

Electronic Supplementary Information

Post-modified porphyrin imine gels with improved chemical stability and efficient heterogeneous activity in CO₂ transformation

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Experimental Section

Materials and methods. Concentrated HCl, concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$, DMSO and glyoxal water solution (40%) were purchased from Damao Chemical Reagent Factory (Tianjin, China), reagents (epoxides, *p*-nitrobenzaldehyde, acetic anhydride, propionic acid, freshly distilled pyrrole, pyridine, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) were obtained from Aladdin (Shanghai, China), PdCl_2 (99%) was purchased from HWRK Chem. Co., LTO (Beijing, China). The free-base porphyrin H_2TAPP was synthesized¹ and subsequently metallated with metal salts ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and PdCl_2) to yield ZnTAPP,² CoTAPP³ and PdTAPP,⁴ respectively, according to the reported procedure. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis was performed using either a Quanta 400F SEM equipped with an INCA energy dispersive X-ray spectrometer or an ultra-high resolution SU8010 FE-SEM. Prior to SEM measurements, gel samples were dispersed in EtOH with the aid of sonication, and then deposited on a silicon plate. Transmission electron microscopy (TEM) investigations were carried out on a FEI Tecnai G2 Spirit 120 kV or 200 kV TEM system. To prepare a sample for TEM measurement, wet gel was dispersed in EtOH using sonication method, and then mounted on a carbon coated copper grid. The absorption spectra were observed with a Shimadzu UV-3600 spectrometer (slit width 5.0 mm). Samples were dispersed in EtOH with the aid of sonication, and then drop on the disc of barium sulfate for testing. X-ray diffraction (XRD) was recorded on a Rigaku Smart Lab diffract meter (Bragg-Brentano geometry, Cu- $K\alpha_1$ radiation, $\lambda = 1.54056 \text{ \AA}$). Cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectroscopy was performed on a Bruker Ascend 300 MHz spectrometer (MAS probe with 4 mm outside diameter, zirconia rotors). Infrared spectra of the aerogels were taken in a KBr disc with nujol on a Nicolet/Nexus-670 FT-IR spectrometer in the range of 4000–450 cm^{-1} . N_2 adsorption–desorption isotherms were measured at 77 K with a Quantachrome Autosorb-iQ analyzer. Prior to analysis, the as synthesized materials were typically degassed at 100 °C for 10 h to remove the solvated molecules. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett–Joyner–Halenda (BJH) model, the volume and size distribution of the mesopores were derived from the adsorption branches of isotherms. The volume and size distribution of the micropores were calculated by the Horvath–Kawazoe (HK) theory.

Synthesis of ZnTAPP. ZnTAPP was prepared following a modified literature procedure.² H_2TAPP (100 mg, 148 μmol) was dissolved in DMF-CHCl_3 (60 mL, *v/v* 1:3), and a solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (130 mg, 593 μmol) in MeOH (100 mL) was added. The resulting reaction mixture was heated under reflux for 24 h. After cooled down to room temperature, the mixture was washed with water (15 mL \times 3), and filtered to yield ZnTAPP as green solid (45 mg, 41%). ^1H NMR ($\text{DMSO-}d_6$, 400 MHz): 8.83 (8H, s, β -pyrrole H), 7.81 (8H, d, $J = 7.92$, Ph-H meta to NH_2), 6.97 (8H, d, $J = 7.92$, Ph-H ortho to NH_2), 5.44 (8H, s, NH_2).

Synthesis of CoTAPP. CoTAPP was prepared following a modified literature procedure.³ H₂TAPP (75 mg, 0.11 mmol) was dissolved in CH₂Cl₂ (15 mL), and a solution of CoCl₂·6H₂O (493 mg, 2 mmol) in MeOH (7.5 mL) was added. The reaction mixture was stirred overnight at room temperature, and then the reaction mixture was washed with water (15 mL × 3) and 10% NaHCO₃ (10 mL), dried over Na₂SO₄, and the solvent was evaporated and resulting solid was collected as purple crystals (64 mg, 80%). UV-vis (in DMF): 436, 550, 600 nm. MS (MALDI-TOF): *m/z* found (calcd.) for C₄₄H₃₂N₈Co (M⁺): 731.283 (731.208).

Synthesis of H₂TAPP-GO gel. A solution of glyoxal (6.8 μL, 40%) in DMSO (0.5 mL) was added into a solution of H₂TAPP (0.03 mmol, 20.2 mg) in DMSO (0.5 mL), and then HOAc (30 μL, 3 mol L⁻¹ in DMSO) was added whilst stirring. Heating the precursor solution at 80 °C gave a brown gel within 4 h. The resulting gel was further aged for 24 h. The gel was subsequently washed with DMSO (8 mL × 3) at RT. DMSO was replaced every day by fresh solvent and solvent exchange was finished after three days. Then the gel was washed with anhydrous EtOH (8 mL × 3) for three days in similar way. The gel was then placed in a high-pressure Soxhlet stainless-steel autoclave extractor (0.75 L). The solvent in the wet gel was extracted with liquid CO₂ (ca. 270 g) for 24 h, and the extraction temperature was kept at 35.0 °C (pressure 5.9 MPa). After the extractor was depressurized slowly at room temperature over ca. 2–3 h, H₂TAPP-GO aerogel was obtained (20.4 mg, 96%).

Following similar procedures, ZnTAPP-GO aerogel (21.6 mg, 96%), CoTAPP-GO aerogel (12.2 mg, 56%) and PdTAPP-GO aerogel (16.2 mg, 66%) were prepared from ZnTAPP, CoTAPP and PdTAPP, respectively.

Synthesis of H₂TAPP-GO-r gel. The above H₂TAPP-GO gel reacted with a saturated ethanol solution of NaCNBH₃ (5 mL) at RT for three days. The NaCNBH₃ solution was replaced every day and solvent exchange was finished after three days. Then the gel was washed with anhydrous EtOH (9 mL × 3), and a H₂TAPP-GO-r gel was obtained. After subcritical CO₂(l) drying H₂TAPP-GO-r aerogel was obtained (20.0 mg, 93%).

Synthesis of ZnTAPP-GO-r. H₂TAPP-GO-r (0.03 mmol, 1.0 equiv) was dissolved in CH₂Cl₂-MeOH (v/v 9:1, 15 mL). After the solution was refluxed at 75 °C, Zn(OAc)₂·2H₂O (30mg, 1.5 equiv) was added into the flask, stirring at 75 °C overnight. After cooling down to room temperature, the resulting mixture was filtered, washed with water (5 mL × 3), exchanged with EtOH (5 mL × 3). Finally, a dark green gel was obtained. After subcritical CO₂(l) drying ZnTAPP-GO-r aerogel was obtained (14.6 mg, 63%).

Synthesis of CoTAPP-GO-r. H₂TAPP-GO-r (0.03mmol) and CoCl₂·6H₂O (30m g) were added into degassed DMF (ca. 5 mL) at 120 °C under Ar atmosphere in sequence. After reaction for 12 h, the mixture was cooled down to room temperature, and then 10% NaHCO₃ (5 mL) was added

slowly in air. After filtering, washing with water (10 mL), and EtOH (10 mL), CoTAPP-GO-r was obtained as brown gel. After subcritical CO₂(l) drying CoTAPP-GO-r aerogel was obtained (11.2 mg, 49%).

Synthesis of PdTAPP-GO-r. H₂TAPP-GO-r (0.03mmol) and PdCl₂ (11mg, 0.067mmol) were added into degassed DMF (ca. 5 mL) at 120 °C under Ar atmosphere in sequence. After reaction for 24 h, the mixture was cooled down to room temperature. After filtering, washing with water (10 mL), and EtOH (10 mL), the PdTAPP-GO-r product was obtained as brown dark gel. After subcritical CO₂(l) drying PdTAPP-GO-r aerogel was obtained (16.2 mg, 56%).

Cycloaddition of CO₂ and styrene oxide. Reactions were carried out in a 10 mL tube equipped with a rubber septum. In a typical run, the reactor was charged with 3 mmol of styrene oxide, 0.03 mmol of TAPP-GO gel catalyst (prior to the reaction the gel was subjected to solvent exchange with DMSO (5 mL × 3) and EtOH (5 mL × 3) in sequence), 0.21 mmol of co-catalyst *n*-Bu₄NBr, and 1.5 mmol of 1-bromo-3,5-dimethylbenzene used as an internal standard. Carbon dioxide was first bubbled into the solution for 10 min to saturate the liquid phase, was then connected to the reaction tube to maintain an atmosphere pressure of carbon dioxide during the course of the reaction. The reaction mixture was placed in an oil bath at 100 °C. The reaction progress was monitored by GC (TECHCOMP 7890II) and NMR (AVANCE III 400 MHz).

Determination of Zn content. Typical procedure: 5.0 mg ZnTAPP-GO-r aerogel was destroyed by 5 mL aqua fortis and then the mixture was transferred to a flash for a further digestion at 80 °C. The amount of Zn content was determined by Atomic Absorption Spectroscopy (AAS, Hitachi Z-2000).

Determination of the content of imine bonds. 400 mg KBr was evenly ground, and 20 mg potassium bromide was taken for tablet preparation, 1, 2, 4, 6, 8, or 10 μL glyoxal aqueous solution (0.5 mg mL⁻¹) was dropped on the KBr film and then quickly FT-IR absorption spectra was collected on a Perkin-Elmer spectrometer. Then the standard curve of glyoxal was obtained. 7.0 mg of H₂TAPP-GO aerogel was added to 200 mg of KBr, ground uniformly. To guarantee the consistency, several different batches of gel catalyst were mixed. And then 20 mg of the mixture was taken for tablet preparation. FT-IR absorption analysis was performed on a Perkin-Elmer spectrometer. The sample was tested for three times.

References

- 1 A. Bettelheim, B. A. White, S. A. Raybuck and R. W. Murray, *Inorg. Chem.*, 1987, **26**, 1009-1017.
- 2 W. Meng, B. Breiner, K. Rissanen, J. D. Thoburn, J. K. Clegg and J. R. Nitschke, *Angew. Chem. Int. Ed.*, 2011, **50**, 3479-3483.
- 3 P. Muthukumar and S. A. John, *Electrochim. Acta*, 2014, **115**, 197-205.

4 L. Zeng, P. Liao, H. Liu, Z. Liang, J. Zhang, L. Chen and C. Y. Su, *J. Mater. Chem. A*, 2016, **4**, 8328-8336.

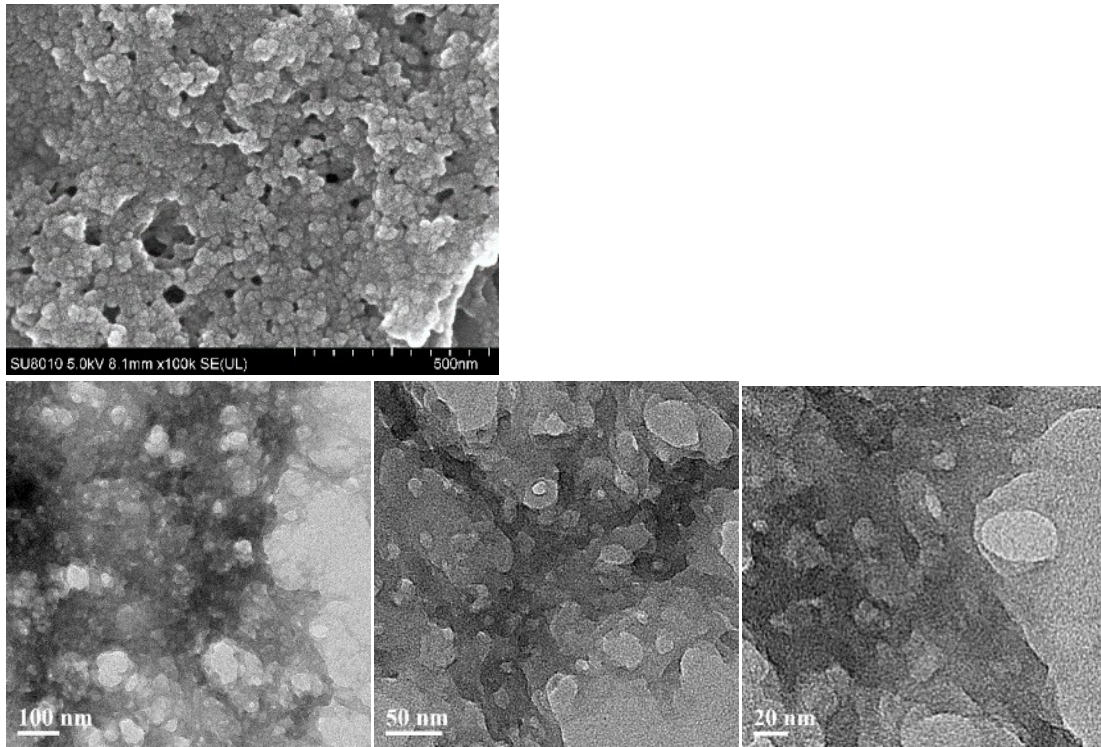


Fig. S1 SEM and TEM images of CoTAPP-GO gel (bars represent 500, 20, 50 and 100 nm, respectively).

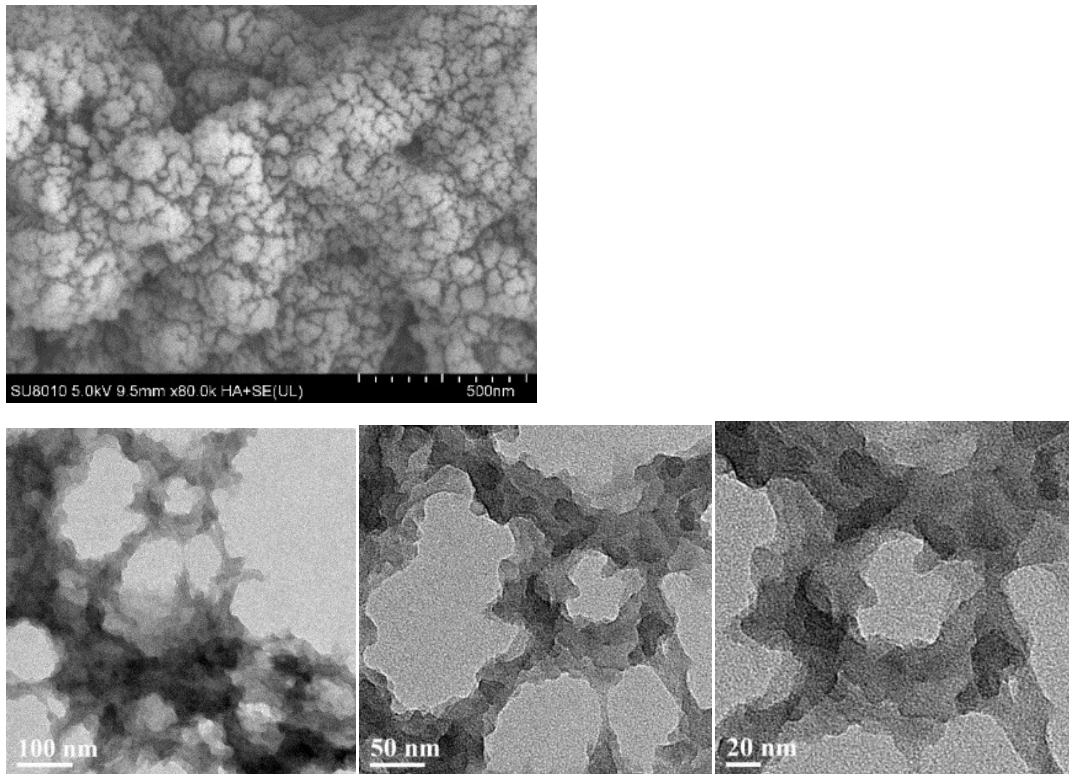


Fig. S2 SEM and TEM images of PdTAPP-GO gel (bars represent 500, 20, 50 and 100 nm, respectively).

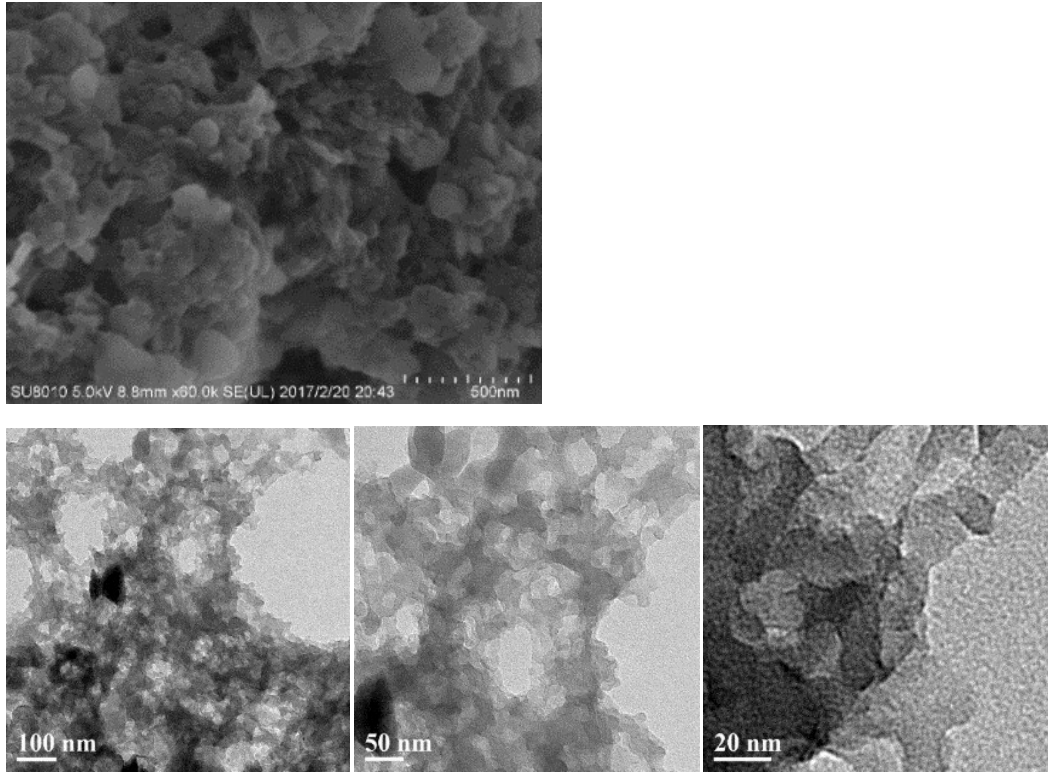


Fig. S3 SEM and TEM images of CoTAPP-GO-r gel (bars represent 500, 20, 50 and 100 nm, respectively).

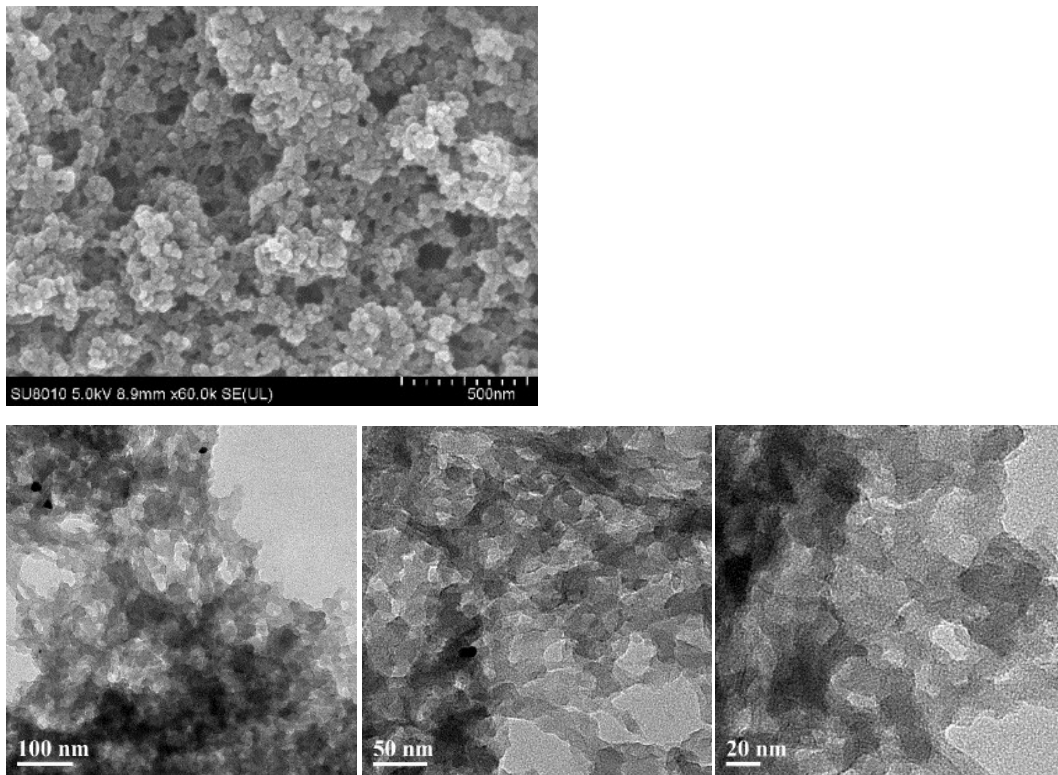
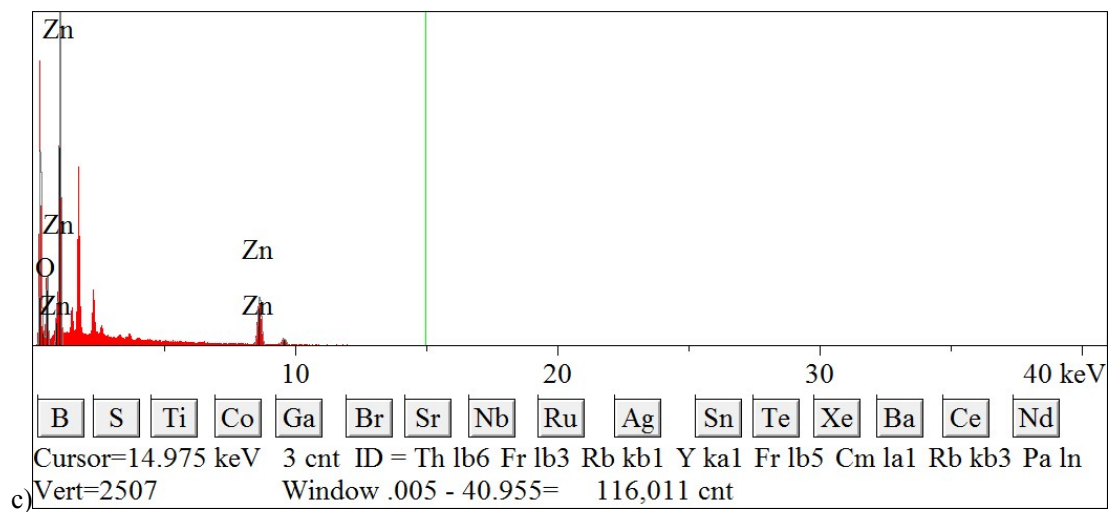
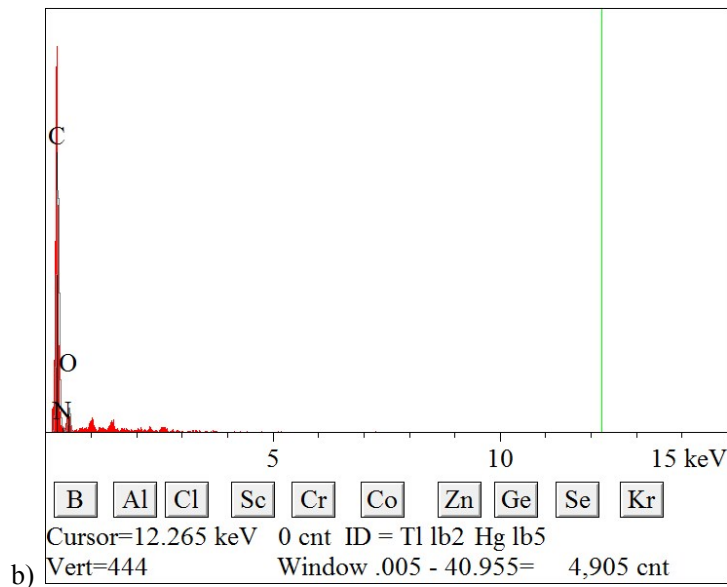
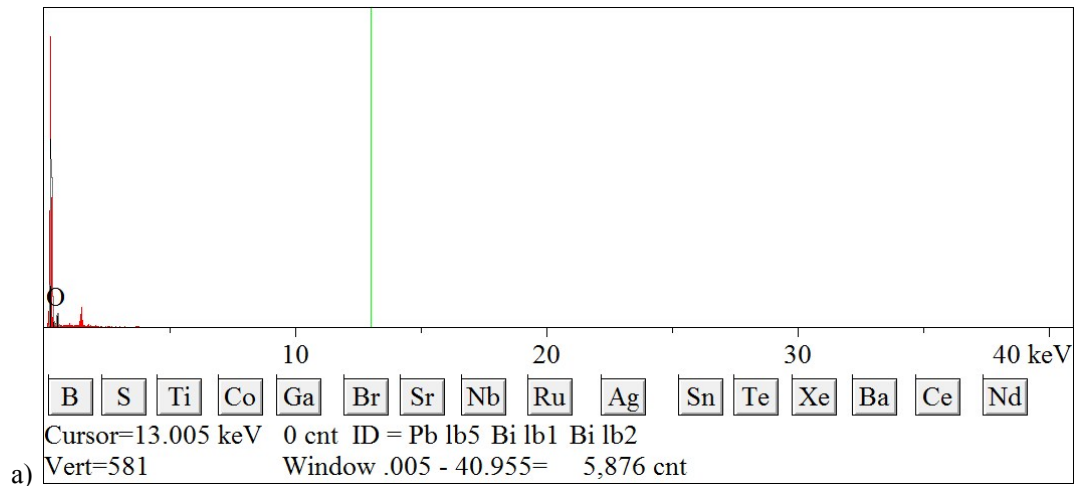
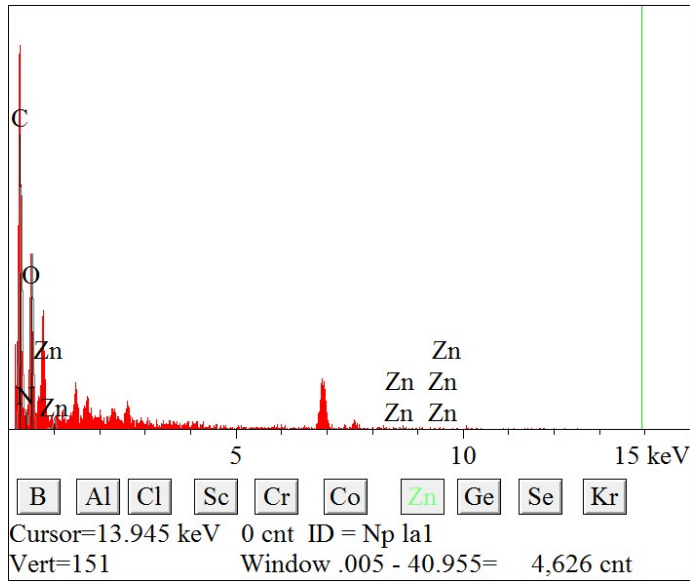
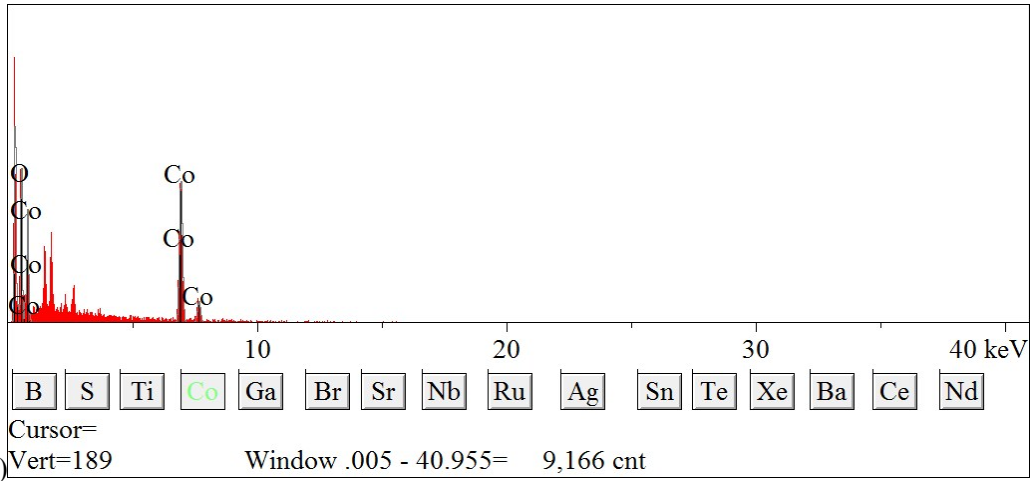


Fig. S4 SEM and TEM images of PdTAPP-GO-r gel (bars represent 500, 20, 50 and 100 nm, respectively).

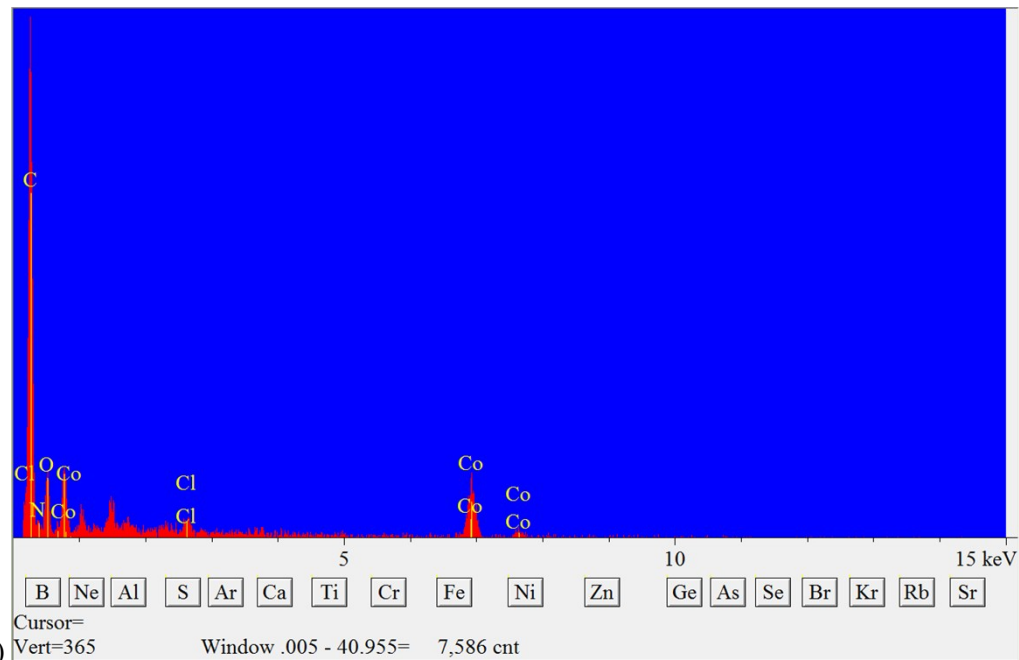




d)



e)



f)

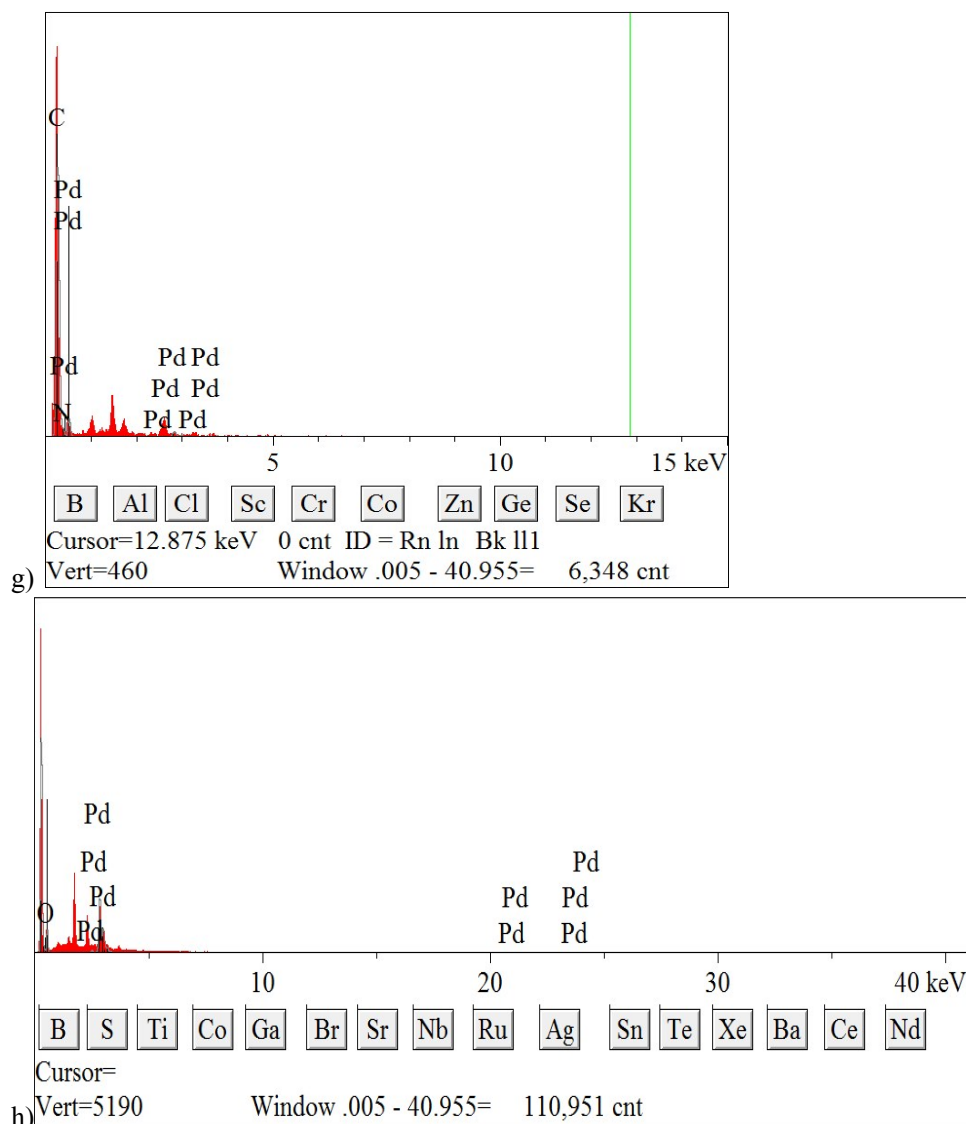


Fig. S5 Energy dispersive X-ray spectra of a) H₂TAPP-GO (Quantitative values/atom%: C 65.330, N, 16.127 and O 18.543); b) H₂TAPP-GO-r (Quantitative values/atom%: C 66.950 N, 12.511 and O 20.539); c) ZnTAPP-GO (Quantitative values/atom%: Zn 6.55, C 59.60, N,12.11 and O 21.74); d) ZnTAPP-GO-r (Quantitative values/atom%: Zn 1.361, C 44.295, N, 11.951 and O 42.394); e) CoTAPP-GO (Quantitative values/atom%: Co 9.57, C 48.51, N, 9.87 and O 32.05); f) CoTAPP-GO-r (Quantitative values/atom%: Co 3.817, C 49.323, N, 12.839, O 19.995, Cl 0.676); g) PdTAPP-GO (Quantitative values/atom%: Pd 0.758, C 66.404, N, 18.790 and O 14.047); h) PdTAPP-GO-r (Quantitative values/atom%: Pd 4.76, C 62.74, N, 15.99 and O 16.51).

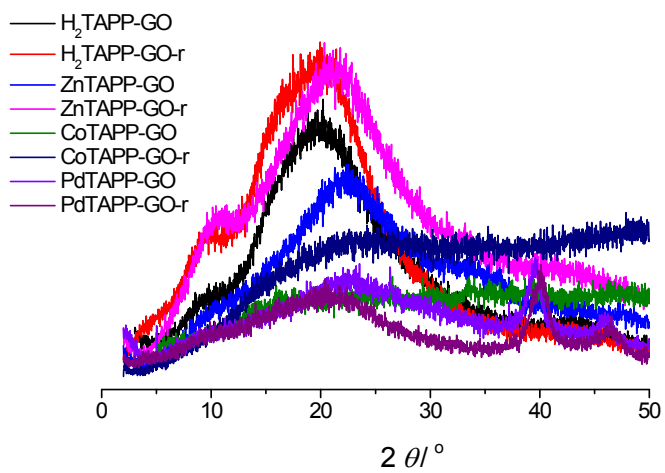


Fig. S6 PXRD patterns of a) H_2 TAPP-GO; b) H_2 TAPP-GO-r; c) ZnTAPP-G; d) ZnTAPP-GO-r; e) CoTAPP-GO; f) CoTAPP-GO-r; g) PdTAPP-GO; h) PdTAPP-GO-r wet gels.

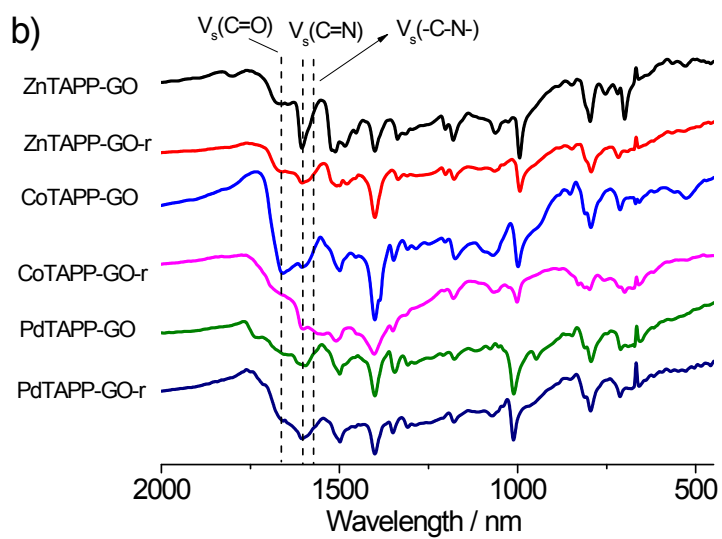
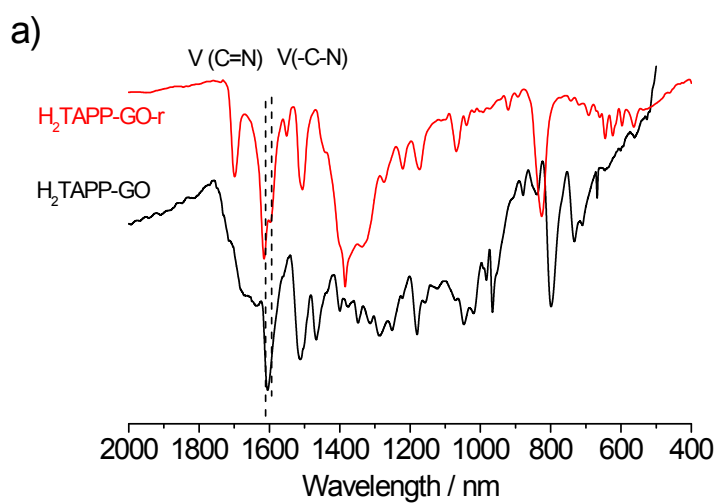


Fig. S7 FT-IR spectra of a) $H_2TAPP-GO$ and $H_2TAPP-GO-r$, b) $ZnTAPP-GO$ and $ZnTAPP-GO-r$, $CoTAPP-GO$, $CoTAPP-GO-r$, $PdTAPP-GO$ and $PdTAPP-GO-r$ aerogels.

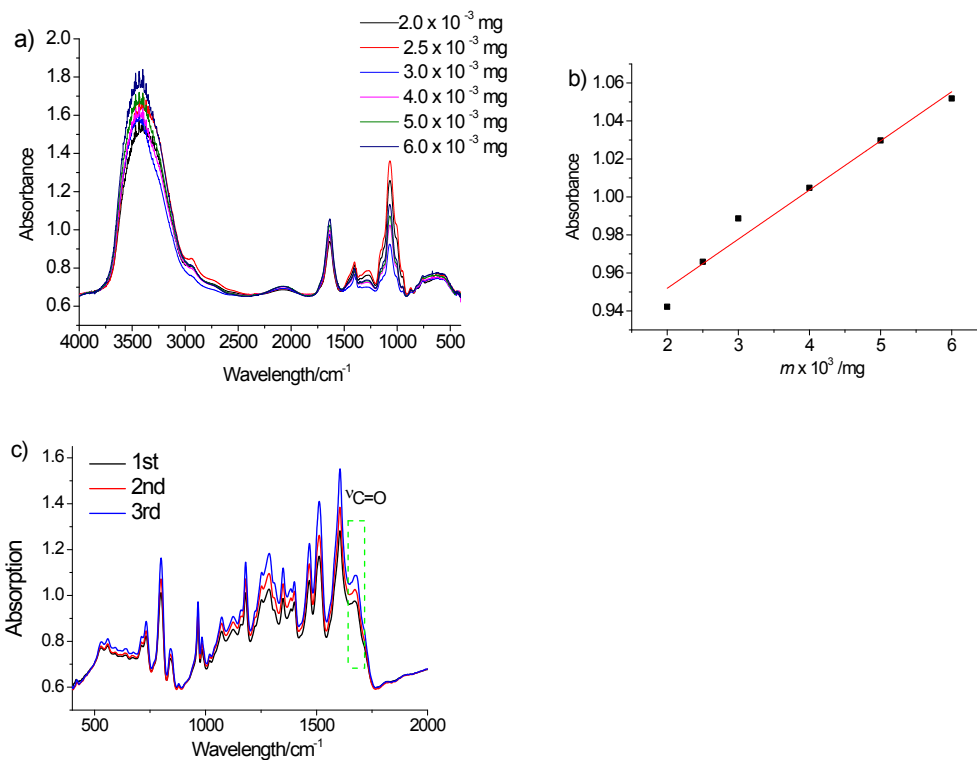


Fig. S8 a) FT-IR absorption spectra of various amount of glyoxal, b) the standard curve of glyoxal showing the relation between absorbance (A) and quality (Q) ($A = 0.9002 + 0.02586Q$, $R^2 = 0.96499$), and c) FT-IR absorption spectra of H₂TAPP-GO aerogels (three parallel samples).

The percentage of formed Ar-C=N- bonds was identically as follow. According to the standard curve of glyoxal, the amount of glyoxal can be cacluated with the absorbance of C=O for H₂TAPP-GO aerogel, corresponding to the amount of unreacted glyoxal in H₂TAPP-GO aerogel. The amount of H₂TAPP-GO aerogel in the KBr film is 0.68 mg (9.5×10^{-4} mmol). The percentage of formed Ar-C=N- bonds is $1 - (\text{the amount of unreacted glyoxal}/\text{the amount of H}_2\text{TAPP-GO aerogel}) \times 100\% = 91\%$ (everage for three times).

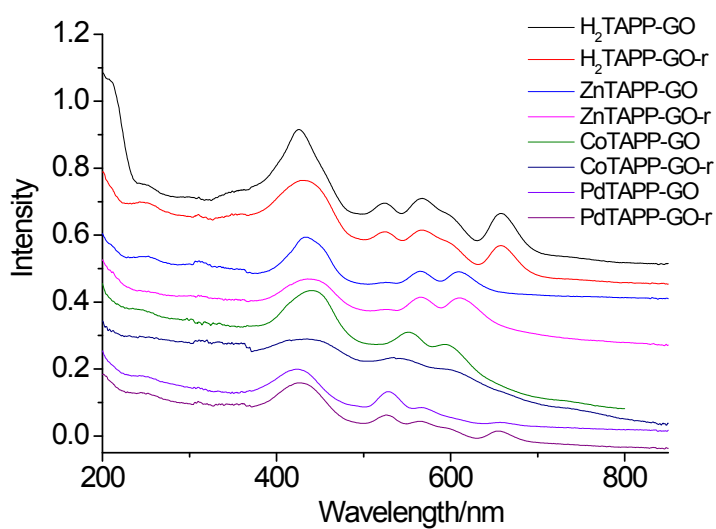


Fig. S9 Solid-state diffuse reflectance UV-vis spectra of H₂TAPP-GO (offset with 0.50), H₂TAPP-GO-r (offset with 0.40), ZnTAPP-GO (offset with 0.35), ZnTAPP-GO-r (offset with 0.20), CoTAPP-GO (offset with 0.05), CoTAPP-GO-r (offset with -0.10), PdTAPP-GO (offset with -0.07) and PdTAPP-GO-r (offset with -0.10) wet gels. The spectra are vertically offset for clarity.

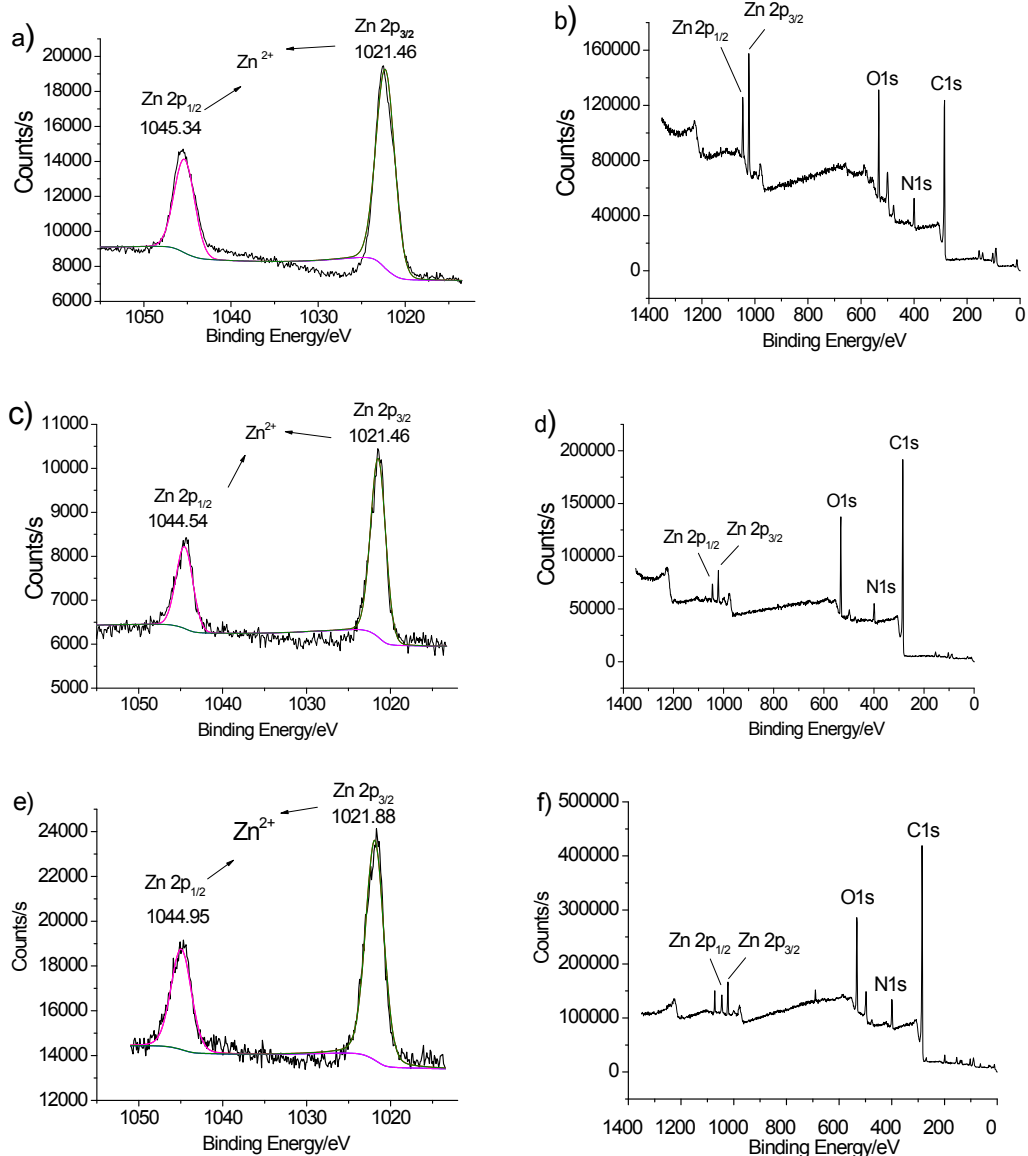


Fig. S10 a) XPS Zn 2p and b) survey spectra of ZnTAPP-GO; c) XPS Zn 2p and d) survey spectra of ZnTAPP-GO-r; e) XPS Zn 2p and f) survey spectra of ZnTAPP-GO immersed in NaBH₃CN ethanol saturated solution for 3 d.

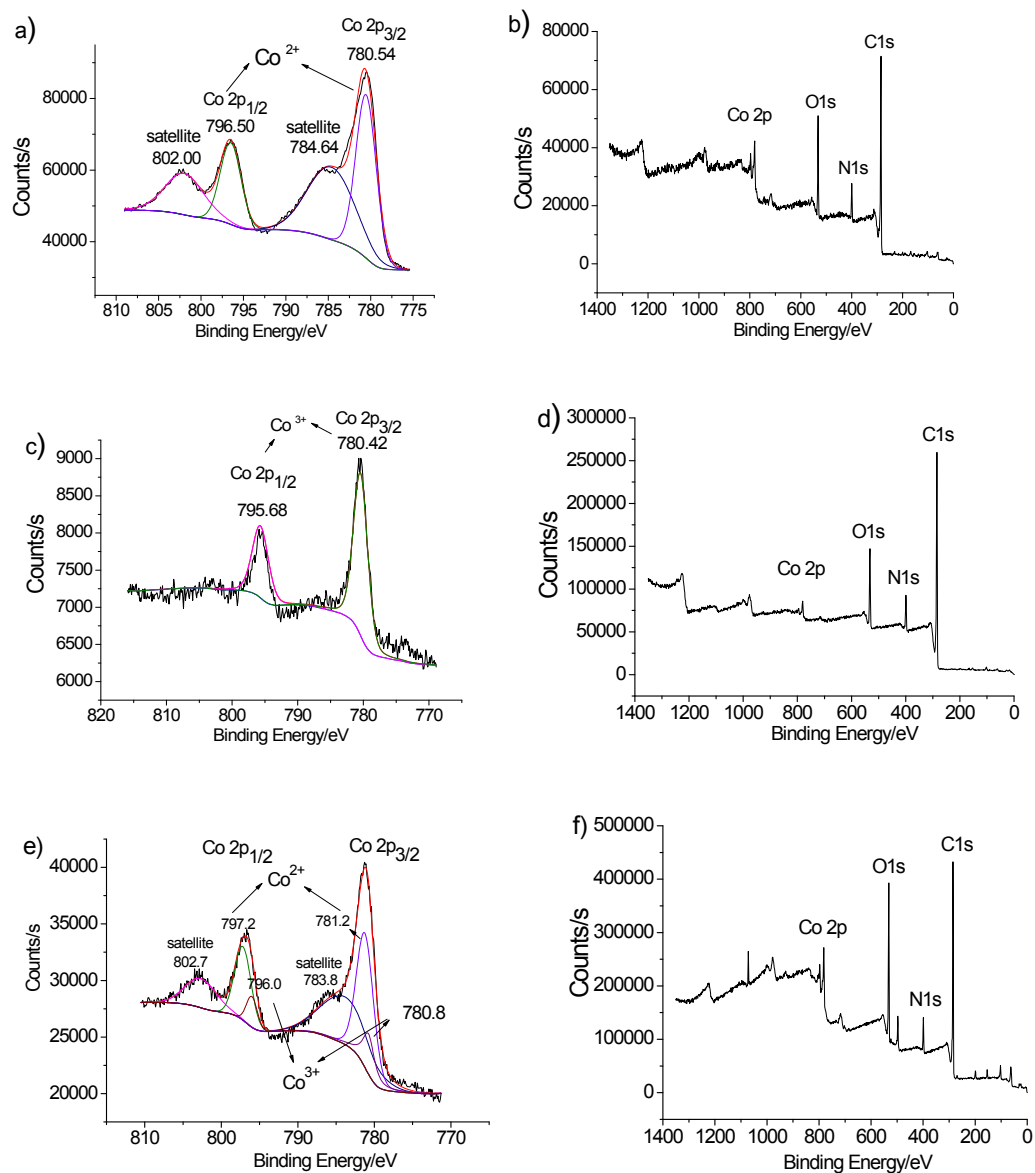


Fig. S11 a) XPS Co 2p and b) survey spectra of CoTAPP-GO; c) XPS Co 2p and d) survey spectra of CoTAPP-GO-r; e) XPS Pd 2p and f) survey spectra of CoTAPP-GO immersed in NaBH₃CN ethanol saturated solution for 3 d.

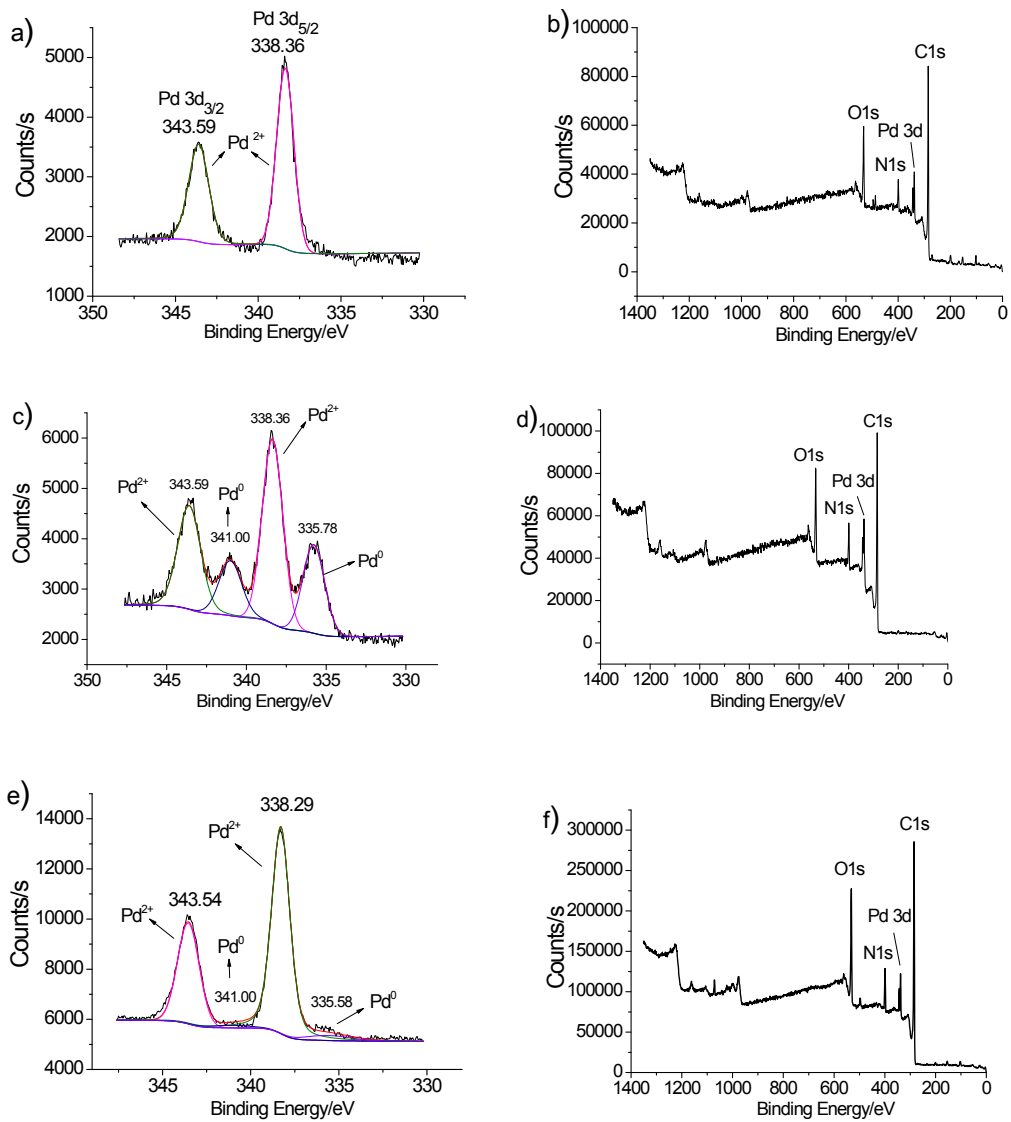


Fig. S12 a) XPS Pd 2p and b) survey spectra of PdTAPP-GO; c) XPS Pd 2p and d) survey spectra of PdTAPP-GO-r; e) XPS Pd 2p and f) survey spectra of PdTAPP-GO reduced by NaBH₃CN.

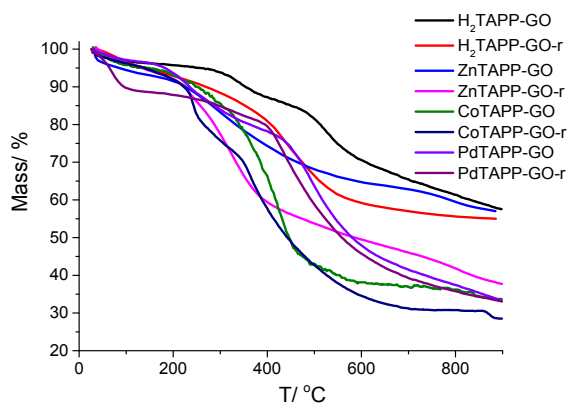


Fig. S13 TG curves of H₂TAPP-GO, H₂TAPP-GO-r, ZnTAPP-GO, ZnTAPP-GO-r, CoTAPP-GO, CoTAPP-GO-r, PdTAPP-GO and PdTAPP-GO-r aerogels under N₂ atmosphere.

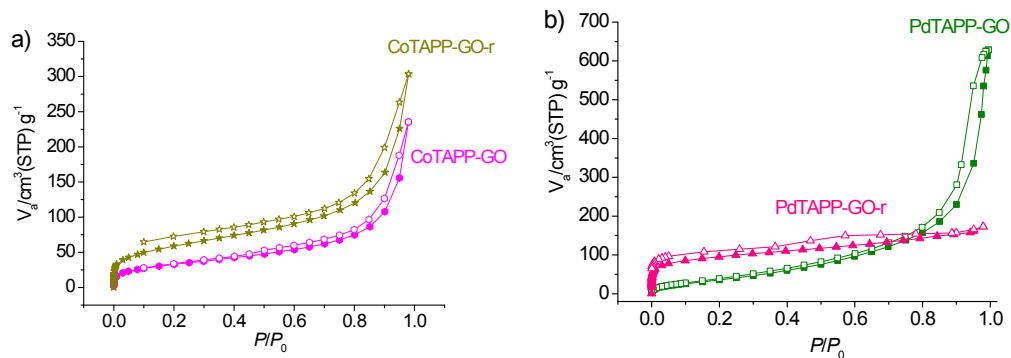


Fig. S14 N₂ adsorption (closed symbols) /desorption (open symbols) isotherms at 77 K for a) CoTAPP-GO and CoTAPP-GO-r aerogels, b) PdTAPP-GO and PdTAPP-GO-r aerogels.

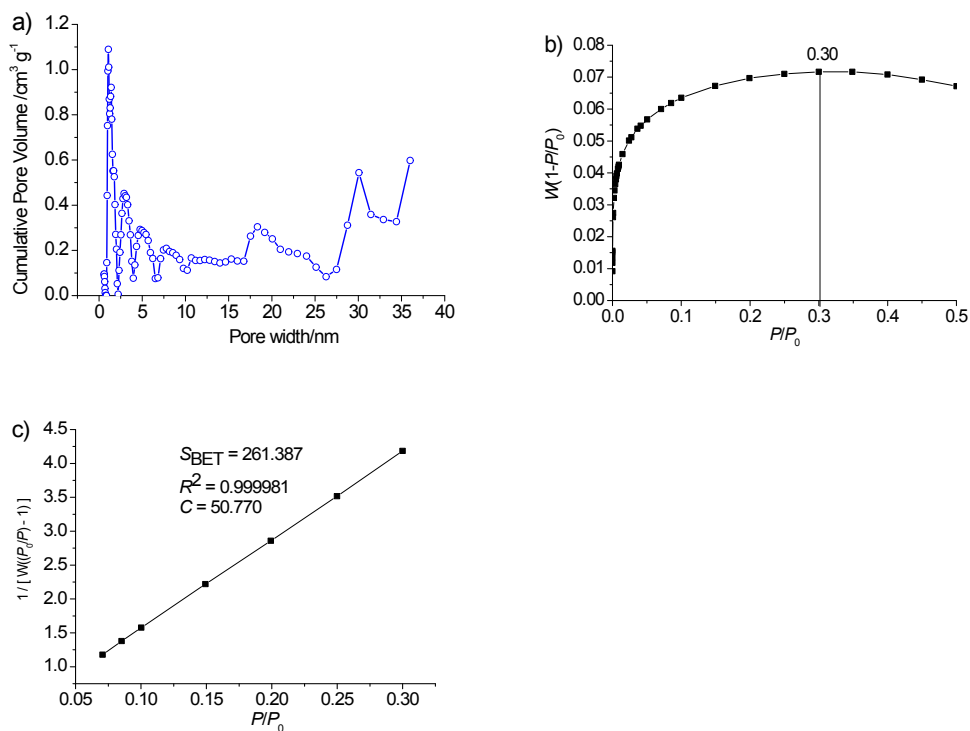


Fig. S15 a) NL-DFT pore size distribution (model: DFT method N₂ at 77 K on carbon (slit pore, NLDFE equilibrium model), b) consistency plot, and c) BET fit and for H₂TAPP-GO aerogel.

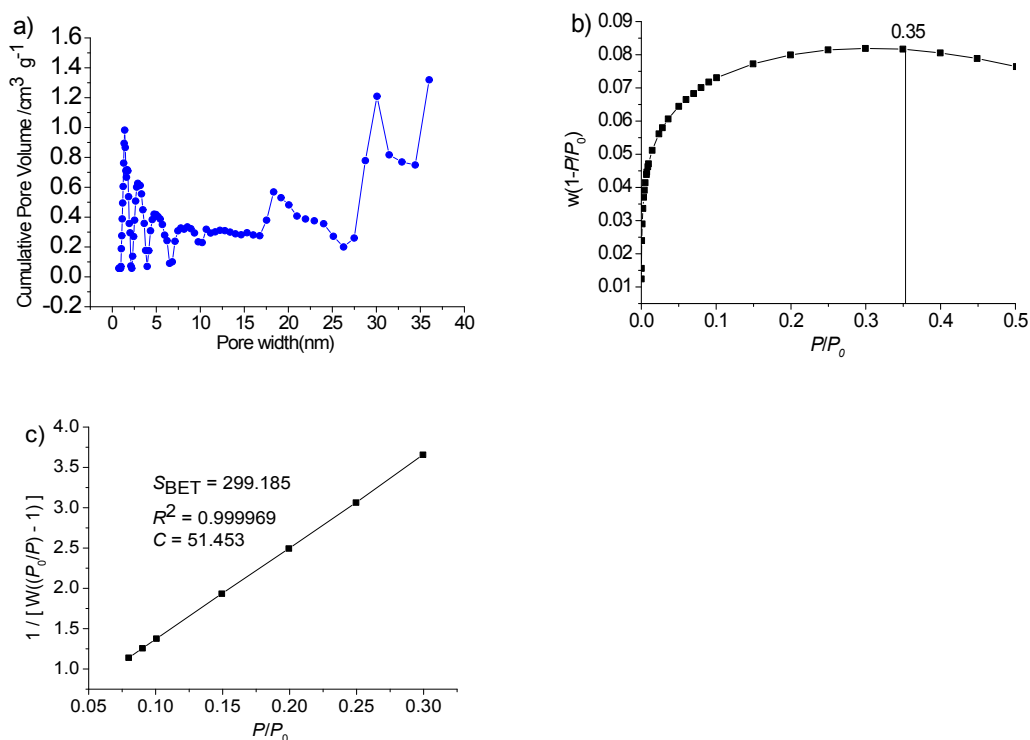


Fig. S16 a) NL-DFT pore size distribution (model: DFT method N₂ at 77 K on carbon (slit pore, NLDFE equilibrium model), b) consistency plot, and c) BET fit and for H₂TAPP-GO-r aerogel.

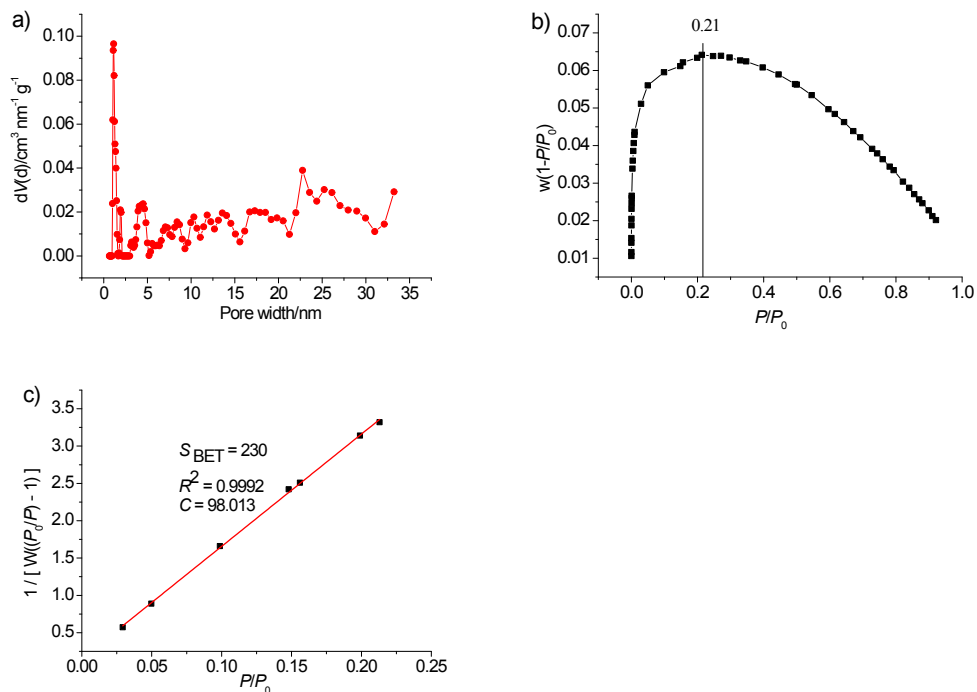


Fig. S17 a) NL-DFT pore size distribution (model: DFT method N_2 at 77 K on carbon (slit pore, NLDFTE equilibrium model), b) consistency plot, and c) BET fit and for ZnTAPP-GO aerogel.

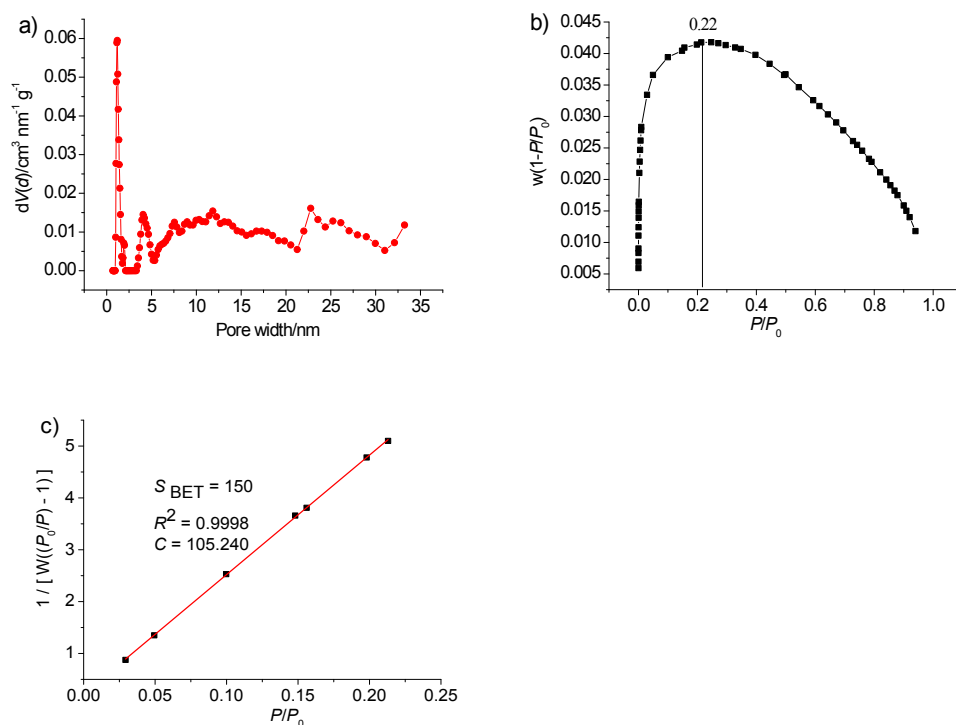


Fig. S18 a) NL-DFT pore size distribution (model: DFT method N_2 at 77 K on carbon (slit pore, NLDFTE equilibrium model), b) consistency plot, and c) BET fit and for ZnTAPP-GO-r aerogel.

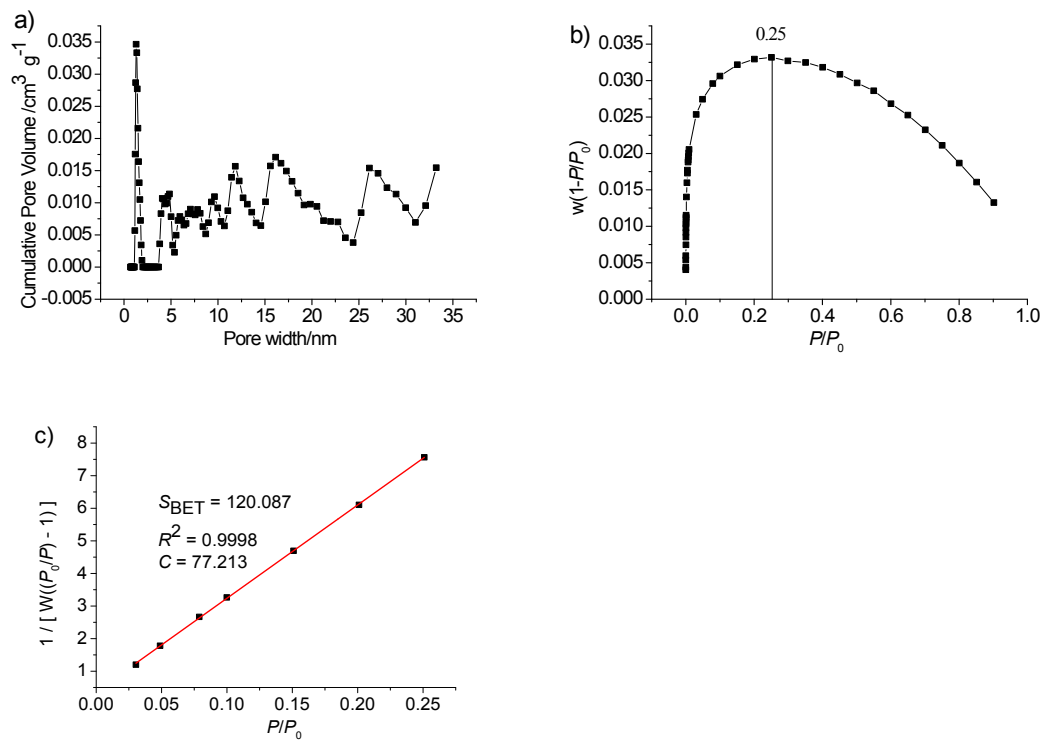


Fig. S19 a) NL-DFT pore size distribution (Model: DFT method N_2 at 77 K on carbon (slit pore, NLDFE equilibrium model), b) consistency plot, and c) BET fit and for CoTAPP-GO aerogel.

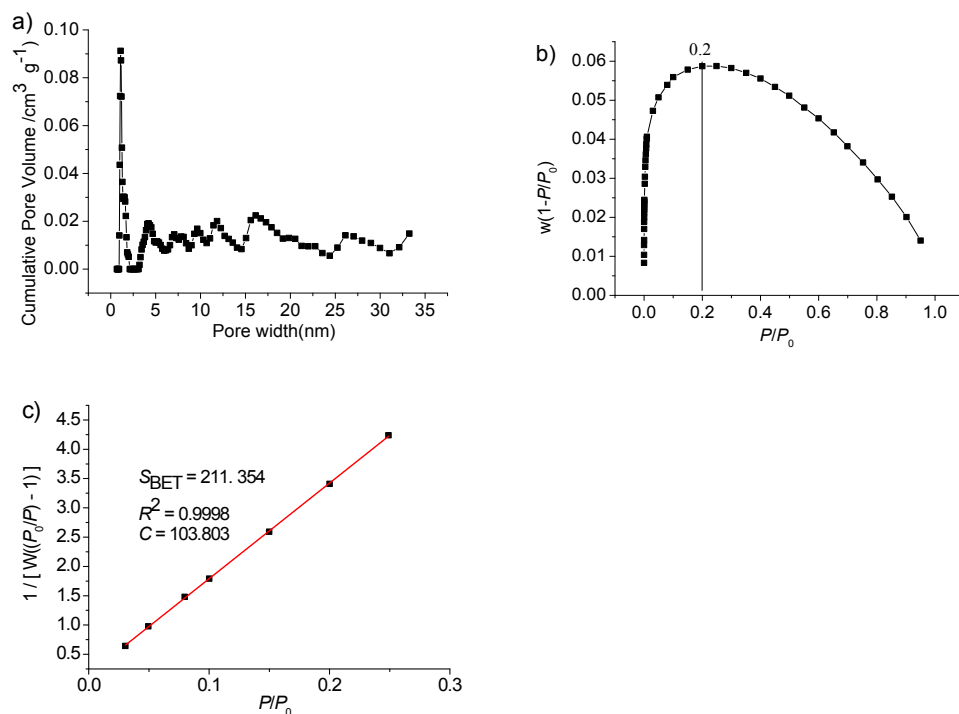


Fig. S20 a) NL-DFT pore size distribution (model: DFT method N_2 at 77 K on carbon (slit pore, NLDFE equilibrium model), b) consistency plot, and c) BET fit and for CoTAPP-GO-r aerogel.

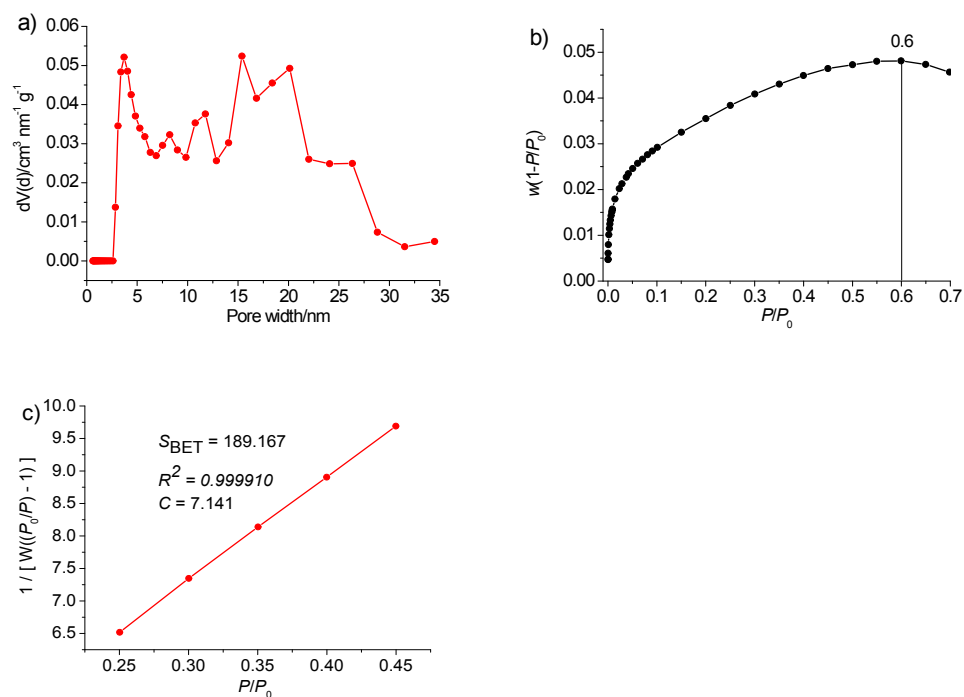


Fig. S21 a) NL-DFT pore size distribution (model: DFT method N_2 at 77 K on carbon (slit pore, NLDFE equilibrium model), b) consistency plot, and c) BET fit and for PdTAPP-GO aerogel.

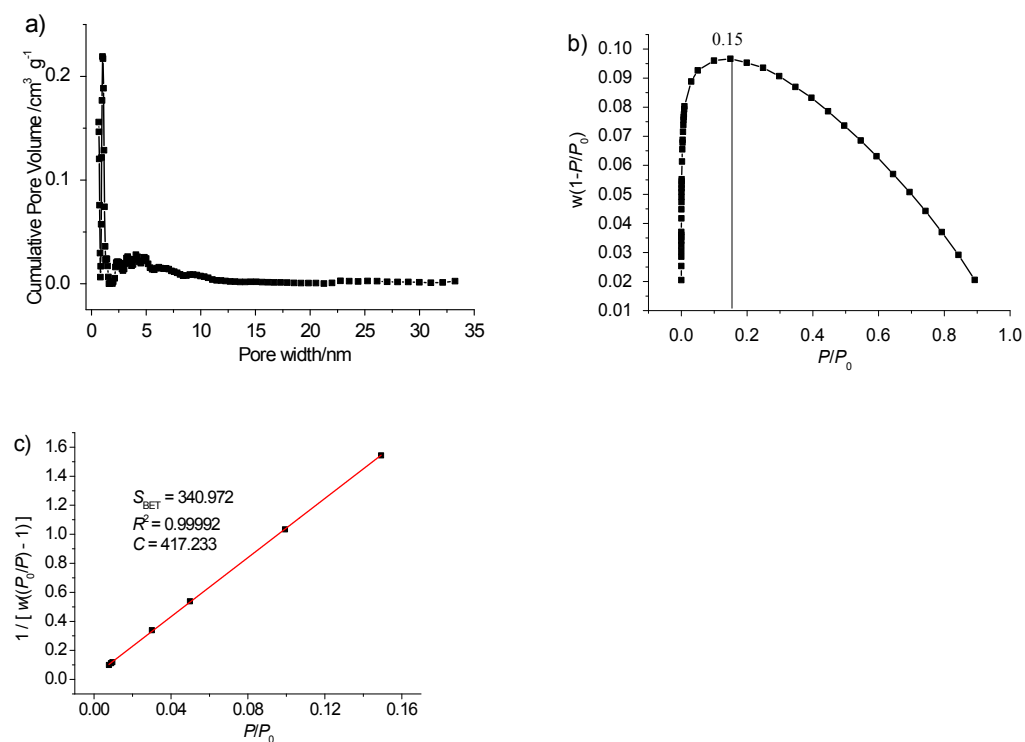


Fig. S22 a) NL-DFT pore size distribution (model: DFT method N_2 at 77 K on carbon (slit pore, NLDFE equilibrium model), b) consistency plot, and c) BET fit and for PdTAPP-GO-r aerogel.

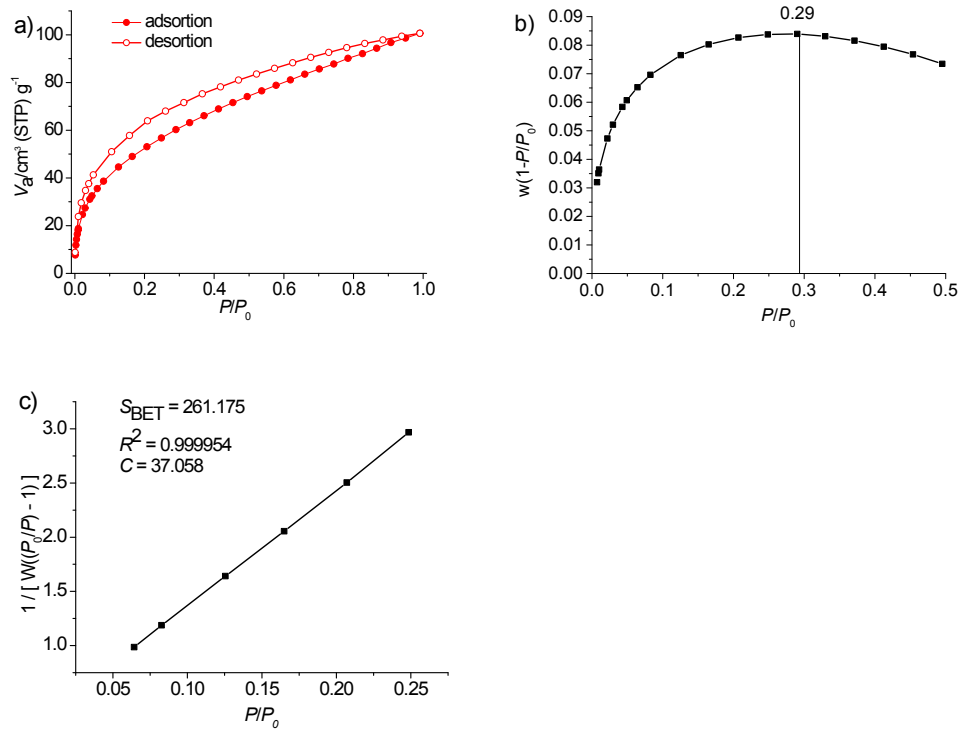


Fig. S23 a) CO₂ adsorption (closed symbols)/desorption (open symbols) isotherms for H₂TAPP-GO aerogel at 195 K b) consistency plot and c) BET fit of H₂TAPP-GO aerogel.

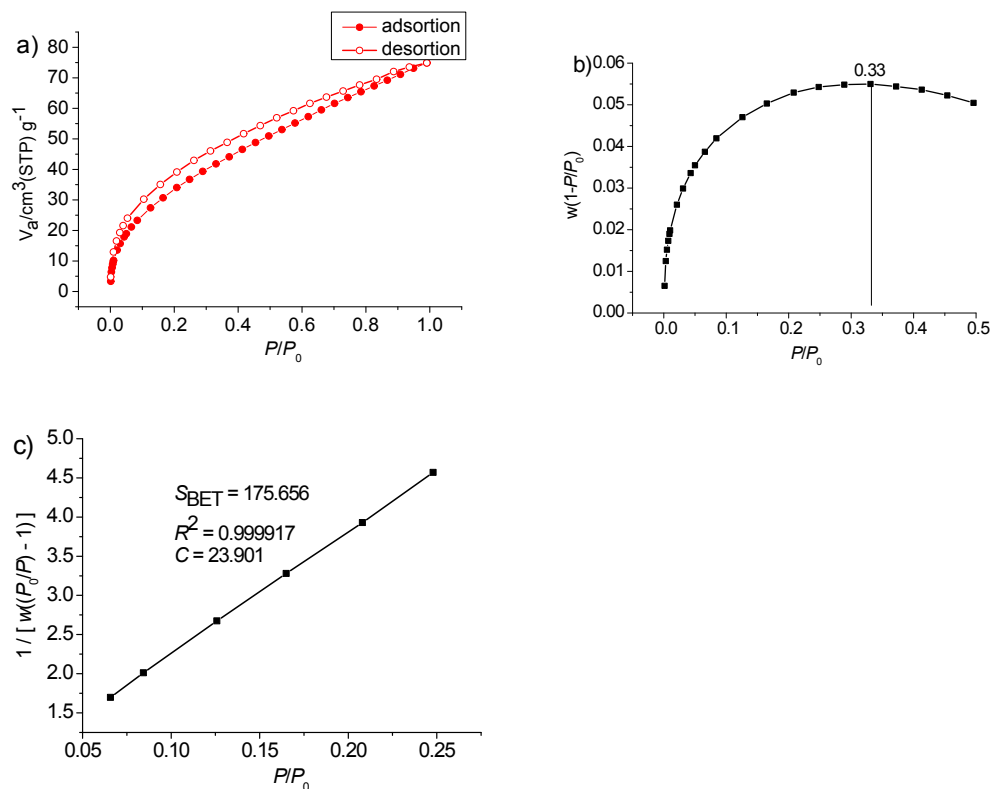


Fig. S24 a) CO₂ adsorption (closed symbols) /desorption (open symbols) isotherms for H₂TAPP-GO-r aerogel at 195 K b) consistency plot and c) BET fit of H₂TAPP-GO-r.

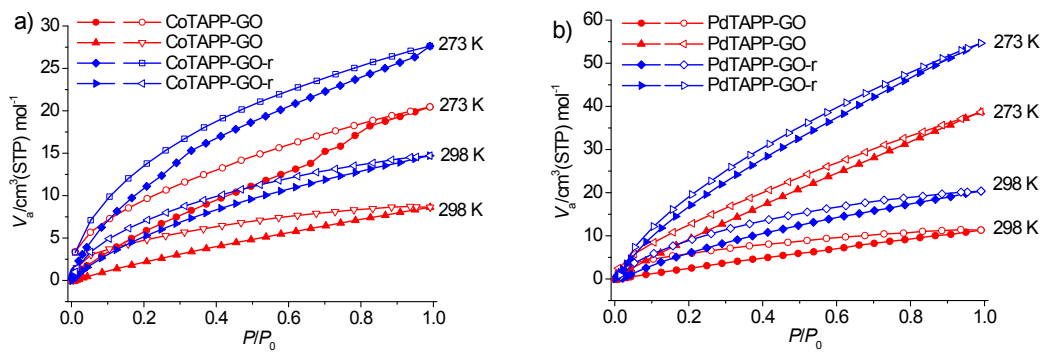


Fig. S25 CO₂ adsorption (closed symbols)/desorption (open symbols) isotherms for a) CoTAPP-GO and CoTAPP-GO-r aerogels, b) PdTAPP-GO and PdTAPP-GO-r aerogels at 273 and 298 K.

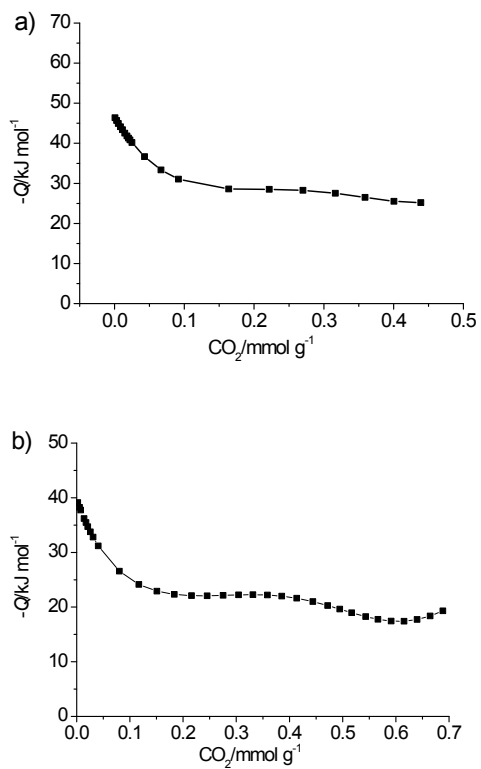


Fig. S26 Isothermic heats of adsorption (Q_{st}) as a function of gas loading for a) H₂TAPP-GO and b) H₂TAPP-GO-r aerogels, estimated from low pressure isotherms at 273 and 298 K by applying the virial equation.

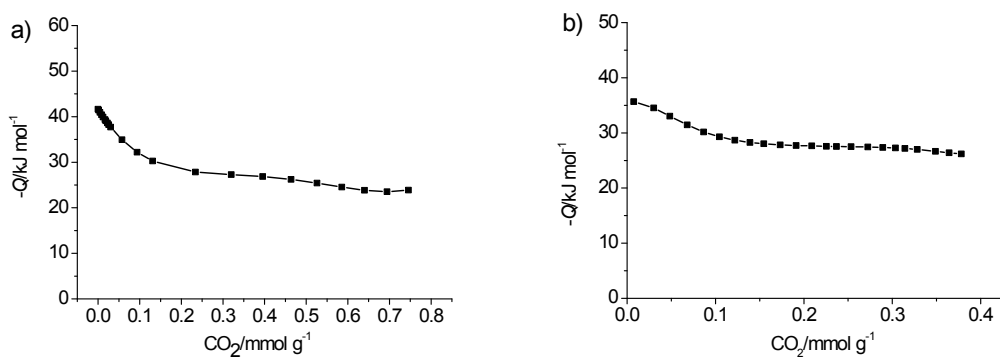


Fig. S27 Isosteric heats of adsorption (Q_{st}) as a function of gas loading for a) ZnTAPP-GO and b) ZnTAPP-GO-r aerogels, estimated from low pressure isotherms at 273 and 298 K by applying the virial equation.

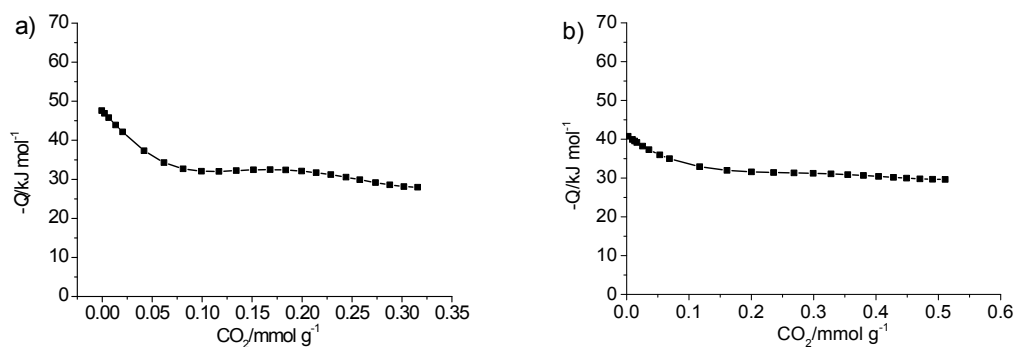


Fig. S28 Isosteric heats of adsorption (Q_{st}) as a function of gas loading for a) CoTAPP-GO and b) CoTAPP-GO-r aerogels, estimated from low pressure isotherms at 273 and 298 K by applying the virial equation.

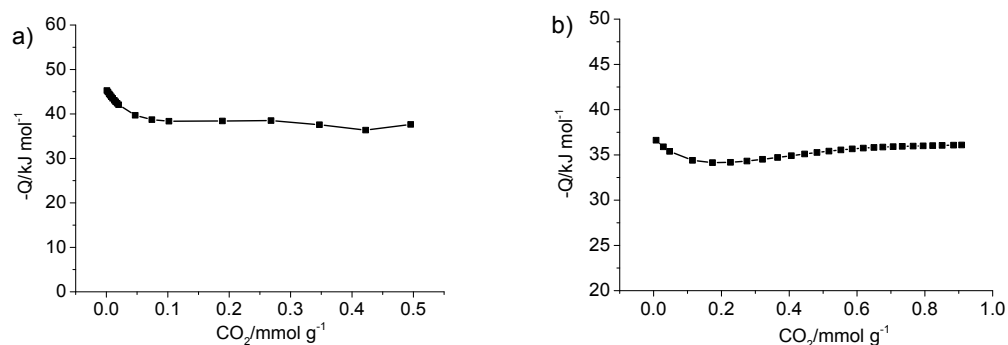


Fig. S29 Isosteric heats of adsorption (Q_{st}) as a function of gas loading for a) PdTAPP-GO and b) PdTAPP-GO-r aerogels, estimated from low pressure isotherms at 273 and 298 K by applying the virial equation.

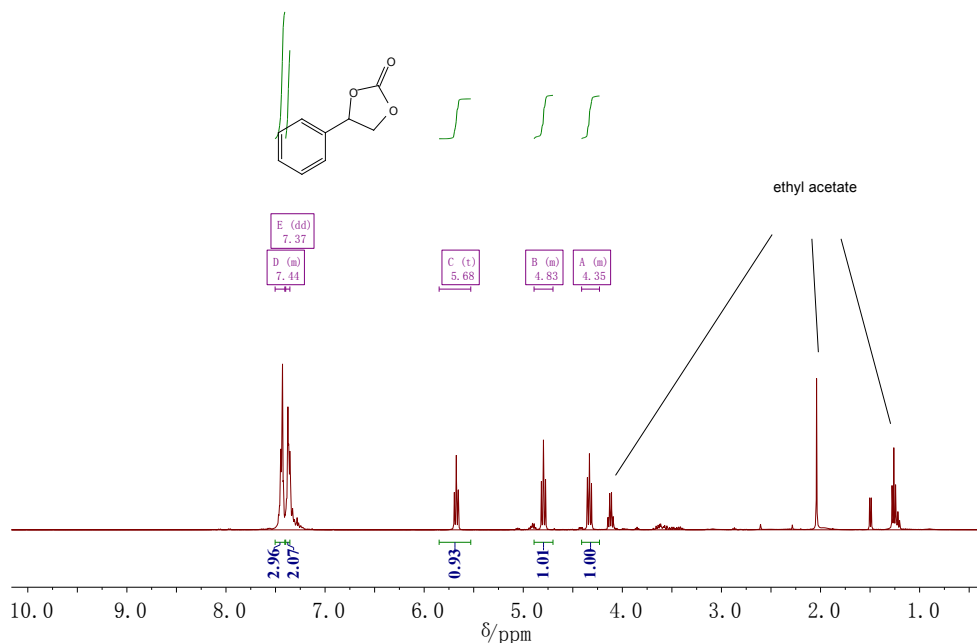


Fig. S30 ^1H NMR spectrum of 1-phenyl-1,2-ethylene carbonate in the cycloaddition of CO_2 with styrene oxide (400 MHz, 298 K, CDCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.50-7.41 (m, 3H), 7.37 (dd, $J = 8.1, 5.5$ Hz, 2H), 5.68 (t, $J = 8.0$ Hz, 1H), 4.89-4.70 (m, 1H), 4.41-4.23 (m, 1H).

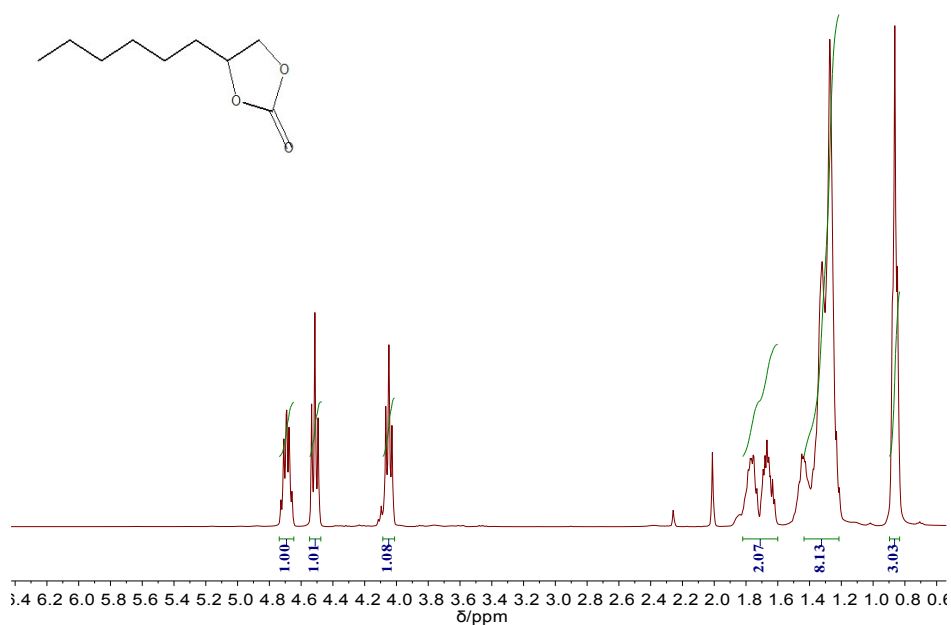


Fig. S31 ^1H NMR spectrum of 4-hexyl-1,3-dioxolan-2-one in the cycloaddition (400 MHz, 298K, CDCl_3). ^1H NMR (400 MHz, CDCl_3): δ 4.65-4.75 (m, 1H), 4.48-4.54 (m, 1H), 4.00-4.09 (m, 1H), 1.62-1.84 (m, 2H), 1.30-1.46 (m, 8H), 0.93 (t, 3H).

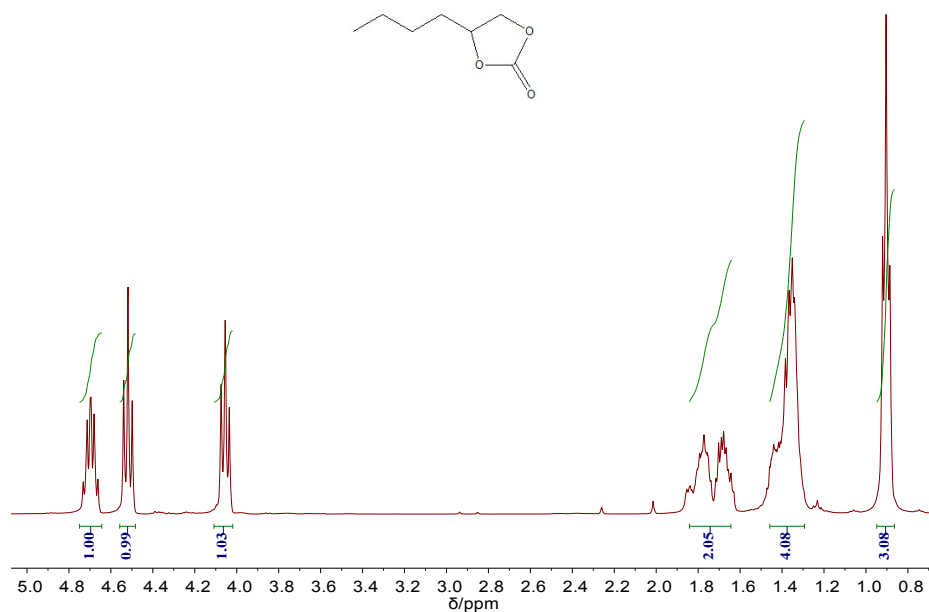


Fig. S32 ^1H NMR spectrum of 1,2-hexylene carbonate in the cycloaddition (400 MHz, 298 K, CDCl_3). ^1H NMR (400 MHz, CDCl_3) δ 4.63-4.74 (m, 1H), 4.49-4.55 (m, 1H), 4.03-4.09 (m, 1H), 1.62-1.84 (m, 2H), 1.30-1.46 (m, 4H), 0.93 (t, 3H).

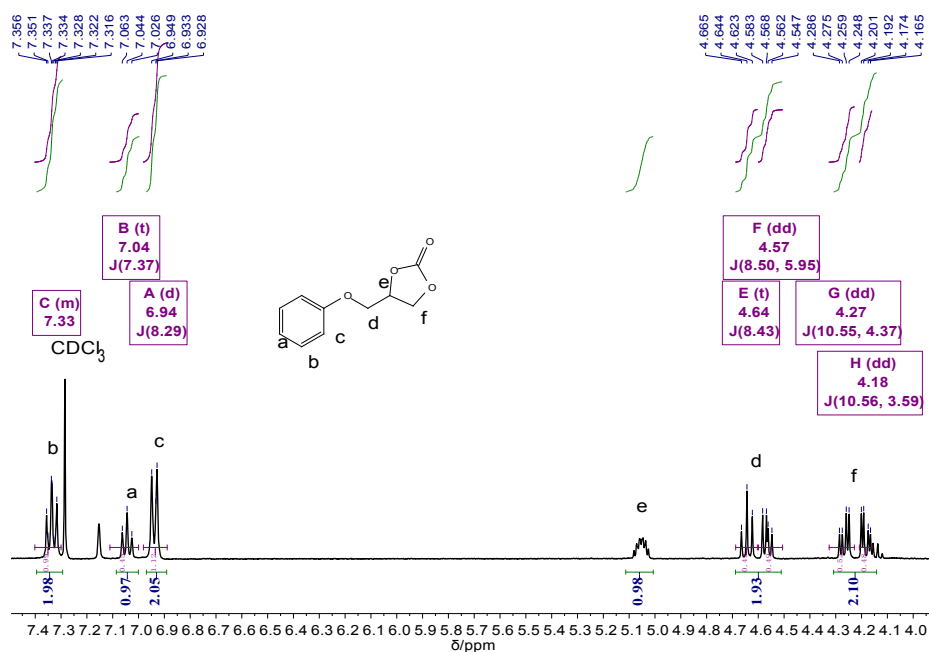


Fig. S33 ^1H NMR spectrum of 3-phenoxypropylene carbonate in the cycloaddition (400 MHz, 298 K, CDCl_3). ^1H NMR (400 MHz, CDCl_3): δ ^1H NMR (400 MHz, CDCl_3): δ 7.40 – 7.30 (m, 1H), 7.04 (t, $J = 7.4$ Hz, 0H), 6.94 (d, $J = 8.3$ Hz, 1H), 5.06 (m, 1H), 4.64 (t, $J = 8.4$ Hz, 1H), 4.57 (dd, $J = 8.5, 6.0$ Hz, 1H), 4.27 (dd, $J = 10.6, 4.4$ Hz, 1H), 4.18 (dd, $J = 10.6, 3.6$ Hz, 1H).

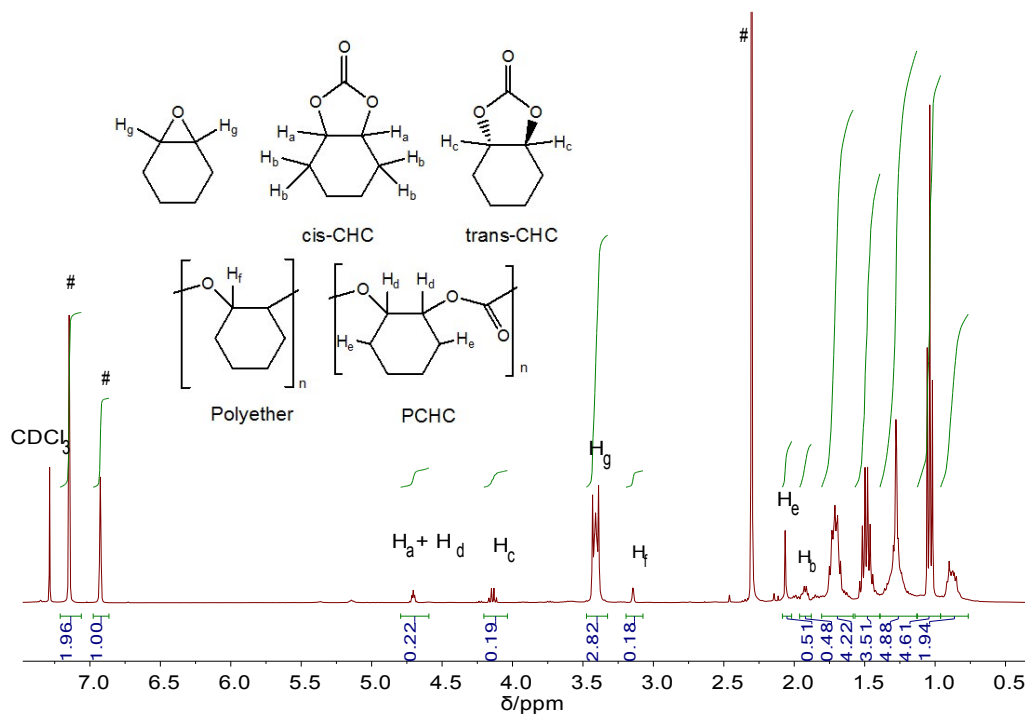


Fig. S34 ¹H NMR spectrum of the products in the cycloaddition of epoxycyclohexane with CO₂ (400 MHz, 298 K, CDCl₃) (# signals are attributed to the internal standard 1-bromo-3,5-dimethylbenzene).

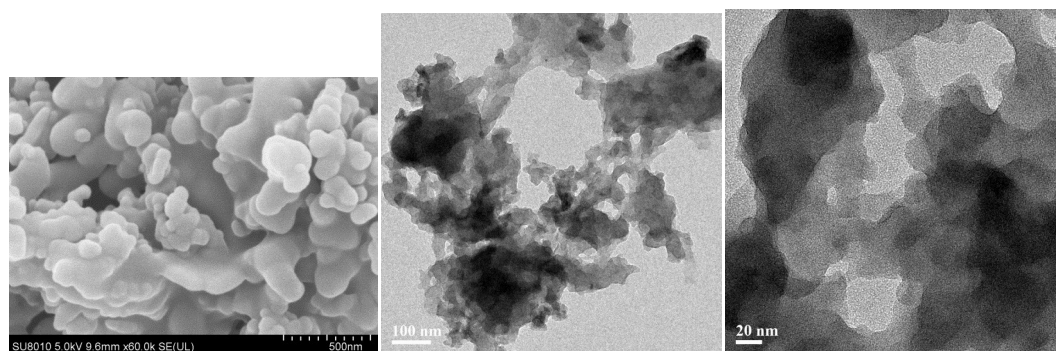


Fig. S35 SEM and TEM images of ZnTAPP-GO-r recycled after the 5th catalytic run.

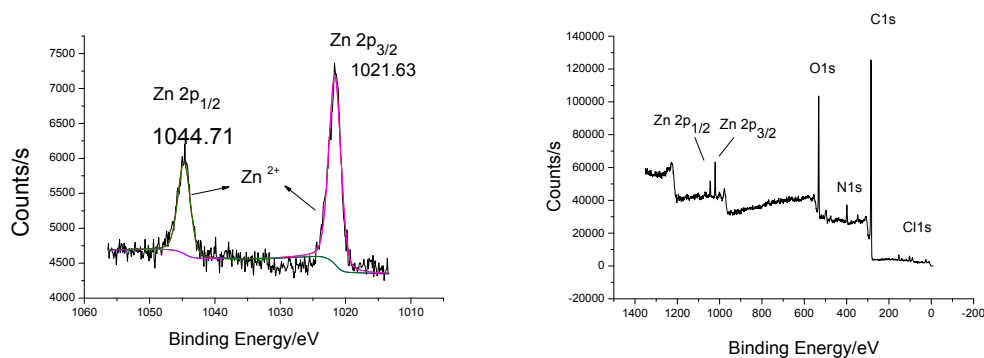


Fig. S36 a) XPS Zn 2p and b) survey spectra of ZnTAPP-GO-r recycled after the 5th catalytic run.

Table S1 Porosity of various porphyrin-based aerogels.

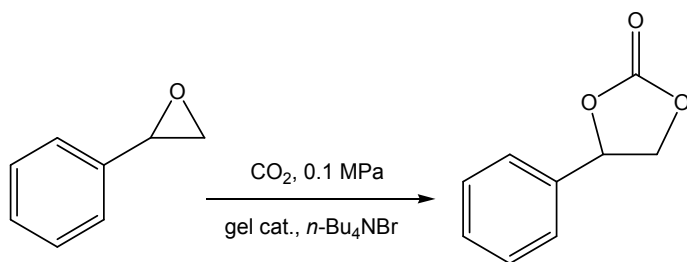
	$S_{\text{BET}}^{\text{a}}/\text{m}^2 \text{ g}^{-1}$	$V_{\text{total}}/\text{cm}^3 \text{ g}^{-1}$	$V_{\text{micro}}^{\text{c}}/\text{cm}^3 \text{ g}^{-1}$	$V_{\text{meso}}^{\text{d}}/\text{cm}^3 \text{ g}^{-1}$
H ₂ TAPP-GO	261 (261 ^b)	1.748	0.062	1.694
H ₂ TAPP-GO-r	299 (176 ^b)	2.878	0.070	2.830
ZnTAPP-GO	230	0.8434	0.066	0.780
ZnTAPP-GO-r	150	0.4903	0.042	0.450
CoTAPP-GO	120	0.3642	0.031	0.340
CoTAPP-GO-r	211	0.4696	0.059	0.414
PdTAPP-GO	189	0.9719	0.000	0.999
PdTAPP-GO-r	341	0.2674	0.111	0.130

^a S_{BET} was calculated from the N₂ adsorption at 77 K unless otherwise stated; ^b calculated by the CO₂ adsorption at 195 K; ^c V_{micro} was calculated by the SF method; ^d V_{meso} was calculated by the BJH method.

Table S2 CO₂ adsorption properties of porphyrin-based aerogels.

	CO ₂ uptake /cm ³ g ⁻¹ at 1 bar, 273 K	CO ₂ uptake /cm ³ g ⁻¹ at 1 bar, 298 K	initial Q_{st} of CO ₂ /kJ mol ⁻¹
H ₂ TAPP-GO	21.2	11.0	46.4
H ₂ TAPP-GO-r	24.9	15.4	39.1
ZnTAPP-GO	30.5	16.8	41.6
ZnTAPP-GO-r	21.5	8.5	35.6
CoTAPP-GO	20.5	8.6	48.7
CoTAPP-GO-r	27.6	14.7	41.2
PdTAPP-GO	38.7	11.3	45.3
PdTAPP-GO-r	54.7	20.4	36.6

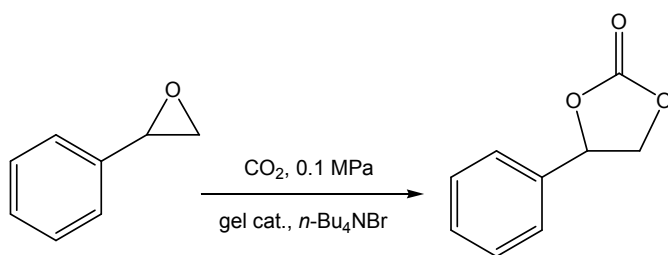
Table S3 Catalytic tests of H₂TAPP-GO and H₂TAPP-GO-r gels for the conversion of CO₂ and styrene oxide to styrene carbonate.



catalyst	co-catalyst (<i>n</i> -Bu ₄ NBr)	<i>T</i> /K	<i>V</i> _{EtOH} /mL	conversion/% (time/h)	yield/% (time/h) ^b
H ₂ TAPP-GO (3%)	10 mol%	373	-	55 (42)	57 (42)
H ₂ TAPP-GO (3%)	30 mol%	373	-	51 (40)	17(40)
H ₂ TAPP-GO (0.24%)	10 mol%	RT	-	28 (39)	16 (39)
H ₂ TAPP-GO (0.24%)	7 mol%	RT	-	36 (40)	19(40)
H ₂ TAPP-GO (1%)	7 mol%	323	-	44(24)	62 (24)
H ₂ TAPP-GO (1%)	-	323	-	0 (24)	0 (24)
H ₂ TAPP-GO-r (0.5%)	7 mol%	323	-	53 (24)	13 (24)
H ₂ TAPP-GO (0.5%)	7 mol%	323	-	54 (23)	41 (23)
H ₂ TAPP-GO (0.3%)	7 mol%	RT.	-	6(28)	12 (28)
H ₂ TAPP-GO (0.3%)	7 mol%	RT.	-	38(28)	13 (28)
H ₂ TAPP-GO (0.3%)	7 mol%	323	2	62(42)	39(42)
H ₂ TAPP-GO (0.3%)	7 mol%	323	3	55 (42)	24(42)
H ₂ TAPP-GO (0.3%)	7 mol%	373	2	>99 (24)	>99 (24)
H ₂ TAPP-GO (0.3%)	7 mol%	323	2	41 (24)	17 (24)

Reaction conditions: styrene oxide, 0.03 mmol of gel catalyst (1 mol% based on TAPP), co-catalyst *n*-Bu₄NBr, and 0.015 mmol 1-bromo-3,5-dimethylbenzene used as an internal standard.

Table S4 Catalytic tests of MTAPP-GO and MTAPP-GO-r gels for the conversion of CO₂ and styrene oxide to styrene carbonate.



Catalyst	Conversion/% (time/h)	Selectivity/% (time/h)
H ₂ TAPP-GO	97(3), 97(4), 98(6), 98(8), 99(10)	1(4), 9(6), 16(8), 27(10)
H ₂ TAPP-GO-r	66(1), 90(4), 86(6), 92(10)	1(1), 3(4), 38(6), 75(10)
ZnTAPP-GO	22(4), 66(6), 72(8), 90(10)	100(2), 100(6), 100(8), 100(10)
ZnTAPP-GO-r	62(4), 74(8), 88(10)	65(4), 100(8), 100(10)
CoTAPP-GO	24(4), 38(6), 51(8), 67(10)	48(4), 54(6), 81(8), 90(10)
CoTAPP-GO-r	21(2), 41(4), 45(6), 43(10)	9(2), 11(4), 18(6), 31(10)
PdTAPP-GO	52(2), 71(4), 82(6), 83(8), 89(10)	21(2), 56(4), 85(6), 100(8), 100(10)
PdTAPP-GO-r	27(2), 38(4), 77(8), 75(10)	6(2), 14(4), 22(8), 49(10)
PdTAPP-GO(r)	28(1), 30(4), 28(6), 28(10)	4(1), 57(4), 100(6), 100(10)
ZnTAPP	95 (10)	94 (10)
None	92 (10)	68 (10)

Reaction conditions: 3 mmol styrene oxide, 0.03 mmol of gel catalyst (1 mol% based on TAPP), 0.21 mmol co-catalyst *n*-Bu₄NBr and 1.5 mmol 1-bromo-3,5-dimethylbenzene used as an internal standard at 373 K. The yields and conversion were determined by GC and NMR. PdTAPP-GO(r) was prepared by reacting PdTAPP-GO gel with a saturated ethanol solution of NaCNBH₃ at RT, followed by solvent exchange with EtOH.

Table S5 Reusability tests of ZnTAPP-GO and ZnTAPP-GO-r for the conversion of CO₂ and epoxides to cyclic carbonates.

catalyst	ZnTAPP-GO-r		ZnTAPP-GO	
	conversion/% (time/h)	selectivity/% (time/h)	conversion/% (time/h)	selectivity/% (time/h)
Run 1	92(10)	100(10)	96(10)	100(10)
Run 2	93(10)	100(10)	84(10)	100(10)
Run 3	91(10)	100(10)	83(10)	100(10)
Run 4	91(10)	100(10)	81(10)	95(10)
Run 5	97(10)	100(10)	64(10)	75(10)

Reaction conditions: 3 mmol styrene oxide, 0.03 mmol of gel catalyst (1 mol% based on TAPP), 0.21 mmol co-catalyst *n*-Bu₄NBr and 1.5 mmol 1-bromo-3,5-dimethylbenzene used as an internal standard at 373 K. The yields and conversion were determined by GC and NMR.