Electronic Supplementary Information

Dilute Magnetic Semiconductor Cu₂MnSnS₄ Nanocrystals

with a Novel Zincblende and Wurtzite Structure

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Experiment section

I. Chemicals.

 $Cu(Ac)_2 \cdot H_2O$, $Mn(Ac)_2 \cdot 4H_2O \cdot 4H_2O$, $SnCl_4 \cdot 5H_2O$, sulfur powder (99.999%), thiourea, oleylamine (OM, 80%~90%) were purchased from Aladdin Inc. All chemicals were used as received.

II. Preparation of two type of sulfur precursors.

a) 1.0 M S/OM solution was prepared by dissolving 0.64 g (20 mmol) of sulfur powder in 20.0 mL of OM at 120 $^{\circ}$ C.

b) 0.5 M thiourea/OM solution was prepared by dissolving 0.76 g (10mmol) of thiourea in 20.0 mL of OM at 170 $^{\circ}$ C.

III. Synthesis of zincblende Cu₂MnSnS₄ nanocrystals.

In a typical synthesis, 17.0 mg (0.1 mmol) of $CuAc_2 \cdot 2H_2O$, 17.0 mg (0.05 mmol) of $SnCl_4 \cdot 5H_2O$, 10.0 mg (0.05 mmol) of $MnAc_2 \cdot 4H_2O$, and 5.0 mL OM were added to a 50 ml three-neck flask, and the reaction mixture was heated to $120^{\circ}C$. The inside of

the flask was degassed by a vacuum pump for 10 min and argon gas was charged from the balloon. This procedure was repeated three times to remove the oxygen and water. Next, the temperature was increased to 270 °C, and 0.5 ml of S/OM solution was swiftly injected into the flask. After 30 min, the crude solution was cooled to 60 °C and then precipitated with 30 mL of ethanol and further isolated by centrifugation and decantation.

III. Synthesis of wurtzite Cu₂MnSnS₄ nanocrystals.

All the procedures were the same as those of the synthesis of zincblende Cu_2MnSnS_4 , except that 1.0 ml of thiourea/OM solution was used as the sulfur source.

IV. Characterization

X-ray diffraction (XRD) pattern was recorded by a Bruker D8 FOUCS X-ray diffractometer using Cu K α radiation. The simulated XRD patterns for zincblende and wurtzite Cu₂MnSnS₄ were obtained by using Diamond 3.0 program. UV-vis-NIR absorption spectrum was measured by Shimadzu UV-3600. The optical band gap (*Eg*) was obtained by extrapolating the linear portion of the absorption spectrum to *hv* axis. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were taken on a FEI Tecnai G2 F20 with an accelerating voltage of 200 kV. Energy Disperse Spectroscopy (EDS) spectra were obtained by using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. The magnetic properties of Cu₂MnSnS₄ nanocrystals were obtained by SQUID (MPMS-XL-7, Quantum Design, Ltd.) between 2-300 K using zero-field-cooled (ZFC) and field-cooling (FC) procedures in an applied field of 100 Oe.



Figure S1. Unit cells of zincblende (left) and wurtzite (right) Cu₂MnSnS₄.

Crystal data

Formula	Cu_2MnSnS_4	
Crystal system	Zincblende	Wurtzite
Space group	<i>F</i> -43 m (No. 216)	<i>P</i> 63mc (No. 186)
Unit cell dimensions	a = b = c = 5.4323 Å	<i>a</i> = <i>b</i> = 3.8428 Å, <i>c</i> = 6.3313 Å

Atomic coordinates

Atom	Wyck.	x/a	y/b	z/c	Atom	Wyck.	x/a	y/b	z/c
S	4c	1/4	1/4	1/4	S	2b	1/3	2/3	0
Sn	4a	0	0	0	Sn	2b	1/3	2/3	0.3752
Mn	4a	0	0	0	Mn	2b	1/3	2/3	0.3752
Cu	4a	0	0	0	Cu	2b	1/3	2/3	0.3752

Notice that both Cu^+ , Mn^{2+} , and Sn^{4+} occupy the same position, and the occupancy possibilities of Cu^+ , Mn^{2+} , and Sn^{4+} are 1/2, 1/4 and 1/4, respectively.

hkl	Observed 20	Simulated 20	$\Delta 2\theta$
111	28.432	28.435	-0.003
220	47.297	47.290	+0.007
311	56.100	56.107	-0.007

Table S1. Comparison of experimental and simulated peaks for zincblende Cu_2MnSnS_4 .

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hkl	Observed 20	Simulated 20	$\Delta 2\theta$
100	26.770	26.766	+0.004
002	28.208	28.166	+0.042
101	30.324	30.317	+0.007
102	39.237	39.247	-0.010
110	47.227	47.270	-0.043
103	51.158	51.215	-0.057
112	55.899	55.935	-0.036



Figure S2. Selected area electron diffraction (SAED) images of zincblende (left) and wurtzite (right) Cu₂MnSnS₄ nanocrystals.



Figure S3. EDS spectra of zincblende (left) and wurtzite (right) Cu_2MnSnS_4 nanocrystals.

Table S3. EDS results (atomic percent) of zincblende and wurtzite Cu_2MnSnS_4 nanocrystals.

Phase	Cu%	Mn%	Sn%	S%
Zincblende	27.63	11.92	12.77	47.68
Wurtzite	28.08	10.30	13.76	47.87



Figure S4. (a) Temperature dependence of the magnetization for Cu_2MnSnS_4 nanocrystals with a zincblende structure, measured under conditions of zero-field-cooled (ZFC) and field-cooled (FC) in a magnetic field of 100 Oe; (b) The field dependence of the magnetization for zincblende Cu_2MnSnS_4 nanocrystals; inset: the magnification of the hysteresis loop at 2 K.