

Supporting Information

A General Route to High Surface Area Covalent Organic Frameworks and Their Metal Oxide Composites as Magnetically Recoverable Adsorbents and for Energy Storage

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1. Experimental Section

1.1. Materials

1,3,5-Triformylbenzene, 1,4-diaminobenzene, Fe₃O₄ (powder, particle size: 500-1200 nm, purity: 99%), Co₃O₄ (powder, mean size: 2-5 μm, purity: 99%), NiO (powder, mean size: 200-500 nm, purity: 99%), 1,4-dioxane, mesitylene, acetic acid, toluene, and methanol with A.R. and C.R. grades were purchased from Sigma-Aldrich and used as received.

1.2. Synthesis of COFs and Fe₃O₄, Co₃O₄, and NiO-based COF Composites

Firstly, 81 mg 1,3,5-Triformylbenzene and 81 mg 1,4-diaminobenzene were placed in a mortar (diameter: 75 mm). Three droplets (one droplet: 60 μL) of 1,4-dioxane and three droplets of 6 M acetic acid were added and then grinded for 2 h. Soxhlet of the product with acetone afforded amorphous polymer precursor i.e. COF-0d. Secondly, 80 mg COF-0d was added into 6.4 mL 1,4-dioxane/mesitylene (4/1) mixture, and then sonicated 2 min. After added 1.3 mL water and 1.9 mL ice acetic acid, the mixture was undergo crystallization for 3, 5, and 7 days. Washing the product by toluene and methanol afforded crystal COF-3d, COF-5d, and COF-7d, respectively. Following the procedure, adding Fe₃O₄ powders during mechanical grinding offered Fe₃O₄/COF composites i.e. Fe₃O₄/COF-0d, Fe₃O₄/COF-3d, Fe₃O₄/COF-5d, and Fe₃O₄/COF-7d; replacing Fe₃O₄ powders with Co₃O₄ or NiO afforded Co₃O₄ and NiO-based COFs.

2. Characterization and Measurements

2.1. Material Characterization

Fourier transform infrared (FT-IR) spectra of samples as KBr pellets were taken on a Nicolet 670 spectrometer. Solid-state ¹³C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra were taken on an AVANCE400 spectrometer. Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer (40 kV, 30 Ma) using Cu Kα radiation ($2\theta = 2-70^\circ$). UV-vis adsorption spectra were obtained on a

Shanghai Metash UV-9000S. Thermal gravimetric analysis (TGA) was carried out on a TGA Q500 apparatus under a nitrogen atmosphere in the temperature range 30-900 °C (heating rate 10 °C/min). Scanning electron microscope (SEM) images were obtained on a HITACHI S-4800 and transmission electron microscope (TEM) images were obtained on a JEM-2100 TEM microscope. The content of iron in the polymers was analyzed using a Leeman Labs Prodigy inductively coupled plasma atomic emission spectrometer (ICP-AES). N₂ adsorption/desorption measurements at 77.4 K, CO₂ adsorption/desorption measurements at 273 and 298 K were performed after degassing the samples under high vacuum at 120 °C for 15 hours using a Micro ASAP2046 machine.

2.2. Electrochemical Measurements

The cyclic voltammetry (CV) scans was conducted in a conventional three-electrode cell configuration, employing platinum as the counter electrode, an aqueous Ag/AgCl as the reference electrode. The working electrode was prepared by mixing COF-5d or Fe₃O₄/COF-5d materials with carbon black and poly-tetrafluoroethylene (PTFE) binder at a mass ratio of 80:10:10. The potential range for CV scans was kept between -0.1 to 0.7 V (SCE vs. Ag/AgCl) at different scan rates. The galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were carried out in a two-electrode cell configuration with two same prepared electrodes bundled together. The GCD cycling experiments were conducted at room temperature using a LAND CT2001A battery testing system (Wuhan, China). All the experiments were carried out in 0.5 M H₂SO₄ solution at ambient temperature. The specific capacitance (C) from GCD measurements was calculated using the standard equation:

$$C = 2I\Delta t / (m\Delta V)$$

where C (F g⁻¹), I (A), Δt (s), m (g) and ΔV (V) represent the specific capacitance, the discharge current, the discharge time, the mass of the active materials in one electrode, and the potential window, respectively.

3. Supplementary Figures and Tables

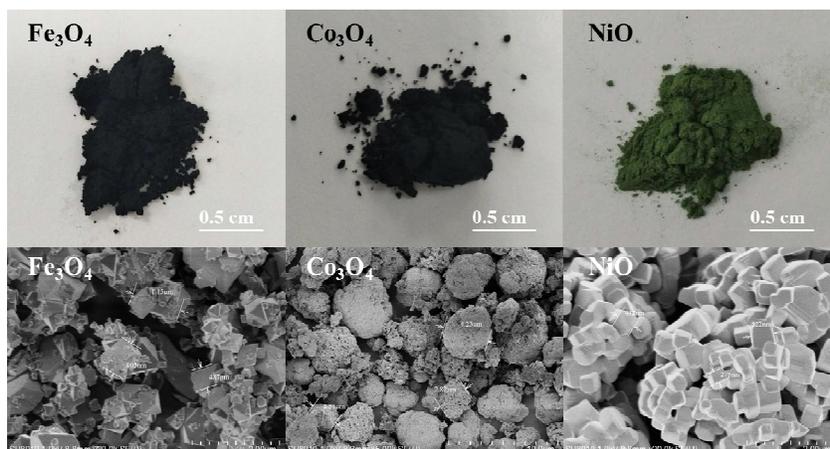


Figure S1 The appearances and SEM images of metal oxides used in this study.

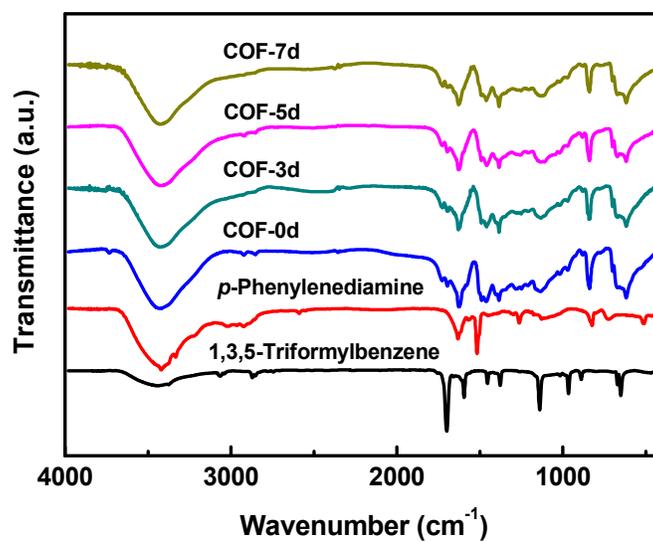


Figure S2 FT-IR spectra of COFs before and after crystallization.

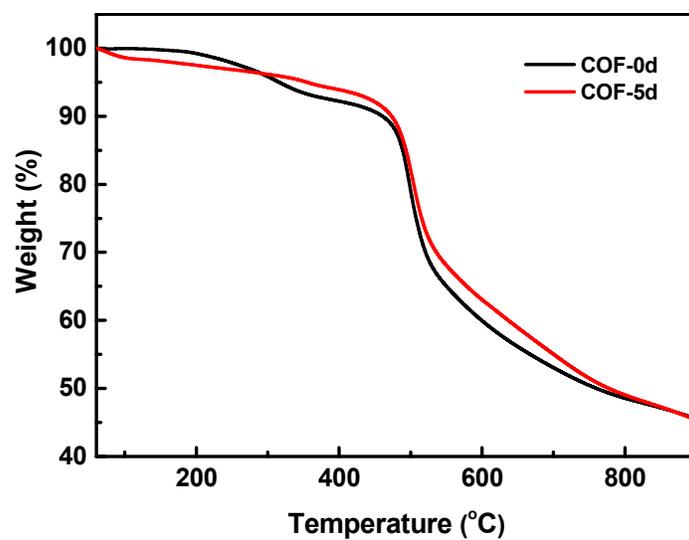


Figure S3 TGA scans of COF-0d and COF-5d.

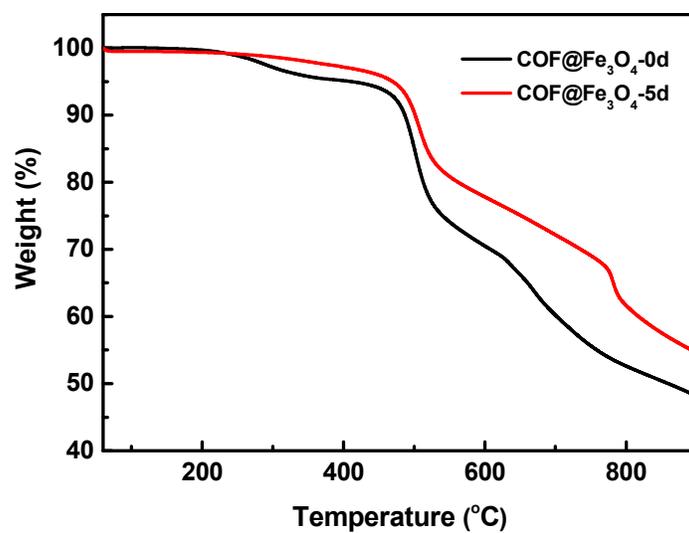


Figure S4 TGA scans of Fe₃O₄/COF-0d and Fe₃O₄/COF-5d.

Table S1 Porous properties of COFs and their Fe₃O₄ composites.

Samples	S _{BET} (m ² /g)	Pore size (nm) ^a	PV (cm ³ /g) ^b	CO ₂ (wt%, 1 bar)		HOA (kJ/mol) ^c
				273 K	298 K	
COF-0d	32	-	-	2.3	1.4	34.7
COF-3d	573	1.3	0.39	n.d.	n.d.	n.d.
COF-5d	1500	1.3	0.77	8.1	3.9	26.9
COF-7d	792	1.3	0.43	n.d.	n.d.	n.d.
Fe ₃ O ₄ /COF-0d	28	12.9	0.04	1.5	1.2	24.1
Fe ₃ O ₄ /COF-3d	389	1.3	0.28	n.d.	n.d.	n.d.
Fe ₃ O ₄ /COF-5d	872	1.3	0.45	7.3	3.5	20.4
Fe ₃ O ₄ /COF-7d	462	1.3	0.30	n.d.	n.d.	n.d.

a: determined by NLDFT method, b: determined by pores with pore width < 40 nm at $p/p_0 = 0.95$, c: determined at an adsorbed amount of 1.9 cm³/g.

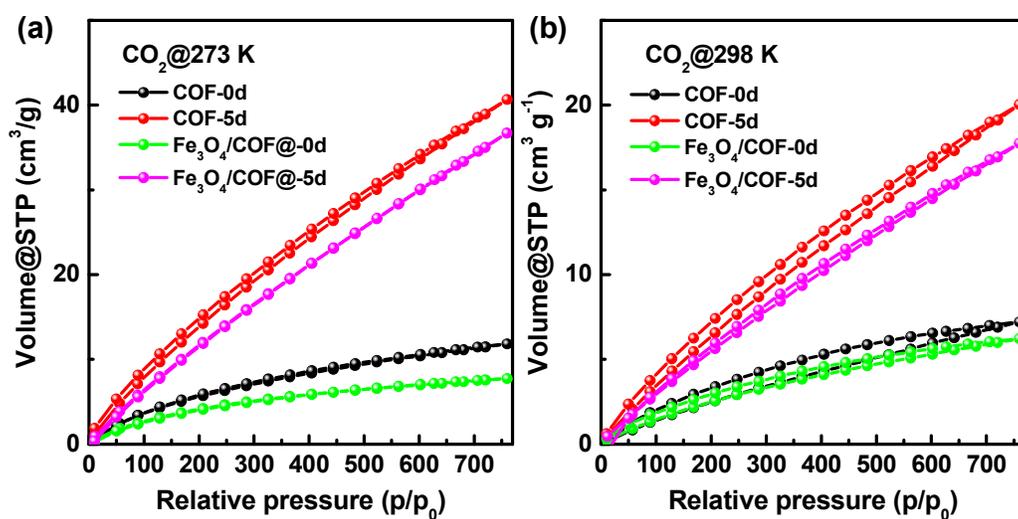


Figure S5 CO₂ adsorption/desorption isotherms of COF-0d, COF-5d, and Fe₃O₄/COF-5d at (a) 273 and (b) 298 K.

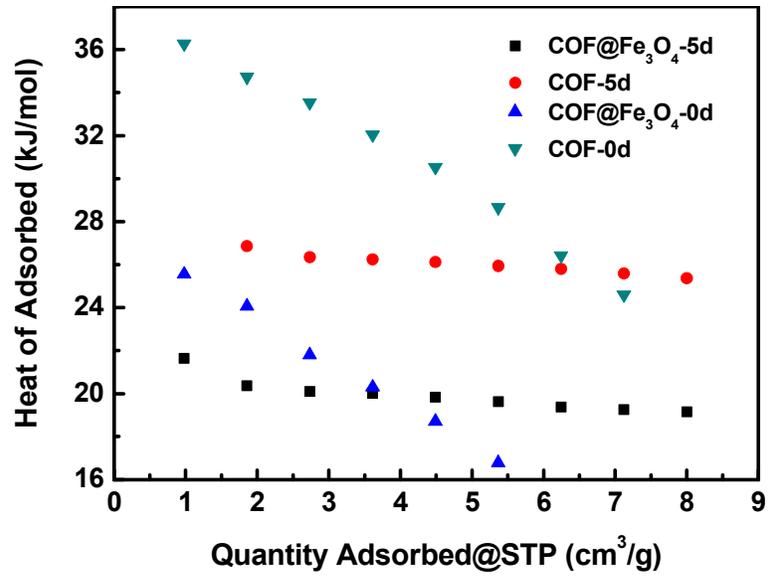


Figure S6 Heat of adsorption of COF-0d, COF-5d, and Fe₃O₄/COF-5d.

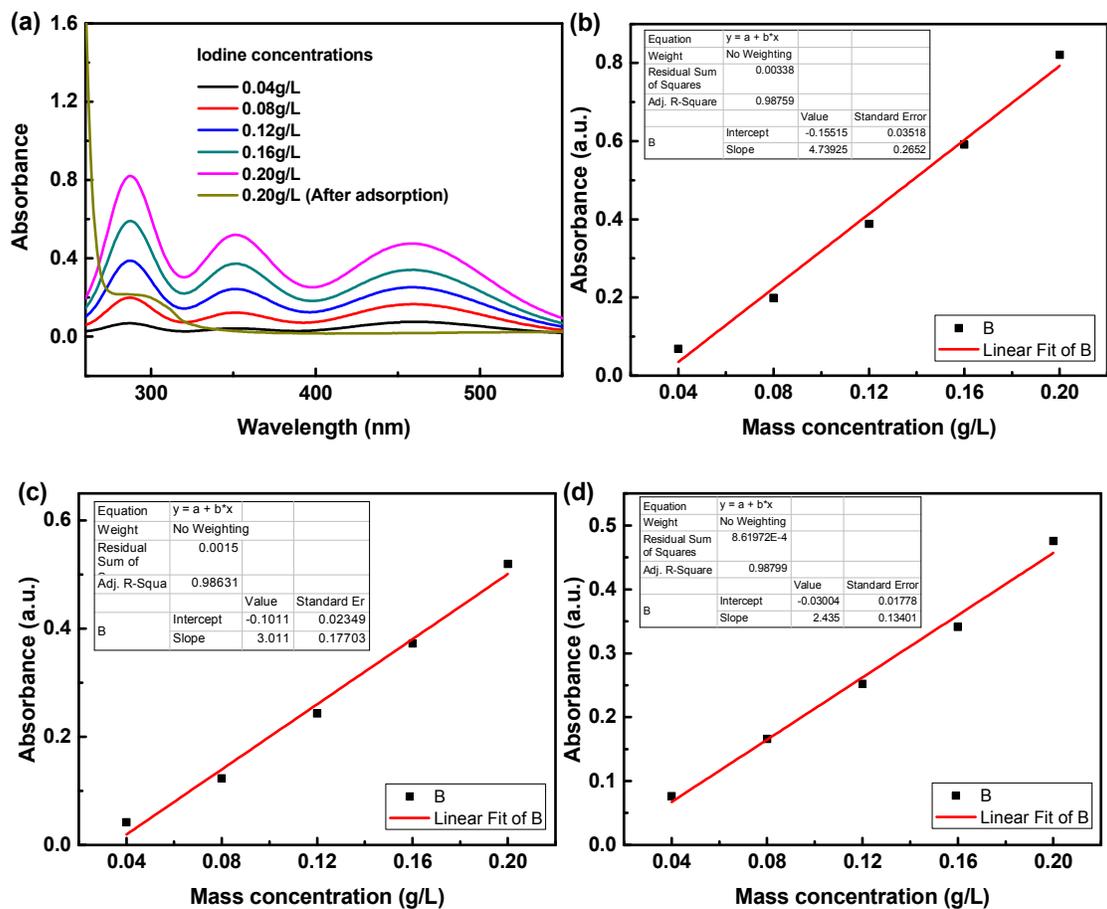


Figure S7 (a) UV-vis adsorption spectra of iodine aqueous solution with different mass concentrations, (b-d) the standard curves obtained *via* absorbance functions mass concentration of iodine aqueous solution, using the absorbance at 287 (b), 351 (c), and 460 nm (d), the adsorption ability of Fe₃O₄/COF-5d was determined by 797, 738, and 700 mg/g, respectively, upon using the corresponding standard curves.

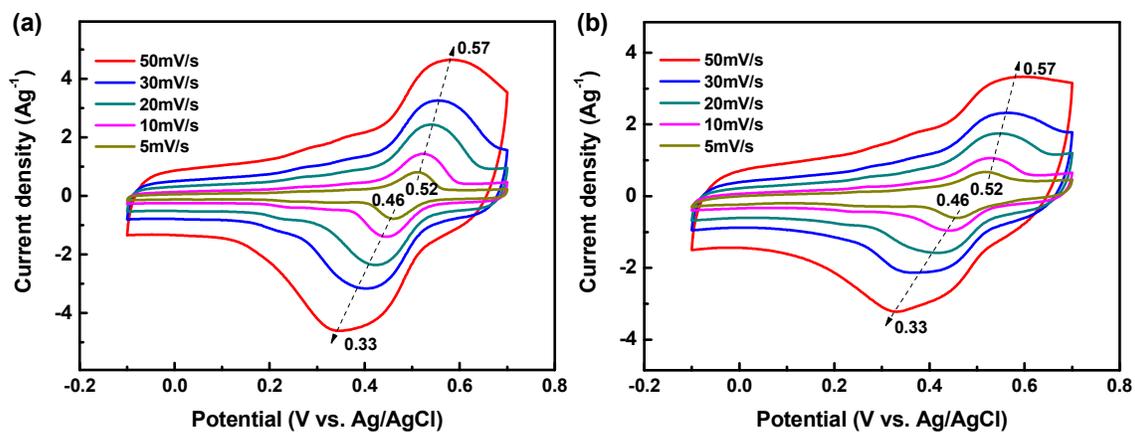


Figure S8 CV scans of (a) COF-0d and (b) COF-5d.

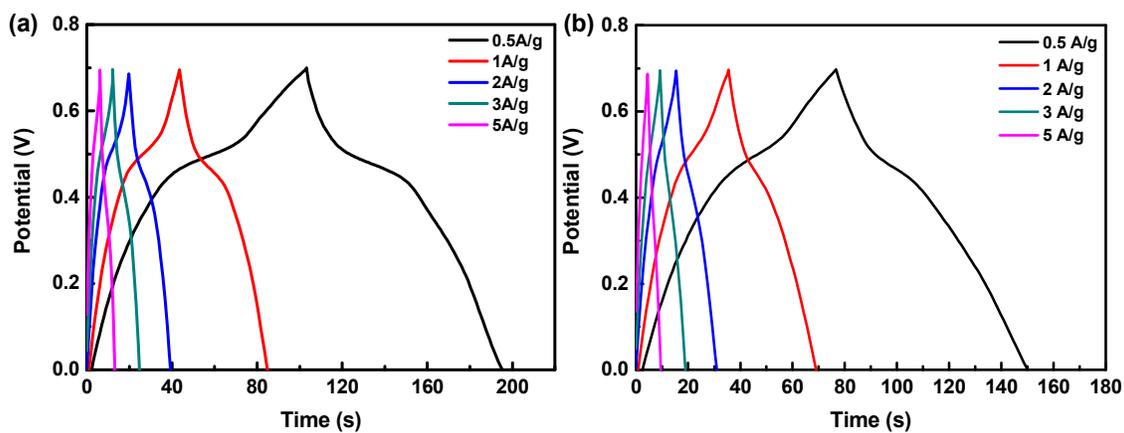


Figure S9 GCD curves of (a) COF-0d and (b) COF-5d.

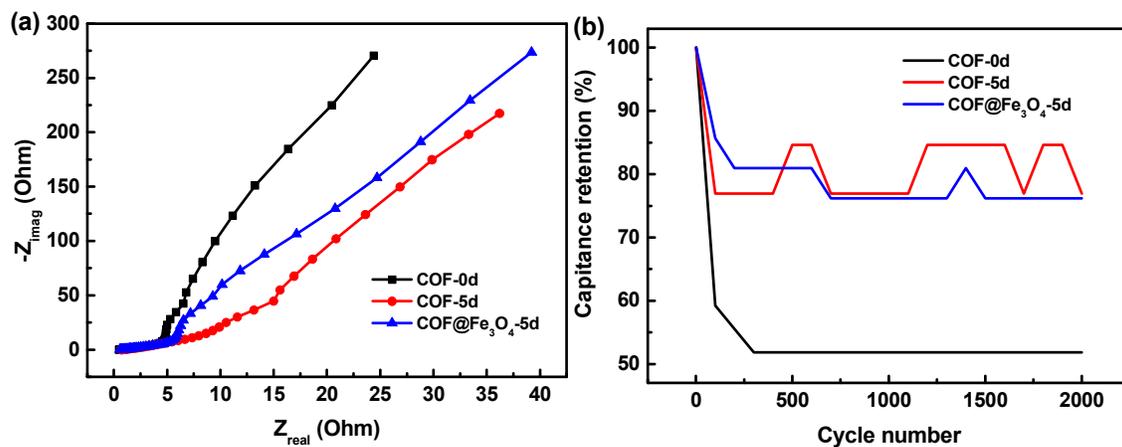


Figure S10 (a) Nyquist plots and (b) cyclability tests of COF-0d, COF-5d, and Fe₃O₄/COF-5d.

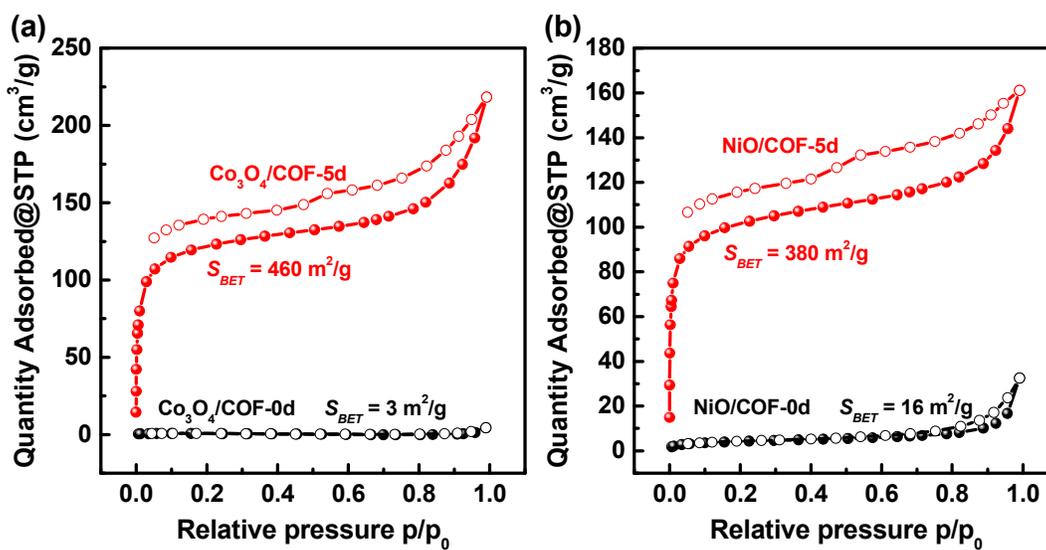


Figure S11 N₂ adsorption/desorption isotherms of (a) Co₃O₄/COF-0d and Co₃O₄/COF-5d and (b) NiO/COF-0d and NiO/COF-5d composites.

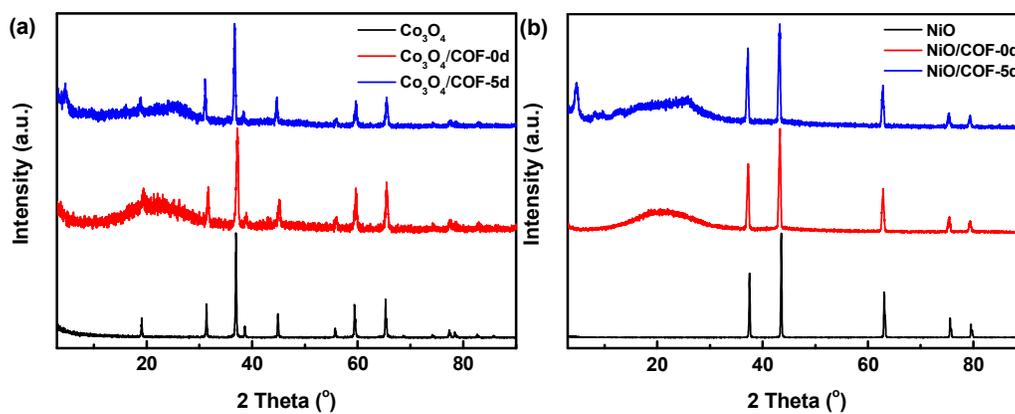


Figure S12 Powder XRD patterns of (a) Co₃O₄/COF-0d and Co₃O₄/COF-5d and (b) NiO/COF-0d and NiO/COF-5d composites, Co₃O₄ and NiO are also showed for comparisons.