ABSTRACT: Owing to many problems of the detriment by large amount of organic reagents, high cost and difficulty of industrialization, development of high-efficiency economical technologies for uranium extraction is an irresistible trend to support steady supply of nuclear energy. Herein, a novel fibrous adsorbent, named as AO-HPE fibers, was prepared by introduction of amidoxime groups using the green vapor-phase grafting polymerization (VPGP) technology of monomer acrylonitrile (AN). Gaseous AN was grafted onto the ultra high molecular weight polyethylene (UHMWPE) fibers at 80 °C in the enclosed evaporation and condensation reflux system. The innovative technology not only endowed synthetic process high monomer utilization ratio but also excellent environmental friendliness. The AO-HPE fibers exhibited an appreciable calculated maximum adsorption capacity \( (Q_m) \) of 1144.94 mg g\(^{-1}\) in uranium solution and an adsorption capacity of 14.11 mg g\(^{-1}\) in simulated seawater. Meanwhile, the higher uranium selectivity than main competing ion vanadium (adsorption mass ratio was almost 5) was achieved. The adsorption process accorded closely with chemisorption mechanism. This work provided a novel idea for the synthetic method of adsorbents for uranium extraction, and inspired the sustainable technologies for grafting polymerization of monomer AN.

1. INTRODUCTION

The special and essential application in the nuclear industry determined that uranium has become an economic resource rather than just a natural resource.\(^1\) Estimated at rate of global energy consumption, the current global terrestrial uranium reserves can only meet the use of nuclear power generation for 80–120 years.\(^2\)–\(^4\) The ocean is main supplier of uranium, and the total reserves of uranium in terrestrial ores are only one-thousandth of those in the oceans. Therefore, uranium in natural seawater will still be a desirable source for nuclear energy in the future, and uranium extraction from seawater (UES) meets the requirements of industrial efficiency and environmental protection. Although uranium is abundant in the ocean, it exists in highly stable Ca\(_2\)(UO\(_2\))(CO\(_3\))\(_3\) complex form with an average concentration of only 3.3 ppb.\(^5\)–\(^7\) Besides V(III), Na(I), Mg(II), Ca(II) and Zn(II) et al. also have strong competition with uranium. Therefore, more and more advanced adsorbents that have high-efficiency and economical advantages are indispensable to extraction of uranium from such low concentrations.\(^8\)

Until now the amidoxime-based (AO) adsorbents are still one of the most potential materials for uranium extraction due to the specific and excellent chemical complexation.\(^9\)–\(^10\) A variety of AO adsorption materials have been developed, including covalent-organic frameworks (COFs),\(^11\)–\(^12\) metal–organic frameworks (MOFs),\(^13\)–\(^14\) porous organic polymers (POPs),\(^15\)–\(^16\) inorganic adsorbents\(^17\) and genetic engineered materials.\(^18\) In terms of the performance, lots of excellent adsorbents have been fabricated via multifarious technologies with a high uranium adsorption capacity in natural seawater or radioactive effluent. Xu et al. first reported a kind of groundbreaking 3D hierarchical porous AO adsorbents via multi-step grafting polymerization which achieved a high capacity of 11.50 mg g\(^{-1}\) after trimestral successive adsorption in natural seawater.\(^19\) Recently, a novel functionalized magnetic Fe\(_3\)O\(_4\)@TiO\(_2\) core-shell microspheres were designed by Zhao et al. via classical solvent hydrothermal method exhibited the maximum uranium adsorption capacity of 313.6 mg g\(^{-1}\) at pH 6.0.\(^20\) For uranium extraction from high salinity seawater, an outstanding investigation has reported a photoelectric-assisted method by exploiting a kind of bifunctional nitride material. The result indicated that the extraction capacity of the adsorbent could be significantly improved to reach 1556 mg g\(^{-1}\) under light illumination.\(^21\) In addition, based on the technology of surface self-assembly, researchers fabricated the macroporous resin by a simple one-step method, which
achieved a high uranium adsorption capacity of 157 mg g⁻¹ in 32 ppm uranium-spiked seawater.²²

In spite of these, there are still two major inescapable problems with existing traditional technologies for preparation of AO adsorbents. The first is low monomer utilization ratio of less than 20 wt. %,²³,²⁴ and the other is serious environmental toxicity attributed to the large use of organic reagents. The comprehensive uranium adsorption performance of existing adsorbents has been able to gradually meet the strategic requirement of UES. However, the development of UES gradually tends to industrialization and scale.⁶,²⁵ Accordingly, referring to the uranium spot price ($28.33 per pound of uranium, Mar., 2021),²⁶ maximizing the matching of adsorbents’ adsorption capacity, cost of the preparation and cost of uranium extraction should be the focus of current researches. It can be further acknowledged that the reusability, easy management and economic benefit of the adsorbents will be the priorities to be investigated in future researches.

Due to a series of advantages such as simplicity of operation and production, substrate diversification, reusability of monomer, low investment and environmental friendliness, the vapor-phase technology has been widely used in industrial production.²⁷,²⁸ Based on the original intention to solve foregoing problems, herein, we first reported an innovative technology to fabricate the AO-HPE fibers with the layered channel architecture and high AN monomer utilization ratio for uranium extraction. As shown in Figure 1, the schematic diagram illustrated the synthesis of the AO-HPE fibers using a two-step grafting involving pre-irradiation induced grafting polymerization (PIGP) of AA onto the ultra high molecular weight polyethylene (UHMWPE) fibers followed by the green vapor-phase grafting polymerization (VPGP) of AN onto the poly-AA (PAA) chains. In this work, as a simple and efficient modification technology, the VPGP with an enclosed evaporation and condensation reflux system not only gave birth to the repetitive utilization of monomers but also exhibited excellent environmental friendliness. The obtained adsorbents exhibited a stable structure and remarkable adsorption performance. A suite of characterization methods including Fourier transform infrared spectrometry (FT-IR), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and differential scanning calorimeter test (DSC) were used to investigate the physicochemical properties of the fibers before and after the application. The thermal analyses demonstrated that the AO-HPE fibers could maintain good stability during the modification and adsorption. Then, the adsorbents were used for uranium extraction from simulated seawater, and the effect of the pH value and coexisting ions of the solution were discussed. All the results suggested the AO-HPE fibers prepared via VPGP technology could be used as a high-efficiency economical uranium adsorbent from seawater and radioactive effluents in the future.

### 2. RESULTS AND DISCUSSION

#### 2.1. The PIGP of AA and VIGP of AN onto UHMWPE Fibers

The effect of the reaction time on the DG of HPE-PAA fibers was investigated. As shown in Figure 2a, the DG of PAA on modified fibers increased slowly before grafting for 1.5 h, and increased sharply to 127.6% from 29.4% for 2 h. The results were attributed to the high radicals’ initiation activity
and relatively easy diffusion of monomer AA to the surface of irradiated UHMWPE fibers in the early stage of the grafting reaction. After that, the increase of the DG slowed down again and reached relative saturation of 168.9% for 5 h, which could be intuitively interpreted as the restricted diffusion by a great deal of homopolymers produced after a long reaction. In the process of VPGP, as shown in Figure 2b, the grafting polymerization of AN onto HPE-PAA fibers started at 70.2 °C closed to its boiling point of 77.3 °C. The DG of PAN reached peak value at 80 °C, and decreased sharply with the increase of reaction temperature. At low temperature below 70 °C, vapor of AN was insufficient for effective contact with HPE-PAA fibers. While higher temperature than 80 °C did not show any merit of grafting due to the phenomenon that most of gaseous AN resulted in its homopolymers and part of AN vapor was refluxed to the bottom of the reaction vessel. Accordingly, a reaction temperature of 80 °C was identified as the optimum temperature and exploited for the further investigation for effect of the reaction time. As shown in Figure 2c, with the extension of reaction time, the DG of PAN increased almost linearly and could reach more than 70% after grafting for 20 min. After grafting for 40 min, the DG still increased rapidly despite the presence of the homopolymers on the surface of fibers. Therefore, this independent and enclosed evaporation-condensation reflux system endowed a liquid—vapor severance and loop contact of the monomer with fibers. On the other hand, compared to traditional approaches, less homopolymer was produced on the surface of the grafted fibers during this process. Finally, the process of VPGP not only prevented the emission of monomer to environment but also gave birth to the repetitive utilization of monomers. These results all significantly illustrated the efficient advantages and excellent environmental friendliness compared with traditional grafting polymerization in solutions.

2.2. Characterization of the Pristine and Modified Fibers. 2.2.1. FT-IR Characterization. To characterize the chemical structure of UHMWPE, HPE-PAA, HPE-PAN, AO-HPE and AO-HPE alkali fibers, FT-IR tests were employed. As shown in Figure 3, the characteristic absorption peaks at 2914 and 2845 cm\(^{-1}\) were attributed to the asymmetric and symmetric stretching of the -CH\(_2\) groups, and also appeared in the modified fibers. In addition, absorption peaks at 1472 and 721 cm\(^{-1}\) belonged to the bending and swaying vibration of -CH\(_2\) groups on the main chain of UHMWPE fibers. The spectrum of HPE-PAA fibers presented a new peak at 1715 cm\(^{-1}\), which was attributed to the adsorption peak of -C=O in PAA chains. The new feature revealed that AA was successfully grafted onto the UHMWPE fibers. After VPGP, an evident peak at 2250 cm\(^{-1}\) was assigned as -C ≡ N, which indicated that AN was successfully grafted onto the modified fibers. New characteristic peaks of -NH\(_2\) -OH, -C≡N, -C-N- and -N=O - in the spectrum of the AO-HPE fibers appeared at 3140–3450, 1646, 1387 and 920 cm\(^{-1}\), respectively. Meanwhile, the disappearance of the -C ≡ N - peak at 2250 cm\(^{-1}\) and the sharp increasing of -C≡N - peak confirmed that the successful transformation of nitrile groups into the amidoxime groups after reaction with NH\(_2\)OH-HCl.

2.2.2. SEM Characterization. SEM images of the pristine and modified UHMWPE fibers were obtained to investigate their morphologies during the modification processes, as shown in Figure 4. For the original UHMWPE fibers, an average diameter of 18.0 ± 0.07 μm and relatively smooth surface could be observed (Figure 4a). After PIGP of AA, the surface of the UHMWPE fibers was wrapped in PAA gel, and the hydrophilic PAA chains made the surface morphology of the HPE-PAA fibers smoother (Figure 4b). After VPGP, the morphology of the HPE-PAN fibers with a DG of 81.0% was relatively rough, which was attributed to the grafted PAN particles of 75 to 123 nm diameters on surface of the HPE-PAA fibers. The diameter of HPE-PAN changed slightly, illustrating the homogeneous distribution of grafted PAN chains onto the surface of the HPE-PAA fibers (Figure 4c). After ammoximation with NH\(_2\)OH-HCl, the diameter of the AO-HPE fibers increased obviously, and the surface of AO-HPE fibers was wrapped in polymeric particles. Meanwhile, many tiny pits and micro-channels could be observed in superficial region of the AO-HPE fibers (Figure 4d), which might provide a larger specific surface and stable structure for firm loading of uranyl ions. Additionally, X-ray energy dispersive spectrum (EDS) mapping of C and N illustrated that -C ≡ N was distributed throughout the particles and amidoxime groups were widely distributed across the surface of the AO-HPE fibers (Figure 4d).

2.2.3. XPS Characterization. To further analyze the detail chemical components of modified fibers and uranium loaded AO-HPE fibers, XPS test was carried out as shown in Figure 5. From the XPS spectra (Figure 5a), a sharp peak attributed to C 1 s (284.5 eV) was observed in the pristine UHMWPE fibers. Comparatively speaking, the HPE-PAA fibers exhibited a new peak at 531.6 eV (O 1 s), indicating that successful grafted PAA onto the pristine UHMWPE fibers after PIGP. Furthermore, two new peaks of 400.6 eV (N 1 s) and 531.6 eV (O 1 s) emerged at both the HPE-PAN and AO-HPE fibers. There were two peaks at 399.2 and 400.5 eV in the N 1 s spectrum of AO-HPE fibers, as shown in Figure 5b, indicating that C=N and C-N groups were successfully introduced, which was consistent with the results of XPS spectra. From Figure 5c, further analysis from the high-resolution O 1 s spectrum of the AO-HPE fibers, three peaks at 530.7, 532.1 and 533.0 eV could be observed, which were assigned to C=O, N-O and C-O groups, respectively. Furthermore, compared with the original AO-HPE fibers, the specific double peaks at 391.1 and 381.5 eV of the U-uptake AO-HPE (AO-HPE-U) could indicate the uranyl ions have been adsorbed in the AO-HPE fibers (Figure 5d). The high resolution XPS spectra (U4f: U4f5/2, U4f7/2) of the AO-HPE-U further confirmed the existence of uranyl ions (Figure 5e and f). These results demonstrated that the AO-HPE fibers that could provide available complexion sites for uranium adsorption were successfully prepared.

Figure 3. The FT-IR spectra of UHMWPE, HPE-PAA, HPE-PAN, AO-HPE and AO-HPE alkali fibers.
Figure 4. Morphology characterization: SEM images of (a) UHMWPE, (b) HPE-PAA and (c) HPE-PAN fibers. (d) SEM image and EDS mapping of AO-HPE fibers. The insets showed high-magnification images.

Figure 5. The XPS survey spectra of UHMWPE, HPE-PAA, HPE-PAN and AO-HPE fibers: (a) overall spectrum, (b) the N 1s spectrum of AO-HPE fibers, and (c) the O 1s spectrum of AO-HPE fibers. The XPS spectra of AO-HPE and AO-HPE-U fibers: (d) overall spectrum, (e) high-resolution XPS spectra of U 4f5/2 and (f) high-resolution XPS spectra of U 4f7/2.

Figure 6. TG and DTG curves for (a) UHMWPE, (b) HPE-PAA, (c) HPE-PAN and (d) AO-HPE fibers, respectively. (e) DSC patterns for UHMWPE, HPE-PAA, HPE-PAN and AO-HPE fibers.
2.2.4. Thermal Analyses. The amount of grafted groups on fibers was determined by TGA. As shown in Figure 6a, the pristine UHMWPE fibers exhibited high thermal stability up to 453 °C, without residue remained at 472 °C. Two main decomposition processes could be clearly observed in TG-DTG curves of the HPE-PAA fibers (Figure 6b) which included that the first in the temperature range from 151 to 348 °C and the second occurred from 340 to 521 °C. The weight loss was attributed to the complex thermal decomposition of the carboxylic groups and grafted chains. For the HPE-PAN fibers (Figure 6c), the processes including dehydration, decarboxylation of AA groups, cyclization, carbonization of the PAN and carbonization of the PAA chains resulted in five regions of weight loss (30.3 to 150 °C, 150 to 210 °C, 210 to 291 °C, 292 to 403 °C, and 418 to 586 °C, respectively). Apparently, due to the fibers in the process of synthesis with good hydrophilic groups and a layered channel architecture, the first region within 100 °C could be interpreted as the evaporation of physisorbed water.39,40 After amidoximation, the AO-HPE fibers became less thermally stable than the UHMWPE and HPE-PAN fibers with main degradation beginning at approximately 136 °C, which could be precisely attributed to excess combustion product from carbonization of the PAA chains (Figure 6d). The shoulder peak from DSC in Figure 6e suggested a slight increase in the full width at half maximum (FWHM) and a slight decrease in the crystalline regularity, which can be explained within a normal range due to the damage to material from the radiation modification.41 The thermal and chemical stability of the main chain all indicated that the adsorbent would be suitable for uranium extraction from complex environment.

2.3. Uranium Adsorption of the AO-HPE Fibers. The adsorbents were screened using a simulated seawater system with an initial concentration 100 times higher than that of ions in natural seawater. The result was shown in Figure 7a, which exhibited a high uranium adsorption capacity of 14.11 mg g⁻¹ of the AO-HPE fibers after 24 h. Furthermore, the adsorption capacities of the AO-HPE fibers followed the order of U > Ca > Mg > Fe > Pb > Cu > V > Zn > Ni > Co, which indicated that the adsorbent exhibited higher uranium selectivity than all the competing ions, especially the main competing ion of V (an actual U/V mass ratio was up to almost 5). These results revealed the high capacity and selectivity of AO-HPE fibers exhibited its considerable potential application for UES. Due to the influence of optimal pH on the application range of the adsorbents, the tests of uranium uptake at a range of pH values were indispensable exploration. As shown in Figure 7b, the highest uranium adsorption capacity of 314.20 mg g⁻¹ at pH 7.0 was exhibited, corresponding to our previous work.19

The 20 mg adsorbents treated by alkali were soaked in 1 L uranium-spiked simulated seawater of different uranium concentration to investigate the adsorption behavior of the AO-HPE fibers. The concentrations of uranium in the adsorption system were determined at an interval of hrs. As shown in Figure 8a, the results showed that adsorbents reached equilibrium adsorption capacity of 66.10 mg g⁻¹ after 60 hrs from 2 ppm simulated seawater. Meanwhile, in simulated seawater with uranium initial concentration of 8 ppm and 32 ppm, the equilibrium adsorption capacity of 300.81 mg g⁻¹ and 712.00 mg g⁻¹ were achieved after approximately 140 hrs, respectively. Moreover, two conventional models of pseudo-first-order and pseudo-second-order were used to evaluate the adsorption kinetics and adsorption rate (Figure 8b and c). As expressed by linear eq 1 and 2, the pseudo-first-order and pseudo-second-order models were exhibited, respectively.42,43

\[
\ln \left(1 - \frac{Q_t}{Q_e}\right) = -k_1t
\]

(1)

\[
\frac{t}{Q_t} = \frac{1}{k_2} + \frac{t}{Q_e}
\]

(2)

where \(Q_e\) (mg g⁻¹) and \(Q_t\) (mg g⁻¹) were the uranium uptake at equilibrium time (h) and specific time (h), respectively; \(k_1\) (h⁻¹) and \(k_2\) (g·mg⁻¹·h⁻¹) represented the kinetic rate constants of the pseudo-first-order and pseudo-second-order models, respectively. Apparently, according to the kinetic parameters (\(k_1\), \(k_2\) and \(R^2\)) listed in Table 1, the kinetic behaviors of AO-HPE fibers in 2, 8 and 32 ppm simulated seawater was described more adequately by the pseudo-second-order model due to the close calculated equilibrium adsorption capacity (\(Q_{cal}\)) and relatively higher correlation coefficients (\(R^2\)). The result indicated that the chemisorption mechanism in this adsorption process was the rate-controlling step. Furthermore, the adsorption isotherm was used to evaluate the maximum adsorption capacity of AO-HPE fibers for uranium. As shown in Figure 8d, the uranium adsorption capacity of the adsorbent increased rapidly with the increase of uranium concentrations, and then slowed down gradually. To further reveal the adsorption behavior of the AO-HPE fibers, the Langmuir and Freundlich adsorption models were used to fit the adsorption data at room temperature, as described by eq 3 and 4:

\[
\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}
\]

(3)

\[
\lg Q_e = \lg K_f + \frac{1}{n} \lg C_e
\]

(4)

where \(C_e\) (ppm) was the concentration of uranium when the adsorption amounts for uranium at equilibrium, \(Q_{m}\) (mg g⁻¹) was the maximum adsorption capacity. \(K_L\) (L·mg⁻¹) was the Langmuir constant. \(K_f\) (mg g⁻¹·(L·mg⁻¹)⁻¹/n) and \(n\) were the Freundlich constants.44

The fitted curves of the Langmuir and Freundlich adsorption models and adsorption isotherm parameters (\(Q_{max}\), \(K_L\), \(K_f\) and \(n\)) of AO-HPE fibers for uranium were showed in Figure 8e and f and Table 2, respectively. Based on the above tests and data, the calculated value of \(Q_{max}\) could reach 1144.94 mg g⁻¹ in uranium-spiked simulated seawater, which was close to the
valid prediction from experimental data. Additionally, the adsorption data accorded with the Langmuir and Freundlich models, primarily indicating that uranium was adsorbed on AO-HPE fibers in a homogeneous and monolayer manner. Additionally, the uranium adsorption process of AO-HPE fibers was more consistent with the Freundlich model by comparing $R^2$ of two different adsorption isotherm models. Also, the value of $1/n$ was close to 0.5. These results all visually illustrated that a relatively easy and rapid absorption of uranium by AO-HPE fibers could be achieved.

The morphology of uranium loaded on the AO-HPE fibers was observed by SEM image. As shown in Figure 9, the result indicated the original fibers had the legible layered channel architecture. The relatively compact surface and a hierarchical groove structure were observed after adsorption of uranium in uranium-spiked simulated seawater. The change of gelation might be attributed to the sorption of uranyl ions, which resulted in the further integrated arrangement on surface of the AO-HPE fibers. Furthermore, EDS analysis revealed the wide distribution of uranium on the AO-HPE fibers, which illustrated the successful load of uranium by the adsorbents (Figure 9).

![Figure 8. Adsorption performance of AO-HPE fibers: (a) adsorption kinetics in uranium-spiked simulated seawater of different uranium concentration, (b) the curve of $t/Q_t$ by fitting with the pseudo-second-order kinetic model, (c) the curve of $\ln(1-Q/Q_e)$ by fitting with the pseudo-first-order kinetic model, (d) adsorption isotherm of AO-HPE fibers for uranium, the Langmuir (e) and Freundlich (f) isotherms for uranium adsorption by AO-HPE fibers (pH 7.0, T = 25 °C).](image1)

![Figure 9. SEM and EDS analyses of the uranium loaded on the AO-HPE fibers surface.](image2)

Table 1. Kinetic Parameters of Adsorption for Uranium in Pseudo-First-Order and Pseudo-Second-Order Models

| $C_e$ (ppm) | $Q_e$ (mg·g$^{-1}$) | $Q_e$ cal (mg·g$^{-1}$) | $k_1 \times 10^{-2}$ (h$^{-1}$) | $R^2$ | $Q_e$ cal (mg·g$^{-1}$) | $k_2 \times 10^{-4}$ (g·mg$^{-1}$·h$^{-1}$) | $R^2$ |
|-----|----------------|------------------|-----------------|-----|----------------|------------------|-----|
| 2   | 66.10          | 69.47            | 7.3             | 0.8844 | 66.94          | 5.10             | 0.9641 |
| 8   | 308.81         | 308.22           | 3.0             | 0.9652 | 304.80         | 1.04             | 0.9861 |
| 32  | 712.00         | 740.33           | 3.7             | 0.9755 | 715.41         | 0.64             | 0.9945 |

Table 2. Adsorption Isotherm Parameters of AO-HPE Fibers for Uranium

| Isotherm model | Langmuir | Freundlich |
|---------------|----------|------------|
| $T$ (°C)  | $Q_m$ (mg·g$^{-1}$) | $K_L$ (L·mg$^{-1}$) | $R^2$ | $K_F$ (mg·g$^{-1}$·L$^{-1}$) | $1/n$ | $1/n$ | $R^2$ |
| 25   | 1144.94  | 0.12       | 0.9316 | 152.27 | 0.539 | 0.9918 |
3. CONCLUSIONS
In summary, a high-efficiency green technology for the adsorbents synthesis has been developed using the commercially available UHMWPE fibers as the substrate material. The PAA chains was grafted onto the UHMWPE fibers by VPGP, followed by green VPGP of AN and further amidoximation to obtain the AO-HPE fibers. The sustainable process of VPGP endowed the adsorbents a pretty appreciable calculated maximum adsorption capacity \((Q_0)\) of 1144.94 mg g\(^{-1}\) in uranium-spiked solution. Furthermore, the adsorption capacity of 14.11 mg g\(^{-1}\) in simulated seawater and the higher uranium selectivity than main competing ion vanadium (adsorption selectivity than main competing ion vanadium (adsorption % selectivity than main competing ion vanadium (adsorption %) were achieved. More importantly, the VPGP implemented in an enclosed evaporation and condensation reflux system also endowed the high monomer AN utilization ratio nearly 100% and excellent environmental friendliness, which exhibited its unique advantages compared with traditional grafting polymerization in solutions. Therefore, the AO-HPE fibers fabricated via the green technology of VPGP have great potential to meet the requirements as an efficient and cost-effective material for extraction of uranium. This work provided a novel idea for the synthetic method of adsorbents for uranium extraction, and inspired sustainable technologies for grafting polymerization of AN in industrial.

4. EXPERIMENTAL SECTION
4.1. Materials and Reagents. UHMWPE fibers (TYZ Safetex FT-103) were supplied by Beijing Tongzhihong Advanced Material Co., Ltd. Acrylic acid (AA, ≥ 99.0% (w), analytical reagent grade (AR)), sulfuric acid (\(\text{H}_2\text{SO}_4, 95.0 \sim 98.0\%\) (w), AR), ammonium ferrous sulfate hexahydrate \((\text{NH}_4)_2\text{Fe(SO}_4\text{)}_2\cdot 6\text{H}_2\text{O}, \text{AR})\), ceric ammonium nitrate \((\text{Ce} (\text{NH}_4)_2\text{NO}_3)_6\cdot \text{w} \text{AR})\), acrylonitrile (AN, ≥ 99.0% (w), AR), methanol (\(\text{CH}_3\text{OH,} \geq 99.5\%\) (w), AR), hydroxylamine hydrochloride (\(\text{NH}_2\text{OH-HCl, AR})\), sodium hydroxide (NaOH, AR), hydrochloric acid (HCl, AR), sodium chloride (NaCl, AR), sodium carbonate (\(\text{Na}_2\text{CO}_3\cdot \text{AR})\), potassium hydroxide (KOH, AR), and nitric acid (HNO\(_3\), 65.0 \sim 68.0\%\) (w), AR) were purchased from Sinopharm Chemical Reagent Company and used without further purification. Standard solutions of metal ions with 1000 ppm concentration were purchased from SPEX CertiPrep, Inc. Nitrogen (99.999%) gas was supplied by Shanghai Luoyang Gas Canned Co., Ltd. Deionized water was used from water purification instrument (Milli-Q Direct, Millipore Company, USA) for all experiments.

4.2. Preparation of the Fibrous Adsorbent. Primarily, the AO-HPE fibers were modified via pre-irradiation grafting of AA in a reaction vessel, followed by the VPGP of monomer AN onto the PAA chains and further amidoximation. The UHMWPE fibers (approximately 1.0 g) were irradiated directly by using high-energy electron-beam (EB) by the Shanghai Institute of Applied Physics (Chinese Academy of Sciences) under air condition at room temperature with an absorbed dose of 70 kGy (Figure 1). The energy of EB was 1.5 MeV. Each path the absorbed dose of the sample was 5 kGy within 8 s. Then the irradiated UHMWPE fibers were placed into the reaction vessel containing 10 wt. % AA, 0.06 M \(\text{H}_2\text{SO}_4\) 1 wt. \%(\text{NH}_4)_2\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O} and deionized water (total weight of 80 g), and the grafting polymerization was performed at 70 °C. Sufficient nitrogen gas was required before the reaction. The modified fibers were washed with water and hot water for 3–5 times, respectively. Subsequently, the fibers were denoted as HPE-PAA after dried in a vacuum oven at 60 °C. The degree of grafting \((DG)\) was calculated by the weight increase of samples before and after the PIGP as shown according to eq 5

\[
DG = \left(\frac{W_0 - W_f}{W_0}\right) \times 100\%
\]

where \(W_0\) (g) is the weight of the pristine UHMWPE fiber, and \(W_f\) (g) is the weight of HPE-PAA fibers. The selected DG of HPE-PAA fibers in this work was 121.0%.

Further modification of the HPE-PAA with the cyano groups was conducted via green VPGP of AN. As shown in Figure 1, firstly, the HPE-PAA fibers with 0.03 mol/L Ce(\(\text{NH}_4\)\(_2\)\text{NO}_3\))\(_6\) initiator solution adsorbed in the fibers in advance were placed into a special reactor containing pure monomer AN (approximately 6–8 g) injected into the bottom of the reactor. Then nitrogen gas was charged into the reaction system for 10–15 min to remove oxygen and the reactor was placed in a constant temperature water bath with a range of 80 °C to 110 °C. The process of VPGP was performed rely on the sufficient contact of monomer AN vapor with the fibers. Meanwhile, the excess monomer AN passed quickly through the fibers and was condensed back to the bottom of the reactor. This process of cyclic reaction not only endowed the adsorbents close to 100% of high AN monomer utilization ratio but also the certain environmental friendliness due to no use of any organic solvent. After reaction, the fibers were washed with deionized water for three times and extracted with solvent dimethyl formamide (DMF) for 24 h. Finally, the fibers were dried in a vacuum oven at 60 °C and denoted as HPE-PAN. The DG was calculated by the weight increase of samples before and after the VPGP, and shown according to eq 6

\[
DG = \left(\frac{W_2 - W_1}{W_1}\right) \times 100\%
\]

where \(W_2\) (g) is the weight of the HPE-PAN fibers. The selected DG of HPE-PAN fibers in this work was 81.0%.

Furthermore, the HPE-PAN fibers were amidoximated with \(\text{NH}_2\text{OH-HCl}\) in a solution composed of 50 vol. % \(\text{CH}_3\text{OH}\) and 50 vol. % deionized water, added with \(\text{NaOH}\) until the pH value was adjusted to 7.0. The process was performed for 24 h at 75 °C. In like manner, the fibers were washed with deionized water repeatedly to remove the remaining solvents and dried in a vacuum oven. Eventually, the novel fibrous adsorbent was successfully prepared, denoted as AO-HPE fibers.

4.3. Characterization of the Modified Fibers. A FT-IR spectrometer (instrument Nicolet Avatar 370) supplied by Thermo Nicolet Company (USA) was used in attenuated total reflectance mode with 32 scans and a resolution of 4 cm\(^{-1}\). The scanning range of FT-IR spectra was 500–4000 cm\(^{-1}\) and background spectra were deducted from all tests. The chemical composition of the fibers was analyzed by XPS using a Thermo instrument SCIENTIFIC ESCALAB 250Xi. The XPS data were acquired through wide scans ranged from 0 to 1300 eV with monochromatic Al Ka radiation (hv = 1486.7 eV, working voltage = 15 kV). The first sample was prepared and ensured that the surface was clean and carefully transferred to a separate setup. Then, the ultra-high vacuum state was kept in the analysis chamber so that the air pressure was less than 10\(^{-7}\) Pa. And then the video camera was used to select the analysis position on the sample. Finally, the original data were...
generated and analyzed using related software to indicate group peak positions.

The surface morphologies of fibers were observed using a field-emission SEM (instrument Merlin Compact) from Zeiss Company of Germany. Before observation by SEM, all the samples were sputtered with gold to enhance the conductivity and the necessary testing voltage range was 5–10 kV.

A NETZSCH STA449F3-QMS instrument (Switzerland) was used to carry out DSC tests from 30 to 200 °C with a heating rate of 10 °C/min and a nitrogen gas flow rate of 20 mL/min. Finally, the test crystallinity $X_c$ of fiber samples was calculated according to eq 7 as follows:

$$X_c = \frac{\Delta H}{\Delta H_{00}} \times 100\% \quad (7)$$

where $\Delta H$ is measured melting enthalpy of the crystallite and $\Delta H_{00}$ is the heat of fusion of the 100% crystalline fiber sample, taking 291 J/g.46

A TG209 F3 device (NETZSCH Company, Germany) was used to perform TGA from 25 to 800 °C with a heating rate of 10 °C/min under a nitrogen gas flow.

The concentrations of the metal ions in simulated seawater were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (PerkinElmer Optima 8000). The tests were repeated an average of three times per sample to calibrate the uranium and other coexisting ions. Meanwhile, a four-point curve was generated and calibrated utilizing the standard solutions with different gradients. Inductively coupled plasma mass spectroscopy (ICP-MS) (PerkinElmer, NexION 300D) was used for the more precise quantitative analyses.

4.4. Adsorption of Uranium by the AO-HPE Fibers.

According to previous work, the uranium adsorption test by the AO-HPE fibers could be achieved in 5 L simulated seawater adsorption system. Firstly, 175.0 g sea salt was dissolved in 5 L deionized water to produce a practical salinity unit (psu) of 35. Next, quantitative standard solutions of uranium and competing ions including VO$_3^-$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and Pb$^{2+}$ were added into the 5 L adsorption system. These ions are prepared at concentrations up to 100 ppm and 32 ppm, respectively. Finally, the concentrations of uranium loaded onto the AO-HPE fibers at different times were also analyzed by ICP-AES and ICP-MS according to an appropriate dilution. The adsorption capacity $Q$ of the AO-HPE fibers for metal ions could be evaluated using eq 9

$$Q_t = \frac{(C_0 - C_t) \times V}{M} \quad (9)$$

where $C_0$ (mg L$^{-1}$) and $C_t$ (mg L$^{-1}$) are the concentrations of uranium at initial time and specific time in adsorption process tested by ICP-AES and ICP-MS, respectively. $V$ (L) is the volume of the adsorption system and $M$ (g) is the weight of the dried AO-HPE fibers that was used.

**AUTHOR INFORMATION**

**Corresponding Author**

Hong-Juan Ma — Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; Shanghai Applied Radiation Institute and Key Laboratory of Organic Compound Pollution Control Engineering (MOE), Shanghai University, Shanghai 200444, China; Dalian National Laboratory for Clean Energy, Dalian 116023, China; orcid.org/0000-0001-8160-7194; Phone: +86 (021) 39194080; Email: hongjuanma@shu.edu.cn

**Authors**

Ren-Hao Ding — Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0002-4823-3853

Xiao Xu — Center for Molecular Imaging and Translational Medicine, School of Public Health, Xiamen University, Xiamen 361102, China

Chen Huang — Shanghai Applied Radiation Institute and Key Laboratory of Organic Compound Pollution Control Engineering (MOE), Shanghai University, Shanghai 200444, China; orcid.org/0000-0003-1626-8549

Lin Ma — Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0001-7122-8422

Feng Ye — Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; University of Chinese Academy of Sciences, Beijing 100049, China

Lu Xu — Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; Dalian National Laboratory for Clean Energy, Dalian 116023, China

Zi-Qiang Wang — Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04048

**Notes**

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