Synthesis and Magnetic Properties of Cr₂Te₃ and CuCr₂Te₄ Nanocrystals

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NaBH₄ + Te + TOA
$$\rightarrow$$
 2[TOA-H]⁺ Te²⁻
CrCl₃.6H₂O \rightarrow Cr-OA \rightarrow Cr₂Te₃

Scheme S1

NaBH₄ + Te + TOA $\xrightarrow{350-355 \circ C}$ 2[TOA-H]⁺ Te²⁻ CrCl₃.6H₂O + CuCl₂ \xrightarrow{OA} CuCr-OA $\xrightarrow{2[TOA-H]^+ Te^{2-}}$ CuCr-OA $\xrightarrow{2[TOA-H]^+ Te^{2-}}$

Scheme S2



Fig S1. Transmission electron microscope (TEM) images of Cr_2Te_3 nanocrystals synthesized at 350-355 °C.



Fig S2. SEM-EDX spectra of CuCr₂Te₄ nanocubes.



Fig S3. (a) Raman spectra of $CuCr_2Te_4$ nanocrystals with 633 nm (1.99 eV) excitation; (b) Raman modes of $CuCr_2Te_4$ spinel.



Fig S4. Magnetization (*M*) as a function of temperature for field-cooled (*FC*) and zero-field-cooled (*ZFC*) measurements at 100 Oe and 50 Oe for (a) Cr_2Te_3 and (b) $CuCr_2Te_4$ nanocrystals.



Fig S5. (a) Isothermal magnetization around $T_{\rm C}$ for Cr₂Te₃ nanocrystals; (b) the Arrott plot (isotherms of M^2 vs. H/M) for Cr₂Te₃ in the temperature range of 130-230 K.



Fig S6. (a) Isothermal magnetization around $T_{\rm C}$ for CuCr₂Te₄ nanocrystals; (b) the Arrott plot (isotherms of M^2 vs. H/M) for CuCr₂Te₄ in the temperature range of 250-350 K.

Materials. All chemicals were used as received, and the solvents were dried in molecular sieves and purged with high purity argon for 30 minutes before use. Tellurium powder and chromium chloride (CrCl₃.6H₂O, 99.5 %) were received from Alfa Aesar; anhydrous copper chloride (CuCl₂, \geq 99.0%) and trioctylamine (TOA, \geq 99.0%) were obtained from Acros organics; oleylamine (OLA, 70%) was purchased from Aldrich Chemical Co. Analytical grade hexane and ethanol were also obtained from Aldrich.

Synthesis. Standard Schlenk techniques were used for all the experiments in a fume hood under a N₂ atmosphere. For the synthesis of Cr₂Te₃ nanocrystals, 0.4 mmol of Te powder, 0.4 mmol of NaBH₄ in 25 mL of TOA (98 %) were degassed at room temperature for 10 min and then backfilled with N2 for 10 min. The mixture was subsequently heated to 170-180 °C under vacuum and then to 350-355 °C under N2, and maintained at this temperature for 1h. In another vessel, 0.4 mmol of CrCl₃.6H₂O and 2 mL of oleylamine (OLA) was placed under vacuum for 10 min and then in N₂ atm for 10 min at room temperature. The vessel was heated in stages to 80-90 °C under vacuum and then to 180-190 °C under N2 (but not exceed 200 °C). The CrCl_{3.6}H₂O and oleylamine mixture was then rapidly injected into the Te-containing vessel. The vessel was then quickly reheated to the original temperature (350-355 °C), and the resulting mixture continually stirred for 30 min. Following this, the mixture was cooled to 60-70 °C and a 1:3 mixture of hexane and ethanol was added to precipitate the nanocrystals. The black precipitate was then isolated via centrifugation. The washing process was repeated four times to ensure removal of any excess capping agent. A similar procedure was used for the synthesis of CuCr₂Te₄ nanocrystals but using excess of tellurium powder (0.8 mmol) and NaBH₄ (0.8 mmol), and a mixture of CuCl₂ and CrCl₃.H₂O (with 1:2 stoichiometry of Cu:Cr) in oleylamine was

injected into the Te-containing vessel. The experiment reproducibly yielded 70-75 % of Cr_2Te_3 and 40-45 % of $CuCr_2Te_4$ nanocrystals

Measurements. Transmission electron microscopic (TEM) analysis was performed using a FEI-Tecnai, 200 kV transmission electron microscope equipped with a CCD camera for STEM, HAADF detector, and EDX. TEM image non-linear processing carried out using Gatan digital micrograph version 3.4. Powder XRD patterns were recorded on a Bruker D8 instrument equipped with a Cu K α radiation source operated as a rotating anode at 40 kV and 20 mA. Raman spectroscopy was performed with a Raman spectrometer (Jobin Yvon, HR800 UV), excitation using the 633 nm HeNe line. Scanning electron microscope (SEM) analysis was carried out using a JEOL 7000 FE SEM equipped with EDX, WDS, EBSD, SE, BE and TE detectors. Magnetic measurements were performed using a superconducting quantum interference device (SQUID) with MultiVu application. Crystal structure data were obtained from the Inorganic Crystal Structure Database (ICSD) database.