

# Silver Tip Formation on Colloidal CdSe Nanorods by a Facile Phase Transfer Protocol

Tanushree Bala,<sup>[a]</sup> Ambarish Sanyal,<sup>[a, #]</sup> Ajay Singh,<sup>[a, b]</sup> Dervla Kelly,<sup>[a]</sup> Catriona O'Sullivan, Fathima Laffir<sup>[a]</sup> and Kevin M. Ryan<sup>\*[a, b]</sup>

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A facile phase transfer procedure is described for the formation of uniform silver metal tips on II-VI semiconductor nanorods. Judicious choice of a functional ligand, dimethyl phenol (DMP), which binds to the semiconductor rod in the organic phase enables the transfer of metal ions from the aqueous phase and their reduction onto the nanorod. The metal tips initially form as random sub-2 nm particles surrounding the nanorod which ripen to dual tips at the nanorod ends. The nanorod hybrids can be assembled into perpendicularly aligned arrays by simple solvent evaporation. The hybrid nanostructures are characterised by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), photoluminescence (PL), ultraviolet-visible spectroscopy (UV-vis) and X-ray photoelectron spectroscopy (XPS). A detailed FTIR analysis is also carried out to predict the role of the ligands in the tipping procedure.

## Introduction

Colloidal semiconductor nanorods synthesised by precise shape control of nanocrystals have found significant application in photovoltaics, photocatalysis and field emission devices.<sup>1-5</sup> These bulk applications are possible as the nanorods can be readily assembled into scaleable perpendicular architectures where length dependent properties such as total absorption or emission can be independently tuned from diameter dependent properties such as band gap.<sup>2,6,7</sup> Recent advances allow the formation of gold tips on the ends of the semiconductor nanorods as a sequential synthetic step in solution or by post-synthetic spin casting on a preformed assembly.<sup>8-17</sup> This heterojunction, while long understood as critical to bulk devices, has particular significance in the nano size domain where quantized energy levels in the semiconductor and plasmonic resonances in the metal allow the possibility of unique size defined heterojunctions to be realized.<sup>18</sup> In Au-CdSe, as an example, enhanced photocatalytic reactions are possible in solution through charge separation at the M-SC interface.<sup>6, 17, 19</sup> A facile route to Au tip formation has been achieved where the metal precursor either (AuCl<sub>3</sub>) or more recently (AuCl) and a reducing agent are solubilized in the organic phase using surfactants. Control of reaction time, temperature and light activation can tune the structure from double tipped (both ends) to single tip to enlarged single tip.<sup>8-11</sup> The organic phase reduction methods while extremely successful with Au-tipping, limit the extension of the tipping protocol to other metals due to the insolubility of their metal salts in non-polar solvents. Tipping using organometallic precursors has been successful with Pt and Co although complex reaction schemes are necessary for these non-commercially available precursors.<sup>20-23</sup> A successful approach allowed Au and Pt tipping on rods from their water soluble salts whereby the nanorod was transferred to the aqueous phase using ligand exchange followed by reduction of the water soluble metal precursor. The tip growth is pH dependent and reaction times of up to 2 days are required.<sup>20, 24</sup>

Here we describe a simplified protocol to yield instantaneous Ag-semiconductor nanorod hybrid structures where instead of transferring the nanorod to the aqueous phase, the metal ions are phase transferred from the aqueous to the organic phase. This we achieved by the introduction of suitable organic ligand molecules onto the surface of the nanorods possessing the bi-functionality of phase transfer and reducing capability. Tipping by this phase transfer protocol was successful at room temperature on CdSe nanorods. This method also avoided the preference for the Ag ion to cation exchange with Cd forming Ag<sub>2</sub>Se. The tipped nanorods also readily assemble into close packed superlattices from solution with the c-axis of the rod perpendicular to the substrate. The density of packing will likely find significant application where silver metal-semiconductor hybrids are needed in high density arrays such as photovoltaics or photocatalysis.<sup>25-27</sup>

## Results and Discussion

Stirring a biphasic mixture of organically soluble di-methyl phenol (DMP) with aqueous AgNO<sub>3</sub> in presence of 5×10<sup>-5</sup>M KOH resulted in the formation of Ag nanocrystals (Figure 1A) in the organic medium (Yellow colour). Nanocrystals were FCC Ag of the order of 5-10 nm in size with a density dependent on the concentration of the DMP (Figure 1B). The introduction of CdSe nanorods that were pre-treated with 10<sup>-1</sup>M DMP into the organic phase, with similar concentrations of AgNO<sub>3</sub> and KOH in the aqueous phase resulted in metal tip nucleation onto the rod surface without additional free metal nanocrystal formation. The formation of the hybrid is schematically represented in Figure 1C. The tip growth was reaction time dependent with multiple tips (~1 nm) (TEM image, Figure 1D) occurring after 1 hour stirring of the biphasic mixture, ripening to a single tip on one or both ends of the nanorod on further stirring (TEM image, Figure 1E). HRTEM of a single tipped rod allowed characterisation of the CdSe (100) and Ag (111) lattice spacings at 3.69 and 2.40 Å respectively, Figure 1F.

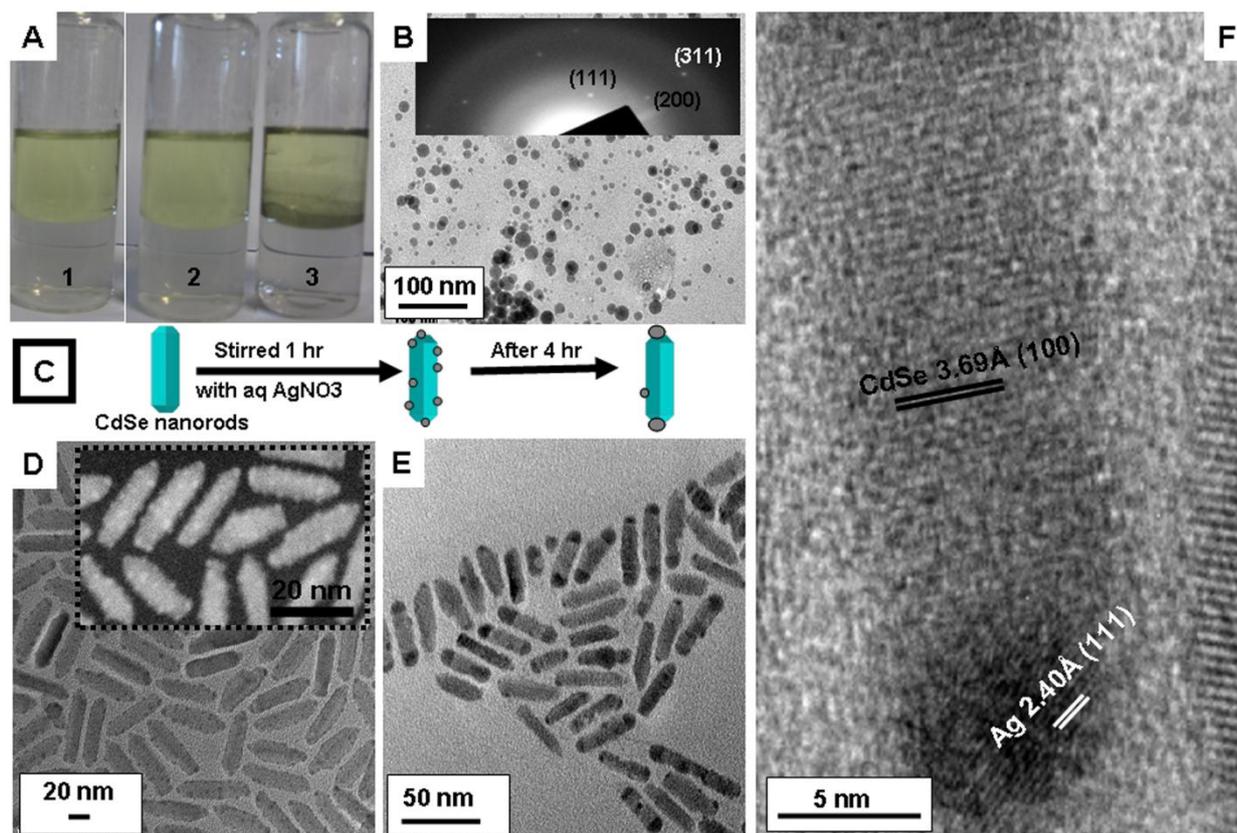


Figure 1. (A) photographs of the Ag nanoparticles formed using  $1 \times 10^{-4}$  (photo 1),  $1 \times 10^{-3}$  (photo 2) and  $1 \times 10^{-2}$  M (photo 3) aqueous  $\text{Ag}^+$  and  $10^{-2}$  M DMP in toluene. (B) TEM and SAED of Ag nanoparticles. (C) Schematic representation of the formation of Ag tips on bare CdSe nanorods. (D) TEM of the anisotropic growth of Ag nanoparticles all over the surface of the nanorods at  $t=1\text{hr}$ . Inset shows STEM of Ag tipped CdSe nanorods. (E) Ag tips only at the ends of CdSe nanorods at  $t=3\text{hr}$ . (F) HRTEM of Ag tipped CdSe nanorods aligned horizontally revealing the planes corresponding both to CdSe and Ag.

The presence of the semiconductor nanorods in the organic phase (Toluene) and the surface attachment of the DMP molecules clearly enabled the selective transfer of  $\text{Ag}^+$  from the aqueous phase and its reduction onto the nanorod. Though DMP molecules were not common for reduction of  $\text{Ag}^+$  to form Ag nanoparticles, phenolic OH groups had previously been shown to lead to the reduction of  $\text{Ag}^+$  in an alkaline medium.<sup>28</sup> Crucially, the attachment of the DMP to nanorods resulted in metal formation on the nanorod structure whereas in solution it capped the Ag nanoparticles forming a stable dispersion. The phenomenon of multiple Ag tip formation and their Oswald ripening to form one larger single tip could be explained in terms of significant lattice mismatch for Ag and the semiconductor materials used in this study due to a strain relief mechanism.<sup>26, 29-31</sup> The lattice mismatch and associated strain relief had already been reported to grow small islands of noble metals of a critical atom density which ripen into larger islands as the reaction continued. Robinson and co-workers observed similar strain-dependent island formation on CdS nanorods during the partial cation exchange of  $\text{Cd}^{2+}$  with  $\text{Ag}^+$ .<sup>30</sup> However, as our protocol favoured reduction of the metal under conditions not conducive to Cd ion removal, cation exchange was not expected as confirmed by detailed characterisation.

The UV-Vis spectrum of as synthesized CdSe NRs showed two peaks at 552 and 674 nm (Figure 2A, curve 1), which were characteristic of the excitonic band transitions.<sup>32</sup> The absorption

spectrum of the Ag-CdSe nanorod hybrid retained the peak at 674 nm and showed a peak at 421 nm. The latter corresponded to the surface plasmon resonance peak of Ag nanoparticles (Figure 2A, curve 2). The appearance of a surface plasmon peak characteristic of Ag nanoparticles clearly indicated the reduction of  $\text{Ag}^+$  to form Ag nano-tips onto the semiconductor nanoparticles.<sup>33</sup>

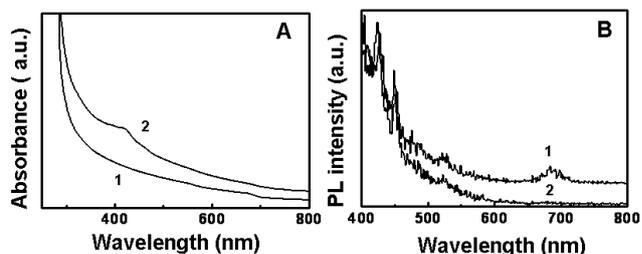


Figure 2. (A) UV-Vis spectra and (B) Photoluminescence spectra of CdSe nanorods, before and after the hybrid formation. In both cases, curve 1 indicates the as synthesized nanorods whereas curve 2 corresponds to Semiconductor-Ag hybrids.

The PL peak for CdSe nanorods was found to be centred at  $\sim 684$  nm with a small shoulder at 529 nm, after exciting the sample at 400 nm (Figure 2B, curve 1). The emission was found to be quenched heavily after the formation of Ag-CdSe nanorod hybrid structures (Figure 2B, curve 2). This kind of quenching of

emission peak due to hybrid formation had previously been observed and could be explained due to efficient electron transfer from semiconductors to metal nanoparticles,<sup>8, 26, 35</sup> The dramatic quenching of emission was strongly suggestive of charge separation at a silver metal-CdSe semiconductor interface. The CdSe-Ag<sub>2</sub>Se interface in contrast is an abrupt n-n heterojunction which has a limited affect on the PL intensity as observed in previous studies.<sup>36</sup>

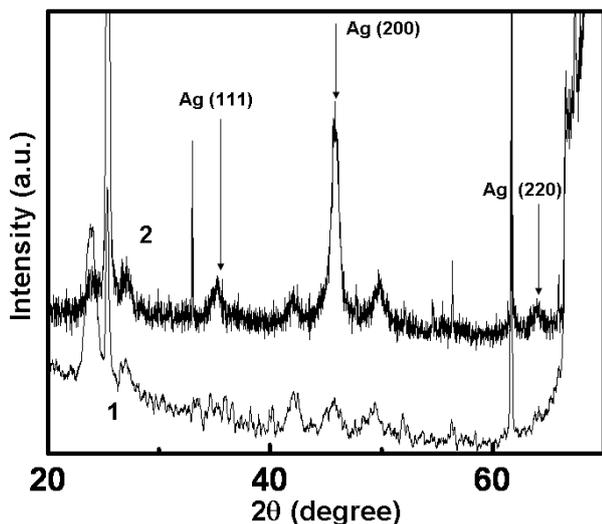


Figure 3. X-ray diffractograms of CdSe nanorods, curve 1 indicates the as synthesized nanorods whereas curve 2 corresponds to Semiconductor-Ag hybrids.

Comparison of the X-ray diffractograms of CdSe nanorods and CdSe nanorods after reaction with AgNO<sub>3</sub> (Figure 3A) revealed the presence of Ag (111), (200) and (220) peaks in curve 2 confirming the presence of fcc Ag with a lattice parameter estimated to be 4.08 Å (PCPDF no. 04-0783).

A systematic XPS analysis was carried out on the pristine CdSe nanorods (SI-1) as well as on the hybrids (Figure 4A-C). In both the cases Cd 3d peak was fitted with two components corresponding to 3d<sub>5/2</sub> and 3d<sub>3/2</sub> at 405.0 and 411.7 eV respectively, Figure S1A and Figure 4A. The fitting clearly showed the presence of single species for Cd coming from CdSe. The deconvolution of Se 3d peak showed the presence of two decoupled components at 53.5 and 54.6 eV (Figure S1B and Figure 4B) due to 3d<sub>5/2</sub> and 3d<sub>3/2</sub> which appeared from CdSe. Absence of any extra components in the fitted curve ruled out the probability of the presence of un-reacted Se. The Ag 3d doublet obtained from the hybrids appear at 367.9 and 373.9 eV, with a separation of 6.0 eV and full width at half maximum of 0.9 eV, characteristic of metallic silver<sup>37</sup> (Figure 4C). However, since the energy differences between the different chemical states of Ag were < 0.5 eV, formation of Ag compounds could not be ruled out entirely solely depending on XPS.<sup>38</sup> However in combination with HRTEM, UV-Vis, XRD the characterizations were indicative of metallic Ag tips on rods instead of Ag<sub>2</sub>X (X=S, Se)<sup>38</sup> suggesting the phase transfer of Ag<sup>+</sup> ions and their reduction by DMP occurred faster than cation exchange processes.<sup>39</sup>

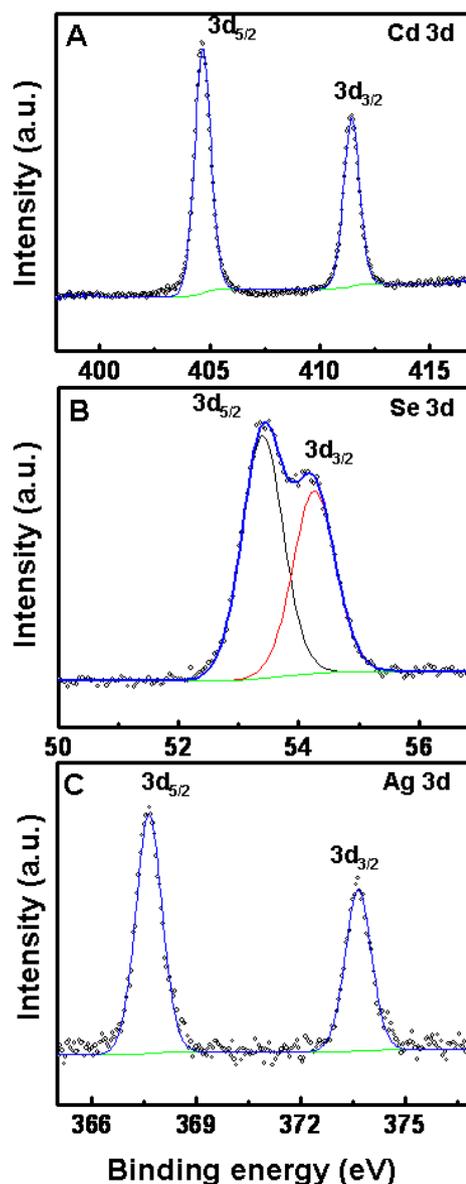


Figure 4. (A-C) X-ray photoelectron spectroscopic analysis of Cd 3d, Se 3d and Ag 3d from Ag tipped CdSe nanorods. The Ag 3d peak could be matched with Ag<sup>0</sup> level.

FTIR analyses were also carried out on CdSe rods capped with TOPO and alkyl phosphonic acid (Figure 5) showing the characteristic peaks at 1463, 1376, 1151 and 1087 cm<sup>-1</sup> which were related to -CH<sub>3</sub> groups of the capping ligand, P=O of alkyl phosphonic acids,<sup>40</sup> P=O of TOPO<sup>41</sup> and P-O-H of alkyl phosphonic acids<sup>41</sup> respectively. After modification of the surface with DMP, curve 2, a new peak at 1409 cm<sup>-1</sup> and a broad band at 3250 cm<sup>-1</sup> emerged corresponding to -OH in plane bending vibration and stretching vibration respectively of the molecule. The -OH stretching frequency was found to be damped out after the formation of Ag tips on the particles (Figure 5, curve 3). This further confirmed the role of phenolic-OH of DMP in the formation of Ag tips on the CdSe rods. It was interesting to note that in absence of DMP molecules none of the nanorods allowed the growth of any Ag tips (SI-2) which again validated our

proposition that DMP played the important roles of phase transfer and reduction of the metal ions site selectively on the surface of the semiconductor materials to synthesize these hybrids.

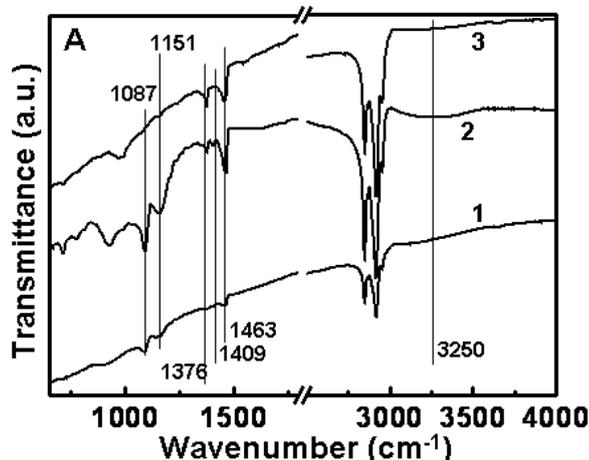


Figure 5. FTIR analysis of the pristine CdSe rods (curve 1), CdSe nanorods after modifying the surface with DMP (curve 2) and after the formation of CdSe rod-Ag hybrid (curve 3).

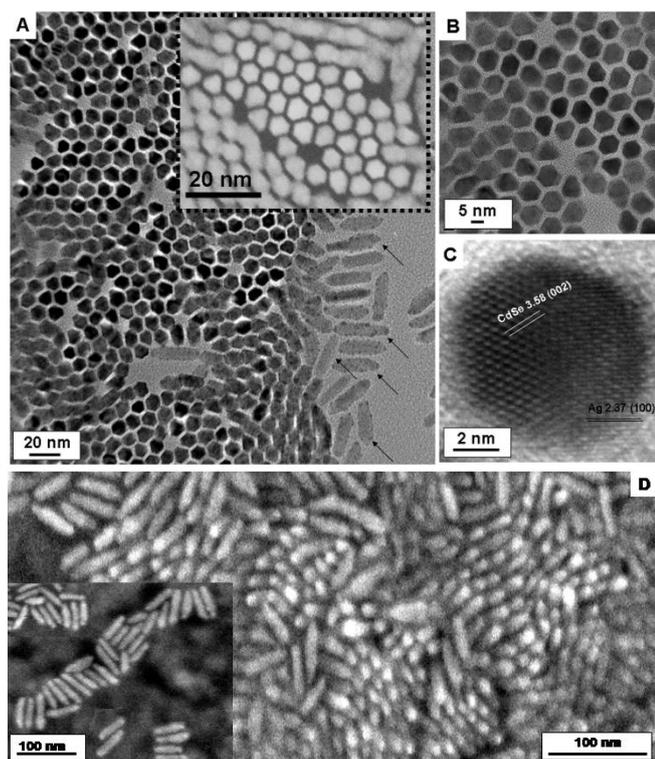


Figure 6. Vertically assembled Ag-tipped CdSe nanorods at lower (A) and at higher magnification (B). (C) HRTEM of the vertically aligned hybrid nanorod showing the planes corresponding to both CdSe and Ag. (D) SEM image of the Ag-tipped CdSe nanorods mainly aligned vertically on substrate along with few horizontally aligned rods in the inset.

Through careful control of concentration, Ag-tipped CdSe rods readily organized into close packed vertical assemblies

from solution, as observed from TEM and STEM analyses (Figure 6A and inset). Arrows highlighted the non-assembled Ag-CdSe rods at the edge of the superlattice. A further magnified TEM image clearly showed the vertically arranged Ag tipped wurtzite rods adopted a hexagonal close packed super-structure with individual rods separated at 1-2 nm by interdigitation of the surfactant ligands, Figure 6B. The planes corresponding to both CdSe and Ag could be distinguished on the top end of a vertical rod through HRTEM imaging (Figure 6C). The tipped rods adopted an orthogonal orientation with the CdSe component in contact with the substrate similar to Au-tipped CdSe structures reported by Zhao et al.<sup>14</sup> and O'Sullivan et al.<sup>26</sup> Brighter contrast due to Ag tips was also clearly visible on vertically aligned CdSe rods under scanning electron microscope, Figure 6D.

## Conclusion

In summary, we demonstrated a novel synthetic protocol for the formation of Ag noble metal tips on semiconductor nanorods where water soluble metal precursors were transferred to organic media and selectively reduced on nanorods in a single step. This facile route was mediated an organic ligand (phenolic -OH) which could mediate phase transfer in addition to metal ion reduction at room temperature, thus avoiding the use of costly organometallic precursors and/or toxic organic solvents. The procedure can be extended to a generalized method for different noble metal tipping on semiconductor nanorods through judicious selection of suitable precursors and ligands. The facile hierarchical assembly of the metal tipped nanorods may allow scaleable application for bulk devices where nanoscale metal-semiconductor interfaces are required in high density.

## Experimental Section

### Synthesis of CdSe nanorods:

**Materials:** Cadmium oxide (CdO) was purchased from Fluka, Trioctylphosphine (TOP, 90%), trioctylphosphine oxide (TOPO, 99%), sulphur (S), Silver nitrate (AgNO<sub>3</sub>), Dimethyl phenol (C<sub>8</sub>H<sub>16</sub>O, mentioned as DMP in this paper), Toluene were purchased from Aldrich, and n-octadecylphosphonic acid (ODPA), was obtained from PolyCarbon Industries Inc (PCI).

**Method:** CdSe nanorods were synthesised with slight modifications to the published procedure.<sup>42</sup> The general approach for the synthesis of nanorods involves the stepwise addition of cadmium precursor and followed by chalcogenide precursor at a high temperature. Briefly, CdO (0.2 g) as a cadmium precursor was dissolved in mixture of surfactants like n-tetradecylphosphonic acid (TDPA, 0.71 g), n-hexylphosphonic acid (HPA, 0.160 g) and tri-n-octylphosphine oxide (TOPO, 3.00 g) in 25 ml three-neck flask equipped with a condenser and a thermocouple adapter. The mixture was heated to 120° C in an atmosphere of Ar and then degassed for 60 min with pressure range between 150 – 300 mTorr and followed by heating at 300°C under Ar atmosphere, during which the CdO decomposed and gave an optically clear solution. Once clear solution was achieved 1.5g of trioctylphosphine (TOP) was added to the mixture and the temperature was further raised to 310°C. Next stock solution of Selenium (~500µl) containing 0.073 g of selenium in 0.416 g of TOP was injected rapidly to the vigorously stirring precursors and the resulting particles were further allowed to grow for 5-10 min at 310°C. The nanorods growth was terminated by removal of the heating mantle, and at 80°C 2-4 ml anhydrous toluene was added to the mixture to quench the reaction. The nanorods were purified by dissolution in toluene and precipitation from anhydrous isopropanol. They were cleaned thrice with toluene and isopropanol mixture and redispersed in toluene toluene and stored inside an air-free glove box. for further measurements.

### Synthesis of Ag-semiconductor hybrids:

**Method:** In a typical reaction, 10 mL of 10<sup>-1</sup> M DMP in toluene was injected into 15 mL of nanorod solution and the resulting mixture was sonicated before precipitating with acetone/toluene mixture. The solution was then centrifuged at 5000 rpm for 10 min. The colorless supernatant was decanted off and the above process was repeated

for 3 times. The precipitate was then re-dispersed in toluene maintaining a concentration of 0.06 mg/mL, a part of which (~5 mL) was then stirred with  $5 \times 10^{-3}$  M aqueous  $\text{AgNO}_3$  in presence of  $5 \times 10^{-5}$  M KOH solution. Aliquots of the top toluene layer were separated from the biphasic mixture at different time intervals for 5 characterization.

#### Characterizations techniques:

**Transmission electron microscopy.** Samples for TEM were prepared by putting a drop of the solution on a carbon-coated copper grid. TEM analysis was performed 10 on a JEOL 2011 at an accelerating voltage of 200 kV.

**X-ray diffraction analysis.** X-ray diffractograms of drop-cast films of the sample on Si (111) substrate were carried out on a PANalytical X'Pert MPD Pro using  $\text{Cu K}\alpha$  radiation with a 1-D X'Celerator strip detector.

15 **Fourier transform infrared spectroscopy.** FTIR measurements for the drop casted samples on Si substrates were carried out on a Perkin-Elmer-Spectrum One FTIR spectrometer operated at a resolution of  $4 \text{ cm}^{-1}$ .

20 **X-ray photoelectron spectroscopy.** XPS measurement of the pristine particles and the hybrids were carried out using a Kratos Axis 165 spectrometer. High resolution spectra were taken using monochromated Al  $\text{K}\alpha$  radiation of energy of 1486.6 eV at fixed pass energy of 20 eV. For peak synthesis, a mixed Gaussian-Lorentzian function with a Shirley type background subtraction was used. Samples were 25 flooded with low energy electrons for efficient charge neutralisation. Binding energies (BE) were determined using C 1s at 284.8 eV as charge reference.

**UV-Vis and fluorescence spectroscopy.** UV-Vis spectroscopy and fluorescence measurements of the phase transferred solutions were carried on a Cary-300 Bio 30 UV-Vis spectrophotometer operated at a resolution of 1 nm and a Varian Cary Eclipse Fluorescence Spectrophotometer respectively.

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## Notes and references

<sup>a</sup> Dr. T. Bala, Dr. A. Sanyal, <sup>#</sup> Mr. A. Singh, Ms. D. Kelly, Ms. C. O'Sullivan, Dr.

40 F. Laffir, Dr. K. M. Ryan\*

Materials and Surface Science Institute and Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland.

Fax:

E-mail: [kevin.m.ryan@ul.ie](mailto:kevin.m.ryan@ul.ie)

45 <sup>#</sup> Present address: JISCE College, Kalyani, West Bengal, INDIA

<sup>b</sup> Mr. A. Singh, Dr. R. D. Gunning, Dr. K. M. Ryan\*

SFI-Strategic Research Cluster in Solar Energy Research, University of Limerick,

50 Limerick, Ireland

† Electronic Supplementary Information (ESI) available: [XPS of pristine CdSe nanorods, EDAX analysis, STEM image of CdSe-Ag hybrids and detailed control experiment are available]. See DOI: 10.1039/b000000x/

55 ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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