

Supporting information

Chemical shaping of CPO-27-M (M = Co, Ni) through an *in-situ* crystallization within chitosan hydrogels

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Experimental details

Chemicals. The reagents used were cobalt(II) nitrate hexahydrate (CAS: 10026-22-9, 99%; Fisher Scientific), nickel(II) nitrate hexahydrate (CAS: 13478-00-7; Merck), 2,5-dihydroxyterephthalic acid ($C_8H_6O_6$) (CAS: 610-92-4; Fisher Scientific), chitosan (CS) – low molecular weight (CAS: 9012-76-4; Sigma Aldrich), acetic acid glacial (Alfa Aesar Carlo Erba), N,N-dimethylformamide pure (CAS: 68-12-2; Carlo Erba), ethanol (CAS: 64-17-5, 100%; VWR Chemicals), and methanol extra pure (CAS: 67-56-1, 99%; Fisher Scientific) All chemicals were used as received without any further treatment.

Synthesis procedures.

CS@CPO-27-M (M = Co, Ni) beads. To prepare CS@CPO-27-Co (R) {R representing the molar ratio $n(\text{Co})/n(\text{NH}_2)_{\text{CS}}^1$ } composites beads, we first dissolve the appropriate amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 15 ml of distilled water. Subsequently, 0.5 g of chitosan (CS) and 0.8 ml of acetic acid were added under mechanical stirring, and the mixture is stirred at 600 rpm at 30 °C overnight. The resulting viscous solution is then coagulated by adding it drop by drop into a 4M NaOH solution (60 ml). The obtained CS@Cobalt oxide hydrogels are washed with distilled water until reaching a neutral pH and then refluxed at 100 °C in a solution of the organic ligand (2,5-dihydroxyterephthalic acid) dissolved in a mixture of DMF, ethanol, and water. The brown beads obtained are washed with 3x 30 ml of DMF and 6x 30 ml of methanol, followed by storage in methanol for three days (with methanol changed twice daily for 3 days) before being dried at room temperature under atmospheric conditions. A general illustrative scheme is proposed in Fig. S1.

CS@CPO-27-Ni (R=2) beads were prepared similarly by replacing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and the beads were refluxed for 24 h instead of overnight.

CPO-27-M (M = Co, Ni) powder. The pristine powder was prepared as follows: Initially, 1.02 g of 2,5-dihydroxyterephthalic acid ($H_4\text{dhtp}$) was dissolved in a mixture of DMF and ethanol. Once complete dissolution was achieved, a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) dissolved in water was added. The mixture was then refluxed at 100 °C overnight (24 h in the case of CPO-27-Ni). The resulting powder was obtained through centrifugation at 1200 rpm,

¹ 1 gram of chitosan contains about 5.8 mmol of NH_2 groups.

and rinsing with 3x 30 ml of DMF and 6x 30 ml of methanol. The final powders were obtained after vacuum drying overnight at 150 °C.

Characterization. Powder X-ray diffraction (PXRD) was performed using Bruker D8 Advanced AXS diffractometer equipped with Cu anticathode generating a monochromatic radiation $K\alpha_1$ ($\lambda = 1.5418 \text{ \AA}$) at 30 mA and 40 kV. The diffractograms were registered between 0 and 80° with a step of 0.2°/second. Fourier transform infrared spectra (FTIR) were measured using a PerkinElmer Spectrum equipped with an ATR sampling module between 450 and 4000 cm^{-1} . The specific surface areas (S_{BET}) of the samples were determined by N_2 physisorption at 77 K, performed using a Micromeritics Tristar II device. Before measuring, the composites beads were outgassed at 120 °C for one night, and CPO-27-Co powder was outgassed at 150 °C for one night. Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) were performed by means of a JEOL JSM 6700F microscope operated at a voltage of 15 KV. TG analysis was performed by a Mettler Toledo TGA/DSC 3+ ranging from 25 °C to 1000 °C under air flow (80 ml/min) with a heating rate of 5 °C. min^{-1} . CO_2 sorption isotherms were measured using a Micromeritics Tristar II device. Before measuring, the composites beads were outgassed at 120 °C for one night except in the case of the cycling experiments where only 4 hours of degassing were applied.

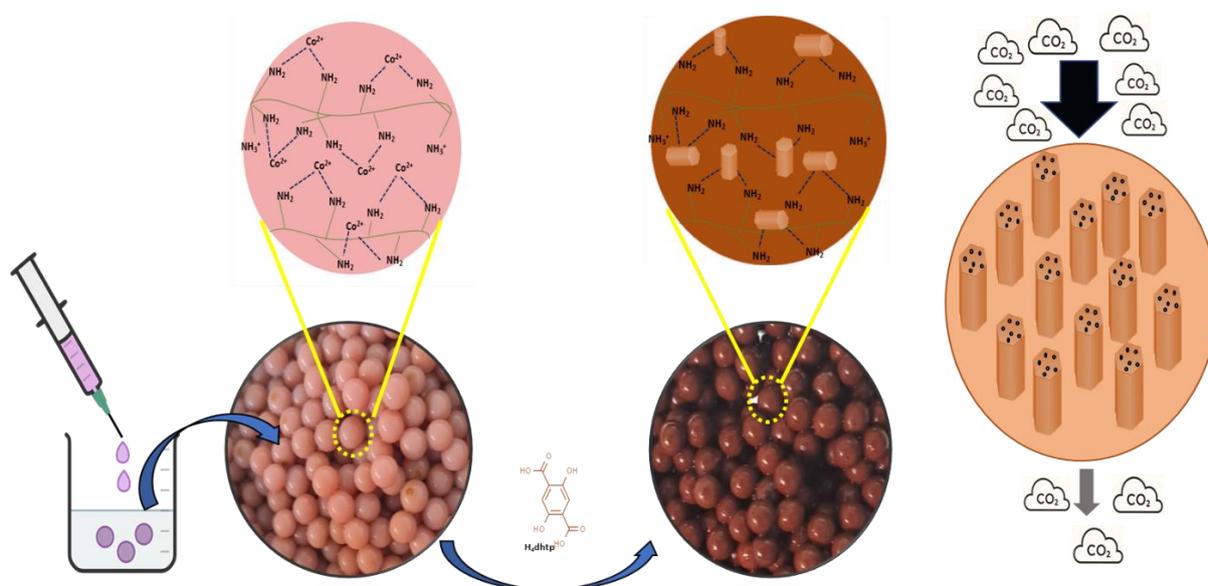


Fig. S1. General scheme illustrating the preparation approach developed herein.

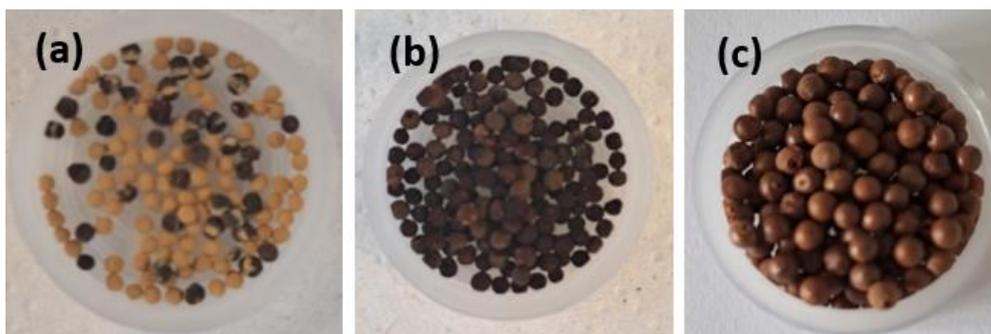


Fig. S2. The as-prepared CS@CPO-27-Co (R) beads with R =1/2 (a), R=1 (b), and R=2 (c).

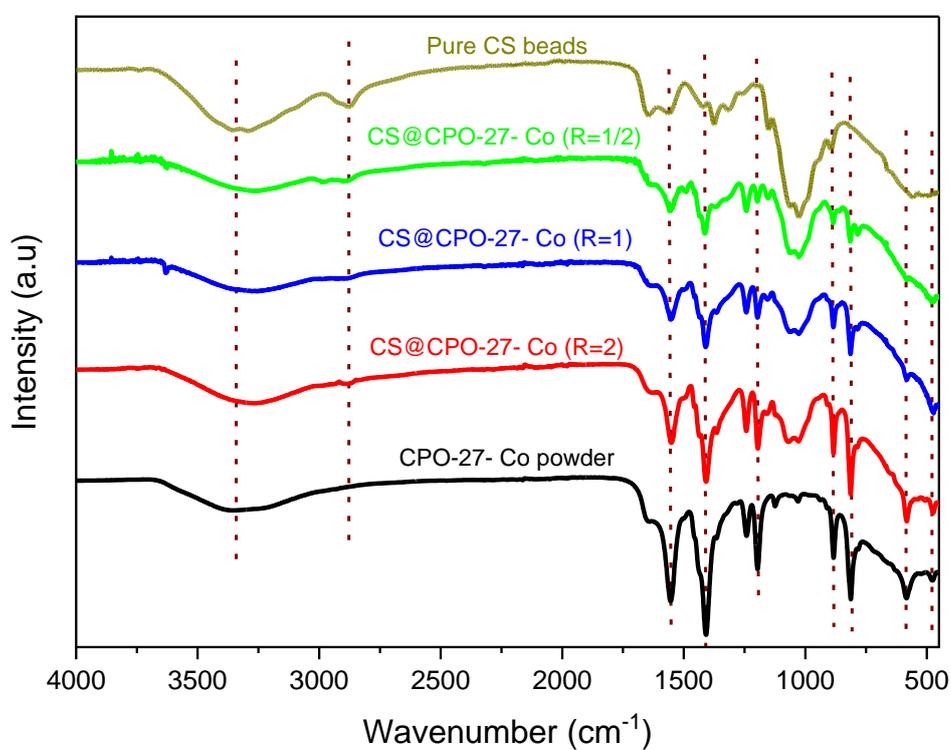
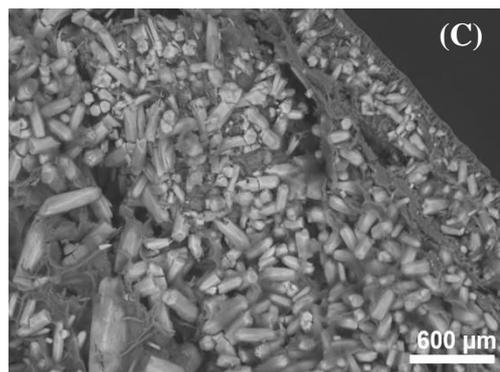
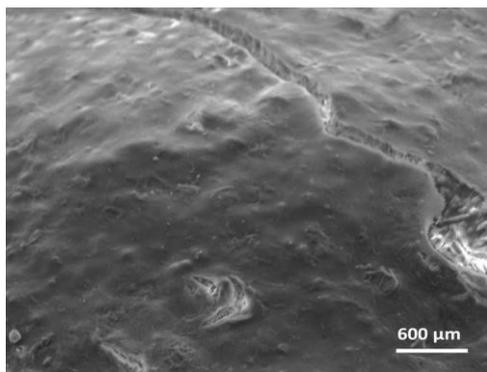
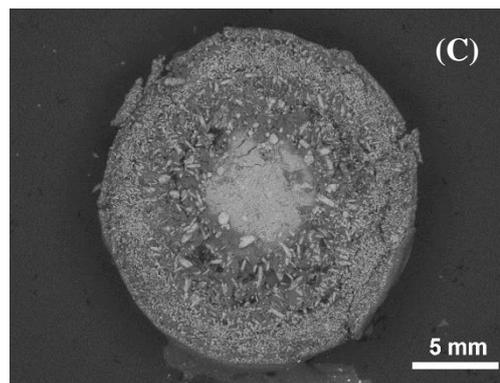
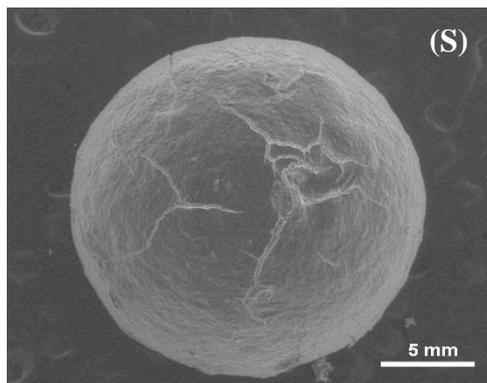


Fig. S3. IR spectra of CS@CPO-27-Co (R) beads and CPO-27-Co powder.

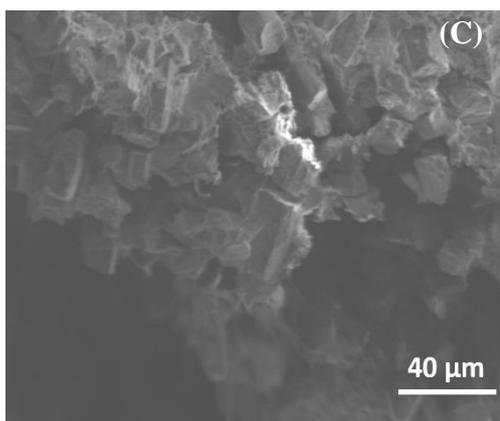
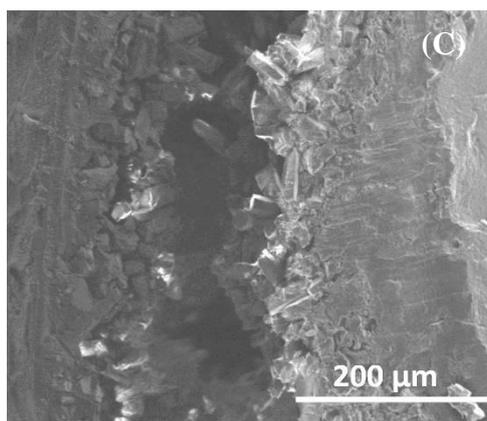
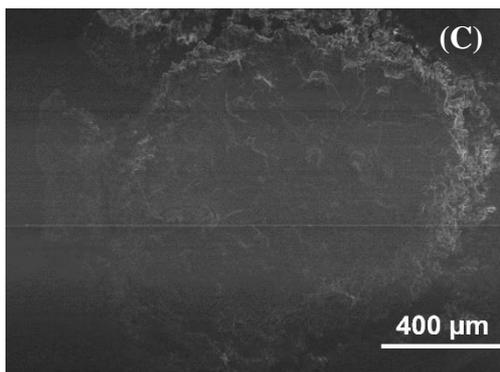
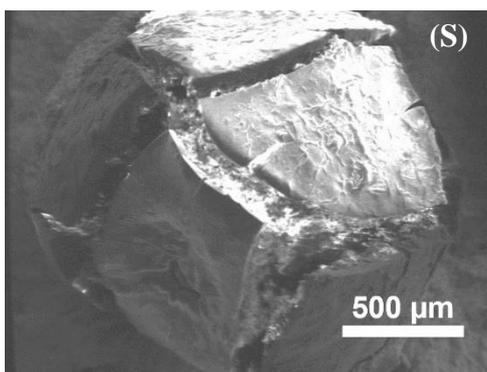
Table S1. Vibrational wavenumbers (cm^{-1}) of chitosan typical peaks.

	C-O-C	Amide I & amide II	C-H	-OH and -NH
CS bands (cm^{-1})	1032	1561&1650	2890	3010-3680

CS@CPO-27- Co (R=2)



CS@CPO-27- Co (R=1)



CS@CPO-27-Co (R=1/2)

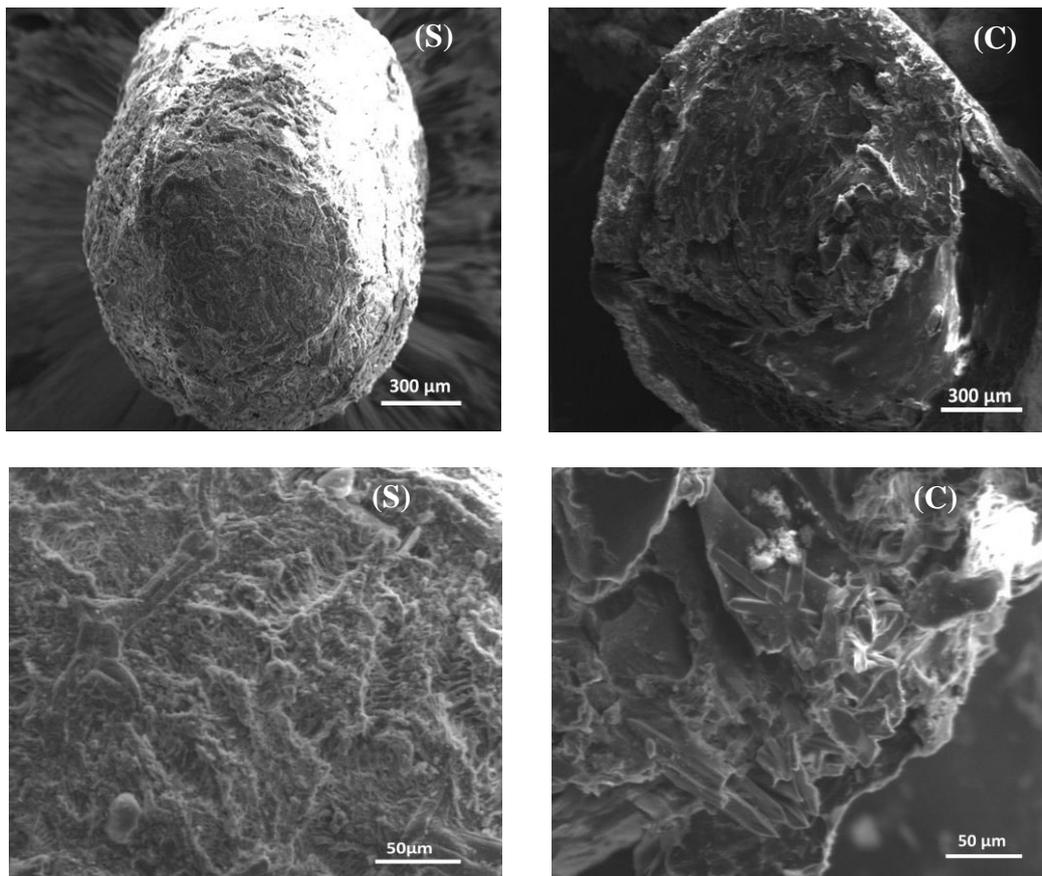


Fig. S4. SEM external surface (S) and cross-section (C) images of CS@CPO-27-Co (R).

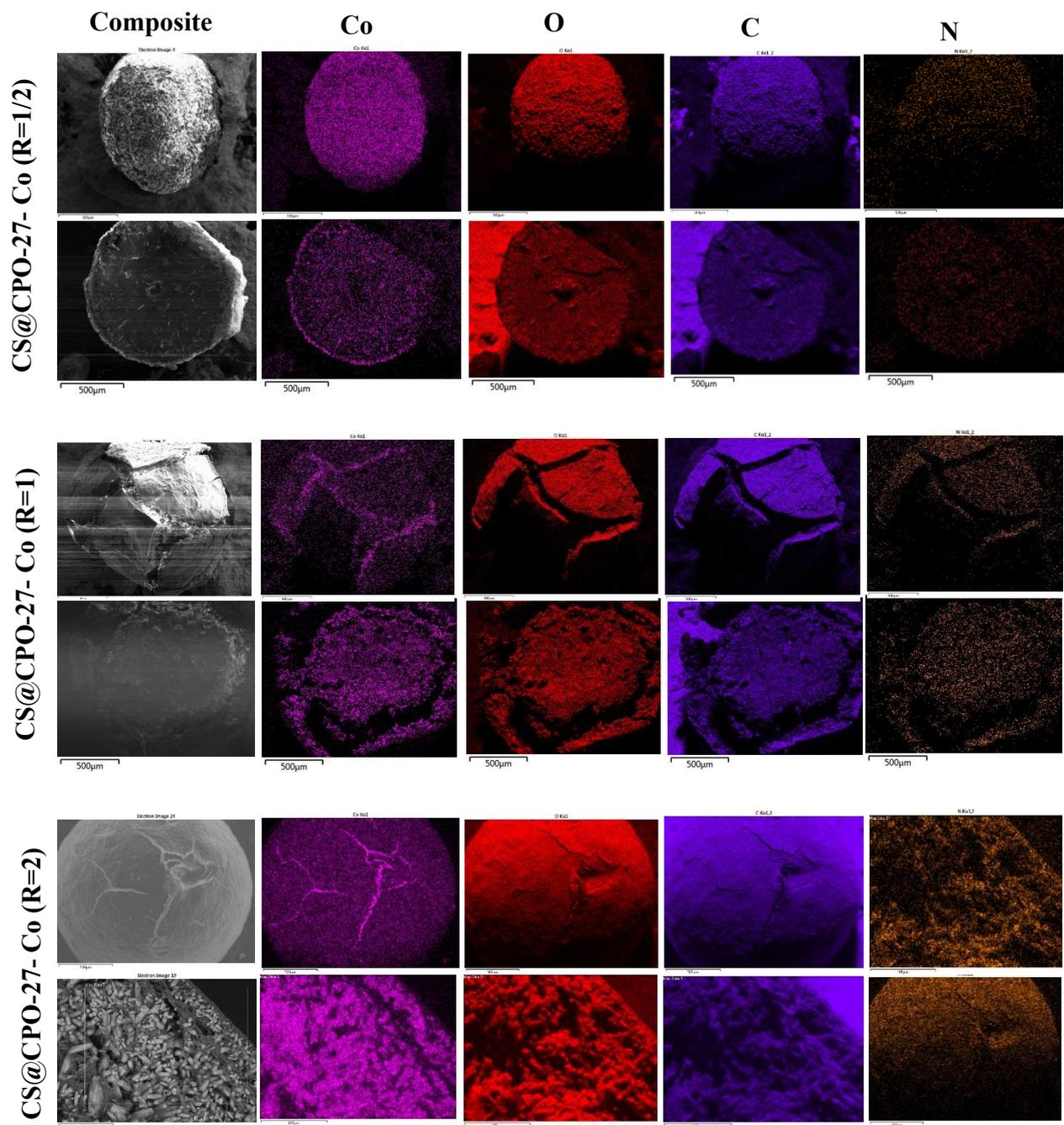


Fig. S5. Surface and cross-section EDS images of CS@CPO-27-Co (R) composites.

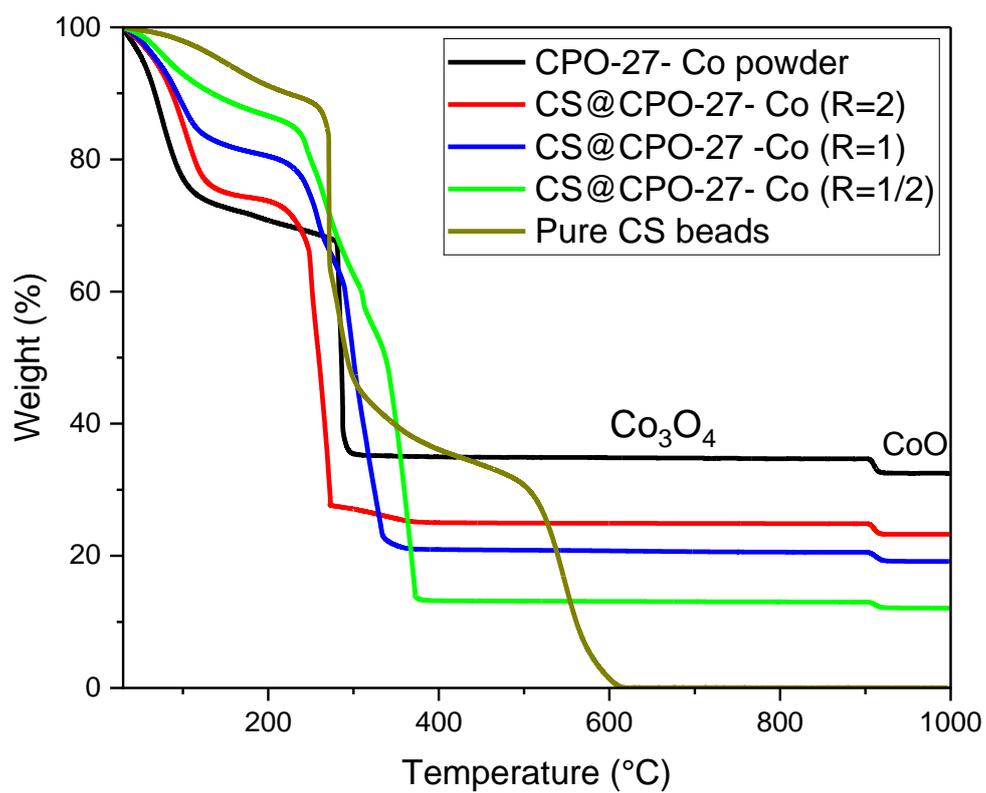


Fig. S6. TGA curves of CPO-27- Co powder, pure CS beads, and CS@CPO-27- Co (R) composites.

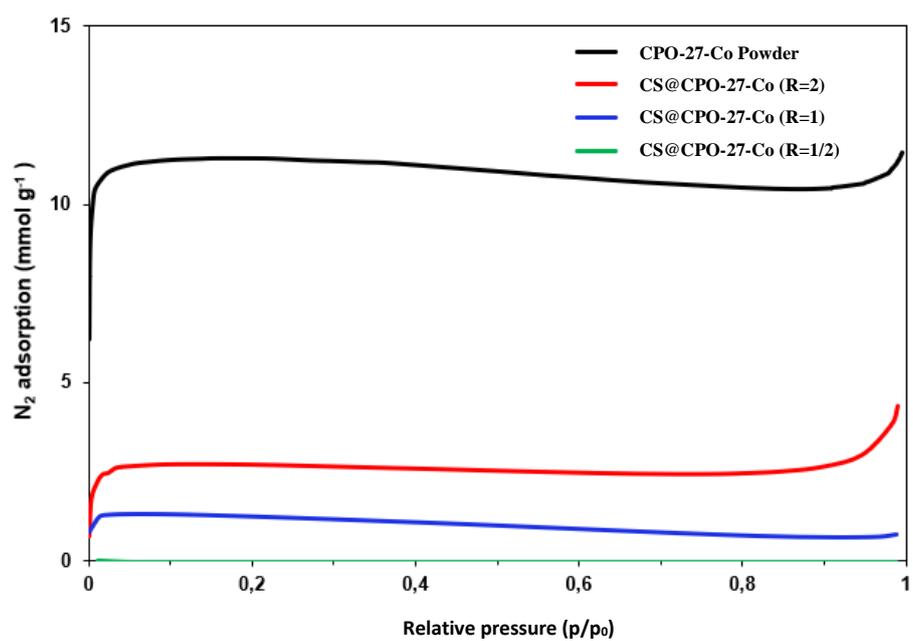


Fig. S7. N₂ adsorption isotherms of CPO-27-Co powder and CS@CPO-27-Co (R) composites at 77 K.

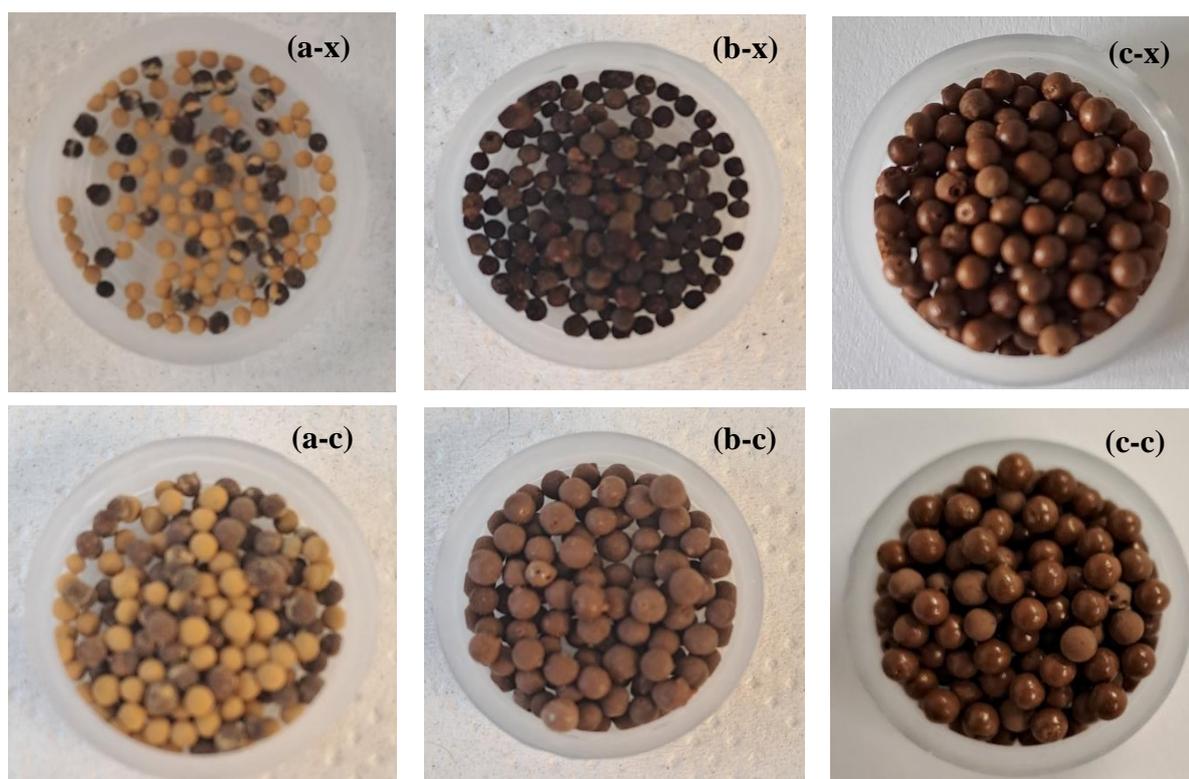


Fig. S8. Composites beads of CS@CPO-27-Co ($R=1/2$) (a), CS@CPO-27-Co ($R=1$) (b), and CS@CPO-27-Co ($R=2$) (c) – x: for xerogels (atmospheric drying), c: Cryogels (freeze drying).

Table S2. Average diameter (D_m) of CS@CPO-27-Co (R) composites beads after air drying (Xerogels) and after air freeze drying

	CS@CPO-27-Co (1/2)	CS@CPO-27-Co (1)	CS@CPO-27-Co (2)
D_m Xerogels (mm)	1.1	1.4	1.9
D_m Cryogels (mm)	1.6	2.1	2.2

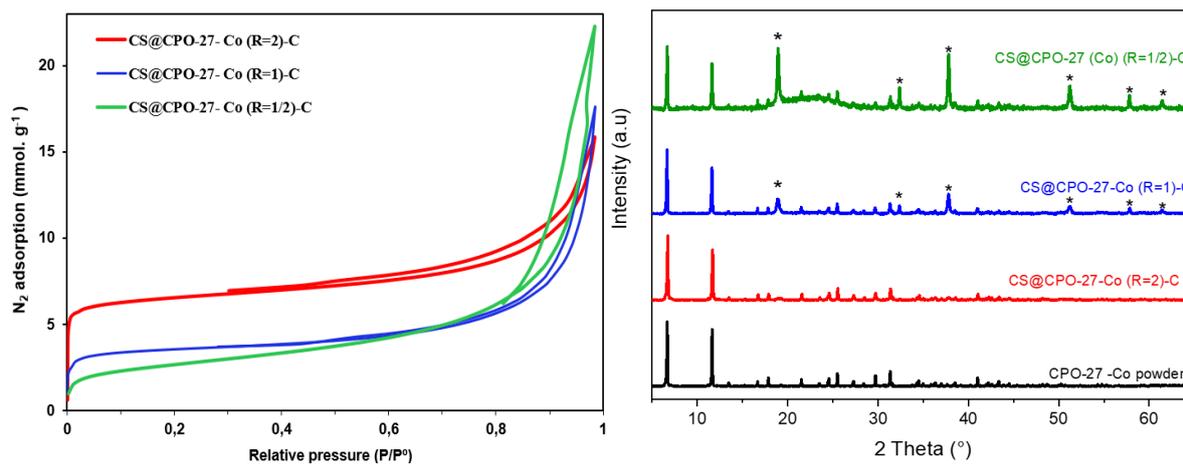


Fig. S9. N₂ physisorption isotherms (left) and PXRD (right) of beads of CS@CPO-27-Co (R)-C beads.

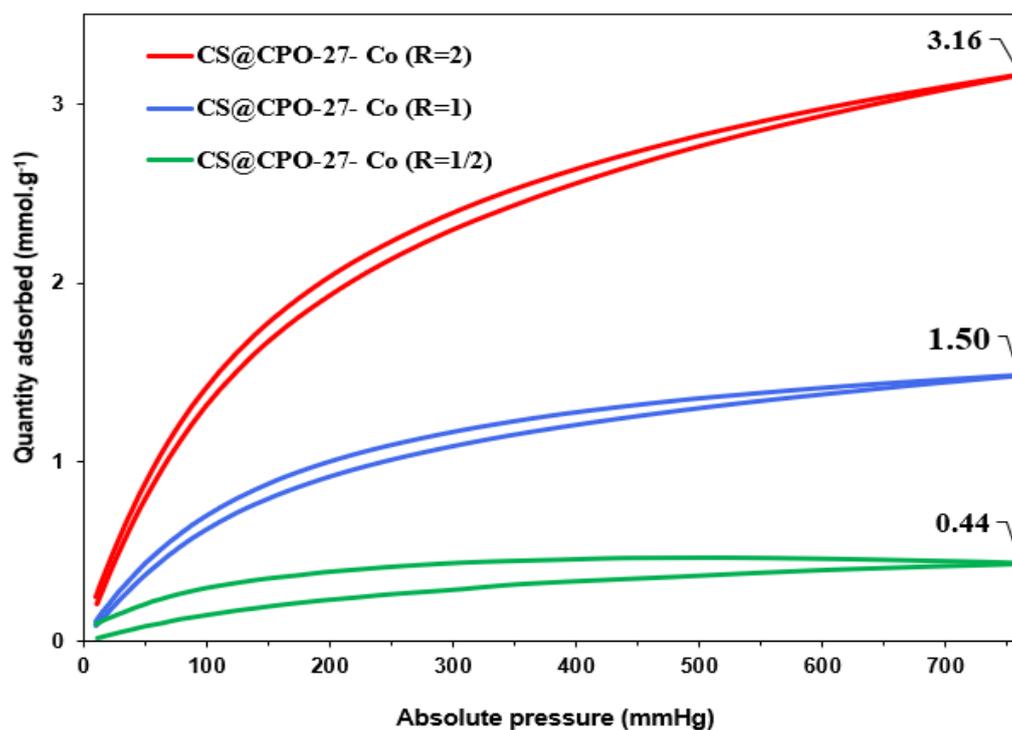


Fig. S10. CO₂ physisorption isotherms of CS@CPO-27-Co (R) xerogel beads measured at 298 K.

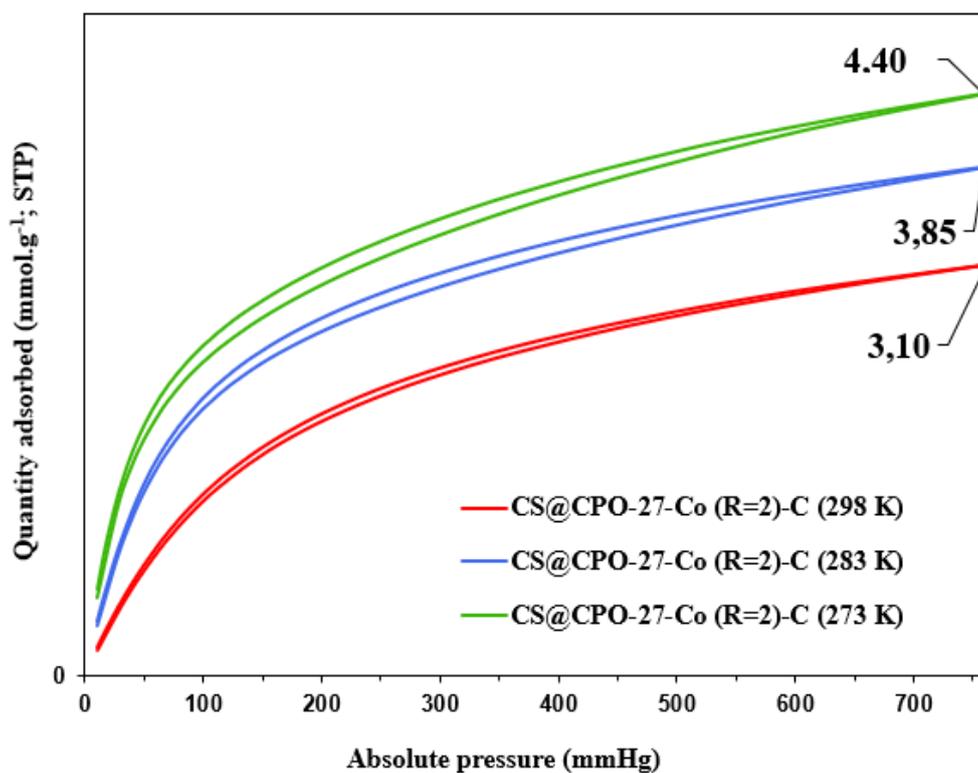


Fig. S11. CO₂ physisorption isotherms of CS@CPO-27-Co (R=2) cryogel beads measured at 273, 283, and 298 K.

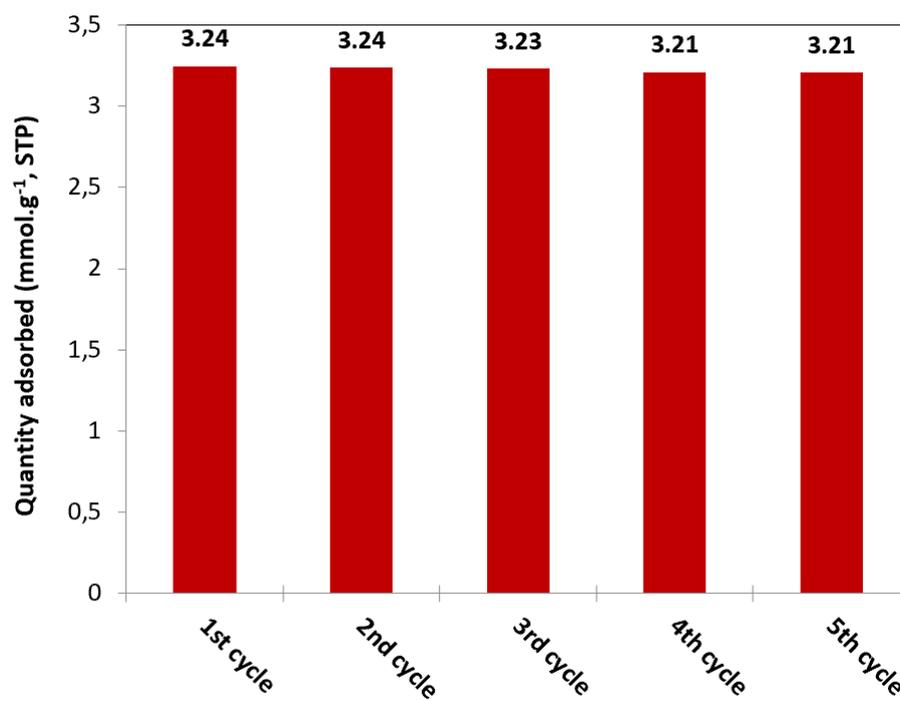


Fig. S12. CO₂ maximal uptake measured over adsorption-desorption cycles using CS@CPO-27-Co (R=2) at 298 K. A degassing step at 393 K for 4 hours was applied between two cycles.

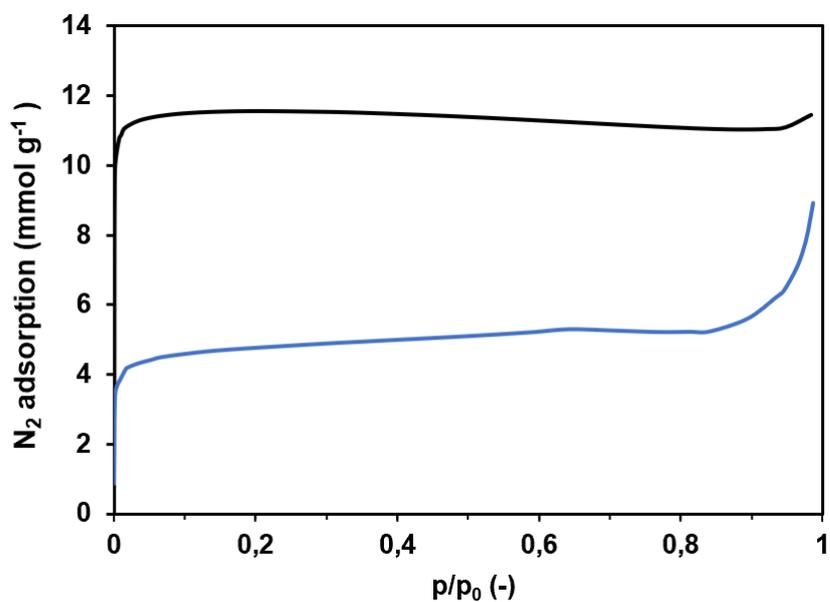


Fig. S13. N₂ adsorption isotherms of CPO-27-Ni powder (black) and CS@CPO-27-Ni (blue) at 77 K.

Table S3. Textural properties of CPO-27-Ni powder and CS@CPO-27-Ni.

	S_{BET} (m ² /g)
CPO-27-Ni	1070
CS@CPO-27-Ni	315