

Sewage Free Preparation of 2D Metal Oxides by Rapid Freezing Soft Templated Method for Extraordinarily Activating Solar Driven Humidity VOCs Combustion

Experimental Section

1.1 Chemicals

Cobaltous nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Copper nitrate hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Ferric nitrate hexahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were purchased from Kermel. Formaldehyde solution (37 wt%) was purchased from Damao. Polyvinyl pyrrolidone (PVP, K30) was purchased from Macklin. Deionized water (resistance > 18.2 M Ω per cm) was used for all experiments. All chemicals were directly used as received without further treatment.

1.2 Synthesis of 2D metal oxides

We take Co_3O_4 as an example. 1.5 g PVP was dissolved in 30 ml deionized water at room temperature with stirring. Then 0.6 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to the PVP solution, and the mixture was stirred for 3 h. After that, the mixed solution was frozen by liquid nitrogen, and then freeze-dried at -45 °C for 48 h. Finally, the obtained powder was calcined at 450 °C for 10 h in the air to form 2D Co_3O_4 . The synthesis of 2D CuO, 2D ZnO, 2D Fe_2O_3 was similar to that of 2D Co_3O_4 , and the only difference is using the $(\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to replace $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

The synthesis of Nano Co_3O_4 procedure was similar to that of 2D Co_3O_4 except that no PVP was added to the solution.

1.3 Catalyst characterizations

The overall composition of the prepared samples were studied by the powder X-ray diffraction (XRD), which was performed on a Bede D1 system operated at 20 kV and 30 mA with Cu K α radiation ($\lambda= 1.5406 \text{ \AA}$). The scanning electron microscopy (SEM) images were tested with the FEI Nova NanoSEM450 (Czech Republic). Transmission electron microscopy (TEM, JEM-2100 Plus) was used to identify the morphology and the crystal structure of the nanostructures. Zennium_Pro (Zahner, Germany) was an electrochemical workstation. The ultraviolet-visible-near infrared absorption spectrum (UV-vis-IR) was tested by Hitachi Limited U4100 (Japan). Infra-red (IR) photographs were taken with a camera (Fluke Ti300, America). Raman spectra were recorded on a HORIBA Raman spectrometer, with an excitation laser wavelength of 532 nm. The FTIR was tested by HYPERION 3000 (Bruker Optics). N₂-sorption isotherms were collected on a Belsorb-Max system. Brunauer-Emmett-Teller (BET) specific surface areas were calculated from adsorption data. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB-250 spectrometer using a monochromatic Al K α radiation source (1486.6 eV), with the binding energy of the C 1s (284.6 eV) as a basis for the deconvolution of others.

1.4 Thermal catalytic test of catalysts

The thermal catalytic activity of 2D Co₃O₄ and Nano Co₃O₄ for VOCs oxidation was tested in a fixed-bed quartz tube reactor (Φ 8 mm) with 50 mg of catalysts. 50 sccm of air (20% O₂/80% N₂) passed through the water tank to form carrier gas with high water content and the concentration of VOCs (formaldehyde, CH₄, acetone), CO was 0.1% (1000 ppm). The composition of the outlet gas was tested by a gas chromatograph (GC, 7890A) equipped with FID detector.

1.5 Sunlight driven catalysis

The laboratory light source was AM 1.5 G light source. For the photocatalytic VOCs combustion, 50 mg of catalyst was loaded in the quartz tube to ensure the direct sunlight irradiation to catalysts. For the sunlight driven thermal VOCs combustion, 50 mg of

catalyst was loaded in the light selective absorbing device.¹ The light source was used to irradiate the reactors and the ambient temperature was constant at 30 °C. Then, 50 sccm of air (20% O₂/80% N₂) passed through the water tank to form carrier gas with high water content and the concentration of VOCs (formaldehyde, CH₄, acetone), CO was 0.1%. To test the real sunlight driven thermal combustion rate for formaldehyde, the water with the flow rate of 0.08 sccm was injected into 500 sccm of air (20% O₂/80% N₂) by peristaltic, which was passed through the catalysts and the concentration of formaldehyde was tuned by the injection amount. The outlet gases were tested by gas chromatograph (GC) 7890A equipped with an FID detector.

For the turnover frequency (TOF) test, we assumed that all Co sites in 2D Co₃O₄ participated in the reactions. The TOF = α/γ .

Where $\alpha = \delta * 500 / 22.4$, δ was the combust formaldehyde concentration. γ was the mole number of Co sites (0.207 mmol).

Table S1. The Sunlight-driven formaldehyde oxidation turn over frequency (TOF) rate in terms of new photothermal device supported 2D Co₃O₄ (2D Co₃O₄+Device), in comparison with the reported best formaldehyde decomposition performances of photocatalysis.

Catalysts	Light intensity (mW cm ⁻²)	Condition	TOF (min ⁻¹)	References
2D Co ₃ O ₄ +Device	100	Humidity	5.1	This work
Bi ₂ SiO ₅ /AgI	100	Humidity	0.138	2
g-C ₃ N ₄ -TiO ₂	25	Humidity	7.36×10 ⁻²	3
Au/TiO ₂	19	Humidity	1.84×10 ⁻³	4
TiO ₂ @NH ₂ -MIL	150	Humidity	1.76×10 ⁻⁴	5
graphene/TiO ₂	100	Humidity	1.5×10 ⁻²	6
g-C ₃ N ₄	100	Humidity	3.98×10 ⁻³	7
Cu-TiO ₂	10.2	Humidity	2.29×10 ⁻⁴	8
Silicate-TiO ₂	11	Humidity	3.35×10 ⁻³	9
g-C ₃ N ₄ -TiO ₂ -zeolites	100	Humidity	1.27×10 ⁻²	10

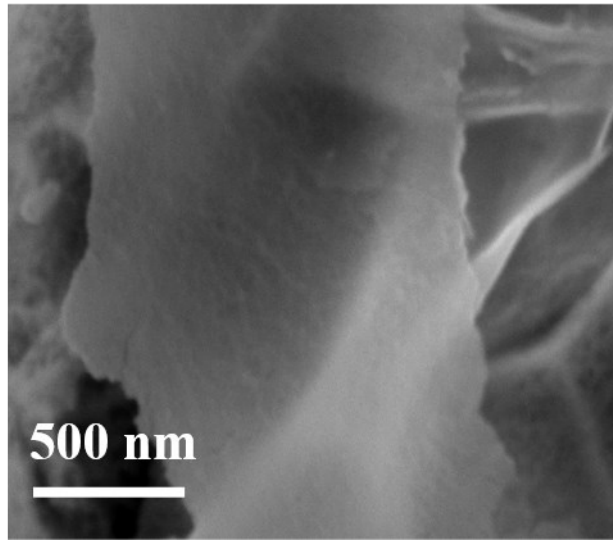


Figure S1. SEM image of Co-PVP shown in Figure 1e.

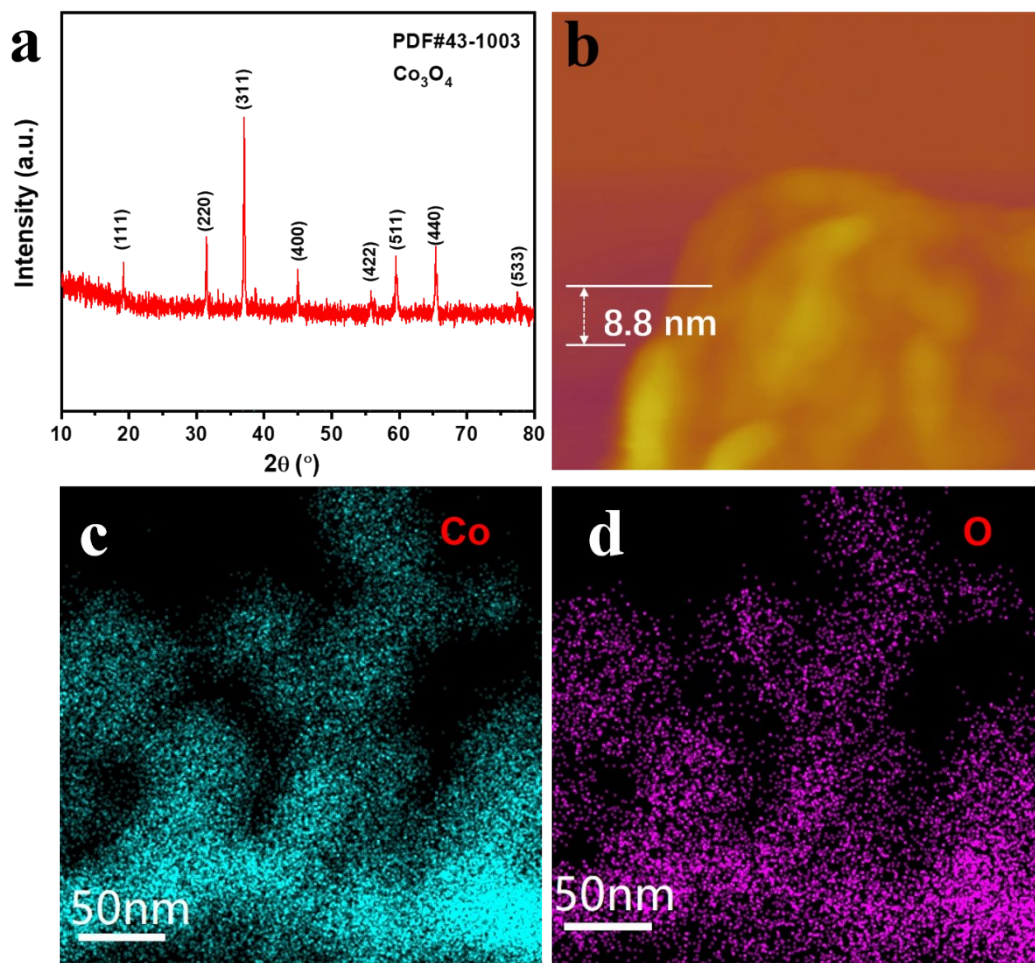


Figure S2. XRD pattern (a), AFM image (b), Co (c) and O (d) elemental mappings of 2D Co_3O_4 .

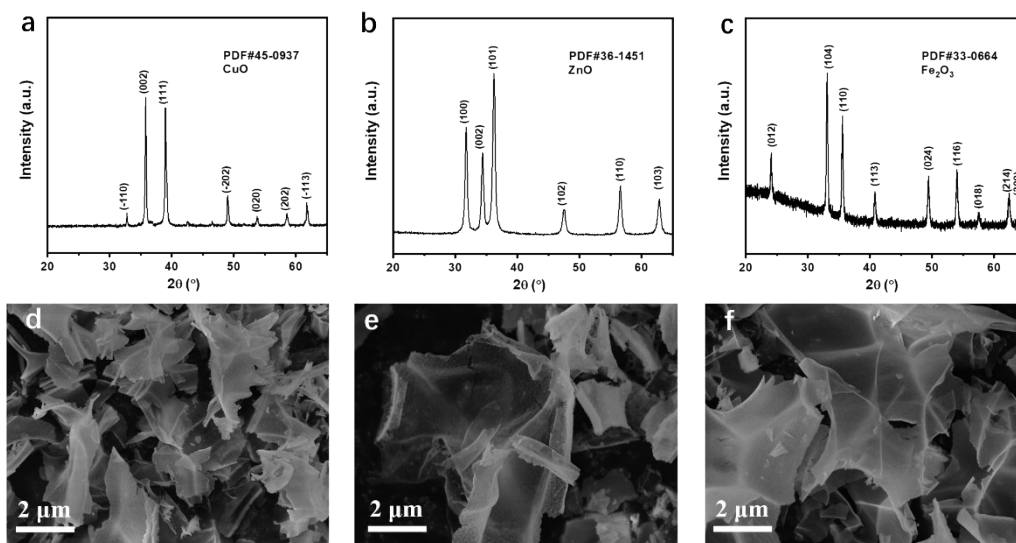


Figure S3. XRD patterns and SEM images of CuO (a, d), ZnO (b, e), Fe₂O₃ (c, f) synthesized by our method.

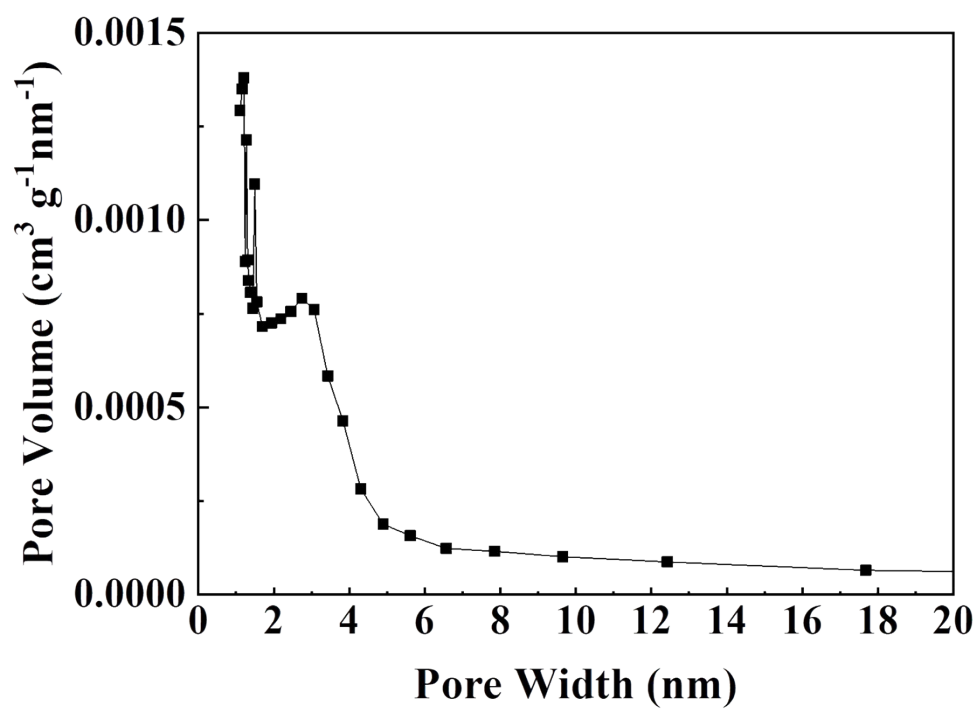


Figure S4. Pore size distributions of the 2D Co₃O₄.

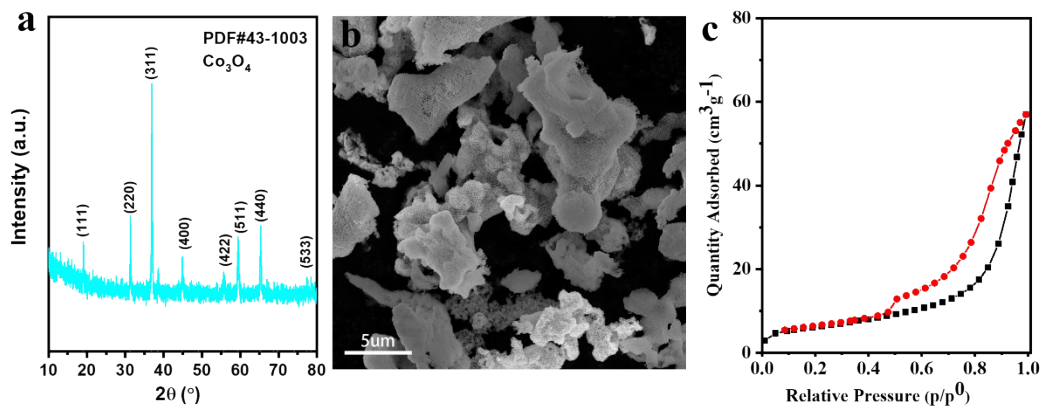


Figure S5. (a) XRD pattern, (b) SEM image and (c) N_2 adsorption-desorption isotherm of SEM image of Nano Co_3O_4 .

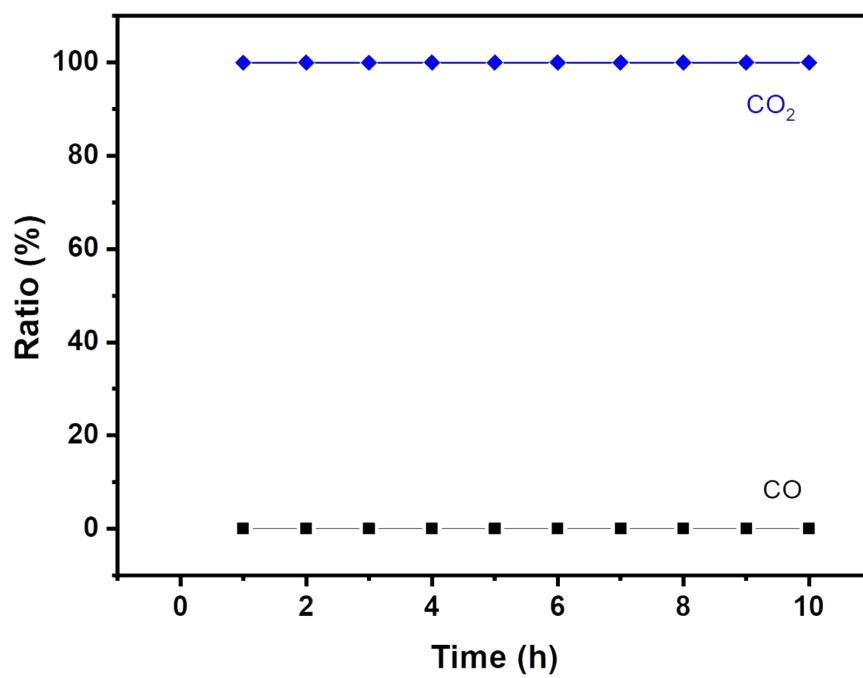


Figure S6. The CO₂ and CO ratio of the exhausted gas shown in Figure 4a at 120 °C.

The Ratio=CO₂ or CO/ CO₂+CO

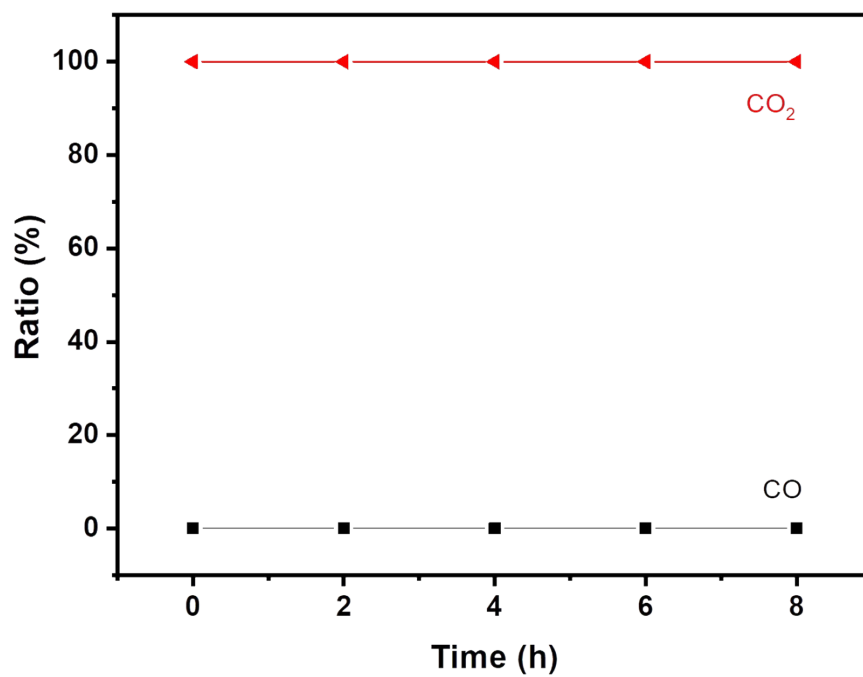


Figure S7. The CO₂ and CO ratio of the exhausted gas shown in Figure 4b at 300 °C.

The Ratio=CO₂ or CO/ CO₂+CO

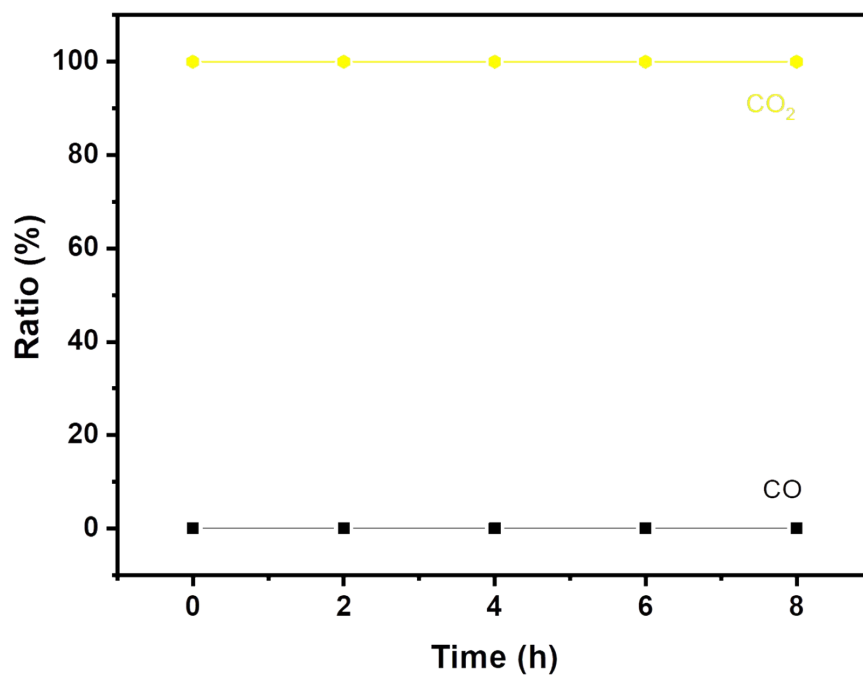


Figure S8. The CO₂ and CO ratio of the exhausted gas shown in Figure 4d at 300 °C.

The Ratio=CO₂ or CO/ CO₂+CO

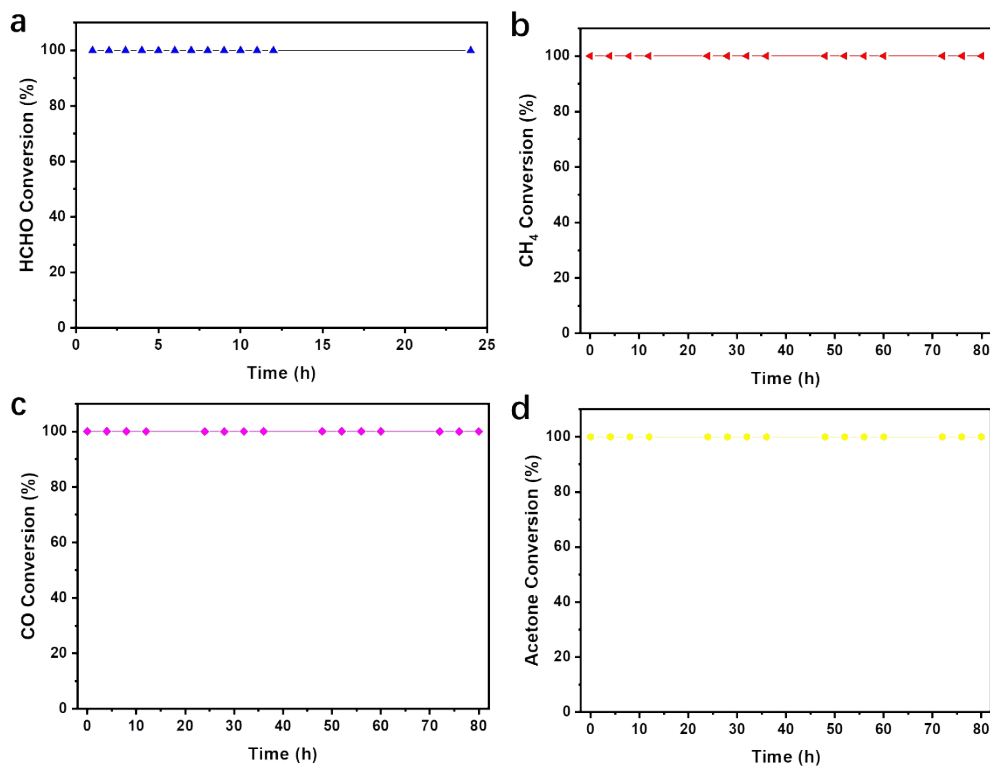


Figure S9. (a) Formaldehyde catalytic performances with time over 2D Co₃O₄ catalyst under the temperature of 120 °C. (b) CH₄ catalytic performances with time over 2D Co₃O₄ catalyst under the temperature of 300 °C. (c) CO catalytic performances with time over 2D Co₃O₄ catalyst under the temperature of 150 °C. (d) Acetone catalytic performances with time over 2D Co₃O₄ catalyst under the temperature of 300 °C.

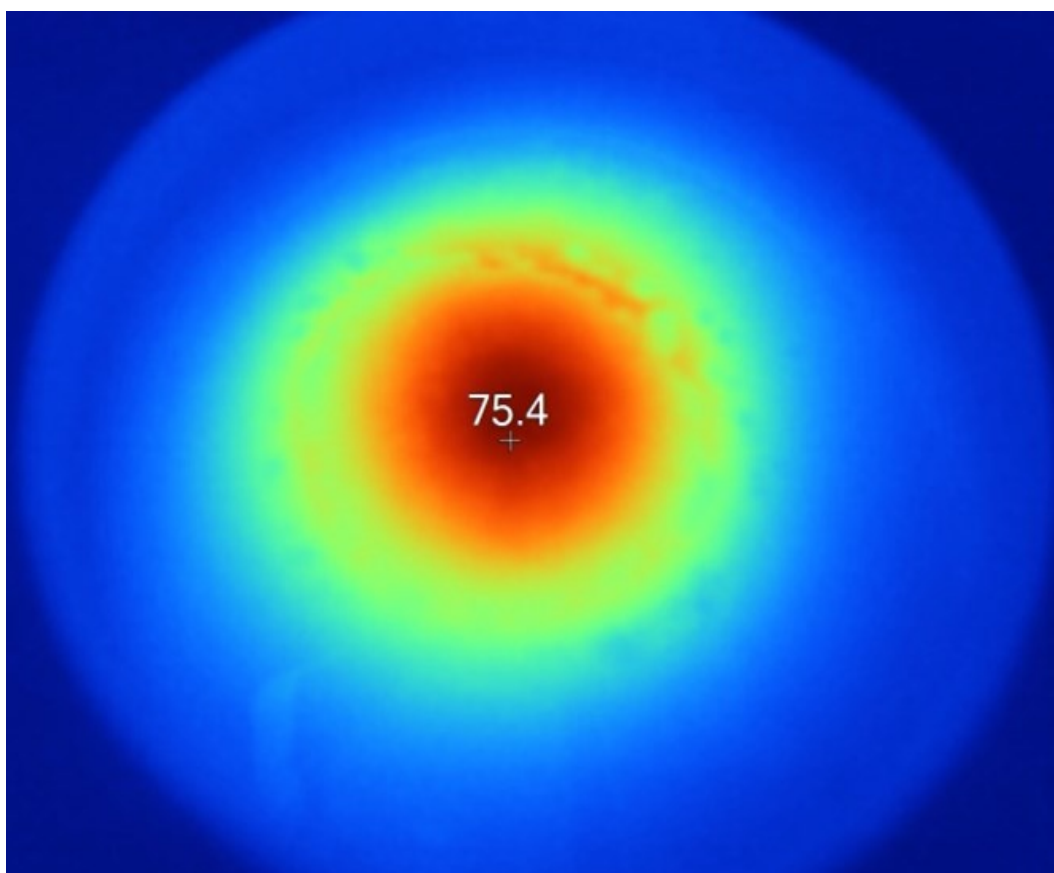


Figure S10. The IR image of 2D Co₃O₄ directly irradiated by 1 sun.

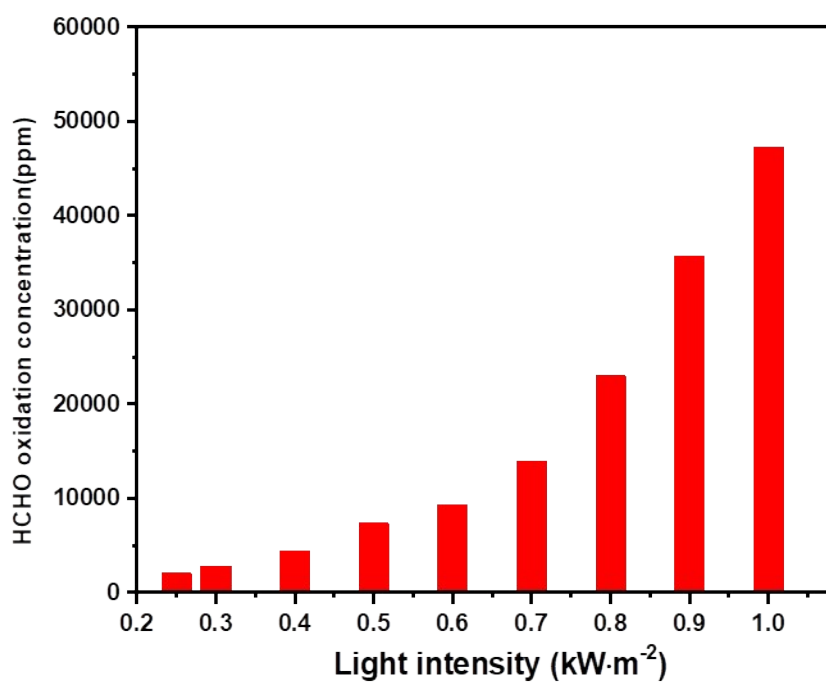


Figure S11. The maximum formaldehyde oxidation concentration and temperature of 2D Co₃O₄ +Device under sunlight irradiation with different intensity.

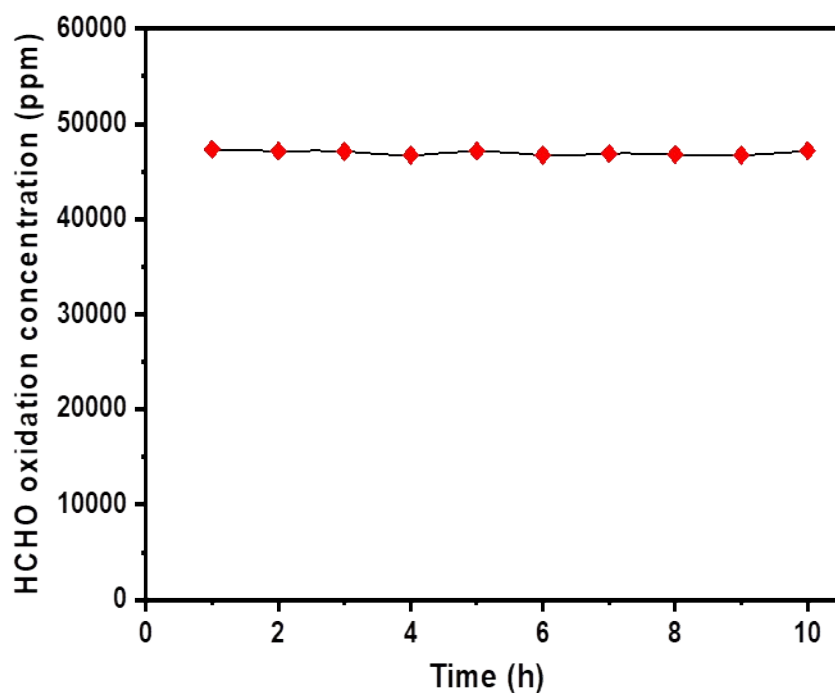


Figure S12. The different oxidation of 2D Co_3O_4 +Device under 1 sun irradiation.

References

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