Polyvinylpyrrolidone-induced anisotropic growth of gold nanoprisms in plasmon-driven synthesis

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Experimental Procedures

Materials

Tetrachloroauric acid (HAuCl₄), silver nitrate (AgNO₃), sodium iodide (NaI), polyvinylpyrrolidone (PVP, MW = 40,000), N-methyl-2-pyrrolidone (99.5%), methanol (99.8%), formaldehyde (36.5-38% in H₂O), formic acid (> 95%), ethanol, hydrochloric acid (HCl), and sodium borohydride (NaBH₄) were purchased from Sigma Aldrich (St. Louis, MO). Trisodium citrate (Na₃C₆H₅O₇) and sodium hydroxide (NaOH) were purchased from Fisher Scientific (Hampton, NH). All chemicals were used as received without further purification. All glassware was cleaned with aqua regia solution, followed by copious rinsing with Nanopure™ H₂O (Barnstead, 18.2 MΩ cm) prior to use. Caution! Aqua regia is highly corrosive and toxic: handle with care and use appropriate personal protection equipment.

Instrumentation

Ultraviolet–visible–near infrared (UV–vis–NIR) spectra of Au nanoprisms were collected on a Shimadzu UV-1800 spectrophotometer. The complete Au nanoprism extinction spectrum (400-1600 nm) was obtained on a Cary-5000 UV–vis–NIR spectrophotometer by dispersing the sample in D₂O to avoid interference from H₂O in the NIR region. Zeta potential analysis of PVP was conducted at 25 °C on a Zetasizer Nano-ZS (Malvern). Scanning electron microscopy (SEM) analysis of the Au nanoparticles was conducted on an FEI Nova Nano 430 SEM operated at 15 kV at the Nanoscale Research Facility at the University of Florida (UF). Transmission electron microscopy (TEM) samples were prepared by dropping 6 µL of the Au nanoparticle suspension onto a Holey Carbon 400 mesh Cu grid (Ted Pella, Inc.) and allowing the grid to dry in ambient air. TEM analysis was then performed using a JEOL 200CX TEM (located at the Major...
Analytical Instrumentation Center at UF) operated at 200 kV. Additional high-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL 2100F HRTEM equipped with a Schottky field-emission gun (FEG) with Cs = 1.0 mm operated at 200 kV (located at Brookhaven National Lab (BNL), Upton, NY). Annular dark-field scanning transmission electron microscopy (ADF-STEM) imaging was conducted on a Cs-corrected Hitachi HD-2700C microscope equipped with a Cold-FEG and operated at 120 kV (located at BNL, Upton, NY). Images were acquired using a probe convergence semi-angle of 23 mrad, with the inner collection angle of the ADF detector at 53 mrad. Electron energy loss spectroscopy (EELS) data was acquired with a Gatan Enfina spectrometer. The collection angle was approximately 15 mrad while the dwell time was 0.032 s and the spectrometer dispersion was set to 0.05 eV per channel. Energy resolution of the system, as defined by the FWHM and FWTM of the zero loss peak (ZLP), was approximately 0.35 eV and 0.85 eV, respectively. The ZLP was removed using a fitted logarithmic tail model in Gatan Digital Micrograph. The distribution of plasmon modes was plotted by integrating over a 0.1 eV-wide window centered on the indicated energy value. Lastly, to account for variation in the EELS signal, the intensity of each mode was normalized at each point. This normalization was accomplished by dividing its value by the total intensity of the corresponding EELS spectrum. The thickness of individual Au nanoprisms on the Si substrate was measured using an atomic force microscope (AFM, Asylum Research MFP-3D™) operated in tapping mode (located at Pacific Northwest National Lab (PNNL) in Richland, WA). The 2 × 2 μm² scan was conducted with a scan rate of 1.0 Hz using the non-contact AFM probes (TETRA15 from K-TEK Nanotechnology). Nanoscale secondary ion mass spectrometry (NanoSIMS) multi-element maps were acquired from Au nanoprisms on a Si wafer using a Cameca NanoSIMS 50L (located at PNNL, Richland, WA). The as-synthesized
nanoparticles were first washed via centrifugation at 5,000 rpm for 5 min and redispersed in Nanopure™ H₂O. This procedure was repeated two times to remove excess surfactants from the solution. The cleaned nanoparticles were then deposited onto the Si substrate by drop casting and allowed to dry in a desiccator. A 16.0 keV Cs⁺ primary ion beam was used to focus a spot size of ca. 50 nm for imaging negative secondary ions. The Cs⁺ beam was scanned on 6 × 6 µm² or 8 × 8 µm² areas to obtain ion images with a definition of 256 × 256 pixels. The mass spectrometer was fine-tuned to detect ¹²C¹⁴N⁻, ¹²⁷I⁻, and ¹⁹⁷Au⁻ species. For the characterization of Ag nanoprisms, the spectrometer was fine-tuned to detect ¹²C¹⁴N⁻ and ¹⁰⁷Ag⁻ species. The secondary ion signals were recorded with electron multipliers. It should be noted that all secondary ion maps were acquired without any pre-sputtering process to specifically collect signals from the top-most surface of the nanostructures. Image processing was carried out using the software ImageJ 1.46r (Wayne Rasband, National Institute of Health, USA, http://rsbweb.nih.gov/ij/index.html) equipped with the OpenMIMS plugin (http://www.nrims.harvard.edu/software.php). To identify the products of methanol oxidation, the reactor headspace gas was examined by gas chromatography both before and after 2 h of light irradiation. The composition of the gas sample (0.2 mL) was detected using a Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity detector (TCD) and Ar was used as the carrier gas at a flow rate of 25 mL/min. The reference sample was a mixture containing methanol, formaldehyde, and formic acid. Electrochemical experiments were conducted using a three-electrode electrochemical cell controlled by a potentiostat (EC Epsilon, Bioanalytical Systems, Inc.). The Au nanocrystal photoelectrode served as the working electrode (area of 2 cm²), with a Pt wire auxiliary electrode and a Ag/AgCl reference electrode all immersed in a supporting electrolyte of 0.1 M NaSO₄ with 10% (vol.) methanol (tuned to pH 3.0
via HCl addition). All error bars indicate the standard deviation of the mean value obtained from three independent trials.

**Figure S1 | Structural characterization of Au nanoprisms.**

**a**, TEM image of a Au nanoprism produced by irradiating the growth solution for 2 h with 500 ± 10 nm light. The inset shows an HRTEM image of the Au nanoprism surface, which displays a lattice spacing of 0.24 nm, consistent with the {111} facet. **b**, A typical selected area electron diffraction (SAED) pattern taken from an individual Au nanoprism supported on the TEM grid. The spot (circle) was indexed to the {220} reflection; the spot (square) was assigned to the {422} reflection; and the spot (triangle) corresponds to the formally forbidden 1/3{422} reflection.**c**, AFM image of a single Au nanoprism. **d**, Cross-sectional scan of the Au nanoprism along the blue line shown in (e), indicating a nanoprism thickness of ca. 22 nm.
Figure S2 | Time-dependent evolution of Au nanostructures. a, Extinction spectra of the growth solution with (b-e) SEM images and (f-m) corresponding size distribution histograms taken every 30 min to monitor the photochemical growth of Au nanostructures under visible-light excitation ($\lambda_{\text{inc}} = 500 \pm 10$ nm) over the course of the 2 h reaction. These spectra exhibit two distinctive features in the visible ($\lambda_{\text{max}} \sim 550$ nm) and near-infrared ($\lambda_{\text{max}} > 1100$ nm) regions attributed to the SPR of the Au nanospheres and the Au nanoprisms, respectively. These assignments are consistent with prior reports involving the synthesis of Au nanoprisms$^{20,22,33,43}$. The simultaneous emergence and continued growth of both SPR features demonstrate that both
nanospheres and nanoprisms grow independently of each other; that is, they evolve from different initial seed structures into larger pseudo-spherical nanoparticles or hexagonal nanoprisms. The independent growth of both Au nanospheres and nanoprisms is also demonstrated by periodic inspection of these Au nanostructures over the course of the 2 h reaction by SEM (b-e), along with the corresponding size distribution histograms for both nanospheres (f-i, red) and nanoprisms (j-m, blue). Both nanostructures simultaneously increase in size over the course of the 2 h reaction. It must be emphasized that this result indicates that there is no interconversion of these larger (~20–100 nm) spherical Au nanoparticles into hexagonal Au nanoprisms, as has previously been observed in the plasmon-mediated growth of Ag nanostructures\(^1,^2,^5,^{11}\). This difference is due to the greater chemical stability of Au compared to Ag\(^15\), since Au seeds are not readily susceptible to photo-oxidation during plasmon excitation like Ag seeds\(^1,^2,^5\). We emphasize this difference between the Au and Ag systems to clarify the distinction in growth mechanisms between these otherwise very similar noble metals. As such, the Au precursors are supplied by AuCl\(_4^–\) species in the growth solution, rather than from the sacrificial oxidation of unstable Au seeds. It is also noted that the yield of nanoprisms (~21%) is roughly consistent with the percentage of planar-twinning nanocrystals present in the initial seed solution (~30%), implicating a seed-mediated growth process. Taken together, these data show that all the Au nanocrystals grow under visible light, and that only those with the proper crystal structure evolve into the nanoprisms. The multiply-twinning nanocrystals, on the other hand, continually increase in size without developing anisotropy, as evidenced by the fact that the feature \(\lambda_{\text{max}}\sim550\) nm continually increases in amplitude while exhibiting a slight red-shift in its spectroscopic position.
Figure S3 | Plasmon-driven growth rate of Au nanostructures. The plasmon-driven growth rate of Au nanostructures was obtained by periodically measuring the average diameter of Au nanospheres (red curve) or the average edge length of Au nanoprisms (blue curve) from SEM images every 30 min over the course of the 2 h reaction (see Fig. S2). The average particle volume after each 30 min growth period was then computed based on geometric shape. As shown in this plot, the growth rate of these Au nanocrystals actually increases with time as the nanoparticles become larger. Inset shows a magnified plot to demonstrate that the pseudo-spherical nanocrystals follow the same trend as the nanoprisms, albeit with significantly reduced overall magnitude.
Figure S4 | Identification of diverse nanocrystal structures in the Au seed solution. a-d, HRTEM images of various Au seed structures indicated by blue circles: (a) single-crystalline, (b) planar-twinned, (c) penta-twinned, and (d) complex multiply-twinned structure. Dashed white lines serve as a guide to highlight the twin boundaries. All scale bars represent 2 nm.
Figure S5 | Influence of incident excitation wavelength on Au nanostructure growth. a, Extinction spectra of growth solution with (b-g) corresponding SEM images after 2 h of irradiation with the following incident wavelengths (\( \lambda_{\text{inc}} \)): (b) 480 ± 10 nm, (c) 500 ± 10 nm, (d) 520 ± 10 nm, (e) 540 ± 10 nm, (f) 580 ± 10 nm, and (g) 620 ± 10 nm. As shown in the SEM images, Au nanospheres and Au nanoprisms were produced regardless of the incident wavelength (\( \lambda_{\text{inc}} \)), and only the relative size and total number density of Au nanocrystals changed. For instance, the average edge length of Au nanoprisms obtained after 2 h of irradiation with 500 nm light was ca. 496 nm (c) while under 620 nm light the nanoprism edge length only reached ca. 260 nm (g).
Further quantification of the amount of Au precursors (HAuCl₄) left in the growth solution by UV-Vis spectroscopy after the 2 h reaction further correlates the reduction of Au precursors in the growth solution (Fig. 1b, red points) with the SPR of the Au nanocrystals (Fig. 1b, black curve). Taken together, these results demonstrate that the incident excitation wavelength directly determines the total consumption of Au precursors in the growth solution over the course of the reaction and therefore affects the final size of the Au nanostructures produced.
**Figure S6 | Photothermal control experiment conducted in the dark at 32 °C for 2 h.**

Extinction spectra of the growth solution after 2 h of incubation in the dark while immersed in a water bath maintained at 32 °C (denoted “a”). The extinction spectrum of the growth solution after irradiation with 500 ± 10 nm light for 2 h is also shown for comparison (denoted “b”). The hot electrons produced during plasmon decay quickly equilibrate with the metal lattice via electron-phonon coupling (~1 ps), thereby elevating the surface temperature of the metal nanoparticles. Since the heat transfer from a plasmonic-metal nanoparticle to the surrounding solution is ultrafast (~1 ns), the bulk solution temperature (32 °C measured after 2 h) can be used as a surrogate for the nanoparticle surface temperature under low-power visible-light irradiation. The growth solution was therefore incubated at 32 °C in the dark for 2 h; however, no noticeable SPR features were observed via UV-Vis spectroscopy (a), indicating that no Au nanoparticle growth ensued. This result shows that the bulk solution temperature observed under visible-light irradiation is not high enough to enable PVP to directly reduce the HAuCl₄ precursors, confirming a negligible contribution from photothermal heating to the plasmon-driven growth of Au nanostructures.
Figure S7 | Detection of the methanol oxidation product using gas chromatography.

a, Gas chromatogram spectrum obtained from the growth solution before light irradiation. Only methanol (CH$_3$OH) is observed. 

b, Spectrum obtained from the same solution after 2 h of light irradiation with 500 ± 10 nm light, showing a second feature indicative of formaldehyde (CH$_2$O).

c, Gas chromatogram spectrum obtained from a mixture of methanol (CH$_3$OH), formic acid (CHOOH), and formaldehyde (CH$_2$O) used as a standard for comparison. These results confirm that formaldehyde is the photochemical byproduct of methanol oxidation.
Figure S8 | Synthesis of Au nanoprisms using various hole scavengers. a-d, SEM images of the Au nanoprisms produced using (a) methanol, (b) formaldehyde, (c) citrate, or (d) ethanol as a hole scavenger. All scale bars represent 500 nm. Au nanoprisms were produced regardless of which hole scavenger was used, confirming that the sacrificial reagent exerts no influence over the nanopism morphology.
Figure S9 | Control experiments without methanol in the photochemical growth solution.

a, The extinction spectrum of the final products obtained after 2 h of irradiation with 500 ± 10 nm light without methanol in the growth solution. Only the absorption features of the initial Au precursor were observed, indicating no appreciable growth occurred in the absence of the hole scavenger methanol. b,c, SEM images of single-nanoparticle growth experiments conducted with a collection of Au nanospheres and a single Au nanoprinm immobilized on a Si substrate before (b) and after irradiation with 500 ± 10 nm light for 2 h (c). Both scale bars represent 200 nm. In agreement with the results presented in (a), no noticeable growth occurred without methanol present as a hole scavenger to complete the photocatalytic cycle. These results further confirm that PVP itself is incapable of reducing the HAuCl₄ precursor in the absence of the hole scavenger under these experimental conditions.
Figure S10 | Zeta potential measurement of PVP as a function of solution pH. A positive surface charge is observed for PVP under acidic conditions (pH 3.0 and pH 5.0), while a negative charge was observed under neutral and alkaline conditions (pH 7.0 and pH 9.0). It is noted that around pH 6.0 there was hardly any surface charge detected for PVP. These data demonstrate that the surface charge of PVP is dependent upon the solution pH.
Figure S11 | Influence of growth solution pH on Au nanoprisms synthesis. SEM images of Au nanostructures obtained in the growth solution with different pH values: (a) pH 3.0, (b) pH 5.0, (c) pH 6.0, (d) pH 7.0, and (e) pH 9.0. These results illustrate that the pH of the growth solution is crucial for the formation of Au nanoprisms. Au nanoprisms were only observed at pH 3.0 and pH 5.0, when a positive surface charge was imparted to PVP by the acidic growth solution (see Fig. S10). Furthermore, the growth rate at pH 3.0 is higher than that at pH 5.0 based on the significant difference in Au nanoprisms size [compare images (a) and (b)]. With increasingly alkaline conditions (pH 6.0, 7.0, and 9.0), the Au seeds (ca. 7 nm) only marginally increased in size (ca. 20 nm) over the 2 h reaction. These results demonstrate that the positive surface charge of PVP is crucial for promoting nanoparticle growth, and implies that PVP forms an electrical adlayer on the Au nanocrystal capable of coulombically stabilizing hot electrons generated via SPR excitation to facilitate the reduction of Au precursors on the nanocrystal surface.
Figure S12 | Control experiment with PVP monomer in the growth solution.

SEM image showing Au nanoprisms are produced if the PVP polymer is replaced with its monomer: N-methyl-2-pyrrolidone. This result illustrates that the γ-lactam ring constitutes the critical chemical moiety in the PVP surfactant that facilitates anisotropic growth during the plasmon-driven reaction.
Figure S13 | Influence of PVP on open-circuit photovoltage of Au nanocrystals.

Transient open-circuit voltage \( V_{oc}(t) \) rise/decay from the same Au nanoparticle photoelectrode with (blue) and without (black) the modification of PVP during excitation/termination of visible-light irradiation \( (\lambda_{inc} > 495 \text{ nm}) \). Horizontal dashed lines represent the open-circuit voltage \( V_{oc} \) baselines obtained under dark conditions. This electrochemical technique has been widely used to study the role of citrate in the plasmon-driven synthesis of Ag nanoprisms\(^6,10,41\) and Au nanoparticles\(^31\). We adopted a similar approach herein to directly probe the involvement of PVP in the plasmon-driven growth of Au nanostructures. The photovoltage \( V_{ph} = V_{oc}(\text{light}) - V_{oc}(\text{dark}) \) established within the photoelectrode during irradiation corresponds to the displacement of the Fermi level \( (E_F) \) of the Au nanocrystals from their ground state in the dark.
\([E_{F_{\text{dark}}}]\) to an excited state under light irradiation \([E_{F_{\text{light}}}]\) with respect to the redox couple in solution [where \(E_{F_{\text{redox}}} = E_{F_{\text{dark}}}]^{46}. The production of hot electrons within the Au nanocrystals during optical excitation can therefore be probed electrochemically by monitoring the open-circuit voltage \((V_{\text{oc}})\) of the photoelectrode, since the \(V_{\text{oc}}\) shifts to more negative potentials as electrons accumulate within the plasmonic-metal nanostructures\(^6,10,31,41\). Au nanocrystals were specially prepared in the absence of any surfactants to unambiguously determine the role of PVP in stabilizing hot electrons within the metal nanocrystals (see “Electrochemistry” section in Methods for experimental details). Only a modest photovoltage \((V_{\text{ph}} \sim 6 \text{ mV})\) was established in the bare nanoparticle electrode without any PVP molecules (black curve). This same nanoparticle electrode was then modified with PVP (see “Electrochemistry” section). After surface modification with PVP, a shift in the rest potential \((\sim 11 \text{ mV})\) of the Au nanoparticle electrode was observed to more positive potentials (blue curve). This positive shift in \(V_{\text{oc}}\) under dark conditions is indicative of a lower Fermi level, suggesting a redistribution of charge from the Au nanocrystals to adsorbed PVP molecules\(^31,41\). Upon photoexcitation of the Au nanocrystals, a prompt shift in \(V_{\text{oc}}\) was observed to more negative potentials and a significant photovoltage \((V_{\text{ph}} \sim 27 \text{ mV})\) was established within the Au nanocrystals modified with PVP (blue curve). It is noted that the photovoltage observed herein is similar to what has been previously observed for Au nanocrystals modified with adsorbed citrate molecules\(^31\). No photoresponse was observed from the bare FTO substrate, confirming that these signals arise from the Au nanocrystals themselves. Taken together, these results indicate that PVP molecules assist with the accumulation of plasmon-generated electrons over extended timescales to establish a significant photovoltage on the Au nanocrystal surface under visible-light irradiation.
Figure S14 | Au nanoparticles produced without PVP in the growth solution.

SEM image showing only large aggregates and irregularly shaped nanoparticles are produced if the standard growth solution is irradiated for 2 h with 500 ± 10 nm light without PVP. This result illustrates the importance of PVP in facilitating anisotropic growth during the plasmon-driven reaction.
**Figure S15 | Influence of PVP concentration on the thickness of Au nanoprisms.**

*a-d*, SEM images of Au nanoprisms produced using the standard 0.4 mg/mL PVP (*a* and *b*) or 8 mg/mL PVP in the growth solution (*c* and *d*). *a*, Multiple Au nanoprisms in the stack can be seen through the top nanoprism, indicating the relatively thin dimensions of these nanoprisms obtained from standard growth conditions. In contrast, the prisms were no longer transparent after increasing PVP concentrations, as shown by the blue square in (*c*). The thickness measured by AFM (Fig. S1d) was confirmed through SEM by finding nanoprisms oriented perpendicular to the Si wafer substrate (*b* and *d*). A series of SEM images were used to determine the average thickness, which was ca. 22 ± 3 nm for nanoprisms produced with the standard growth solution (*b*) and ca. 49 ± 8 nm for nanoprisms produced with 20 times more PVP (*d*). These results further confirm that the PVP concentration is important for regulating the direction of Au nanoprism growth.
Figure S16 | NanoSIMS data of Au nanoprisms produced using high quantities of PVP.

a, SEM image of the thicker Au nanoprism sample obtained with 8 mg/mL PVP characterized by NanoSIMS. b, Elemental distribution of gold (\(^{197}\text{Au}^-\)) in the sample. c, Elemental distribution of \(^{12}\text{C}^{14}\text{N}^-\) signals obtained from the entire surface of each Au nanoprism, confirming the adsorption of PVP onto their top and bottom \(\{111\}\) facets with increased surfactant concentrations. These results confirm that PVP performs a unique function as a photocatalytic intermediary, directing the growth trajectory of Au nanostructures by sequestering \(\text{AuCl}_4^-\) ions from solution and stabilizing hot electrons produced via plasmon excitation at the nanoprism perimeter to preferentially promote lateral growth. The scale bar in (a) applies to all images (a-c).
Figure S17 | Identification of defects near twin boundaries on Au nanocrystals.

a-d, HRTEM images of Au nanoparticles showing planar-twinned (a and b) and penta-twinned (c and d) nanocrystals containing defects such as surface steps, kinks, and stacking-faults. All scale bars represent 1 nm. Dashed white lines serve as a guide to highlight the twin boundaries. The red and blue lines indicate steps near twinned boundaries (a to c), and the area within the blue rectangle (d) shows a kink of the crystal lattice.
Figure S18 | Au nanoparticles obtained from various incubation periods in the dark.

a-d, SEM images of Au nanoparticles obtained after incubation in the dark for (a) 2 h, (b) 6 h, (c) and (d) 12 h along with (e) corresponding extinction spectra after 12 h, and (f) size distribution histogram after 12 h. 

a, Only small Au nanospheres were obtained after 2 h of incubation in the dark. 

b, Larger pseudo-spherical nanoparticles and many decahedral structures were identified after 6 h (red circles). 

c, Large ($d \sim 100$ nm) spherical Au nanoparticles were obtained if the dark reaction was extended to 12 h; however, no Au nanoprisms were observed. 

d, High magnification SEM image showing that multiply-twinned structures were the dominant nanocrystals produced during the 12 h dark incubation period. These results show that the reduction of AuCl$_4^-$ by methanol in the dark is driven by the innate surface activity of the Au nanostructures. For multiply-twinned Au nanoparticles (e.g. penta-twinned decahedrons), the five-fold twin boundaries exhibit lattice rotation coupled with shear strains that elevate the surface energy of the metal nanocrystal$^{47}$. These multiply-twinned seeds thereby inherently
possess a large proportion of active surfaces for $\text{AuCl}_4^-$ reduction, leading to faster growth kinetics in the dark compared to the more stable planar-twinned nanoparticles. e, Extinction spectrum of the growth solution after 12 h in the dark exhibits a single feature at ca. 588 nm due to the pseudo-spherical Au nanoparticles, confirming the absence of nanoprism.s. f, Histogram of Au nanoparticle size exhibits a roughly Gaussian distribution with an average diameter of $d = 97 \pm 19$ nm.
Figure S19 | Comparison of the Au nanoparticle growth rates in light and dark conditions.

The growth rate was calculated by assuming a spherical shape for the nanoparticles and using the average radius of the Au nanoparticles obtained from SEM and TEM images. The nanoparticles were counted from a suite of SEM images (a) and TEM images (b) to construct the size distribution histograms shown for incubation in the dark for 2 h (c) and irradiation with 500 ± 10 nm light for 2 h (d).

\[
\frac{V_{\text{SPR}}}{V_{\text{dark}}} = \frac{\frac{4}{3} \pi R_{\text{SPR}}^3 - \frac{4}{3} \pi R_{\text{seed}}^3}{\frac{4}{3} \pi \left(\frac{105.1}{2} \text{ nm}\right)^3 - \frac{4}{3} \pi \left(\frac{7}{2} \text{ nm}\right)^3} = 496
\]
Figure S20 | Investigation of Au seed composition after reaction in the dark. 

**a**, TEM image of Au nanoseeds after 12 h dark reaction. Besides the large Au nanoparticles (average particle size was 97 ± 23 nm), there were still many tiny Au nanoparticles present (highlighted by the red circle). 

**b**, HRTEM image of these tiny Au nanoparticles (average particle size was 15 ± 1 nm) shows an increase in nanocrystals containing planar-twinned boundaries (indicated by blue arrows) relative to the initial Au seed solution.

Comparison of the growth rate ($\nu$) between multiply-twinned (MT) and planar-twinned (PT) Au nanoseeds in the dark:

$$
\frac{\nu_{\text{dark-MT}}}{\nu_{\text{dark-PT}}} = \frac{\frac{4}{3} \pi R^3_{\text{dark-MT}}}{\frac{4}{3} \pi R^3_{\text{dark-PT}}} = \frac{\frac{4}{3} \pi \left(\frac{96.6}{2} \text{ nm}\right)^3}{\frac{4}{3} \pi \left(\frac{14.6}{2} \text{ nm}\right)^3} = \frac{4}{3} \pi \left(\frac{7}{2} \text{ nm}\right)^3 = 325
$$
Figure S21 | Single-particle tracking experiment of Au nanoparticles in the dark. a,b, SEM images of a single Au nanoprism and several pseudo-spherical nanoparticles (a) before and (b) after growth in the dark for 6 h. Both scale bars represent 100 nm. White and red dashed lines were added to illustrate the initial dimensions of the Au nanoprism and nanospheres, respectively. These images reveal that only the spherical nanoparticles grew to a noticeable extent in the dark. This experiment further shows that the growth process in the dark is seed-mediated, as no new nanoparticles were observed on the bare Si substrate.
Figure S22 | Influence of nanocrystal twinning on open-circuit photovoltage.

Transient open-circuit voltage \( [V_{oc}(t)] \) rise/decay from photoelectrodes exclusively composed of either planar-twinned Au nanoprisms (blue) or multiply-twinned Au nanoparticles (black) during excitation/termination of visible-light irradiation \( (\lambda_{inc} > 495 \text{ nm}) \). This electrochemical technique was used to demonstrate the influence of nanocrystal twinning on the plasmon-driven growth of Au nanostructures. The separation of these two nanocrystals in high purity was accomplished via the method outlined in Scheme S1. These data show that the planar-twinned nanoprisms exhibit larger photovoltages \( (V_{ph} \sim 60 \text{ mV}) \) than the multiply-twinned nanocrystals \( (V_{ph} \sim 30 \text{ mV}) \), in agreement with our expectation that the planar-twinned nanoprisms should sustain a greater number of hot carriers capable of catalyzing HAuCl\(_4\) reduction under steady-state illumination. It is noted that such a result is consistent with the previously proposed theory on polycrystalline Ag-based nanocrystal electrodes, whereby the high density of defects in the nanocrystal increased the hot carrier decay rate and lowered the overall photochemical quantum yield\(^{41}\).
Figure S23 | Nanocrystal composition of the Au seeds after incubation in the dark.

HRTEM image of the Au nanocrystals left in the seed solution after removing the larger multiply-twinned nanocrystals by high-speed centrifugation (10,000 rpm for 10 min) following 36 h of dark reaction. The blue arrows indicate the planar-twin boundaries.
Figure S24 | Influence of dark incubation time on the yield of Au nanoprisms.

a-d, SEM images showing the yield of Au nanoprisms obtained after reaction in the dark for (a) 0 h, (b) 12 h, (c) 24 h, and (d) 36 h. The % yield (by shape) of nanoprisms is clearly dependent on the amount of dark reaction time, as noted in the upper right-hand corner of each image. This dark incubation period is critical to obtaining high yields of Au nanoprisms, as it excludes the multiply-twinned nanocrystals from the starting seed solution prior to irradiation (see Scheme S1). All scale bars represent 2 μm.
Figure S25 | Optical properties of Au nanoprisms dispersed in D₂O.

The extinction spectrum for the Au nanoprism solution exhibits a single SPR dipole peak at 1220 nm. The absence of a spherical SPR peak around 550 nm confirms the high yield of nanoprisms obtained using the light-driven method.
Figure S26 | NanoSIMS of PVP and iodide distribution on triangular Au nanoprisms.

a, SEM image of the Au nanoprisms inspected by NanoSIMS. b, Elemental distribution of gold (197Au⁻) signals detected from the sample. c, Elemental distribution of 12C¹⁴N⁻ signals detected from the sample. d, Elemental distribution of iodide (127I⁻) signals detected from the sample. e, Overlay of both 12C¹⁴N⁻ and 127I⁻ signals from (c) and (d) to show the physically separate locations of these two complementary ligands on the Au nanoprism surface. Scale bar in (a) applies to all images (a-e).
Figure S27 | Plasmon-driven synthesis of silver nanoprisms with PVP. a, SEM image of the final products obtained via irradiation of the growth solution with $\lambda_{\text{inc}} = 400 \pm 10$ nm light for 8 h (full experimental details given below). The Ag nanoprisms (ca. 10% yield by shape) are indicated by yellow circles. b, SEM image of Ag nanoparticles produced without PVP in the photochemical growth solution under otherwise identical conditions. No Ag nanoprisms are produced. c, High-magnification SEM image of a single Ag nanoprin. d,e, NanoSIMS images collected from an individual Ag nanoprin, showing the elemental distributions of $^{107}$Ag$^-$ (yellow) signals (d) and $^{12}$C$^{14}$N$^-$ (green) signals (e). It is noted that $^{107}$Ag$^-$ signal is weaker than $^{197}$Au$^-$ because the ionization yield of $^{107}$Ag$^-$ species is generally about 1-2 orders of magnitude lower than $^{197}$Au$^-$ species. These data reveal that PVP adsorbs along the Ag nanoprin perimeter, which is exactly where it was observed in the Au system. Such similarity between material systems confirms that the adsorption location of PVP determines the anisotropic growth direction during plasmon-driven nanoprin synthesis.

The synthesis of Ag nanoprisms was conducted through a similar fashion as for the Au
nanoprisms. Ag seeds were first synthesized according to a previously described method. A photochemical growth solution was prepared by adding 5 mg of PVP to a mixture of 8 mL Nanopure™ H₂O and 2 mL methanol. Then, 40 μL of 50 mM AgNO₃ aqueous solution and 50 μL of the above-mentioned Ag seed solution were added to the growth solution and gently mixed. The growth solution was then illuminated for 8 h with a halogen lamp (Dolan Jenner, Model No. MI-150) equipped with a 400 ± 10 nm bandpass filter (Thor Labs, Inc.) under an incident power density of I₀ ~12 mW/cm² on the sample surface. Nanostructure growth products were collected after synthesis by centrifugation at 5,000 rpm for 5 min and redispersed in Nanopure™ H₂O. This procedure was repeated two more times to remove excess surfactants from the nanostructure surface before the characterization of the sample by electron microscopy. These nanoparticles were washed the same way for the preparation of NanoSIMS samples.
Table S1: Comparison of nanocrystal growth rates under dark and light conditions.

The growth rates (ν) show remarkable differences under dark and light conditions, as well as between nanocrystal morphologies. All growth rates are given relative to the planar-twinned seeds in the dark (ν_{PT, Dark}) to enable direct comparison. For instance, the growth of the multiply-twinned decahedrons is about 500 times faster in the light (ν_{MT, Light}) than in the dark (ν_{MT, Dark}), and the decahedron growth rate in the dark (ν_{MT, Dark}) is about 400 times faster than the planar-twinned nanocrystals in the dark (ν_{PT, Dark}). However, under visible-light irradiation, the growth rate of the planar-twinned nanocrystals (ν_{PT, Light}) is about 10 times faster than that of the decahedrons (ν_{MT, Light}). Similarly, the growth of the planar-twinned nanocrystals increases under light irradiation, but much more dramatically than that of the decahedrons, with a growth rate that is ca. 2 × 10^6 times faster in the light (ν_{PT, Light}) than in the dark (ν_{PT, Dark}). These remarkable differences in growth rate between nanocrystals inspired the development of a new seed separation strategy for producing Au nanoprisms (see Scheme S1).
Scheme S1: Seed separation method for the high-yield synthesis of Au nanoprisms.

a, The dark reaction is first carried out for 36 h to significantly enlarge the multiply-twinned Au nanocrystals over the planar-twinned nanocrystals due to the different growth rate between these nanocrystals under dark and light conditions (see Table S1). The optimal incubation time typically ranged from 18 h to 36 h. b, After this dark incubation period, the multiply-twinned structures were large enough to be removed from the growth solution by centrifugation at 10,000 rpm for 10 min (as shown in the SEM image on the left). c, The entire supernatant, now highly enriched in planar-twinned nanocrystals, is then redispersed in a clean vial and irradiated with 500 ± 10 nm light for 2 h. d, After the reaction, the nanoprisms dominate the distribution (~90% yield by shape) and can be isolated from the reaction solution by centrifugation at 5,000 rpm for 5 min (as shown in SEM image on the right).
References


