Supplementary Information

Co-irradiation induced graft polymerization of pre-swollen polyacrylonitrile nanofiber membrane for Uranium Extraction from Seawater

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1. Experimental section

1.1 Characterization methods

Fourier-transform infrared (FT-IR) spectra were collected on a Nicolet Avatar 370 FTIR spectrometer (Thermo Nicolet Company, USA) in attenuated total reflectance mode with a resolution of 4 cm^{-1} and 16 scans. The elemental composition and chemical states of the membranes were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo SCIENTIFIC ESCALAB 250Xi instrument. The XPS data were acquired through wide scans ranging from 0 to 1300 eV.

TGA was performed (NETZSCH, TG209, F3) in the temperature range from 25 to 800°C with a heating rate of 10 °C per minute under a nitrogen flow. Mechanical tests were conducted on a universal material testing machine (TIDJ-1000, Suzhou Zhuo Xu Precision Industry Co. Ltd., China). Nitrogen adsorption–desorption isotherms were measured by a surface aperture adsorption instrument (ASAP2010C, Micromeritics). The specific surface areas of the samples were calculated using Brunauer–Emmett–Teller (BET) method within a relative pressure (P/P_0) range of 0.0–1.0, and the pore size distribution were calculated by the Barret–Joyner–Halenda (BJH) algorithm.

The surface and cross-sectional morphologies of the membrane samples and the energy dispersive spectroscopy (EDS) analysis was performed using field-emission scanning electron microscopy (SEM) (JSM-6700F, JEOL, Japan). All the membranes were frozen and cracked in liquid nitrogen to investigate the original cross-section morphologies. All nanofiber membrane samples were sputtered with gold to enhance the electron conductivity before observation by SEM.

Contact angle experiment was used to analyze the hydrophilic and hydrophobic properties of materials by a KSV Instrument. The samples were fixed upon the specimen stage. A drop of 5 μL distilled water was dropped onto the surface of the sample. Photographs were recorded with a NAVITAR camera to analyze the contact angle. The angle of the contact point between water droplets and the sample surface was regarded as the contact angle of the sample. Each sample was measured five times at different locations of the surface. The concentrations of U and other metals were analyzed by Inductively Coupled Plasma Mass spectrometry (ICP-MS, NexION 300D) and an Atomic Emission Spectrometer (ICP-AES, Optima 8000).

1.2 Simulated seawater screening and reusability of HMWPAO-g-PAO nanofiber membrane

Prepare 5 L of simulated seawater for adsorption-desorption cycling experiments. Begin by accurately measuring 5 L of H_2O. Sequentially add standard metal ion solutions to the H_2O, including UO_2^{2+}, VO_3^-, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}, in the following volumes: 1.65 mL, 0.75 mL, 0.5 mL, 0.025 mL, 0.50 mL, 3.0 mL, 2.0 mL, and 0.015 mL, respectively. Dissolve 175 g of sea salt in the prepared solution. Next, add 0.25 g of Na_2CO_3 to adjust the pH to approximately 8.0 ± 0.1, simulating the pH of natural seawater. Subsequently, introduce approximately 0.02 g of the nanofiber membrane into the 5 L of simulated seawater. Perform the adsorption experiments at 26°C with agitation at 120 rpm for 24 hours using a rotary shaker. Following the adsorption process, elute uranium and competing metal ions from the nanofiber membrane using a 0.1 M HCl solution. The elution is performed at room temperature with agitation at 100 rpm for 30 minutes using a rotary shaker. After appropriate dilution, determine the concentration of eluted uranium by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The adsorption capacity of HMWPAO-g-PAO nanofiber membrane for metal ions is quantified using Equation. Regenerate the HMWPAO-g-PAO nanofiber membrane in a 0.4 M NaOH solution for 30 minutes.

After regeneration, rinse the nanofiber membrane with deionized water to remove residual NaOH, ensuring that the pH of the remaining water in the nanofiber membrane is adjusted to 7.0. Next, approximately 0.02 g of the membrane was added to 5 L of simulated seawater. The adsorption experiment was conducted on a rotary shaker at 26 °C and 120 rpm for 24 h. After the adsorption, the uranium and competing metal ions loaded onto the membrane were eluted with 0.1 M HCl solution at room temperature with a rotary shaker at 100 rpm for 30 min. The concentration of the eluted uranium was analyzed by ICP-OES with an appropriate dilution.

$$Q = C \cdot V/M \quad \text{(S1)}$$

where Q (mg/g) is the adsorption capacity of the metal ions from HMWPAO-g-PAO nanofiber membrane, C (mg/L) is the metal ion concentration measured by ICP-AES, V (L) is the eluted solution volume, and M (g) is the weight of the dried HMWPAO-g-PAO nanofiber membrane that was used. After elution, the HMWPAO-g-PAO nanofiber membrane were immersed in 0.1 M NaOH solution at room temperature for 30 min for regeneration. Then they have rinsed with deionized water until the pH of the excess water in the HMWPAO-g-PAO nanofiber membrane was neutral. The adsorbent was used for the next adsorption–desorption cycle following the same procedure described above.

1.3 The calculation of adsorption model

The solid-liquid ratio for adsorption experiments was 0.01 g of adsorbent in 1 L of uranyl solution. The adsorption experiment was conducted on a rotary shaker at 26 °C and 120 rpm for 24 h. To study the mechanism of uranium adsorption, the experimental kinetic data of the HMWPAO-g-PAO nanofiber membrane for uranium adsorption were simulated using the following pseudo-first-order and pseudo-second-order models.

$$\ln(Q_e - Q_t) = lnQ_e - k_1 t \quad \text{(S2)}$$

$$t/Q_t = 1/(k_2 \cdot Q_e^2) + t/Q_e \quad \text{(S3)}$$

where Q_t (mg/g) and Q_e (mg/g) are the uranium adsorption capacities at time t and equilibrium time, respectively; t is the contact time (h); k_1 and k_2 represent the kinetic rate constants of the pseudo-first-order (/h) and pseudo-second-order models, respectively (g/ (mg·h)).

To further clarify the uranium adsorption mechanism of the HMWPAO-g-PAO nanofiber membrane, the Langmuir and Freundlich equilibrium models were employed to fit the experimental data using eqs. (S4) and (S5), respectively:

$$C_e/Q_e = C_e/Q_m + 1/(K_L \cdot Q_m) \quad \text{(S4)}$$

$$\ln Q_e = lnK_F + (1/n) \cdot \ln C_e \quad \text{(S5)}$$

where Q_e is the uranium adsorption capacity at equilibrium (mg/g), C_e is the equilibrium concentration of uranium (mg/L), Q_m is the maximum uranium-adsorption-capacity or saturation capacity at complete monolayer coverage (mg/g), K_L is the Langmuir adsorption constant, which represents the affinity between the adsorbates and adsorbents (L/mg), and K_F and n are the Freundlich constants characteristic of a particular adsorption isotherm (L/g).

2. Supplementary Figures S1-S4

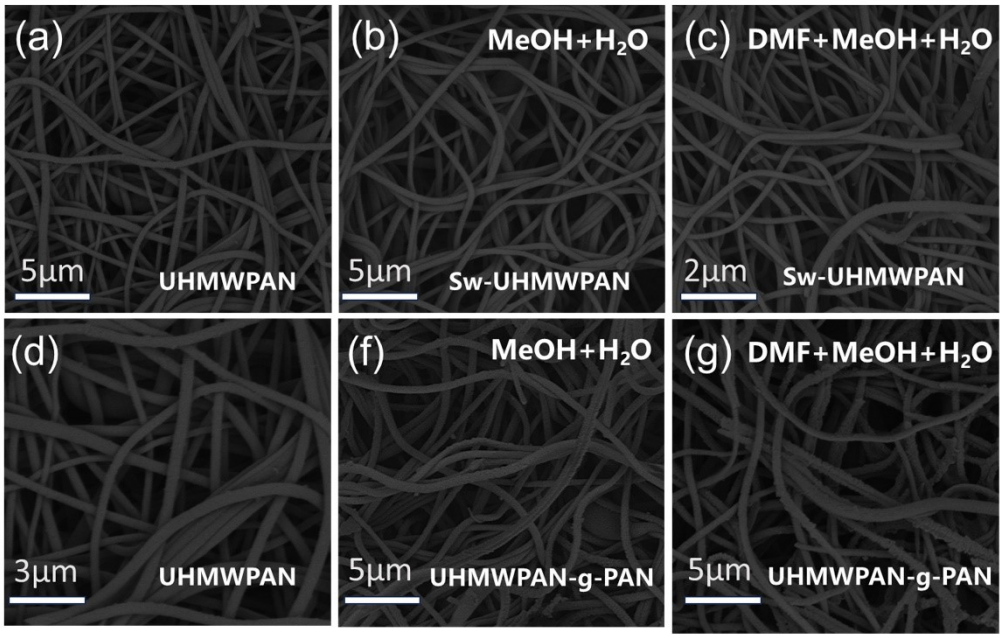


Fig. S1. SEM images of (e) HMWPAN, (f) Sw-HMWPAN, (g) HMWPAN-*g*-PAN, and (h) HMWPAO-*g*-PAO.

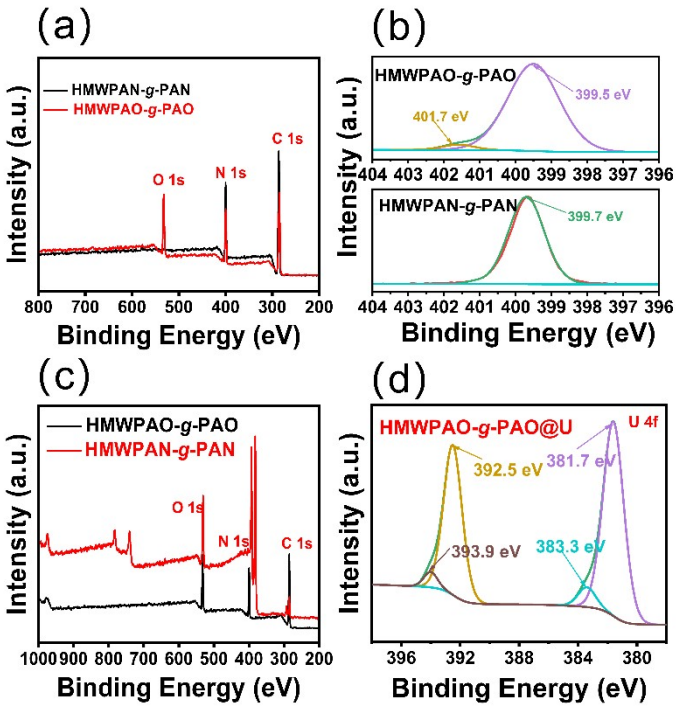
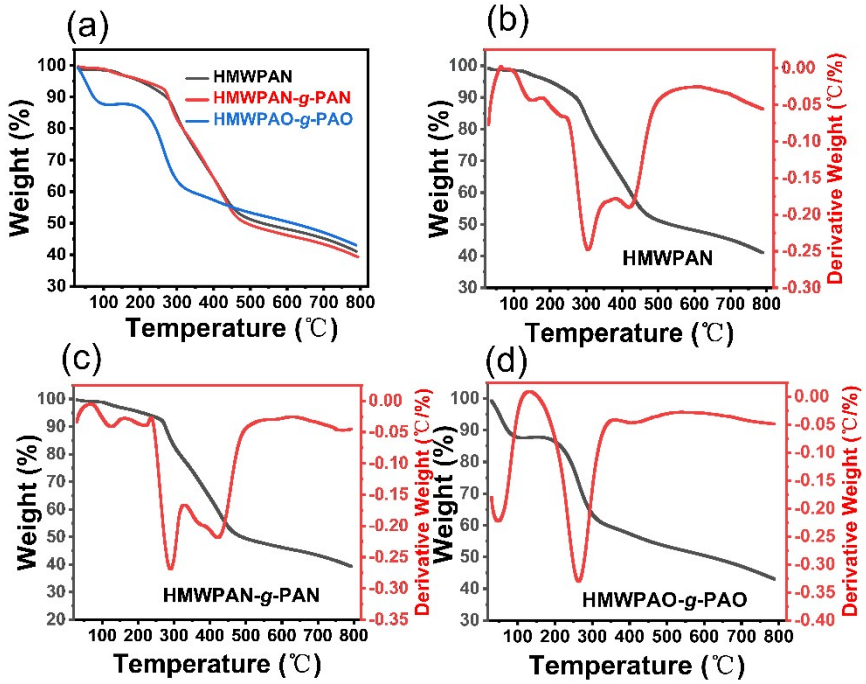


Fig. S2. Full spectrum XPS spectra of HMWPAN, HMWPAN-g-PAN, and HMWPAO-g-PAO nanofiber membrane.



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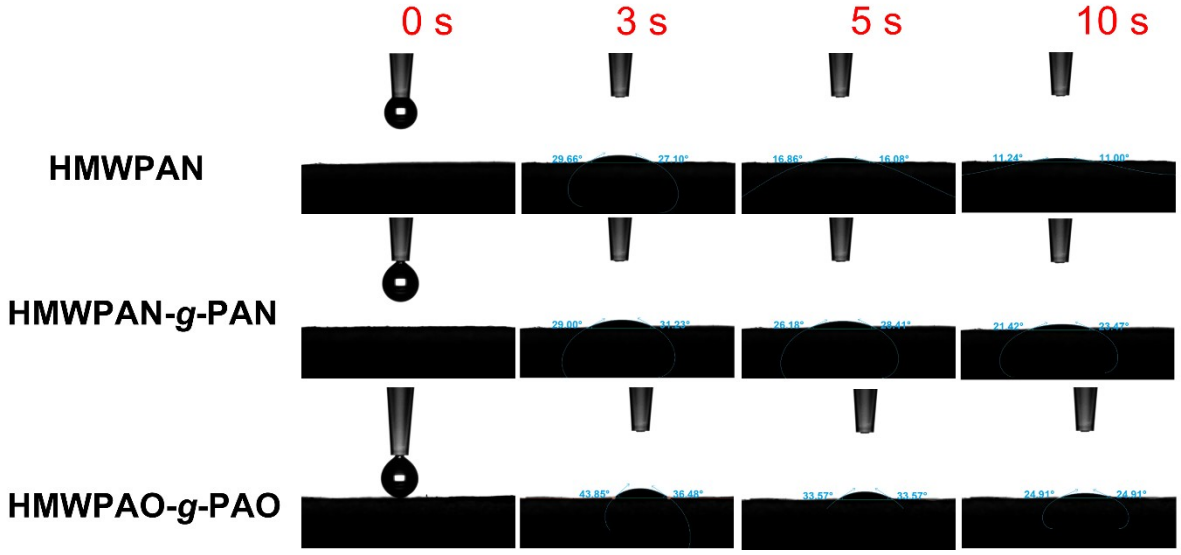
100 Fig. S3. TGA and DTG curves of (a) HMWPAN, (b) HMWPAN-g-PAN, (c) HMWPAO-g-PAO

101 nanofiber membrane in N_2 atmosphere.



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103 Fig. S4. HMWPAN, HMWPAN-g-PAN, and HMWPAO-g-PAO water contact angle photo of

104 nanofiber membrane.

105 3. Supplementary Tables

106 Table S1. A comparison of the tensile strength of different materials.

Materials	The tensile strength MPa	Ref.
This work	≈18	/
PVDF/MXene	7.24	[41]
HA-PAO NFMs	13.6±0.9	[42]
PA-PAO/CS/PEO NFs	8.33 ± 0.15	[43]
c-PVA-g-PAO NFs	10.39	[44]
AO10-CPAN	10.6	[45]
PIDO NF	2.5	[46]
EVOH/MXene NFs	1.43	[47]
PAO/PAN	3.2	[48]
EVOH-g-PAO-PAA NFs	2.24	[49]

Table S2. A comparison of the monomer utilization ratio of various materials through radiation grafting is presented.

Materials	Monomer		Utilization ratio	Ref.
	Name	Density/(g/cm^3)	%	
PP-RIGP-(PAAc-co-Pam)	AM	1.13	0.54	[52]
NWF-g-PGMA-AO	AN/AA	0.806/1.051	2.00	[53]
PES-g-PAAc	AA	1.051	2.09	[54]
PES-co-AMS	AMS	0.909	5.13	[55]
PAO-AMS-A	AMS	0.909	12	[56]

PE-g-P(AN-co-AA)	AN	0.806	14.47	[57]
AO-HPE	AN	0.806	26.19	[58]
DPNR-g-PAN	AN	0.806	46	[59]
This work	AN	0.806	83.02	/

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111 Table S3. **A** comparison of adsorption capacities in natural seawater among adsorbent materials.

Adsorbents	Adsorption from natural seawater		Ref.
	mg-U/g-ads	time(d)	
MSF@PAO-PEI	1.102	20	[60]
PP	1.15	15	[61]
PAO-Y	1.969	15	[62]
HFAO-QPEI	2.45	21	[63]
PP@MeP-H	3.12	21	[64]
PAO-PHMB-A	3.19	30	[65]
FF-PT	3.22	30	[66]
AI10-AI17	3.35	56	[67]
AF8	4.48	56	[68]
PVC-co-CPVC	5.2	49	[69]
AM	6.03	70	[70]
AFM	7.46	56	[71]
This work	8.32	50	/
CID NFs	11.39	87	[72]

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113 Table S4 Ions concentration in simulated seawater

Element	U	V	Fe	Co	Ni	Cu	Zn	Pb	Mg	Ca
Simulated Seawater Conc. in system (ppb)	330	152	141	5.3	101	65	408	34.6	1.2×10^5	0.6×10^5

114