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Size Controlled Gold Tip Growth onto II-VI Nanorods†

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Gold tip size and multiplicity is controlled in hybrid gold-semiconductor nanorods (CdS-Au, CdSe-Au and CdTe-Au) in fast reaction times of less than 2 minutes by optimising precursor type, concentration, and temperature. Controllable gold tips up to as large as 40 nm on a rod diameter of 7 nm are reported with the tip size shown to be directly related to the redox potentials of the dangling atoms on the nanorod and the gold chloride precursors (mono or trivalent). The preference for symmetric (both ends) over asymmetric (single end) is achieved by simply elevating the reaction temperature to 80°C without changing the reaction time. TEM and XRD analysis were performed to verify both the gold nanoparticle size and crystallinity of the hybrid nanostructures. Increased quenching of nanorod emission is observed as the size of the gold tip increases suggesting optimisation of charge transfer between the semiconductor and the metal.

Introduction

Solution formation of metal tips on semiconductor nanocrystals (nanorods) offer a new paradigm in materials design where discrete nano-sized heterojunctions can be created en-masse by a relatively facile chemical reaction on a colloidal nanocrystal dispersion.¹⁻⁴ Gold tip growth is the most widely investigated with hybrid structures demonstrated with CdS, CdSe, CoPt₃, CdSe seeded CdS, InAs and CdTe nanorods using AuCl₃ or HAuCl₄ as a precursor.⁵⁻¹⁰ The gold tip has significant promise as anchor points for nanoscale connectivity, facilitating optimal (ohmic) interfacing with the semiconductor in nanoelectronics and selectivity for thiol linkages in nanobiotechnology.^{11, 12} Charge separation at metal semiconductor interface has already shown promise in photocatalysis with considerable interest for exciton separation in nanocrystal photovoltaics emerging.¹³

The preference for tip formation with gold in contrast to encapsulation (core-shell)¹⁴ or cation exchange^{15, 16} (e.g. Ag or Cu) is mainly due to the large lattice mismatch between the semiconductor and the gold metal. We recently observed that the use of a monovalent (AuCl) instead of a trivalent gold precursors (AuCl₃, HAuCl₄) allows instantaneous gold tip formation onto CdS nanorods. This was further optimised to a scalable spin casting process achieving gold tipping on nanorods predeposited in a perpendicular aligned array.⁴ The rate of the reaction with the monovalent gold chloride with respect to the trivalent gold precursor is remarkable with the former occurring instantaneously and the latter requiring several hours to days for optimal growth on CdS and CdSe nanorods.¹⁰ The longest reaction times allow the formation of single tipped nanorods using the trivalent precursor which ripen from dumbbells (both ends tipped) after x hours.¹ Recently the rate of tip growth was accelerated by irradiating the sample with UV-light during the tipping reaction.¹⁷ Using

this process it was shown to be possible to control the size of gold tip growth on CdS-CdSe and CdSe nanorods up to 15 nm in a two hour reaction with gold tip size increasing as a function of UV exposure. In contrast, to achieve gold tip sizes of up to 10 nm on similar nanorods a three day reaction is required with AuCl₃ in the absence of external irradiation³. The reaction rate is not however limited to the gold precursor with faster reaction rates (5 min for 13 nm tip) observed for CdTe gold tipped tetrapods with HAuCl₄ largely due to the greater reduction potential of Te dangling bonds.¹⁰

Here we demonstrate very fast yet size controlled gold growth on CdS, CdSe and CdTe nanorods in solution without external irradiation. Tip sizes from 1 nm to as large as 40 nm on a 7 nm diameter CdSe nanorods rod were achieved by varying the concentration of the monovalent gold precursor in a solution based reaction for a duration of two minutes. Under similar conditions, tip size ranged from 2 to a maximum of 15 nm with CdS nanorods. A facile route to control preference for symmetric or asymmetric growth is also reported with the former occurring at the elevated temperature and the latter occurring at room temperature. Gold tipping of CdTe nanorods was more difficult to control with the monovalent gold precursor but gave similar size control to CdS in a 10 second reaction when the reagent was changed to AuCl₃. The kinetics of the gold tip growth is correlated to the reduction potentials of the gold precursors and the respective elements (dangling bonds) on the surface of the II-VI rods.

Experimental

Chemicals

Triethylphosphine (TOP, 90%), cadmium oxide (≥99%), dodecylamine (DDA, 99.5%) were purchased from Fluka;

trioctylphosphine oxide (TOPO, 99%), gold (III) chloride (99.99%), gold (I) chloride (99.99%) sulfur (99.98%), selenium (99.9%), Tellurium, (99.9%), gold(I) chloride (99.9%), and didodecyldimethylammonium bromide (DDAB, 97%) were purchased from Aldrich; and *n*-octadecylphosphonic acid (ODPA) was obtained from PolyCarbon Industries Inc. All Chemicals were used as received.

CdS/CdSe/CdTe nanorod synthesis

Cadmium Sulphide (CdS), Cadmium Selenide (CdSe) and Cadmium Telluride (CdTe) nanorods were prepared using standard air free techniques, and redispersed in toluene before use (0.1%w/v).^{18, 19} In this method CdS (CdSe, CdTe) nanorods were synthesized by the injection of a sulfur (selenium, telluride)/tri-*n*-octylphosphine solution into a cadmium oxide and surfactant mixture.

CdS, CdSe Gold tip growth

Gold tip growth is performed in a 25 ml 3 neck flask consisting of CdS (CdSe) nanorods in toluene at room temperature under argon. The gold solution was injected swiftly into a vigorously stirring mixture and the reaction was allowed to proceed for two minutes before being quenched with methanol. A typical gold solution consisted of 22.5 mg of Dodecylamine (DDA), 12.5 mg of didodecyldimethylammoniumbromide (DDAB), 4 mg (0.017 mmol) of AuCl in 2 ml of anhydrous toluene according to a previous method.⁴ This quantity of gold was varied to manipulate gold tip size, with the surfactant ratio kept constant. All chemicals were weighed in a glove box under nitrogen.

CdTe gold tip growth

To achieve gold tip growth onto CdTe nanorods the nanorods were placed in a 3 neck flask where the gold solution was injected swiftly. A typical gold solution consisted of 8 mg (0.026mmol) of AuCl₃ in 2 ml of chloroform, 48 mg of Dodecylamine (DDA) and 88 mg of didodecyldimethylammoniumbromide (DDAB). The substitution of AuCl with AuCl₃, utilisation of chloroform and increasing the amount of DDAB used was necessary to achieve gold growth on the tips of the nanorods.

Characterisation

Transmission electron microscopy (TEM) was performed using JEOL 2011 TEM with an accelerating voltage of 200kV. The nanorods solvated in toluene was drop cast directly onto a carbon coated copper TEM grid and allowed to dry. Powder X-ray Diffraction (XRD) spectra were obtained with a Philips X'Pert PRO MPD (Multi-purpose X-ray Diffractometer) using Cu K α . However because the volume being used was minute the sample was drop cast and allow to dry directly on the glass slide. Photoluminescence spectra were measured with a Varian Cary Eclipse Fluorescence Spectrophotometer. Ultraviolet-visible spectroscopy was performed on solutions solvated in chloroform on a Varian Cary Eclipse Spectrophotometer. X-Ray Photoelectron Spectroscopy (XPS)

were obtained by a Kratos Axis 165 spectrometer using monochromatic Al K α radiation ($\lambda\nu = 1486.58$ eV) and fixed analyser pass energy of 20 eV. All spectra were calibrated using the C 1S at 284.18 eV.

Results and Discussion

TEM images in Fig. 1 a-c shows the effect of sequential increases in the concentration of the monovalent gold precursor (AuCl) on the resultant tip size growth on 30 \times 7 nm CdSe nanorods. Addition of the lowest gold concentration (0.0086 mmol) leads to gold nanocrystal tips of \sim 1-2 nm on each of the CdSe nanorods as shown in Fig. 1a and further magnified in Fig. 1d. A two minute reaction was found sufficient to tip all rods with complete monodispersity in tip size. The tip growth is inherently asymmetric in these reactions with only a single tip occurring in all cases. Quadrupling the AuCl concentration (0.034 mmol) results in monodisperse tip formation of 12 nm which are significantly larger than the rod diameter (Fig. 1b). High resolution transmission electron microscopy (HRTEM) imaging of a single tipped nanorod from this sample shows lattice fringing from both the gold tip and the semiconductor nanorod (Fig. 1e). The faint fringes from the gold tip is only seen at the edges due to the height offsets from the gold tip and rod diameter at 12 nm and 7 nm respectively. The largest gold tips (40 nm) were observed when the concentration was further increased to (0.155 mmol) (Fig. 1c). Here the volume occupied by the tip is a remarkable 20 times that of the host nanorod and represent the largest tip sizes reported to date (Fig. 1f). The nanorods (7 nm diameters) are encapsulated to half their length by the gold nanocrystal yet in all cases there is asymmetry in the tip formation without complete core shell formation. This is likely due to the large lattice mismatch between the cubic gold and the wurtzite rod which favours island formation rather than conformal coverage. XPS analysis further confirmed the large ratio of Au: Cd, see ESI†, Table S1 for relative concentrations. The images shown are a selection of the results on size control and intermediate tip sizes were achieved as a function of AuCl concentration with the full data set plotted in Fig. 4. The substitution of the trivalent gold precursor with a monovalent gold precursor in our study is believed necessary for spontaneous controlled gold growth.

Fig. 2 shows a selection of TEM results with a similar concentration study when the nanorods are CdS with similar diameters and lengths. Here the lowest gold chloride concentration (0.0086 mmol) leads to polydispersed tip growth, ranging from < 1 nm to 4.5 nm, Fig. 2a. A higher gold concentration (0.0344 mmol) leads to the formation of uniform gold tips on each of the nanorods, (Fig. 2b) however the diameter of \sim 8 nm is less than the that observed for gold tip growth onto CdSe nanorods under identical conditions (Fig. 1b). The largest tips possible for CdS were 12-15 nm using a concentration of 0.103 mmol AuCl. Further increases in concentration had no impact on tip size suggesting the maximum possible tip size is related to the elemental composition of the nanorod.

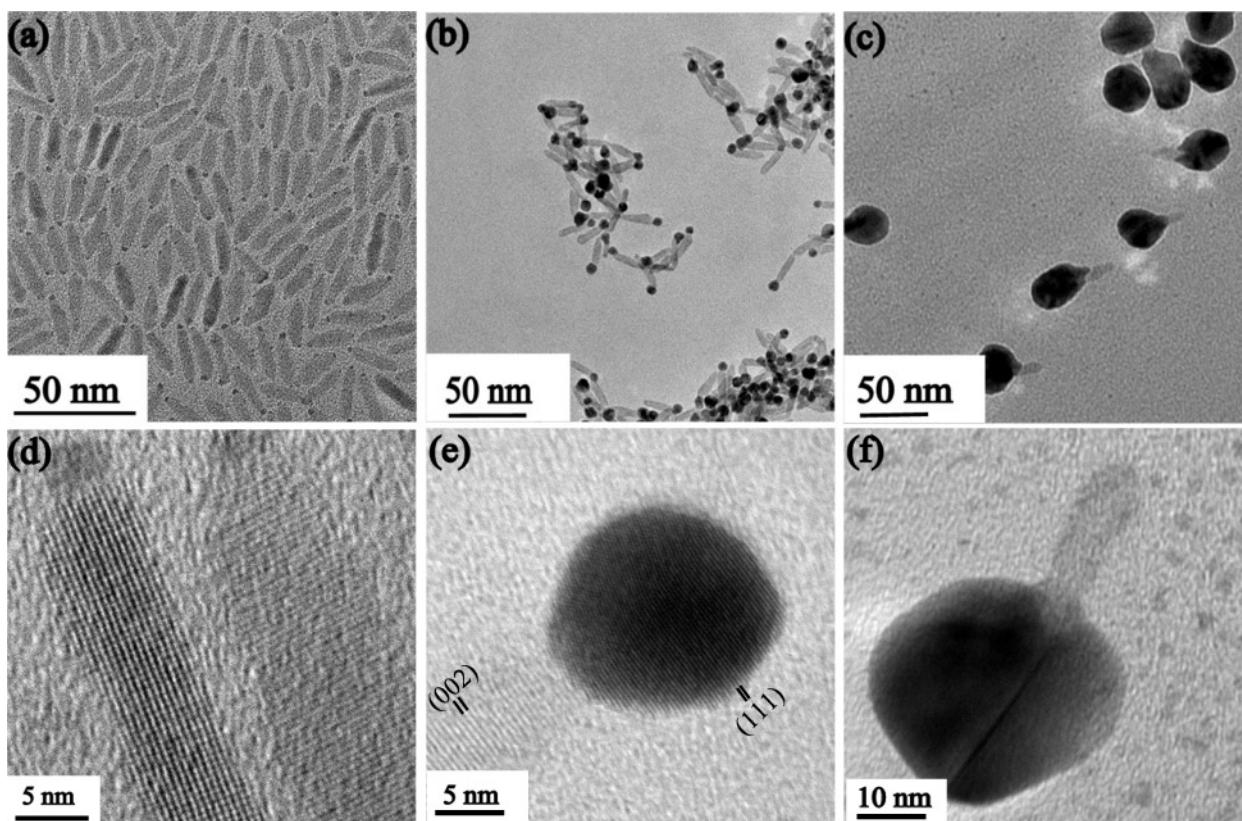


Fig. 1. TEM images showing the change in tip size due to a variation in starting gold concentration on CdSe nanorods in a two minute reaction. (a) Gold tip growth with 0.0086 mmol gold (I) chloride on CdSe nanorods (d) HRTEM image using the latter gold concentration (b) Gold tip growth with 0.034 mmol gold (I) chloride on CdSe nanorods (e) corresponding HRTEM image (c) Gold tip growth with 0.155 mmol gold (I) chloride on CdSe nanorods growth (f) corresponding HRTEM image.

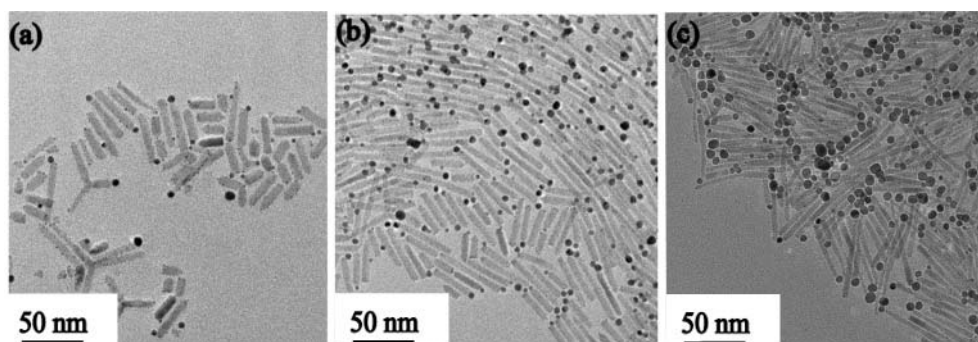


Fig. 2. Varied gold tip size variation on CdS nanorods due to a manipulation of starting gold concentration (a) Gold tip growth using 0.0086 mmol gold (I) chloride on CdS nanorods (b) Gold tip growth with 0.0344 mmol gold (I) chloride on CdS nanorods (c) Gold tip growth with 0.103 mmol gold (I) chloride on CdS nanorod.

Gold tip growth onto CdTe nanorods differs significantly from that observed for CdS and CdSe under similar reaction conditions. Using the monovalent precursor the reaction is so vigorous that controlled tip growth was not possible. Switching to the trivalent precursor (0.013 mmol) and using chloroform as the solvent resulted in uniform 5 nm tips after a 10 second reaction (Fig. 3a) and further magnified for an individual nanorod (Fig. 3d). Addition of 0.026 mmol AuCl₃ leads to tips that are approximately 10 nm in diameter, Fig. 3b, whereas gold tip growth of approximately 15 nm in diameter are achievable after subjection to 0.05 mmol AuCl₃, Fig. 2c. Increasing the AuCl₃ concentration to 0.066 mmol leads to large, less monodispersed tips of approximately 20

nm in diameter, (see ESI†, Fig. S2).

The data presented so far shows that when precise reaction conditions are followed controllable gold tip growth is possible on CdS, CdSe and CdTe nanorods in short reaction times (< 120 s). Clearly the reaction rate for tip growth is dependent on the elemental composition of the starting nanorod in addition to the precursor concentration. This has previously been linked to the respective reduction potential of the dangling atoms on the rods surface in the case of tip growth on CdTe tetrapods.¹⁰ Extrapolating, the effect of reduction potentials to the observations in our work allows rationalisation of how much

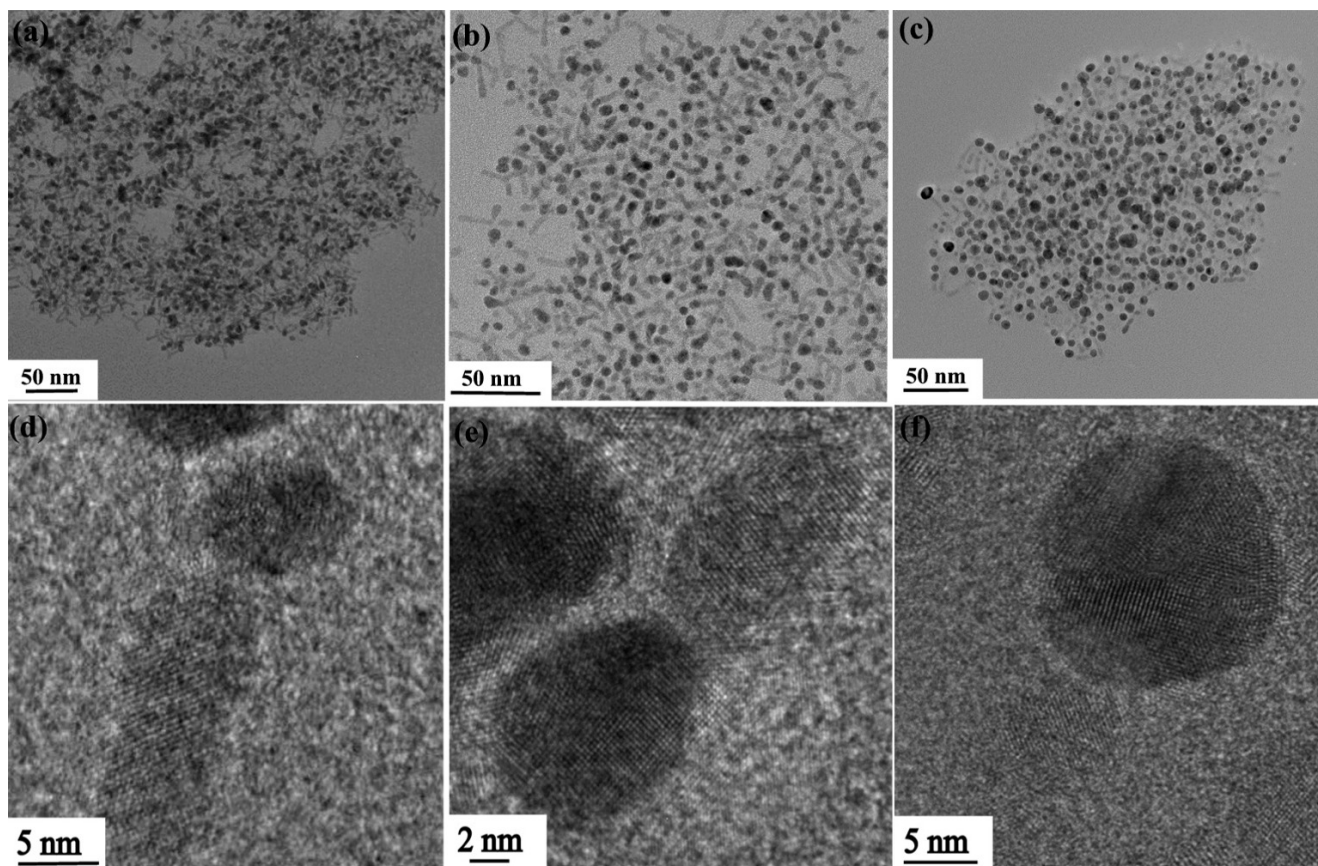


Fig 3. Gold tip size variation on CdTe nanorods after a 10 second reaction by a manipulation of starting gold concentration (a) Gold tip growth using 0.0086 mmol gold (I) chloride on CdS nanorods (b) Gold tip growth with 0.0344 mmol gold (I) chloride on CdS nanorods (c) Gold tip growth with 0.103 mmol gold (I) chloride on CdS nanorod, (d,e,f) corresponding HRTEM images to the above images.

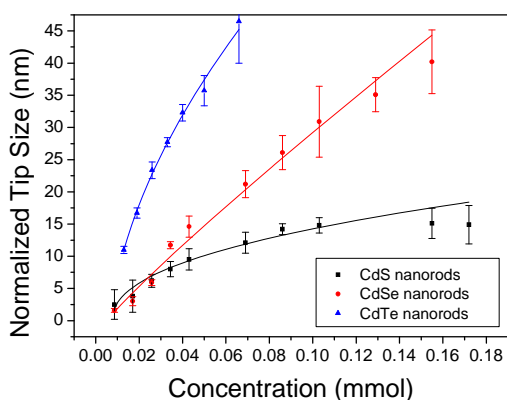


Fig 4. Gold tip size variation and corresponding concentration of gold for CdS, CdSe and CdTe nanorods.

larger tips could be achieved in the case of CdSe. The reduction potential of Se^{2-} ions (-0.924V) is large compared to that of S^{2-} ions (-0.476 V), leading to increased reactivity during the tipping process.²⁰ The Te^{2-} ion, with an even more negative potential of -1.143 V, should have an even higher reaction rate which causes the uncontrolled reactions with AuCl . The more controlled reaction possible on CdTe with the trivalent precursor can be understood when the difference in oxidation potential of the two gold cations is considered. The

15 monovalent Au^+ cation – used for the CdS and CdSe nanorods – has an oxidation potential of 1.692 V, while the Au^{3+} cation has an oxidation potential of 1.498 V. Therefore, while there is a difference of 0.2 V in the reduction potentials of the Se^{2-} and Te^{2-} anions, there is an almost equal difference in the
20 oxidation potentials of the Au^+ and Au^{3+} cations, resulting in an overall equal relative redox potential for the Au^+ - Se^{2-} and the Au^{3+} - Te^{2-} systems. Fig. 4 shows the relationship between tip size (after a reaction of 120 seconds) and concentration of gold used in the reaction. The growth of a particle due to
25 Ostwald ripening can be described by the following equation:²¹

$$D = k_1 t^{\frac{1}{n}}$$

where D is the particle diameter, k_1 is the kinetic rate of the reaction, t is the time of the reaction and n is the
30 dimensionality of the growth – in this case, $n = 3$. For the CdS and CdSe, the reaction time was 120 s, but for the CdTe, the reaction time was 10 s. Reaction times longer than this resulted in less controlled multiple tip growth. To normalize all three reactions, the particle size for the CdTe was
35 extrapolated from the above equation. However this equation only holds for a given concentration, a more complete equation must be considered in order to analyze the

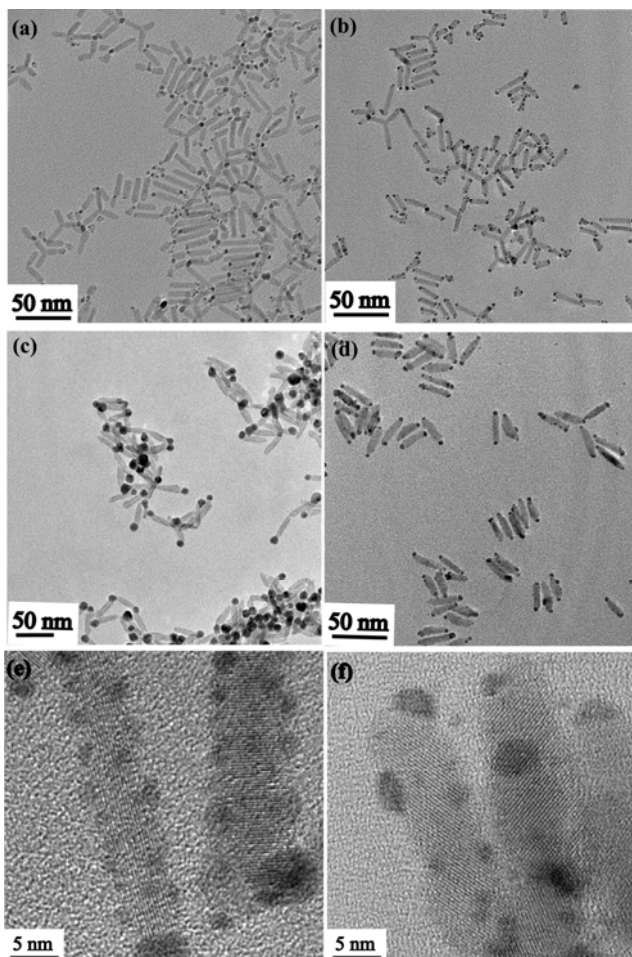


Fig 5. TEM image showing how a change in the reaction parameters such as temperature and duration can lead to a variation in tip positioning. (a) gold growth onto CdS nanorods at room temperature for 2 minutes leading to an asymmetric tip (b) gold growth at 80°C for 2 minutes leading to symmetric gold tipping on CdS nanorods (c) gold tip growth onto CdSe nanorods at room temperature leading to asymmetric tip growth (d) gold tip growth at 80°C leading to symmetric gold tip growth onto CdSe nanorods. Multiple tipping on the side of (e) CdS and (f) CdSe nanorods resulting from increased reaction duration

concentration dependence, given by

$$D = k_1 (c - c_0)^p t^{\frac{1}{n}}$$

where c is the concentration of the gold precursor and p and c_0 are constants. Given that t and k_1 are constants, this reduces to a Belehradek equation

$$D = A(c - c_0)^p$$

with A , c_0 and p as fitting parameters. The data in Fig. 4 was fitted using this equation, the fitting parameters are given in ESI†, Table S2. A would represent the kinetic rate of the tipping reaction. As expected, the rate for CdS is much lower than that of the other materials. The CdSe and CdTe have, within uncertainty, almost the same kinetic rate. All other factors being equal and assuming similar activation energies

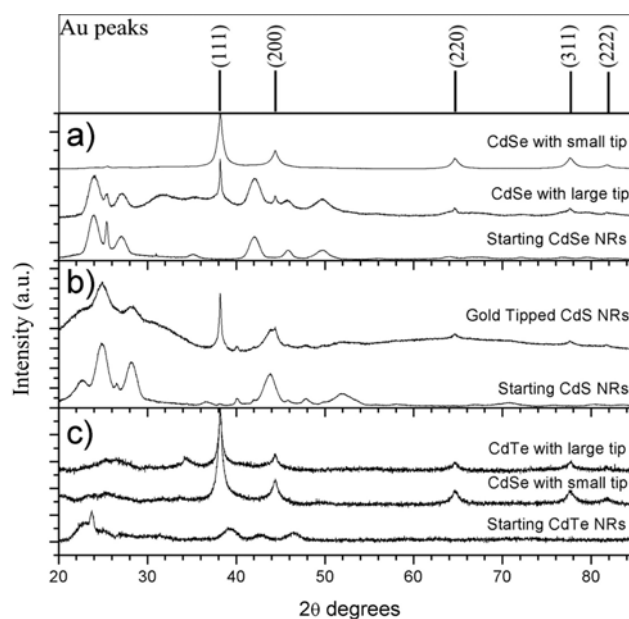


Fig 6. Powder X-ray diffraction pattern of (a) as synthesized CdSe nanorods, CdSe nanorods with small gold tips (10 nm) and CdSe nanorods with large gold tips (38 nm) (b) as synthesized CdS nanorods and CdS nanorods with Au tips (10nm) (c) as synthesised CdTe nanorods, CdTe nanorods with small (~5 nm) gold tips and CdTe nanorods with larger gold tips (~10 nm).

for all materials, a similar reaction rate can be expected for the two systems.

While external factors such as light, dark, aerobic and anaerobic conditions have been shown to effect previous gold tip growth reactions,²² the effect of these on the gold tip growth in our study was shown to be negligible, most likely due to the short reaction times. However the addition of heat to the reaction has a pronounced effect on the multiplicity of tip formation. A typical gold tip reaction favours asymmetric growth (single end tipping), however it is observed that elevating the reaction temperature to 80°C resulted in symmetric growth (both end tipping) under the same conditions. Fig. 5a shows CdS nanorods subjected to gold tip growth at room temperature giving a typical tip size of 4.5 nm on only one end of the rod. The corresponding result from subsection of the same batch of nanorods to the tipping reaction at 80°C results in dumbbell structures. Interestingly, the effective doubling of the tipping sites did not affect the average tip size that occurred on each rod which remained constant at 4.5 nm. This suggests that the elevated temperature does not increase the rate of tip growth but lowers the activation barrier for tipping at the lesser reactive rod end for CdS. The results for CdSe are shown in Fig. 5c and d. Similar results were obtained with the elevated temperature favoring symmetric over asymmetric growth. Again the 100% selectivity of this reaction to temperature is remarkable with all rods forming a single tip at room temperature and dual tips at the elevated temperature. However, in the case of CdSe larger asymmetric tips (12 nm) occurred in comparison to (6 nm) to symmetric tips suggesting that the availability of a

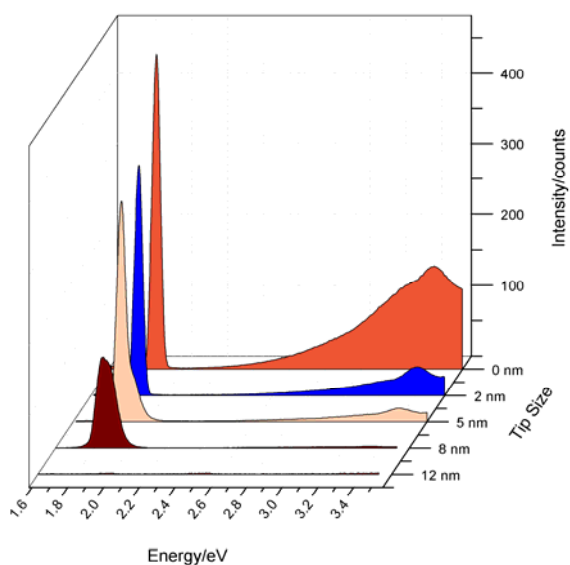


Fig 7. PL spectra of as synthesised CdSe nanorods and CdSe nanorods with various gold tip sizes

second site for nucleation reduces the critical tip size for gold tip growth on CdSe at this concentration. Extending the reaction time beyond 2 minutes at room temperature resulted in multiple tipping occurring on both CdS and CdSe nanorods. Fig. 5 e and f shows the pattern of gold nucleation on CdS and CdSe nanorods respectively after subjection to 0.0344 mmol AuCl for a 10 minute reaction. The side wall tips (1-2 nm) are typically much smaller than the tips localised at the nanorod ends and most likely occur at crystallographic stacking faults between zinc-blende and wurzite typical of II-VI nanorods.²³

The XRD spectra of as synthesised nanorods and selected small and large tips for each of the three chalcogenides is shown in Fig. 4a. The as synthesised nanorods for each of the CdSe, CdS and CdTe are in excellent agreement with the literature JCPDS values #77-002, #41-1049 and #73-2871 respectively. The Au formation corresponds with the emergence of peaks at $2\theta = 38.20, 44.41, 64.60, 77.61$ and 81.81 degrees which matches closely with cubic gold ref. (JCPDS) # 71-4615. These 2θ positions can be indexed to (111), (200), (220), (311) and (222) lattice planes. Scherrer analysis of each of the Au peaks yielded an average gold particle size in good agreement with the TEM analysis (see ESI†, Table S3).

Photoluminescence (PL) spectra of CdSe nanorods with sequentially increasing gold tip sizes; 0 nm, 3 nm, 5 nm, 8 nm and 12 nm are shown in Fig. 7. In the as synthesized CdSe nanorods two significant emission peaks were detected centred around 3.2 eV (370 nm) and 1.8 eV (670 nm) which denote the surface defect emission and the band gap emission respectively. As the gold tip increases, the intensity of both peaks reduces; particularly the surface defect emission, which eventually disappears in the case of tip size larger than 8 nm. The quenching of the band gap emission is observed in nanorods with tip size greater than 12 nm. This quenching

effect in the band gap emission is due to the rapid transfer from the conduction band (CdSe) to the gold tip leading to charge separation and a reduction in charge recombination.

The size dependence of this effect as shown highlights the strong coupling of the gold to the nanorod and suggests that tips larger than the rod diameter are needed for optimal charge separation in photocatalysis or photovoltaics. Similar quenching behaviour has also been observed for CdS nanorods of similar tip sizes,⁴ and for CdTe nanorods with gold tips, (see ESI†, Fig. S4).

Conclusion

Size controlled growth of gold tips onto CdS, CdSe and CdTe nanorods has been demonstrated in fast reaction times (< 120 seconds). Tip sizes of up to 40 nm were achieved on CdSe which are the largest reported to-date. The rate of tip growth is shown to correlate with the concentration of the gold precursor in addition to the reduction potentials of both the gold precursor and the nanorod dangling atoms. A greatly simplified protocol for dictating symmetric over asymmetric tip growth was shown to occur with 100% selectivity when the temperature of the reaction is raised to 80°C. The tunability of tip size and localisation coupled to the fast reaction times is attractive for practical application where bulk concentrations of tipped rods are needed on demand. Additionally, the ability to tune the volume ratio of the metal to semiconductor may allow optimisation of distinct size dependent properties of both materials such as plasmonic properties in the metal and quantum confinement in the semiconductor for enhancement of photovoltaic devices.

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40