

Supporting Information

A simple and general route to prepare functional mesoporous double-metal oxy(hydroxide)

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Experimental procedure

Materials and Sample Preparation

All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd and used without further purification.

Fabrication of ZnSn(OH)₆ Nanocubes

To synthesize ZnSn(OH)₆ nanocubes, 15 mL of ZnCl₂ (3 mmol) solution was added into 15 mL of Na₂SnO₃·4H₂O (3 mmol) solution. The mixture solution was stirred for 1 h at room temperature. Afterwards, the white precipitation was obtained by centrifugation and washed with distilled water and absolute ethanol for three times, and dried at 60 °C for 12 h in a vacuum oven.

Fabrication of CuSn(OH)₆ Nanorods

CuSn(OH)₆ nanorods were synthesized as following. Briefly, SnCl₄·5H₂O (0.79 g) was completely dissolved in 100 mL of distilled water, then NaOH (0.76 g) was added to the solution under vigorous stirring. Subsequently, CuCl₂·H₂O (0.044 M, 50 mL) solution was dropped into the above mixed solution. After stirring for another 10 min, blue precipitates were then kept standing at room temperature for 5 h. CuSn(OH)₆ nanorods were obtained by centrifuged, washed, and dried in a vacuum oven.

Fabrication of CoAl-LDH (Co₂Al(OH)₇) 2D Nanosheets

Co₂Al(OH)₇ 2D layered double hydroxide (LDH) nanosheets were prepared as following. In a typical synthesis, 6 mmol of Co(NO₃)₂·6H₂O, 2 mmol of Al(NO₃)₃·9H₂O and 20 mmol of CO(NH₂)₂ were dissolved in 40 mL of distilled water under vigorous stirring. Subsequently, the above mixture solution was transferred into a Teflon-lined stainless steel autoclave, and the autoclave was sealed and maintained at 110 °C for 8 h. After hydrothermal reaction, CoAl-LDH nanosheets were obtained by centrifuged, washed, and dried in a vacuum oven.

Synthesis of double-metal oxy(hydroxides) with Mesoporous Structure

0.8 g of as-prepared double-metal hydroxide was dispersed in 40 ml absolute ethanol under continuous stirring and ultrasonication for 30 minutes, then the

mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and heated at 220 °C for 24 hours. The obtained products were collected by centrifugation and washed with absolute ethanol several times and dried at 60 °C for 12 h in a vacuum oven.

Characterization

The X-ray powder diffraction (XRD) of the samples were characterized by Philips X'Pert Pro Super diffractometer, which was radiated by graphite monochromatized Cu K α ($\lambda = 1.54178 \text{ \AA}$). The operating voltage was kept at 40 kV and the current was kept at 200 mA. Scanning electron microscopy (SEM) images were taken on a field-emission scanning electron microscopy (JEOL JSM-6700F, 15 kV). High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and elemental mapping analysis were recorded on FEI Talos F200X. Fourier transform infrared (FTIR) spectra were recorded on Nicolet 8700 FT-IR spectrophotometer by using the pellets of sample mixed with KBr (0.5:100). The X-ray photoemission spectroscopy (XPS) measurements were performed at the Catalysis and Surface Science end station in National Synchrotron Radiation Laboratory (NSRL, Hefei), and the surface adventitious carbon (C 1s at 284.6 eV) was used to calibrate the binding energy. The UV-Vis absorption spectra were measured on a Shimadzu UV-2510 spectrophotometer, the wavelength region was from 250 to 550 nm. JEOL JES-FA200 EPR spectrometer was used to obtain the electron paramagnetic resonance (EPR) spectra, and operating parameters were 140 K, 9064 MHz, 0.998 mW, X-band. The actual atom contents were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) on the optima 7300 DV, PerkinElmer. Thermogravimetric analysis (TGA) was tested on a TGA Q5000IR thermogravimetric analyzer with a heating rate of 10 °C min⁻¹ under N₂ flow. Nitrogen adsorption-desorption isotherms were measured under a Micromeritics ASAP 2020 system at 77 K. Barrett-Emmett-Teller (BET) and

Barrett-Joyner-Halenda (BJH) methods were adopted to calculate the specific surface areas and pore size distribution, respectively.

General Experimental Procedures for Photocatalytic Aerobic Oxidation of amines to imines

The photocatalytic aerobic oxidation reactions were carried out in an oxygen atmosphere (1 atm) at the temperatures of 25-80 °C. Typically, mesoporous $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$ photocatalyst (20 mg) was suspended in acetonitrile (4 mL) containing benzylamine (0.03 mmol) and 1, 3, 5-trimethylbenzene (internal standard) (0.03 mmol) in a 10 mL round-bottomed flask. The temperature was controlled by water bath. A 300 W Xe lamp (CEL-HXF300, CeauLight) in conjunction with a cut-off filter ($\lambda \geq 420$ nm) was used as the light source. The reaction progress was monitored at different time intervals by gas chromatograms (GC) (Agilent HP-5), which is equipped with a SGE BP1 non-polar 100 % dimethylpolysiloxane with capillary column dimensions of 30 mm \times 0.32 mm \times 0.25 mm. The products were determined by mass spectrometry (GC-MS) using the Agilent technologies 7890A GC and a mass spectrometer Agilent technologies 5975C as detector.

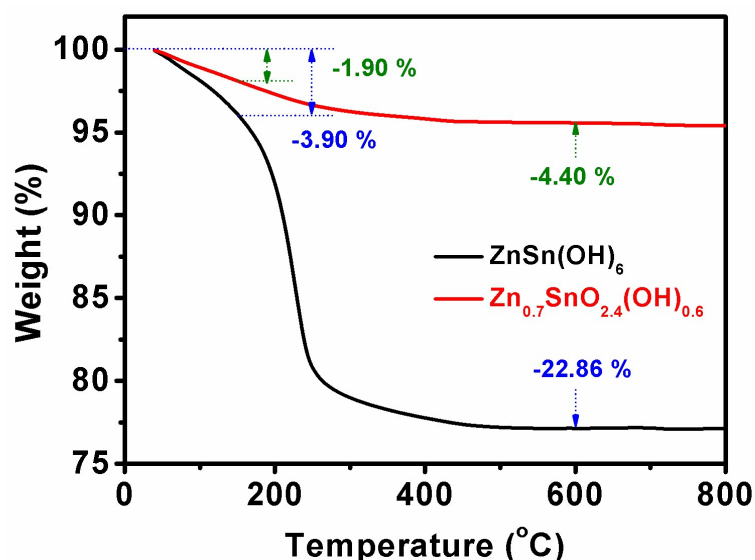


Fig. S1 Thermogravimetric analysis (TGA) curves of $\text{ZnSn}(\text{OH})_6$ (ZSH) and $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$ nanocubes measured at a temperature ramp of 10 °C min⁻¹ in air.

Fig. S1 shows the thermogravimetric analysis (TGA) curves of ZSH and $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$ samples measured in air with a heating rate of 10 °C min⁻¹. From the

curve of ZSH, it can be seen that the first weight loss occurs before 150 °C, mainly due to the elimination of adsorbed water in the sample. Then it starts to decompose upon further heating and undergoes a quick weight loss (18.96%) covering the temperature from 150 to 600 °C, which corresponds to the thermal decomposition of ZSH to ZnSnO_3 . In comparison with ZSH, the TG curve of the oxygen-deficient $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$ recorded at the same condition shows a remarkably decreased weight loss owing to partial dehydration of ZSH by solvothermal treatment with ethanol. This assignment is reasonable since a weight loss of about 2.50% from 150 to 600 °C is in good agreement with the calculated one (2.53%) on the basis of the empirical formula, $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$. Inductively coupled plasma mass spectroscopy (ICP-MS) analysis shows that the molar ratio of Zn to Sn is decreased to 0.7:1 after solvothermal treatment in ethanol, indicating the leaching of some Zn^{2+} into solution.

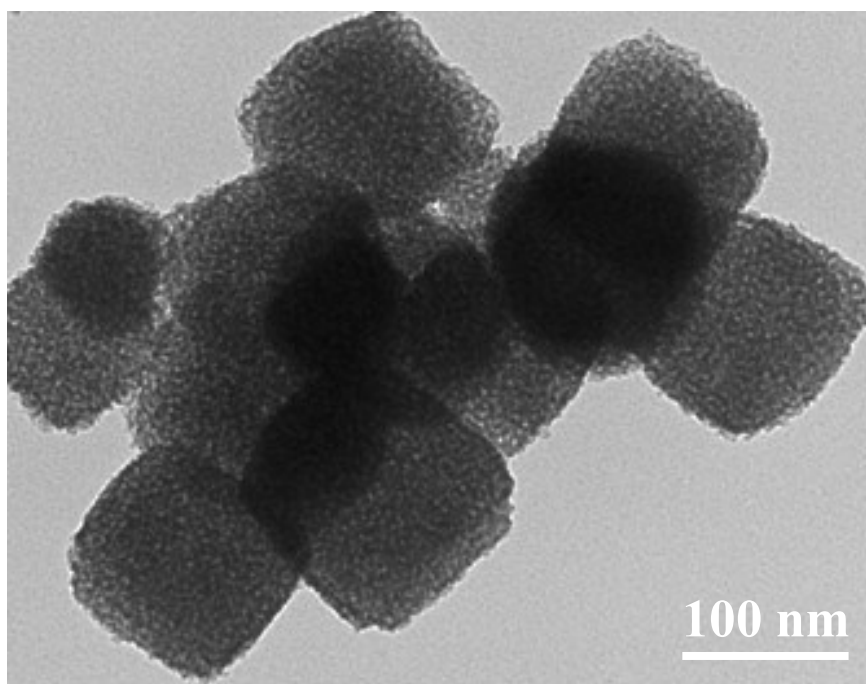


Fig. S2 TEM image of mesoporous $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$ nanocubes.

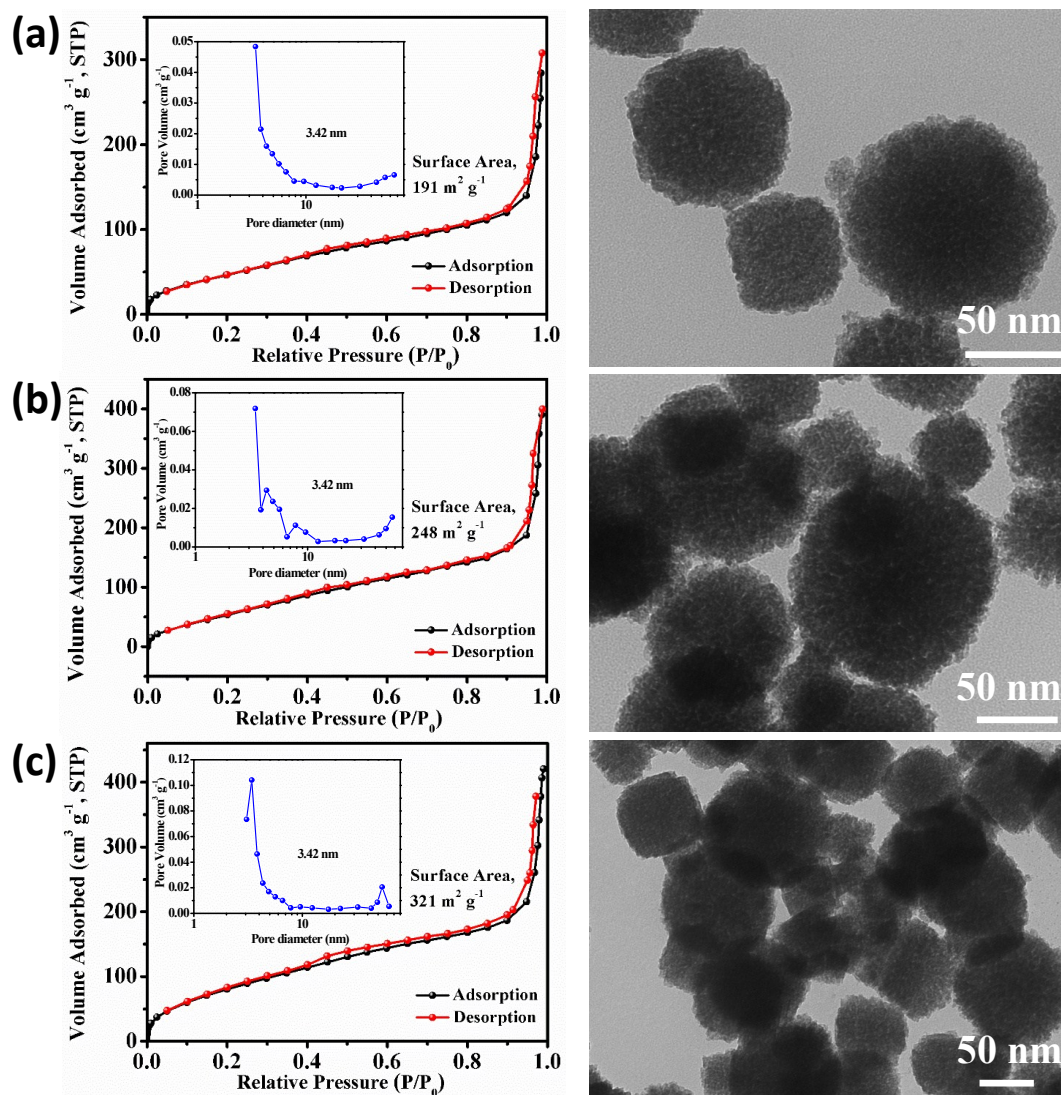


Fig. S3 Nitrogen adsorption-desorption isotherms and the corresponding TEM images of products treated at different solvothermal temperature. (a) 160 °C (b) 180 °C (c) 200 °C (Inset: the corresponding pore size distribution curves).

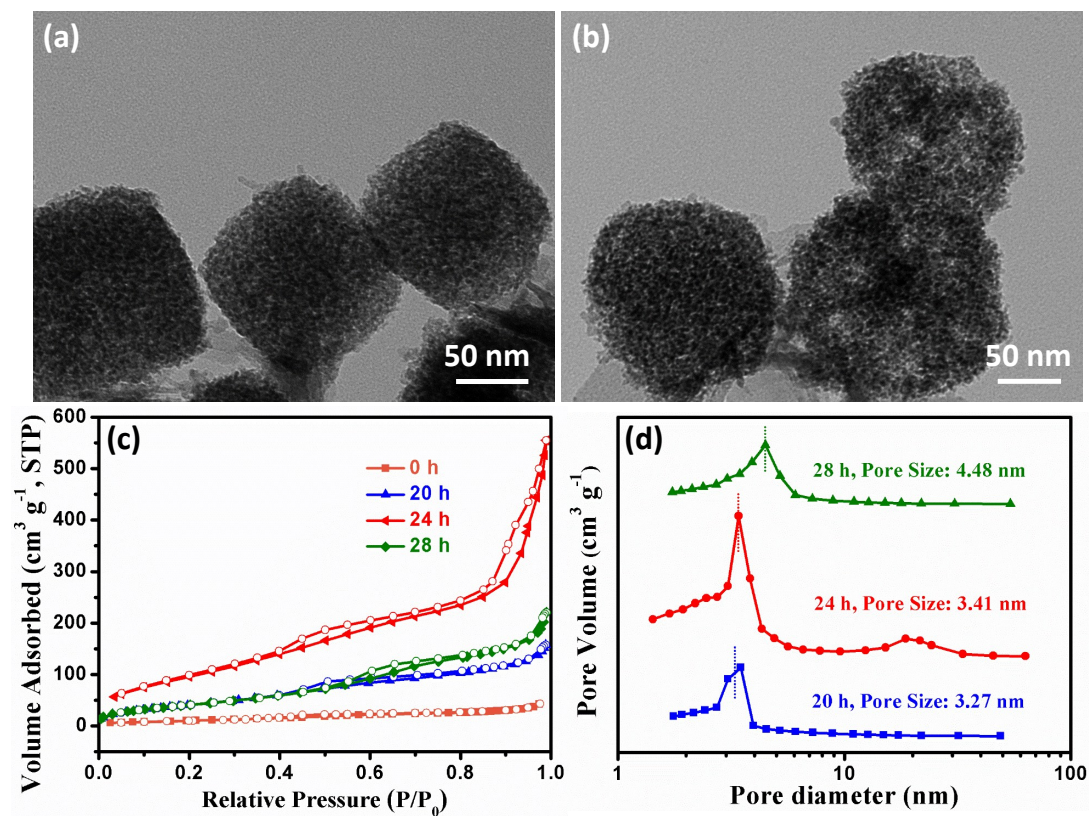


Fig. S4 TEM images of ZSH treated at different solvothermal time. (a) 20 h and (b) 28 h. (c) Nitrogen adsorption-desorption isotherms and (d) the corresponding pore size distribution curves of products treated at different reaction time.

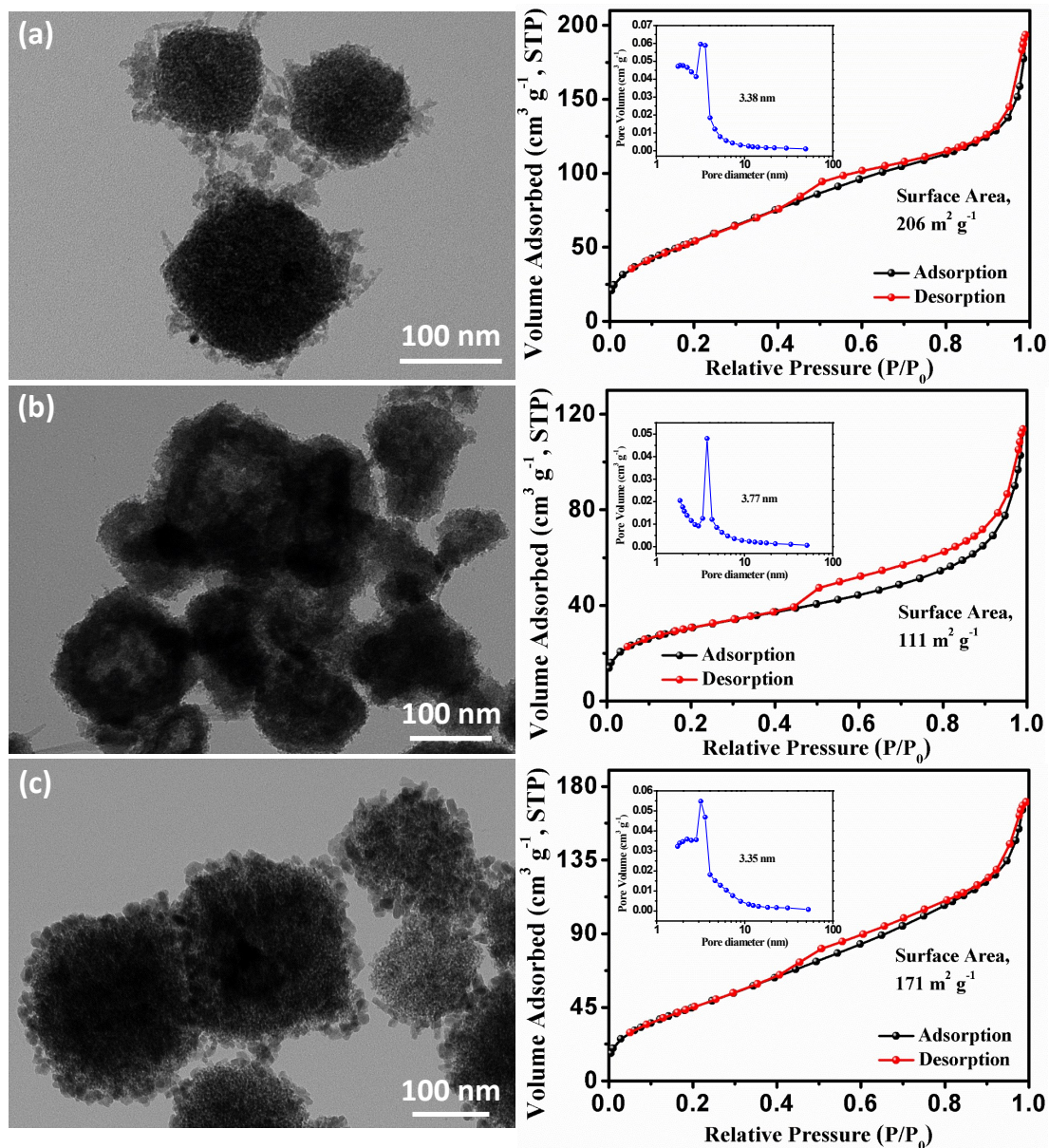


Fig. S5 TEM images and the corresponding Nitrogen adsorption-desorption isotherms of ZSH treated in different solvents. (a) methanol, (b) ethylene glycol and (c) polyethylene glycol, molecular weight: 400 (Inset: the corresponding pore size distribution curves).

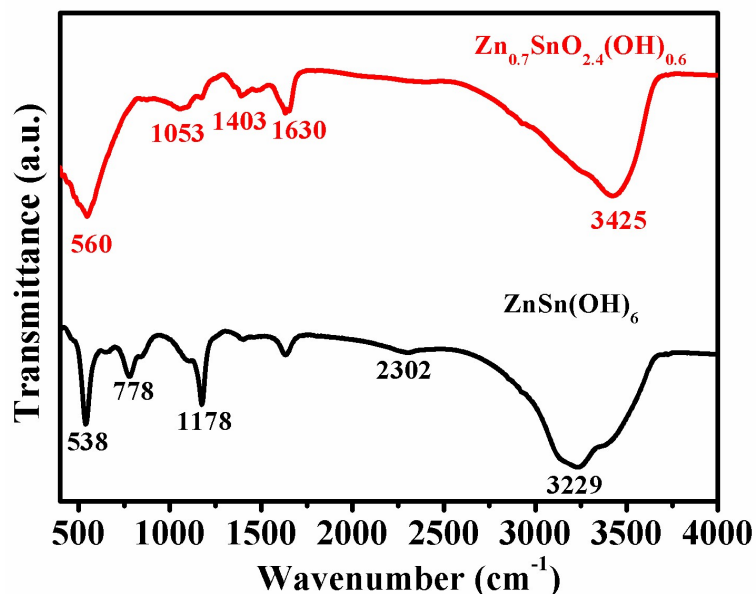


Fig. S6 FTIR spectra of ZnSn(OH)_6 precursors and mesoporous $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$ nanocubes.

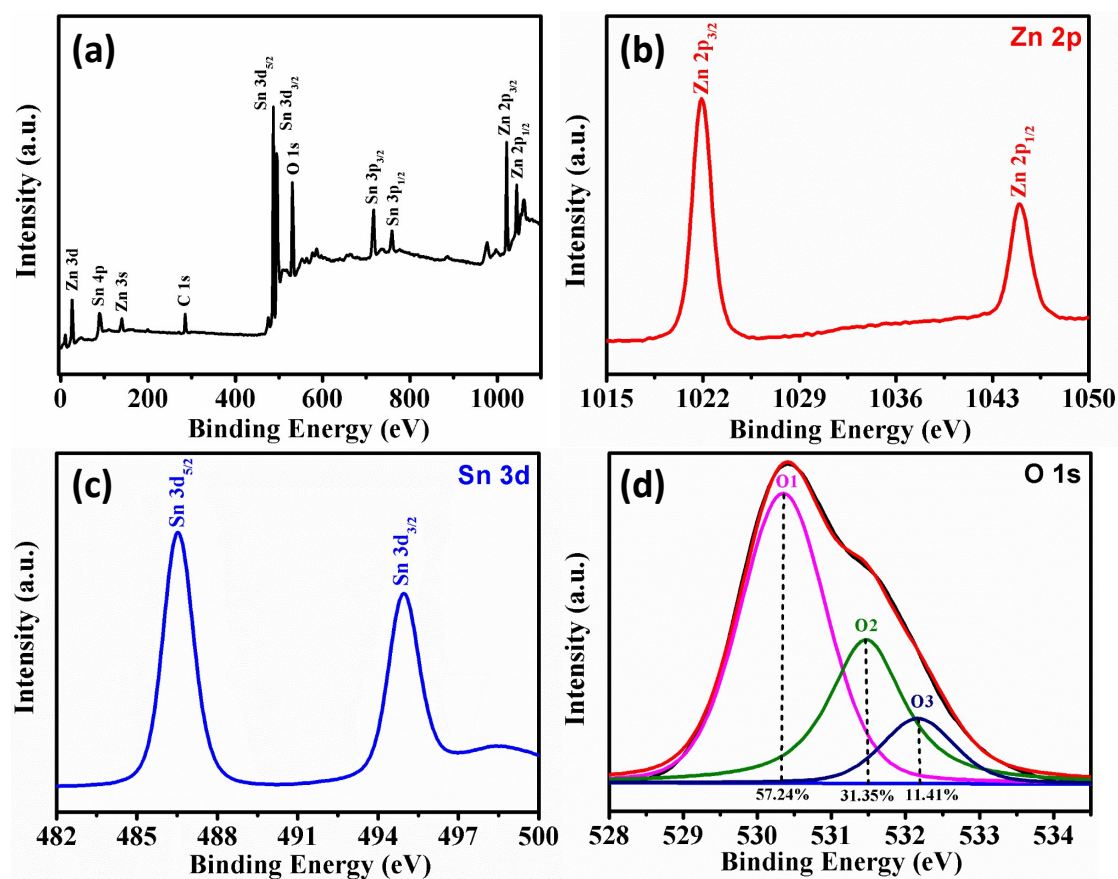


Fig. S7 XPS spectra of mesoporous $\text{Zn}_{0.7}\text{SnO}_{2.4}(\text{OH})_{0.6}$ sample: (a) survey spectrum, high-resolution XPS spectra of (b) Zn 2p, (c) Sn 3d and (d) O 1s.

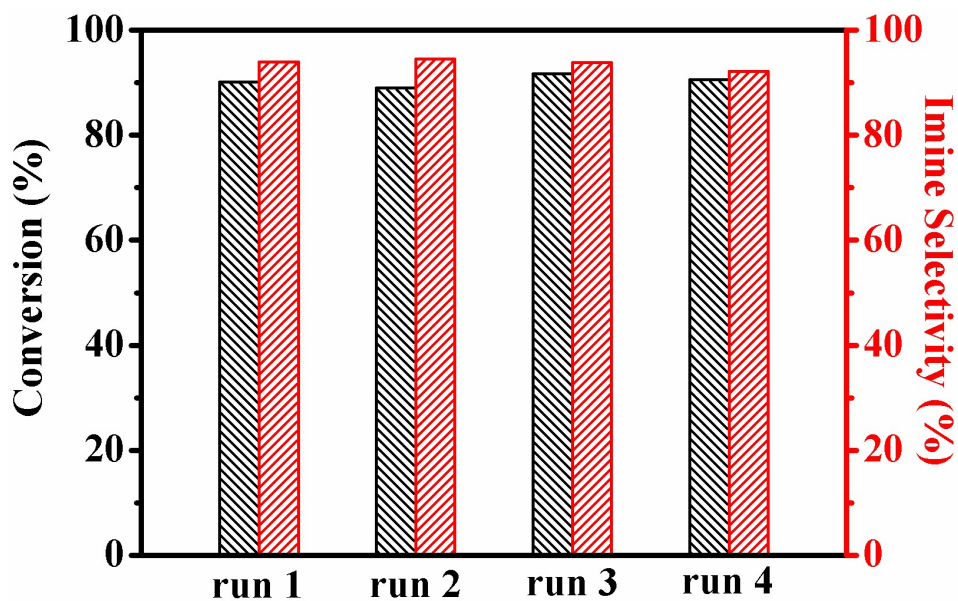


Fig. S8 Evaluation of the conversion in the benzylamine aerobic oxidative coupling over $\text{Zn}_{0.7}\text{Sn}_{2.4}(\text{OH})_{0.6}$ nanocatalyst for four catalytic cycles. Reaction conditions: O_2 (1atm), temperature (60 °C), 300 W Xe lamp ($\lambda \geq 420$ nm); time (8 h).

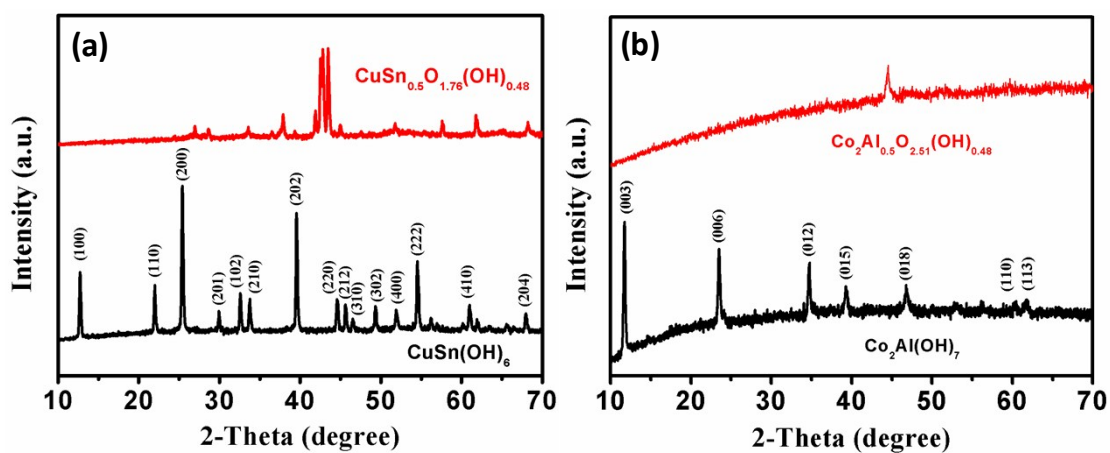


Fig. S9 XRD patterns of (a) $\text{CuSn}(\text{OH})_6$ and $\text{CuSn}_{0.5}\text{O}_{1.76}(\text{OH})_{0.48}$, (b) $\text{Co}_2\text{Al}(\text{OH})_7$ and $\text{Co}_2\text{Al}_{0.5}\text{O}_{2.51}(\text{OH})_{0.48}$.

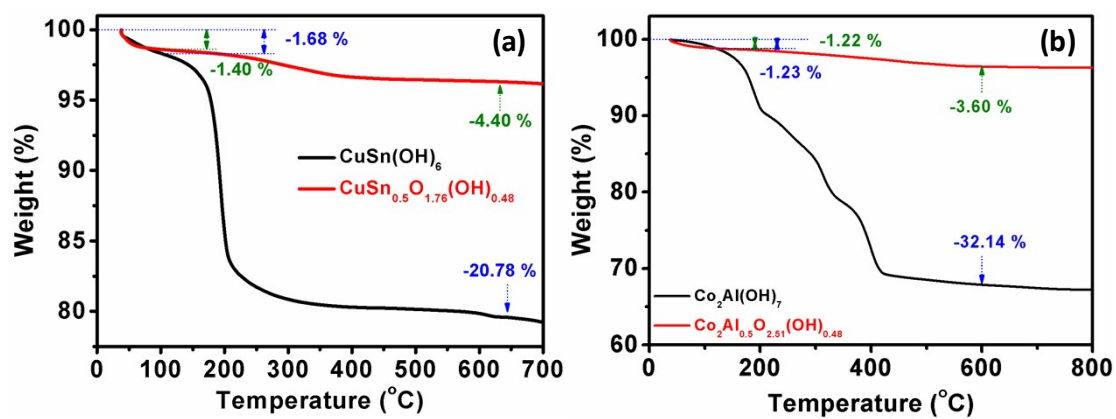


Fig. S10 Thermogravimetric curves of (a) CuSn(OH)₆ and CuSn_{0.5}O_{1.76}(OH)_{0.48} NRS, (b) Co₂Al(OH)₇ and Co₂Al_{0.5}O_{2.51}(OH)_{0.48} NSs measured in N₂ flow with a heating rate of 10 °C min⁻¹.