A Molecular Coordination Template Strategy for Designing Selective Porous Aromatic Framework Materials for Uranyl Capture

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ABSTRACT: Uranium capture from seawater could solve increasing energy demand and enable a much needed relaxing from fossil fuels. Low concentration (~3 ppb), competing cations (especially vanadium) and pH-dependent speciation prohibit highly efficient uranium uptake. Despite intensive research, selective extraction of uranyl ions over vanadyl units remains a tremendous challenge. Here, we adopted a molecular coordination template strategy to design a uranyl-specific bis-salicylaldoxime entity and decorated it into a highly porous aromatic framework (PAF-1) by programmable assembly. The superstructure (MISS-PAF-1) gives a strong affinity that removes 99.97% of uranium in 120 min. Notably, it binds to the uranyl ion at least 100 times more selectively than 14 different cations tested, including the vanadyl ion, in simulated seawater at ambient pH. Real seawater samples collected from the Bohai Sea achieve 5.79 mg g⁻¹ of uranium capacity over 56 days without PAF degradation, exceeding a 4-fold higher amount than commercial adsorbents.

1. INTRODUCTION

Uranium is a desirable ingredient with significant implications in many technical applications, for instance, the nuclear energy industry, but the uranium reserve on land (~4.85 million tons in total) will be exhausted in the next few decades when taking into consideration of current global consumption.¹ To address this issue, the extraction of uranyl (UO₂²⁺) ions from seawater (4.5 billion tons) has attracted enormous attention in past years.²⁻³ A number of adsorbents with reasonable adsorption capability such as porous carbon, mesoporous silica, metal–organic frameworks, and ionic liquids have been developed to cope with the steady increase in uranium demand worldwide.⁴⁻¹¹ However, the uranyl ion coexists with a number of transition metal ions including Co²⁺, Ni²⁺, Fe³⁺, and VO₃⁻, among others, commonly referred to as interfering metal ions, in seawater at an exceedingly low concentration, which seriously suppresses the extraction capacity and selectivity of currently available adsorbents toward uranyl ions for practical applications.³ It is a daunting challenge to effectively and selectively capture uranium from seawater.

Porous organic materials have been recently recognized as an emerging class of functional platforms, which enable versatile inclusion of functionalized groups thanks to their modular structure, rich stability, and reticular variety.¹²⁻²⁰ This flexibility of tuning the chemical compositions and spatial structures promotes a myriad of applications, for instance, gas separation and storage, optoelectronics, and catalysis.²¹⁻²⁹ Dai et al. and Ma et al. pioneered porous materials with amidoxime groups, which exhibited excellent capability for uranium extraction.³⁰⁻³² However, traditional adsorbents (including oxime-bore products) with flexible and randomly distributed groups lack the selectivity for binding uranyl ions in the presence of interfering ions.³³

To overcome this limitation, two objectives provide such improvement to satisfy the thought-provoking features of capacity and selectivity: First, an adsorption site with the customized size, shape, and composition is required to create both specific and directional interaction with the uranyl ion.
Second, a large contact surface in a robust architecture will provide a huge number of accessible spaces for a reciprocity interaction between adsorption sites and target species. These basic necessities rely on the shape persistent structure and suitable directional anchor to enforce specific bonding geometries for uranyl ions (Figure 1). With that in mind, a molecular coordination template strategy is adopted to prepare the selective sites with assembled and arrayed salicylaldoxime groups. Using the porous aromatic framework (PAF-1) as a scaffold, its pore surface was encoded with the salicylaldoxime-based units into dynamic adsorption sites. As a result of the uranyl-specific interaction of bis-salicylaldoxime entity, the resulting porous material (MISS-PAF-1) exhibited excellent adsorption capacity, outstanding selectivity, and good reusability for extraction of UO$_2^{2+}$ ions from real seawater.

2. RESULTS AND DISCUSSION

First of all, salicylaldoxime molecules together with uranyl ions were mixed at 80 °C for 1 h to produce the uranyl coordination complex with a predetermined configuration of oxime fragments. In addition, the rigid PAF-1 with three-dimensional open channels and an ultralarge surface area was selected as the scaffold to perform a comparative case study. To immobilize the uranyl-specific salicylaldoxime unit, acetyl groups were grafted onto PAF-1 to prepare the acetylated porous material, denoted as A-PAF-1, which was followed by condensation of the acetyl group (A-PAF-1) with 2-bromobutyric acid to yield B-PAF-1 (Figure 1a). Meanwhile, succinic acid was immobilized into A-PAF-1 to obtain S-PAF-1, which contained adjacent carboxylic groups to retain the structural integrity of postmodified oxime groups (Figure S1). Then, a coordination complex was tethered on the B-PAF-1 and S-PAF-1 through hydrogen-bond interaction, respectively. After the uranyl centers were removed, MIBS-PAF-1 and MISS-PAF-1 were obtained for ion rebinding (Figure 1c). As controls, pure salicylaldoxime molecules were affixed onto B-PAF-1 and S-PAF-1 frameworks to produce traditional adsorbents, BS-PAF-1 and SS-PAF-1, respectively (Figure 1b). As compared with PAF-1, Fourier transform infrared (FTIR) spectra of B-PAF-1, S-PAF-1, BS-PAF-1, and SS-PAF-1, MIBS-PAF-
1, SS-PAF-1, and MISS-PAF-1 showed the C–Br peak centered around 602 cm\(^{-1}\), which indicated the existence of carboxylic groups on the PAF-1 skeleton (Figure S2). To assess the bonding mode of salicylaldoxime fragments in the carboxylated PAF-1 structures, the hydrogen-bond-coupled dimers of 2-bromobutyric acid and salicylaldoxime were synthesized. As shown in Figure S3a, the \(^1\)H nuclear magnetic resonance (NMR) spectra showed that the chemical shift of the -O–H group moved from 13.15 ppm for 2-bromobutyric acid to 13.17 ppm for the dimer, and the chemical shift of the -N–O–H group increased from 11.31 ppm for salicylaldoxime to 11.34 ppm for the dimer, whereas the phenol hydroxyl group in salicylaldoxime remained its original chemical activity. As shown in FTIR spectra (Figure S3b), the red shift of the -O–H band of carboxylic groups from 1226 to 1218 cm\(^{-1}\) was assigned to the hydrogen bonding of these carboxyl groups with the -N–O–H in salicylaldoxime. Correspondingly, the red shift of the -C=N band in salicylaldoxime from 1713 to 1702 cm\(^{-1}\) was attributed to the hydrogen bonding between these groups with the -O–H groups in carboxyl group. Similar red shifts were observed in the FTIR spectra of as-prepared oxime-bore PAFs (BS-PAF-1, MIBS-PAF-1, SS-PAF-1, and MISS-PAF-1) (Figure S2). The out-plane flexural vibration of the aromatic building unit at 702 cm\(^{-1}\) for PAF-1 ranged to 706 cm\(^{-1}\) for oxime-bore PAF materials, proving the \(\pi-\pi\) interaction between salicylaldoxime and the PAF skeleton. In solid state \(^{13}\)C NMR spectra, the carbon resonances ranging from 0 to 150 ppm corresponded to each carbon atom in the PAF frameworks (Figure S4); the peaks, centered at 72, 58, and 19 ppm, were attributed to the salicylaldoxime fragments in the PAF products. In addition, the aromatic carbon centered at 145.4 ppm for PAF-1 disappeared in the oxime-bore PAFs (Figure S4). All these results implied that the salicylaldoxime fragments were tethered on the carboxylic groups of PAFs via double-hydrogen binding (Figure 1c) and fixed on the PAF-1 skeleton through \(\pi-\pi\) interaction (Figure 3c).

According to the elemental analysis, the nitrogen contents in BS-PAF-1, SS-PAF-1, and MISS-PAF-1 remained little changed after being consecutively washed by NaHCO\(_3\) solution and ethanol. In contrast, the nitrogen content of MIBS-PAF-1 reduced from 2.57 to 1.37 wt %, which was ascribed to the fact that the coordination complex was composed of more salicylaldoxime fragments. Although the single carboxylic group in B-PAF-1 could fasten only one salicylaldoxime fragment of the coordination complex through hydrogen bonding, other salicylaldoxime components of the coordination complex were unfastened and washed away from the MIBS-PAF-1 framework, resulting in the loss of the selective feature. The eventual amounts of nitrogen were 1.59, 1.37, 2.66, and 2.68 wt % for BS-PAF-1, MIBS-PAF-1, SS-PAF-1, and MISS-PAF-1, respectively, corresponding to 1.13, 1.01, 1.91, and 1.94 mmol g\(^{-1}\) of salicylaldoxime components (Table S1). Scanning electron microscopy (SEM) imaging showed that all PAF samples were the submicron-sized particles of PAF aggregates (Figure S5). Transmission electron microscope (TEM) images and powder X-ray diffraction (PXRD) patterns indicated that the porous frameworks were short of long-range ordered structure (Figures S6 and S7).

The stability of adsorbents is a significant character for practical application. Because of the existence of double-hydrogen bonds, all oxime-bore PAFs including BS-PAF-1, MIBS-PAF-1, SS-PAF-1, and MISS-PAF-1 exhibited good...
structural integrity after incubation in various organic solvents such as methanol, 2-methoxyethanol, acetone, and DMSO for 24 h. The poor solubility of salicylaldoxime in aqueous solution guaranteed the immovability of adsorption sites in PAF skeletons for the capture of UO$_2^{2+}$ ions. To further prove the role of hydrogen bonding, original PAF-1 powder was placed in the solution of the coordination complex to graft the porous skeleton with salicylaldoxime fragments. However, ∼96% of the salicylaldoxime components loaded within PAF-1 channels was washed away by ethanol, which suggested that the salicylaldoxime groups were tethered in the oxime-bore PAF architectures via hydrogen bonds. Thermogravimetric analysis (TGA) showed noticeable weight loss as temperature increased from 270 to 350 °C because of the escape of salicylaldoxime constitutions from porous frameworks (BS-PAF-1, MIBS-PAF-1, SS-PAF-1, and MISS-PAF-1) (Figure S8), whereas the entire PAF structures were carbonized in the range of 400−500 °C, and little residue was left after burning at 800 °C, indicating few inorganic impurities in the PAF samples.

Nitrogen adsorption−desorption isotherms were conducted at 77 K to investigate the porosity of as-prepared PAF materials (Figure S9). The BET surface areas of PAF-1, A-PAF-1, B-PAF-1, S-PAF, BS-PAF-1, MIBS-PAF-1, SS-PAF-1, and MISS-PAF-1 are 4783, 1505, 1078, 923, 644, 368, and 412 m$^2$ g$^{-1}$, respectively. The decrease in surface area is assigned to the increased content of salicylaldoxime fragments fixed within the PAF skeletons, which increases the weight per structural unit. Using nonlocal density functional theory (NL-DFT), all PAF samples show hierarchical porosity, which is conducive to the entrance of ions into the porous channels to access the adsorption sites (Figure S9).

Inductively coupled plasma mass spectrometry (ICP-MS) was adopted to investigate the adsorption performance of PAF materials toward UO$_2^{2+}$ ions at pH ≈ 6.5. As shown in Figures 2a and S10, the adsorption capacity increased with the concentration of UO$_2^{2+}$ ions. There was a sharp jump in uptake during the initial adsorption because of the close contact between the external surface of adsorbents and UO$_2^{2+}$ ions in solution; the sorption rate reduced obviously because of the gradually slow diffusion of UO$_2^{2+}$ ions from large cavities to small ones. Finally, the adsorption equilibrium was reached when the adsorption sites were almost completely occupied. The maximum uptakes of the UO$_2^{2+}$ ion by B-PAF-1, S-PAF-1, BS-PAF-1, MIBS-PAF-1, SS-PAF-1, and MISS-PAF-1 were 60, 108, 219, 239, 411, and 253 mg g$^{-1}$, respectively, when the
initial concentration of UO$_2^{2+}$ ions was in the range of 50–200 ppm. The adsorption capacity of BS-PAF-1, MIBS-PAF-1, and SS-PAF-1 toward UO$_2^{2+}$ was in good agreement with the content of salicylaldoxime fragments in BS-PAF-1, MIBS-PAF-1, and SS-PAF-1, increasing from 1.13 and 1.01 to 1.91 mmol g$^{-1}$, respectively. Although MISS-PAF-1 and SS-PAF-1 had a similar amount of the salicylaldoxime fragment (1.94 mmol), the former adsorption capacity toward UO$_2^{2+}$ ions was nearly half of the latter, which implied that one UO$_2^{2+}$ ion was bound to two salicylaldoxime components in each selective site of MISS-PAF-1.

The as-prepared PAF samples were utilized to adsorb UO$_2^{2+}$ ions in aqueous media in the presence of one type of interfering metal ion, such as Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, and CrO$_4^{2-}$; the concentration of UO$_2^{2+}$ ions and that of the interfering ions were set to be comparable and about 7 ppm in deionized water at pH ≈ 6.5. As shown in Figure S11, because of the random distribution of carboxyl groups in the porous structures, BS-PAF-1, SS-PAF-1, and MIBS-PAF-1 with traditional adsorption sites showed a notable capacity for interfering ions, whereas MISS-PAF-1 with clearly endorsed selective sites revealed a maximum uranium adsorption uptake of 79.8 mg g$^{-1}$ with a selectivity coefficient over 821 (821, 203, and 1057 based on mass ratio, molar ratio, and distribution coefficients, respectively) for UO$_2^{2+}$/Co$^{2+}$ (Figure S12). Its performance is much higher than that reported in the literature, including those of inorganic materials (ND-AO), metal−organic frameworks (MIL-101-DETA), and polymers (PAF-1-CH$_2$AO, DQ$_2$VP, SA-VP, IIP resins, nanoﬁbrous polymer) (Figure 2b and Table S2).

Many metal ions (such as Co$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Fe$^{3+}$) are liable to coordinate with salicylaldoxime fragments. To unravel the mechanism of adsorption selectivity toward UO$_2^{2+}$ ions, we have examined the uranyl binding mode to as-prepared PAF adsorbents. Uranium present in aqueous solution is in the state of uranium(VI) oxidation, which is dominated by the uranyl ion, [UO$_2$(H$_2$O)$_5$]$^{2+}$, ambient pH. After adsorbing onto the PAF adsorbents, the UO$_2^{2+}$-ion-loaded PAFs, denoted as PAF@Us, showed a weak vibrational band centered at 986 cm$^{-1}$ assigned to the uranyl-OH and U=O stretch (Figure S13). The vibrational bands of the −OH and −C=O groups in PAF adsorbents decreased from 1125 to 1122 cm$^{-1}$ and from 1713 to 1699 cm$^{-1}$, respectively, suggesting the coordination of these two units to UO$_2^{2+}$ ion. Similarly, the vibrational bands centered at 589 and 457 cm$^{-1}$ were an indication of the formation of U−O and U−N coordination bonds, respectively (Figure S13b). Using [(UO$_2$)$_2$Co$_2$(bpd)$_4$]$^{2-}$ and [UO$_2$L(H$_2$O)$_5$]NO$_3$ as references, X-ray photoelectron spectroscopy (XPS) analysis revealed the coordination mode of uranium in the resulting PAF@Us. As illustrated in Figures S14 and 3a, the observed binding energies of U 4f$_{7/2}$ and U 4f$_{5/2}$ are located at 382.6 and 393.4 eV, respectively, in B-PAF-1@U and S-PAF-1@U, which corresponds to the monocarboxylic coordination structure to the UO$_2^{2+}$ ion. For BS-PAF-1, MIBS-PAF-1, and SS-PAF-1, the binding energies of U 4f$_{7/2}$ and U 4f$_{5/2}$ positioned at 382.2 and 393.1 eV, respectively, and were assigned to the dominating structure of single-salicylaldoxime chelation with a UO$_2^{2+}$ ion. As to MISS-PAF-1, the selective sites possessed a unique coordination geometry, where two salicylaldoxime fragments bound with one UO$_2^{2+}$ ion as demonstrated by element analysis.

To probe the spatial structure of the selective sites in MISS-PAF-1, the crystallization of the UO$_2^{2+}$ ion coordination complex from aqueous solution yielded a complex crystal, the structure of which was determined to be [(UO$_2$)$_2$(SA)$_2$(H$_2$O)] by means of single-crystal X-ray diffraction. The crystallographic analysis indicated that [(UO$_2$)(SA)$_2$(H$_2$O)] was in a monoclinic phase with a $P2_1/m$ space group (Table S3), in which the asymmetric unit consisted of one uranyl ion, two SA$^-$ ligands, and one aqua ligand. Figure S3b (inset) showed that the uranium center in the coordination complex adopted a 7-fold coordinated pentagonal bipyramid, and its terminal, short U=O groups had a bond length of 1.76(9) Å with an O=U=O angle of 176.8(7)°. The salicylaldoxime bonds, coordinated with the UO$_2^{2+}$ ion, were ~2.25(15) Å for U−O and ~2.61(13) Å for U−N (Table S4). The detailed crystallographic data for the UO$_2^{2+}$ ion exhausted selective site was described in CCDC 1839164. As illustrated in Figure S15, the same binding energy for U 4f$_{7/2}$ and 4f$_{5/2}$, in XPS analysis proved that the uranium atom environments were identical for [(UO$_2$)(SA)$_2$(H$_2$O)] and MISS-PAF-1@U. To gain further insight, X-ray absorption fine structure (XAFS) spectroscopy was adopted to investigate the coordination environment of the U atom in MISS-PAF-1@U. In normalized the U L$_3$ XAFS spectrum (Figure 3b), the similar trend curves together with an identical U absorption edge energy (17173 eV) for both [(UO$_2$)(SA)$_2$(H$_2$O)] and MISS-PAF-1@U revealed the same conclusion as predicted by XPS analysis that MISS-PAF-1 binds uranyl ions in the same fashion as [(UO$_2$)-(SA)$_2$(H$_2$O)]. In this scenario, the selective mechanism is attributed to that the spatial structure and size of the coordination complex matches well with the segments in the PAF-1 skeleton according to the minimal energy principle (Figure 3c). Therefore, the biosalicylaldoxime entity will keep its structural integrity via π−π interaction to preserve the special direction and settled bond (U−O and U−N) for the rebinding of UO$_2^{2+}$ ions. As to interfering ions, for example, vanadium, the varied coordination bond lengths and unmatched orientation will destroy the original π−π interaction between the biosalicylaldoxime entity and PAF-1 skeleton, which results in the high selectivity for UO$_2^{2+}$ ions against other interfering ions.

Because MISS-PAF-1 exhibited the best adsorption selectivity toward UO$_2^{2+}$ ions, the static adsorption isotherms were fitted with Langmuir and Freundlich models, respectively. The correlation coefficients ($R^2$) based on the Langmuir and Freundlich calculations were 0.9938 and 0.8352, respectively (Figure S16); a better fitting by the Langmuir model reveals the monolayer chemical adsorption of the target ions (UO$_2^{2+}$) onto MISS-PAF-1. The maximum adsorption capacity for the UO$_2^{2+}$ ions was calculated to be 253 mg g$^{-1}$ for MISS-PAF-1 (Figure 2a). The energy-dispersive X-ray (EDX) spectroscopy showed distinct maps of elemental uranium and oxygen to confirm the uniform distribution of salicylaldoxime groups and bound UO$_2^{2+}$ ions across the MISS-PAF-1 skeleton (Figure S17). The molar ratio of adsorbed uranium species (0.92 mmol g$^{-1}$) to the decorated biosalicylaldoxime entity (0.97 mmol g$^{-1}$) suggested the utilization of selective sites was 92.6% in MISS-PAF-1. The adsorption capacity of MISS-PAF-1 was about 28 times higher than that of the traditional molecularly imprinted polymer (7.51 mg g$^{-1}$) and about 9 times higher than that of commercial adsorbents such as METSORB (27 mg g$^{-1}$) and Dyna Aqua (21 mg g$^{-1}$).
The kinetic adsorption behavior of MISS-PAF-1 was investigated in 100 mL of aqueous solution of UO$_2^{2+}$ ions (7.05 ppm) at room temperature and pH $\approx 6.5$ (Figure S18). MISS-PAF-1 showed a rapid capture of UO$_2^{2+}$ ions during the first 40 min and reached the adsorption equilibrium with a uranium capacity of 82.5 mg g$^{-1}$ after 200 min. The correlation coefficients ($R^2$), calculated based on the pseudo-first-order and pseudo-second-order kinetic models, were 0.7643 and 0.9996, respectively (Figure S19). The higher value indicated the best fitting by pseudo-second-order kinetic model, implying the adsorption of UO$_2^{2+}$ ions onto MISS-PAF-1 was chemical interaction. As known, the uranyl iodon would form different oligomerizations at different pH including pH < 5 for monomeric pentagonal bipyramids, 5 < pH < 7 for $[(\text{UO}_2)_3\text{O(OH)}_3]_n$ trimers, and 7 < pH < 8 for $[(\text{UO}_2)-(\text{OH})_2]_n$ chains. The adsorption capability of MISS-PAF-1 was also examined against different pH including 2, 4, and 8. As indicated in Figure 2c, the sample revealed similar adsorption behaviors, as it was at pH $\approx 6.5$. The maximum uranium capacities were 17.3, 36.6, and 48.0 mg g$^{-1}$ corresponding to the pH values of 2, 4, and 8, respectively, manifesting the strong extraction capability of MISS-PAF-1 for uranyl ions. The difference in UO$_2^{2+}$ capacity is attributed to how the varied uranyl species affect the interactions with the bis-salicylaldoxime entity in MISS-PAF-1. The distribution coefficient ($K_d$) was calculated by the incubation of MISS-PAF-1 (10 mg) in 50 mL of aqueous solution under shaking with the reduced concentration of UO$_2^{2+}$ ions from 5 to 0.0016 ppm in 120 min. The obvious decrease of uranium concentration (from 5 to 0.0016 ppm) calculated an outstanding removal ratio of 99.97%. The $K_d$ value for UO$_2^{2+}$ ions was over 1.4 x 10$^5$, demonstrating there was a strong affinity of UO$_2^{2+}$ ions to the selective sites in MISS-PAF-1.

Reusability of MISS-PAF-1 was also investigated to evaluate the possibility for actual utilization. Washing with NaHCO$_3$ (100 mL, 1 mol L$^{-1}$) just three times was sufficient to remove the adsorbed UO$_2^{2+}$ ions from MISS-PAF-1@U. After reuse for four times, the adsorption capacity of MISS-PAF-1 was reduced by 2% from the original value, proving the excellent reusability (Figure 3d). All these features suggested that MISS-PAF-1 could serve as a novel adsorbent for selective extraction of uranium element from seawater. As a result of the rich hydrochemical stability, strong binding affinity, high adsorption capacity, and great selectivity, MISS-PAF-1 was further examined in 200 mL of simulated seawater (salinity of 30) containing 7.05 ppm of UO$_2^{2+}$ ions and a mixture of interfering ions including 9500 ppm of Na$^+$, 1130 ppm of Mg$^{2+}$, 360 ppm of Ca$^{2+}$, 350 ppm of K$^+$, 7 ppm of Li$^+$, 7 ppm of Co$^{2+}$, 7 ppm of Cr$^{3+}$, 7 ppm of Zn$^{2+}$, 7 ppm of Mn$^{2+}$, 7 ppm of Pb$^{2+}$, 7 ppm of Cd$^{2+}$, 7 ppm of Ni$^{2+}$, 7 ppm of Fe$^{3+}$, 7 ppm of VO$_2^{2+}$, 8000 ppm of Cl$^-$, and 2400 ppm of SO$_4^{2-}$ ions. As shown in Figure 2d, MISS-PAF-1 showed the uranium adsorption capacity of 73.26 mg g$^{-1}$ with a selectivity adsorption coefficient of 113 (UO$_2^{2+}$ over VO$_2^{2+}$ ions for instance). After that success, MISS-PAF-1 was examined in the nonspiked real seawater. MISS-PAF-1 (5 mg) was dispersed in 5 gallons of seawater (initial concentration of 4.4 ppb from Bohai Sea, China) at room temperature. After incubation for 56 days under shaking, MISS-PAF-1 showed the uranium adsorption uptake of 5.79 mg g$^{-1}$, which is approximately 4 times higher than the value reported by Singh and Mishra. This result proved the superior adsorption performance of MISS-PAF-1 toward uranium ions at the extremely low level, thus showing a great promise in practical applications.

3. CONCLUSIONS

Using a molecular coordination template strategy, salicylaldoxime groups were encoded on the porous skeleton of PAF-1 to produce the uranyl-specific bis-salicylaldoxime adsorption sites. Consequently, one resultant (MISS-PAF-1) exhibits excellent capture capacity and ultrahigh selectivity toward UO$_2^{2+}$ ions over interfering species. The selective mechanism is established with the aid of single-crystal X-ray diffraction and XAFS spectroscopy, unraveling that the assembly of salicylaldoxime fragments creates the special coordination environment and settled bond lengths for the uranyl ion. Our work highlights the sharp increase in ion adsorption capacity with high selectivity and good reusability. These results demonstrate that the novel PAF material has proven to be a promising candidate for effective capture of UO$_2^{2+}$ ions from seawater. This therefore resolves the longstanding challenge in the field of uranium extraction.

4. EXPERIMENTAL SECTION

4.1. Acetylation of PAF-1. Anhydrous AlCl$_3$ (2 g), 4 mL of acetyl chloride, and 100 mg of PAF-1 were added to a flask, followed by the addition of 10 mL of 1,2-dichloroethane. The mixture solution was stirred at room temperature for 8 h and then slowly poured into ice-cooled concentrated HCl solution (100 mL). Afterward, the precipitate was filtered and washed with methanol, water, and dichloromethane three times, respectively, and then dried at 100 °C under vacuum for 3 days to yield acetylated PAF-1, denoted as A-PAF-1.

4.2. Carboxylation of PAF-1. Activated A-PAF-1 (100 mg) and 2 g of sodium hydride were mixed to 15 mL of dry dimethylformamide (DMF) and stirred for 1 h. Then, 2 g of carboxylic reactant (2-bromobutyric acid or dibromosuccinic acid) was added to the reaction solution and stirred for another 2 h. The resultant was filtered, washed with water and methanol three times, respectively, and then dried at 100 °C under vacuum for 3 days to remove all the solvents. The final products were denoted as B-PAF-1 and S-PAF-1, respectively.

4.3. Preparation of Coordination Complex. Salicylaldoxime (1 g), 1 g of UO$_2$(NO$_3$)$_2$·6H$_2$O, and 10 mL of 2-methoxyethanol were added into a flask. Then, the mixture solution was heated at 80 °C for 1 h to produce a coordination complex.

4.4. Preparation of Oxime-Based Adsorbents. Salicylaldoxime (1 g) and 10 mL of 2-methoxyethanol were added to a flask, and then, the resulting mixture solution was heated at 80 °C for 1 h. Carboxylic functionalized PAF (B-PAF-1 or S-PAF-1) (100 mg) was poured into the reaction solution, followed by stirring for another 8 h. The solid product was collected through filtration and washed with water and ethanol, respectively, to yield BS-PAF-1 and SS-PAF-1.

4.5. Preparation of MIBS-PAF-1 and MISS-PAF-1. Salicylaldoxime (1 g), 1 g of UO$_2$(NO$_3$)$_2$·6H$_2$O, and 10 mL of 2-methoxyethanol were added into a flask in order to form a uniform mixture solution, followed by heating at 80 °C for 1 h. Afterward, carboxylic functionalized PAF (B-PAF-1 or S-PAF-1) (100 mg) was added to the mixture solution and stirred for another 8 h. The solid product was collected through filtration and washed with water and ethanol, respectively. The PAF sample was added into NaHCO$_3$ solution (100 mL, 3 M).
and 2-methoxyethanol (100 mL) for 3 h to release the uranium ion and salicylaldehyde molecules, which was repeated for four times to yield MIBS-PAF-1 and MISS-PAF-1, respectively.

No unexpected or unusually high safety hazards were encountered.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00494.

Linker syntheses and characterization, PXRD patterns, TGA curves, NMR spectroscopy, and adsorption isotherms (PDF)

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Notes

The authors declare no competing financial interest.

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