Supporting Online Information

Light-Controlled One-Sided Growth of Large Plasmonic Gold Domains on Quantum Rods Observed on the Single Particle Level

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Methods

Materials. All chemicals, except ethanol, were used as received without further purification. Chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%), Magnesium metal (Mg, 99% for Grignard reactions), Sulfur (S, 99.998%), Selenium (Se, powder 100 mesh 99.5%), Cadmium Oxide (CdO, 99.99%), Bis(trimethylsilyl) sulfide ($(\text{TMSi})_2\text{S}$, synthesis grade), anhydrous Chloroform, Toluene and Hexane were purchased from Sigma-Aldrich. Dodecylamine (DDA, $\geq 99.5\%$), Trioctylphosphine (TOP, 97%) and 3-(Mercaptopropyl)trimethoxysilane (MPTS, $\geq 97\%$) were purchased from Fluka. (Di-n-dodecyl)dimethylammonium bromide (DDABr, 99%) was from Alfa Aesar; Iodine crystals, denaturated Ethanol were from Roth ($\geq 99.8\%$). Trioctylphosphine oxide (TOPO, 99%) and Tributylphosphine (TBP, 99%) were purchased from Strem Chemicals; Octadecylphosphonic acid (ODPA, 99%) and Hexylphosphonic acid (HPA, 99%) were from Polycarbon Industries. SH-PEG-OCH₃ (MW 5000) was from Iris Biotech.

Dry ethanol preparation. Dry ethyl alcohol is obtained by refluxing 100 ml of denaturated ethanol in the presence of 2.5g of Mg metal and a small amount of iodine (tip of a spatula) under inert atmosphere (Ar in this case). The solvent is refluxed until the metal is consumed (about 20-24 hours). The ethanol is distilled off, and the alcohol vapor is condensed in a flask and stored in the glovebox.

Optical characterization. Photoirradiation is carried out in the glovebox using an ordinary UV-lamp (Roth) with a central wavelength of 366 nm and with a full width at half maximum (FWHM) of 18 nm. The UV lamp produces emission intensities of about 1-3 mW/cm² as measured using a digital COHERENT power meter calibrated at 366 nm (FM/GS, sensor COHERENT LM-3HTD) depending on the lamp-sample distance (see table below).

Lamp Power (mW/cm ²)	Lamp-Sample Distance (cm)
0.95	15
1.41	4
2.47	2
2.82	1

UV-visible absorption spectra are recorded in an Omega 20 Bruins Instruments equipped with 1 cm quartz cells.

Structural characterization. Low-magnification TEM analysis is performed on a Philips CM12 electron microscope operating at 120 kV. High-resolution (HR)-TEM images are acquired in a FEI Tecnai-F30 microscope operating at 300 kV. High-resolution SEM images are obtained on a FEI Magellan system in STEM mode at 30 kV. TEM samples are prepared by spray-casting (Hielscher ultrasound technology) dilute solutions of nanocrystals onto carbon coated copper grids. Afterwards, the deposited samples are allowed to completely dry at 60°C for one night before examination.

Nanoparticle synthesis

Synthesis of CdSe nanoseeds. All syntheses are carried out under Ar atmosphere in a glovebox. CdSe quantum dots are synthesized according to the procedure of Manna *et al.*¹ In brief, 3.700g of TOPO, 0.280g of ODPA and 0.060g of CdO are stirred in a 50 mL flask, heated to 150°C and exposed to vacuum for 1 hour. Afterwards, the solution is heated to approx. 300°C while flushing the flask with Ar until it turns optically clear and colorless in order to decompose CdO. At this point, 1.5 g of TOP is injected into the flask and the temperature set to the value required for the injection of the Se:TOP solution (0.063g Se + 0.575g TOP). The Se:TOP solution is swiftly injected at 370°C and the heating mantle is removed after 1 min of growth reaction. Later, the CdSe nanoseeds are transferred to the glovebox and washed twice by precipitating them and then re-solubilizing them with methanol and anhydrous chloroform, respectively. In the last precipitation step, the nanoseeds are dissolved in TOP in a final CdSe dots concentration of 150μM (calculated according to X. Peng *et al.*²).

Synthesis of CdS nanoseeds. CdS quantum dots are synthesized according to the procedure of Manna *et al.*¹ In brief, 3.300 g of TOPO, 0.600 g of ODPA and 0.100 g of CdO are stirred in a 50 mL flask, heated to 150°C and exposed to vacuum for 1 hour. Afterwards, the flask is flushed with Ar, and the solution is heated to 320°C until it turns optically clear and colorless in order to decompose CdO. When the temperature has settled to the required value, a sulfur solution (0.190 g $(\text{TMSi})_2\text{S}$ + 3.000 g TBP) is swiftly injected and the growth reaction interrupted after 8 min by interrupting the heating. Thereafter, the CdS nanoseeds are transferred in the drybox and washed twice. In the last step, the seeds are dissolved in TOP to a final CdS dots concentration of 2.3 mM.²

Figure S1. a) Low-resolution TEM image of CdS nanorods grown from seeds of CdSe. The sketch in the picture depicts the rod (pale blue cylinder) surrounding the seed (orange sphere). (b) Gold-tipped CdSe/CdS dumbbells. The optical spectra below display the absorption curves of the CdSe/CdS nanorods before (black line) and after (red line) Au growth. The

presence of very small gold tips (2.2 ± 0.2 nm) partially weakens the CdSe absorbance peak at 580 nm.

Synthesis of CdSe/CdS nanorods. CdSe/CdS nanorods are synthesized using a seeded-growth approach.¹ In a typical nanoparticle synthesis, 0.085 g of CdO is mixed together in a flask with 3.000 g of TOPO, 0.297 g of ODPa and 0.084 g of HPA. The flask is pumped to vacuum for about 1 hour at 150°C. Then, the resulting solution is heated to 350°C and flushed with Ar. At this point, 1.5 g of TOP is injected. After the temperature has recuperated the set value (350°C), a solution of S precursor-TOP-CdSe nanodots is swiftly injected into the flask. This kind of solution is prepared by dissolving 0.120 g of S in 1.5 g of TOP and adding 570 μ L of a solution of CdSe dots (see above) dissolved in TOP (150 μ M). After the injection, the dark red CdSe/CdS nanocrystal solution is allowed to grow for 6 min. The reaction is then stopped by removing the heating mantle. When the solution temperature cools down to about 60-70°C, the nanoparticles are transferred into the glovebox and purified twice by precipitating them with methanol and re-solubilizing them in anhydrous chloroform. If we assume that there is a CdSe seed inside every CdS rod, we obtain a nanoparticle mother solution concentration of $1.72 \cdot 10^{-5}$ M (calculated from seeds). 14.5 μ L of this mother solution diluted in 1 mL of CHCl_3 give an absorbance $A=0.48$ at 452 nm (which is the first CdS absorption peak), which we use as a reference point for dilutions.

Synthesis of Au-CdSe/CdS-Au nanodumbbells. Gold-tipped CdSe/CdS nanorods are prepared according to the procedures described by Banin *et al.*^{3,4} By performing the Au growth on the semiconductor nanoparticles under anaerobic conditions, it is possible to induce the gold nucleation exclusively on the CdS tips (see Figures S1, S2). The Au precursor solution is prepared by dissolving 0.009 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 0.054 g of DDABr, 0.086 g of DDA in 10 ml of toluene. The solution is sonicated for 3 min in order to completely solubilize the gold salt. In another vial, a volume of CdSe/CdS nanorod solution containing 10^{-9} moles of nanoparticles is diluted with 15 ml of toluene. While stirring, the Au-salt solution is slowly added (drop-wise) within about 25 min to the diluted nanorods and left reacting under N_2 for an additional 60 min. The final pale-yellow sample is precipitated with acetone, dried under vacuum and re-dissolved with 4 ml of anhydrous chloroform. Since the absorption of the nanodumbbell suspension is identical to the pure nanorods below 450 nm (Figure S1c), we can estimate their concentration from the starting nanorods as $2.5 \cdot 10^{-7}$ M.

Gentle chemical and physical reaction conditions (room temperature, inert atmosphere and a slow drop-wise Au injection over 25 min) is essential for the selective growth of Au on both semiconductor rod tips (Fig. S2 a/b). More rough reaction conditions such as a moderately high growth

temperature (50°C)⁵, or considerably large injection rate of the gold solution (drop-wise in 2-3 min), mostly produce Au nucleation at the CdSe seed position along the overall CdS rod length (Fig. S2 c/d). Thus, subtle differences between the chemical potentials at the tips and near the CdSe seed position seem to be the driving factor for the initial location of the gold deposition. Dorfs and Banin had argued that strain from a lattice mismatch of CdSe and CdS could not be the reason for the gold deposition at the seed position since this phenomenon was not observed for gold grown on ZnSe seeded CdS nanorods.⁶

Figure S2. Low and High resolution TEM images of Au-CdSe/CdS-Au nanodumbbells. The pictures a and b show how the mild reaction conditions (room temperature, 25 min drop-wise Au injection and N_2 atmosphere) induce Au nucleation preferably on the tips (with the exception of very few cases). Conversely, an Au injection over 2-3 min with the rest of the reaction conditions kept constant causes a sharp increase of gold concentration and Au nucleation influenced by the internal CdSe seed position (pictures c and d).⁵ In the latter case, gold is allowed to react for 1 hour after the injection.

Synthesis of CdS/CdS nanorods. CdS/CdS nanorods are synthesized using a seeded-growth approach.¹ Briefly, in a typical nanoparticle synthesis, 0.100 g of CdO are mixed together in a flask with 3.000 g of TOPO and 0.462 g of ODPa. The flask is pumped to vacuum for about 1 hour at 150°C, then heated to 380°C and flushed with Ar. In this step, 1.5 g of TOP is injected. After the temperature has recuperated the set value, a solution of S precursor-TOP-CdS nanodots is swiftly injected into the flask. This kind of solution is prepared by dissolving 0.060 g of S in 0.75 g of TOP and adding 22 μ L of the formerly prepared CdS nanoseeds (2.3 mM). After the injection, the yellow CdS/CdS nanocrystal solution is allowed to grow for 8 min, after which the reaction is stopped by removing the heating mantle. When the solution temperature cools down to about 60-70°C, the nanoparticles are transferred to the glovebox and purified three times by

precipitating them with methanol and re-dissolving them in anhydrous chloroform. Considering the similar size dimensions with the CdSe/CdS nanorods (see Figure S4), we adjust the absorption of the first CdS absorption peak in order to have identical concentrations.

Figure S3. Low-resolution TEM image of CdS nanorods seeded-grown by injecting CdS seeds. The sketch symbolizes a CdS nanorod with a CdS dot inside.

Photo-induced Au reduction on semiconductor rods

The photocatalysis experiments are performed under Ar atmosphere (glovebox) using dry solvents.

A volume of 1 ml of a chloroform based solution of the nanoparticle sample is added to a glass vial at a concentration of $2.5 \cdot 10^{-7}$ M. As nanoparticles, we use either CdS/CdS rods, CdSe/CdS rods, or Au-CdSe/CdS-Au nanodumbbells. Afterwards, 400 μ L of dry EtOH is slowly added (for a final ratio of 10:90 v/v to chloroform). Keeping the ethanol concentration below 10% prevents precipitation of the hydrophobic nanoparticles. Finally, we inject (drop-wise) 3 ml of a chloroform based Au solution (9 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) containing the surfactants DDA (70 mg) and DDABr (42 mg). The resulting mixture is then UV irradiated ($\lambda = 366$ nm) in the darkness while stirring. The sample is allowed to grow under UV irradiation for up to 120 min with aliquots withdrawn at scheduled times (see main text). Finally, the growth reaction is stopped by interrupting the irradiation, precipitating the sample with acetone, applying 10 min of centrifugation at 1300 g, drying, and re-solubilizing the precipitate in chloroform. Depending on the dilution, the final sample appears dark or pale violet. In order to rule out any light absorbance of the glass vial for the UV irradiation (366 nm), a few control experiments with identical results were performed in a quartz cuvette.

The resulting gold-capped nanorods are shown in Figure S4 together with the starting material (CdS/CdS rods, CdSe/CdS rods, or Au-CdSe/CdS-Au nanodumbbells) and the resulting nanoparticles in a parallel control experiment without UV irradiation. Without UV irradiation, only small

domains form (Figure 2g-i), with particles often sharing one gold domain and creating network-like structures in the case of nanodumbbells as starting material.

Figure S4. The strategy of depositing gold with light driven reduction works just as well for all investigated starting materials (a-c): pure CdS rods (length 32.9 ± 4.8 nm; diameter 4.0 ± 0.5 nm) (left column), CdSe(seed)/CdS(shell) (length 28 ± 2 nm; diameter 3.8 ± 0.4 nm) rods (middle column), and Au-CdSe/CdS-Au dumbbells (right column). After 60 min of UV irradiation, each particle forms exactly one large gold domain at one end, irrespective of the starting material (d-f). After the same amount of time without UV irradiation, only small gold islands form (g-i). (All scale bars 50 nm)

Table S1. Summary of the control experiments**Control Experiments**

In order to test the role of each component in the reaction mixture, we carried out several control experiments. See Table S1 for a summary of the procedures and Figure S5 for the corresponding results. We used nano dumbbells as starting material.

(a) Without EtOH

In de-aerated organic solutions, the holes h^+ generated by the semiconductor photo-excitation are supposed to be scavenged according to reactions (R1) and (R2) by the two organic solvents EtOH and CHCl_3 .⁷

The absence of EtOH does not prevent the asymmetric gold growth entirely, although the growth is less uniform and the size of the gold domain is visibly decreased (Figure S5a).

(b) In storage conditions

In this control experiment, nanodumbbells are irradiated for a long-time (ca 30 min) *before* gold injection with the purpose of accumulating charge carriers in the metal. Surprisingly, there is no noticeable etching of the starting dumbbells from the irradiation probably due to the ability of the dumbbell's gold domains to store electrons.⁸ The gold injection after pre-irradiation seems to induce dumbbell network-formation and randomly creates a few large gold islands (Figure S5b). However, no large gold domains form on each particle as in our standard conditions.

Figure S5 TEM images of the control experiments. (a) Experiment with no EtOH. The sample shows gold deposition on one dumbbell's end although the deposition is less uniform and much smaller than in the presence of EtOH. (b) This experiment describes the sample in conditions of charge carrier storage: *before* Au injection, the nanodumbbells have been irradiated for 30 min. The particles show a tendency to network perhaps due to an attempt of the system to either delocalize as much as possible the charge carriers or to attract opposite charges localized on the small gold domains. (c) Control experiment achieved irradiating the Au growth solution without dumbbells. The experiment tests the tendency of gold to nucleate under 60 min of 366 nm UV irradiation. Without semiconductor seeds, only small gold crystals form. The scarce quality of the image reflects the difficulty to purify the small gold particles from the unreacted species.

(c) Without semiconductor nano-rods or dumbbells.

To test the influence of UV irradiation on Au nucleation in the normal reaction conditions, we performed a control experiment without any semiconductor particles. 60 min of irradiation leads to the formation of small gold crystals in the range of 2-3 nm in diameter (Figure S5c).

Figure S7. a) High resolution TEM image showing small gold domains on the sides and tips of the semiconductor rod (scale bar 10 nm). Dark (b) and bright-field (c) STEM images of hybrid nanoparticles also showing the presence of small gold domains (scale bar 50 nm)

Figure S8. TEM images with successive tilting angle. The three picture sequences, (A), (B), and (C) (wide field of view) distinctly prove the non-centrosymmetrical Au growth with respect to the semiconductor cross-section. The (A) tilting sequence shows how the corresponding 2D projections depict a rod moving around the spherical Au domain for three nanoparticles. The sequence suggests a nanoparticle structure where the semiconductor shares with Au a lateral facet. In addition, the (B) sequence establishes how the different angles of view can be responsible for an apparently different semiconductor rod length (for example (B) at 10° and at 35°). The (C) sequence shows several tilting steps for a wide field of view. When the single particles are favorably aligned with respect to the tilting axis, it is possible to follow more particles at the same time (see the differently colored arrows). (D) HR-TEM picture of a gold sphere aligned non-centrosymmetrically with respect to the semiconductor nanorod *c*-axis.

Figure S9. Effect of irradiation at 562 nm. a) shows the original spectra of the CdS and CdSe/CdS nanorods. Irradiation at 562 nm induces excitation only in CdSe seeds. b-c) show TEM images of the CdSe/CdS and pure CdS nanorods (respectively, as indicated by the insets) after one hour of irradiation at 562 nm in the presence of a Au^{3+} solution. For the CdSe/CdS rods, gold nucleates preferentially in the area where the CdSe seed is localized and some isolated gold domains form (b). For CdS nanorods, gold nucleates on random positions on the nanorod surface (c) and again some isolated gold particles form (d).

Figure S10. Test of the effect of gold ions at very long reaction times without UV irradiation. A solution of CdSe/CdS nanorods in the presence of gold ions in a mixture of $\text{EtOH}:\text{CHCl}_3=10:90$ (v:v) is stirred in darkness for two days. (a) A TEM image of the resulting particles shows two effects: a reaction of gold with the surface of CdS producing small gold islands on the rod facets (3.83 ± 1.12 nm) and the nucleation of isolated gold spheres (12.93 ± 1.11 nm). The graph in (b) shows the extinction spectra of the particles after stirring for one and two days.

Figure S11. (a) TEM image of short CdSe/CdS nanorods (length 18.9 ± 1.4 nm diameter 4.6 ± 0.5 nm). UV irradiation of the starting sample dispersed in a mixture of EtOH:CHCl₃=10:90 (v:v) ratio and in the presence of excess of Au³⁺ ions produces growth of a large gold domain on one tip of the semiconductor particles (b). No significant etching is observed.

Figure S12. Transferability to polar solvents. The TEM image shows hybrid particles deposited from an ethanolic solution. The sample is prepared starting from CdSe/CdS nanorods irradiated in the presence of Au³⁺ ions for 1 hour. After precipitation with acetone and re-suspension in CHCl₃, 150 μ L of HS-PEG-OCH₃ (MW=5000 g/mol) in CHCl₃ (0.002 M) is added and the solution shaken for 25 minutes. Afterwards, the particles are precipitated with hexane and re-suspended in a polar solvent such as EtOH or H₂O.

Figure S13. Effects of long UV exposure. The panel shows low and high resolution TEM pictures of particles irradiated for three hours. The particle's metal domains coalesce together helped by a large number of unreacted gold ions still present in the solution.

Single particle optical characterization

Preparation of flow cells: For single-particle optical characterization in an oxygen-free environment, we use a flow cell made from a flat borosilicate glass capillary glued with epoxy to polyethylene tubing (see Figure S6). After the flow cell is produced, motorized syringes allow for the addition of constant flow of liquids to the flow cell. First, washing stages are performed in order to ensure a complete removal of contaminants and to tune the glass wall's contact angle in the direction of the organic mercapto-silane solution. Then, the capillary is functionalized with mercapto-silane, which covalently binds to the cell walls through silanolic bonds. When a diluted nanoparticle solution is flowing in, the thiol groups of the mercapto-silane bind to the semiconductor particles. Before optical measurements, the unbound nanoparticles are washed out and the cell is filled with a mixture of EtOH and CHCl_3 . The detailed 10-step protocol is as follows (the injection rates are always 1 mL/min):

- 1st The cell is washed with 60mL of Hellmanex (Hellma)/Millipore H_2O solution 4% v/v
 - 2nd washing with 60 mL of Millipore H_2O
 - 3rd washing with 60 mL of pure EtOH
- The flow cell is transferred into the glovebox for the following steps and anhydrous solvents are used hereafter
- 4th washing with 6 mL of pure CHCl_3
 - 5th functionalizing with 12 mL of mercapto-silane in CHCl_3 (5% v/v)
 - 6th washing with 6 mL of pure CHCl_3
 - 7th 4 mL of chloroformic solution $1.4 \cdot 10^{-10}\text{M}$
 - 8th washing with 2 mL of pure CHCl_3 ;
 - 9th washing with 4 mL of EtOH in CHCl_3 (30% v/v)
 - 10th The glass capillary is filled again with a solution 30% (v/v) of EtOH in CHCl_3 and sealed tightly with two syringes at both ends of the flow cell.

At this point, the flow cell is taken out of the glovebox and investigated under the microscope.

Figure S6. Flow cell composition.

Single particle microscopy: Single particle scattering was recorded in a self-made dark-field microscope setup. The setup allows for the recording of scattering intensities and single particle spectra with an imaging spectrometer (Figure 4). The flow-cell was glued to a microscope slide at both ends and placed on the sample stage. Immersion oil is placed between the dark field condenser and the microscope slide, and between the microscope slide and the flow cell to avoid refraction of the illuminating light. The sample is observed with an oil immersion microscope objective for the highest possible magnification and contrast (Carl-Zeiss Achroplan 100x, oil iris). Images are recorded in regular time intervals using an imaging spectrometer (SP2300i, Acton Research) equipped with a Peltier-cooled CCD camera (Pixis 400 Princeton Instruments). For observing the CdS/CdSe quantum dot blinking, we use 1 s exposure time with zero delay between exposures for 5 minutes. For observing the growth of the gold domains, we use 30 ms exposure time in 30 sec time intervals for 60 minutes. The intensity of a structure-free area in close vicinity to the particle under investigation is used for background correction of the particle signal.

Estimation of laser illumination intensity: To estimate the laser light intensity at the sample level, we measured the response of a regular photodiode (Siemens BPW 34). The diode is initially calibrated using the diode laser, an optical power sensor (Thorlabs S130A), neutral optical filters, and a $10\text{k}\Omega$ resistor as load. If the diode is positioned in the place of the sample, the measured voltage drop is 88 mV, which corresponds to a laser power of 0.8 mW over the field of view or an irradiance of 6 W/cm^2 .

Figure S14. More examples for the temporal evolution (exposure time: 1000ms, 29sec delay) of the gold domain growth (main graphs) observed on single particles (see Figure 4b). The position of the quantum rods were identified by their blinking behavior (insets) before addition of gold ions. The growing gold domains start to be detectable at diameters of approx. 15 nm. The gold domains diameter grows linearly in time in the observable period for all particles.

Figure S15. (a) Fluorescence image of CdSe/CdS quantum rods and (b) dark field plasmon scattering image of the same area showing the Au domains after photo-assisted gold growth. The green rectangles indicate areas where the positions of the quantum rods and the gold domains are correlated. A few gold particles form also at places where no quantum rod signal was detected and a few places showing fluorescence signal displayed no gold domain formation.

Figure S16. Temporal evolution of hybrid nanoparticles during growth. Representative TEM images taken from aliquots extracted during the growth process (scale bars 50 nm). Here, for CdS nanorods as starting material. Statistical results from these images are shown in Figure 3 in the main text.

Figure S17. Temporal evolution of hybrid nanoparticles during growth. Representative TEM images taken from aliquots extracted during the growth process (scale bars 50 nm). Here, for CdSe/CdS nanorods as starting material. Statistical results from these images are shown in Figure 3 in the main text.

Figure S18. Temporal evolution of hybrid nanoparticles during growth. Representative TEM images taken from aliquots extracted during the growth process (scale bars 50 nm). Here, for Au-CdSe/CdS nano-dumbbells as starting material. Statistical results from these images are shown in Figure 3 in the main text.

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