

Electronic Supplementary Information

**Size-tunable Zn_2SnO_4 octahedra possessing two lattice phases for thiol-ene
Reaction**

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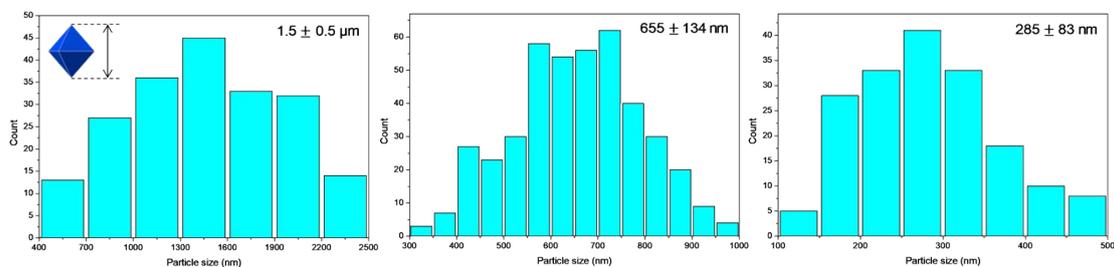


Fig. S1 Size distribution histograms of the synthesized Zn_2SnO_4 octahedra.

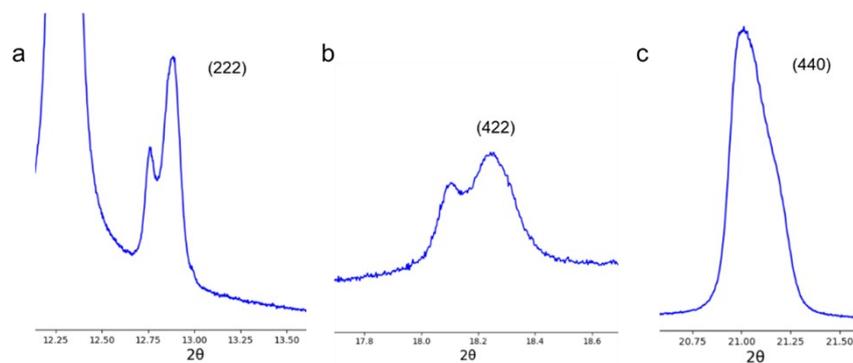


Fig. S2 Selected peaks in synchrotron XRD pattern of 285 nm Zn_2SnO_4 octahedra.

Table S1 Changes in atomic positions while transforming from the cubic phase to the trigonal phase.

cubic $FD\bar{3}m$ phase				
Atom	x	y	z	Fraction
Zn1	0.3750	0.3750	0.3750	1
Zn2	0.0000	0.0000	0.0000	0.5
Sn1	0.0000	0.0000	0.0000	0.5
O1	0.2416	0.2416	0.2416	1
trigonal $R\bar{3}m$ phase				
Zn5	0.6667	0.3333	0.2044	1
Zn6	0.6667	0.3333	-0.1667	0.5
Zn7	1	0.5	0	0.5
Sn1	0.6667	0.3333	-0.1667	0.5
Sn2	1	0.5	0	0.5
O3	0.6667	0.3333	0.0788	1
O4	1.0137	0.5068	0.2044	1

Atoms with a fractional occupancy of 0.5 indicate that they share the same atomic site with equal probability. Atoms highlighted in red denote those whose coordinates along the a, b, or c directions are variable.

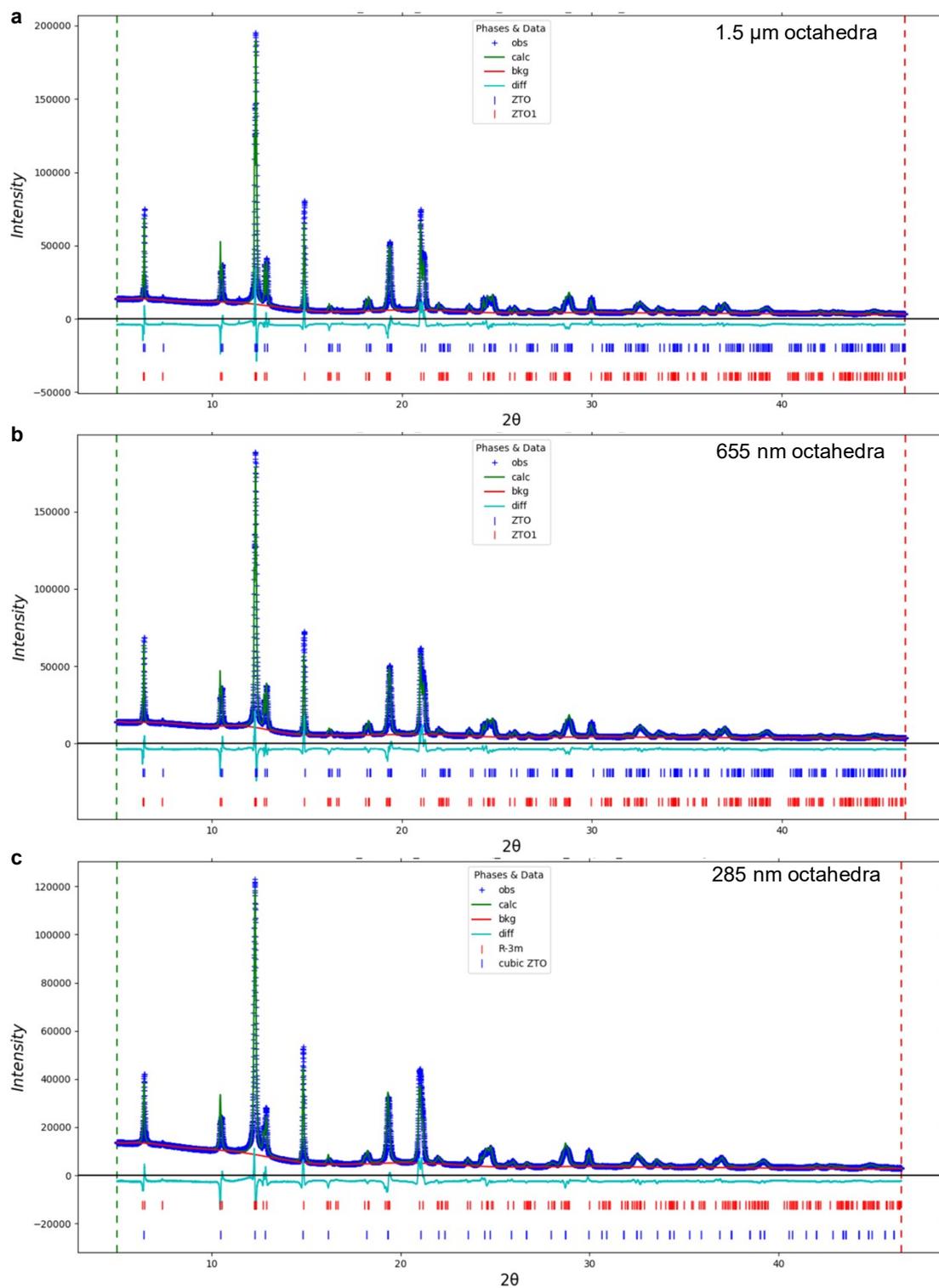


Fig. S3 Rietveld refinement of Zn_2SnO_4 octahedra with sizes of (a) 1.5 μm and (b) 655 nm using two $R\bar{3}m$ phases, and (c) 285 nm using one $R\bar{3}m$ and one $Fd\bar{3}m$ phase for peak fitting.

Table S2. Crystallographic data of Zn₂SnO₄ octahedra.

Formula	Zn ₂ SnO ₄					
Wavelength (Å)	0.56025					
2 θ range (°)	5.0 to 46.5					
<i>d</i> resolution (Å)	0.710					
Zero-point shift (°)	0.00546		0.00468		0.00777	
Morphology	1.5 μ m octahedra		655 nm octahedra		285 nm octahedra	
Space group	<i>R</i> $\bar{3}$ <i>m</i>	<i>R</i> $\bar{3}$ <i>m</i>	<i>R</i> $\bar{3}$ <i>m</i>	<i>R</i> $\bar{3}$ <i>m</i>	<i>R</i> $\bar{3}$ <i>m</i>	<i>Fd</i> $\bar{3}$ <i>m</i>
Phase	bulk	surface	bulk	surface	bulk	surface
Weight percentage (%)	17.0(2)	82.9(8)	16.4(3)	83.5(7)	56.5(5)	43.4(5)
Unit cell <i>a</i> (Å)	6.0879(6)	6.1080(3)	6.0885(7)	6.1084(4)	6.0950(5)	8.6730(4)
Unit cell <i>c</i> (Å)	15.103(2)	15.128(1)	15.080(1)	15.130(1)	15.138(1)	
Equatorial μ strain $\Delta d/d$ ($\times 10^6$)	6946.6	11185.7	8248.6	12077.4	10114.9	7620.8
Axial μ strain $\Delta d/d$ ($\times 10^6$)	6481.4	5580.7	4880.5	6863.7	6387.9	25514.7
μ strain unique axis [<i>hkl</i>]	001		001		001	111
wR (%)	10.702		9.411		8.509	
<i>R</i> (<i>F</i>) ² (%)	16.470	15.192	16.765	13.194	12.120	12.390

Table S3. Refined Zn–O and Sn–O distances.

Morphology	1.5 μm octahedra		655 nm octahedra		285 nm octahedra	
Phase	bulk	surface	bulk	surface	bulk	surface
Zn5–O (\AA)	2.36(6)	1.826(13)	2.48(5)	1.848(11)	1.922(24)	1.871(4)
T_d site	2.223(25)	1.889(7)	2.172(25)	1.891(7)	1.983(13)	
	2.223(25)	1.889(7)	2.172(25)	1.892(7)	1.983(13)	
	2.223(25)	1.889(7)	2.172(25)	1.891(7)	1.983(13)	
Sn1–O4 (\AA)	1.582(25)	2.111(8)	1.706(22)	2.108(7)	1.967(11)	2.172(8)
O_h site	1.583(25)	2.111(8)	1.706(22)	2.109(7)	1.967(11)	
	1.582(25)	2.111(8)	1.706(22)	2.108(7)	1.967(11)	
	1.583(25)	2.112(8)	1.707(22)	2.109(7)	1.968(11)	
	1.583(25)	2.111(8)	1.706(22)	2.109(7)	1.967(11)	
	1.583(25)	2.112(8)	1.707(22)	2.109(7)	1.968(11)	
	1.995(26)	2.155 (7)	1.912(21)	2.153(7)	2.132(14)	
	1.995(26)	2.155(7)	1.912(21)	2.153(7)	2.132(14)	
Sn2–O (\AA)	2.252(27)	2.208(7)	2.183(25)	2.202(6)	2.187(14)	
O_h site	2.252(21)	2.208(4)	2.184(17)	2.202(4)	2.187(8)	
	2.252(27)	2.208(7)	2.183(25)	2.202(6)	2.187(14)	
	2.252(21)	2.208(4)	2.184(17)	2.202(4)	2.187(8)	

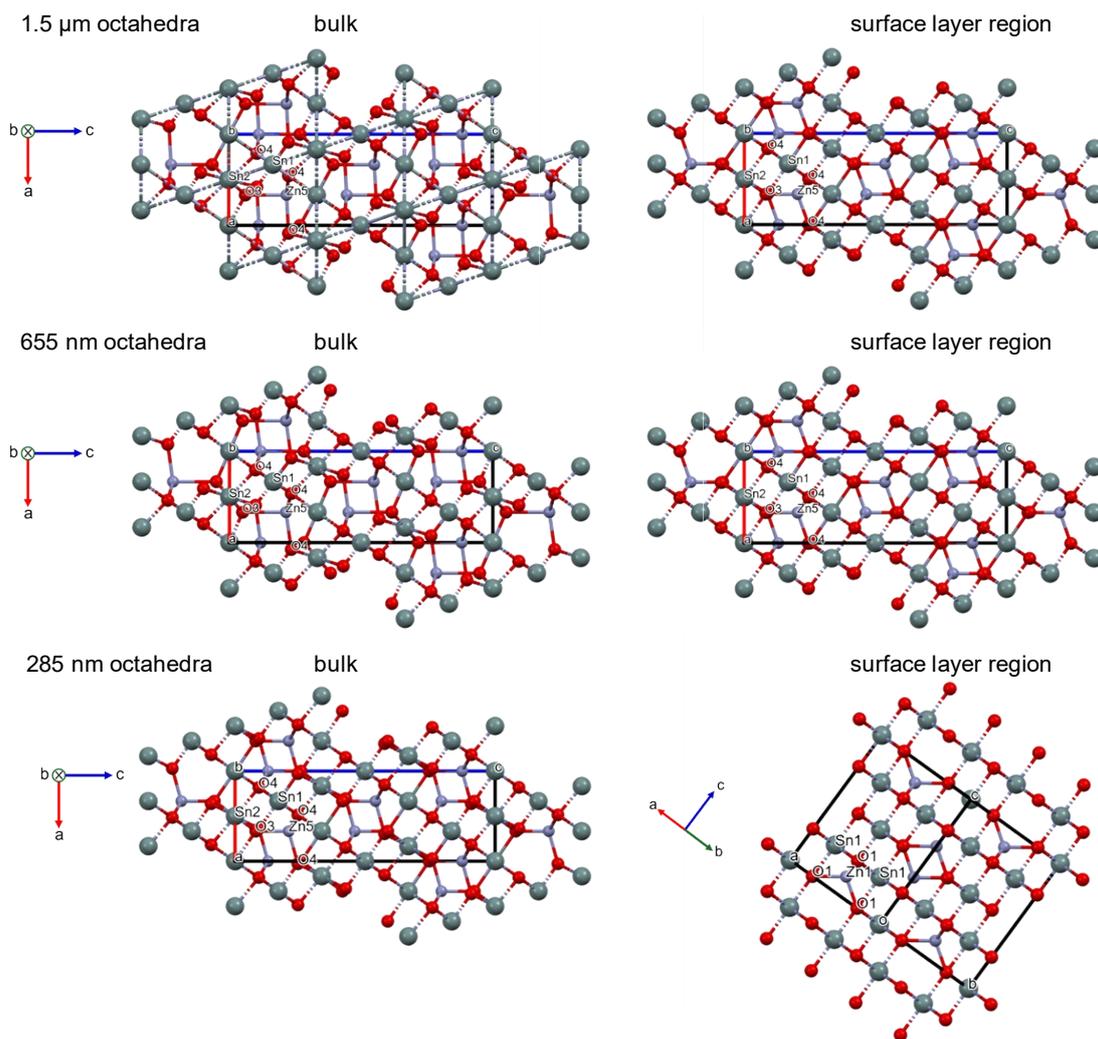


Fig. S4 Additional crystal structure models of the bulk and surface layer lattices of size-tunable Zn_2SnO_4 octahedra.

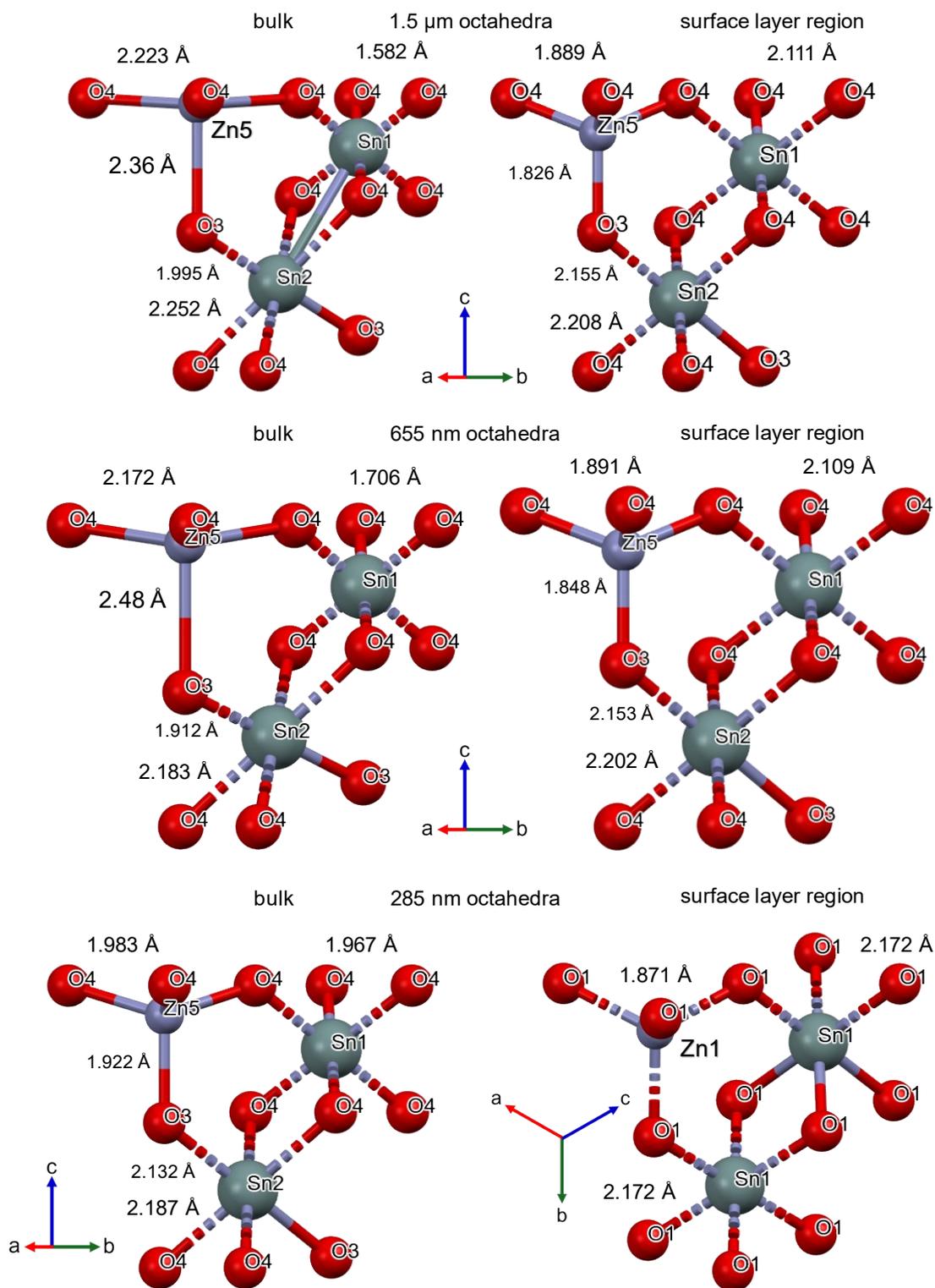


Fig. S5 Local bonding geometries in the crystal lattices of the Zn_2SnO_4 octahedra. Zn–O and Sn–O bond lengths are indicated.

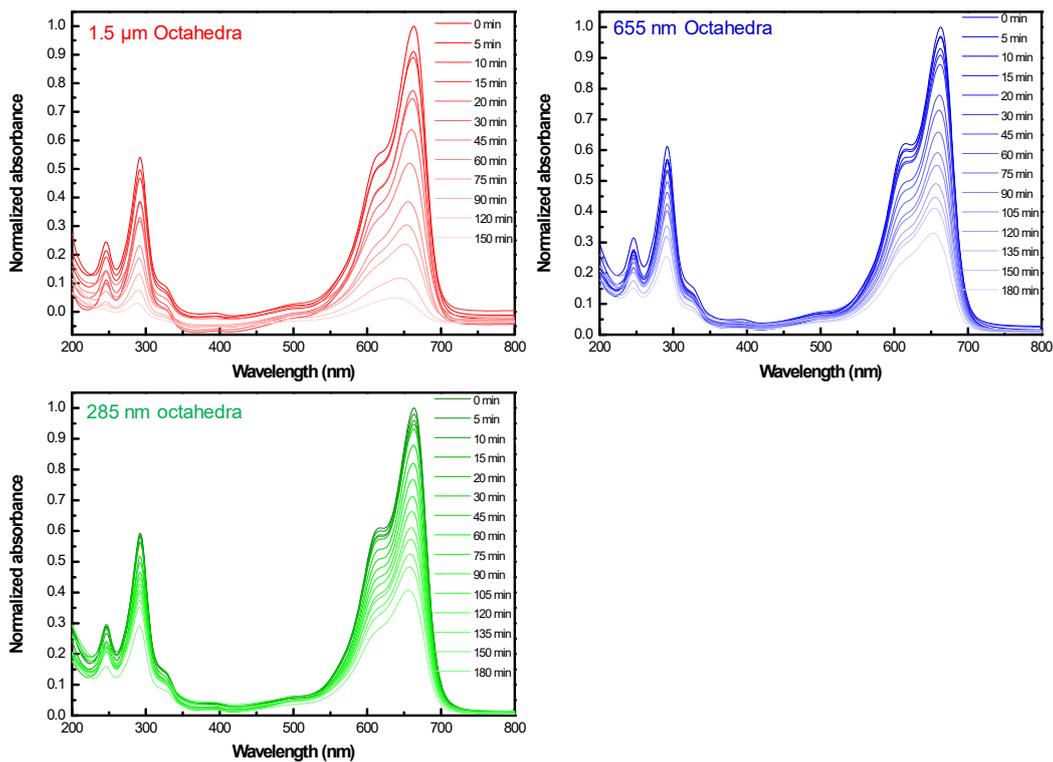


Fig. S6 UV-vis absorption spectra of methylene blue as a function of irradiation time on size-tunable Zn_2SnO_4 octahedra.

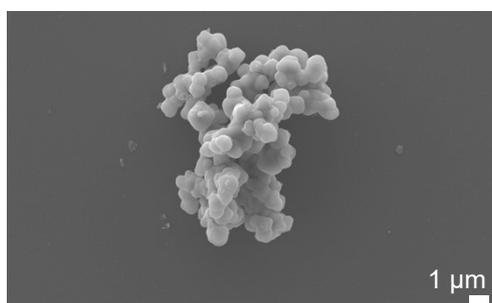


Fig. S7 SEM image of the 1.5 μm Zn_2SnO_4 octahedra after the thiol-ene reaction.

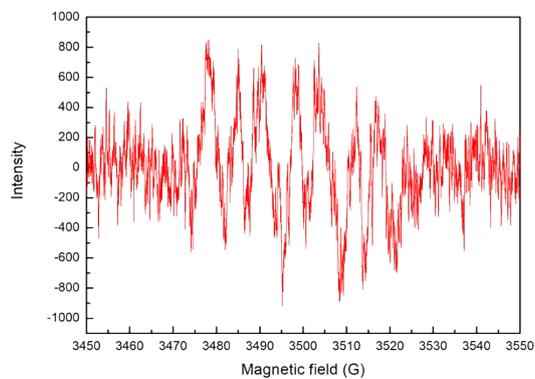


Fig. S8 EPR spectrum of DMPO upon 370 nm light irradiation on Zn_2SnO_4 octahedra in methanol.

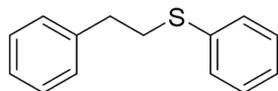
Table S4 Reagent amounts used for the synthesis of Zn₂SnO₄ octahedra.

Octahedra	H ₂ O (mL)	SnCl ₄ (mmol)	ZnSO ₄ (mmol)	0.8 M LiOH (mL)	Temp.	Time
1.5 μm	5.5			3.5		
655 nm	5	0.25	0.5	4	180 °C	9 h
285 nm	4.5			4.5		

Table S5 Calculated amounts of catalysts for photocatalytic dye degradation.

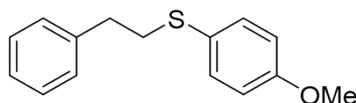
Zn ₂ SnO ₄	1.5 μm Oct	655 nm Oct	285 nm Oct
surface area of one particle (nm ²)	3.95 × 10 ⁶	7.46 × 10 ⁵	1.40 × 10 ⁵
volume of one particle (nm ³)	5.74 × 10 ⁸	4.71 × 10 ⁷	3.83 × 10 ⁷
weight of one particle (g)	3.55 × 10 ⁻¹²	2.91 × 10 ⁻¹³	2.37 × 10 ⁻¹⁴
fixed total surface area (nm ²)		1.11 × 10 ¹⁶	
number of particles	2.80 × 10 ⁹	1.49 × 10 ¹⁰	7.96 × 10 ¹⁰
weight needed (mg)	10	4.3	1.9

Spectroscopic Data



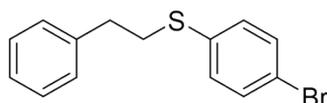
Phenethyl(phenyl)sulfane (1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.27 (d, $J = 7.8$ Hz, 2H), 7.21-7.13 (m, 11H), 7.13-7.03 (m, 13H), 5.48 (s, 1H), 3.08-3.01 (t, $J = 8.0$ Hz, 2H), 2.83 (t, $J = 8.0$ Hz, 2H).



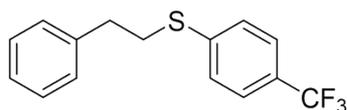
(4-methoxyphenyl)(phenethyl)sulfane (2)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36-7.29 (m, 2H), 7.23 (m, 2H), 7.16-7.07 (m, 3H), 6.83-6.76 (m, 2H), 3.69 (s, 3H), 3.05-2.97 (t, $J = 12.0$ Hz, 2H), 2.82 (t, $J = 8.0$ Hz, 2H).



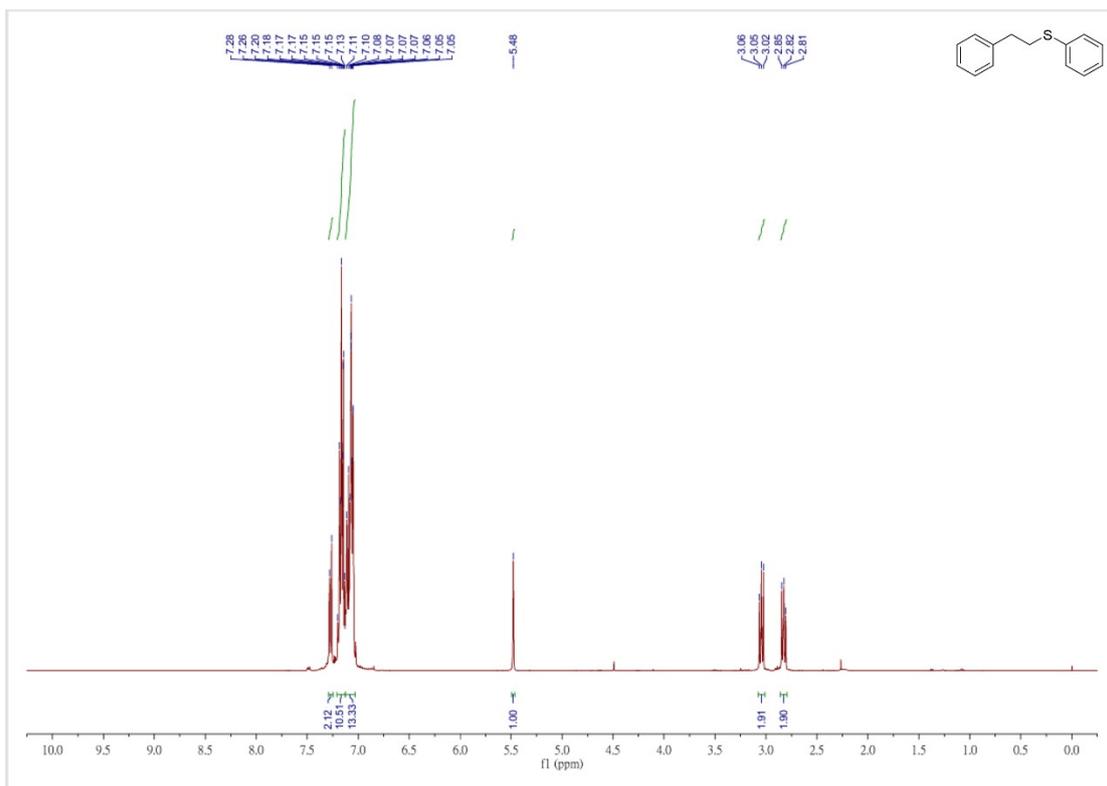
(4-bromophenyl)(phenethyl)sulfane (3)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.29 (m, 2H), 7.24-7.17 (m, 2H), 7.16-6.98 (m, 5H), 3.05 (t, $J = 8.0$ Hz, 2H), 2.84 (t, $J = 8.0$ Hz, 2H).

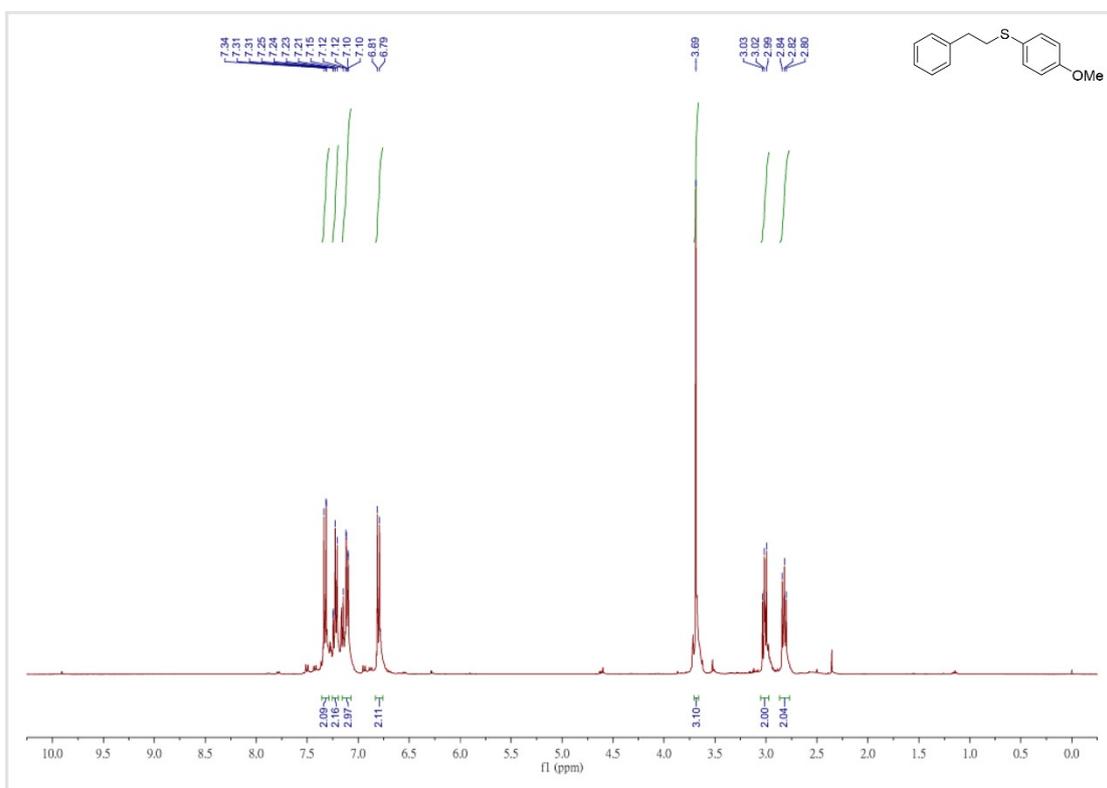


Phenethyl(4-(trifluoromethyl)phenyl)sulfane (4)

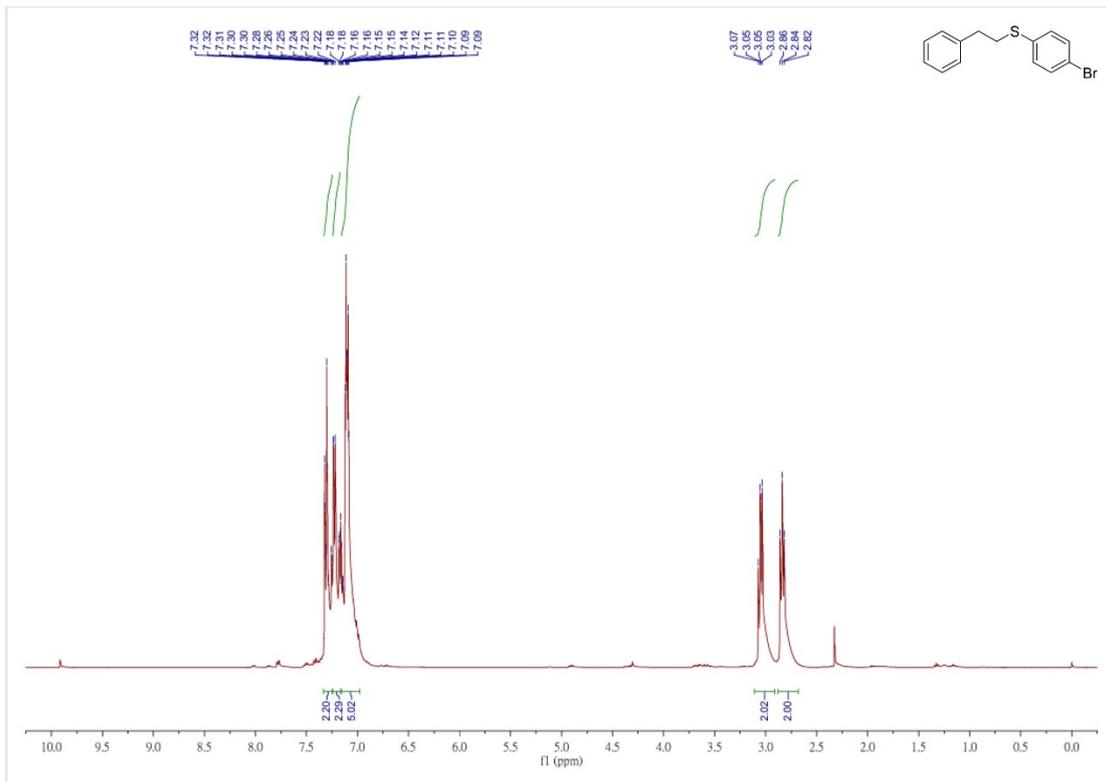
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.46-7.41 (m, 2H), 7.25 (m, 4H), 7.20-7.12 (m, 3H), 3.13 (t, $J = 8.0$ Hz, 2H), 2.89 (t, $J = 8.0$ Hz, 2H).



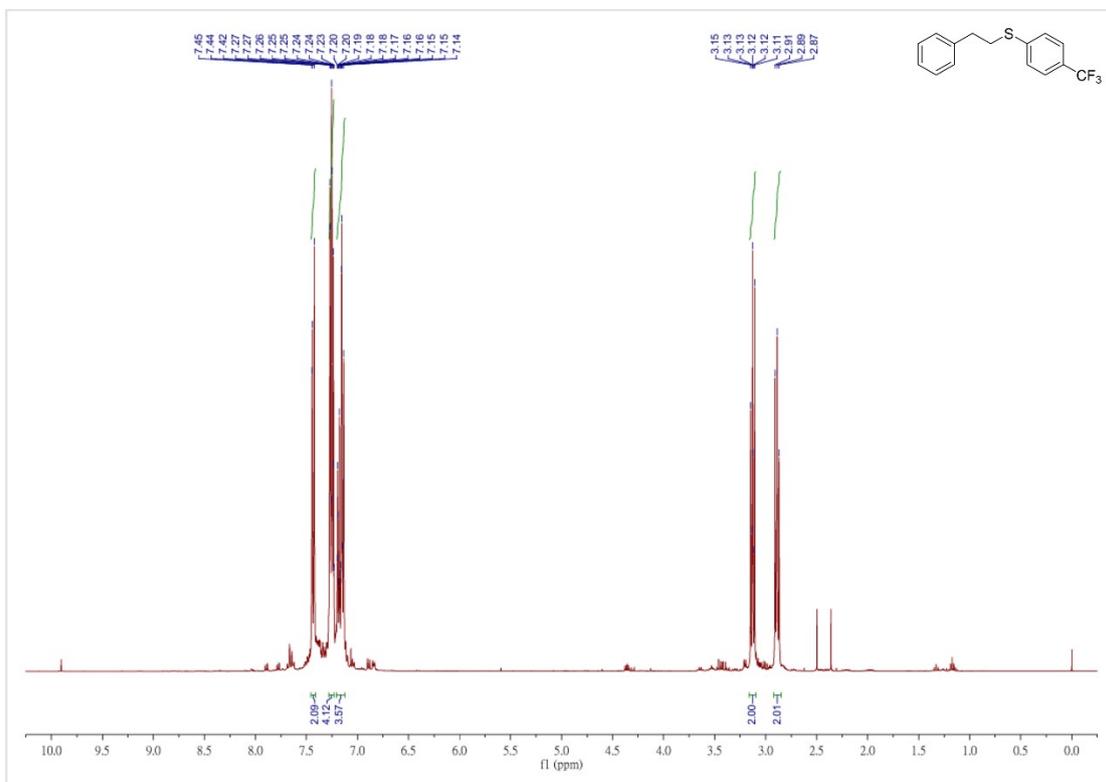
Spectrum S1 Crude ^1H NMR spectrum of compound 1 (CDCl_3 , 400 MHz).



Spectrum S2 Crude ^1H NMR spectrum of compound 2 (CDCl_3 , 400 MHz).



Spectrum S3 Crude ¹H NMR spectrum of compound 3 (CDCl₃, 400 MHz).



Spectrum S4 Crude ¹H NMR spectrum of compound 4 (CDCl₃, 400 MHz).