Supporting Information

# Surface Chemistry of Cadmium Sulfide Magic-sized Clusters: A Window into Ligand-Nanoparticle Interactions

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## Synthesis Procedures and Chemical Treatments

### Materials

The following chemicals were used as received 1-octadecene (ODE, >90%), oleic acid (OA, >90%), cadmium oxide (>99.5%), ethyl acetate (99.5%) and elemental sulfur (purified by sublimation, particle size~100 mesh) were purchased from Sigma-Aldrich. Hexanes (BDH ACS Grade) and ethanol (Ethanol, 200 proof, Anhydrous KOPTEC USP) were purchased from VMR International. Tri-noctylphsosphine (TOP, 90%) was purchased from Sigma-Aldrich. 1-dodecanethiol (DDT, >98%) from Sigma-Aldrich. 1-Butylamine (>99%) from Alfa Aesar.

### Synthesis of ultra-pure 324 nm family MSCs

In a typical synthesis, a 1.0 M solution of CdOleate is prepared by mixing 1.28 g of CdO (10.0 mmol) in 10.0 mL of oleic acid (8.95 g, 31.6 mmol) in a 25 mL round bottom flask. The mixture is heated to 50°C and placed under vacuum for 15 min. The mixture is then placed under $N_2$ and heated to 160°C until clear with a tan to orange color. The solution is cooled to 100°C and put under vacuum until bubbling stops (~1 hr). The solution is cooled to 50°C (solution may become turbid) and placed under $N_2$. The 2.5 M tri-n-octylphosphine sulfide (TOPS) solution is prepared in a glovebox by dissolved 0.16 g (5.0 mmol) of elemental sulfur in 2.0 mL of tri-n-octylphosphine (TOP) in a scintillation vial. The mixture takes ~10 min to dissolve and has a yellow-green tint. While dissolving, the mixture releases heat (*Precaution: At greater volumes (>20 mL solutions), this heating becomes significant and additional precautions may become necessary*). The TOPS solution is loaded into a 3 mL syringe, removed from glovebox, and injected into 1.0 M CdOleate solution at 50°C. The CdOleate and TOPS mixture is heated to 140°C within 15 min. Nearing 140°C, the mixture will become suddenly more viscous and turbid. The synthesis soaks at 140°C for up to 60 min. The reaction is stopped by removing the colloidal mixture from the heating mantle and quenching with ethyl acetate (EtAc) in equal parts with reaction volume (~12 mL) in a centrifuge tube. The sample is spun at 4400 rpm for 5 min. The supernatant is discarded and the precipitate is suspended in hexane (~10 mL). During resuspension, the solution gels substantially. Once fully dissolved, the product is again precipitated with EtAc (~10 mL) and centrifuged for 5 min at 4400 rpm. The supernatant is discarded and the sample is dried under vacuum for 24 hr. This reaction procedure of ultra-pure MSCs has been scaled to volumes of 5 – 100 mL with no effect on quality or production rate of MSCs.

### Synthesis of high-quality NPs

The synthesis of high-quality NPs is adopted from Peng et al.[2] In a typical synthesis, a 0.02 M solution of CdOleate is prepared by mixing 0.069 g of CdO in 0.8 mL (0.72 g, 2.5 mmol) oleic acid and 9.2 mL (7.26 g) ODE in a 100 mL round bottom flask. The mixture is heated to 50°C and placed under vacuum. While under vacuum the mixture is heated to 120°C for 1 hr; after which, the mixture is placed under $N_2$ and heated to 300°C (approaching 240°C the mixture will become a clear solution). The sulfur solution is prepared by dissolving 0.003 g of elemental sulfur in 1.0 mL of ODE and heated slightly to dissolve the sulfur. The sulfur solution is loaded into a 1 mL syringe and rapidly injected into the CdOleate mixture at 300°C. After 3 min the mixture is quickly cooled to 200°C and then quenched to room temperature with ~20 mL EtAc. The colloidal suspension is added to 4 50-mL centrifuge tubes and EtAc is added to each

tube until solution becomes turbid (~ 45 mL of EtAc to 3 mL of reaction solution). The centrifuge tubes are spun at 8800 rpm for 15 min to maximize collection of NP product. The supernatant is discarded and the precipitated is combined and suspended in a total of 0.5 mL of hexane. The solution is again precipitated with EtAc (~45 mL) and spun at 8800 rpm for 15 min. The supernatant is discarded and the product is dried under vacuum.

*Additional Comments:*

- Total approximate anti-solvent for dilute NP synthesis is ~ 300 mL of solvent for 15 mg of product.
- Total approximate anti-solvent for concentration MSC synthesis is ~20 mL solvent for 1000 mg of product.

**Ligand Treatment Conditions**

We consider several ways to match the ligand treatment conditions between the MSCs and NPs because of their fundamental different sizes. The true identical treatment condition between MSCs and NPs is to have identical ratio of added ligand to ligand sites. We approximate the number of surface sites per sample using two methods (see **Table S1**): total surface area of the species and total number atoms in within the distance of a Cd-S bond of the surface. The second method was previously used by Bawendi and Murry groups to estimate surface sites.[3, 4] Based on propagation of error analysis, samples with the same total mass of MSCs and NPs have the same total inorganic surface area and same total surface sites between the MSCs and the NPs samples. The largest source of uncertainty in these calculations is the uncertainty of an empirical sizing curve that was used to determine the particle size (reported sizing curve uncertainty: 10-15%[5]). This is the large source of uncertainty; even though, we used the lower limit (*e.g.*, best case scenario uncertainty) of the sizing curve uncertainty (*i.e.*, 10%).

**Table S1:** Comparison of the calculated total inorganic surface area and total surface sites available within the total mass of MSC and NP samples that were treated with ligands. The uncertainty is calculated using standard propagation of error analysis, and the values used the in calculations are provided in the sample calculations section.

| Species | Total Mass of Sample (mg) | Total Inorganic Surface Area ($cm^2$) | Total Surface Sites (µmol) | Fraction of Surface Atoms |
|---|---|---|---|---|
| **Magic-sized Clusters** | 4±1 | 10000±4500 | 6.2±3.5 | 0.68 |
| **Nanoparticles** | 4±1 | 4500±2000 | 3.4±2.0 | 0.26 |

**Chemical Treatment of MSCs and NPs - Alcohol**

**MSC** – To transform the 324 nm family (F324) into a 313 nm family (F313), 4 mg of F324 and 0.5 mL of ethanol (EtOH) is added to a scintillation vial. The mixture is stirred at room temperature (in air) for 24 hrs. Over 24 hrs, the resin-like F324 sample breaks down into a fine white powder as it converts into F313. To remove the ethanol, the mixture is centrifuged at 4400 rpm for 5 min. The supernatant is discarded and the precipitate is dried under vacuum for 24 hr. The product is suspended in THF (sample is turbid in alkanes) for absorption spectroscopy. The use of THF rather than hexane as a solvent does not change the MSC excitonic peak position, rather it merely reduces scattering due to aggregation. If residual alcohol is still present, there is a broad 348 peak in the absorption spectrum. The dried product is used for FTIR analysis.

**NP** – 4 mg of NPs and 0.5 mL of EtOH is added to a scintillation vial. The mixture is stirred at room temperature (in air) for 24 hrs. The mixture is centrifuged at 4400 rpm for 5 min. The supernatant is discarded and the precipitate is dried under vacuum for 24 hr. The product is suspended in hexane for absorption spectroscopy. The dried product is used for FTIR analysis.

**Chemical Treatment of MSCs and NPs - Thiol**

**MSC** – To transform the 324 nm family (F324) into a 348 nm family (F348), 4 mg of F324 is dissolved in 0.5 mL of octane in a scintillation vial. The mixture is precipitated with EtAc (~5 mL) and centrifuged at 4400 rpm for 5 min. The supernatant is discarded and the precipitate is dried under vacuum for 24 hr. Once the sample is completely dry, the product is a colorless, clear, brittle material with plastic-like texture and does not dissolve in solvent (but swells). Absorption spectroscopy is performed prior to drying under vacuum by suspending a small fraction of product in THF (sample is turbid in alkanes). The dried product is used for FTIR analysis.

**NP** – 4 mg of NPs and 0.5 mL of DDT is added to a scintillation vial. The mixture is stirred at room temperature (in air) for 1 hr. The mixture is precipitated with EtOH (~100 mL) and centrifuged at 8800 rpm for 15 min to maximize collection of NP product (**Note:** EtAc does not precipitate product and EtOH is required, and the use of EtOH for precipitation did not affect excitonic peak). The supernatant is discarded and the precipitate is dried under vacuum for 24 hr. The product is suspended in hexane for absorption spectroscopy. The dried product is used for FTIR analysis.

**Chemical Treatment of MSCs and NPs - Amine**

**MSC** – To transform the 324 nm family (F324) into a 360 nm family (F360), 4 mg of F324 and 0.5 mL of n-butylamine is added to a scintillation vial. The mixture is stirred at room temperature (in air) for 1 hr. The resin-like F324 sample dissolves into a clear fluid solution with a green tint. The solution is precipitated with EtAc (~40 mL) and centrifuged at 4400 rpm for 15 min to maximize collection of the MSC product. The supernatant is discarded and the precipitate is dried under vacuum for 24 hr. Once the sample is completely dry, the product is a colorless, clear, brittle material and does not readily dissolve in solvents. Absorption spectroscopy is performed prior to drying under vacuum by suspending a small fraction of product in hexane. The dried product is used for FTIR analysis.

**NP** – 4 mg of NPs and 0.5 mL of n-butylamine is added to a scintillation vial. The mixture is stirred at room temperature (in air) for 1 hr. The mixture is precipitated with EtOH (~100 mL) and centrifuged at 8800 rpm for 15 min (**Note:** EtAc does not precipitate product and EtOH is required, and the use of EtOH for precipitation did not affect excitonic peak). The supernatant is discarded and the precipitate is dried under vacuum for 24 hr. The product is suspended in hexane for absorption spectroscopy. The dried product is used for FTIR analysis.

## Characterization Methods

### Absorption Spectroscopy

Absorbance measurements were performed on Ocean Optics USB 2000+ UV-Vis spectrometer with a DH-2000-BAL light source. Each sample was background subtracted with its respective solvent (hexane or THF). The samples were washed with ethyl acetate to remove unreacted or removed ligands/species prior to characterization. Integration time for each spectrum was 400 ms and 150 scans were averaged. The particle size was estimated from the lowest energy absorption peak using Peng et al.'s sizing curve[5], which has uncertainty of 10-25%.

### Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) Spectroscopy

FTIR measurements were performed on Thermo Scientific Smart iTR diamond ATR. A background scan was collected before each measurement (64 scans), sample scan were an average of 64 scans, and resolution was set 4 with a data spacing of 0.482 $cm^{-1}$.

### Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES was measured at the Cornell Soil & Water Laboratory, Cornell University, Ithaca, New York on an ICP-OES spectrometer equipped with an argon torch. Cd and S standards were prepared in 2% HNO3, and the instrument was calibrated using ICP model: Thermo iCAP 6500 series. Samples were digested in concentrated nitric acid (~3-50 mg in 4-5 mL), and then diluted with 2% nitric acid for analysis.

### Thermogravimetric Analysis (TGA)

TGA measurements were performed on a TGA Q500 (TA Instruments Inc.). All samples were washed with ethyl acetate prior to characterization. F324 samples were prepared by added ~1 mg of clusters to a platinum pan to create thin film either as a dissolved solution in hexane. Then, the clusters were dried under vacuum to remove solvent. The following temperature profile was used 15°C/min ramp from 25°C to 700°C. Analysis was performed under nitrogen. Analysis of F324 as a particulate rather than thin-film sample led to foaming, which to inaccuracy and noisy in the mass loss curve.

### Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) analysis was performed on an FEI Tecnai T12 transmission electron microscope operating at 120 kV with a LaB6 tip. All samples were washed with ethyl acetate and dried in vacuum prior to characterization. Samples for TEM analysis were prepared by placing a drop of MSCs solution in hexane on top of a copper grid coated with an amorphous carbon film. Particle counting was done manually using ImageJ. A 50 nanoparticle count was used to measure average size and relative size distribution.

### X-ray Diffraction (XRD)

XRD data were collected on a Bruker D8 Discover (Cu Kα radiation, wavelength 1.54 Å) with a 0.5-mm collimator. All samples were washed with ethyl acetate and dried in vacuum prior to characterization. The powders were analyzed on silicon wafer, and spots from the silicon were masked before integration of the 2D x-ray image. Scherrer analysis was performed after background subtraction.

## Figures and Tables

### Absorption Fits and TEM

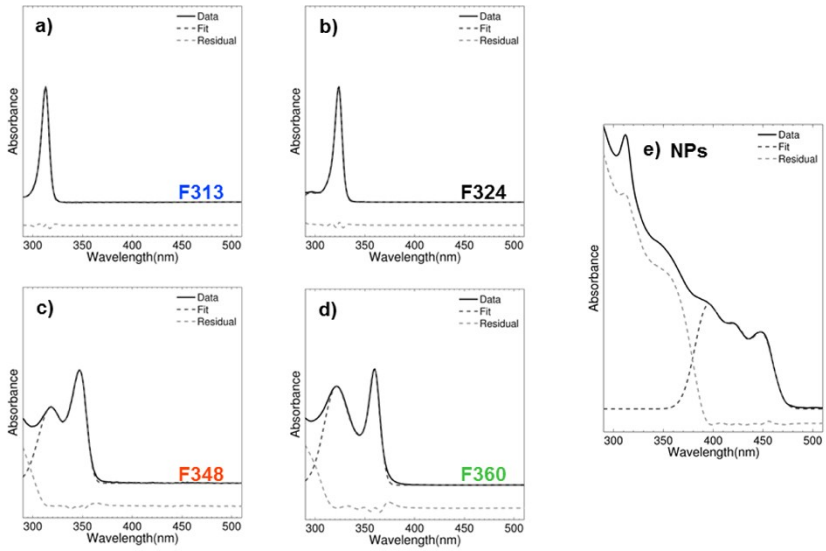


***Figure S1*:** Absorption spectra for each MSC family (a-d) and the initial NP spectrum. All spectra are fitted with 3 normal distribution functions. See **Table S2** for fitting parameters. For the NPs, the sharp peak at 313nm is trace MSCs.

**Table S2:** Fitting parameters to the absorption spectra above in **Figure S1**. The normal-distribution function has 3-fitting parameters: the mean (peak position), the standard deviation (std. dev.), and a scalar. The FWHM is related to the size standard. deviation (std. dev.) by multiplying a factor of $2\sqrt{2ln(2)}$.

| | 1st Peak | | | | 2nd Peak | | | 3rd Peak | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Species** | **Position* (nm)** | **FWHM (nm)** | **Std.dev. (nm)** | **Intensity** | **Position (nm)** | **Std.dev. (nm)** | **Intensity** | **Position (nm)** | **Std.dev. (nm)** | **Intensity** |
| F313 | 313.1 | 8.1 | 3.46 | 7.3 | 307.5 | 6.0 | 4.0 | 290.0 | 6.0 | 0.6 |
| F324 | 323.8 | 8.0 | 3.40 | 7.0 | 318.0 | 6.7 | 4.0 | 296.0 | 8.0 | 1.6 |
| F348 | 348.9 | 13.9 | 5.90 | 12.0 | 339.5 | 6.0 | 5.5 | 318.2 | 12.5 | 20.6 |
| F360 | 360 .2 | 13.0 | 5.50 | 12.3 | 348.0 | 8.5 | 6.1 | 321.5 | 12.5 | 26.8 |
| NPs | 450.0 | 25.0 | 10.6 | 24.3 | 422.6 | 12.0 | 29.4 | 394.0 | 12.5 | 40.6 |

*These values are the fitted peak positions for the exciton

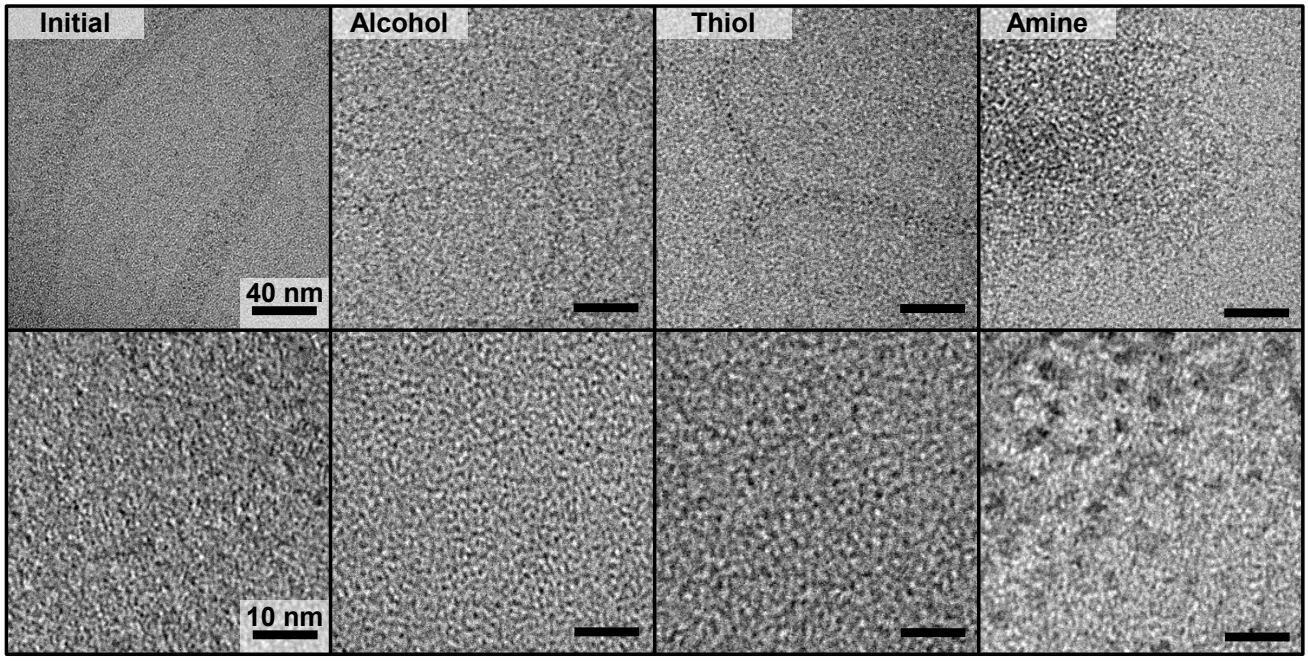


***Figure S2*:** TEM images of the MSCs at two different magnifications. The top row shows the presence of MSCs and the bottom row illustrates the difficulty in the imaging of MSCs. The size and size distribution are reported in **Table S3**.

**Table S3:** Analysis of TEM images of the bottom row in **Fig. S2**. The mean size and size distribution are determined using a normal distribution function on a count of 50 particles. The relative size distribution is a ratio of the size distribution to the mean particle size.

| Species | Mean Size (nm) | Size Distribution (nm) | Relative Size Distribution (%) | Pixel Resolution (nm/pixel) |
|---|---|---|---|---|
| **Initial** | 0.6 | 0.1 | 16.7 | 0.2 |
| **Alcohol** | 0.7 | 0.1 | 14.3 | 0.1 |
| **Thiol** | 1.1 | 0.2 | 18.2 | 0.2 |
| **Amine** | 2.5 | 0.3 | 12.0 | 0.2 |

**FTIR Spectra**

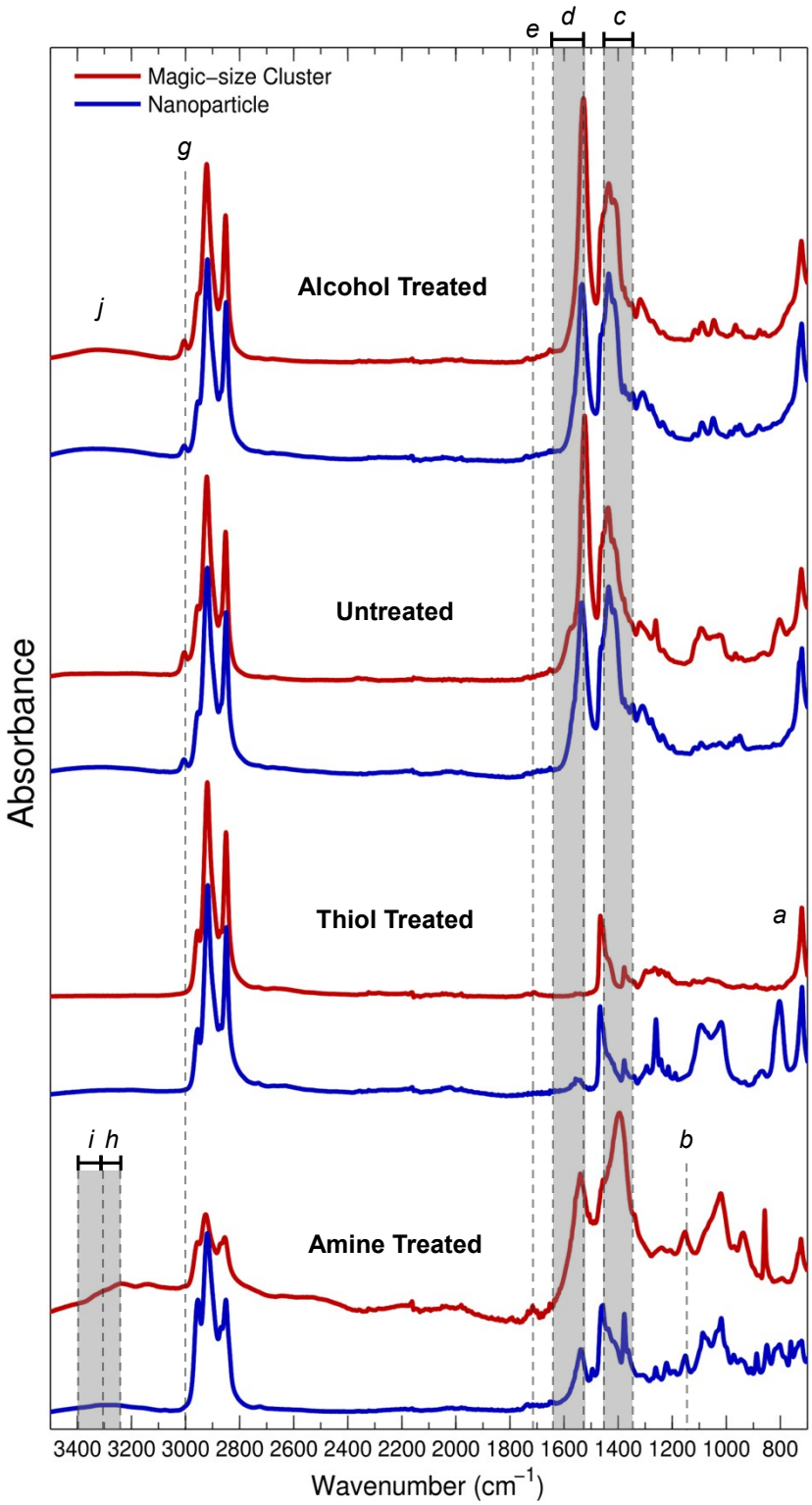


***Figure S3*:** Full FTIR spectra for chemically treated MSCs (red) and NPs (blue). The alcohol treated MSC is the F313, the untreated MSC is the F324, the thiol treated is the F348, and the amine treated is the F360. Key peaks (a-j) are labeled in each spectrum and the values and ranges are reported in **Table S4.**

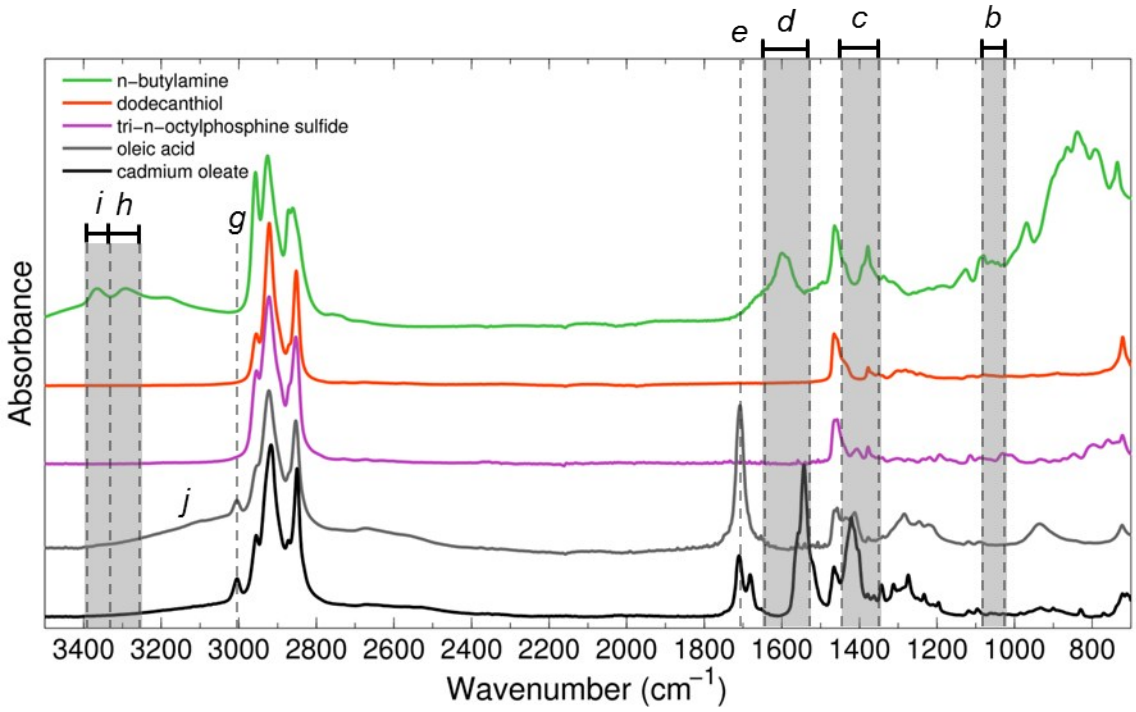


***Figure S4:*** Full FTIR reference spectra for the reaction precursors (i.e. oleic acid, Cd-oleate and TOPS) and chemical treatment liquids (DDT and n-butylamine). Key peaks are labeled in each spectrum and the values and ranges are reported in are in **Table S4**. The broad base between 2400-3400 cm$^{-1}$ of the oleic acid and Cd-oleate are due to O-H stretches (*j*).

**Table S4:** Peak positions for selected peaks in FTIR spectra of MSCs, NPs, and reference materials. All values in the table are reported in cm$^{-1}$. Symmetric and asymmetric stretches are denoted by *s* and *as*, respectively. Stretches that are not present in the spectra are identified by *n.a.* (not applicable).

| | | Magic-sized Clusters | | | | Nanoparticles | | | | Reference Materials | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Graph Label** | **Chemical Stretches** | **Alcohol** | **Initial** | **Thiol** | **Amine** | **Alcohol** | **Initial** | **Thiol** | **Amine** | **CdOleate** | **Oleic Acid** | **DDT** | **Butyl-amine** | **Literature[1]** |
| *a* | C-S | n.a. | n.a. | 803 | n.a. | n.a. | n.a. | 803 | n.a. | n.a. | n.a. | n.a. | n.a. | 585-750 |
| *b* | C-N | n.a. | n.a. | n.a. | 1144 | n.a. | n.a. | n.a. | 1144 | n.a. | n.a. | n.a. | 1120 | 1020-1090 |
| *c* | C-O (*s*) | 1419 | 1436 | n.a. | 1407 | 1435 | 1435 | n.a. | 1435 | 1421 | 1435 | n.a. | n.a. | 1350-1450 |
| *d* | C-O (*as*) | 1541 | 1524 | n.a. | 1553 | 1533 | 1533 | n.a. | 1538 | 1542 | n.a. | n.a. | n.a. | 1525-1650 |
| *e* | C=O | 1705[a] | 1655[b] | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 1682/1710 | 1708 | n.a. | n.a. | 1710 |
| *f* | S-H | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 2560-2590 |
| *g* | =CHR | 3005 | 3005 | n.a. | 3005 | 3005 | 3005 | n.a. | n.a. | 3004 | 3005 | n.a. | n.a. | 3000-3040 |
| *h* | N-H (*s*) | n.a. | n.a. | n.a. | 3157 | n.a. | n.a. | n.a. | 3157 | n.a. | n.a. | n.a. | 3290 | 3300-3250 |
| *i* | N-H (*as*) | n.a. | n.a. | n.a. | 3257 | n.a. | n.a. | n.a. | 3257 | n.a. | n.a. | n.a. | 3365 | 3400-3330 |
| *j* | O-H | 3330[a] | 3330[b] | n.a. | n.a. | 3300[a] | 3300[a] | 3300[b] | n.a. | n.a. | 3100[a] | n.a. | n.a. | 3200-3570 |

[a] Broad peak. [b] Trace and broad peak

## Compositional Analysis

**Table S5:** Compositional analysis of MSCs (core Cd and S and Ligand) in mass and mole percent. Values are based on ICP-OES and TGA analysis (see calculations for conversion from mass to mole percent). Error refers to the standard deviation and is determined using propagation of error analysis.

| | Mass Percent (wt%) | | | Mole Percent (mol%) | | | |
|---|---|---|---|---|---|---|---|
| Species | Cd | S | Ligand (ICP-OES)[a] | Cd | S | Ligand (ICP-OES) | Cd/S ratio |
| F313 | 26.2±0.1 | 3.9±0.1 | 69.9±0.1 | 38.7±0.2 | 20.2±0.3 | 41.1±0.2 | 1.91±0.02 |
| F324 | 25.5±0.1 | 3.6±0.1 | 70.9±0.1 | 38.3±0.2 | 19.2±0.3 | 42.5±0.3 | 2.00±0.02 |
| F348[c] | 32.1±0.4 | 4.4±0.2 | 63.5±0.9 | 38.7±0.3 | 18.7±0.7 | 42.6±0.5 | 2.07±0.07 |
| F360 | 27.9±0.1 | 6.9±0.1 | 65.2±0.2 | 18.3±0.1 | 15.8±0.2 | 65.8±0.6 | 1.16±0.01 |

[a]The ligand values from ICP-OES are determined by the balance of mass not accounted for by Cd and S for the analyzed MSCs samples. The ICP-OES ligand percentages were used in calculations for consistent and to avoid complication due to the thiol sulfur atom, potentially not burning off in the TGA. [c] The thiol treated sample (F348) analysis was completed by the presence of sulfur in ligand. ICP-OES detects both core and thiol sulfur; thus the values were corrected to distinguish core S and thiol S. First, the molecular weight of DDT less the weight of a sulfur atom was used to calculate the mole percent, then the mole percent of ligands was subtracted from mole percent of sulfur, and finally the mole percentages were re-scaled to total 100%. Then, the mass percentages were calculated from the corrected mole percentages (see calculation for details).

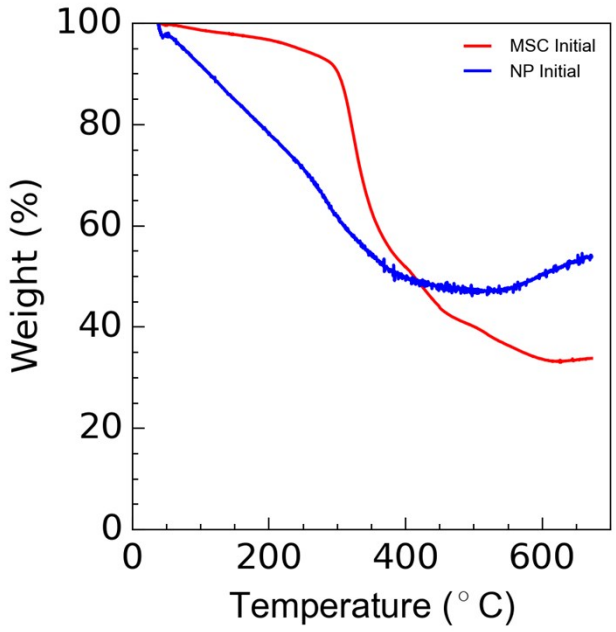


**Figure S5**: TGA scan of MSCs and NPs (Initial sample) to determine the inorganic mass fraction, which is 33 and 48 wt%, respectively.

## Scherrer Analysis (XRD)

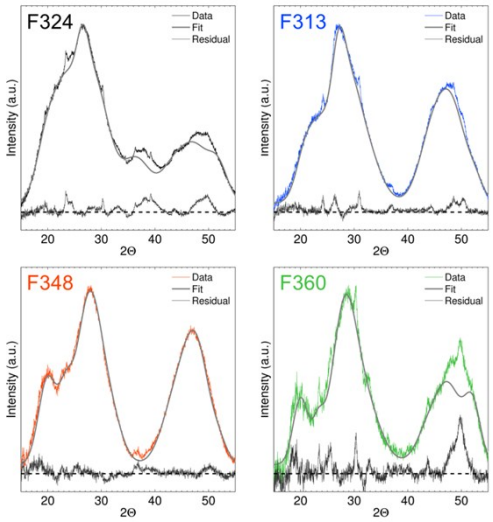


**Figure S6**: XRD patterns of MSCs. Each pattern is fit with eight normal distribution functions (see **Table S6**) corresponding to the bulk peak positions and 2 float peaks possibly associated with the organics.

**Table S6**: XRD peak fitting parameters. Initial F324 is best fit to a wurtzite standard (light gray) while other samples are best fit to zinc blende (white) with two additional peaks from wurtzite to provide a more accurate fit. Each pattern has two float peaks (dark gray) that may be associated with the organics. Scherrer size is the average of the crystallite sizes of the fitted peaks (means).

| | **F324** | **F313** | **F348** | **F360** |
|---|---|---|---|---|
| **Phase** | **Wurtzite** | **Zinc Blende** | **Zinc Blende** | **Zinc Blende** |
| **Mean 1** | 26.5 | 26.5 | 26.5 | 26.5 |
| **Std. Dev. 1** | 1.10 | 1.20 | 2.30 | 2.90 |
| **Intensity 1** | 0.59 | 0.79 | 0.57 | 0.12 |
| **Mean 2** | 28.2 | 30.8 | 30.8 | 30.8 |
| **Std. Dev. 2** | 3.00 | 2.90 | 2.40 | 3.30 |
| **Intensity 2** | 0.60 | 0.31 | 0.40 | 0.33 |
| **Mean 3** | 36.6 | 44.0 | 44.0 | 44.0 |
| **Std. Dev. 3** | 2.50 | 2.50 | 2.60 | 2.30 |
| **Intensity 3** | 0.24 | 0.36 | 0.35 | 0.22 |
| **Mean 4** | 43.7 | 52.1 | 52.1 | 52.1 |
| **Std. Dev. 4** | 2.50 | 1.50 | 1.50 | 1.50 |
| **Intensity 4** | 0.22 | 0.15 | 0.15 | 0.53 |
| **Mean 5** | 47.8 | 28.2 | 28.2 | 28.2 |
| **Std. Dev. 5** | 2.30 | 2.00 | 1.80 | 2.00 |
| **Intensity 5** | 0.28 | 0.50 | 0.50 | 0.63 |
| **Mean 6** | 51.8 | 47.8 | 47.8 | 47.8 |
| **Std. Dev. 6** | 1.80 | 2.50 | 2.30 | 2.30 |
| **Intensity 6** | 0.28 | 0.48 | 0.65 | 0.43 |
| **Mean 7** | 20.0 | 20.0 | 20.0 | 20.0 |
| **Std. Dev. 7** | 2.00 | 1.60 | 1.70 | 1.40 |
| **Intensity 7** | 0.48 | 0.25 | 0.71 | 0.64 |
| **Mean 8** | 23.3 | 23.3 | 23.3 | 23.3 |
| **Std. Dev. 8** | 2.00 | 2.50 | 1.20 | 1.00 |
| **Intensity 8** | 0.55 | 0.44 | 0.50 | 0.40 |
| **Scherrer Size (nm)** | 2.0±0.9 | 2.1±0.8 | 1.9±0.5 | 1.8±0.6 |

## Calculations

### Particle Size Calculation

The size of the MSCs and NPs is determined from its excitonic peak position (see **Table S2**) using an equation proposed by Peng et al (Eq. 1)[5], where *D* is the nanoparticle diameter and λ is the excitonic wavelength.

$$D = -6.65 \times 10^{-8}\lambda^3 + 1.96 \times 10^{-4}\lambda^2 - 9.24 \times 10^{-2}\lambda + 13.29 \quad \textbf{(1)}$$

$$D = -6.65 \times 10^{-8}(324)^3 + 1.96 \times 10^{-4}(324)^2 - 9.24 \times 10^{-2}(324) + 13.29 = 1.64\ nm \quad \textbf{(1s)}$$

### Compositional Analysis

To convert ICP determined mass percentages into mole percentages the following analysis was used (see **Table S5**).

$$mol\%_{Cd} = \frac{\frac{wt\%_{Cd}}{Mw_{Cd}}}{\frac{wt\%_{Cd}}{Mw_{Cd}} + \frac{wt\%_{S}}{Mw_{S}} + \frac{wt\%_{ligand}}{Mw_{ligand}}},$$

where wt% is the species mass percent, and Mw is the molecular weight.

For instance to calculate the Cd mole percent in the F324 and F313 samples, the following equation was used:

$$mol\%_{Cd} = \frac{\frac{26.03g}{112.411g/mol}}{\frac{26.03g}{112.411g/mol} + \frac{3.66g}{32.065g/mol} + \frac{70.31g}{282.46g/mol}} \cdot 100 = 38.9mol\%$$

For the F348 sample, the S wt% needs to be corrected for thiol sulfur detected by ICP. This was accomplished by 1) calculating the mole percent as shown above, but using the molecular weight of DDT less the weight of a sulfur atom, 2) subtracting the mole percent of ligands from the mole percent of S (to remove the thiol S from the S mol%) and 3) finally re-scaling the mole percentages to total 100%.

### Scherrer Analysis

The crystallite size is calculated with the following (Scherrer equation):

$$d_{crystallite} = \frac{K\lambda}{\beta cos\theta},$$

where K is shape factor (0.94), λ is X-ray wavelength (1.54 Å), β is line broadening (FWHM) minus the instrument line broadening (0.005236) in radian, and θ is the angle of the Bragg peak. FWHM is equal to the standard deviation multiplied by a factor of 2.355. For example for the first fitted for the initial sample (see **Table S6**), the Scherrer size is

$$d_{crystallite} = \frac{0.94 \cdot 0.154nm}{(\frac{4.0° \cdot \pi \cdot 2.355}{180} - 0.005236) \cdot cos(\frac{24.8°}{2})} = 0.93nm.$$

**Calculation of Clusters' Total Surface Area and Surface Sites**

This calculations assumes spherical particles with bulk inorganic cadmium sulfide molecular weight (144.47 g/mol ) and density (4.82 g/cm$^3$), and surface shell or layer, $r_{Surface\_Layer}$, equivalent to the distance of a Cd-S bond distance (2.5 Å). Additional values used in the calculations are provided in the Table below.

| Property | Value | Error |
|---|---|---|
| **Total sample mass (mg)** | 4 | 1 |
| **Total chemical volume (mL)** | 0.5 | 0.01 |
| **MSC Diameter (nm) (Sizing Curve)** | 1.6 | 0.16 |
| **NP Diameter (nm) (Sizing Curve)** | 5.3 | 0.53 |
| **Percent Inorganic Mass MSC (%) (TGA)** | 33 | 0.1 |
| **Percent Inorganic Mass NP (%) (TGA)** | 48 | 1 |

## Total Surface Area of a Cluster Sample

To calculate the total surface area of the mass of nanomaterial, the number of particles and their surface area is needed. The surface area is calculated using the surface area of a sphere and the particle radium from Peng's sizing curve.[5]

$$Surface\ Area\ of\ Individual\ Species\ (NP\ or\ MSC) = 4\pi r^2$$

The number of particles ($N_{part}$) is calculated by calculated the total inorganic volume of the sample, and volume of an individual MSC or NP.

$$Total\ Inorganic\ Volume\ of\ Sample = \frac{Total\ Mass\ of\ Sample \cdot Mass\ Percentage\ Inorganic}{Inorganic\ Density}$$

$$Volume\ of\ Individual\ Species\ (NP\ or\ MSC) = \frac{4}{3}\pi r^3$$

$$N_{part} = \frac{Total\ Inorganic\ Volume\ of\ Sample}{Volume\ of\ Individual\ Species\ (NP\ or\ MSC)}$$

Finally, the total surface area can be calculated as follows.

$$Total\ Surface\ Area = N_{part} \cdot\ Surface\ Area\ of\ Individual\ Species\ (NP\ or\ MSC)$$

**For example**

$$Surface\ Area\ of\ Individual\ Species\ (MSC) = 4\pi(\frac{1.6\ nm}{2})^2 = 8.04\ x\ 10^{-14} cm^2$$

$$Total\ Inorganic\ Volume\ of\ Sample = \frac{4mg \cdot 0.33}{4.82\ g/cm^3} = 2.7x10^{-4}cm^3$$

$$Volume\ of\ Individual\ Species\ (MSC) = \frac{4}{3}\pi(\frac{1.6\ nm}{2})^3 = 2.14x10^{-21}cm^3$$

$$N_{part} = \frac{2.5x10^{-4}cm^3}{2.14x10^{-21}cm^3} = 1.27x10^{17}$$

$$Total\ Surface\ Area = 1.27x10^{17} \cdot\ 8.04\ x\ 10^{-14}cm^2 = \sim 1000\ cm^2$$

## Total Surface Sites in a Cluster Sample

To calculate the number of surface sites, the number of atoms at the surface of a particle is needed. This is determined by calculating the volume of the surface layer, which is the difference between the volume of NPs or MSCs and the volume of that particle excluding the surface layer.[3, 4]

$$Volume\ of\ Individual\ Species\ Excluding\ Surface\ (NP\ or\ MSC) = \frac{4}{3}\pi(r - r_{Surface\_Layer})^3$$

Where r is the particle radius and $r_{Surface\_Layer}$ is the thickness of the surface layer (*i.e.*, that is the Cd-S bond distance).

The volume of occupied by the surface layer is calculated as the difference between the total spherical volume and spherical volume of the species excluding the surface layer.

$$Volume\ of\ Individual\ Species\ Surface\ Layer\ (NP\ or\ MSC) = Volume\ of\ Individual\ Species\ (NP\ or\ MSC) - Volume\ of\ Individual\ Species\ Excluding\ Surface\ (NP\ or\ MSC)$$

From the volume of the surface layer, the total number of surface atoms is calculated.

$$Moles\ of\ Cadmium\ Sulfide\ at\ Surface\ of\ Species\ (NP\ or\ MSC) = \frac{Volume\ of\ Individual\ Species\ Surface\ Layer \cdot Bulk\ CdS\ Density}{Molecular\ Weight\ CdS}$$

Finally, the total number of surface sites in the mass of nanomaterial sample is calculated as follows.

$$Total\ Surface\ Sites = Moles\ of\ Cadmium\ Sulfide\ at\ Surface\ of\ Species\ (NP\ or\ MSC) \cdot N_{part}$$

**For example**

$$Volume\ of\ Individual\ Species\ Excluding\ Surface\ (\ MSC) = \frac{4}{3}\pi(\frac{1.6\ nm}{2} - 0.25nm)^3 = 6.97x10^{-22}\ cm^3$$

$$Volume\ of\ Individual\ Species\ Surface\ Layer\ (\ MSC) = 2.14x10^{-21}cm^3 - 6.97x10^{-22}cm^3 = 1.4\ x10^{-21}\ cm^3$$

$$Moles\ of\ Cadmium\ Sulfide\ at\ Surface\ of\ Species\ (MSC) = \frac{1.4x10^{-21}cm^3 \cdot 4.82g/cm^3}{144.47\ g/mol} = 4.8\ x10^{-23}mol$$

$$Total\ Surface\ Sites = 4.8\ x10^{-23}mol \cdot 1.27 * 10^{17} = \sim 6.1\ \mu mol$$

## Fraction of atoms on the surface

To estimate the fraction of atoms on the surface, we compare the volume of the surface layer to the volume of the total particle

$$Fraction\ of\ Surface\ Atoms\ (NP\ or\ MSC) = \frac{Volume\ of\ Individual\ Species\ Surface\ Layer\ (NP\ or\ MSC)}{Volume\ of\ Individual\ Species\ (NP\ or\ MSC)}$$

For example,

$$Fraction\ of\ Surface\ Atoms\ (MSC) = \frac{1.4\ x10^{-21}\ cm^3}{2.14x10^{-21}cm^3} = \sim 0.68$$

## References


1. D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press Inc., San Diego, San Diego, CA, 1991.
2. W. W. Yu and X. Peng, *Angew. Chem. Int. Ed. Engl.*, 2002, **41**, 2368-2371.
3. M. Kuno, J. K. Lee, B. O. Dabbousi, F. V. Mikulec and M. G. Bawendi, *The Journal of Chemical Physics*, 1997, **106**, 9869-9882.
4. G. Kalyuzhny and R. W. Murray, *The Journal of Physical Chemistry B*, 2005, **109**, 7012-7021.
5. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2854-2860.