

Gold Tip Formation on Perpendicularly Aligned Semiconductor Nanorod Assemblies

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Received (in XXX, XXX) 1st January 2007, Accepted 1st January 2007

5 First published on the web 1st January 2007

DOI: 10.1039/b000000x

A facile spin cast process is used for the instantaneous asymmetric formation of gold tips on perpendicularly aligned CdS nanorod superlattices. Tip size varies as a function of precursor solution concentration and growth time. A single uniform tip occurs on the end facets of each
10 nanorod in the array when an optimised gold chloride solution is used, with multiple tipping occurring with variations in precursor concentration. HRTEM shows that the gold tip growth does not always occur centro-symmetrically on the nanorods, with growth occurring on the (101) or the (001) facet of the wurtzite nanocrystal depending on the rod shape. X-ray diffraction confirms that the gold tips are crystalline with a 60% lattice mismatch with the wurtzite CdS nanocrystal
15 suggesting strain relief may be a factor in tip formation. The gold tipped nanorods are further characterised by photoluminescence spectroscopy.

Introduction

Directed and self-assembly of vertically aligned nanorods into hexagonal superlattices is a recent development in nanocrystal
20 assembly. Electric fields applied across a drying nanorod solution can direct orientation perpendicular to the substrate during packing.^{1, 2} Perpendicular alignment of nanorods in hexagonal arrays without external fields is also possible. We have recently reported the vertical alignment of CdS nanorods
25 (25 nm × 7 nm) over micron squared areas by controlled evaporation under highly oriented pyrolytic graphite (HOPG) whereas Carbone *et al* achieved similar structures by evaporation control at the toluene water interface.^{3, 4} These perpendicularly aligned nanorods separated from their nearest
30 neighbour by organic spacers offer a route to integrating useful properties of discrete nanorods in ordered high density applications. Individual nanorods have been shown for example to function as single electron devices, interconnects, linearly polarised emitters and biospecific sensors.⁵⁻⁹ The
35 organisation of such discrete functionalities into ordered arrays on a substrate allows the possibility of self assembled macroscale devices with unprecedented properties defined by precise positioning at the nanoscale.

Post synthetic functionalisation of individual nanorods can
40 allow more complex hybrid metal/semiconductor nanorods to be developed. Banin and co-workers formed gold tips symmetrically and asymmetrically on CdSe nanorods using a solution phase reflux reduction of gold (III) chloride.^{10, 11} This was further extended to gold tip growth on CoPt₃ and InAs
45 nanocrystals using a similar solution process by Pellegrino and Mokari.^{12, 13} The selectivity for asymmetric over symmetric growth was shown to occur by nanorod specific Ostwald ripening of the gold eventually favouring a single uniform tip.¹⁰ The gold tips are expected to provide an ideal
50 anchor point for nanorod integration across a range of disciplines in nanoelectronics, nanophotonics and nanobiology. For example, Salant *et al.* used the selectivity of

a biomolecular species for binding at the gold tip to arrange the nanorods end to end on a substrate.¹⁴ The selectivity of
55 gold sulphur bonds means any organic moiety that can be functionalized with a thiol linkage can be attached to a semiconductor nanorod using the gold tip interface. This has particular advantages for the binding of complex molecular species such as DNA which are routinely terminated with
60 sulphur functional groups.¹⁵ Specific applications in bio-labelling can be realised whereas specific biosensor properties are feasible in arrayed structures. In nanoelectronic applications, the gold tip can potentially provide a low barrier interface to reduce contact resistance in discrete nanocrystal
65 devices. The greater conductivity of the metallised end of hybrid rods has been established by conductance AFM although the effect of tipping on the electronic properties of the remnant semiconductor has yet to be fully established.¹¹ Recently, Costi *et al.* showed that charge separation can occur
70 at the metal nanorod interface under photoexcitation suggesting that the metal nanorod interface functions as a type II heterojunction with electron transfer occurring from the conduction band of the semiconductor to the gold tips.¹⁶ In the solution state sufficient retention of charge was possible to
75 affect photocatalytic redox reactions.

In this paper we report a method to form vertically aligned arrays of gold tipped nanorods by a facile spin casting process. This sequential approach involves nanorod synthesis followed by perpendicular alignment on a substrate with
80 subsequent tipping using a gold(I)chloride solution. The instantaneous reaction results in a single uniform tip on each of the exposed end facets of the wurtzite nanorods with the tip positioning largely determined by facet size. Such arrays of gold terminated nanorods precisely positioned on a substrate
85 are likely to greatly facilitate their hierarchical integration into functional devices.

Results and discussion

The novel sequential process used to form superlattice arrays of gold tipped nanorods is schematically shown in figure 1. Monodisperse nanorods can be aligned into perpendicular arrays either by trapping a solution of the nanorods under an electric field of 1kV or by pinning the nanorod solution between a Highly Oriented Pyrolytic Graphite block and a gold substrate according to previously published methods.¹⁻³ An optimized gold(I)chloride solution is spin cast onto the nanorods on a substrate for 30 seconds followed by a couple of drops of methanol to quench the reaction. This procedure leads to the instantaneous and reproducible formation of an individual gold tip on the end of each nanorod in the array.

Figure 2a-c shows TEM images at successive magnifications of the optimum growth of single gold tips on perpendicularly aligned CdS nanorods. Tip growth in this case is inherently asymmetric occurring only on the exposed ends of the vertically aligned nanorods with an average tip size of 2.9 nm. In figure 2a and further magnified in figure 2b, the non-centrosymmetric positioning of the gold tips on the nanorods are clearly visible. The predominant gold tip position is on or near the edge of the anisotropic nanocrystal when viewed as a 2D projection as in TEM. Centered gold tip nucleation with respect to the rod axis occurred in less than 10% of aligned nanorods (fig. 2c). It is expected that the tip positioning is related to the facet topography at the end of the nanorod. During the nucleation of the CdS nanorod, growth occurs in the <001> direction however it is not expected that the termination of growth is abrupt. Manna *et al* showed that the end structure of nanorods is terminated by small (101) facets at 45 degrees to the rod direction and a planar (001) facet.¹⁷ The respective sizes of the (001) facet and the (101) facets terminating the nanorod are affected by how fast or slow the termination of growth in the solution state occurs. This can vary from rod to rod as highlighted in figure 4a where nanorods from the same batch have either a pointed pencil shape (labeled α) or a flattened pencil shape (labeled β). Depending on the shape of the exposed end structure of the CdS nanorods in the supercrystal, tip growth appears to occur on the (101) facet if pencil shaped or on the (001) facet if flattened pencil shaped. This is shown schematically where a 3D projection of CdS nanorods shows how the positioning of the gold nanocrystals on the respective facets will lead to centered (fig. 2d) or off centered positioning (fig. 2e) of the gold tip when viewed using TEM.

The instantaneous reduction of gold (I) chloride to Au⁰ gold tips in this procedure contrasts with several hours required for the reduction of gold (III) chloride in solution reflux. The size and distribution of the tips in our study was found to have a concentration dependence. Figure 3a-c shows pre-aligned nanorods from the same batch (8 nm × 20 nm) which have been subjected to different concentrations of gold chloride. Figure 3a shows the tip formation after spin casting with 5 μ L of 6.5×10^{-3} mol dm⁻³ gold chloride solution. The gold tips (< 1nm) are barely perceptible occurring on multiple sites on each rod typically close to the edge. The optimal gold chloride concentration used in Fig. 3b, equivalent to the concentration used in Fig. 2 is 8.6×10^{-3} mol dm⁻³ solution. Again a single

uniform gold tip occurs on each nanorod with an average tip size of 2.5 nm. A higher concentration of gold (1.2×10^{-2} mol dm⁻³) leads to the multiple tipping on the CdS nanorods with an average tip size of 1.3 nm (fig. 3c). The upper left hand corner of figure 3c shows an area of nanorods aligned parallel to the substrate where it is evident that the multiple tipping occurs uniformly along the long axis of the nanorod. The number density of tips appears greater on the end facets of the perpendicularly aligned rods in this image. However, as this is a 2D representation of the entire C-axis of the nanorod, all gold tips will appear to occur on the end facets. The image of the parallel aligned nanorods is a truer reflection of the structure with uniform distribution of the sub-1.5 nm tips. It was shown that multiple tip growth occurs on defects along the nanorod surface which are most likely at stacking faults between the wurtzite and Zinc-blende crystal growth. It is known that on average a II-VI nanorod can have up to 10 stacking faults in each 30 nm of length. The positioning and multiplicity of tip growth was unaffected by the aspect ratio of the nanorod. Figure 3d shows nanorods from a different synthesis batch, (aspect ratio: L/D = 6) which were subjected to the optimum gold concentration for tip formation similar to figure 3b. Again, single uniform tip sizes were observed (average 2.9 nm in diameter) with non-centrosymmetric positioning on the rod axis. In this synthesis the spin-casting experiment resulted in single uniform tip growth occurring both on rods aligned perpendicular and parallel to the substrate. The tip growth on the perpendicularly aligned nanorods is expected to be inherently asymmetric due to the passivation influence of the bonded surface. However the occurrence of asymmetric tip growth on the parallel aligned rods suggests that asymmetric tip growth is preferred in this rapid spin casting process regardless of rod orientation.

Instantaneous gold tip formation also occurred in the solution state when CdS nanorods were refluxed in the gold (I) chloride solution under argon. Figure 4b shows TEM images of uniform gold tip growth after an aliquot is taken after two minutes. In comparison, several hours growth was needed to achieve tip formation with AuCl₃ on CdS with similar gold tip diameter to rod diameter ratios in non aerobic conditions. High resolution TEM, Fig. 4c of a single nanorod with asymmetric tip growth shows that tip formation favours the pencil shaped end of the nanorod. The size, asymmetric growth and density of the gold tips after 2 minutes reflux were similar to that obtained by the optimized spin cast method. Figure 4d shows pre deposited nanorods (25 nm × 7 nm) lying parallel to the substrate after 30 s spin casting with 8.6×10^{-3} mol dm⁻³ of AuCl. Predominantly asymmetric tip growth has also occurred with an average tip size of 3.5 nm. The quality of the image is reduced slightly as the spin-casting process results in the deposition of excess surfactant on to the grid. Typically the largest tip size obtainable using the spin casting process is equal in diameter to the radius of the nanorod. Slower spin speeds (60 s) in a saturated solvent atmosphere yielded tips from 5-7 nm in diameter. Tips larger than the rod diameter were only achievable in the solution reflux.

XRD spectra of CdS nanorods and CdS nanorods after 2 minutes reaction with gold (I) chloride is shown in figure 5.

The CdS nanorod spectrum was indexed to CdS ref. (JCPDS) #41-1049. Additional peaks were observed after gold tipping at 38.20, 44.45, 64.67 and 77.60 2θ which match closely to gold metal reflections (111), (200), (220) and (311) respectively (JCPDS) #73-9564. The XRD data confirmed that the gold nanoparticle tips are crystalline cubic with a basal lattice parameter of 4.08 Å.

A 60% lattice mismatch exists between the hexagonal CdS nanocrystal and the cubic gold nanocrystal along the c -direction which is reflected in a large misfit in d -values. This lattice mismatch suggests that strain relief may be a significant factor in gold tip formation. A parallel for this phenomenon is that which is observed in the molecular beam heteroepitaxy of Cu on a Ni(100) wafer.¹⁸ The lattice mismatch and associated strain relief results in the growth of small islands of copper of a critical atom density which ripen into larger islands on continued deposition. Similar strain dependent island formation on CdS nanorods was recently reported by Robinson et al during the partial cation exchange of Cd²⁺ with Ag⁺.¹⁹ Initially random islands of Ag₂S were distributed around the rod which merged into larger segments along the rod axis by Ostwald ripening. It is expected that the occurrence of multiple tips on the nanorod (fig. 2c) occurs when the gold clusters are below a critical atom density beyond which ripening occurs into larger islands or tips. The sub-1 nm particles are most likely stable gold clusters in the anticubic octahedron geometry which aggregate into superclusters in the observed cubic close packed arrangement. One very stable form of gold superclusters is [(Au₁₃)₁₃]n which is a cubic nanocrystal with a typical diameter of 2.5 nm similar to the optimum gold tips observed.²⁰

Photoluminescence (PL) data of the as synthesised CdS nanorods and the CdS nanorods after 2 and 30 minutes reaction with AuCl respectively is shown in figure 6. The nanorods were excited at 540 nm. The quenching of the emission peak > 2 eV from the CdS nanorod due to the presence of the gold tip has previously been observed in such structures.¹¹ The emission quenching shows a direct correlation with gold tip size highlighting the strong coupling of the gold tip to the CdS nanorod.

Experimental

Chemicals

Trioctylphosphine (TOP, 90%), cadmium oxide ($\geq 99\%$), dodecylamine (DDA, 99.5%) were purchased from Fluka; trioctylphosphine oxide (TOPO, 99%), sulfur (99.98%), 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.

Synthesis and perpendicular alignment of CdS nanorods

The CdS nanorods used in this study were synthesized using the pyrolysis route²¹, and redispersed in a toluene solution before use (0.1% w/v). In this method CdS nanorods were

synthesised by the injection of a sulfur/tri- n -octylphosphine solution into a hot cadmium oxide and surfactant mixture at a high temperature.

The nanorods can be perpendicularly aligned using either electric field methods or by highly ordered pyrolytic graphite (HOPG) (20 mm \times 20 mm \times 1 mm, SPI Supplies). The electric field method utilises a combination of a DC electric field and slow evaporation of solvent (toluene) to generate large CdS superlattices. The CdS nanorods dispersed in toluene are trapped between parallel electrodes (Fig 1) and allowed to dry under a DC electric field. Slower evaporation is achieved through near-saturation of the entire assembly in a toluene atmosphere. As the solvent evaporated the size of the trapped droplet decreases the CdS nanorods pack into a 2D superlattice.¹ Using HOPG the nanorods can be assembled into large superlattices without the use of an external electric field. The nanorods are trapped between a block of HOPG and a substrate eg TEM grid or silicon wafer. The assembly was covered in an airtight container to allow slower evaporation of the solvent, and the solution was allowed to dry over several hours.

Spin cast gold tips

The CdS nanorods were perpendicularly aligned on a carbon coated copper TEM grid and the grid was placed on a glass slide in the spin coater (Fig 1d). A drop of AuCl solution (~ 5 μ L) was placed on the grid and another after 10 seconds. The total spin time was 30 seconds at a spin rate of 100 rpm. The gold growth was subsequently quenched with 1 ml of methanol. Excess surfactant was removed by suspending the grid in acetone. The typical gold solution consisted of 22.5 mg of Dodecylamine (DDA), 12.5 mg of didodecyldimethylammoniumbromide (DDAB), 4 mg of AuCl and suspended in 2 ml of anhydrous toluene. All chemicals were weighed in a glove box under nitrogen. The gold solution was sonicated for 5 minutes before use.

Solution grown gold tips

The solution method involved a reflux set-up in a three neck flask consisting of CdS nanorods in toluene at room temperature under argon. The gold solution was injected swiftly into a vigorously stirring mixture. The reaction is allowed to proceed for two minutes until quenched by injection of methanol. The nanorods with the Au tips can subsequently be deposited onto the desired substrate depending on analysis.

Characterisation

Photoluminescence spectra were measured with a Varian Cary Eclipse Fluorescence Spectrophotometer. X-ray Diffraction (XRD) spectra were obtained with a Philips X'Pert PRO MPD (Multi-purpose X-ray Diffractometer) using Cu $K\alpha$ radiation. Transition electron microscopy (TEM) was performed using a JEOL 2011 TEM with an accelerating voltage of 200kV.

Conclusions

The controllable formation of gold tips on each nanorod in a superlattice is a promising route for their higher integration into functional device architectures. In effect each gold tipped nanorod in the assembly is an individual substrate bonded probe insulated from its nearest neighbour by organic ligands. The assembly is an ideal architecture for sensor and screening applications using the gold as the functional component. For example, DNA-functionalized gold particles have been used as targeted sensors for biomolecular species and biomolecular activity and in more diverse applications such as heavy metal detection.²²⁻²⁶ The integration of such functionalities in aligned gold-nanorod probes would allow for significant miniaturization and greater sensitivities to detection through electrical response. Gold is also an excellent seed for the mediation of semiconductor nanowire growth and aligned arrays of such seed structures at specific separation may allow the templation of directional arrangements of silicon nanowires at ultra high densities which have not been achieved by other methods.^{27, 28} Gold tipped II-VI nanorods have also been demonstrated in visible light photocatalysis where charge separation occurs between the metal and semiconductor component of the particle. The organization of 2D arrays of gold tipped nanorods on a substrate would potentially allow high efficiency photovoltaic device fabrication where the separated holes and electrons are harnessed in an external circuit.

Acknowledgements

The work was supported principally by Science Foundation Ireland (SFI) under the Principal Investigator Program under contract No. 06/IN.1/I85. Funding and support from Intel Ireland is acknowledged under the Irish Research Council for Science, Engineering and Technology (IRCSET) embark initiative for COS. The authors acknowledge Juan P. Camacho and Amy Rudd, Intel Ireland for useful discussions and Wynette Reddington, MSSI for XRD measurements.

Notes and references

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Figure Captions

Fig. 1 Schematic showing the process to achieve instantaneous gold tips via the spin cast method: Starting with a blank substrate, (a), the nanorods are perpendicularly aligned using either electric field or highly ordered pyrolytic graphite directed assembly.(b). The gold solution is then spin cast onto the aligned nanorods for 30s before quenching with methanol (c) resulting in perpendicularly aligned nanorods with gold tips (d).

Fig. 2 Transmission electron micrograph (TEM) image of vertically aligned CdS nanorods (10 nm × 25 nm) after the formation of gold-tips by spin-casting technique (scale bar = 10 nm) (a). Further magnified TEM image of gold tipped CdS nanorod superlattice (scale bar = 5 nm) (b). High resolution TEM showing single CdS nanorod with gold tip growth on the 001 facet(c) Schematic showing 3D view of tip growth on 001 facet of CdS nanorod(d), 3D schematic of tip growth on respective 101 facets(e).

Fig. 3 TEM image showing gold tip growth on CdS nanorod superlattice using 6.5×10^{-3} mol dm⁻³ gold (I) chloride after 30 s reaction (Scale bar = 10 nm)(a). Gold tip growth with 8.6×10^{-3} mol dm⁻³ gold (I) chloride (scale bar = 20 nm) (b). Gold tip growth with 1.2×10^{-2} mol dm⁻³ gold (I) chloride (scale bar = 20 nm) (c). Gold tip growth on higher aspect ratio batch of nanorods using 8.6×10^{-3} mol dm⁻³ gold (I) chloride (scale bar = 10 nm) (d)

Fig. 4 TEM image of CdS nanorods (10 nm × 25 nm) before gold tipping (a), TEM image of gold tip growth after two minutes solution reflux (scale bar = 25 nm) with AuCl (b). HRTEM of single nanorod with large gold tip(c). TEM image of nanorods after 30 seconds spin casting with AuCl (d).

Fig. 5 Powder X-ray diffraction patterns comparing CdS nanorods before (i) and after (ii) Au-tip growth. CdS and Au peaks are labeled to JCPDS-41-1049 and JCPDS-73-8564 respectively.

Fig. 6 Photoluminescence patterns of CdS nanorods prior to reaction (square markers), with gold tip growth after 2 min reaction (diamond markers) and 30 min reaction (circle markers). Samples were excited at 540 nm.