

Supporting Information

Construction of PPIL@COF Core–Shell Composite with Enhanced Catalytic Activity for CO₂ Conversion

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Section 1. Material and Instrumentation

Divinylbenzene (DVB, mixtures of isomers, 78~80% grade) was distilled under vacuum and azobisisobutyronitrile (AIBN) was recrystallized in ethanol before use. 1-vinylimidazole, 2-bromoethylamine hydrobromide and terephthalaldehyde (Tp) were bought from Adamas Reagent, Ltd. 1,3,5-Tris-(4-aminophenyl)triazine (TAPT) and 2,5-dihydroxyterephthalaldehyde (DHTP) were bought from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. Solvents (AR grade) were obtained from Beijing Chemical Works. Powder X-ray diffraction (PXRD) was conducted on the PANalytical X'Pert PRO MPD with Cu K α radiation ($\lambda = 0.1541$ nm), from $2\theta = 2.5^\circ$ to 30° with 0.02° increments at room temperature. The N₂ sorption isotherms were measured on an automatic volumetric adsorption equipment (Micromeritics ASAP 2020) at 77 K. Prior to the measurements, the samples were activated under vacuum at 120 °C for 10 h. The Brunauer-Emmett-Teller (BET) method was applied for the specific surface areas and pore volume. Pore size distribution was obtained through the nonlocal density functional theory (NLDFIT) method. CO₂ adsorption measurements were recorded using a Quantachrome Nova 4000e. The Fourier transform infrared (FT-IR) spectra were collected on a Thermo Nicolet 380 with KBr tableting method in a range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. The ¹H and ¹³C NMR data were detected *via* a Bruker Avance III 600 MHz spectrometer. The CP-MAS ¹³C NMR measurements were carried out with a Bruker AVANCE III HD 500MHz spectrometer. The morphologies and structures were investigated by the Hitachi SU8020 Field emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 5 kV

and all the samples were mounted on a carbon tape and coated with gold prior to measurement. Transmission electron microscopy (TEM) images were obtained with JEM-2100F at 200 kV. Thermogravimetric analysis (TGA) was performed on the Shimadzu TA-60WS Thermal analyser in a range of 30~500 °C with a heating rate of 10 °C min⁻¹ under nitrogen. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250Xi spectrometer by get the sample on the aluminized sheet.

Section 2. Figures S1-S13

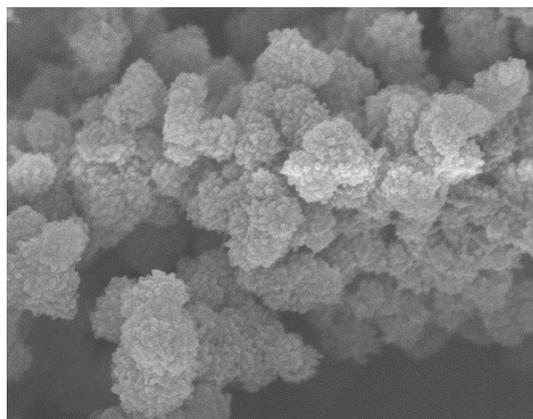


Fig. S1 The SEM images of PPIL@COFA-20.

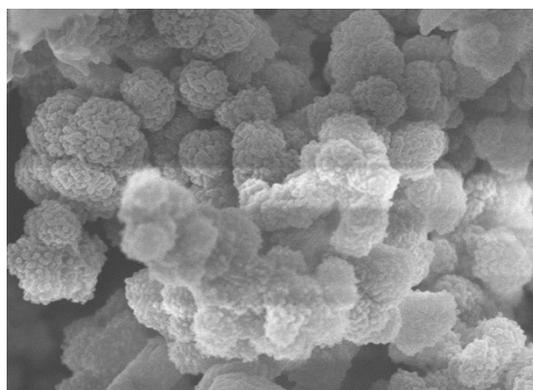


Fig. S2 The SEM images of PPIL@COFA-60.

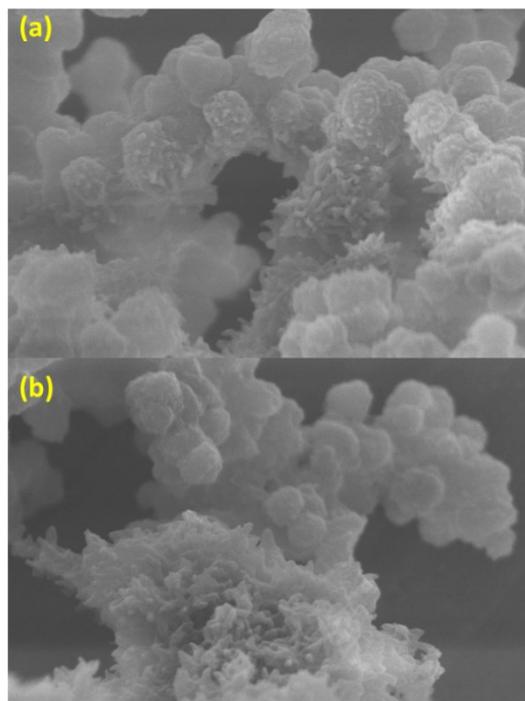


Fig. S3 SEM image of the hybrids directly using PPIL as without surface functionalization. (a): inhomogeneous growth of COF on the surface of PPIL, (b): uncontrollable bulk COF and PPIL.

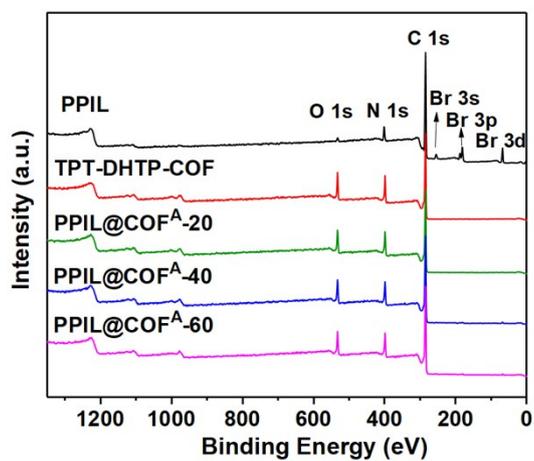


Fig. S4 The survey XPS spectra of TPT-DHTP-COF, PPIL and PPIL@COF^A hybrids.

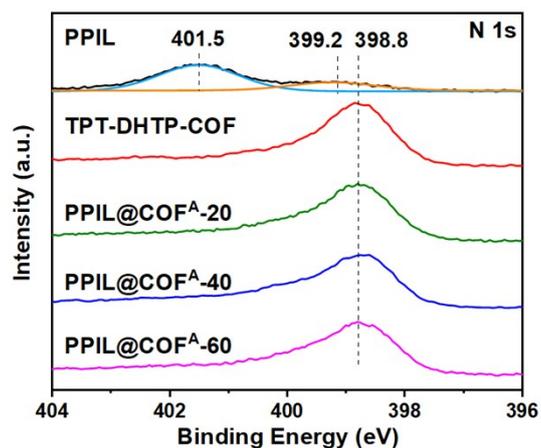


Fig. S5 N 1s XPS spectra of TPT-DHTP-COF, PPIL and PPIL@COF^A hybrids.

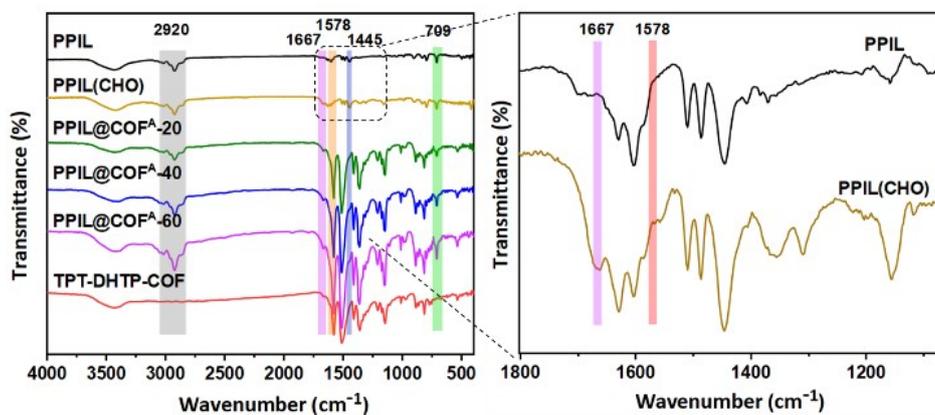


Fig. S6 FT-IR spectrum of TPT-DHTP-COF, PPIL, PPIL(CHO) and PPIL@COF^A hybrids.

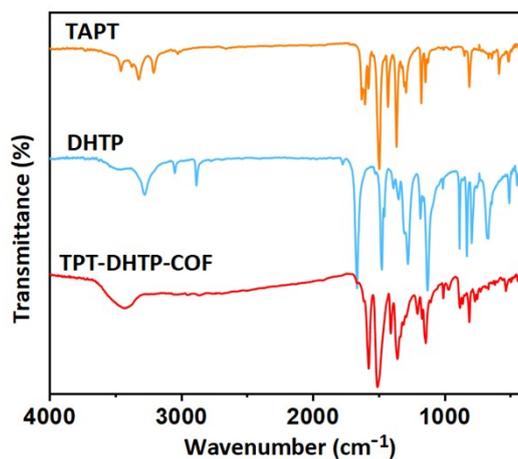


Fig. S7 FT-IR spectra of TAPT, DHTP and TPT-DHTP-COF.

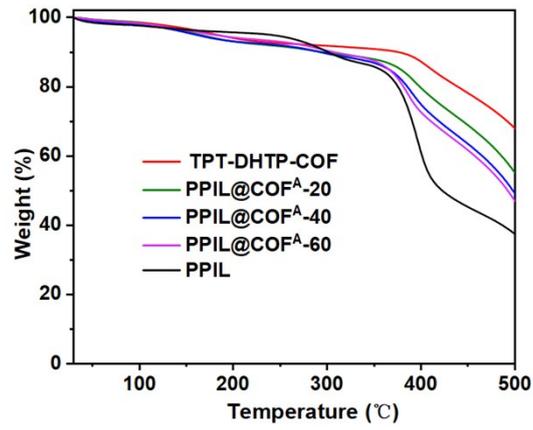


Fig. S8 TGA curve of PPIL, TPT-DHTP-COF and PPIL@COF^A hybrids.

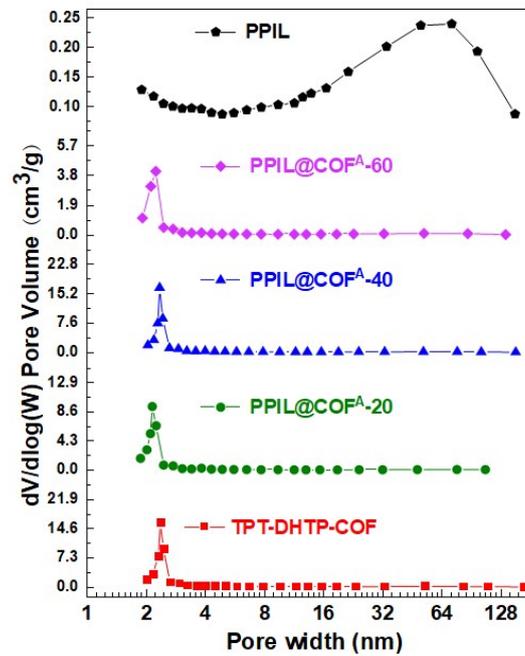


Fig. S9 Pore width distributions of PPIL, TPT-DHTP-COF and PPIL@COF^A hybrids.

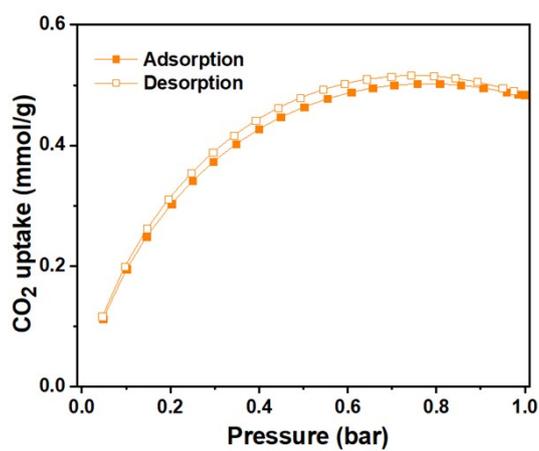


Fig. S10 CO₂ adsorption isotherms of PPIL@COF^B-40.

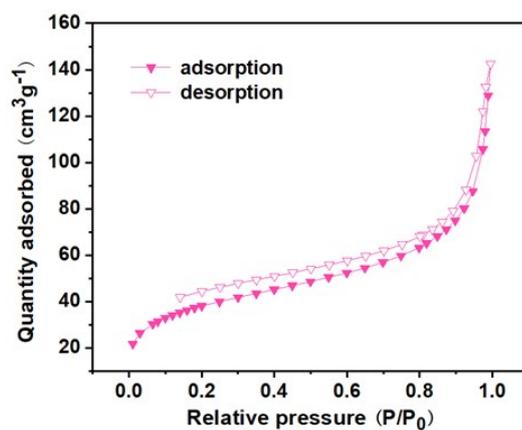


Fig. S11 BET studies on PPIL@COF^B-40.

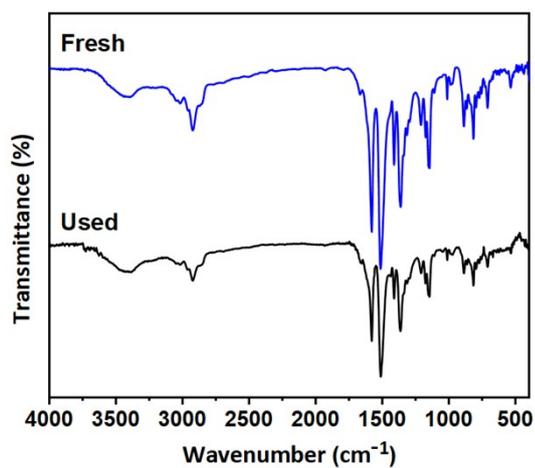


Fig. S12 FT-IR spectra of the PPIL@COF^A-40 before use (fresh) and after use for five runs (used).

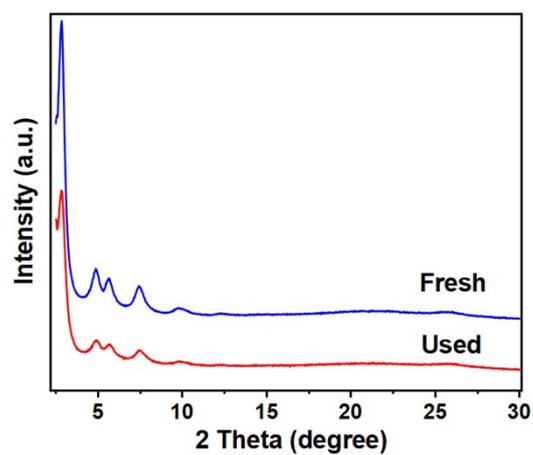


Fig. S13 XRD spectra of the PPIL@COF^A-40 before use (fresh) and after use for five runs (used).

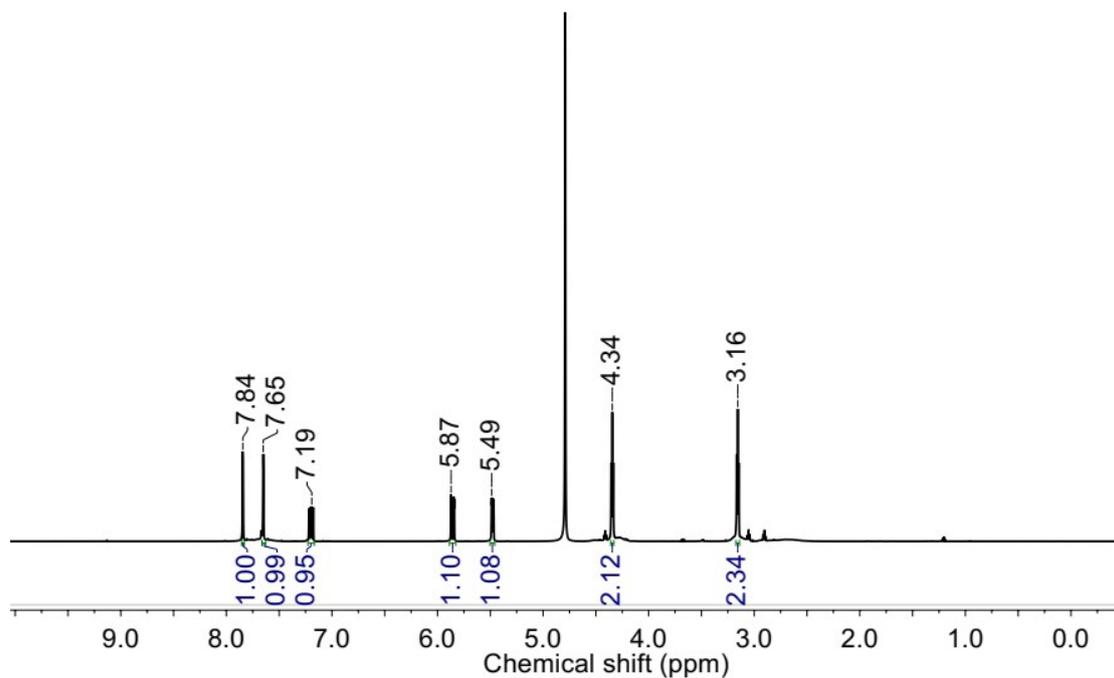
Section 3. Tables S1

Table S1. Bromine mass fraction of PPIL and varied PPIL@COF hybrids.

Entry	Catalyst	Br element content (wt.%)	Loading amount (mmol/g)
1	PPIL	5.67	0.71
2	PPIL@COF ^A -20	1.84	0.23
3	PPIL@COF ^A -40	2.72	0.34
4	PPIL@COF ^A -60	3.36	0.42
5	PPIL@COF ^B -40	3.04	0.38

Section 4. NMR spectrum

^1H NMR (600 MHz, $\text{D}_2\text{O}-d_2$, 298 K): $\delta = 7.84$ (s, 1H), 7.65 (s, 1H), 7.19 (m, 1H), 5.87 (m, 1H), 5.49 (m, 1H), 4.34 (m, 2H), 3.16 (m, 2H).



NMR Spectrum 1 ^1H NMR (600 MHz, $\text{D}_2\text{O}-d_2$, 298K) of [AVIM]Br.