Covalent Organic Framework Sponges for Efficient Solar Desalination and Selective Uranium Recovery

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1. INTRODUCTION

With the advantages of high energy density and low carbon emission, nuclear energy will become the main clean energy supply in the near future. Uranium is a key element of nuclear energy, and recovering uranium from seawater is one of the most promising strategies to solve the problem of uranium resources. In addition, since 97% of the earth’s water is stored in the ocean, seawater desalination plays a growingly important role in freshwater production. Solar-driven evaporation has a low carbon footprint and is one of the most promising sustainable freshwater production technologies. Current research is mainly focused on either uranium recovery or solar desalination but has not yet jointly solved these two important issues, despite the fact that both are focused on the same sample: seawater. A synergistic platform for solar desalination and uranium recovery may solve the shortage of fresh water and clean energy.

Covalent organic frameworks (COFs) are considered to be the most promising uranium adsorbents because of their robust stability, large specific surface area, and well-defined pore environments. Since 2018, several examples of amidoxime-based COFs for uranium extraction have been reported, such as COF-TpAb-AO, NDA-TN-AO, and PT-BN-AO. However, these COFs are usually in a powder form, which is difficult to process and recover from natural seawater. In addition, amidoxime-based COFs exhibit much higher affinity for vanadyl than uranyl. The efficiency of solar-driven vapor evaporation mainly depends on the property of absorbers. However, most absorbers suffer from poor water transport, low photothermal conversion efficiency, or short service life. Notably, the application of COFs in solar desalination has not yet been explored.

Herein, we constructed a new platform for concurrent solar desalination and selective uranium recovery. By integrating benzoxazole-linked COFs into a low-cost 3D porous polymer scaffold (polydimethylosiloxane, PDMS), we report the first example of COF-based sponge (BHMS) as a synergistic platform for solar desalination and uranium recovery. Under solar irradiation, the rough surface of the BHMS can produce multiple scattering of incident sunlight, which can convert more incident light into heat at the air/water interface, thereby increasing the photothermal conversion efficiency. The increase in temperature can promote the thermal movement of uranium near BHMS and enhance the interaction between uranium and binding sites. Meanwhile, the introduction of conjugated alkylnyl groups in the skeleton of the benzoxazole-linked COF endows BHMS with high anti-biofouling activity, so that BHMS can withstand the complex environment of the ocean and realize long-term synergistic seawater desalination and uranium recovery. In summary, the BHMS has a desirable structural hierarchy, elastic macroporous open cells, and excellent mechanical stability, providing adequate water...
transport for evaporation, selective binding sites of uranyl, excellent photothermal performance and photocatalytic activity, and achieving long-term synergistic desalination and uranium recovery.

2. EXPERIMENTAL SECTION

2.1. Synthesis of BHMS Sponge. PDMS prepolymer (10 g), curing agent (1 g), and DBD-BTTH (300 mg) are mixed together by ultrasonic treatment. Then, the sugar cubes in the mixture were degassed under vacuum for 2 h. PDMS on the surface of cubes was wiped off to expose the sugar after curing at 60 °C under atmospheric conditions for 3 h. The sugar template was then dissolved in hot water (60 °C) and washed away under stirring. After drying in a 60 °C oven for 10 h, BHMS sponges were obtained. To obtain the optimal COF content, five samples were prepared, namely, PDMS sponge, BHMS1, BHMS2, BHMS3, and BHMS4, and their DBD-BTTH:PDMS mass ratios were 0:10, 1:10, 2:10, 3:10, and 4:10, respectively.

2.2. Uranium Recovery Experiments from Uranium-Spiked Filtered Natural Seawater. The pH value of the solutions was adjusted to 5.0 with HNO3 or NaOH aqueous solution. Seawater collected from the East China Sea near the Xiamen City, Fujian Province, was used. The natural seawater was filtered through a 0.22 μm filter to remove insoluble particles and microorganisms, and uranyl nitrate was added into the filtered natural seawater to a final concentration of 35 ppm. The concentrations of various metal ions during all the experiments were measured by inductively coupled plasma mass spectrometry (ICP–MS). All the recovery experiments were performed under ambient conditions. The uranium recovery capacity assay was performed by adding 5 mg of BHMS3 sponge into 500 mL (35 ppm) of uranium-spiked filtered natural seawater with moderate magnetic stirring. The uranium-spiked filtered natural seawater was irradiated with a xenon lamp having an optical power density of 1 kW m−2 with the light wavelength from 250 to 2500 nm. At an interval of 1 h, the treated solution was filtered through a 0.22 μm membrane filter, and the filtrate was collected and analyzed by ICP–MS to determine the remaining uranium content. The recovery capacity at time (qt, mg/g) was calculated using the following equation: qt = (C0 – Ct) / V × M, where V is the volume of the treated solution (L), M is the amount of used adsorbent (g), C0 is the initial concentration of uranium (mg/L), and Ct is the concentration of uranium at time (mg/L).

2.3. Uranium Recovery Experiments from Natural Seawater. The uranium recovery capacity of BHMS3 was also determined in natural seawater without additional uranium. In brief, BHMS3 was fixed in the continuous flow of natural seawater to extract uranium. BHMS3 has a mass of 253 mg. The volume of seawater was 1000 L, and the flow rate was controlled at 500 mL/min. After natural seawater adsorbed uranium, the sponges were immersed in a mixture of 0.1 M HNO3 and 0.5 M ascorbic acid to desorb the uranium adsorbed in the sponges, and then, the mixture was filtered with a 0.22 μm membrane filter. After that, the concentration of uranium was measured by ICP–MS. The amount of uranium is calculated using the following equation: q = C × Vt / M, where q, (mg g−1) is the adsorption capacity of the adsorbents for uranium, C (mg L−1) is the concentration of uranium measured by ICP–MS, Vt (L) is the elution solution volume, and M (g) is the weight of the adsorbent.

2.4. Recyclability Test. After one run of recovery, the adsorbent was regenerated by treatment with the elution solution of HNO3 (0.1 M) and ascorbic acid (0.5 M) and reused for another recovery experiment. We immersed 5 mg BHMS3 sponge in a mixture of 0.1 M HNO3 and 0.5 M ascorbic acid to desorb the uranium adsorbed in the sponge and then filtered the mixture with a 0.22 μm membrane filter, and the concentration of uranium was measured by ICP–MS. After that, the BHMS3 was washed twice with deionized water and dried at 50 °C for subsequent uranium adsorption–desorption cycles. The elution efficiency (E, %) was determined using eq: E = [(C0 − Ct) × Vt] / (C0 × Vd) × 100%, where C0 (mg L−1) is the uranium concentration in elution solution, Vt (L) is the volume elution solution, Ct (mg L−1) is the uranium concentration in uranium-spiked seawater after uranium recovery, Vd (mg L−1) is the initial uranium concentration of uranium-spiked seawater, and Vt (L) is the volume of uranium-spiked seawater used for recovery.

3. RESULTS AND DISCUSSION

We first synthesized an alkynyl-functionalized benzoazoleole-linked COF (named DBD-BTTH, Figure 1a), which had excellent photocatalytic activity, strong stability, good hydrophilicity, and high selectivity to uranium (see Results and Discussion Section in the Supporting Information, Figures S1–S23, and Tables S1 and S2). This COF is rich in hydroxyl groups on the surface. To highlight that the hydroxyl groups could greatly improve the hydrophilicity, visible light absorption, and the selectivity to uranyl, we prepared a reference COF (named DBD-BTTH, Figure 1a) without the hydroxyl groups in the same way.

To explore the new concept of synergistic solar desalination and uranium recovery and to overcome the bottleneck that COF-based adsorbents are difficult to process and recover, we used soft-templated PDMS to prepare DBD-BTTH-integrated sponge (BHMS) as a new platform for solar evaporation and recovery of uranium from seawater. The 3D porous BHMS was prepared by a cost-effective sugar leaching method (Figure 1b). A homogeneous DBD-BTTH and PDMS hybrid gel containing silicone curing/elastomer agents was first mixed, and then, a sugar cube was immersed in the mixed gel for 2 h. After curing, the sugar cube template was dissolved in water to produce 3D porous BHMS. To obtain the optimal COF content, five samples were prepared, namely, PDMS sponge, BHMS1, BHMS2, BHMS3, and BHMS4, and their DBD-BTTH:PDMS mass ratios were 0:10, 1:10, 2:10, 3:10, and 4:10, respectively (Figure S24).

The SEM images of the PDMS sponge and BHMS3 showed similar hierarchical porous structures (Figures 1c,d, S25, and S26), and BHMS3 had a more rough internal surface, which could produce multiple scattering of incident sunlight, improve the heat conversion efficiency of sunlight, and increase the contact area between BHMS3 and uranyl. In addition, BHMS3 also exhibited high flexibility (Figures S27 and S28). Even after 100 cycles of compression testing, BHMS3 could be restored to its original shape without plastic deformation (Figure S29), indicating that BHMS3 had excellent flexibility, mechanical stability, and recyclability, which are essential for practical applications. Owing to the excellent hydrophilicity and robust stability of DBD-BTTH, compared with PDMS sponge,

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BHMS3 has a much smaller static water contact angle (Figure S30) and higher thermal stability (Figure S31). In addition, the liquid flow experiment confirmed the efficient water transport of BHMS3 (Figure S32), and BHMS3 had excellent floatability and thermal insulation (Figures S33 and S34), allowing more incident light to be converted to heat at the air/water interface with minimal heat loss, providing an ideal new platform for solar desalination and uranium recovery.

Compared with PDMS sponge, BHMS showed extremely low light transmittance (<0.5%) and reflectance (<9%) over the entire solar spectrum (Figures S35 and S36), indicating that the BHMS possessed excellent light absorption performance (Figure S37). As shown in Figure 2a, the surface temperature of BHMS3 and BHMS4 could reach 42.9 and 44.0 °C under 1 sun, respectively, while the surface temperature of blank PDMS sponge was only 31.7 °C, indicating that BHMS had much higher photothermal conversion efficiency.
evaporation rate of BHMS was also explored by recording the weight change because of loss of water. To accurately measure the evaporation rate of water, the area outside the sample was covered with an aluminum foil (Figure S38). Through this measurement, the evaporation of water unrelated to the samples would be eliminated. As shown in Figure 2b, the water evaporation rates of the PDMS sponge, BHMS1, BHMS2, BHMS3, and BHMS4 were calculated to be 0.267, 1.01, 1.13, 1.39, and 1.31 kg m⁻² h⁻¹, respectively, with the corresponding conversion efficiencies \( \eta \) being 14.3%, 60.8%, 71.7%, 84.7%, and 79.7% (Figure S39), respectively. Meanwhile, the water evaporation rates and surface temperature of BHMS3 almost increased linearly with the solar irradiation intensity, indicating that the evaporation rate could be further scaled up by using optical concentrators (Figures S40–S42). Surprisingly, the BHMS3 sample still maintained a high evaporation rate after 12 cycles of 1 sun irradiation for 1 h (Figure S43) and after treatment at a high temperature of 100 °C for 48 h (Figure S44). It should be noted that although this work is the first proof of concept for applying COF sponges to solar desalination, it has already achieved performance comparable with recently reported solar absorbers (Table S3).

Encouraged by the excellent water evaporation performance of BHMS3, we conducted further systematic research on the practical application of BHMS3. Obviously, the evaporation rates of four types of water, including seawater, river water, strong acid, and alkaline water, are close to that of pure water (Figures S45 and S46). Consistent with the water mass loss, the surface temperature of BHMS3 showed only minor differences in various types of water (Figure S47). Meanwhile, the shape of BHMS3 had not changed after being exposed to the long-term seawater evaporation for 12 h, further indicating its excellent stability (Figure S48). In addition, the salt-resistant performance of BHMS3 was further assessed by desalination tests. After placing 500 mg of NaCl on the surface of BHMS3 and exposing it to 1 sun irradiation within 3 h, these NaCl salt crystals gradually dissolved (Figure S49), indicating that the BHMS3 possessed an excellent salt resistance property. As shown in Figure S50, even after long-term evaporation tests (soaked for 14 days, once a day for 60 min under 1 sun irradiation), the water evaporation rate of BHMS3 was almost constant. According to the SEM images (Figure S51), it was found that the structure of BHMS3 was well retained, and there was no salt residue on the skeleton. This might be due to the diffusion of salt ions into bulk water through the porous structure of BHMS3. In addition, we also explored the mass changes in seawater (Figure S52), surface temperature (Figure S53), and uranium adsorption capacity before and after durability tests for 14 days. The results showed that the evaporation rate and surface temperature were similar to the initial data of BHMS3, indicating that BHMS3 has long-term durability and good reusability. Furthermore, BHMS3 also showed excellent effects in solar seawater desalination. After evaporation, the four main ion concentrations of Na⁺, Mg²⁺, K⁺, and Ca²⁺ in seawater were reduced by 4 orders of magnitude (Figure 2d). These experimental results confirmed the great potential of BHMS3 in solar desalination.

To explore synergistic solar desalination and uranium recovery, we also studied the uranium adsorption performance of BHMS3 in uranium-spiked filtered natural seawater. We first explored the uranium recovery performance of BHMS3 in the pH range of 3.0–7.0. As shown in Figure S55, BHMS3
exhibited the maximum uranium recovery capacity at pH 5.0, while the PDMS sponge only showed a very small uranium adsorption capacity, demonstrating that the efficient uranium recovery of BHMS3 was mainly derived from DBD-BTTH. Subsequently, we explored the uranium recovery performance of BHMS synthesized at different DBD-BTTH contents at pH 5.0. As shown in Figure S56, as the mass ratios of DBD-BTTH increased from 10% to 30%, the uranium recovery capacity significantly increased from 210.1 ± 7.1 to 402.3 ± 12.6 mg g⁻¹. However, as the mass ratio of DBD-BTTH increased from 30% to 40%, the uranium recovery capacity showed only a small increase (from 402.3 ± 12.6 to 413.7 ± 13.0 mg g⁻¹), which might be caused by the shielding effect. Overall, considering the synergistic demands of high-efficiency solar evaporation and high-capacity uranium recovery, we choose BHMS3 as an ideal platform for synergistic solar desalination and uranium recovery from natural seawater.

To confirm that DBD-BTTH can significantly improve the hydrophilicity and the specific affinity for uranium of BHMS, we prepared a DBD-BTT-integrated sponge (named BTMS) in the same way (Figures S57–S59). Under dark conditions, the uranium adsorption capacity of BHMS3 was much higher than that of BTMS (Figure 3a), which could be attributed to the integration of DBD-BTTH in the 3D sponge, providing abundant uranyl binding sites and improving the hydrophilicity of BHMS. X-ray photoelectron spectroscopy (XPS) was used to verify this speculation. After recovering uranium, intense U 4f double peaks appeared for the BHMS (Figure 3b), while only feeble U 4f double peaks appeared for BTMS (Figure S60), which matched well with the experimental data. In the N 1s high-resolution spectrum of BHMS3, the two peaks centered at 400.10 and 398.50 eV were assigned to C=N and C≡N, respectively (Figure 3c). After uranium binding, the two peaks of C—N and C≡N were shifted to 400.31 and 398.65 eV, respectively (Figure 3d), confirming strong interactions between uranyl ions and the nitrogen atoms in the benzoxazole rings. In the O 1s high-resolution spectrum of BHMS (Figure 3e), the two peaks at 532.87 and 530.60 eV were attributed to C=O and C≡O, respectively. After uranium binding, the two peaks in the O 1s region obviously shifted to higher binding energy, and the ratio of C=O to C—O significantly increased, suggesting that the enol form of DBD-BTTH was oxidized to a keto form after uranium recovery (Figure 3f). However, compared with BHMS, the N 1s and O 1s high-resolution spectrum of BTMS did not change after uranium recovery (Figure S61), indicating a lack of further interactions between BTMS and uranium.

The antifouling activity of BHMS sponge was then explored with bacteria as the target. The BHMS3 sponge showed high antibacterial activity against Gram-positive *Bacillus cereus* and *Staphylococcus aureus* and Gram-negative *Pseudomonas aeruginosa* and *Vibrio alginolyticus* under light conditions (Figures 3a, S53–S55).
Owing to the excellent photocatalytic, photo-thermal, and photoelectric effects of BHMS3, the adsorption capacity and adsorption kinetics of BHMS3 for uranium have been significantly improved after light irradiation (Figures S66 and S67). In addition, BHMS3 showed excellent regeneration performance, which is critical for the recovery of uranium from seawater (Figures S68 and S69). In addition, we used uranium-spiked filtered natural seawater with different NaCl concentrations to study the effect of seawater salinity on the recovery of uranium by BHMS3 (Figure S70). Surprisingly, in a wide range of NaCl concentrations (0.1−0.5 mol/L), no significant inhibition of uranium adsorption was observed, indicating that the salinity has almost no effect on the adsorption of uranium by BHMS3. We also explored the uranium adsorption capacity before and after evaporation tests for 14 days (Figure S71). The results showed that even after the durability test, the uranium capture capacity of BHMS3 was near to the initial data under dark conditions (from 402.3 ± 12.6 to 398.6 ± 11.95 mg/g). All of these indicated that BHMS3 has excellent photocatalytic activity, photothermal effect, and reusability and could achieve a long-term recovery of uranium from natural seawater.

Finally, to realize synergistic solar-driven desalination and uranium recovery under natural sunlight, we designed a new prototype for simultaneous solar desalination and uranium recovery (Figure S72). We fixed the BHMS3 on the predesigned flow device, controlled the flow rate at 500 mL/min, and then irradiated it under natural light from 07:00 to 17:00 for 12 days. BHMS3 showed rapid uranium extraction efficiency in the first 5 days, and the uranium extraction capacity of BHMS3 reached 4.98 ± 0.14 mg/g. Within 12 days, the uranium adsorption capacity of BHMS3 and BTMS reached 5.14 ± 0.15 and 0.57 ± 0.05 mg/g (Figure 4a), respectively. BHMS3 showed excellent selectivity to uranium in natural seawater but not to other metals (such as Na, Mg, K, Ca, V, Zn, Cu, and Fe) (Table S4), and the uranium adsorption capacity of BHMS3 was 12.7 times higher than that of vanadium (Figure 4b). The pH of natural seawater is about 8.0, in which uranyl ions exist in the form of [UO$_2$(CO$_3$)$_3$]$^{4-}$. In addition to excellent photocatalytic activity and photothermal effect, the BHMS3 also showed excellent photoelectric performance (Figure S73), which could effectively form a positive electric field around the BHMS3 sponge, exhibiting a strong electrostatic attraction to the negative [UO$_2$(CO$_3$)$_3$]$^{4-}$, further improving the uranium recovery capacity. Furthermore, the outdoor device for BHMS3 achieved highly pure water generation of ca. 7.1 kg m$^{-2}$ within 12 h (from 07:00 to 17:00), suggesting good performance for practical seawater purification applications (Figure 4c,d). All of these indicated that even under natural light, BHMS3 still exhibited a high evaporation rate and high uranium recovery capacity, providing an attractive platform for solving the current shortage of fresh water and energy.

4. CONCLUSIONS

In summary, we successfully developed the first 3D COF sponge (BHMS) as a synergistic platform for efficient solar desalination and selective uranium recovery. The BHMS was customized with excellent photothermal performance, photocatalytic activity, hydrophilicity, mechanical properties, ideal inbuilt structural hierarchy, and elastic macroporous open cells for adequate water transport and rapid diffusion of uranyl ions. The promotion of thermal movement of uranyl ions and solar desalination through photothermal enhancement can achieve synergistic uranium recovery and freshwater collection. Owing to its outstanding photocatalytic activity and excellent mechanical properties, the BHMS showed ultrahigh antifouling activity on marine biological entities, thus realizing efficient uranium recovery and long-term solar desalination.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c04419.

Additional experimental details and figures including FT-IR spectra; PXRD patterns; solid-state 13C CP−MAS NMR spectra; N2 adsorption−desorption isotherms; SEM images; static water contact angles; TGA results; UV−vis NIR spectra; XPS spectra; antibacterial spectrum; uranium recovery capacity; prototype for concurrent seawater desalination and uranium extraction under natural sunlight; and transient photocurrent response (PDF)

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Notes
The authors declare no competing financial interest.

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