faceting CVNCBs and CCNCBs exhibited catalytic activities much higher than those of the low-index faceting NCBs, and Au NRs showed intermediate catalytic activities due to the coexistence of high-index and low-index facets on their curved surfaces. However, the UV–vis spectroscopic results only allowed us to qualitatively compare the relative apparent activities of various types of Au facets. The UV–vis spectroscopy measured the overall kinetics of multistep processes including adsorption of the reactants, surface-catalyzed molecular transformations, and desorption of reactants, all of which might be further complicated by the surface-adsorbed surfactants. Significant deviation from pseudo-first-order kinetics was observed even though AB was in great excess with respect to 4-NP. In addition, an induction time during which no hydrogenation occurred was observed at the initial stage of the reactions, which arose most likely from diffusion and surface adsorption of 4-NP and AB.

The strong plasmonic field enhancements on Au NCBs, CVNCBs, and CCNCBs provided unique opportunities for us to more quantitatively study the catalytic hydrogenation of surface-adsorbed 4-NTP by AB through time-resolved SERS measurements. We used a confocal Raman microscope with an excitation volume of \( \sim 10 \) to measure the \( \frac{E_0}{E_{\text{Raman}}} \) because 4-NTP molecules were preadsorbed on the nanocatalyst surfaces, no induction time was observed in time-resolved SERS. We chose the Raman peaks at 1076, 1338, and 1570 cm\(^{-1}\) to quantify the fractions of reactant (\( \theta_{\text{4NTP}} \)) and product (\( \theta_{\text{4ATP}} \)) catalytic hydrogenation reaction at different AB concentrations. Both Au CVNCBs and CCNCBs exhibited significantly higher catalytic activities, with \( k_1 \) approximately 10 times larger than that of Au NCBs. The enhanced catalysis on high-index facets can be interpreted in the context of undercoordinated surface atoms at the surface atomic steps, which serve as the active sites for heterogeneous catalysis.\(^{3,31,46,53,54}\)

As illustrated in Figure S12 in Supporting Information, the surface atoms on the \{100\} facet have an atomic coordination number of 8 while significant fractions of surface atoms have a lower coordination number of 6 on the high-index \{730\} and \{830\} facets. The \{730\} facet exhibited catalytic activity even higher than that of the \{830\} facet because of its higher fraction of surface atoms with a coordination number of 6.

To gain further mechanistic insights into the enhanced catalysis on high-index facets, we studied the kinetics of the catalytic hydrogenation reaction at different AB concentrations. As shown in Figure 4I, the pseudo-first-order rate constants, \( k_1 \) and \( k_2 \), both increased with the AB concentration, \( C_{\text{AB}} \). The rate constants on high-index facets were more sensitively dependent on \( C_{\text{AB}} \) than those on the low-index \{100\} facet. Under our experimental conditions, both \( k_1 \) and \( k_2 \) appeared to be proportional to the surface coverage of AB (\( \theta_{\text{AB}} \)) and the adsorption of AB was found to follow the Langmuir isothermal adsorption. The reaction kinetics could be well-described using the apparent rate laws for an elementary reaction between the

\[ \theta_{\text{4NTP}} = e^{-k_1 x_1} \] \[ \theta_{\text{4ATP}} = 1 + \frac{(k_1 x_1 e^{-k_1 x_1} - k_2 x_1 e^{-k_2 x_1})}{k_2 - k_1} \]
preimmobilized 4-NTP and surface-adsorbed AB, though the detailed mechanisms might be even more complicated. The equilibrium constants for adsorption/desorption of AB on various Au facets were obtained by fitting the experimental data with the following equations:

\[ k_1 = \alpha_1\beta_{AB1} = \alpha_1\frac{K_{EQ1}C_{AB}}{1 + K_{EQ1}C_{AB}} \]  
\[ k_2 = \alpha_2\beta_{AB2} = \alpha_2\frac{K_{EQ2}C_{AB}}{1 + K_{EQ2}C_{AB}} \]

where \( \alpha_1 \) and \( \alpha_2 \) are two fractional factors linking the pseudo-first-order rate constants and surface coverages of AB. \( K_{EQ1} \) and \( K_{EQ2} \) represent two equilibrium constants for adsorption/desorption of AB on Au surfaces preadsorbed with 4-NTP and DMAB, respectively. \( K_{EQ1} \) was significantly smaller than \( K_{EQ2} \) on all three nanostructures (Figure 4K,L), suggesting that the conversion of 4-NTP to DMAB facilitated the adsorption of AB onto the Au surfaces. Therefore, the conversion of 4-NTP into DMAB was the rate-limiting step. While both \( \alpha_1 \) and \( \alpha_2 \) appeared facet-independent, the \( K_{EQ1} \) and \( K_{EQ2} \) values on the high-index facets were significantly higher than those on the \{100\} facet, strongly indicating that the undercoordinated surface atoms on high-index facets facilitated the surface adsorption of AB and thus served as catalytically more active sites for the hydrogenation reaction than the close-packed surface atoms on the low-index facets.

The ratios between \( k_1 \) and \( k_2 \), which determined the fraction of DMAB, were both facet- and \( C_{AB} \)-dependent. As shown in Figure S13A in Supporting Information, the \( k_1/k_2 \) values on the high-index facets were higher than those on the \{100\} facet at the same AB concentrations. Therefore, a higher fraction of the intermediate could be effectively modulated either by tuning the facets of Au nanocatalysts or by changing the concentration of AB.

In summary, we have demonstrated that well-defined low-index and high-index facets can be controllably created on the surfaces of cylindrical Au NRs through overgrowth processes that are synergistically guided by Cu\(^{2+}\) and cationic surfactants. CTAC facilitates the formation of Au NCBs enclosed by \{100\} facets. When binary surfactants, such as CTAC/BDAC and CTAC/CTAB, are used, surface convexity and concavity can be controllably created through which high-index facetting Au CVNCBs and CCNCBs are obtained. This controlled NR overgrowth approach allows us to fine-tailor both the aspect ratios and the facets of anisotropic Au nanostructures, advancing the geometry control of nanoparticles to an unprecedented level of precision and detail far beyond the state-of-the-art seed-mediated Au NR synthesis. The surface convexity and concavity of facetted Au nanostructures provide additional geometric parameters that one can tailor to further fine-tune the far-field and near-field plasmonic properties of nanoparticles. Creation of well-defined facets on optically tunable Au NRs provides unique opportunities of using SERS as a noninvasive in situ spectroscopic tool to fully characterize catalytic molecular transformations at nanoparticle–molecule interfaces in real time, further enabling us to gain quantitative insights into the underlying relationship between the atomic-level surface structures and intrinsic activities of Au nanocatalysts.

## Associated Content

### Supporting Information

Experimental details and additional figures including SEM images, TEM images, extinction spectra, EDS, XPS, and DDA results as noted in the text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b01286.

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**Notes**
The authors declare no competing financial interest.

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