*Electronic Supplementary Information for*

# Using ligands to control reactivity, size and phase in the colloidal synthesis of $WSe_2$ nanocrystals

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**Supplementary tables and figures**

**Table 1. Amounts of ligand present in the reactions (A) before and (B) after $Ph_2Se_2$ injection.**

| OA/W | | mmol TOPO | | mmol OA | | OA/TOPO | | TOPO/W | | Ligand/W | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | B | A | B | A | B | A | B | A | B | A | B |
| 948 | 1000 | 5.2 | 5.2 | 53.9 | 57.0 | 10.42 | 11 | 91 | 91 | 1039 | 1095 |
| 45 | 100 | 57 | 57 | 2.5 | 5.7 | 0.045 | 0.100 | 1001 | 1001 | 1046 | 1101 |
| 10 | 10 | 58 | 61 | 0.6 | 0.6 | 0.009 | 0.009 | 1029 | 1069 | 1039 | 1079 |
| 2 | 2 | 58 | 61 | 0.1 | 0.1 | 0.002 | 0.002 | 1029 | 1067 | 1031 | 1069 |
| 0 | - | 59 | - | 0 | - | 0 | - | 1038 | - | 1038 | - |

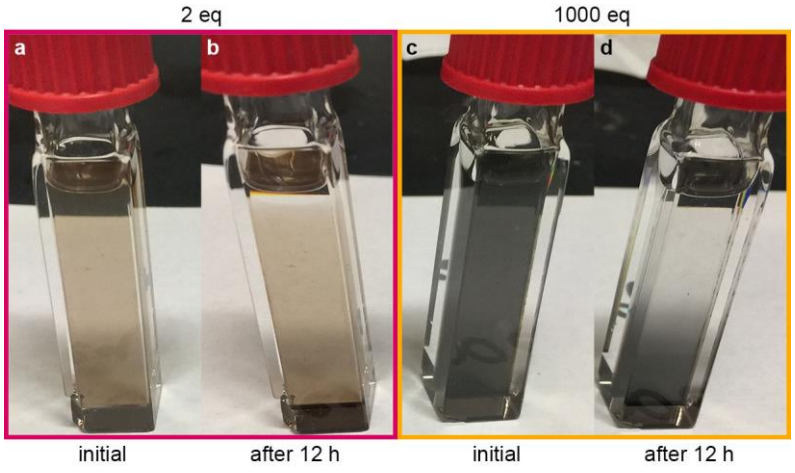


**Figure S1.** Photographs of colloidal suspensions of nanocrystals synthesized with (a,b) 2 eq and (c,d) 1000 eq OA/W. Suspensions were prepared by adding ~12 ml toluene and 1 drop oleylamine to one of the two pellets collected from centrifugation. Photographs were taken (a,c) just after preparing suspensions and (b,d) after 12 h.

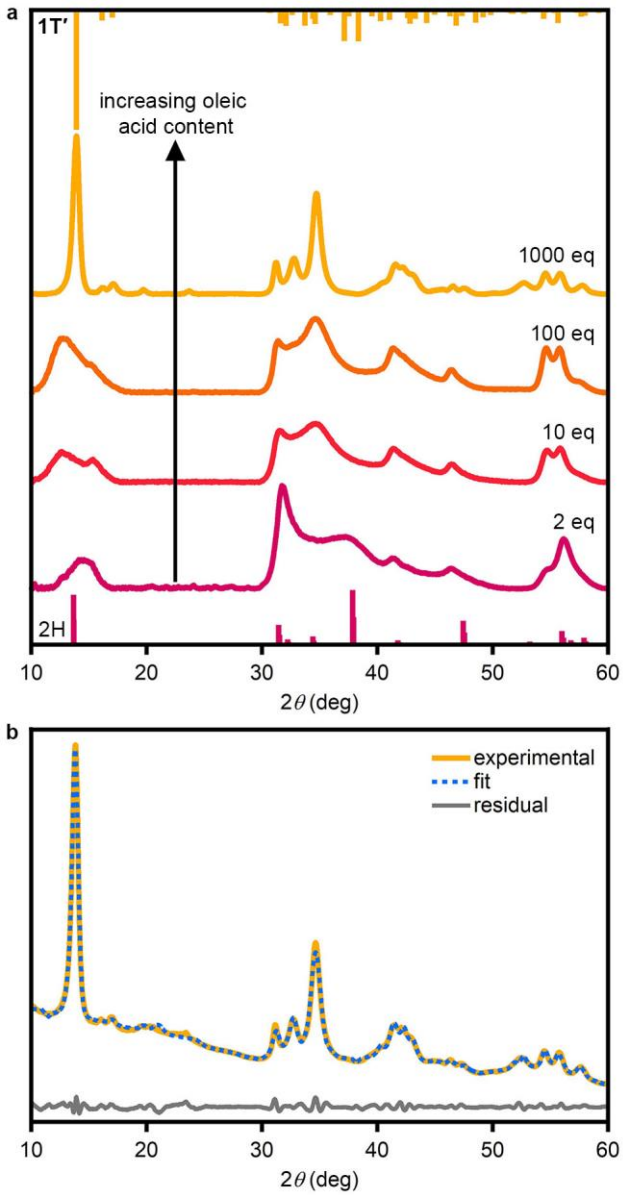


**Figure S2.** (a) Powder X-ray diffraction patterns of nanocrystals synthesized with (bottom to top) 2, 10, 100 and 1000 eq OA/W. The 2H powder pattern is simulated from a published structure.[1] The 1T′ powder pattern was simulated using *a* and *b* parameters obtained from HRTEM ($a$ = 5.9 Å, $b$ = 3.3 Å, Figure 2f) and floating $c$ to match the (002) reflection ($2\theta$ = 13.92 deg, $c$ = 12.74 Å). (b) Le Bail fitting of the 1T′ (1000 eq) powder pattern in the $P2_1/m$ space group yields good agreement with the experimentally observed powder pattern with unit cell parameters $a$ = 5.8543 Å, $b$ = 3.2675 Å, $c$ = 12.7884 Å, $\beta$ = 93.9107 deg.

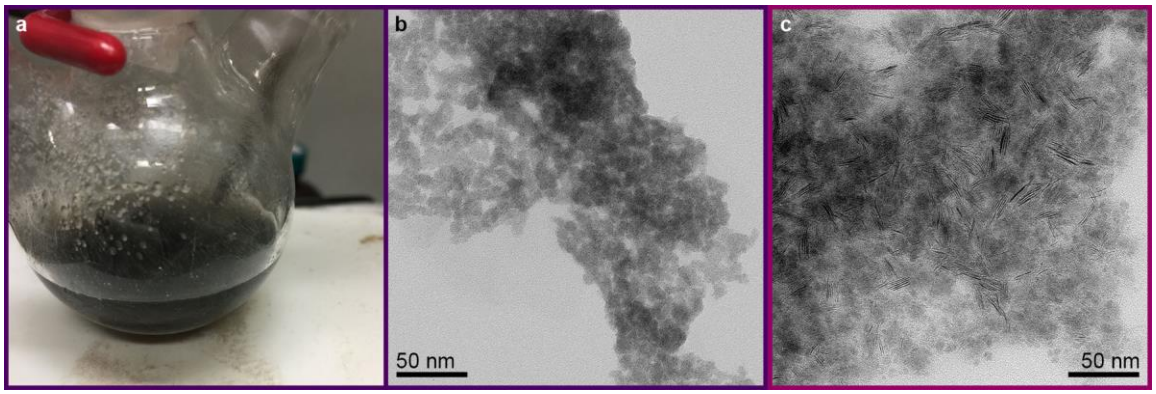


**Figure S3.** (a) Photograph of the reaction of $W(CO)_6$ in TOPO, which results in rapid formation of a cloudy black solution above 260 °C, suggesting nucleation of nanoparticles from $W(CO)_6$ alone. TEM images of (b) amorphous nanoparticles isolated from the reaction of $W(CO)_6$ in TOPO and (c) $WSe_2$ synthesized in TOPO without added OA. The heterogeneity in (c) may be due to a separate nucleation event prior to $Ph_2Se_2$ injection. Because $W(CO)_6$ in all TOPO (0 eq OA) shows this nucleation without $Ph_2Se_2$ injection, $WSe_2$ nanocrystals synthesized with 0 eq OA/W are not included in the trends discussed in this study.

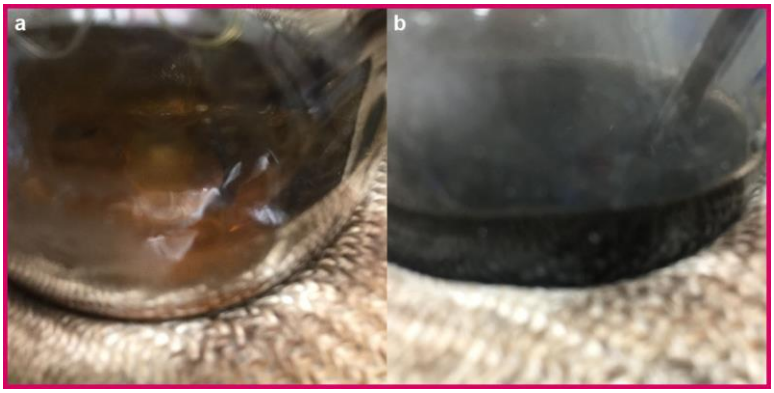


**Figure S4.** Photograph of reaction of $W(CO)_6$ in TOPO with 2 eq OA at 320 °C (a) before and (b) after $Ph_2Se_2$ injection. The lack of cloudy solution prior to $Ph_2Se_2$ injection suggests that inclusion of 2 eq OA prevents nucleation of $W(CO)_6$ alone.

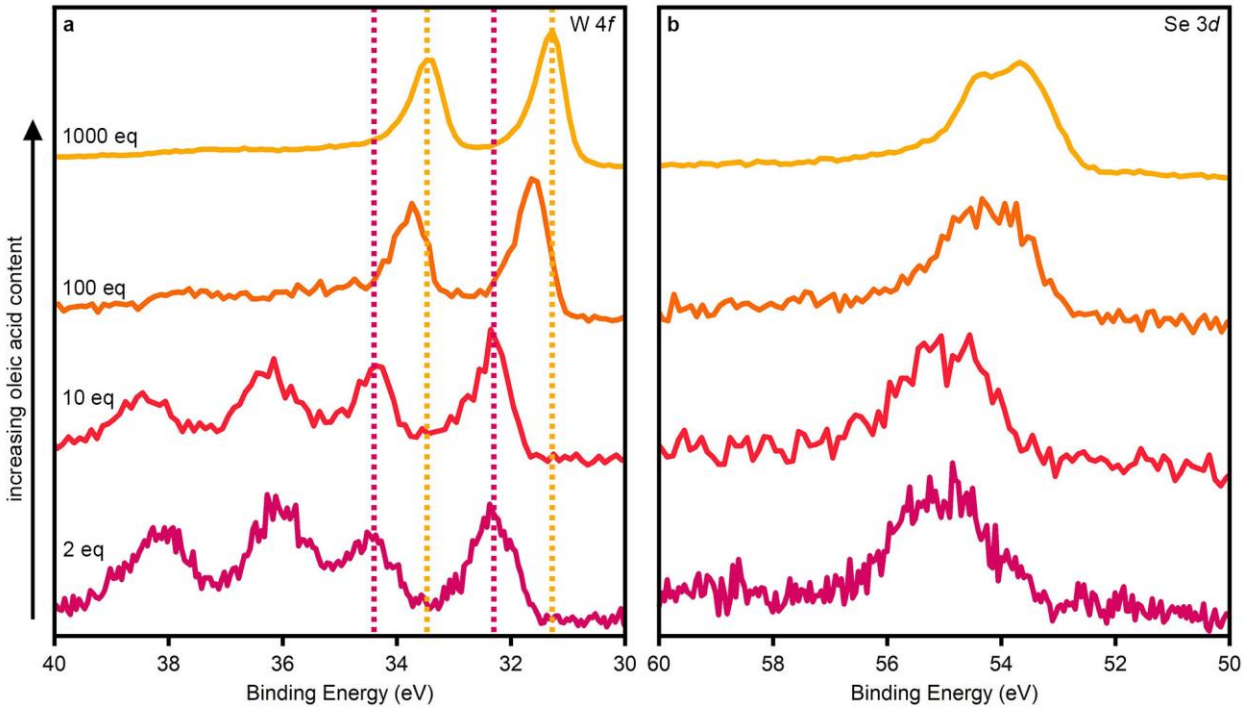


**Figure S5.** (a) W 4*f* and (b) Se 3*d* X-ray photoelectron spectra of nanocrystals synthesized with (bottom to top) 2, 10, 100 and 1000 OA/W. The dashed vertical lines at 32.3 and 34.4 eV show the expected energies for the W $4f_{7/2}$ and W $4f_{5/2}$, respectively in 2H.[2] The dashed vertical lines at 31.8 and 33.5 eV show the energies observed in the nanocrystals synthesized with 1000 OA/W. The shift of these peaks to lower energies is consistent with a change to the 1T′ crystal phase.[3-4] The peaks at higher binding energies (~38 and ~36 eV) are consistent with oxidized W.[5-6] These peaks are more prevalent in the samples synthesized with 2 and 10 eq, likely due to easier surface oxidation of smaller nanocrystals.

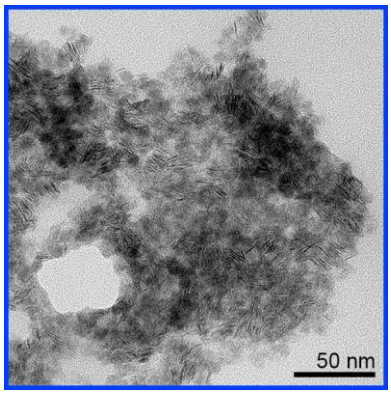


**Figure S6.** TEM image of nanocrystals synthesized with 2 eq OA/W. Aliquot was taken 5 min following $Ph_2Se_2$ injection. The Raman spectrum (Figure 4, bottom) shows peaks indicative of the 1T′ phase, suggesting that nanocrystal size and phase can be tuned independently.

**Experimental methods**

*Chemicals.* Trioctylphosphine oxide (TOPO, 90%) was purchased from Strem Chemicals. Diphenyl diselenide ($Ph_2Se_2$, >96%) was purchased from TCI and stored in a vacuum desiccator. Tungsten hexacarbonyl ($W(CO)_6$, 99%) was purchased from Acros Organics and stored in a nitrogen-filled glovebox. Oleic acid (OA, 90%, stored in freezer), and hexanes (≥98.5%) were purchased from Sigma Aldrich. Toluene (tol, 99.9%), and methanol (MeOH, 99.9%) were purchased from Fischer Scientific. All chemicals were used without further purification. All chemicals were stored in ambient conditions unless otherwise noted.

All reactions were carried out using a glass sheath to prevent contamination from the temperature probe.

*Synthesis of $WSe_2$ with 2 eq OA/W.* In a 100 ml round bottom flask equipped with a Teflon-coated stir bar, 32 mg OA (0.11 mmol) and 22.6 g TOPO (58.5 mmol) were combined. Separately, a stock solution of $Ph_2Se_2$ was prepared by combining 256 mg $Ph_2Se_2$ (0.8 mmol) in 4.88 g (12.62 mmol) TOPO. Both solutions were degassed under vacuum at 100 °C for 1 hr, followed by 4 quick cycles of refilling the flask with argon and evacuating. The evacuated TOPO/OA mixture was brought into a nitrogen-filled glovebox, where 20 mg $W(CO)_6$ (0.057 mmol) was added. This solution was placed back on the Schlenck line and heated to 330 °C under argon, at which point 1 ml $Ph_2Se_2$ stock solution (0.15 mmol $Ph_2Se_2$, 2.3 mmol TOPO) was swiftly injected into the flask. The reaction proceeded for a total of 30 min, at which point the heating mantle was removed and the solution left to cool to room-temperature. The nanocrystals were collected by the addition of ~5 ml MeOH directly to the solution followed by centrifugation for 5 min at 3400 rpm. Nanocrystals were washed 2 additional times by dispersing in 10 ml 2:1 tol/MeOH followed by centrifugation for 5 min at 3400 rpm.

*Synthesis of $WSe_2$ with 10, 100, and 1000 eq OA/W.* Synthesis of $WSe_2$ with higher OA/W was performed similarly to reaction above, with varying amounts of OA and TOPO. Table S1 details the amounts of ligand used for each synthesis. For 10 eq OA/W, $Ph_2Se_2$ was injected using 1 ml of the same stock solution described above. For 100 and 1000 eq OA/W, a new stock solution was prepared by adding 256 mg $Ph_2Se_2$ to 4 ml OA and degassing as described above. All other steps were performed as described above.

*Characterization.* TEM grids were prepared by drop-casting a suspension of nanocrystals in toluene onto a 100-mesh copper TEM grid coated with formvar and carbon (Electron Microscopy Sciences). TEM images were collected on a FEI Spirit operating at 120 keV and HRTEM images were collected using a JEOL JEM-2800 TEM operating at 200 keV. Raman and XPS samples were prepared by drop-casting a suspension of nanocrystals in hexanes onto a polished silicon substrate (Silicon Valley Microelectronics). Raman spectra were collected using a Renishaw inVia confocal Raman microscope with 532 nm laser excitation (10 mW) and a 50× objective lens. XPS measurements were acquired using a Kratos Analytical AXIS Supra surface analysis instrument at an emission current of 15 mA. Powder X-ray diffraction patterns were collected using a D8 Smart diffractometer with a Pt 135 detector equipped with a Rigaku MicroMax-007HF High-intensity Microfocus rotating anode with Cu Kα radiation (λ = 1.5478) at 40 kV, 25 mA and Varimax-HF double bounce optics. Diffraction images were merged/integrated in Diffrac.EVA V.4.3.0.1 (Bruker). Le Bail fitting[7] was performed using the FullProf software package.

**References**


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