

High-temperature Solvothermal Synthesis and Magnetic Properties of Nearly Monodisperse CdCr₂S₄ Nanocrystals

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Table S1. List of publications describing synthesis routes of CdCr₂S₄.

Refs	Raw materials	Synthesis route and conditions	Products
This work	CdCl ₂ , CrCl ₃ ·6H ₂ O, 1- DDT	Solvothermal method Reacted at 375 °C for 72 h	Nanocrystals Spherical, average size: 8.0±1.5 nm
2, 7, 12	Polycrystalline CdCr ₂ S ₄ , Br ₂	Chemical transport reaction Transported at 850 °C and annealed in vacuum at 500-700 °C for 0.5-2 h	Single crystals Octahedral, edge length: ~2 mm
4	Polycrystalline CdCr ₂ S ₄ , TeBr ₄	Chemical transport reaction Grown at 850-900 °C, 10 ⁻³ mbar for 3-4 weeks	Single crystals Octahedral, edge length: ~3 mm
9, 11	Synthesized CdCr ₂ S ₄ powder, Cl ₂ , CrCl ₃	Chemical transport reaction Deposited at 850-900 °C, 10 ⁻⁶ Torr	Single crystals
1, 6	Polycrystalline CdCr ₂ S ₄ , CrCl ₃	Chemical vapor transport	Single crystals
18	CdS, Cr ₂ S ₃	Physical vapor deposition Deposited at 670-900 °C, 2×10 ⁻⁵ Torr for several hours	Polycrystalline films 5840-8170 Å in thickness
19	Cd, CrCl ₃ , S ₂ , He	Open-tube vapor-phase technique Deposited at 740 °C for 2 h	Single crystal films 1-2 μm in thickness
21	Polycrystalline CdCr ₂ S ₄ , Cl ₂	Closed-tube vapor transport Deposited at 775-825 °C for 60-80 h	Single crystals
3	CdS, Cr, S	Solid state reaction	Polycrystals
5, 10	Cd, Cr, S	Solid-state synthesis method Heated from 450 to 850 °C and maintained at 850 °C for 1 week Annealed at 800 °C	Polycrystals
20	CdS, CrCl ₃	Solid state reaction Reacted at 900 °C, 10 ⁻⁴ Torr for 3-4 days	Single crystals

17	CdS, Cr, S	Solid state sintering Heated at 780 °C for 4 days, Sintered at 620 °C for 30 min in vacuum at 4500 kg·cm ⁻² , Annealed at 600 °C for 10 days	Crystals
8	Cr ₂ O ₃ , CdSO ₄ , Na ₂ S ₂ O ₃	Electrochemical deposition Deposited at 80 °C for 45 min at pH = 3.5-6.5 at deposition potential of - 550 ~ -850 mV (versus SCE)	Smooth thin films 1000-1500 nm in thickness, spherical grains with an average size of 0.16 μm
16	CdSO ₄ , CrO ₃ , Na ₂ S ₂ O ₃	Electrochemical deposition Deposited at RT for 90 min at current densities of 15-20 mA·cm ⁻²	Thin films Coarse particle-covered surfaces, overgrowth of particles
13	CdCl ₂ , CrO ₃ , (NH ₂) ₂ CS	Chemical bath deposition Reacted at 70 °C for 30-90 min at pH=10±0.2 using Na ₂ EDTA as complexing agent	Thin films 110-224 nm in thickness, elongated spherical grains with ~50 nm in width and ~300-400 nm in length
14	CdCl ₂ , CrO ₃ , (NH ₂) ₂ CS	Chemical bath deposition Reacted at 80 °C for 2-3 h at pH=10 using N ₂ H ₄ ·H ₂ O as reducing agent	Polycrystalline thin films ~200 nm in thickness
15	CdCl ₂ , CrO ₃ , (NH ₂) ₂ CS	Chemical bath deposition Reacted at >80 °C for 1-2 h at pH=10	Thin films 0.7 μm in thickness

Table S2. Physicochemical characteristics of solid state synthesized CuCr_2Se_4 , CuCr_2S_4 , and CdCr_2S_4 . (Ref. 1-28)

Materials	Electron configuration		Lattice parameter (Å)	Curie Temperature (K)	Conductivity	Micro-hardness ($\text{kg}\cdot\text{mm}^{-2}$)	Single crystal growth temperature by chemical vapor transport ($^{\circ}\text{C}$)	Decomposition temperature (K)	
	A site	Cr site						In vacuum	In air
CuCr_2Se_4	$\text{Cu}^{1+}: e^4t_2^6$	$\text{Cr}^{3.5+}: t_{2g}^{2.5}$	10.34	430	metallic	240	~900	805	770
CuCr_2S_4	$\text{Cu}^{1+}: e^4t_2^6$	$\text{Cr}^{3.5+}: t_{2g}^{2.5}$	9.81	377	metallic	396	~850	870	800
CdCr_2S_4	$\text{Cd}^{2+}: e^4t_2^6$	$\text{Cr}^{3+}: t_{2g}^3$	10.24	84.5	n-type $E_g=1.57$ eV	450	~830	801	1073

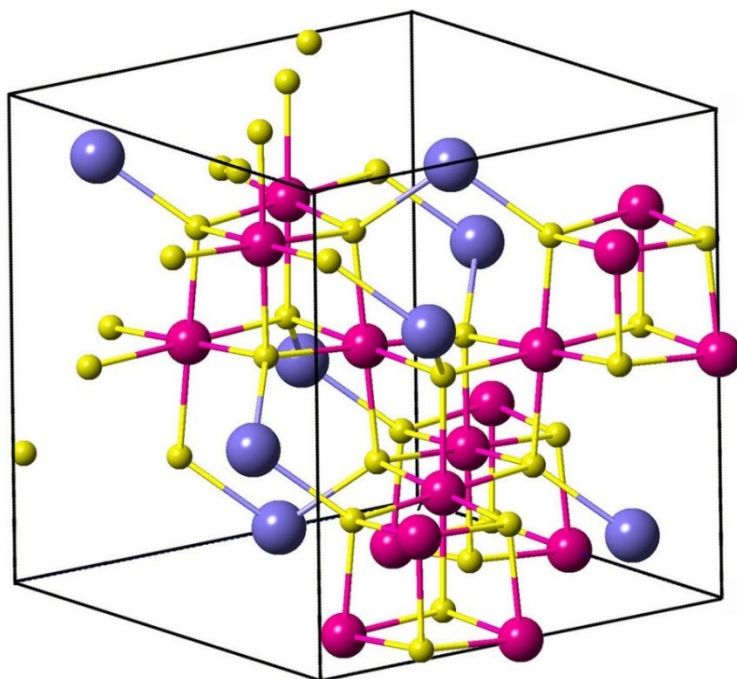


Figure S1. Representative crystal structure of spinel CdCr_2S_4 (Cd, blue; Cr, pink; S, yellow).

Table S3. ICP-OES analysis of the synthesized CdCr_2S_4 nanocrystals.

Analyte	Mean Corrected Intensity	Sample Conc. Units	Std. Dev.	RSD	Atomic %
Cr 267.716	31679.2	7.423 mg/L	0.0222	0.30%	67.38%
Cd 228.802	25678.5	7.767 mg/L	0.0126	0.16%	32.62%

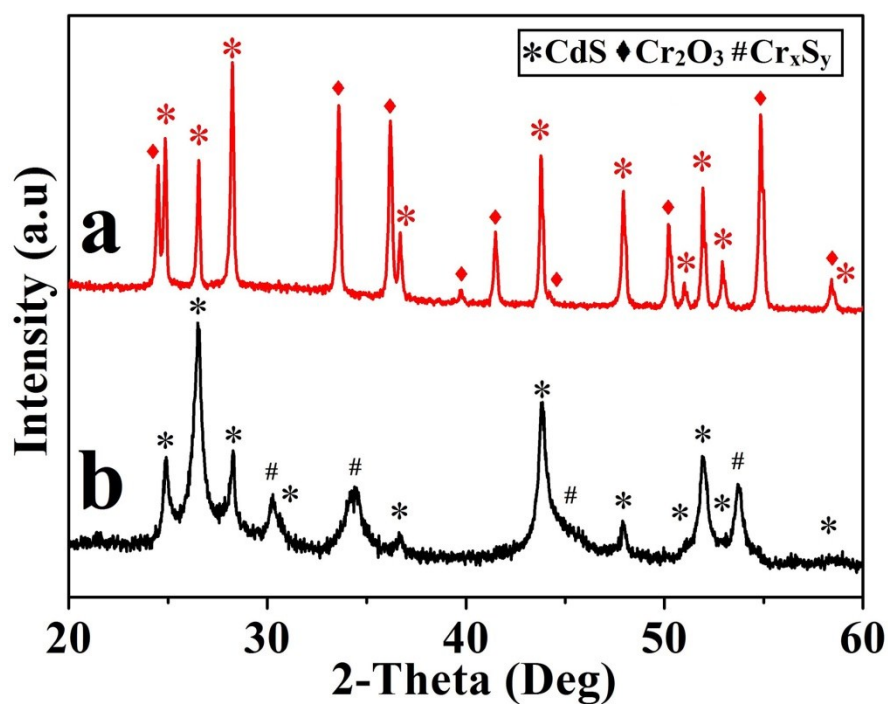


Figure S2. XRD patterns of the products prepared using (a) Cd/Cr sulfates and (b) Cd/Cr acetates as reactants.

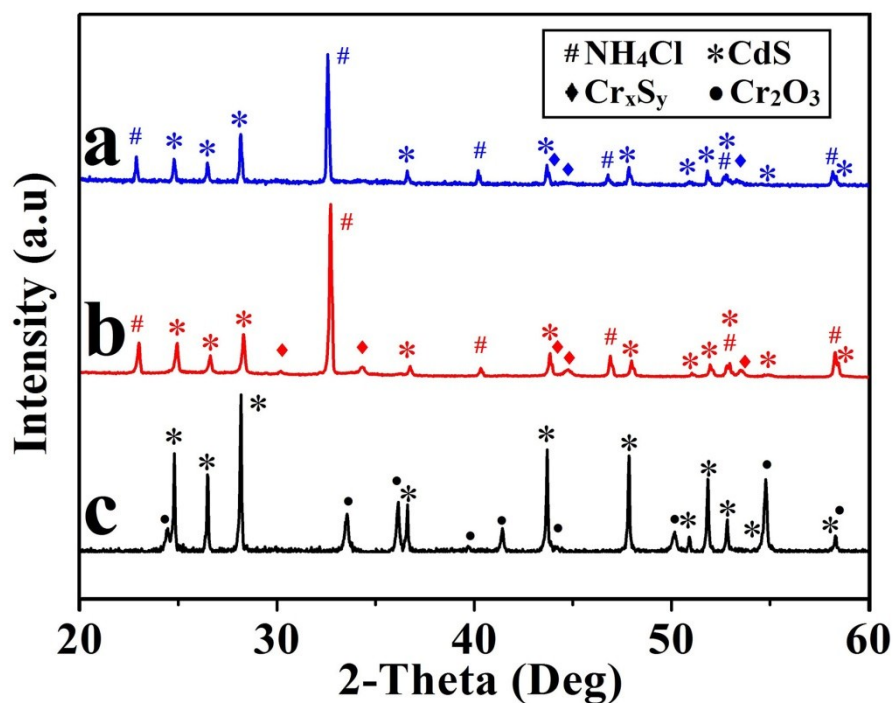


Figure S3. XRD patterns of the products prepared in the solvents (a) oleylamine, (b) octadecylamine, and (c) oleic acid.

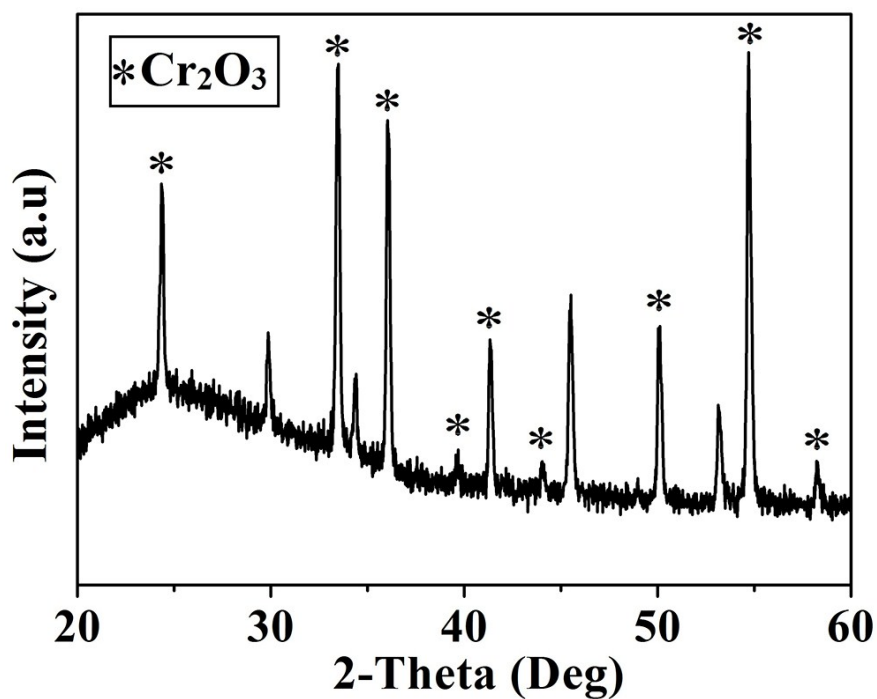


Figure S4. XRD pattern of the products obtained from the reaction of elemental sulfur with cadmium and chromium complexes.

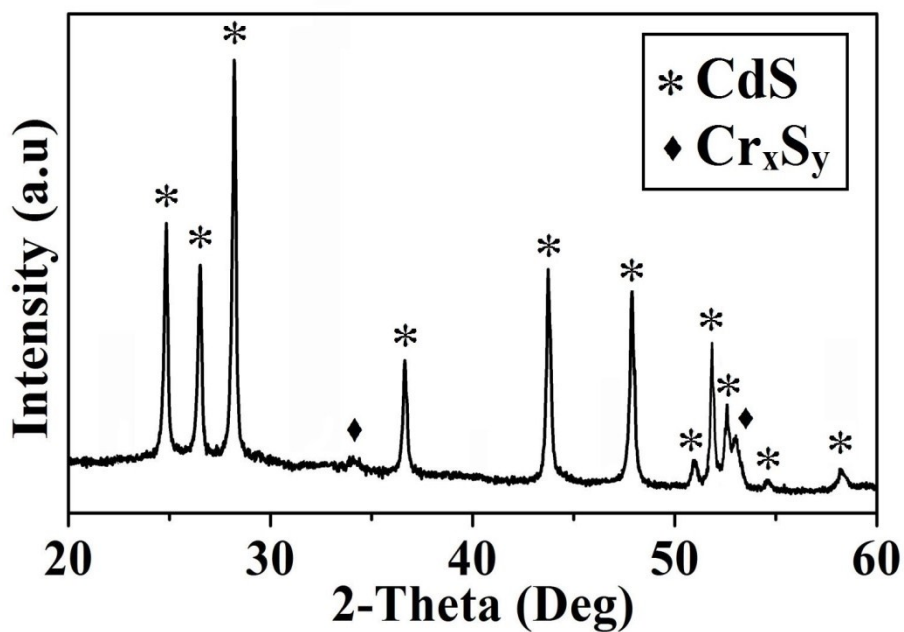


Figure S5. XRD pattern of the products obtained by hot-injection method in an open system at 375 °C in octadecylamine.

Study on the solubility of Cd/Cr chlorides in ODE

In Flask 1, 0.5 mmol CdCl_2 was added to 30 mL ODE, deaerated at room temperature for 15 min, and then back-filled with nitrogen for 50 min (Figure S6a). Flask 1 was then heated to 315 °C (boiling point of ODE) with stirring under N_2 atmosphere. The mixture in Flask 1 gradually turned to a white color during heating and eventually became milky white after being heated at 315 °C for 1 h (Figure S6b). Flask 1 was allowed to cool to room temperature after heating. After sitting overnight, clear and transparent ODE solvent was separated from the white powder settling down at the flask bottom (Figure S6c).

In Flask 2, 1.0 mmol $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was added to 30 mL ODE, deaerated at room temperature for 15 min, and then back-filled with nitrogen for 50 min (Figure S6d). Flask 2 was then heated to 315 °C (boiling point of ODE) with stirring under N_2 atmosphere. With increasing the temperature to ~90 °C, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (melting point of 83 °C) began to melt and formed liquid drops at the bottom of the flask, with the solvent remaining clear and transparent (Figure S6e). With further increasing the temperature, the droplets at the bottom became grey after being heated at 315 °C for 1 h (Figure S6f), due to the release of the water of crystallization in $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. This mixture remained the same as that shown in Figure S6f, while cooled to room temperature.

The solvents obtained from Flask 1 after sitting at RT overnight (Figure S6c), Flask 2 at 90 °C (Figure S6e), Flask 2 after cooling down (Figure S6f), and pure ODE were studied using FTIR. As seen in Figure S7, no significant differences are observed amongst the spectra of the four solvents. This indicates that CdCl_2 can dissolve in ODE at high temperatures, while $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ barely dissolved in ODE. A further PXRD study (Figure S8) confirmed that the solid products obtained from the bottom of Flask 1 after sitting at RT overnight (Figure S6c), Flask 2 at 90 °C (Figure S6e), Flask 2 after cooling down (Figure S6f) are pure CdCl_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and CrCl_3 , respectively.

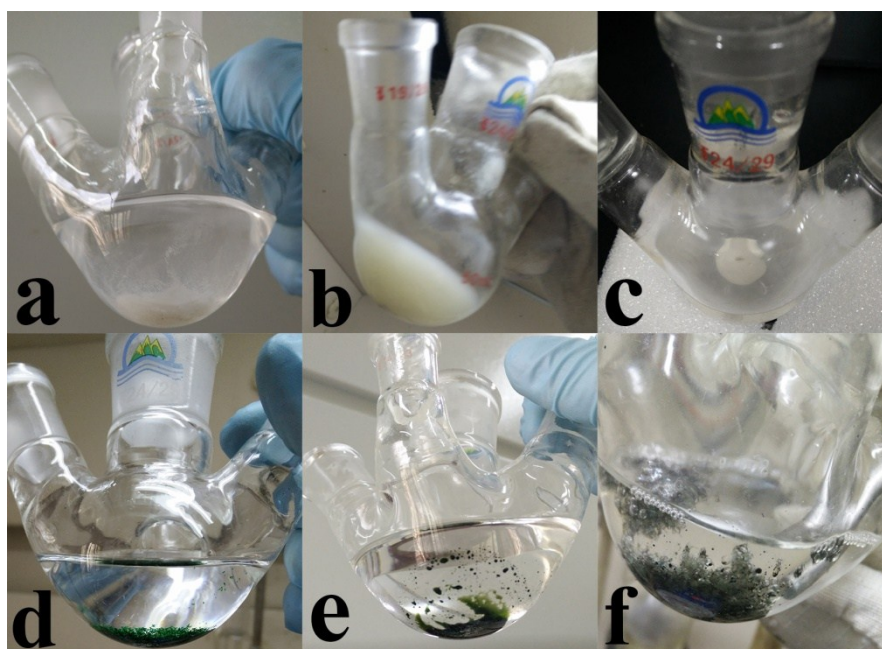


Figure S6. Digital photographs of the CdCl_2 and ODE mixture (a) before heating, (b) after being heated at 315 °C for 1 h, and (c) after sitting overnight at RT. Digital photographs of the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and ODE mixture (d) before heating, (e) after being heated at 90 °C, and (f) after being heated at 315 °C for 1 h.

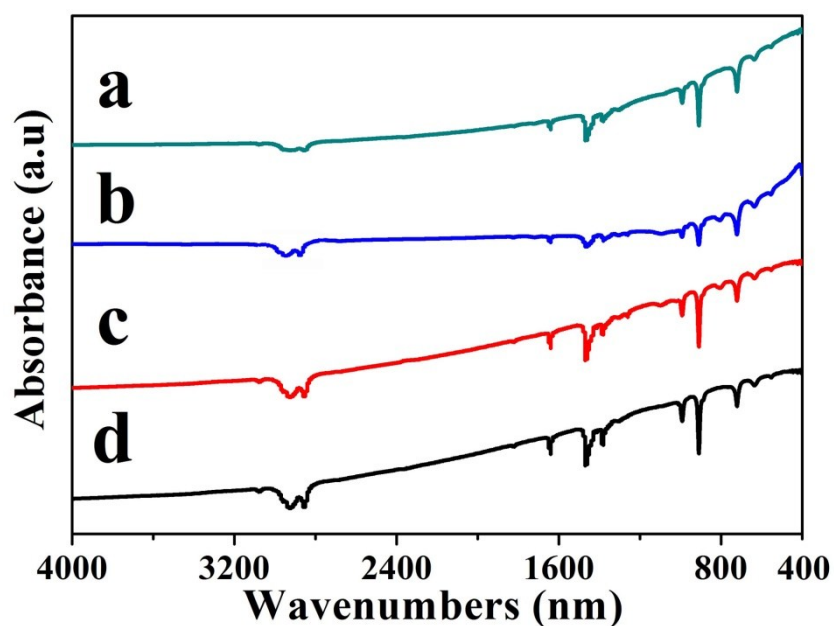


Figure S7. FTIR spectra of the solvents obtained from (a) Flask 1 after sitting overnight at RT (Figure S7c), (b) Flask 2 at 90 °C (Figure S7e), (c) Flask 2 after cooling down (Figure S7f), and (d) pure ODE.

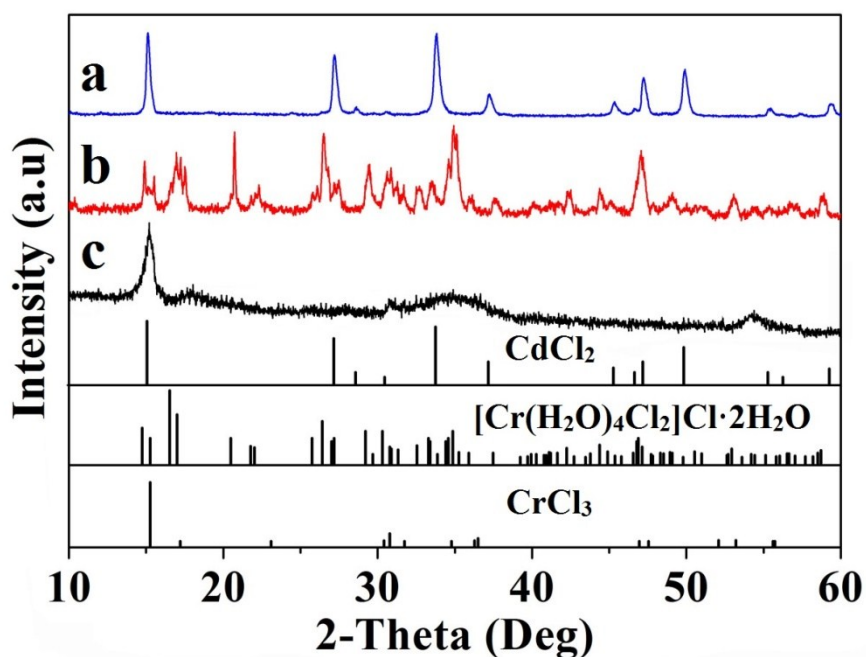


Figure S8. XRD patterns of the solid products obtained from the bottom of (a) Flask 1 after sitting overnight at RT (Figure S7c), (b) Flask 2 at 90 °C (Figure S7e), (c) Flask 2 after cooling down (Figure S7f).

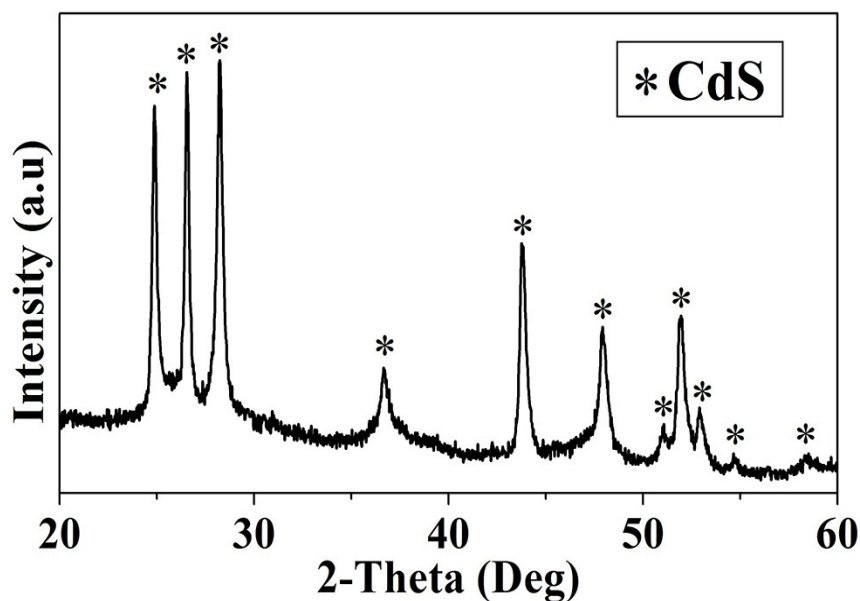


Figure S9. XRD pattern of the product prepared at 370 °C in octadecylamine by solvothermal method with a very-slow heating rate.

Magnetization (M) versus applied field (H) data plot for the CdCr₂S₄ nanocrystals measured at 5 K along with fitted Langevin function²⁹: $M = C_1[\coth(C_2H) - (1/C_2H)] + C_3H$, where C_1 is the saturation magnetization, in emu/gm, $C_2 = (\mu/k_B T)$, and C_3 is a constant accounting for the paramagnetic background contribution. From the fittings, we obtain $C_1 = 19$ emu/g, $C_2 = 1.54125$, and $C_3 = 0.00738$ for the CdCr₂S₄ nanocrystals (Adjusted R-Square = 0.99766). From the value of μ (emu) and the calculated volumes, assuming cubic shape particles, we determine the average size of the nanoparticles to be 17 nm.

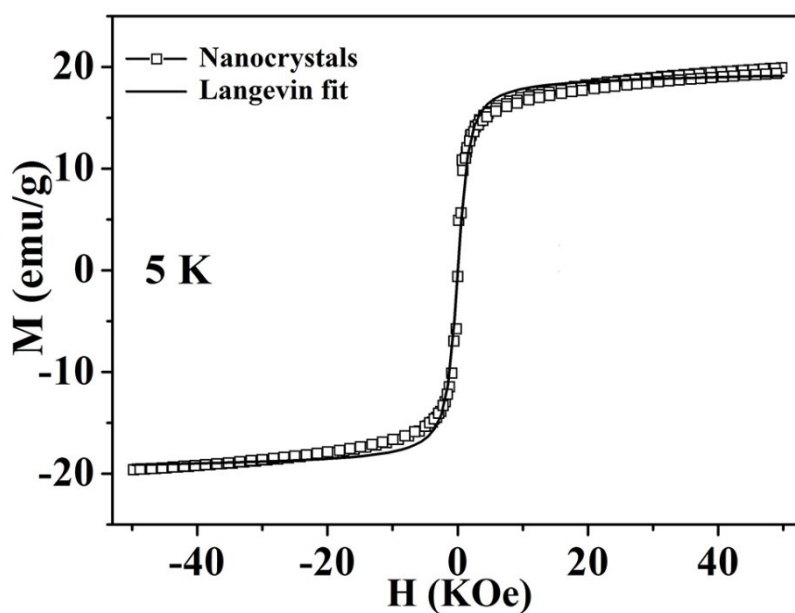


Figure S10. Magnetization (M) versus applied field (H) at 5 K along with the fitted Langevin function for CdCr₂S₄ nanoparticles.

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