Electronic Supporting Information

Heteroaggregation Assisted Wet Synthesis of Core Shell Silver-Silica-Cadmium Selenide Nanowires.

Isabel A. Pita[a], Shalini Singh[b], Christophe Silien[a], Kevin M. Ryan[b], Ning Liu[a]

[a]Department of Physics & Energy, Materials and Surface Science Institute, University of Limerick, Ireland

[b]Department of Chemical and Environmental Science, Materials and Surface Science Institute, University of Limerick, Ireland

Nanoparticle Synthesis

The synthesis routes for each of the nanoparticle sizes/ types are outlined below. As mentioned in the paper, the larger CdSe nanoparticles come from a well-documented literature method[23,24], along with the larger gold nanoparticles[25]. The smaller CdSe method was devised by one of the co-authors, while the 10 gold nanoparticles came from altering the gold nanoparticle conditions.

Synthesis of 6 nm x 6 nm CdSe nanocrystals

To synthesise the smallest nanocrystals, 0.209 g cadmium oxide, 1.89 mL oleic acid, and 3.85 mL squalene were placed in a 3-neck flask with a magnetic stirrer. This solution was heated to 120˚C and degassed. The mixture was then left for 1 hour. Next the temperature was increased to 285˚C, and following this 500 µL selenium/trioctylphosphine (Se/TOP) was added. The reaction was left for 5 minutes, then cooled by removing the heating mantle. Once cooled sufficiently, the mixture was washed three times with toluene and IPA.

Synthesis of 24 nm x 11 nm, and 15 nm x 9 nm CdSe nanorods

0.2 g of CdO was dissolved in 0.71 g tetradecylphosphonic acid (TDPA), 0.20 g n-hexylphosphonic acid (HPA) (0.16 g HPA for 15 nm size) and 3 g tri-n-octylphosphine oxide (TOPO) in a 25 ml 3 neck flask. This mixture was heated to 120˚C in argon and degassed for 60 minutes at a pressure of 0-300 mTorr. The solution was then heated up to 300˚C in Argon to get an optically clear solution. 1.5 g of TOP was then added and the temperature was raised to 310˚C. 500 µl-1 ml of Se/TOP solution (approximately 500 µL for the 24 nm size, and 750 µl for 15 nm size) was then injected in, and the solution was left for 5-10 minutes. The growth was then halted by removing the heating mantle at 80˚C. 2-4 ml of toluene was then injected into the mixture to completely stop the reaction.

Synthesis of 10 nm gold nanoparticles

For 8-10 nm size gold nanoparticles, 2 ml of oleylamine was mixed with 40 mg $HAuCl_4$ or $HAuCl_4.H_2O_3$. 10 mL of oleic acid and 5 mL of oleylamine was heated to 80˚C. The Au solution was then injected into the mixture under magnetic stirring (stop the stirring after 5 minutes) and the reaction was kept going for 1 hour.

Synthesis of 19 nm gold nanoparticles

2.48 mL oleylamine and 49 mL toluene was placed in a three neck flask. The solution was heated in the three neck flask up to 110˚C under reflux. 20 mg $HAuCl_4 3H_2O$ was dissolved in 1.2 ml oleylamine and 1 ml toluene. At 110˚C the gold solution was injected into the flask, and the reaction was left for 1 hr 20 minutes.

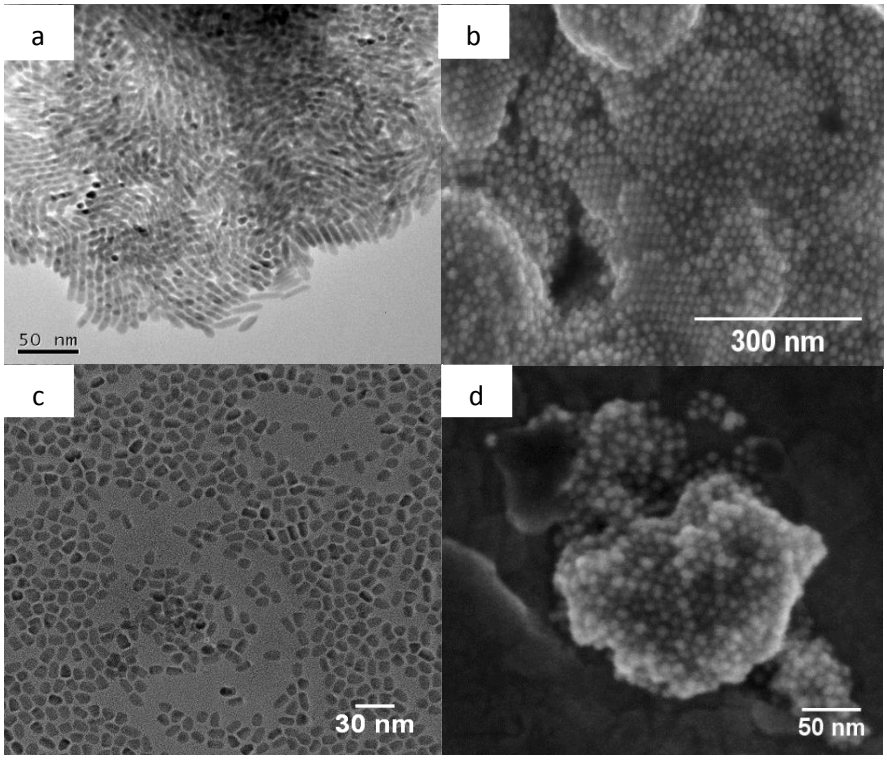

Fig. 1: (a) The 24 nm x 11 nm CdSe nanoparticles and (b) the 19 nm gold nanoparticles synthesised using the above literature procedures. (c) 6-10 nm CdSe nanocrystals synthesised using the above 6 nm x 6 nm synthesis route and (d) 10 nm gold nanoparticles synthesised using the altered procedure. The gold nanoparticles were aggregated with iso-propanol to make them easier to inspect under SEM.

Calculating the van der Waals Interaction Energy

The van der Waals energy for each nanoparticle was calculated in four parts: (1) material-silica-silver, (2) material-silica, and (3) the material-toluene. For part (2) the material-silica interaction is calculated in two parts. The first (2a) is the distance from the nanoparticle to the surface of the silica layer, and the second (2b) is the distance between nanoparticle and the silica layer, including the thickness of the silica. The two separate calculations for material-silica are subtracted to get an estimation of the attractive energy from the thin silica layer, instead of a solid block. Distance d1 was used for (2a) and (3), while distance d2 (d1 + 7.5 nm the average thickness of the silica) was used for (1) and (2b). The total van der Waals interaction energy was then obtained by summing (1) with (2a), and subtracting (2b) and (3). The values for CdSe are included in table 1, while the values for gold are included in table 2. In all cases the optimum distance for particle attachment has been used. For each calculation the correct Hamaker coefficient was used for the system in question. For these calculations equations 6 and 8 from the paper were used.

Table 1: The individual van der Waals values calculated for the different interactions of CdSe nanoparticles with the nanowires in Toluene, and the total van der Waals energy calculated.

Nanoparticle size	Distance used (d1) (nm)	CdSe-silica-silver (x 10^{-21} J)	CdSe-Silica (d1) (x 10^{-21} J)	CdSe-Silica (d2) (x 10^{-21} J)	CdSe-Toluene (x 10^{-21} J)	Total Van der Waals (x 10^{-21} J)
24 nm x 11 nm	1.47	-5.64	-188.13	-12.48	-170.83	-10.46

15 nm x 9 nm	1.48	-3.18	-105.28	-7.04	-95.60	-5.82
6 nm x 6 nm	1.80	-0.99	-25.64	-2.18	-23.28	-1.17

Table 2: The individual van der Waals values calculated for the different interactions of Au nanoparticles with the nanowires in Toluene, and the total van der Waals energy calculated.

Nanoparticle size	Distance used d1 (nm)	Au-silica-silver (x 10^{-21} J)	Au-Silica (d1) (x 10^{-21} J)	Au-Silica (d2) (x 10^{-21} J)	Au-Toluene (x 10^{-21} J)	Total Van der Waals(x 10^{-21} J)
19 nm	1.93	-5.42	-85.94	-6.82	-77.98	-6.56
10 nm	2.06	-1.43	-41.43	-1.80	-37.59	-3.47

Calculation of the Coulomb Interaction Potential

The charge on a TDPA ligand coated CdSe nanoparticle has previously been estimated at 0.2e to 0.4e[20]. When interacting with the nanowire, we can roughly estimate the Coulomb interaction energy between the charged particle and the silver nanowire on the basis that the nanoparticle is producing a mirror charge in the silver nanowire as, in comparison to the size of the nanoparticle, the silver nanowire acts as an infinite conductor. In effect, it is as if the nanoparticle is interacting with another particle, with the opposite charge. The Coulomb interaction potential itself can be calculated using the equation:

$$E_{Coulomb} = \frac{q_1 q_2}{8\pi\varepsilon\varepsilon_0 R}$$

Where q_1 and q_2 are the charges on the two nanoparticles, ε is the dielectric constant of the medium (here taken as the silica layer), ε_0 is the permittivity of free space, and R is the distance between the two nanoparticles. This is half of the value for two real point charges separated by distance R, due to nature that image charge moves as the real charge moves away from the conducting surface. The distance is taken as twice the distance from the nanoparticle core to the silver surface, as the mirror charge would appear at the same distance in the silver nanowire from its surface. As an example, the 24 nm x 11 nm CdSe nanoparticle's distance from the wire would be the radius (5.5 nm) plus the fitted distance (1.47 nm) and the silica thickness (7.5 nm). Doubled, this produces a value of 29.94 nm. The dielectric constant of silica is readily available as 3.9. The calculated values for the Coulomb interaction potential are shown below in table 3.

Table 3: The calculated Coulomb Interaction Potential for the three CdSe nanoparticle sizes.

CdSe Nanoparticle Size	Distance Between the charges (nm)	Interaction Potential (x 10^{-22} J)
24 nm x 11 nm	29.94	-0.39~-1.58
15 nm x 9 nm	26.96	-0.44~-1.75
6 nm x 6 nm	24.60	-0.48~-1.92

As shown, the magnitude of Coulomb interaction potentials all fall below 2 x 10^{-22} J, making them an order of magnitude less than the van der Waals interaction energy. As such, their effects on the total energy of the system is minimal.

Optical Data from the Core-Shell Nanowires

Measurements were made for both the fluorescence peak, and the Raman bands of the core-shell nanowires. The fluorescence was measured using a 532 nm laser connected to a spectrograph, yielding a peak of around 670 nm, matching the CdSe nanoparticles when measured separately. When Raman data was obtained for the nanowires using an 1800 line grating and a separate 532 nm laser the Raman bands were found to match the 1LO and its overtone of CdSe at 221 cm^{-1} and 420 cm^{-1}. This once again highlights the coverage of the nanowires with the nanoparticles once the heteroaggregation step is completed.

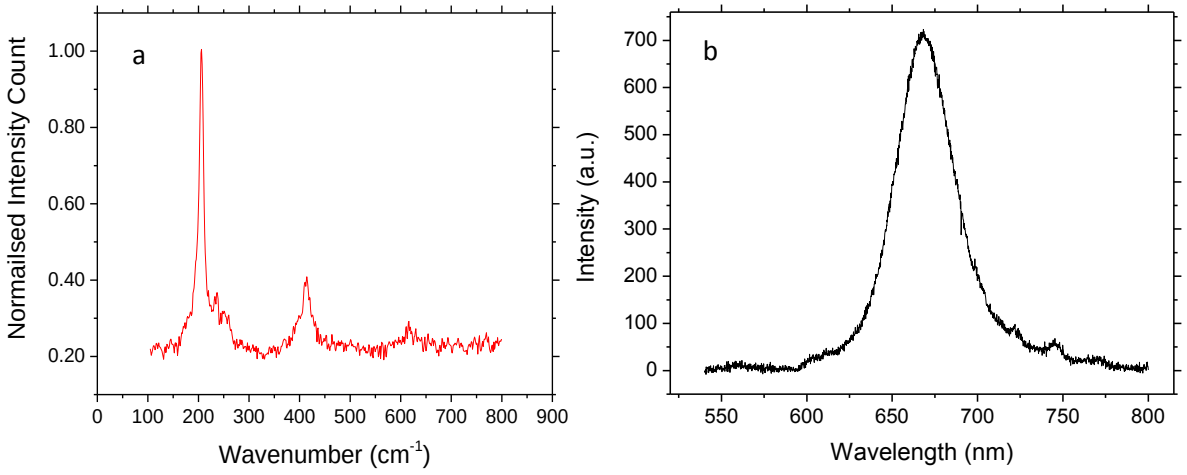

Fig.2: (a) The two Raman bands detected during optical investigation, and (b) the fluorescence peak obtained when the core-shell nanowires are illuminated with a 532 nm laser. The Raman bands match the 1LO and its overtone at 221 cm^{-1} and 420 cm^{-1}, while the fluorescence peak is around 670 nm.

When determining the individual contributions from a single CdSe nanoparticle to the Raman spectrum, either on the nanowire or as part of the monolayer, as mentioned in the paper first the area of the laser spot was calculated as 8.97 x 10^{-14} m^2 and used to estimate how many CdSe nanoparticles were illuminated. The nanoparticle numbers were estimated as 339.8 nanoparticles in the monolayer, and 240.6 nanoparticles on the nanowires surface, assuming that the largest surface area of the nanowire as possible is exposed to the laser while still being end illuminated. Estimating the individual contributions based on existing spectra yields Raman band increases 2-3 times stronger when on the core-shell nanowire surface see fig. 3.

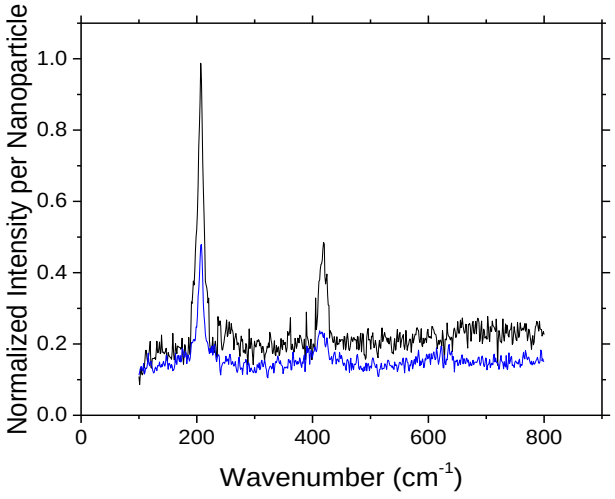

Fig. 3: Raman bands calculated for a single CdSe nanoparticle either (black) on a core-shell nanowire or (blue) as part of a CdSe monolayer. Propagating Surface Plasmons from the core-shell nanowire result in an LO band 2.5 times stronger, and an overtone 2.18 times stronger in this case.

Simulations of nanowires using Comsol Multiphysics Simulation Package

The wave optics module in COMSOL MULTIPHYSICS was used to simulate the core-shell nanowires to determine the effects of end and centre illumination on the backscattered and total fields, along with the intensity. A 3d model was used to properly model the polarisation effect of the reflected/ backscattered fields. A 3d Gaussian beam was applied to simulate the excitation beam and the frequency domain stationary solutions were obtained for a series of simulation parameter sets. The nanowires were simulated using the average dimensions for the nanowire, and separate layers for the silica and CdSe with the nanoparticles assumed to be 100 % covering the surface, and the long axis aligned parallel to the nanowire's long axis. The thickness of the silica layer was taken at an average of 7.5 nm, while the CdSe layer was taken at a thickness of either 11 nm, 9 nm, or 6 nm for each type of CdSe nanoparticle. The simulated nanowire was illuminated both from the end, and the centre to compare to experimental data obtained from core-shell nanowires illuminated with a 532 nm laser.

As shown in figures 4 (c) and (d) the intensity is much stronger when the nanowire is end illuminated than at the centre, due to the generation of a propagating surface plasmon signal, which matches the data obtained from actual experiments with the completed nanowires. While the simulation indicates that the core-shell nanowire would have an intensity approximately 9 times stronger when end illuminated then centre illuminated, instead of about twice, this strong signal is over a very short range in the simulation (1.73×10^{-8} m). In comparison, the intensity from the actual core-shell nanowire was obtained over the area of the laser spot. As a result, the increased intensity is lower within the illuminated area. The total intensity of the centre illuminated nanowire is lower than 1 due to the summation of the reflected and backscattered fields, consistent with the experimental observations in figures 4 (e) and (f).

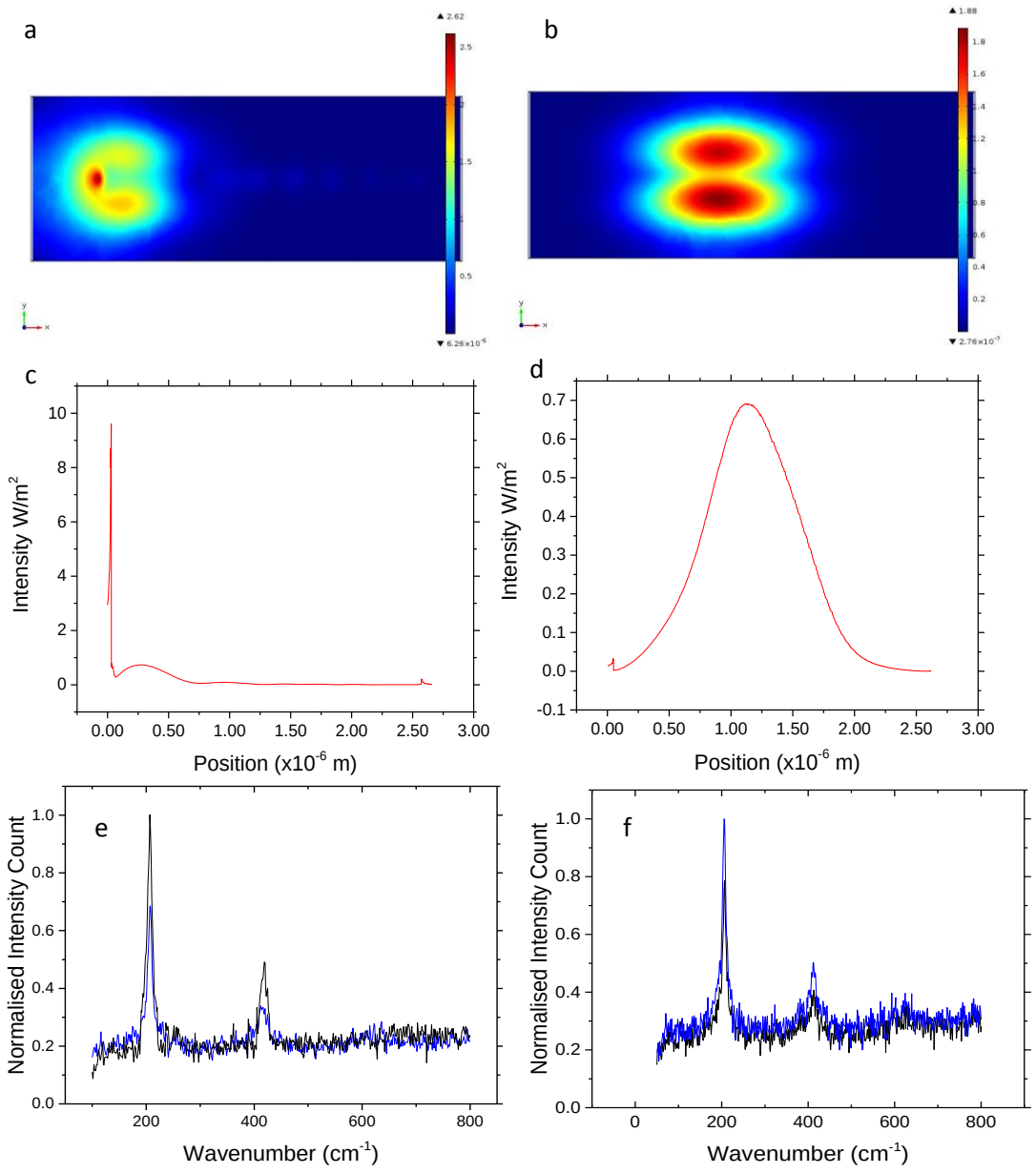

Fig. 4: (a) The intensity profile of an end illuminated core-shell nanowire, and (b) a centre illuminated core-shell nanowire viewed from above. Graphs (c) and (d) show the obtained intensity data from the simulations of (a) and (b) respectively at the CdSe surface layer. (e) The actual experimental data obtained from a core shell nanowire (black) in comparison to a CdSe nanoparticle monolayer (blue) when illuminated with a 532 nm laser from the end of the nanowire, and (f) when illuminated from the centre of the nanowire.