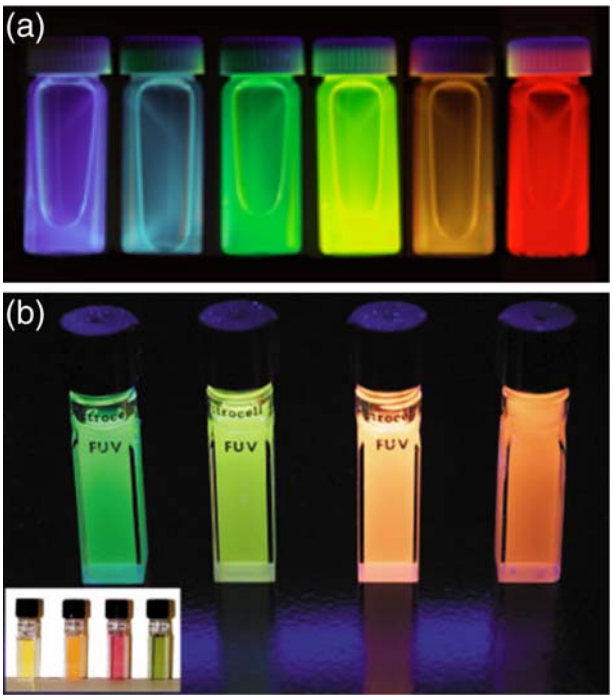
# ND QD Essentials




K. Richter and M. Kuno

6/23/03

## Acronyms

- TOP (trioctylphosphine)
- TOPSe (trioctylphosphine selenide)
- TDPA (tetradecylphosphonic acid)
- CdO (cadmium oxide)
- DDA (dodecylamine)
- HDA (hexadecylamine)
- TOPO (trioctylphosphine oxide)
- $(TMS)_2S$ (bis(trimethylsilyl)sulfide or hexamethyldilsilathiane)
- $ZnEt_2$ (diethyl zinc)

## Equipment

For CdSe Prep:

- 50 or 100 mL 3 neck flask, 14/20 joints or whatever is available
- Condenser with 14/20 joint or whatever is compatible
- Stopcock with 14/20 joint or equivalent
- Magnetic stir bar
- Magnetic stir plate
- Schlenk line or equivalent
- Thermocouple
- Rubber septum
- Variac
- Heating mantle
- 10 mL syringe
- 18 gauge needle for syringe
- 1 mL syringe
- 22 gauge needle for syringe

For overcoating:

- Same equipment as for CdSe prep, except for 1 mL syringe and corresponding needle
- 100 microliter syringe for $(TMS)_2S$
- 100 microliter syringe for $ZnEt_2$
- Addition funnel or syringe pump

# CdSe recipe

## 1M TOPSe solution

- 7.896 grams Se shot (Aldrich)
- 100 mL TOP

This can be scaled down accordingly. Mix the two and stir overnight. The Se will be coordinated by TOP. This solution is air stable and can be kept out on the bench. The only side effect of air exposure is the eventual formation of TOPO (a white solid).

## Traditional Peng prep

Pot:

- 4 grams 99% TOPO (Aldrich)
- 0.3 grams TDPA (Alfa Aesar)
- 0.05 grams CdO (Aldrich)

Injection solution:

- 0.25 mL of 1M TOPSe
- 4 mL 90% TOP (Aldrich)

Heat the pot mixture to 100 C and pull vacuum on the mixture to degas and dry it. After this, raise the temperature to 330 C. At this point the red color of the CdO will begin to disappear. Oxygen is being evolved and TDPA is now coordinating to the Cd ion. Carefully swirl the solution to remove any CdO stuck to the walls of the three-neck flask. Maintain the temperature at 330 C for approximately 5-10 minutes when completely clear.

At this point, load the injection solution into a disposable syringe with an 18 gauge needle. Then penetrate the septum and inject the solution. The temperature of the mixture will drop dramatically with some evolution of gas. Slowly raise the temperature back to 300 C. Watch the color of the solution. Initially it will be clear with a relatively long induction period. Then the color will start to turn slightly yellow, then darker yellow, then orange, then dark

orange, then red and so forth. At each point aliquots can be taken and diluted with hexanes. These aliquots can be UV-Vised to see the growth of the particles.

The growth of the CdSe dots can be stopped by rapid cooling to a temperature somewhere below 200 C rather than allowing the growth to continue until the solution has reached dark red. Growth of the dots only occurs above 200 C.

## Modified Peng prep

Pot:

- 2 grams 99% TOPO (Aldrich)
- 2.88 grams DDA (Acros)
- 0.3 grams TDPA (Alfa Aesar)
- 0.05 grams CdO (Aldrich)

Injection solution:

- 0.25 mL of 1M TOPSe
- 4 mL 90% TOP (Aldrich)

The modified prep is carried out in a manner similar to the traditional prep. After the solution has been degassed and the temperature has been raised, you will notice that the temperature will not go any higher than approximately 300 C. Maintain this maximum temperature until the solution goes clear. This will take approximately 2 hours. Carefully swirl the solution to remove any CdO stuck to the walls of the three-neck flask. Once the solution is completely clear, proceed with the injection and the taking of aliquots as described for the traditional prep. The growth of the dots can be stopped by rapid cooling.

## Processing CdSe dots

Once the prep has been completed, 10 mL of butanol should be added to keep the TOPO from freezing and becoming a solid. Approximately 5 mL of hexanes can also be added if desired. Once the solution has cooled, transfer it to an Erlenmeyer flask and crash the dots out of solution by adding an excess of methanol. The solution will become cloudy after making this addition. Centrifuge and pour off the supernatant. The dots can be redissolved in a minimal amount of hexanes, toluene, chloroform, or other nonpolar solvent.

## Overcoating calculations

These calculations can be done by hand or by computer program.

- Obtain a UV-Vis spectrum from an aliquot of the CdSe stock solution.
- Determine the peak wavelength and optical density from the spectrum.

- From the chart, determine the radius of each dot using the peak wavelength.
- Assuming 0.31 nm per monolayer of ZnS, calculate the volume of the desired ZnS shell. (The number of monolayers can be raised or lowered by any factor, depending on what shell thickness is desired.)
- Using the volume of the shell (in $cm^3$) and the density of ZnS (4.09 g/mL), determine the weight of the shell.
- Convert to moles of ZnS per dot (MW ZnS = 97.456).
- Determine the concentration of the UV-Vis sample by using Beer's Law. (The extinction coefficient can be determined from the chart.)
- Determine the corresponding concentration of the CdSe stock solution (must know the initial volume of stock in mL).
- Multiply this concentration by Avagadro's number to determine the total number of CdSe dots present (something on the order of $10^{17}$ to $10^{18}$).
- Use the moles of ZnS per dot previously determined and the totals number of CdSe dots in order to establish how many moles of ZnS are necessary to overcoat all of the dots.
- Convert the moles of zinc and sulfur needed to grams of each precursor ($ZnEt_2$ and $(TMS)_2S$) needed using their respective molecular weights and densities (MW $ZnEt_2$ = 123.49, MW $(TMS)_2S$ = 178.45).
- Convert grams to volume for each using their respective densities ($\rho_{ZnEt_2}$ = 1.182 g/mL,$\rho_{(TMS)_2S}$ = 0.95 g/mL).

## CdSe overcoating recipe

Pot:

- 5 grams 90% TOPO
- 2.5 grams HDA (Acros)

Overcoating solution:

- Calculated amount of $(TMS)_2S$ (Aldrich)
- Calculated amount of $ZnEt_2$ (Strem)
- 5 mL 90% TOP (Aldrich)

Heat to 150 C. Degas the mixture to remove air and moisture. Then using an addition funnel or syringe pump introduce the overcoating solution (prepared in a glove box) dropwise into the pot. The addition should proceed slowly over the course of half an hour. The overcoating can be monitored real time using a hand-held uv/lamp or portable Ocean Optics fluorimeter with a high temperature fiber probe insert.

## Sizing curves

Table 1: Absorption versus size for CdSe QDs. Sizes are in effective radii.

| Absorption (nm) | Size (Å) | Absorption (nm) | Size (Å) | Absorption (nm) | Size (Å) | Absorption (nm) | Size (Å) |
|---|---|---|---|---|---|---|---|
| 460.00 | 10.41 | 522.00 | 16.33 | 584.00 | 23.76 | 646.00 | 45.07 |
| 462.00 | 10.79 | 524.00 | 16.54 | 586.00 | 24.01 | 648.00 | 46.92 |
| 464.00 | 11.13 | 526.00 | 16.76 | 588.00 | 24.26 | 650.00 | 48.91 |
| 466.00 | 11.43 | 528.00 | 16.98 | 590.00 | 24.51 | | |
| 468.00 | 11.71 | 530.00 | 17.21 | 592.00 | 24.78 | | |
| 470.00 | 11.96 | 532.00 | 17.44 | 594.00 | 25.05 | | |
| 472.00 | 12.19 | 534.00 | 17.68 | 596.00 | 25.33 | | |
| 474.00 | 12.40 | 536.00 | 17.92 | 598.00 | 25.63 | | |
| 476.00 | 12.60 | 538.00 | 18.16 | 600.00 | 25.94 | | |
| 478.00 | 12.78 | 540.00 | 18.40 | 602.00 | 26.26 | | |
| 480.00 | 12.94 | 542.00 | 18.65 | 604.00 | 26.61 | | |
| 482.00 | 13.10 | 544.00 | 18.90 | 606.00 | 26.98 | | |
| 484.00 | 13.25 | 546.00 | 19.15 | 608.00 | 27.37 | | |
| 486.00 | 13.40 | 548.00 | 19.40 | 610.00 | 27.79 | | |
| 488.00 | 13.54 | 550.00 | 19.65 | 612.00 | 28.25 | | |
| 490.00 | 13.68 | 552.00 | 19.90 | 614.00 | 28.74 | | |
| 492.00 | 13.82 | 554.00 | 20.15 | 616.00 | 29.26 | | |
| 494.00 | 13.95 | 556.00 | 20.39 | 618.00 | 29.83 | | |
| 496.00 | 14.09 | 558.00 | 20.64 | 620.00 | 30.45 | | |
| 498.00 | 14.24 | 560.00 | 20.89 | 622.00 | 31.12 | | |
| 500.00 | 14.38 | 562.00 | 21.13 | 624.00 | 31.84 | | |
| 502.00 | 14.53 | 564.00 | 21.38 | 626.00 | 32.62 | | |
| 504.00 | 14.69 | 566.00 | 21.62 | 628.00 | 33.47 | | |
| 506.00 | 14.84 | 568.00 | 21.86 | 630.00 | 34.39 | | |
| 508.00 | 15.01 | 570.00 | 22.10 | 632.00 | 35.39 | | |
| 510.00 | 15.18 | 572.00 | 22.33 | 634.00 | 36.47 | | |
| 512.00 | 15.36 | 574.00 | 22.57 | 636.00 | 37.64 | | |
| 514.00 | 15.54 | 576.00 | 22.81 | 638.00 | 38.91 | | |
| 516.00 | 15.73 | 578.00 | 23.04 | 640.00 | 40.27 | | |
| 518.00 | 15.92 | 580.00 | 23.28 | 642.00 | 41.75 | | |
| 520.00 | 16.12 | 582.00 | 23.52 | 644.00 | 43.35 | | |

Table 2: Emission versus size for CdSe QDs. Sizes are in effective radii.

| Absorption (nm) | Size (Å) | Absorption (nm) | Size (Å) | Absorption (nm) | Size (Å) | Absorption (nm) | Size (Å) |
|---|---|---|---|---|---|---|---|
| 516 | 14.52 | 554 | 18.66 | 592 | 23.69 | 630 | 30.58 |
| 518 | 14.59 | 556 | 18.88 | 594 | 24.03 | 632 | 31.14 |
| 520 | 14.70 | 558 | 19.11 | 596 | 24.36 | 634 | 31.77 |
| 522 | 14.86 | 560 | 19.33 | 598 | 24.70 | 636 | 32.50 |
| 524 | 15.04 | 562 | 19.55 | 600 | 25.03 | 638 | 33.33 |
| 526 | 15.26 | 564 | 19.78 | 602 | 25.37 | 640 | 34.29 |
| 528 | 15.49 | 566 | 20.01 | 604 | 25.71 | 642 | 35.40 |
| 530 | 15.73 | 568 | 20.25 | 606 | 26.05 | 644 | 36.69 |
| 532 | 15.99 | 570 | 20.49 | 608 | 26.39 | 646 | 38.19 |
| 534 | 16.24 | 572 | 20.75 | 610 | 26.72 | 648 | 39.93 |
| 536 | 16.50 | 574 | 21.00 | 612 | 27.06 | 650 | 41.95 |
| 538 | 16.76 | 576 | 21.27 | 614 | 27.39 | 652 | 44.29 |
| 540 | 17.01 | 578 | 21.55 | 616 | 27.74 | 654 | 47.00 |
| 542 | 17.26 | 580 | 21.83 | 618 | 28.08 | 656 | 50.12 |
| 544 | 17.51 | 582 | 22.12 | 620 | 28.44 | 658 | 53.72 |
| 546 | 17.75 | 584 | 22.42 | 622 | 28.81 | 660 | 57.84 |
| 548 | 17.98 | 586 | 22.73 | 624 | 29.20 | | |
| 550 | 18.21 | 588 | 23.05 | 626 | 29.62 | | |
| 552 | 18.44 | 590 | 23.37 | 628 | 30.08 | | |

Table 3: Extinction coefficient versus size for CdSe QDs. Sizes are in effective diameter (nm).

| Dia (nm) | Ext Coeff ($M^{-1}cm^{-1}$) | Dia (nm) | Ext Coeff ($M^{-1}cm^{-1}$) | Dia (nm) | Ext Coeff ($M^{-1}cm^{-1}$) |
|---|---|---|---|---|---|
| 1.5 | 5027.668800 | 3.0 | 210336.8635 | 4.5 | 321060.8133 |
| 1.6 | 22206.55000 | 3.1 | 220358.2435 | 4.6 | 325750.0169 |
| 1.7 | 38851.47660 | 3.2 | 229967.3572 | 4.7 | 330148.6424 |
| 1.8 | 54970.56120 | 3.3 | 239172.3172 | 4.8 | 334264.8026 |
| 1.9 | 70571.91620 | 3.4 | 247981.2359 | 4.9 | 338106.6098 |
| 2.0 | 85663.65420 | 3.5 | 256402.2260 | 5.0 | 341682.1767 |
| 2.1 | 100253.8878 | 3.6 | 264443.4000 | 5.1 | 344999.6158 |
| 2.2 | 114350.7296 | 3.7 | 272112.8705 | 5.2 | 348067.0397 |
| 2.3 | 127962.2921 | 3.8 | 279418.7500 | 5.3 | 350892.5610 |
| 2.4 | 141096.6878 | 3.9 | 286369.1510 | 5.4 | 353484.2921 |
| 2.5 | 153762.0293 | 4.0 | 292972.1862 | 5.5 | 355850.3456 |
| 2.6 | 165966.4292 | 4.1 | 299235.9681 | 5.6 | 357998.8342 |
| 2.7 | 177718.0000 | 4.2 | 305168.6091 | 5.7 | 359937.8703 |
| 2.8 | 189024.8543 | 4.3 | 310778.2220 | 5.8 | 361675.5665 |
| 2.9 | 199895.1046 | 4.4 | 316072.9192 | 5.9 | 363220.0353 |