A Poly(acrylonitrile)-Functionalized Porous Aromatic Framework Synthesized by Atom-Transfer Radical Polymerization for the Extraction of Uranium from Seawater

Yanfeng Yue,[*,†,‡] Chenxi Zhang,[†] Qing Tang,[¶] Richard T. Mayes,[†] Wei-Po Liao,[†] Chen Liao,[†] Costas Tsouris,[η] Joseph J. Stankovich,[†] Jihua Chen,[§] Dale K. Hensley,[§] Carter W. Abney,[†] De-en Jiang,[*,¶] Suree Brown,[⊥] and Sheng Dai[*,†,⊥]

[†]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
[‡]Department of Biology, Geology, and Physical Science, Sul Ross State University, Alpine, Texas 79832, United States
[η]Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
[¶]Department of Chemistry, University of California Riverside, Riverside, California 92521, United States
[§]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
[⊥]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

In order to ensure a sustainable reserve of fuel for nuclear power generation, tremendous research efforts have been devoted to developing advanced sorbent materials for extracting uranium from seawater. In this work, a porous aromatic framework (PAF) was surface-functionalized with poly(acrylonitrile) through atom-transfer radical polymerization (ATRP). Batches of this adsorbent were conditioned with potassium hydroxide (KOH) at room temperature or 80 °C prior to contact with a uranium-spiked seawater simulant, with minimal differences in uptake observed as a function of conditioning temperature. A maximum capacity of 4.81 g-U/kg-ads was obtained following 42 days contact with uranium-spiked filtered environmental seawater, which demonstrates a comparable adsorption rate. A kinetic investigation revealed extremely rapid uranyl uptake, with more than 80% saturation reached within 14 days. Relying on the semiordered structure of the PAF adsorbent, density functional theory (DFT) calculations reveal cooperative interactions between multiple adsorbent groups yield a strong driving force for uranium binding.

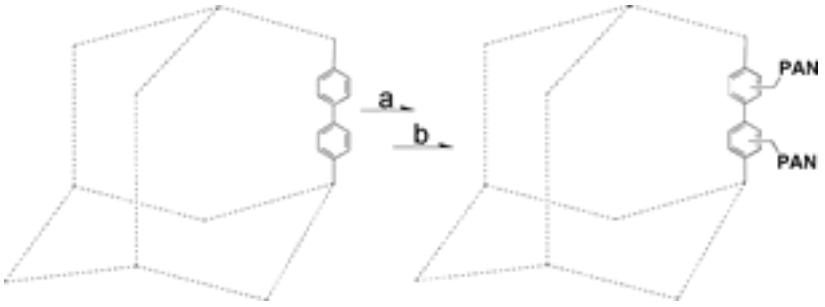
INTRODUCTION

Uranium is one of the primary fuel sources for nuclear power generation, making it an element with considerable technological importance. However, it is anticipated that terrestrial uranium reserves will be exhausted in the next 100 years, motivating research efforts to recovering uranium from nonconventional resources, such as seawater.[1−5] There are ∼4.5 billion tons of uranium in the oceans, which is ∼1000 times greater than the estimated terrestrial reserves.[6−8] However, because the concentration of the uranium in the seawater is very low (∼3.3 ppb), efficient and selective extraction is particularly challenging.

Many types of adsorbents have been developed and tested for the recovery of uranium from seawater, such as hydrous titanium oxide,[9,10] brown coal,[11] chitin/chitosan-bearing materials,[12] composite materials,[13,14] metal−organic hybrids,[15] layered metal sulfides,[16] and chelating resins.[17] However, because of amenability toward industrial-scale preparation, ease of deployment, and comparatively low cost, most preferred adsorbents are based on surface-functionalized polymeric supports. Adsorbents grafted with amidoxime (−C(NH)═N−OH, AO) functionalities have been of particular interest for extracting uranyl, the environmental species of uranium found in seawater, because they possess high affinity stripping with acidic solutions.[18−23] Previously reported poly(amidoxime) (PAO) adsorbents were prepared from poly(acrylonitrile) (PAN) precursors, synthesized by suspension polymerization,[24] radiation-induced grafting polymerization,[25] and even sonochemical functionalization.[26] Atom-transfer radical polymerization (ATRP), which is a common method for controlling polymer growth, has also been applied to graft PAN on porous co-polymer substrates that contain active chlorine species.[27−29]

Adsorbents that combine high surface area with good mechanical properties are of pronounced general interest as adsorbents, as large specific surface areas accommodate higher degrees of grafting than traditional substrates. In this work, we performed ATRP on high-surface-area porous aromatic frameworks (PAFs) to prepare adsorbents for extraction of uranium from seawater. PAFs are a new material at the interface between organic chemistry and materials science, consisting of extended organic structures in which the light elements (H, B, C, N, and

Scheme 1. Schematic Illustration of Synthesis PPN-6-PAN: (a) $CH_3COOH/HCl/H_3PO_4/HCHO$, 90 °C, 72 h; (b) Me_6tren/$CuBr_2$/CuBr/DMSO/AN, 60 °C, 24 h[a]



[a]Me_6tren = tris[2-(dimethylamino)ethyl]amine. DMSO = dimethyl sulfoxide.

O) are interlinked by strong covalent bonds.[30−34] This exciting new class of porous materials has attracted tremendous interest because they possess fascinating structural topologies and chemical stability, enabling potential uses in gas storage, gas separation, catalysis, and sensing. However, no PAF material has been prepared for use as an adsorbent for the extraction of uranium from seawater. Herein, we report the use of a chloride-functionalized PAF as an initiator for surface grafting of PAO by ATRP, and subsequent investigation involving its use in the extraction of uranyl from seawater. For the simulated seawater test, the optimized adsorbent possessed a uranium capacity of 65.2 g-U/kg-ads, exceeding the capacity of benchmark JAEA fiber adsorbents obtained from electron beam irradiation grafting.[29]

RESULTS AND DISCUSSION

The highly porous PAF material, PPN-6 (where "PPN" stands for porous polymer networks), has an extremely robust all-carbon scaffold that is based on biphenyl segments,[30] making it an ideal candidate for surface functionalization with PAO. Pristine PPN-6 was first synthesized using a modified Yamamoto homocoupling polymerization procedure,[34] with PPN-6-CH_2Cl subsequently prepared according to reported literature.[34] The chloride substitutions introduced on the PAF skeleton can be used to initiate the ATRP reaction. Under an inert atmosphere, acrylonitrile (AN) monomers were grafted on the PAF substrate by ATRP, using copper(I) bromide, copper(II) bromide, and tris[2-(dimethylamino)ethyl]amine (Me_6tren) as catalysts, yielding the AN-grafted PAF material PPN-6-PAN (see Scheme 1). Unreacted monomers and homopolymers were removed by washing with N,N′-dimethylformamide (DMF) and ethanol prior to drying the final material at 50 °C under vacuum. As observed in the SEM images (see Figure S3 in the Supporting Information), nanoparticles of PPN-6-PAN were formed, with an average diameter of ∼200 nm. The degree of grafting (DOG) for PPN-6-PAN is 150%, which can be calculated using the expression

$$\mathrm{DOG}\,(\%) = \frac{W_g - W_0}{W_0} \times 100$$

where W_g is the weight of the grafted products and W_0 denotes the weight of the ungrafted PAF precursors.

The surface area and porosity of PPN-6 and PPN-6-CH_2Cl were characterized by nitrogen adsorption/desorption at −196 °C (see Figure 1a). The Brunauer−Emmett−Teller (BET) surface area was calculated from the adsorption branch of the

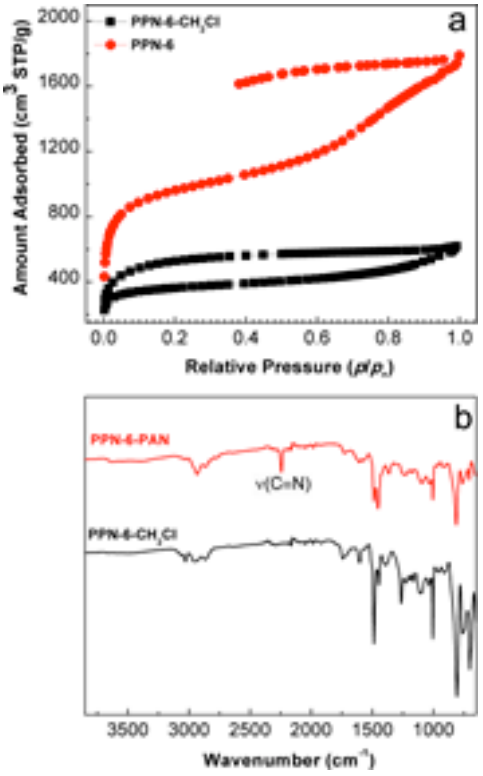


Figure 1. (a) N_2 −196 °C isotherms of PPN-6 and PPN-6-CH_2Cl and (b) Fourier transform infrared (FTIR) spectra of PPN-6-CH_2Cl and PPN-6-PAN.

PPN-6. This surface area is less than the previously reported value, which may be due to impurities trapped in the micropores.[30,31] In contrast, PPN-6-CH_2Cl shows a dramatic decrease in N_2 uptake capacities and a lower BET surface area (1252 m^2/g),[2] because of the introduction of the $-CH_2Cl$ substitutions. Notably, the surface area was further reduced to 19.5 m^2/g for PPN-6-PAN (see Figure S1 in the Supporting Information), indicating that grafting occurs throughout the PPN-6-CH_2Cl. The Fourier transform infrared (FT-IR) spectra of PPN-6-CH_2Cl and PPN-6-PAN are shown in Figure 1b. Compared to the pristine PPN-6-CH_2Cl, the AN-grafted products display a sharp characteristic adsorption band at 2242 cm^{-1}, corresponding to the C≡N stretching vibration, indicative of successful grafting of AN groups onto the PAF substrate (Figure 1b).[35]

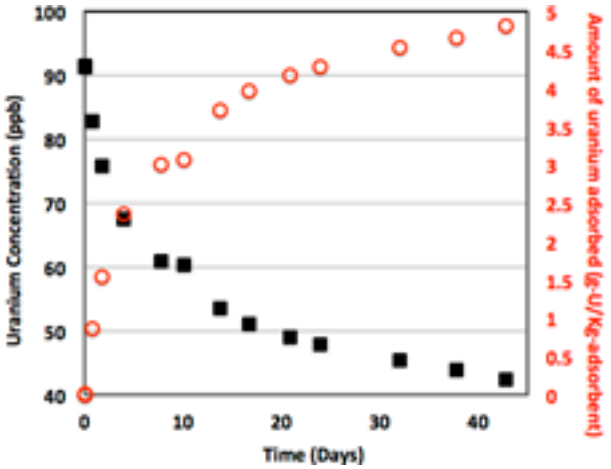


Figure 2. Changes in the concentration of uranium of the spiked seawater and uranium adsorption capacity for PPN-6-PAN-based adsorbents.

for 72 h. From the FT-IR spectra, the sharp peak of the C≡N group disappeared while major features at 3200−3400, 1653, and 933 cm^{-1} were still observed. These bands correspond to the stretching frequencies for the O−H, C═N, and N−O fragments on amidoxime, indicating successful conversion of the nitrile groups to amidoxime (see Figure S2 in the Supporting Information).

Previous literature reports have revealed dramatic increases in uranyl sorption by PAO fibers following treatment with KOH prior to seawater contact.[3] In order to investigate the effect of KOH conditioning, ∼15 mg of PPN-6-PAN were treated with an aqueous 3% KOH solution for 3 h at either room temperature or 80 °C. These samples were lab-screened in the laboratory using simulated seawater with an initial uranyl concentration of 6 ppm at pH 8. After 24 h, the uptake capacities were 64.1 and 65.2 g-U/kg-ads for room-temperature- and 80 °C-conditioned PPN-6-PAO, respectively. These results indicate the KOH conditioning temperature does not affect the final adsorption capacity for the PPN-6-PAO adsorbent. These uranyl uptake capacities were more than two times greater than those of the benchmark JAEA fibrous adsorbents when exposed to uranium under the same conditions.[29] This "apples-to-apples" comparison demonstrates the vast potential of nanostructured, high-surface-area adsorbent materials.

The PPN-6-PAN sample was further tested in real filtered seawater with a spiked uranyl concentration (initial concentration of ∼80 ppb) after being conditioned at 80 °C with 3%

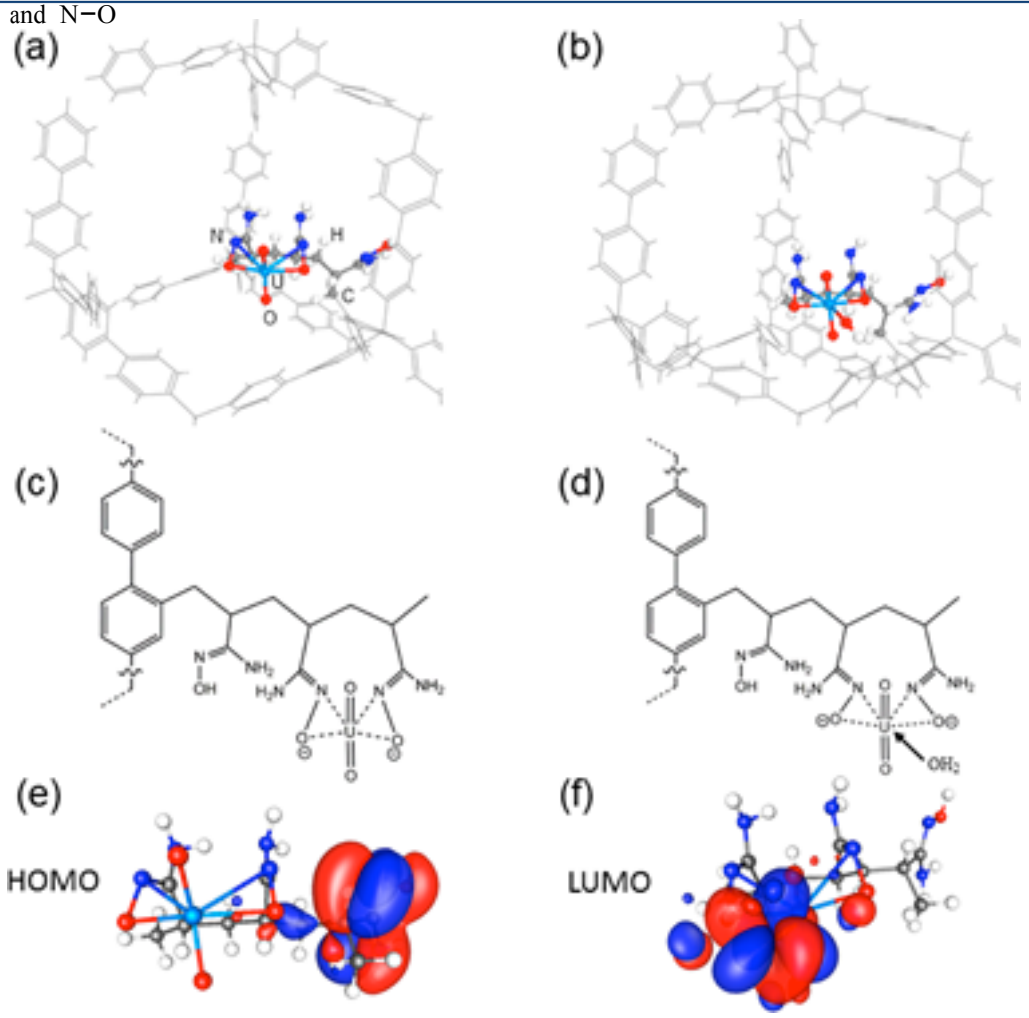


Figure 3. Optimized structures of (a) [(PPN-6-PAO)UO_2] and (b) [(PPN-6-PAO)$UO_2(H_2O)$] complexes; their schematic binding modes are

KOH aqueous solution to ensure capacity performance when competing ions start to be involved. PPN-6-PAN provides comparable uranium adsorption capacity (4.81 g-U/kg-ads) after 42 days. Excitingly, the rapid adsorption kinetics displayed by PPN-6-PAN (Figure 2) reveal that the sorbent is ∼80% adsorbed after only 2 weeks, reducing the amount of time necessary for deployment in seawater. However, no uranyl uptake was measured when deployed in unspiked seawater, possibly because of the very low concentration of uranium under environmental conditions nearing the limits of analytical quantification.

Based on the periodic structure of the PAF skeleton,[34] we performed density functional theory (DFT) calculations to study the binding geometry of PAN-functionalized PAFs with the uranyl (UO_2^{2+}) cation. This is inspired by many previous computational studies of actinide complexes, often in comparison with the experiment.[36−38] The optimized structures of [(PAF−PAO)UO_2] and [(PAF−PAO)$UO_2(H_2O)$] complexes are shown in Figures 3a and 3b, respectively. Previous computational investigations have shown that electron-donating AO functional groups adopt an η^2-type binding motif with the electron-accepting uranyl.[39−41] Because of filling of the equatorial coordination plane with strongly binding amidoxime, we observed that only one H_2O molecule can further bind to the [(PAF−PAN)UO_2] complex, with a U−O distance of 2.57 Å (Figure 3b); we added a second water molecule and found that it does not bind to UO_2 directly but to the first water through a hydrogen bond.

One interesting result of the binding is that the linear uranyl cation becomes distorted after forming the binding motif, with an O═U═O bond angle of 157°, which differs significantly from that in ($[UO_2(CO_3)_3]^{2-}$. 4This bond angle distortion has been previously investigated computationally, and it has been used to rationalize the abrupt change in color observed upon strong uranyl binding.[43] This bent uranyl group in the PAO− UO_2 complex is where the LUMO orbital is located (Figure 3f), while the HOMO is localized on the amidoxime group (Figure 3e). We observed a strong thermodynamic driving force for the PAO−UO_2 binding: compared with the unbound state (where the uranyl cation is at least 5 Å away from the PAO ligand inside the framework), the energy of the bound state is decreased by more than 170 kcal/mol, which is similar to the gas-phase binding energies computed previously.[44]

CONCLUSION

A new porous aromatic framework (PAF)-based adsorbent for uranium was prepared through atom-transfer radical polymerization (ATRP), with the robust porous substrate first modified with chloride to function as an ATRP initiator. The adsorbents were pretreated with potassium hydroxide (KOH) at different temperatures and screened for uranyl extraction with simulated seawater. Similar uranium adsorption results indicate that capacities are not affected by the KOH conditioning temperature, and they reveal that the adsorbents can be conditioned in a more environmentally friendly fashion. The periodic structure of the PAF support facilitates investigation of how the uranyl ions are bound by the poly(amidoxime) (PAO). Short diffusion pathways resulting from the PAF support and the readily accessible metal-binding sites make these functional materials of

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