

Supplementary Information

Cobalt-doped cadmium selenide colloidal nanowires

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Preparation of undoped and doped CdSe colloidal nanowires:

Materials: Cadmium oxide (CdO, 99.99 %), selenium powder (Se, 99 %), octanoic acid (OCA, 99 %), octyl ether (99 %) and phenyl ether (99 %) were purchased from Aldrich. Trioctylphosphine oxide (TOPO, 98 %) and trioctylphosphine (TOP, 90 %) were received from Merck and Fluka, respectively. Cobalt stearate (CoSt₂) was ordered from Acros. Bismuth (Bi) nanoparticles were prepared according to previous reports.¹ Other solvents and chemicals were used as received.

Preparation: Co²⁺-doped and undoped CdSe nanowires were prepared by a solution-liquid-solid (SLS) approach^{2, 3} where Bi nanoparticles were used as catalysts.^{4, 5} The used parameters have been shown in Table S1. It should be noted that the samples with Code 2 – 5 were prepared without activation of Cd-precursor and the other samples were generated by activating Cd-precursor for 30 min. The synthesis procedure has been described using Code 1 as an example.

30.3 mg CdO, 3.04 g TOPO and 0.23 mL octanoic acid were added into a 50-mL three necked flask connected with a reflux condenser and a standard Schlenk line. This mixture was dried and degassed for 60 min at 100 °C under a vacuum. After the flask was filled back with N₂, the temperature was increased to 300 °C to result in clear solution and then decreased to 280 °C. Meanwhile, Co-precursor stock solution was prepared by dissolving 0.44 g cobalt (II) stearate (CoSt₂) in 17.0 mL phenyl ether (or octyl ether) in the presence of 0.5 mL octanoic acid. TOPSe (2.0 M) stock solution was obtained by dissolving 0.63 g Se powder in 4.0 mL TOP. Then a mixture of Bi nanoparticles (100 µL, 3.63 mM), TOPSe (100 µL, 2.0 M) and Co-precursor solution (1.0 mL, 0.04 M) was quickly injected into Cd-precursor solution at 280 °C and the temperature was dropped down to 260 °C. The solution reacted for 1 min and then cooled down to 80 °C, followed by the addition of 2 mL toluene to prevent the TOPO from solidifying. The resultant nanowires were separated from solution through high-speed

centrifugation (14800 rpm, 10 min) and washed with toluene for several times. The purified nanowires were re-dispersed in chloroform for characterization.

Table S1. Preparative parameters of Co²⁺-doped and undoped CdSe nanowires

| Code | CdO (mg) | TOPO (g) ^a | OCA (μL) ^b | TOPSe (μL) ^c | Bi-solution (μL) ^d | Co-solution (mL) ^e | T (°C) ^g | t (s) | D (nm) | Co % |
|------|----------|-----------------------|-----------------------|-------------------------|-------------------------------|-------------------------------|---------------------|-------|----------|------|
| 1 | 30.3 | 3.04 | 230 | 100 | 100 | 1.0 ^f | 280 | 60 | 17.7±1.9 | 0.3 |
| 2 | 24.9 | 3.02 | 230 | 100 | 100 | 0 | 250 | 60 | 30.3±5.8 | - |
| 3 | 24.8 | 3.08 | 230 | 100 | 100 | 0.25 | 250 | 60 | 19.0±7.4 | 0.08 |
| 4 | 24.5 | 3.01 | 230 | 100 | 100 | 0.50 | 250 | 60 | 12.1±3.1 | 0.14 |
| 5 | 24.7 | 3.02 | 230 | 100 | 100 | 1.0 | 250 | 60 | 14.6±4.7 | 0.25 |
| 6 | 25.2 | 3.02 | 230 | 100 | 100 | 0 | 330 | 30 | 13.0±2.6 | - |
| 7 | 24.8 | 3.16 | 230 | 100 | 100 | 0.25 | 330 | 60 | 8.8±1.7 | 0.36 |
| 8 | 24.8 | 3.06 | 230 | 100 | 100 | 0.50 | 330 | 60 | 9.1±1.2 | 0.64 |
| 9 | 25.1 | 3.05 | 230 | 100 | 120 | 1.0 | 330 | 60 | 8.2±1.5 | 2.1 |

^a TOPO: trioctylphosphine oxide; ^b OCA: octanoic acid; ^c Selenium concentration is 2.0 M; ^d Bi concentration is 3.63 mM; ^e CoSt₂ concentration is 41.8 mg/mL; ^f CoSt₂ concentration is 25.1 mg/mL; ^g injection temperature (T).

Characterizations:

Low-resolution TEM images were recorded on a JEOL 1011 electron microscope operating at an acceleration voltage of 100 kV. High-resolution images and energy-dispersive X-ray spectroscopy (EDAX) were collected on a Philips CM 300 UT microscope operating at an acceleration voltage of 200 kV. Energy-filtered TEM (EFTEM) maps were recorded on a FEI Tecnai G² F20 TEM installed with a Gatan GIF200 system and operated at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) measurements were carried out on a Philips X'Pert-diffractometer at 45 kV and 40 mA using a mixture radiation of Cu K α 1 and K α 2 ($\lambda_1 = 1.54056 \text{ \AA}$; $\lambda_2 = 1.54439 \text{ \AA}$, K α 2/ K α 1 = 0.5). Room-temperature absorption was measured with a Cary 50 UV-Vis spectrometer. Fluorescence and MCPL measurements were carried out using a laboratory-constructed spectrometer that has been described previously.⁶ Fluorescence and MCPL signals were detected by a photomultiplier tube (RCA C31034) and lock-in amplifier system. Samples were illuminated in a 0.5 mm path-length quartz cell with 514 nm laser ($\sim 30 \text{ mW/cm}^2$).

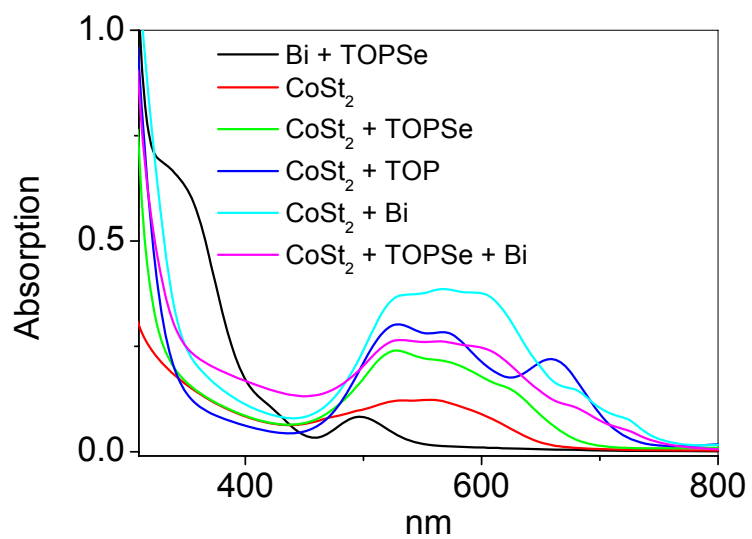
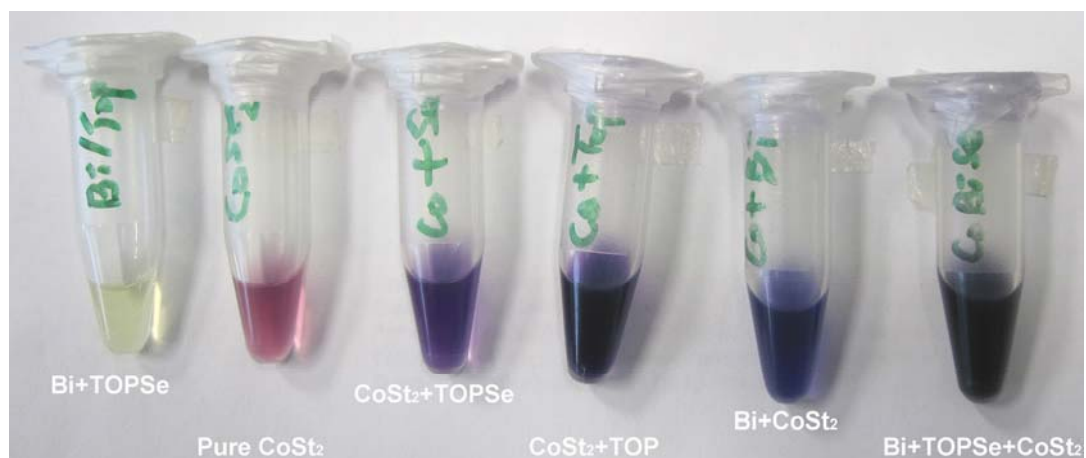


Figure S1. Digital image of precursor solutions and their UV-Vis absorption profiles.

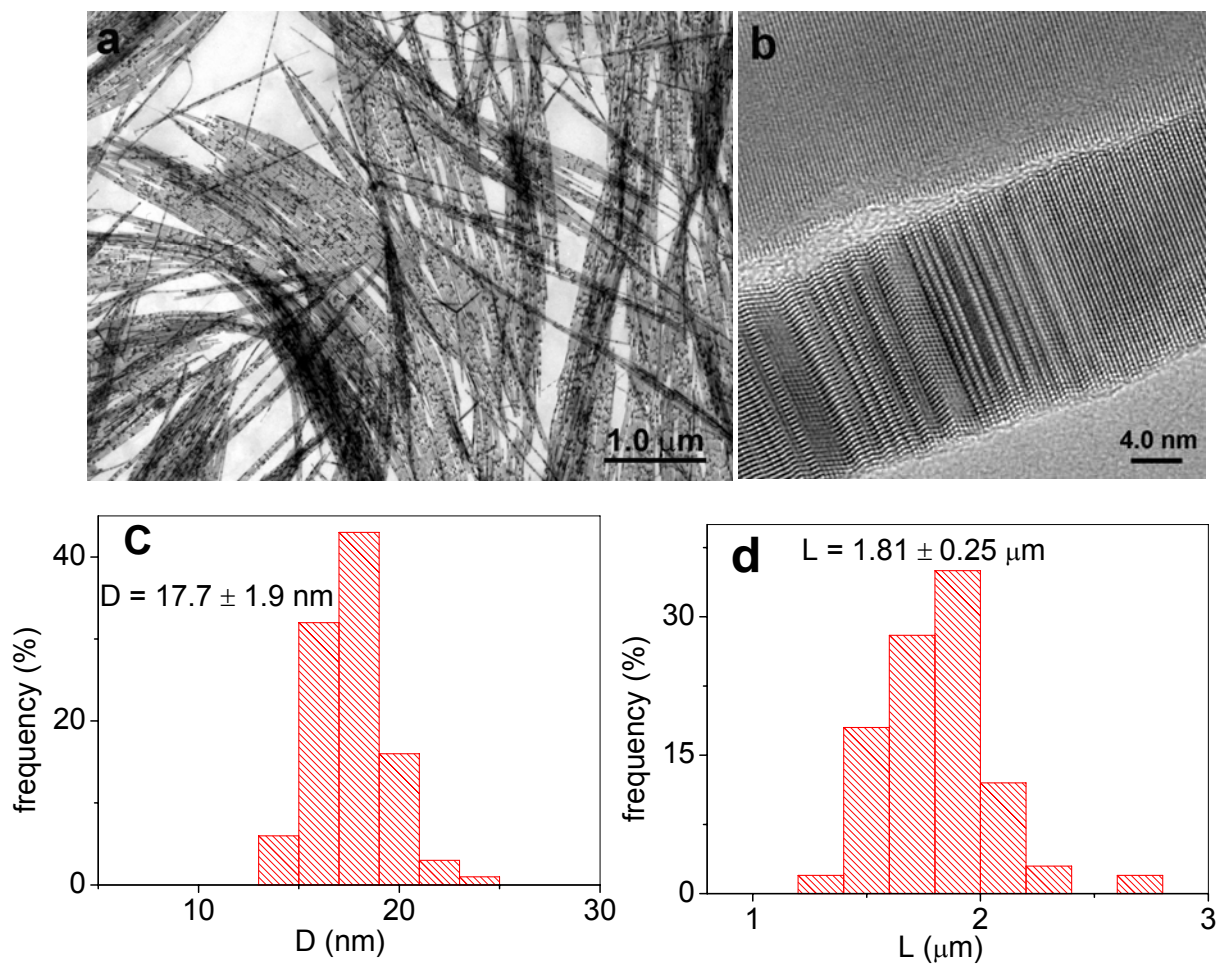


Figure S2. (a-b) low-resolution and high-resolution TEM images of Co^{2+} -doped CdSe nanowires; (c-d) diameter and length distribution of nanowires.

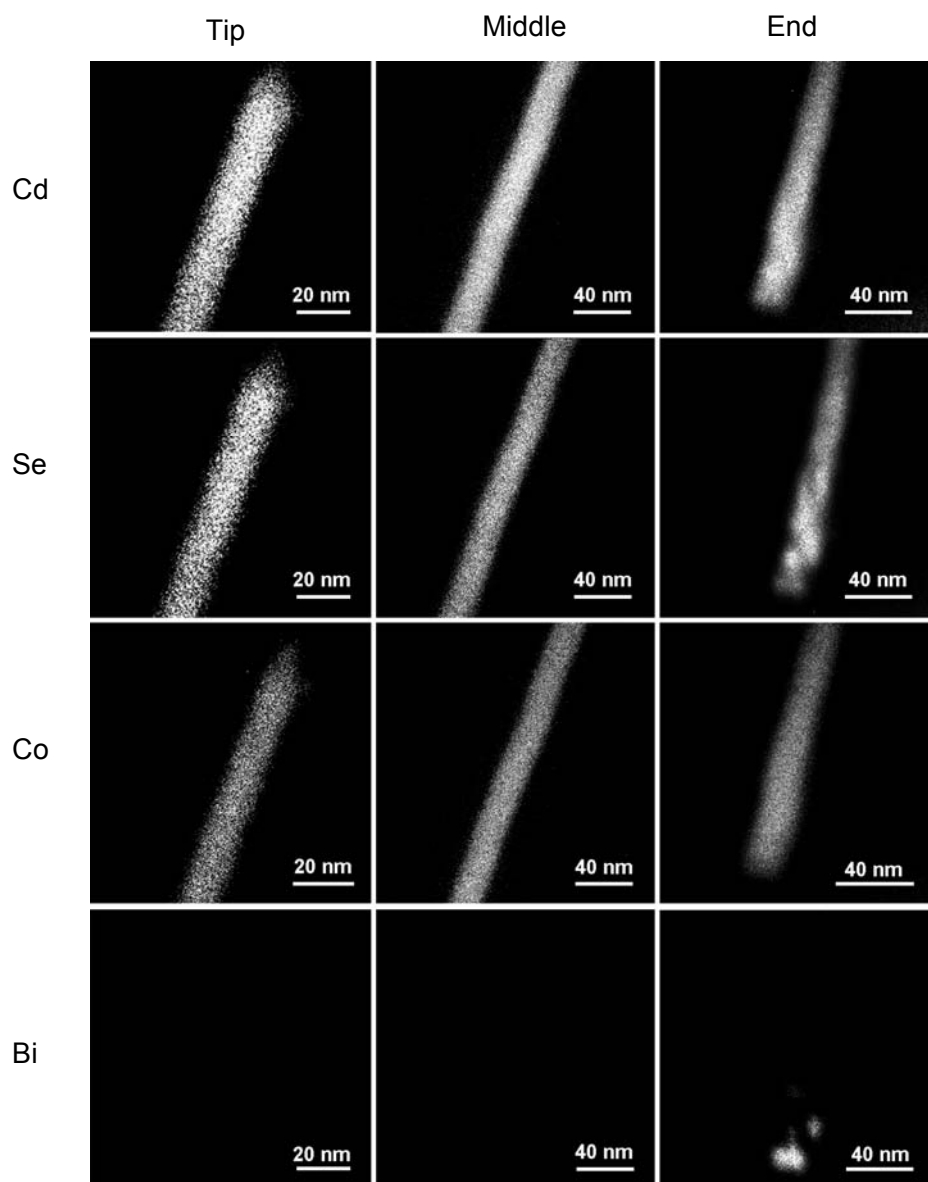


Figure S3. Energy filtered TEM images of different parts of Co^{2+} -doped CdSe nanowires.

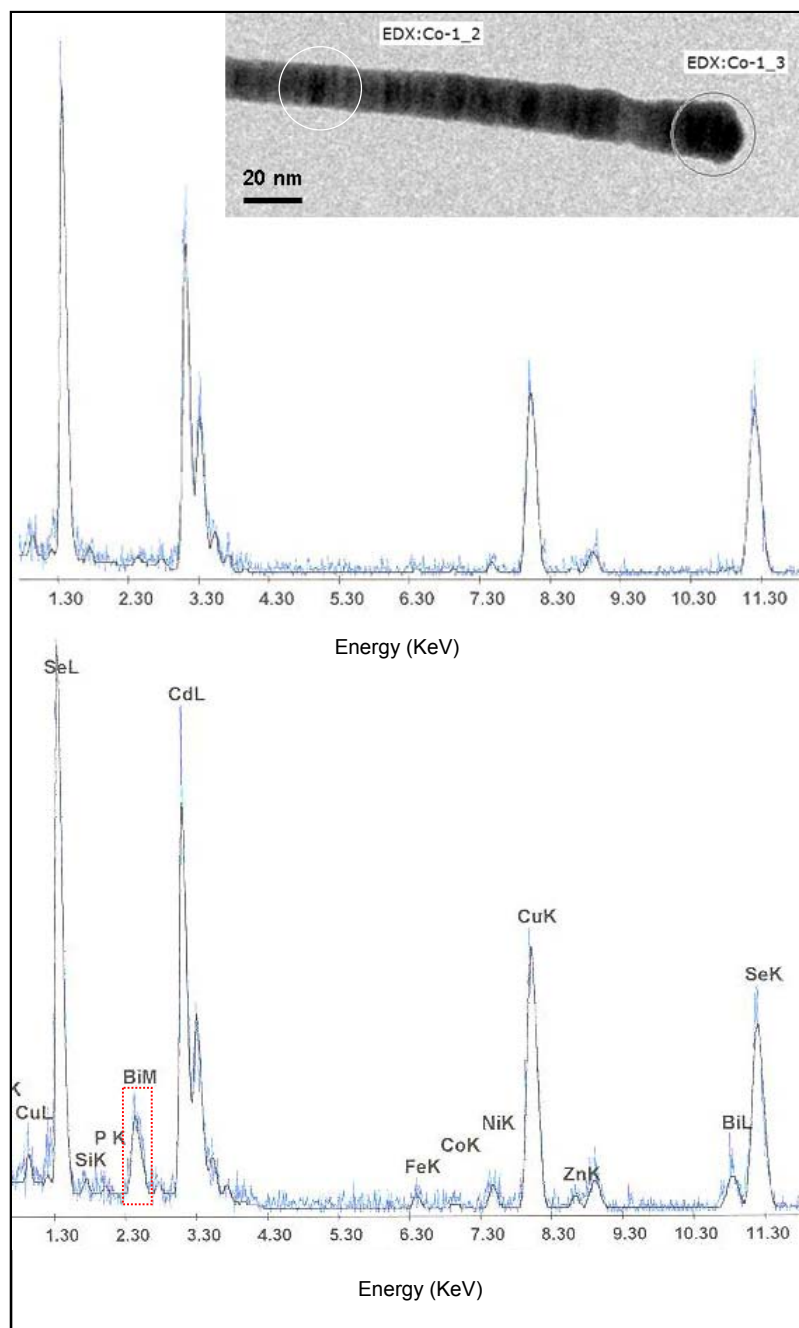


Figure S4. Typical EDAX spectra of middle- and catalyst part of Co^{2+} -doped CdSe nanowire. The red rectangle clearly shows the presence of Bi.

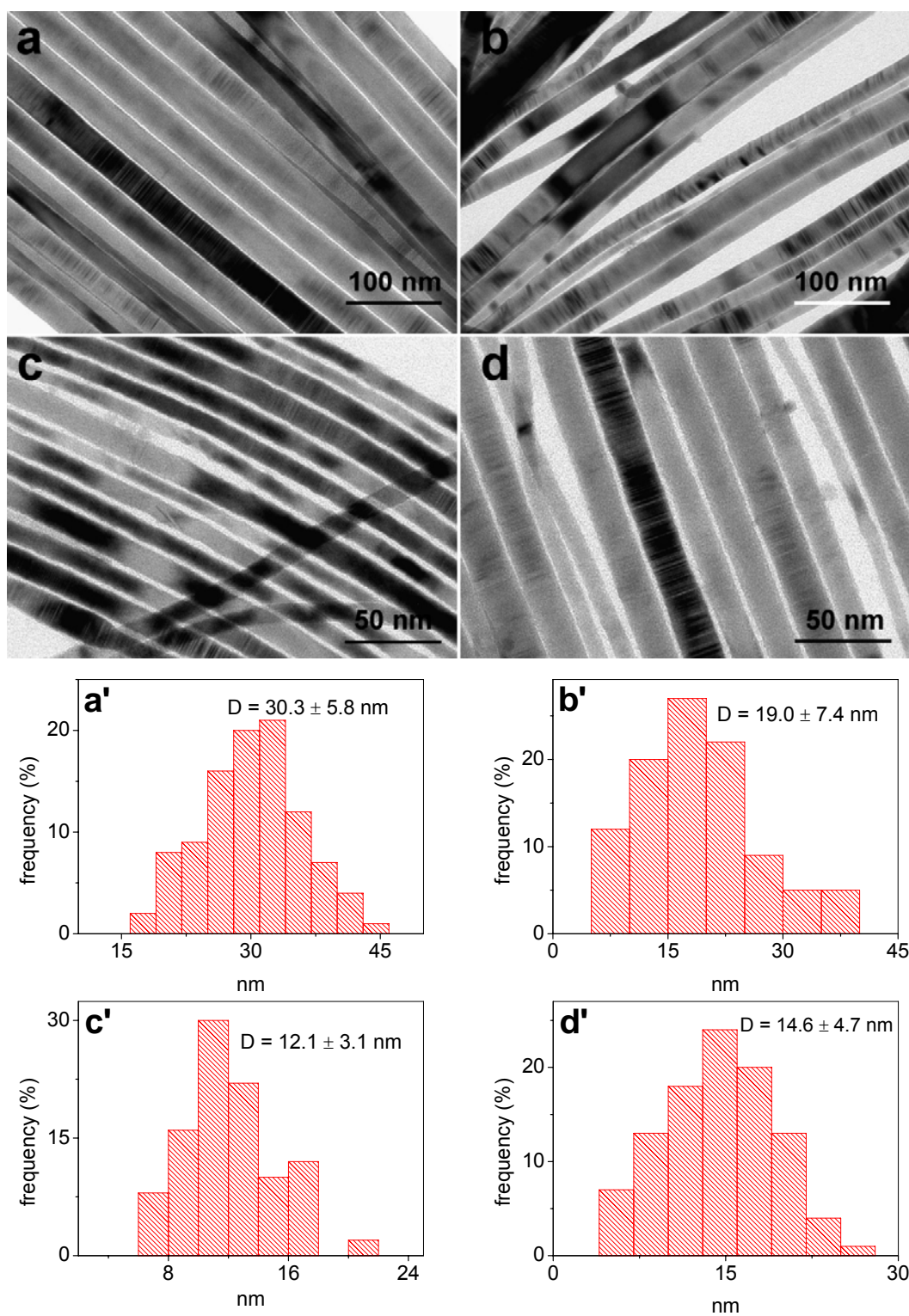


Figure S5. (a-d) TEM images and (a'-d') diameter distributions of $\text{Co}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0, 0.08, 0.14$ and 0.25 %) nanowires prepared at 250 °C.

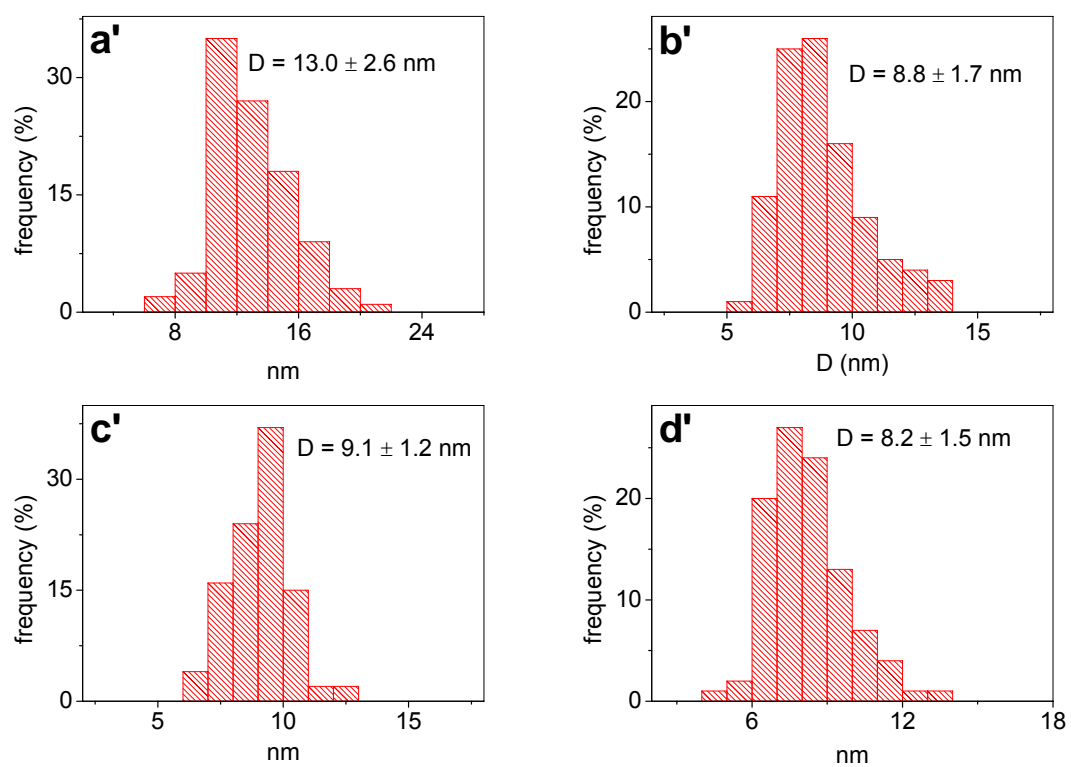


Figure S6. Diameter distributions of $\text{Co}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0, 0.36, 0.64$ and 2.1 %) nanowires shown in Figure 2.

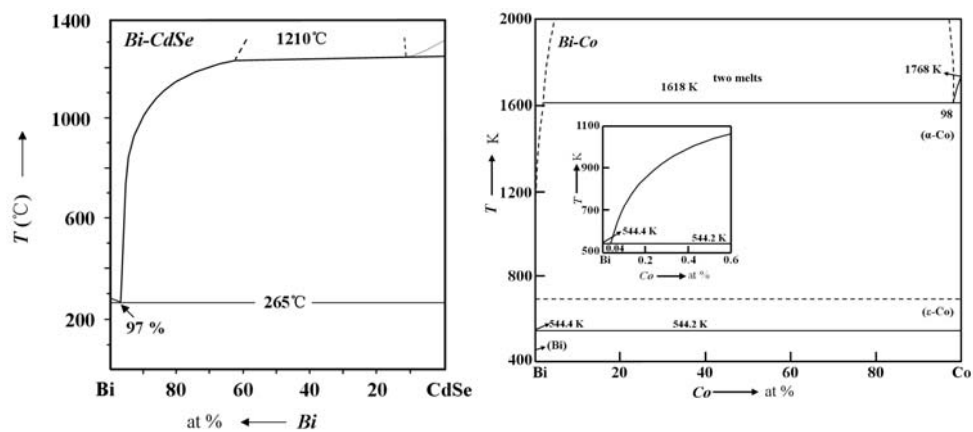


Figure S7. Bulk phase diagrams of Bi-CdSe and Bi-Co.

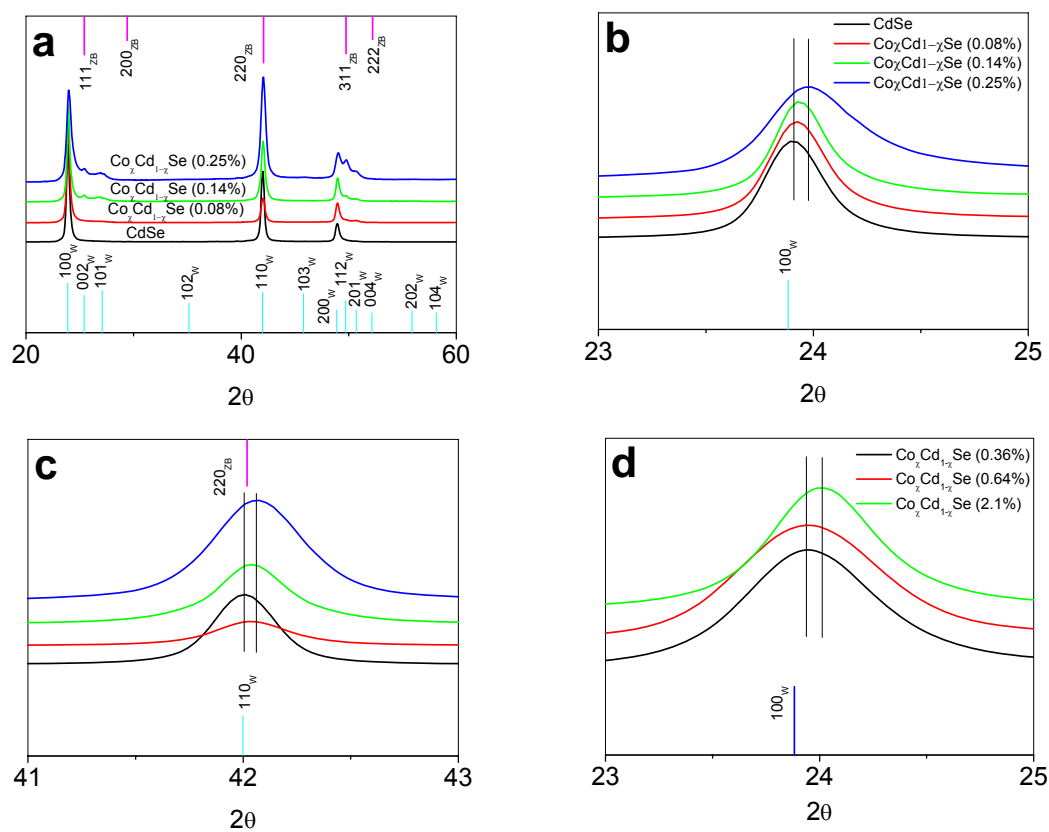


Figure S8. (a-c) XRD patterns of $\text{Co}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0, 0.08, 0.14$ and 0.25 %) nanowires shown in Figure S5; **(d)** Magnified XRD patterns shown in Figure 3a

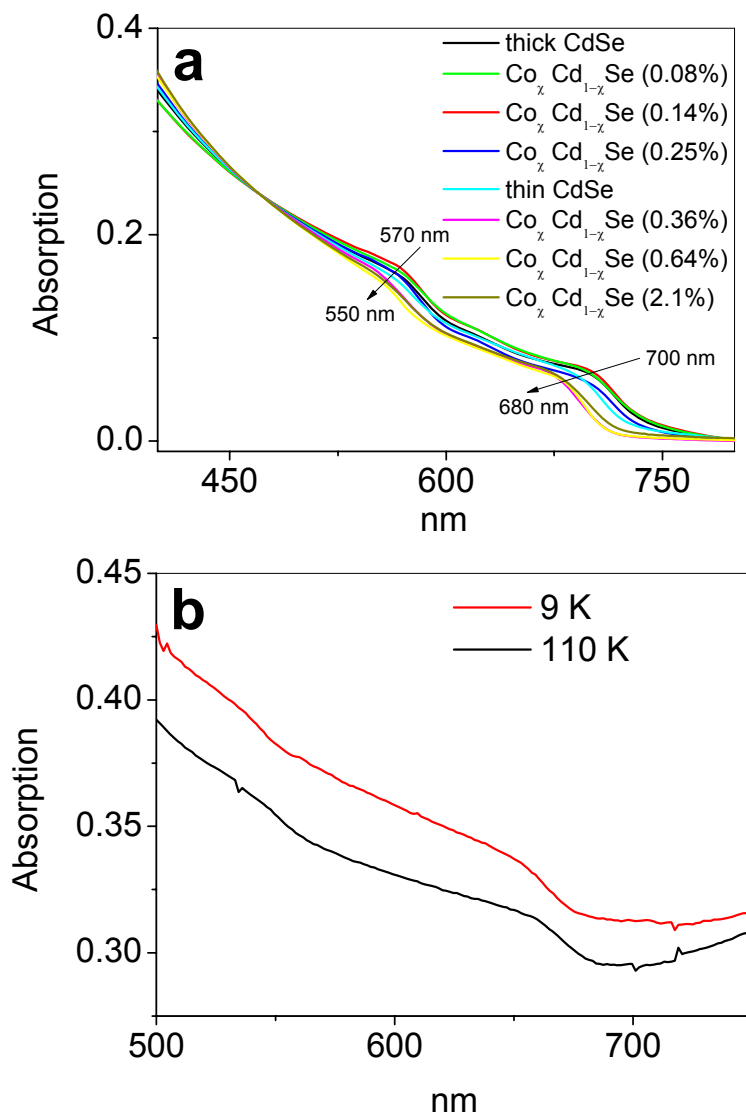


Figure S9. (a) Room temperature UV-Vis spectra of Co²⁺-doped CdSe nanowires shown in Figure S5 and Figure 2; (b) low-temperature absorption of nanowires shown in Figure 2c

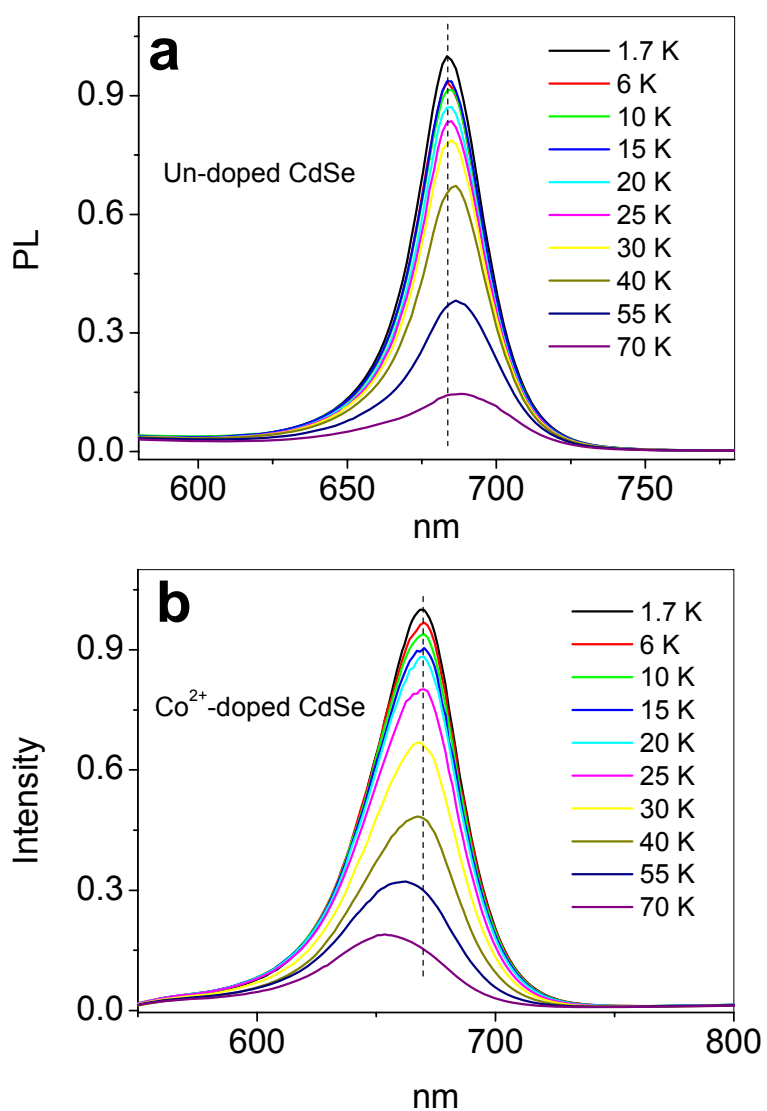


Figure S10. Photoluminescence temperature dependence of (a) undoped and (b) Co²⁺-doped CdSe nanowires measured in the presence of 5-T magnetic field. Their TEM images are shown in Figure 2a, c.

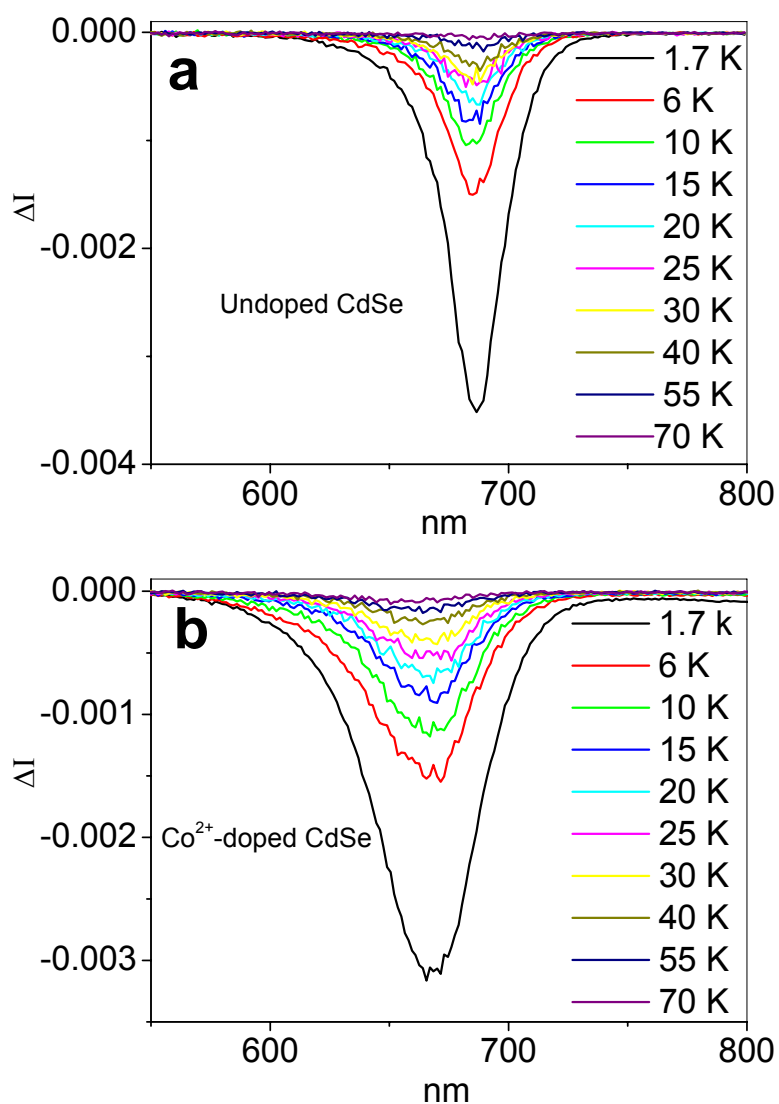


Figure S11. Temperature dependence of magnetic circularly polarized luminescence of undoped and Co^{2+} -doped CdSe nanowires measured in the presence of 5-T magnetic field.

References

1. Z. Li, A. Kornowski, A. Myalitsin and A. Mews, *Small*, 2008, **4**, 1698-1702.
2. F. D. Wang, A. G. Dong, J. W. Sun, R. Tang, H. Yu and W. E. Buhro, *Inorg. Chem.*, 2006, **45**, 7511-7521.
3. M. Kuno, *Phys. Chem. Chem. Phys.*, 2008, **10**, 620-639.
4. Z. Li, Ö. Kurtulus, F. Nan, A. Myalitsin, Z. Wang, A. Kornowski, U. Pietsch and A. Mews, *Adv. Funct. Mater.*, 2009, **19**, 3650-3661.
5. Z. Li, L. N. Cheng, Q. Sun, Z. H. Zhu, M. J. Riley, M. Aljada, Z. X. Cheng, X. L. Wang, G. R. Hanson, S. Z. Qiao, S. C. Smith and G. Q. Lu, *Angew. Chem. Int. Ed.*, 2010, **49**, 2777-2781.
6. R. Stranger, L. Dubicki and E. Krausz, *Inorg. Chem.*, 1996, **35**, 4218-4226.