

Advancements in the Research of COF-Based Materials for Uranyl Enrichment

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Abstract: As a critical fuel for nuclear power operations, uranium plays an important role in ensuring the sustainable development of nuclear energy. In China, the demand for uranium resources is expected to reach 1.0-2.0 million tons per year by 2030. Currently, the principal methods employed for the enrichment of uranyl ions include photocatalysis, electrocatalysis, and adsorption. Covalent organic frameworks (COFs) have emerged as a popular choice for uranyl ion enrichment due to their suitable pore size, substantial specific surface area, and exceptional electrical conductivity. This review primarily focuses on the evaluation and characterization methods pertaining to uranyl enrichment, as well as the utilization of COFs-based materials for uranyl enrichment.

Keywords: Uranium Enrichment; Covalent-Organic Frameworks; Research progress.

1. Introduction

From an environmental perspective, uranium enrichment is crucial due to the radioactive nature of uranium and its potential impact on the ecological balance. Uranium, a naturally occurring radioactive element, can contaminate water bodies and soil, posing significant health risks to humans and wildlife. Therefore, effective methods for uranium enrichment are necessary to minimize its environmental footprint and ensure safe disposal or reuse. In the nuclear industry, uranium enrichment is essential for the production of nuclear fuel. Enriched uranium is required to achieve the desired energy output and safety standards in nuclear reactors^[1]. The purity and concentration of uranium are critical factors in ensuring the efficient and safe operation of nuclear power plants. There are several methods employed for uranium enrichment, including adsorption, reduction, and other techniques. Adsorption, a widely used method, involves the attachment of uranium ions to the surface of adsorbents^[2]. Reduction, on the other hand, involves converting uranium from its oxidized state to a reduced form, often facilitating its separation and purification^[3]. A variety of materials have been studied for uranium enrichment, including metal-organic frameworks (MOFs), porous organic polymers (POPs), and porous aromatic frameworks (PAFs). These materials exhibit unique properties such as high porosity, tunable pore size, and functionalizability, making them promising candidates for uranium adsorption and separation^[4].

Covalent organic frameworks (COFs) are a class of porous crystalline materials composed of light elements (such as C, H, O, N, B, and Si) connected through strong covalent bonds^[5]. They possess high porosity, excellent chemical stability, and tunable pore sizes and functionalities, making them attractive for various applications, including uranium enrichment. Compared to other materials like MOFs, POPs, and PAFs, COFs offer several advantages in uranium enrichment^[6]. First, their covalent bonding nature confers higher thermal and chemical stability, allowing them to withstand harsh conditions encountered during uranium processing^[7]. Second, the tunable pore sizes and

functionalities of COFs enable precise control over uranium adsorption and separation. Finally, the lightweight and crystalline nature of COFs facilitate their synthesis, processing, and recycling, making them environmentally friendly and cost-effective^[8].

This review endeavors to present a thorough examination of the latest advancements in the utilization of covalent organic frameworks (COFs) for the enrichment of radioactive uranium. We will meticulously investigate the evaluation techniques employed to quantify the performance of COFs in uranium enrichment processes. Furthermore, we will delve into the intricate factors that govern the efficiency of COF-based materials in uranium enrichment. Additionally, this review will expound on the adsorption mechanisms, photocatalytic enrichment, and electrocatalytic enrichment of uranium utilizing COFs. By compiling and analyzing the latest research findings and challenges in this domain, we aim to offer profound insights into the potential future development of COF-based materials for uranium enrichment.

2. Enrichment Effect Evaluation and Characterization Methods

2.1. Adsorbing effect

Currently, the concentration of uranyl ions is primarily achieved through photocatalysis, electrocatalysis, and adsorption techniques. The adsorption efficacy is quantitatively assessed by comparing the uranyl ion concentration in the solution prior to and following the reaction. This comparison is typically conducted through ultraviolet absorbance measurements for higher concentrations, while for lower concentrations, inductively coupled plasma mass spectrometry (ICP-MS) is employed for greater precision. Furthermore, the characterization of the adsorbed materials is primarily conducted using X-ray diffractometers and infrared spectrometers. These techniques allow for a detailed analysis of the morphological changes and interactions between the adsorbed uranium and the material surface, providing crucial insights into the enrichment process.

2.2. Cycle performance

To evaluate the durability of the catalyst, we conduct cyclic experiments. The effectiveness of the catalyst over multiple cycles depends heavily on its structural stability. After the reaction, we assess the stability of the material using XRD and FT-IR. We observe any changes in the XRD peaks and check if the specific chemical bonds identified by infrared spectroscopy remain intact. Nowadays, researchers not only conduct material cycling experiments but also perform leaching tests after each reaction to assess the capacity of the catalyst to enrich uranyl ions. This comprehensive approach helps us gain a better understanding of the catalyst's performance and stability, crucial for its practical use in uranium enrichment processes.

2.3. Mechanism study

To understand deeper into the complete mechanism of uranyl ion enrichment and concentration, researchers employ a range of characterization techniques, including theoretical calculations and EXAFS. Theoretical calculations play a critical role in supporting and validating the observed phenomena from performance studies. Through these calculations, key intermediate transformation states are

identified, providing a clearer understanding of the overall reaction mechanism. Advanced techniques like XAFS are utilized to elucidate changes in the valence state of the reaction and the evolution of chemical bonds. By leveraging these tools, we can gain a comprehensive picture of the enrichment process, from start to finish.

3. Enrichment of uranyl in COFs based materials

3.1. Enrichment of uranyl by COFs based adsorption materials

Wu et al.^[9] successfully extracted uranium from highly acidic wastewater in a gentle and efficient way. They also created a sulfonated polyether sulfone (SPES) membrane and a mixed matrix membrane (MMM) using $[\text{NH}_4]^+[\text{COF-SO}_3^-]$ and SPES. These membranes were the first to be used for extracting uranium from acidic solutions with a pH of 1, bridging a gap in the use of SPE-based membranes for uranium absorption. To understand how these MMMs adsorbed uranium on the SPE membrane and $[\text{NH}_4]^+[\text{COF-SO}_3^-]$, Wu et al. conducted tests using SEM, FT-IR, XPS, and EDX.

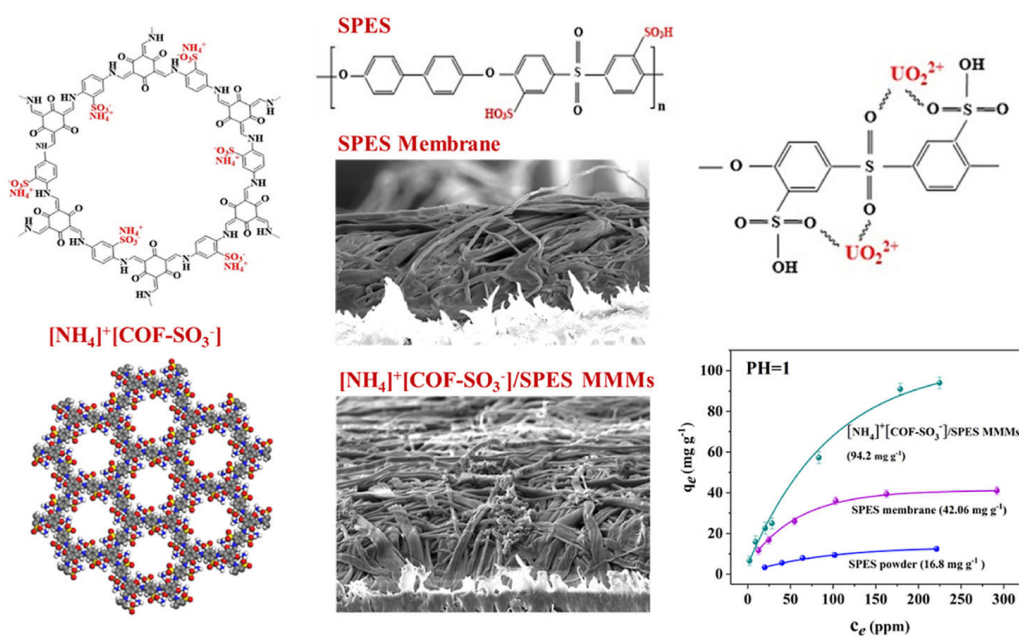


Figure 1. A gentle and efficient way of uranium from highly acidic wastewater extraction^[9].

Xiao et al.^[10] successfully synthesized a porous adsorbent, specifically $[\text{NH}_4]^+[\text{COF-SO}_3^-]$, through the ammoniation of a sulfonic acid-modified covalent organic framework (Fig 2.). This adsorbent exhibited exceptional performance in uranium extraction. In comparison to the original SO_3H functionalized COF ($\text{COF-SO}_3\text{H}$), which demonstrated a uranium adsorption capacity of 360 mg g^{-1} , the ammoniated variant, $[\text{NH}_4]^+[\text{COF-SO}_3^-]$, exhibited a remarkably high uranium absorption rate of up to 851 mg g^{-1} , representing a 2.4-fold enhancement. This adsorption capacity stands as the highest reported among all porous adsorbents for uranium extraction.

3.2. Enrichment of uranyl in COFs-based photocatalytic materials

Cui's team^[11] explored the development of the first covalent organic framework (COF) sponge, designated as BHMS. This innovative sponge was fabricated through the in-situ loading of benzoxazo-linked COF (DBD-BTTH) onto a porous polymer scaffold composed of polydimethylsiloxane. This unique collaborative platform was designed to efficiently facilitate solar desalination and exhibit selective uranium recovery capabilities. After the photo-reaction of 5 mg BHMS in 500ml (35ppm) filtered seawater, the extraction amount can reach 426.7mg/g.

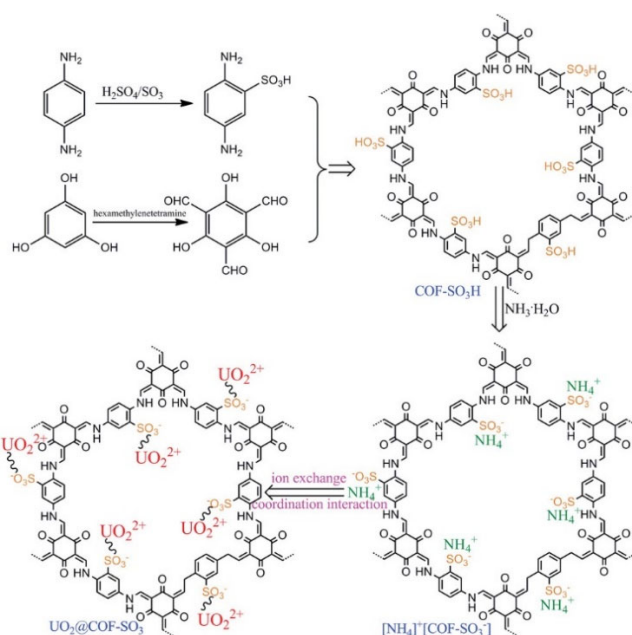


Figure 2. Synthetic scheme of SO_3H -decorated COF ($\text{COF-SO}_3\text{H}$) and the ammoniated material of $[\text{NH}_4]^+[\text{COF-SO}_3^-]$. A proposal of combined approach involved in both ion exchange and coordination interaction^[10].

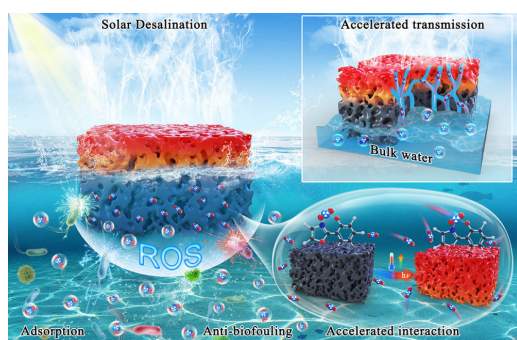


Figure 3. Schematic Depicting BHMS Sponge for Synergistic Solar Desalination and Uranium Recovery

3.3. Enrichment of uranyl in COFs-based electrocatalytic materials

Yang et al. introduce a novel method for the concurrent recovery of uranium (UO_2^{2+}) and rhenium (ReO_4^-) via electroadsorption, offering a non-radioactive alternative for technetium recovery from low-level radioactive waste (Fig 4.). The carboxyl-functionalized covalent organic framework (COF-1) and cationic covalent organic framework (COF-2) were synthesized as electrode materials. The electroadsorption process for uranium and rhenium exhibited kinetics adhering to the quasi-second-order model at pH 7.0 and 298.15 K, achieving rates of 0.45 and 1.05 g/mg/h, respectively. Notably, these rates were twice as fast as those observed with traditional physicochemical adsorption methods. Electroadsorption facilitates ion migration towards the adsorbent by optimizing the utilization of active sites, thereby enhancing both adsorption capacity and kinetics. After 2 hours of electroadsorption, the adsorption efficiencies for uranium and rhenium reached 65.9% and 89.2%, respectively.

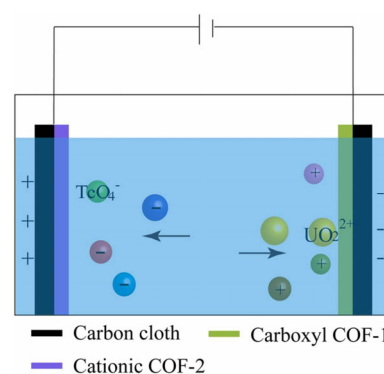


Figure 4. Schematic for simultaneous removal of UO_2^{2+} and ReO_4^- by electro-adsorption using COFs functionalized carbon cloths as asymmetric electrodes.

4. Conclusion

Overall, COFs-based materials have achieved significant advancements in the enrichment of uranyl, primarily attributed to the following key factors: (1) Their exceptional chemical and thermal stability. Current COFs commonly feature covalent bonds such as imine, hydrazone, azine, triazine, amide, and $\text{SP}^2\text{-C}=\text{C}$, among others. Owing to the robust nature of these covalent bonds and the complete assembly of monomers linked by these bonds, COFs exhibit superior chemical and thermal stability compared to other materials, such as MOFs. Notably, they maintain remarkable stability under acidic, alkaline, and redox conditions, with some polyimide COFs exhibiting decomposition temperatures exceeding 500 °C. (2) Their suitable pore size and substantial specific surface area. A catalyst with a larger surface area offers a greater number of active sites, enabling COFs to interact with a broader range of reactants. Consequently, this results in a higher yield of reaction products within a given time frame, leading to faster reaction rates and superior catalytic activity. (3) Their outstanding electrical conductivity. Since the introduction of imide bonds between building units for the synthesis of π - π -conjugated

COFs, various COFs exhibiting π - π -conjugated structures have been developed. The ordered columnar arrangement and π - π stacking between two-dimensional layers facilitate exciton migration and carrier transport within the framework, thereby enhancing electrical conductivity. Furthermore, the vast array of potential structures and innovative designs offered by COFs is noteworthy. The availability of diverse building block types and linkages allows for the creation of COFs with various morphologies and porosity.

References

- [1] Z. Dai, Y. Sun, H. Zhang, D. Ding, L. Li, *Industrial & Engineering Chemistry Research* 2019, 58, 19280-19291.
- [2] S. Ma, L. Huang, L. Ma, Y. Shim, S. M. Islam, P. Wang, L.-D. Zhao, S. Wang, G. Sun, X. Yang, M. G. Kanatzidis, *Journal of the American Chemical Society* 2015, 137, 3670-3677.
- [3] H.-L. Qian, Y. Wang, X.-P. Yan, *TrAC Trends in Analytical Chemistry* 2022, 147, 116516.
- [4] C. W. Abney, R. T. Mayes, T. Saito, S. Dai, *Chemical Reviews* 2017, 117, 13935-14013.
- [5] W.-R. Cui, C.-R. Zhang, R.-H. Xu, X.-R. Chen, W. Jiang, Y.-J. Li, R.-P. Liang, L. Zhang, J.-D. Qiu, *Applied Catalysis B: Environmental* 2021, 294, 120250.
- [6] R.-H. Xu, W.-R. Cui, C.-R. Zhang, X.-R. Chen, W. Jiang, R.-P. Liang, J.-D. Qiu, *Chemical Engineering Journal* 2021, 419, 129550.
- [7] T. Chen, K. Yu, C. Dong, X. Yuan, X. Gong, J. Lian, X. Cao, M. Li, L. Zhou, B. Hu, R. He, W. Zhu, X. Wang, *Coordination Chemistry Reviews* 2022, 467, 214615.
- [8] Z. Wang, Y. Yang, Z. Zhao, P. Zhang, Y. Zhang, J. Liu, S. Ma, P. Cheng, Y. Chen, Z. Zhang, *Nature Communications* 2021, 12, 1982.
- [9] G. Wu, Y. Liu, Q. Zheng, Z. Yu, F. Luo, *Journal of Solid State Chemistry* 2020, 288, 121364.
- [10] X. H. Xiong, Z. W. Yu, L. L. Gong, Y. Tao, Z. Gao, L. Wang, W. H. Yin, L. X. Yang, F. Luo, *Advanced Science* 2019, 6, 1900547.
- [11] W.-R. Cui, C.-R. Zhang, R.-P. Liang, J. Liu, J.-D. Qiu, *ACS Applied Materials & Interfaces* 2021, 13, 31561-31568.