Electronic Supplementary Information

Enhancing photothermal conversion of spinel zinc cobalt oxide through lattice distortion regulation

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1. Experimental details

Materials characterization

X-ray diffractometer (XRD) tests were performed on a SmartLab diffractometer using a Cu Kα radiation source(λ=1.54056Å) to determine the crystal structure. Raman was characterized by Renishaw inVia Raman microscope(λ=532nm), and the laser intensity is 0.2mW. The morphologies were characterized by Scanning Electron Microscope (SEM, FEI Quanta 200F). The macroscopic absorption and intrinsic absorption of powder samples were carried out by Cary 5000 with integrating sphere. The surface temperature under photothermal conversion test was imaged by IR camera (Fluke Thermography).

Materials

$Zn(NO_3)_2 \bullet 6H_2O$(AR), $Co(NO_3)_2 \bullet 6H_2O$, Ethanol(AR), Cu films

Sample preparation

Synthesis of $ZnCo_2O_4$ spinel. First, dissolved Zn $(NO_3)_2 \bullet 6H_2O$(1.203g) in ethanol (10mL) and stirred for about 10 minutes to obtain a colorless solution. The ethanol solution of Co $(NO_3)_2 \bullet 6H_2O$ (2.355g, 15ml) was added dropwise to the obtained solution, and then stirred rapidly at room temperature for more than 6 hours to obtain a deep purple solution. Then slowly heat the solution to 40°C, 60°C, and 80°C, and maintain each temperature step for 2 hours with stirring. Finally, the homogeneous solution is dried at 100℃ for 2 hours to obtain black shiny powder. The obtained powder was calcined at different temperatures from 350 to 600°C for 2 hours to further characterize its structure.

Coatings for photothermal conversion efficiency.

0.5g of $ZnCo_2O_4$ powders were dissolved in 10ml of ethanol. Then ball-milled for 3 hours for spray coating. Then using the above ink to spray on the Cu films.

Photothermal conversion efficiency of coatings.

Then we conducted the photothermal tests of $ZnCo_2O_4$ oxides films under irradiation of a concentrated Xe lamp (P = 1.46 W), which has an irradiation spectrum similar to solar irradiation.

Calculation Details

All the ground state properties are calculated using the Vienna Ab Initio Simulation Package (VASP). Electron–ion interactions are described by using the all-electron projector augmented wave (PAW) method. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is used to approximate correlation of electrons within the many-body wave function. All calculations are performed using a cut-off energy of 520 eV with the 2 × 2 × 7 Monkhorst-Pack grids. The calculations are stopped until the force less than 0.01 eV/Å, and the energy convergence criterion is set to 10^{-8} eV.

2. Supplementary Figures

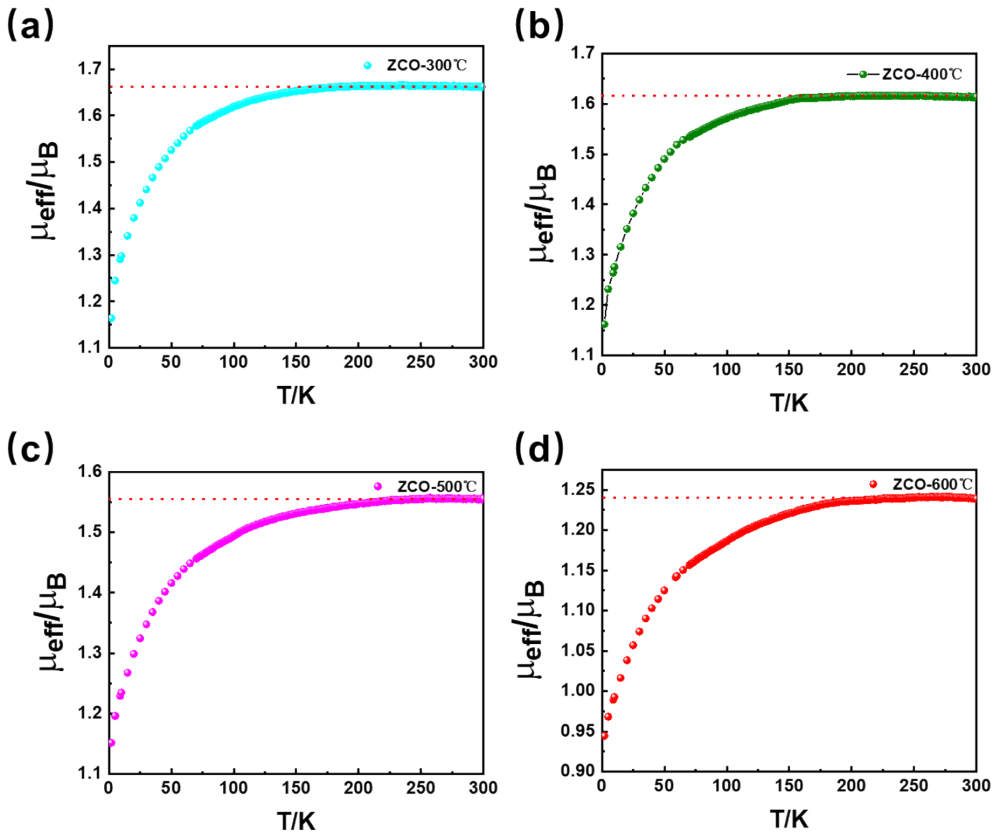

Figure S1. Fitting patterns of μ_{eff}·(a) μ_{eff} of ZCO-300°C (b) μ_{eff} of ZCO-400°C (c) μ_{eff} of ZCO-500°C (d) μ_{eff} of ZCO-600°C

$$f_{HS} = \frac{u^2_{effect} - u^2_{LS}}{u^2_{HS} - u^2_{LS}} \qquad f_{LS} = 1 - f_{HS}$$

f_{HS} *means high spin fraction,*f_{LS} *means low spin fraction,ueffect means effective magnetic moment.*

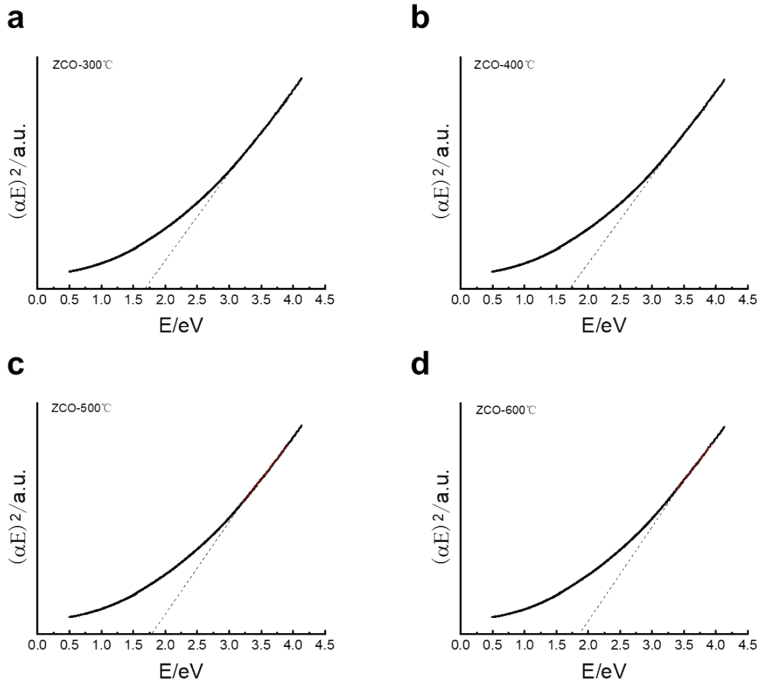

Figure S2. Tauc plot (αE) ² versus photon energy E for $ZnCo_2O_4$.

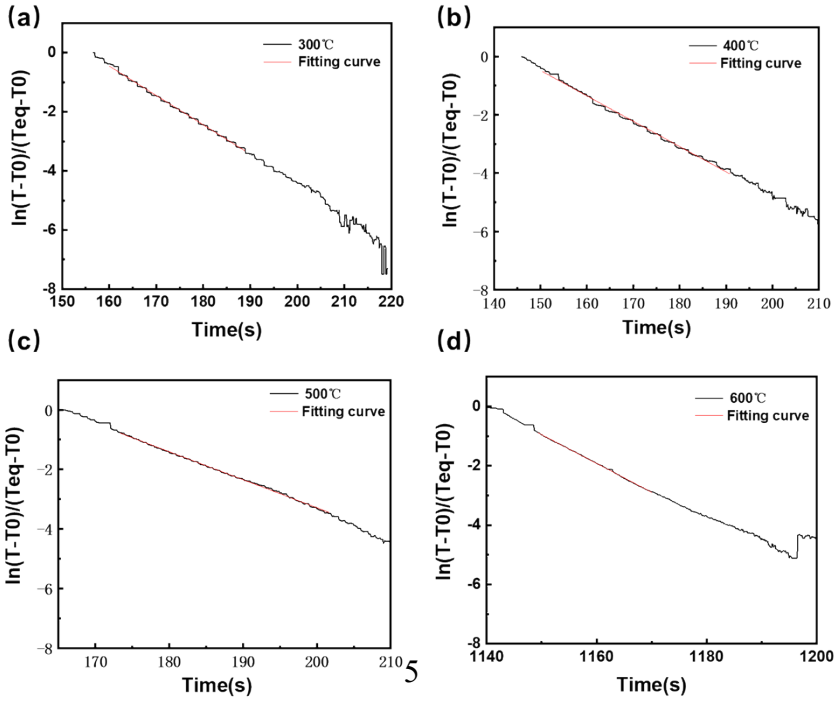

Figure S3. Fitting diagrams of thermal diffusivities of (a) ZCO-300°C and (b) ZCO-400°C (c) ZCO-500°C (d) ZCO-600°C.

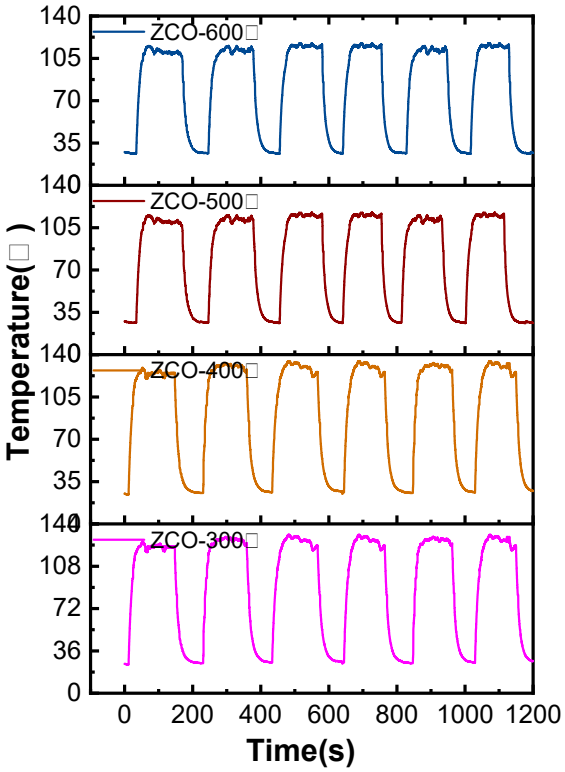

Figure S4. Photothermal stability of samples under repeated illumination cycles.

3. Supplementary Tables

Table S1. Rietveld refinement results of $ZnCo_2O_4$ samples Volume of the unit cell (V), and agreement factors (*R*) for $ZnCo_2O_4$ samples.

	Rp(%)	Rwp(%)	V(g/cm^3)
ZCO-300℃	1.67	2.15	532.1498
ZCO-400℃	1.64	2.11	532.0275
ZCO-500℃	1.70	2.22	531.0605
ZCO-600℃	1.66	2.27	530.6511

Table S2. Rietveld refinement results of $ZnCo_2O_4$ samples Co-O bond length *R* in CoO_6 octahedron site of $ZnCo_2O_4$.

	R1(Å)	R2(Å)	R3(Å)	R4(Å)	R5(Å)	R6(Å)	Δ
ZCO-300 ℃	2.06041	2.06041	2.06041	2.06041	2.06041	2.06041	6.2E-3
ZCO-400 ℃	2.06026	2.06026	2.06026	2.06026	2.06026	2.06026	6.1E-3
ZCO-500 ℃	2.05901	2.05901	2.05901	2.05901	2.05901	2.05901	6.0E-3
ZCO-600 ℃	2.00520	2.00520	2.00520	2.00520	2.00520	2.00520	5.5E-3

Table S3. Magnetic parameter of $ZnCo_2O_4$ samples μ_{eff} and HS/LS of $ZnCo_2O_4$.

	ZCO-300 ℃	ZCO-400 ℃	ZCO-500 ℃	ZCO-600 ℃
$\mu_{eff}/\ \mu_B$	1.66361	1.61508	1.55515	1.24017
HS/LS	34%HS+66%LS	33%HS+67%LS	32%HS+68%LS	25%HS+75%LS

Table S4. DFT calculation of $ZnCo_2O_4$ samples· MAGAMOM,Co-O bond length, cell volume, spin state and Jahn-Teller distortion Δ in CoO_6 octahedron site of $ZnCo_2O_4$.

input MAGMOM of Co	output MAGMOM of Co	Co-O bond 1 (Å)	Co-O bond 2 (Å)	Co-O bond 3 (Å)	cell volume (Å^3)	spin state	Δ
0 0 0 0	0.000 0.000 0.000 0.000	1.92651	1.92651	1.92651	135.313804	LS	1.00
0 0 0 **5**	0.025 0.015 0.022 **3.092**	**Co 1,2,3** 1.94695 **Co4** 1.99219	1.93154 1.99219	1.93154 1.99219	138.720855	IS	1.03
5 5 0 **0**	**3.099** **3.101** 0.037 0.031	**Co 1,2** 2.03356 **Co3,4** 1.93090	1.99287 1.94517	1.99287 1.94517	142.307949	IS	1.03
5 5 5 0	**3.103** **3.093** **3.106** 0.058	**Co 1,2,3** 1.99173 **Co4** 1.93859	2.02992 1.93859	2.02992 1.93859	145.898236	IS	1.05
5 5 5 5	**3.105** **3.097** **3.097** **3.087**	2.02611	2.02611	2.02611	149.522431	HS	1.00

Table S5. Bandgap calculation of samples.

	Bandgap Eg(eV)	R^2
ZCO-300℃	1.72	0.9994
ZCO-400℃	1.73	0.9996
ZCO-500℃	1.77	0.9997
ZCO-600℃	1.80	0.9996

Table S6. Evaluation of photothermal efficiencies of $ZnCo_2O_4$.

	F(J/K)	m(g)	$\eta_{external}$ (%)	$\eta_{external\text{-}average}$ (%)	$\eta_{internal}$ (%)	$\eta_{internal\text{-}average}$ (%)
ZCO-300 ℃	1.2E-2 1.4E-2 1.2E-2	0.3472	76.2 76.4 76.8	76.5 ± 0.3	79.9 80.1 80.5	80.2 ± 0.3
ZCO-400 ℃	1.1E-2 1.2E-2 1.2E-2	0.3498	70.9 70.9 71.5	71.1 ± 0.3	73.7 73.7 74.3	73.9 ± 0.3
ZCO-500 ℃	1.3E-2 1.3E-2 1.3E-2	0.3562	66.0 65.9 65.8	65.9 ± 0.1	69.2 69.1 69.0	69.1 ± 0.1
ZCO-600 ℃	1.3E-2 1.1E-2 1.3E-2	0.3542	59.4 60.2 61.2	60.3 ± 0.9	62.5 63.3 64.3	63.4 ± 0.9

* $mC_p\frac{dT}{dt} + F(T - T_0) = 0$ $P_{in} \cdot \eta = F(Teq - T_0)$ Cp(J/g/K) = 0.385