

*Supporting information for:*

**Novel robust hierarchical porous membrane for uranium enrichment:  
fabrication, degradation behavior, and uranium sorption performance**

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## 1. Adsorption procedure

### Uranium adsorption test of hierarchical porous CAP membrane

Hierarchical porous CAP membrane was soaked in 250 mL uranium aqueous solution. Whether for the adsorption kinetics test or the isothermal uranium sorption process, the sample solution was taken out at regular intervals until the sorption equilibrium. Specifically for the kinetic sorption, hierarchical porous CAP membrane (10 mg) was immersed into 250 mL, 10 ppm uranium aqueous solution (pH=6) at 25 °C, and the mixture was magnetically stirred at 300 r/min. Sample solutions (0.5 mL) were collected at 0, 0.5, 1, 2, 3, 4, 6, 8, 10, 12 hours, respectively.

### Determination of uranium concentration

The uranium concentration was measured *via* UV-Vis with arsenazo III as a chromogenic agent, and the absorbance at the maximum absorption wavelength ( $\lambda_{\max}$ ) of 652nm was recorded. The specific steps were as the following:

The acquisition of the standard curve:  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.21097 g) was carefully transferred into a 100 mL volumetric flask, and the ultrapure water was added to achieve the uranium stock solution (1000 ppm). Subsequently, 40, 80, 120, 160, 200, 240, 280, 320, 360, 400, 440, and 480  $\mu\text{L}$  of the standard solution was separately added into 10 mL volumetric flasks, and standard solutions with uranium concentrations at 4, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48 ppm can be obtained, respectively. Afterwards, the standard uranium solution (0.5 mL), hydrochloric acid (0.1 mol/L, 0.5 mL), arsenazo III (1 g/L, 1 mL) and ultrapure water (2 mL) were sufficiently mixed and poured into a quartz cuvette for UV-Vis tests. The absorbances ( $A$ ) at 652 nm were recorded, and the absorbances *versus* uranium concentration linear regression equation can be thus obtained (Figure S7,  $R^2=0.9995$ ).

Similarly for sample solution with unknown uranium concentration, the sample solution (0.5 mL), hydrochloric acid (0.1 mol/L, 0.5 mL), arsenazo III (1 g/L, 1 mL) and ultrapure water (2 mL) were fully mixed and transferred into a quartz cuvette to measure the absorbance at 652 nm. According to the resultant linear regression equation,

the uranium concentration of each sample can be thus achieved, and the uranium adsorption amount can be further calculated by the following equation.

$$q_t = (C_0 - C_t)V/m$$

Where  $q_t$  (mg/g) is the uranium sorption amount at the contact time.  $C_0$  (ppm) and  $C_t$  (ppm) are the concentrations of uranium at  $t=0$  and  $t$ , respectively.  $V$  (L) is the volume of the solution, and  $m$  (g) is the mass of the adsorbent.

## 2. Equations

### Equation S1:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

Where  $q_t$  (mg/g) and  $q_e$  (mg/g) are the uranium-adsorbed amounts at the contact time and adsorption equilibrium time, respectively.  $t$  (min) is the contact time and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant.

### Equation S2:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Where  $q_t$  (mg/g) and  $q_e$  (mg/g) are the uranium-adsorbed amounts of *CAP* membrane at the contact time and adsorption equilibrium time, respectively.  $t$  (min) is the contact time and  $k_2$  (g/(mg min)) is the rate constant.

### Equation S3:

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} \quad (3)$$

Where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of uranium,  $C_e$  ( $\text{mg L}^{-1}$ ) is the concentration at equilibrium,  $V$  (mL) is the volume of simulated seawater, and  $m$  (g) is the mass of the *CAP* membrane.

### Equation S4 and Equation S5

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \quad (4)$$

$$q_e = k_F C_e^{\frac{1}{n}} \quad (5)$$

Where  $C_e$  (mg/L) and  $q_e$  (mg/g) are separately the uranium concentrations and the uranium adsorption amounts of the adsorbent at equilibrium;  $q_m$  (mg/g) is the adsorption capacity;  $k_L$  (L/mg) is the Langmuir adsorption constants;  $k_F$  and  $n$  are the Freundlich adsorption constants.

### Equation S6

$$q_t = k_{ip} t^{0.5} + C \quad (6)$$

Where  $q_t$  (mg/g) and  $t$  (min) are the uranium-adsorbed amount at the contact time and the contact time, respectively.  $k_{ip}$  is the internal diffusion constant.  $C$  is the intercept of the equation.

### 3. Figures

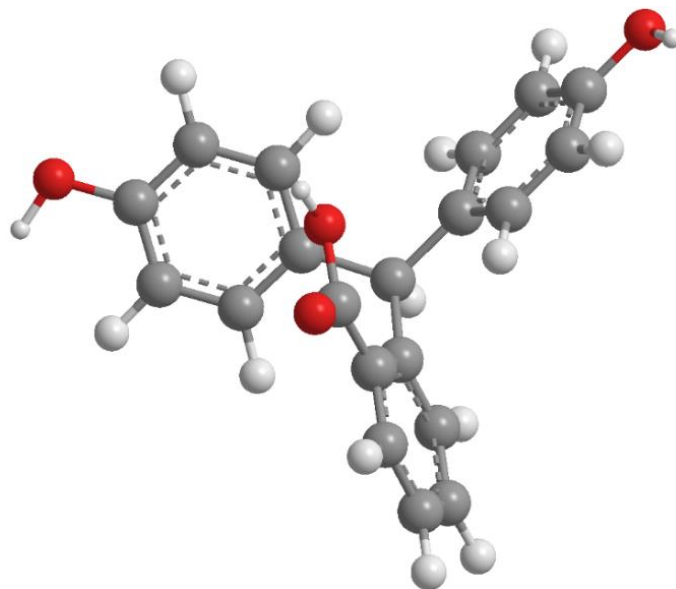


Figure S1 The spatial structure of phenolphthalein.

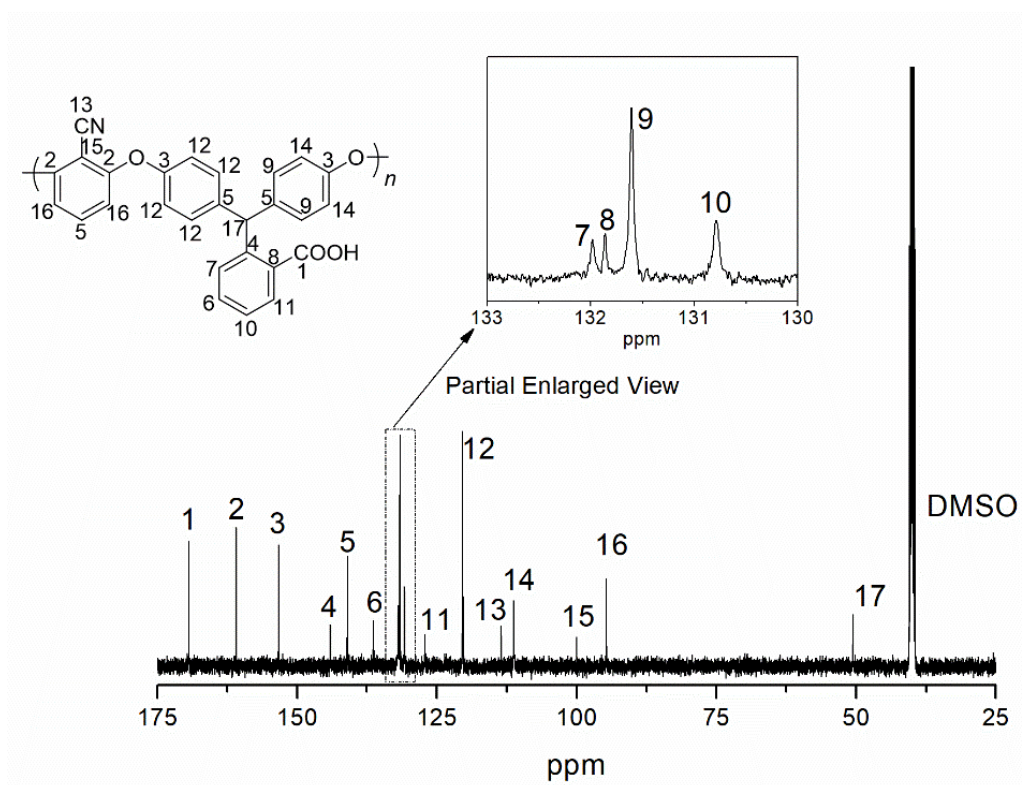
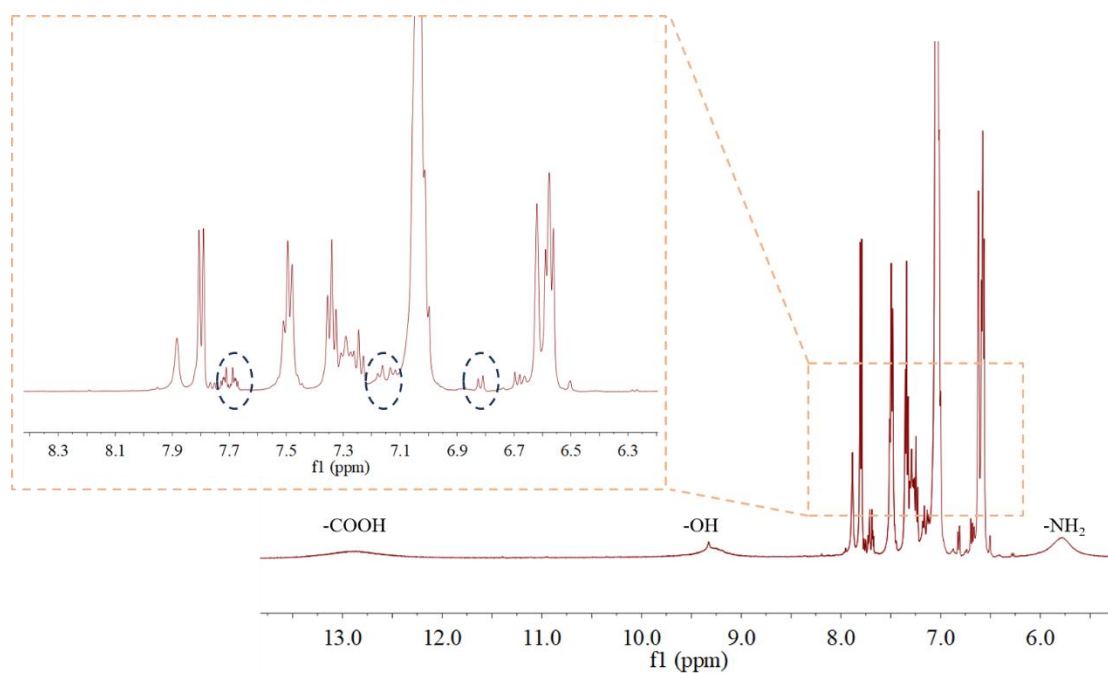
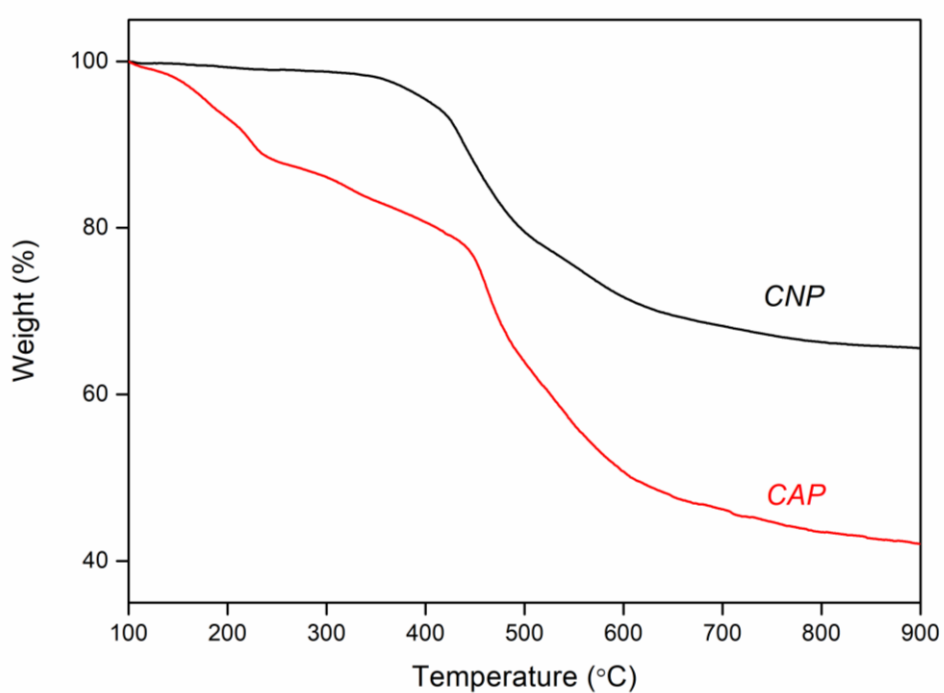


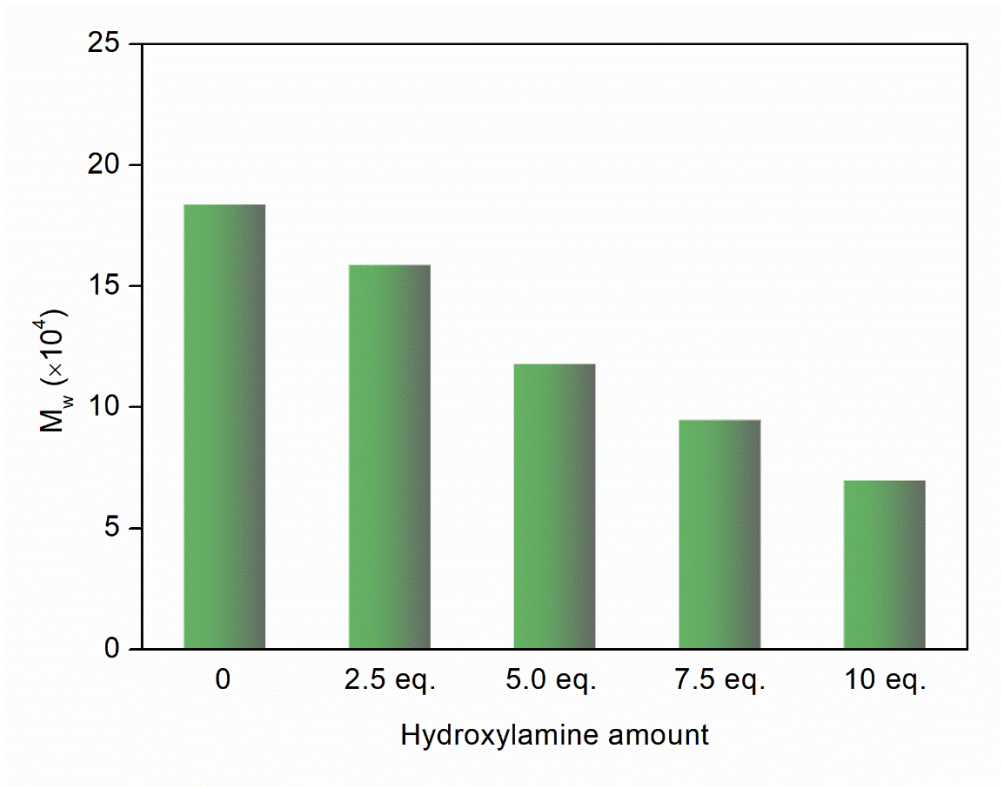
Figure S2  $^{13}\text{C}$  NMR spectrum of *CNP* in  $\text{DMSO-d}_6$ .



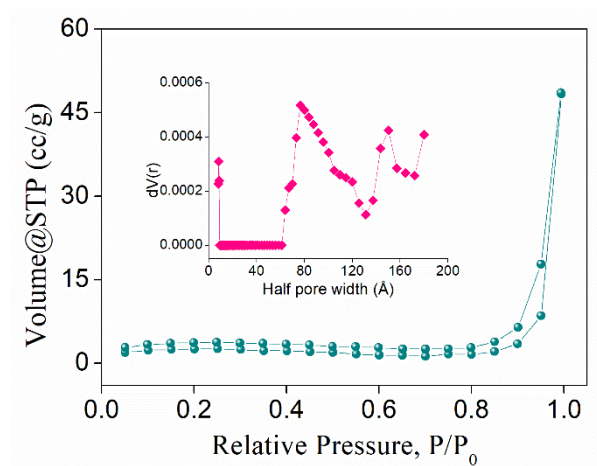
**Figure S3 <sup>1</sup>H NMR spectrum and of *CAP* in DMSO-d<sub>6</sub>. Enlarged image section: chemical shift around 6.3-8.3 ppm.**



**Figure S4 Thermal properties of *CAP* and *CNP* tested by TGA.**

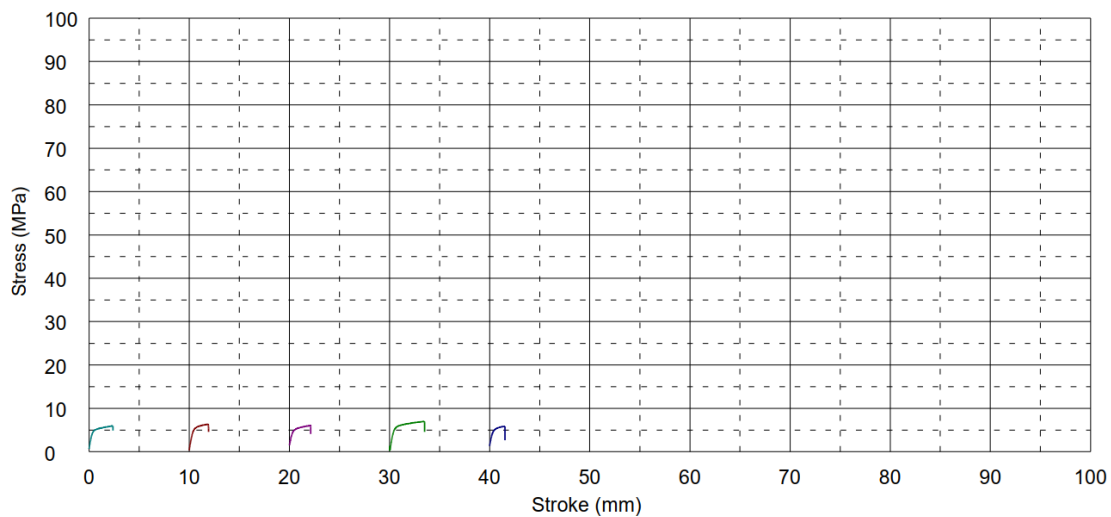


**Figure S5** Changes in *CAP* molecular weight ( $M_w$ ) at different concentrations of hydroxylamine.

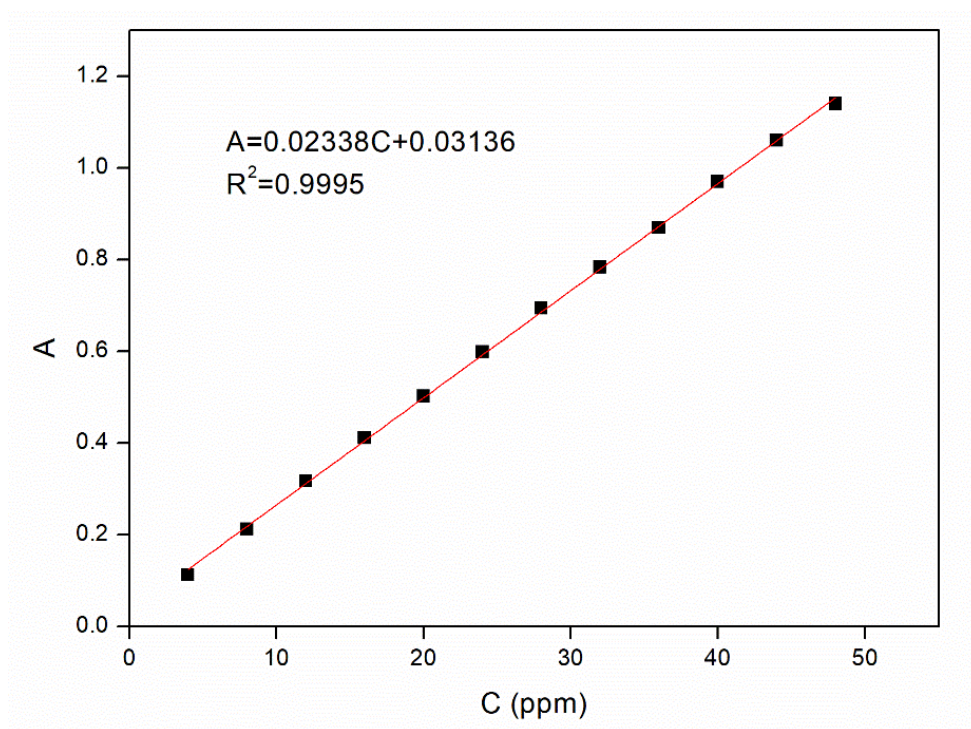


**Figure S6** Isothermal adsorption-desorption curve and pore size distribution via BET analysis (e)

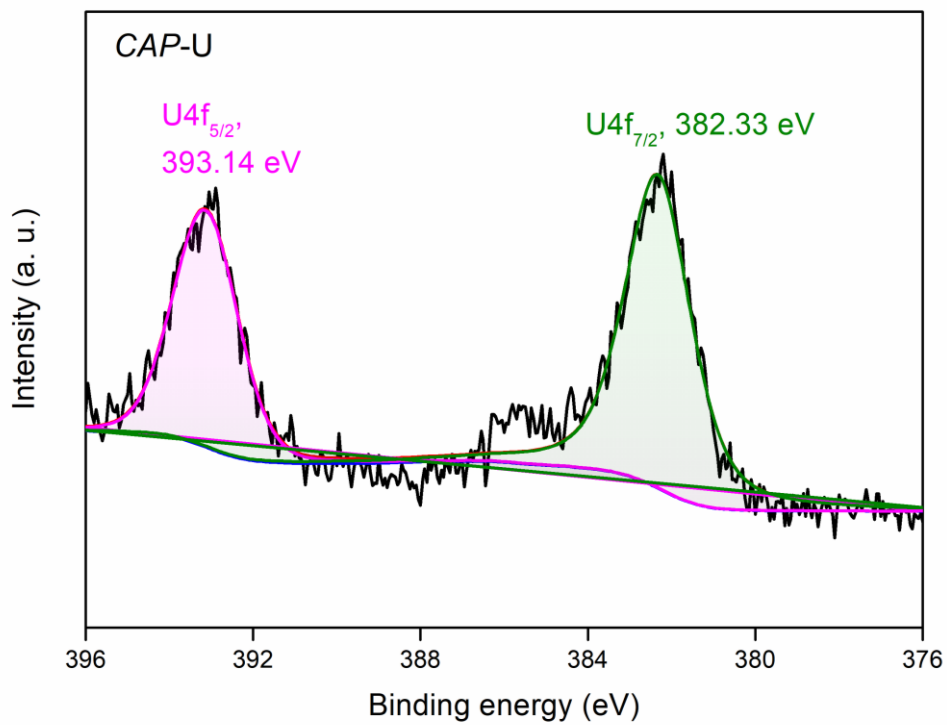




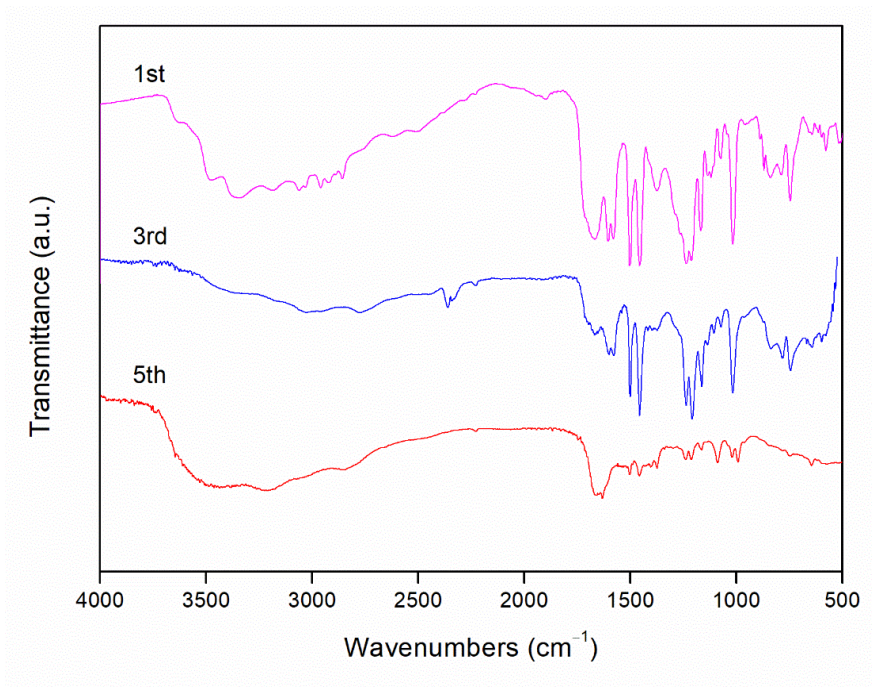
**Figure S7 The tensile property of hierarchical porous *CAP* membrane**



**Figure S8 Liner regression equation of standard curve.**



**Figure S9 High resolution of U4f XPS.**



**Figure S10 FTIR spectra in the 1st, 3rd, and 5th sorption-desorption cycles.**

#### 4. Tables

**Table S1 Soluble property of *CAP* in common organic solvents.**

Solvents	DMF <sup>a</sup>	DMAc	NMP	DMSO	CHCl <sub>3</sub>	THF	1,4-dioxane	Methanol
<i>CAP</i>	++	++	++	++	++	++	+-	-

<sup>a</sup> DMF = *N,N*-dimethylformamide; DMAc = *N,N*-dimethylacetamide; THF = Tetrahydrofuran. NMP = *N*-methyl-2-pyrrolidone; DMSO = Dimethyl sulfoxide; ++, soluble; +-, partial soluble; -, insoluble. All soluble property was tested at 25 °C by dissolving 10 mg of *CAP* in 1 mL of solvent for 24 h.

**Table S2 Detailed *CNP* oximation reaction parameters with the hydroxylamine content at 2.5, 5, 7.5, 10 eq., respectively.**

Term	Solvent	Solid content (wt%)	Temperature (°C)	Stirring speed (r/min)	Reaction time (h)	<i>CNP</i> (mmol)	Hydroxylamine (mmol)
1	DMAc	10	45	300	48	5	12.5
2	DMAc	10	45	300	48	5	25
3	DMAc	10	45	300	48	5	37.5
4	DMAc	10	45	300	48	5	50

**Table S3 Molecular weight of *CAP* in different hydroxylamine concentrations.**

Term	hydroxylamine	Mn (×10 <sup>4</sup> )	Mw (×10 <sup>4</sup> )
<i>CNP</i>	-	16.4	18.4
<i>CAP</i> -2.5	2.5	11.6	15.9
<i>CAP</i> -5.0	5.0	11.8	12.3
<i>CAP</i> -7.5	7.5	5.9	9.5
<i>CAP</i> -10.0	10.0	6.9	7.0

**Table S4 Mechanical performance of hierarchical porous CAP membrane.**

Term	1	2	3	4	5	Mean
Ts (MPa)	5.97	6.35	6.07	6.98	5.87	6.25
E <sub>B</sub> (%)	11.92	9.62	10.7	17.4	7.68	11.48

**Table S5 Distribution coefficient and adsorption kinetic parameters.**

Item	$C_0$ (ppm)	$K_d$ (mL/g)	Pseudo second order			Pseudo first order		
			$R^2$	$q_e$ (mg/g)	$k_2$ (g/(mg min))	$R^2$	$q_e$ (mg/g)	$k_1$ (/min)
CAP	10	$3.84 \times 10^7$	0.9972	244	$5.36 \times 10^{-5}$	0.9968	233	$8.62 \times 10^{-3}$
CAP	20	$1.63 \times 10^5$	0.9956	476	$1.70 \times 10^{-5}$	0.9942	513	$8.14 \times 10^{-3}$

**Table S6 Langmuir and Freundlich models parameters.**

Langmuir model			Freundlich model		
$R^2$	$q_m$ (mg/g)	$k_L$ (L/mg)	$R^2$	$k_F$	$n$
0.9940	499	1.7279	0.8527	289.0875	5.2664