Growth and reductive transformation of a gold shell around pyramidal cadmium selenide nanocrystals.

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1. Materials and Methods
All reactions were conducted in a nitrogen atmosphere. CdSe-dispersions were purged with nitrogen for at least 30 minutes prior to incubation with gold solution.

1.1. Synthesis of CdSe dihexagonal pyramids

1.1.1. Reagents
Cadmium oxide (CdO; 99.99+ %) was purchased from ChemPur. Tri-n-octylphosphine cytec quality (TOP; ≥ 90%, stored in a glovebox) and selenium shots (amorphous, 2-4 mm, 0.08-0.16 in, 99.999+% stored in a glovebox) were ordered from Aldrich, while 1,2-dichloroethane (DCE; p.A.), tri-n-octylphosphine oxide (TOPO; >98%) and toluene were obtained from Merck. All chemicals were used without further purification.

1.1.2. Synthetic Procedure
A mixture of 0.025 g (0.19 mmol) CdO, 0.14 g (0.42 mmol) n-octadecylphosphonic acid and 3.0 g (7.8 mmol) tri-n-octylyphosphine oxide was heated to 120 °C in a three necked flask for 30 minutes. During this time, several switches from vacuum to nitrogen and back were carried out. For complexation, the temperature of the brownish-red dispersion was further increased under moderate stirring until it became an optically clear solution (270 °C). After cooling down to 80 °C, 10 µL of dichloroethane were injected and the temperature was raised again. At 265 °C 0.42 mL (0.42 mmol) of TOPSe were injected before reducing the temperature to 255 °C for growth. The color of the solution turned from colorless via yellow and orange to brownish-red, indicating the formation of CdSe NPs. The reaction was quenched by cooling down to 70 °C and
injecting 3.5 mL of toluene. Resulting CdSe nanocrystals were purified by two cycles of precipitation with methanol (addition until turbidity occurs), centrifugation (4500 rpm/1856*g, 3 minutes), removal of the supernatant and re-dispersion in toluene.

1.2. Synthesis of CdSe rods

1.2.1. Reagents
See 1.1.

1.2.2. Synthetic Procedure
CdSe rods were obtained by extracting 0.8 mL of reaction solution from a pyramid synthesis 30 minutes after addition of the selenium precursor. When the temperature of the aliquot reached 70 °C, it was injected into toluene to prevent solidification. Resulting CdSe nanoparticles were purified by two cycles of precipitation with methanol (addition until turbidity occurs), centrifugation (4500 rpm/1856*g, 3 minutes), removal of the supernatant and re-dispersion in toluene.

1.3. Synthesis of CdSe-Au nanostructures

1.3.1. Reagents
Gold(III) chloride (AuCl₃; 99%) and oleylamine (OA; 70%; tech.) were ordered from Aldrich. 1-Dodecanethiol (DDT; 98%) was produced by Acros, tetra-n-butylammonium borohydride (TBAB; 98%, stored in a glovebox) by Fluka. Dodecyltrimethylammonium bromide (DTAB, 99%) was purchased from Alfa Aesar. All chemicals were used without further purification.

1.3.2. Determination of Au/CdSe ratio
Studies on the extinction coefficient ($\varepsilon$) of pyramidal CdSe NCs for the determination of the molar concentration by UV-vis spectrophotometry have not been published so far. The present experiments were interrelated by ratios of the micromolar amount of gold and the product of optical density and volume of the respective receiving CdSe-NC solution (Au/CdSe ratio). The optical density of the CdSe particle stock solution was obtained by diluting 100 µL with 2900 µL of toluene and multiplying the absorbance of the respective CdSe sample at the first exciton
transition band with 30. The maximum of the band and the optical density were determined by graphically fitting straight lines to the slopes and metering the wavelength and absorbance at their crossing.

1.3.3. **Gold stock solution**

In a volume of 15.0 mL toluene, gold(III) chloride and dodecyltrimethylammonium bromide (1:1.5) were dissolved by sonication and slight warming to give a clear orange-red solution with a concentration of 5.3 mmol/L. The resulting solution was stored in darkness and sonicated or warmed slightly before use if necessary (orange needles formed that could easily be re-dissolved).

1.3.4. **Incubation of CdSe pyramids with Au-DTAB/OA**

Cadmium selenide nanoparticles were purified by one cycle of precipitation and re-dispersion with methanol/toluene. The optical density was determined and an appropriate volume was diluted with toluene to 4 mL with an optical density of OD_{rec} (675.0 nm) = 0.270. Oleylamine (18.6 mg, 48.7 µmol) was mixed with 0.590 mL of a 5.27 mM gold stock solution (3.11 µmol Au, Au/CdSe: 2.88) and 3.41 mL toluene and sonicated for 5 minutes. The light yellow solution was injected into the receiver at once. Upon addition of the gold solution, the color of the reaction solution lost its reddish touch. After 20 minutes of incubation at room temperature or 80 h at 80 °C, particles were precipitated with ethanol, centrifuged (3 min, 4500 rpm/1856*g), separated from the supernatant and re-dispersed in toluene twice.

1.3.5. **Incubation of CdSe rods with Au-DTAB/OA**

CdSe nanorods synthesized in the presence of dichloroethane were purified by two cycles of precipitation and re-dispersion with methanol/toluene. The optical density was determined and an appropriate volume was diluted to give a receiving dispersion of 2 mL with. OD_{rec} (648.0 nm) = 0.27. Oleylamine (9.3 mg, 24 µmol) was mixed with 0.20 mL of a 5.3 mM gold stock solution (1.0 µmol Au, 1.6 µmol DTAB, Au/CdSe: 1.92) and 1.8 mL toluene before being sonicated for 5 minutes. The light yellow solution was injected into the receiver at once and to give a brown mixture. After 20 minutes of incubation, particles were precipitated with ethanol, centrifuged (3 min, 4500 rpm/1856*g), separated from the supernatant and re-dispersed in toluene for characterization.
1.3.6. Incubation of CdSe pyramids with Au-DTAB/OA and addition of TBAB

The details of the experiments are listed in table S1, while the general procedure was as follows. After a sufficient amount of CdSe nanocrystals was precipitated with methanol, centrifuged and re-dispersed in toluene twice, the optical density was determined and an aliquot was diluted to give a dispersion with a volume of 4 mL and an optical density of OD_{receiver} (674.5 nm) = 0.269.

To prepare the gold precursor, a volume $V_{Au-sol}$ of a 5.3 mM gold stock solution containing an amount $n_{Au}$ of gold and $n_{DTAB}$ of dodecyltrimethylammonium bromide was mixed with oleylamine or dodecanethiol ($m_{OA/DDT}$, $n_{OA/DDT}$), diluted with toluene to a volume of 4 mL and sonicated for 5 minutes. The color changed immediately from orange to faint yellow or colorless (DDT) upon contact between stock solution and stabilizer. Subsequently, the solution was injected to the receiving CdSe NC dispersion under vigorous stirring. The solution was left to stir for 1 hour before a volume $V_{TBAB}$ of a freshly prepared solution of TBAB and DTAB (1:1, 3.9 mM) in toluene was added. The molar ratio between gold and reducing equivalents in form of hydride (H-) was kept at 4:1. Upon addition of the reducing agent, the color of the mixture lost its reddish touch; in case of the experiment with DDT it turned to gold-brown. After 20 minutes, the particles were precipitated with ethanol, centrifuged (3 min at 4500 rpm/ 1856xg), separated from the supernatant and re-dispersed in toluene.

Table S1: Experiments with additional reduction by TBAB are listed with the volume of gold solution ($V_{Au-sol}$), amounts of gold ($n_{Au}$) and DTAB ($n_{DTAB}$), the ratio of the amount of gold to the optical density and volume of the receiver (Au/CdSe ratio), the amount of amine or thiol ($m_{OA/DDT}$, $n_{OA/DDT}$), the volume of TBAB solution ($V_{TBAB}$) and molar amount of TBAB ($n_{TBAB}$) employed.

| Exp. | $V_{Au-sol}$ [mL] | $n_{Au}$ [µmol] | $n_{DTAB}$ [µmol] | $n_{Au}/(OD_{rec}*V_{rec})$ | $m_{OA/DDT}$ [mg] | $n_{OA/DDT}$ [µmol] | $V_{TBAB}$ [µL] | $n_{TBAB}$ [µmol] |
|------|------------------|-----------------|-------------------|-----------------------------|------------------|-------------------|-----------------|-----------------|
| OA 1 | 0.20             | 1.0             | 1.6               | 0.96                        | 9.2              | 24                | 17              | 0.066           |
| OA 2 | 0.39             | 2.1             | 3.1               | 1.9                         | 19               | 48                | 34              | 0.13            |
| DDT  | 0.39             | 2.1             | 3.1               | 1.9                         | 10               | 48                | 34              | 0.13            |
2. Characterization techniques

2.1. Sample Preparation and instruments

2.1.1. UV-Vis spectroscopy
For the optical measurements an aliquot of the respective sample was diluted in toluene after purification. CdSe samples were precipitated with methanol, separated by centrifugation (4500 rpm, 3 minutes) and re-dispersed in toluene one to three times. Samples with CdSe and gold were precipitated with ethanol, sedimented by centrifugation (4500 rpm, 3 minutes) and re-dispersed in toluene one to two times. The optical density of the CdSe particle solution was obtained by diluting 100 µL with 2900 µL of toluene and multiplying the absorbance of the respective CdSe sample at the first exciton transition band with 30. The maximum of the band and the optical density were determined by graphically fitting straight lines to the slopes and metering the wavelength and absorbance at their crossing. All measurements were carried out in quartz vessels with an optical path length of 10 mm. UV-vis spectra were obtained with a Varian Cary 50 Spectrophotometer (one-beam), fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence Spectrophotometer.

2.1.2. Transmission Electron Microscopy (TEM) - Energy Dispersive X-ray diffraction (EDX) – Scanning Transmission Electron Microscopy (STEM)
CdSe NC samples for TEM inspection were precipitated with methanol and re-dispersed in toluene twice. CdSe-Au hybrid structures were precipitated from solution with ethanol and re-dispersed in toluene. One drop of the dispersions was left to dry on copper grids covered with a carbon film. TEM-images were obtained with a JEOL Jem-1011 instrument at an acceleration voltage of 100 kV, high resolution images and EDX measurements were accessible with a CM 300 Philips microscope at 200 kV acceleration voltage. STEM measurements and high resolution images of the interface were obtained with a field emitter JEOL JEM-2200FS microscope operated at an accelerating voltage of 200 kV. Lengths for histograms were obtained by measuring the length along the c-axis and the longest axis perpendicular to it (diameter) in CdSe pyramids and the longest distance visible in gold deposits with the help of ImageJ freeware software.
2.1.3. X-ray diffraction

A CdSe sample for XRD-measurement was prepared by deposition of particle dispersion onto a silicon wafer and evaporation of the solvent. Spectra were obtained on an X'Pert system with Bragg Brentano geometry manufactured by Philips, operated with monochromatic X-ray radiation from a copper anode (CuKα: 0.1542 nm).
3. Supplementary Results

3.1. CdSe pyramidal NCs

3.1.1. HRTEM, TEM

Figure S1. High resolution TEM images of dihexagonal particles with different orientation (left) and schematic representation of CdSe pyramid structure (right).

3.1.2. X-ray diffraction pattern

Figure S2. X-ray diffraction pattern of dihexagonal pyramidal CdSe NCs. The reflexes fit with the pattern of hexagonal wurtzite CdSe (reference values: X Pert software\(^1\)).
3.1.3. **Size histograms**

![Figure S3](image)

**Figure S3.** Size histograms of CdSe pyramids obtained after 4 hours of reaction. Mean values of 200 nanocrystals: 12.6 ± 1.3 nm in length (c-axis, left) and 11.2 ± 1.6 nm in diameter (right). Deviations not only occur due to size distributions but also because of different orientations of particles on the TEM grid.

3.2. **CdSe-Au hybrid NCs**

3.2.1. **Synthesis with rod-shaped CdSe nanoparticles**

![Figure S5](image)

**Figure S5.** (A) TEM images of CdSe rods after 30 minutes of reaction. (B) Hybrid particles obtained by incubating the CdSe rods with Au-DTAB/OA for 20 minutes at RT. Au dots grew exclusively on the tips of the CdSe rods and neither the formation of shell-like structures nor transformation processes under the TEM beam was observed.
3.2.2. **Absorption spectra**

The optical absorption of the CdSe-Au hybrids shows similar tendencies when compared with the data for bare CdSe NCs, as observed with other semiconductor-Au systems.\(^2\)\(^3\) The absorption bands of CdSe are smoothed and the absorption at short wavelengths is increased with higher amounts of Au on the surface, a slight tail towards longer wavelengths occurs.

![Absorption spectra of CdSe-Au particles with oleylamine as ligand and Au/CdSe ratios of 0.96 and 1.92 (upper figure) and with dodecanethiol as ligand and an Au/CdSe ratio of 1.92 (lower figure). Spectra are adjusted by multiplication to match at 300 nm.](image)

**Figure S6.** Absorption spectra of CdSe-Au particles with oleylamine as ligand and Au/CdSe ratios of 0.96 and 1.92 (upper figure) and with dodecanethiol as ligand and an Au/CdSe ratio of 1.92 (lower figure). Spectra are adjusted by multiplication to match at 300 nm.
3.2.3. EDX measurements with time of an Au shell on CdSe nanoparticles

Table S2. Consecutive EDX measurements of CdSe nanoparticles with an Au shell transforming to Au clusters. The ratio of cadmium to gold content is roughly the same during the transformation of the gold shell to gold clusters. The scattering of the data is due to a small number of counts.

| Time of exposure / s | Ratio Atom-% Cd / Atom-% Au |
|---------------------|-----------------------------|
| 100                 | 53.4 / 46.6                 |
| 200                 | 44.7 / 55.3                 |
| 300                 | 37.9 / 62.1                 |
| 400                 | 48.9 / 51.1                 |
| 500                 | 45.5 / 54.5                 |

Figure S7. TEM images of CdSe nanoparticles with an Au shell and after exposure for 400s.
3.2.4. Size histograms and table of EDX results

Figure S8. Histograms of Au dot sizes after addition of TBAB (n_{Au}/n_{TBAB}: 4:1) to CdSe NCs incubated with AuCl_{3}-DTAB/OA at Au/CdSe ratios of 0.96 and 1.92 (a, b) and incubated with AuCl_{3}-DTAB/DDT at Au/CdSe ratio of 1.92 (c). The average values for the longest distance in gold dots are a) 2.5 ± 0.7 nm, b) 3.9 ± 1.1 nm and c) 1.4 ± 0.3 nm. The total number of counts was 200 in all three cases.

Table S3. Results of EDX analyses of CdSe-Au HNCs after the addition of TBAB.

| Au/CdSe | Ligand     | Size          | Cd (%) | Se (%) | Au (%) | S (%) |
|---------|------------|---------------|--------|--------|--------|-------|
| 0.96    | Oleylamine | 2.5 ± 0.7 nm  | 38.8   | 45.9   | 15.3   | ----  |
| 1.92    | Oleylamine | 3.9 ± 1.1 nm  | 30.1   | 39.8   | 30.1   | ----  |
| 1.92    | Dodecanthiol| 1.4 ± 0.3 nm  | 42.8   | 38.8   | 8.2    | 2.1   |
3.2.4 Video of transformation of hybrid structures under a TEM beam

A sample of CdSe nanocrystals incubated for 20 minutes with AuCl$_3$-DTAB/OA (1:1.5:23) at a Au/CdSe ratio of 2.88 was inspected by TEM with a constant beam intensity of 8.5 pA/cm$^2$. The growth of spherical gold domains from a thin shell-like structure on the surface of CdSe NCs is visible.

4. References

[1] X'Pert HighScore Plus, Version 2.2c (2.2.3) by PANalytical B.V. Almelo, The Netherlands.

[2] Mokari, T.; Rothenberg, E.; Popov, I.; Costi, R.; Banin, U. Science 2004, 304, 1787–1790.

[3] Yang, J.; Elim, H. I.; Zhang, Q.; Lee, J. Y.; Ji, W. J. Am. Chem. Soc. 2006, 128, 11921-11926.