

Selective reactions on the tips of colloidal semiconductor nanorods†

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A strategy to access several types of Au-tipped dumbbell-like nanocrystal heterostructures is presented, which involves the selective oxidation of either PbSe or CdTe sacrificial domains, initially grown on CdSe and CdS nanorods, with a Au(III) : surfactant complex. The formation of gold patches is supported by TEM, XRD and elemental analysis. This approach has allowed us to grow Au domains onto specific locations of anisotropically shaped nanocrystals for which direct metal deposition is unfeasible, as for the case of CdS nanorods. We believe that this strategy may be of general utility to create other types of complex colloidal nanoheterostructures, provided that a suitable sacrificial material can be grown on top of the starting nanocrystal seeds.

1. Introduction

Colloidal inorganic nanocrystals (NCs) represent a class of materials which is under intensive investigation in various fields of nanoscience. Advances in the fabrication methods of such nanoscale objects have led to systematic tuning of their size and shape for a wide range of materials^{1–3} and, recently, to fine topological control over their composition.^{4–12} Hybrid NCs formed by sections of two or more materials joined in a unique particle would be technologically advantageous, because they could perform multifunctional tasks based on the specific properties (such as, for instance, fluorescence and magnetism) which are characteristic of each domain. Examples of these novel nanostructure types are heterodimers made of spherical domains of two materials (for instance CdS and FePt,⁴ CoPt₃ and Au,⁵ γ -Fe₂O₃ and Au, Ag and Au,⁶ Fe₃O₄ and Au,⁷ and so on), linear and branched junctions of two different types of semiconductors,⁸ dumbbell-like^{9,10} and matchstick-shaped NCs,^{10–12} in which domains of a metal or a semiconductor are grown on one or both tips of a starting semiconductor nanorod. In the latter cases, selective growth of the second material on such locations is possible, as the basal facets are not as efficiently passivated by surfactant molecules as the lateral facets of the rods.^{9–12} Recently reported examples are nanodumbbells in which the starting rod is either CdS or CdSe and the domains at the tips are either Au^{9,12} or PbSe.¹⁰ The presence of Au patches on NCs is especially desirable because such domains can be used as preferential anchoring points onto which organic molecules or biomolecules can be selectively attached.^{6,9} Unfortunately, it is not easy to grow Au domains on any type of nanocrystal. While, for instance, this

has been demonstrated for CdSe nanorods^{9,12} and for roughly spherical CoPt₃,⁵ Ag⁶ and iron oxide NCs,^{6,7} on other types of nanocrystals such growth still represents an open challenge. As an example, we have tried in our labs to grow Au directly onto CdS nanorods using these established approaches,^{5–7,9} however with no success. Here, we report a method by which Au can be grown on both CdSe and CdS nanorods, by performing a two-step reaction. First, a sacrificial material, that can be either PbSe or CdTe, is nucleated on the tips of the rods. Later, these domains are oxidized by means of a Au(III) : surfactant complex, which partially replaces them, leading to the formation of Au patches on the rod terminations. The structure of the hybrid nanocrystals was verified by a combination of low resolution Transmission Electron Microscopy (TEM) investigation, Powder X-ray Diffraction (XRD) measurements, and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) elemental analysis.

2. Experimental

All syntheses were carried out in a standard Schlenk line set-up under nitrogen flow. Gold growth on the dumbbells was carried out in a glove-box under nitrogen atmosphere. The samples were washed and stored in the glove-box.

2.1. Chemicals

Cadmium oxide (CdO, 99.999%), tri-n-octylphosphine oxide (TOPO, 99%), tri-n-octylphosphine (TOP, 97%), tri-n-butylphosphine (TBP, 97%), tellurium powder (99.999%), sulfur powder (99%), selenium powder (99.99%) and hydrogen tetrachloroaurate(III) hydrate (HAuCl₄, 99.9%) were purchased from Strem Chemicals. n-Octadecylphosphonic acid (ODPA, 99%) and n-hexadecylphosphonic acid (HPA, 99%) were purchased from Polycarbon Industries. Lead(II) acetate trihydrate (99.95%), diphenyl ether (99%), oleic acid (90%), n-dodecylamine (DDA, 98%) and didodecylmethyl-ammonium bromide (DDAB, 98%) were purchased from Sigma Aldrich. All solvents, such as toluene or chloroform, were anhydrous and purchased from Aldrich.

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Stock precursor solutions of Te:TOP (10% wt), S:TOP (6% wt) and Se:TBP (8% wt) were freshly prepared in a glove-box before use.

2.2. Synthesis of semiconductor nanodumbbells

PbSe–CdSe–PbSe nanodumbbells. These nanodumbbells were prepared by a two-step synthesis as described in ref. 10, with minor modifications. For the preparation of the CdSe nanorods, a mixture of TOPO (3 g), OHPA (0.430 g), HPA (0.130 g) and CdO (0.160 g) was heated to 350 °C in a flask under inert atmosphere. Then, 2.5 g of the Se:TBP stock solution was added rapidly to the hot surfactant mixture under vigorous stirring and the temperature was kept at 280 °C for 6 min. After the synthesis, the flask was cooled to room temperature, and methanol was added to induce the precipitation of the CdSe nanorods. The CdSe precipitate was collected by centrifugation, then washed twice, and finally solubilized in 10 mL of toluene. PbSe–CdSe–PbSe nanocrystal dumbbells were synthesized by growing PbSe tips selectively onto the basal facets of the CdSe nanorods in a subsequent synthesis step. For this purpose, 1 mL of the purified CdSe nanorod solution described above was diluted with 10 mL of previously degassed diphenyl ether and heated to 130 °C. Then, a Pb–Se precursor solution consisting of oleic acid (1.5 mL), diphenyl ether (2 mL), lead acetate (0.660 g), and Se:TOP (1.3 g) was injected dropwise over a period of 10 min.

After the synthesis the reaction mixture was cooled to room temperature, and the PbSe–CdSe–PbSe nanodumbbells were extracted and purified as described above for the CdSe nanorods.

CdTe–CdS–CdTe nanodumbbells. These nanodumbbells were prepared following the one-pot approach described in ref. 8. CdS nanorods were grown in a mixture of TOPO (3 g), OHPA (0.385 g), CdO (0.050 g) and TOP (1.5 mL) at 360 °C. The synthesis was started by rapid injection of 0.600 g of the S:TOP stock solution into the vigorously stirred surfactant mixture. After 1 min of reaction, the heat source was removed temporarily and the solution was allowed to cool and stabilize at 320 °C. To grow CdTe tips onto the CdS nanorods, 0.180 g of Te:TOP stock solution was rapidly injected into the flask and allowed to react for an additional 5 min.

After the synthesis, the reaction mixture was cooled to room temperature, and the CdTe–CdS–CdTe nanodumbbells were extracted and purified as described above.

2.3. Deposition of metallic gold onto the tips of the nanocrystal dumbbells

A Au(III) : surfactant stock solution was prepared as follows: HAuCl₄ (0.011 g), DDA (0.078 g) and DDAB (0.034 g) were co-dissolved in 7 mL of toluene by sonication. During this process, the colour of the solution changed from orange to pale yellow. 0.5–2 mL of this stock solution was added dropwise to a vigorously stirred diluted solution of nanocrystal dumbbells (roughly 5 mg of dumbbells in 3 mL of toluene) at a rate of 0.2 mL min⁻¹. The formation of metallic gold was accompanied by a progressive darkening of the solution which occurred in 1–5 min. After Au(III) addition, the mixture was

allowed to react for an additional 5 min, after which the nanocrystals were precipitated with methanol, washed once, and finally redispersed in toluene.

2.4. Characterization

Transmission electron microscopy (TEM). Samples for TEM were prepared by dropping dilute solutions of nanocrystals onto carbon coated copper grids and leaving the solvent to evaporate. TEM images were recorded on a JEOL Jem 1011 microscope operating at 100 kV.

Powder X-ray diffraction (XRD) analysis. XRD measurements were performed with a NONIUS KappaCCD single crystal diffractometer equipped with a 3 kW generator molybdenum tube, a high precision four circle goniometer, and a low noise and high sensitivity CCD detector. Folding of the images into powder diffraction patterns was done using the FIT2D software¹³ after calibrating the detector with Si-NIST (640c) powder standard. The samples were measured in Debye–Scherrer configuration using Lindemann capillaries (0.5 mm diameter) that were filled with dried NC powder.

Elemental analysis. ICP-AES analysis was performed with a Varian Vista AX spectrometer. Samples were dissolved in HCl–HNO₃ 3 : 1 (v/v) by using a CEM “MARS 5” microwave digester.

3. Results and discussion

Representative TEM images of different types of nanodumbbells are shown in Fig. 1 and 2. Fig. 1 displays an overview of: starting CdSe nanorods (Fig. 1a), PbSe–CdSe–PbSe dumbbells synthesized from these nanorods before and after reaction with the Au(III) solution (Fig. 1b and c, respectively). Fig. 2 reports representative images of: initial CdS nanorods (Fig. 2a), CdTe–CdS–CdTe dumbbells grown from these rods before and after reaction with Au(III) (Fig. 2b and c, respectively). In PbSe–CdSe–PbSe and CdTe–CdS–CdTe dumbbell samples, the formation of the PbSe and CdTe domains, respectively, can be inferred from both the small increase in the rod length (Fig. 1b and 2b) and the slightly different image contrast observable at the nanorod terminations.¹⁰ When the dumbbells reacted with the Au(III) solution (approximately 1 mL of the above described solution was used), Au patches appeared to partially replace the original PbSe (or CdTe) domains at the tips of the rods. The metallic domains can be distinguished clearly at this stage as they exhibit a higher TEM contrast than that of the rod sections (Fig. 1c and Fig. 2c).

A comparison between the TEM images of samples taken before and after the reaction with Au(III) indicated that the mean length of the dumbbells as well as their diameter were reduced to some extent, an effect that was previously observed in the case of the direct Au growth on CdSe nanorods and ascribed to dissolution induced by the DDA and DDAB surfactants used to dissolve the gold salt in toluene.^{8,11} However, when the amount of Au(III) added was increased even more, additional topological changes were observed. A representative example of such a growth regime is reported in

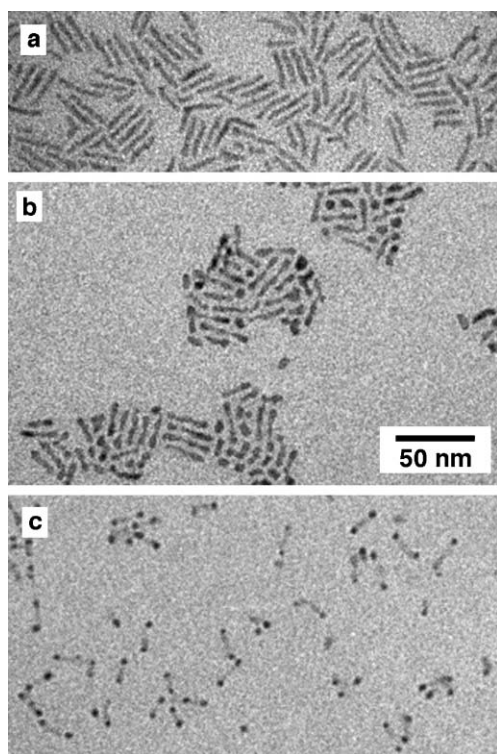


Fig. 1 TEM images of dumbbell-like nanocrystals synthesized from CdSe nanorods (a): PbSe–CdSe–PbSe dumbbells before (b) and after Au(III) reaction on their tips (c).

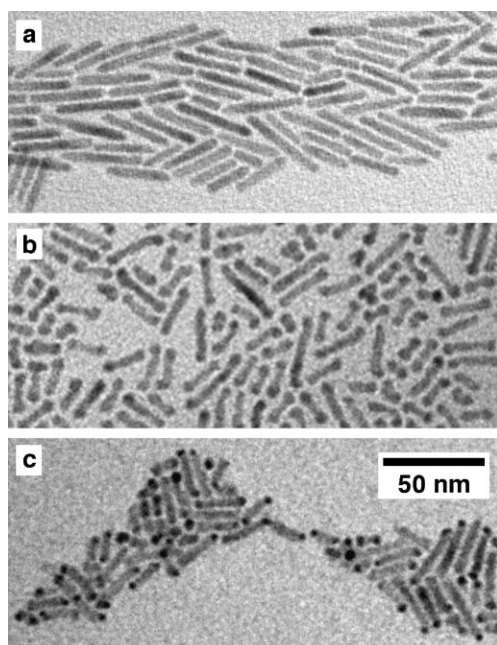


Fig. 2 TEM images of dumbbell-like nanocrystals prepared from CdS nanorods (a): CdTe–CdS–CdTe dumbbells before (b) and after Au(III) reaction on their tips (c).

Fig. 3 for the case of CdTe–CdS–CdTe nanodumbbells. Upon reaction with excess Au(III) stock solution (approximately 2 mL), the CdTe–CdS–CdTe structures evolved into remarkably thinner and shorter nanorods, most of which carried a

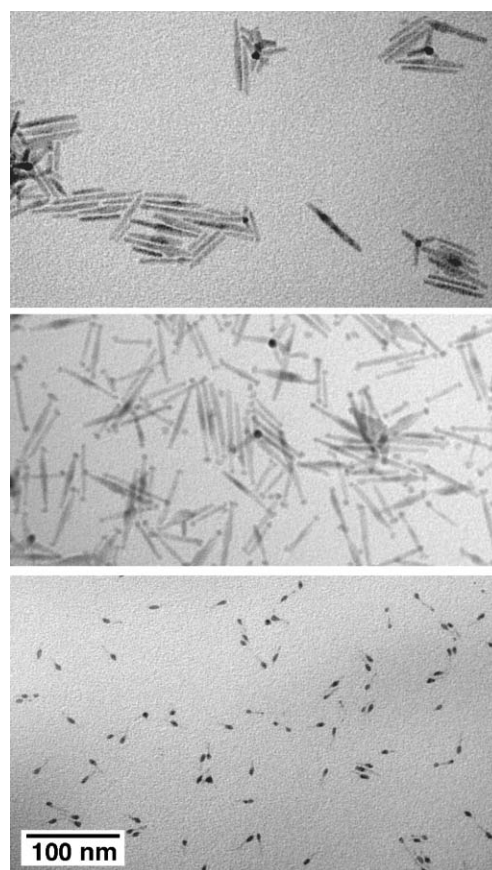


Fig. 3 TEM images illustrating the formation of asymmetric semiconductor–gold heterostructures at the expense of initial CdTe–CdS–CdTe nanodumbbells upon reaction with Au(III). Onto CdS rods (top), CdTe tips were first grown (middle), and then exposed to an excess quantity (2 mL) of Au(III) precursors (bottom).

single Au domain that was mainly located on one side of the rod section. These findings closely resembled the two-side to one-side Au tip growth reported for bare CdSe nanorods.¹² In agreement with this previous study, in our case it could be assumed that the initially formed symmetric Au–CdS–Au dumbbells (such as those shown in Fig. 2c) underwent a transformation into asymmetric CdS–Au matchstick-like nanocrystals when an excess of Au(III) species was present in the solution. Under such conditions, the difference in the chemical potential between Au tips of dissimilar sizes can sustain an intra-particle Ostwald ripening mechanism that can lead to the dissolution of the most unstable metal patches.¹²

XRD patterns provided further structural and compositional information on the various samples, as shown in Fig. 4 for the case of CdTe–CdS–CdTe heterostructures. In the original CdTe–CdS–CdTe dumbbells, a prominent peak at a low angles can be attributed to either the (111) planes of the cubic sphalerite structure or eventually to the (002) planes of the wurtzite structure of CdTe. Notably, this peak is asymmetrically broadened, due to its convolution with CdS wurtzite reflections, and is slightly shifted to higher angles (smaller d spacings) with respect to its bulk position. It is known that, for linear and branched NC heterojunctions based on CdS, CdSe and CdTe, the growth of one material on the

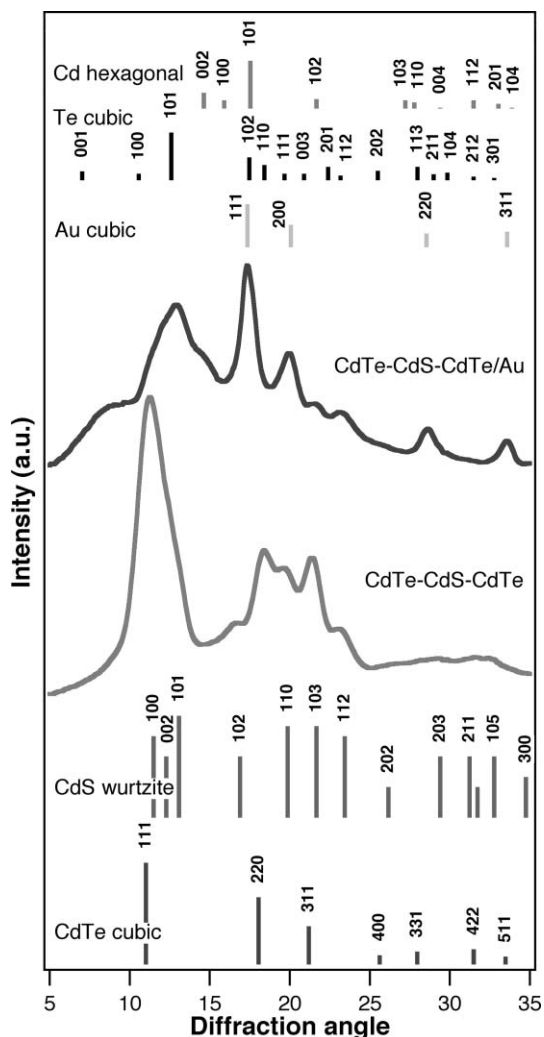


Fig. 4 XRD patterns of CdTe–CdS–CdTe dumbbells (lower spectrum) and CdTe–CdS–CdTe/Au dumbbells (upper spectrum). For comparison, the reference peaks of bulk wurtzite CdS, cubic CdTe, fcc gold, cubic Te, and hcp Cd are displayed.

top of the other occurs epitaxially.⁸ Therefore, the observed CdTe peak shift may be due either to a compressive strain of the CdTe domain, or to the presence of an interfacial region in which CdS and CdTe form an alloy.¹⁴ After the dumbbells reacted with the Au(III) solution (upper spectrum in Fig. 4), the CdTe reflection vanished almost completely, and the CdS contribution was clearly disclosed. More importantly, new distinguishable signals appeared, which confirmed the presence of fcc metallic gold in the final heterostructures. Furthermore, a tiny contribution from metallic Cd and Te can be also noted.

Further support to the TEM observations was provided by ICP-AES elemental analysis. As a representative case, we discuss the experiments on the CdSe rod-based samples

in Fig. 1. The measured concentrations (mol L^{-1}) of the individual species are reported in Table 1 for a sample of PbSe–CdSe–PbSe dumbbells before and after reaction with the Au(III) stock solution. In the initial CdSe nanorod sample, we measured a Cd : Se ratio of 1.14, which is in agreement with surface enrichment with Cd atoms, as ascertained earlier for CdSe nanocrystals.^{15–17} Similarly, in the PbSe–CdSe–PbSe dumbbells, the cations (Cd + Pb) were found to be in stoichiometric excess relative to the anions (Se). The ratio $([\text{Cd}] + [\text{Pb}]) : [\text{Se}]$ was, however, found to be as high as 1.4. For isolated PbSe nanocrystals, a $[\text{Pb}] : [\text{Se}]$ molar ratio of about 1.3 was usually measured, which allowed us to conclude that the unusually high $([\text{Cd}] + [\text{Pb}]) : [\text{Se}]$ molar ratio in the PbSe–CdSe–PbSe dumbbells could indeed result from the presence of the PbSe domains in the nanostructures.

Upon Au(III) reaction, a simultaneous decrease in the $[\text{Cd}] + [\text{Pb}]$ and in the $[\text{Se}]$ concentrations was detected. As the gold reduction yield could be easily explained by oxidation of only a small fraction of the total Se^{2-} anions lost, major consumption of the CdSe and PbSe materials could arise from the surfactant-driven nanocrystal dissolution, as detected by TEM (Fig. 1–3). Interestingly, the net amount of Cd removed was almost two orders of magnitude smaller than the Pb loss, so that it could be presumed that the Au growth mainly proceeded at the expense of PbSe. This was consistent with the TEM observations, which indeed showed Au patches forming almost exclusively at the dumbbell terminations.

At present, the mechanism of Au formation is only partially understood. Control experiments in the absence of DDA revealed that the sole Au(III):DDAB complex could react efficiently with both the PbSe and CdTe sacrificial domains, leading to Au metal deposition. However, under these circumstances, nanocrystal precipitation was prone to occur. TEM investigation showed that the latter event proceeded through the formation of a disordered network of nanorod chain-like segments, in which individual dumbbells fused with each other *via* their gold terminations. An example is reported in Fig. 5. This evidence suggested that, unlike the bare CdSe nanorod system,⁹ DDA did not serve as a reducing agent for Au(III), but was necessary as a surface stabilizer for the gold patches. Therefore, other chemical species should be responsible for the reduction of the Au(III) precursor.

The formation of complexes with the surfactants and size-dependent variation of the redox power of nanoscale materials^{12,18–20} can be expected to alter the absolute values of the electrochemical potentials of the chemical species in our system. Nevertheless, at a first approximation, one can assume that the relative scale of the standard redox potentials, measured in aqueous media, is still applicable to the species involved in the present system.^{18–21} Therefore, from the electrochemical potential point of view, Au(III) reduction to Au(0) could occur directly through oxidation of Te^{2-} in CdTe

Table 1 ICP-AES elemental analysis of nanocrystal dumbbells (mol L^{-1})

	Au	Cd	Pb	Se
PbSe–CdSe–PbSe (initial)		4.37×10^{-7}	1.06×10^{-5}	7.87×10^{-6}
PbSe–CdSe–PbSe (after reaction with Au ^{III})	7.41×10^{-7}	1.30×10^{-7}	3.61×10^{-6}	2.66×10^{-6}

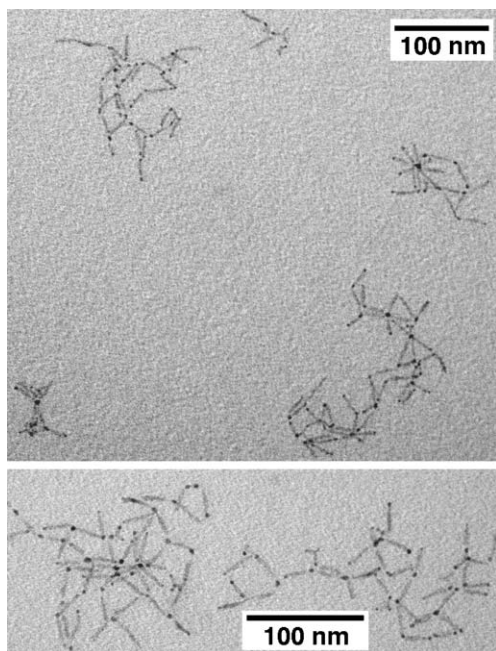


Fig. 5 Examples of aggregates formed by Au-tipped CdSe nanorods fused with each other through their Au terminations.

domains to Te(0) (or of Se²⁻ in PbSe).²¹ This would actually agree with both the TEM and ICP-AES analyses, thus further corroborating the hypothesis that the PbSe and CdTe tips were sacrificially consumed during Au metal production. However, while the formation of Te(0) could be rationalized by these arguments, it remains unclear how the reduction of Cd²⁺ to Cd was also triggered. One possibility could be that the formed Au patches themselves acted as efficient redox catalysts^{19,20} for electron transfer to Cd²⁺ ions. Experiments are currently under way to elucidate the nature of the various chemical processes that accompany gold deposition on the nanocrystal dumbbells under the present reaction conditions.

4. Conclusions

The possibility to perform selective chemical reactions on the tips of CdSe and CdS nanorods has been demonstrated. The developed method involves the growth of additional semiconductor domains on the tips of the rods and subsequent selective oxidization reaction of only these materials. This approach has allowed us to grow Au domains onto specific locations of rod-shaped CdS NCs for which direct metal deposition is unfeasible. We believe that this strategy may be of general utility to create other types of complex colloidal

nanoheterostructures, provided that a suitable sacrificial material can be purposely grown on top of the starting nanocrystals.

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