ISSN 2616-5880 Vol. 4, Issue 7: 8-12, DOI: 10.25236/AJMC.2023.040702

Research progress on the application of sp^2C covalent organic framework materials on uranium extraction from seawater

Bowen Cui[1,a,#], Xingshen Lu[2,b,#]

[1]*Shandong First Medical University, Tai'an, China*
[2]*Shandong University, Weihai, China*
[a]*cuibowen200204@icloud.com,* [b]*2256627408@qq.com*
[#]*Co-first author*

Abstract: *Extracting uranium from ocean plays a key role in ensuring the supply of uranium resources and the benign development of nuclear energy, and the key for which is to obtain uranium extraction materials with excellent properties. sp^2C covalent organic framework materials have reflected the application of many important aspects in catalysis, adsorption, and energy storage because of their high stability, designability, and as well as specific surface area. In this paper, the latest research progress of sp^2C covalent organic framework materials for extracting uranium from the seawater is summarized. The synthesis, characterization, separation, and mechanism of the materials are systematically summarized, and the future development prospect is prospected.*

Keywords: *Uranium, Covalent organic frameworks, Amidoxime, Photoinduced, Adsorption*

1. Introduction

Nuclear energy, an important alternative to oil and coal, plays a unique and indispensable role in contemporary energy demand due to its relatively clean, low-carbon, no greenhouse-gas emission, and sustainable characteristics. Nuclear energy could optimize the global energy structure and ease the energy contradiction and environmental pressure. As vital raw material for nuclear energy, the global land reserves of uranium are only 5.5 million tons. However, the consumption rate of uranium has brought about a serious shortage of nuclear material for at least a century, which is an important problem facing the accord development of nuclear power. There is about 4.5 billion tons amount of uranium in seawater, which is about a thousand times larger than the amount found in land reserves[1]. Therefore, if uranium can be efficiently extracted from seawater, the healthy development of nuclear energy will be greatly guaranteed. At the same time, a large amount of wastewater containing uranium will be inevitably produced in uranium mining, which will cause environmental pollution and serious harm to human health, if we do not take effective measures[2]. Therefore, extracting uranium from seawater is a strategic way to ensure the sustainable development of the nuclear industry and reduce environmental radioactive pollution[3]. At present, uranium extraction from seawater still faces troublesome problems, such as slow kinetics, poor selectivity, low adsorption capacity, poor material stability, and poor reusability. At the same time, due to the large number of microorganisms present in the ocean, biological fouling is also a major obstacle to the uranium extraction from seawater[4].

The current research on uranium extraction from seawater focuses on how to improve the adsorption efficiency of the material. A variety of functional materials have been developed for uranium extraction from seawater, including metal organic frameworks (MOFs)[5], porous aromatic frameworks (PAF)[6], and porous organic polymers (POPs)[7], but most adsorption materials have been reported to have various defects. For example, PAF, because of its irregular channels, to a certain extent, limits the rapid transfer of uranium in these channels. Compared with PAF, MOFs have a more regular pore structure and more stable structure[7], but their performance under extreme conditions is not satisfactory. Based on the above problems, people turn their attention to covalent organic frame materials (COFs)[1,7-9], which have periodic topological structure[1], regular channels, and high stability[1,10], and can better meet the requirements of uranium extraction from seawater.

COFs materials are mainly containing two-dimensional (2D) and three-dimensional (3D) topological structure. Compared with 2D COFs, 3D COFs has advantages such as larger specific

ISSN 2616-5880 Vol. 4, Issue 7: 8-12, DOI: 10.25236/AJMC.2023.040702

surface area, lower mass density, more open pores, and more exposed functional groups. Therefore, 3D COFs are more conducive to the capture of uranium as adsorption material. However, compared with the relatively mature 2D COFs, the study of 2D COFs is very challenging. The main reason is that the driving force of 3D COFs synthesis comes from the formation of covalent bonds, and it is difficult to accurately control the bonding process from the atomic level. In addition, there are still many problems to be solved in 3D COFs[11], including few topological synthesis strategies, difficult structural characterization, and few functional precursors and applications.

Common COFs materials are based on the connection of B-O or C=N[9]. Due to their reversibility, the stability of COFs constructed by these structural unit has its limitations, which seriously hinder its potential application. Compared to B-O and C=N, sp^2C COFs benefit from the vinyl bond[12] and possess remarkable chemical stability under high acid, strong base, and even strong irradiation conditions[13]. This kind of COFs material has important application prospects in many fields such as photoelectric catalysis, chemical sensing, adsorption separation, seawater desalination, precious metal extraction, and so on. Amidoxime is an important functional group, which has good chelating ability with uranyl. Therefore, COFs materials based on a sp^2C skeleton, combined with an amidoxime functional group with a strong chelating ability to uranyl, show special advantages in uranium extraction from seawater. In this article, the research progress of sp^2C-based covalent organic framework materials for extracting uranium from seawater in recent years is reviewed, its advantages, application prospects, and shortcomings are analyzed, and the future development prospects are prospected.

2. Advances in sp^2C-based covalent organic framework materials

In 2021, the research group of Jianding Qiu from Nanchang University successfully introduced alkynes into the sp^2C skeleton amidoxime functionalized covalent organic framework material BD-TN-AO[9] to achieve efficient adsorption of uranium in seawater. The material uses KOH as a base and *o*-dichlorobenzene and *n*-butanol as mixture solvent. The mixture can be successfully obtained by heating and reacting at 120°C for 4 days. Due to the high conjugation properties of the diacetylene unit contained in BD-TN-AO[9], and its -C=C- bond contains unique π-electronic communication[9,14], BD-TN-AO exhibits remarkable photoelectric characteristic and photocatalytic activies. Due to its high sensitivity to light and electricity[14], it can produce biotoxic ROS[9] and photogenic electrons, which in turn is well resistant to biological pollution, and can effectively reduce U(VI) to U(IV). Meanwhile, the positive surface charge exhibits a great electrostatic interaction to the anionic $[UO_2(CO_3)_3]^{4-}$ in seawater[15]. To verify the superiority of the diacetylene skeleton, another COF material ED-TN-AO was constructed from the monomer 4,4'-(acetylene-1,2-diyl) dibenzaldehyde of monomer alkyne[16]. The above two materials were identified and characterized by powder XRD, IR, nitrogen adsorption and desorption, thermogravimetry, and scanning electron microscopy. The material stability experiments show that excellent crystalline was maintained under high acid conditions, high radiation conditions (200 kGy γ-rays), and different alkaline, indicating that these two materials have high stability[18]. To verify the material's applicability in real-world scenarios, they immersed amidoxime-functionalized COFs in a complex Marine environment for 30 days. The results show that the two kinds of materials still have good stability. At the same time, BD-TN-AO showed a better adsorption effect than ED-TN-AO. To give full play to the advantages of amidoxime-functionalized COFs, the author further studied the photoeffect of BD-TN-AO. Through photoelectric chemical characterization, the extraction capacity of BD-TN-AO in natural seawater containing bacteria under irradiation of light was about 1.5 times that under no-light conditions. The results reflects that irradiation could promote the adsorption of uranyl by BD-TN-AO. With uranium extraction capacity, the latter can extract uranium values up to 6.0 $mg \cdot g^{-1}$, that is 1.5 times that of the former[17]. In addition to its control, the extraction capacity of BD-TN-AO for uranium is also better than other adsorbents. Electron paramagnetic resonance (EPR) experiments revealed that singlet oxygen or superoxide radical anion was generated under the condition of light, which inhibited colony enrichment[18]. At the same time, the photoelectric effect causes the material to show a positive charge, which is conducive to the adsorption of $UO_2(CO_3)_3^{4-}$. This work provides a new strategy for constructing COFs with excellent photoelectric performance.

In addition, because of the limited binding sites of TFFM-PDAN-AO adsorbent and the low content of uranium in seawater, the traditional uranium extraction method is inefficient. Inspired by Liu's work on using electrochemical technique to electrodeposit precursor compounds of uranium into UO_2^{2+}. Qiu's group proposed an electrochemical extraction method, which takes advantage of the unique properties of the adsorbent (regular pore channels, good photoelectric performance) and uranyl ion

ISSN 2616-5880 Vol. 4, Issue 7: 8-12, DOI: 10.25236/AJMC.2023.040702

adsorption performance, and applies cyclic voltammetry analysis (positive electrode: platinum, negative electrode: TFFM-PDAN-AO coated graphite felt), it is concluded that the adsorption level of electroextraction is more than that of physicochemical adsorption. It may be that the conversion of uranyl ions into electrodeposited sediments greatly improves the adsorption capacity of the electrode surface, so it effectively prevents the leakage of uranium and improves the recycling of UO_2^{2+}. It is worth mentioning that the variability of the electric field makes CF-COF-AO have good selectivity, which effectively inhibits the interference of vanadium during the process of adsorption of uranium ions. At the same time, it also has a good service life.

In 2022, Qiu's group successfully realized the efficient adsorption of uranium through reliable functional group coordination, chemical and photocatalytic reduction, and ethylene chain covalent organic framework (Tp-TMT). The material can be obtained by introducing dense hydroxyl functional groups onto a rigid skeleton. The synthetic Tp-TMT, with rigid skeleton, exhibits good selectivity for U(VI) and excellent catalytic reduction upon U(VI) to U(IV). Thus, the processing level of Tp-TMT to uranium is greatly improved. At the same time, the cooperative relation of the triazine and hydroxyl group in the skeleton importantly reduces the bandgap and increases an adjacent electronic conduction, thus photocatalytic reduction of Tp-TMT was effectively strengthened. Therefore, alternative path for [19] photocatalytic reduction of U(VI) take place with the irradiation of visible light, and the adsorption kinetics was accelerated and the adsorption capacity was obviously increased. The U(VI) photocatalytic reduction process further accelerates the kinetics and increases the adsorption level. The crystalline of COFs were optimized under different conditions containing acid, base, solvent, as well as temperature. Under alkaline catalysts, such as EtONa, NaOH, or piperidine, the crystallinity of COFs is shown to be either non-crystallinity or only weakly crystallinity. The porosity of Hb-TMT, Tp-TMT, and Tb-TMT was assessed through N_2 adsorption-desorption process. sp^2C COFs exhibit excellent stability because of their irreversible vinyl bonds in the framework. Under harsh conditions, such as 600 kGy gamma radiation, strong acid, strong base, boiling water, and visible light, the crystalline of ethylene chain COFs Hb-TMT, Tp-TMT, and Tb-TMT was maintained and showing excellent chemical stability of The authors also used UV-VIS[20] absorption spectroscopy to investigate the effects of visible light-stimulated and various donor elements in ethylene chain COFs were studied. The absorption edge of Tp-TMT at about 1407 nm is significantly redshifted by about 516 nm compared with that of Tb-TMT at about 891 nm, implying that a stronger donor Tp monomer could reduce the band gap. The XPS study of HB-MTT-U, TP-MTT-U, and TBMTT-U showed that the u4f peak disappeared completely after washing with vitamin C solution(1.0M) and nitric acid(1.0M)[20], thus confirming the successful desorption of uranium. This work reveals a new strategy for promoting the adsorption capacity of Tp-TMT[21] to uranium and obtains high photocatalytic property of COFs.

In 2022, Wang's research group successfully used the Knoevenagel condensation reaction to prepare a new adsorbent named HDU-102, and on this basis, synthesized amidoxime functionalized COF(named HDU-102-AO) by post-modification[22]. The modification of functional adsorbent and the selection of U(VI) by the amidoxime functional group were realized. They used a variety of characterization methods to investigate the crystalline of COFs. Scanning electron microscope(SEM) and transmission electron microscope(TEM) were used to the microstructure of HDU-102-AO and HDU-102. The result indicated that there was little disparateness between them. In addition, based on high-resolution TEM images, HDU-102-AO and HDU-102 showed highly fine crystalline, which means that functional modification of the cyanide group has little effect on the microstructure. Overall, the pore size distribution data further confirm the mesoporous materials of two COFs[23]. In addition, the authors also conducted a qualitative exploration of the synthetic materials by NMR analysis. At 5.7 ppm, an obvious ^1H NMR chemical shift represents H-substituent on aniline ring. Thermogravimetric analysis showed that pyrolysis occur at the stage of 200 ºC ~ 800 ºC, but the decomposition is still going on above 800 ºC, indicating high thermal stability over a wide range of temperature. In the adsorption experiment of U(VI), 436 mg/g uranium was obtained within 10 min using 9.25 ppm (VI) solution. The regeneration property of adsorption-desorption cycle experimental material is also deeply investigated. The experimental results revealed that the removal capacity of U(VI) by the two COFs decreased severely. It's comforting, though, that the removal rate of HDU-102-AO remains above 65%, indicating that the latter has better recyclability after amino oxime treatment. This work is designing and synthesizing novel COF materials and exploring the selective effect of the amidoxime functional group of COFs on U(VI).

In 2023, Qiu's group synthesized 3D COFs with fast adsorption kinetics (TFFM-PDAN-AO) by a selective combination of uranium and amidoxime ligands. TFFM-PDAN-AO was obtained by the Knoevenagel condensation reaction between the acetaldehyde and acetonitrile group, and then the cyanide group in TPMM-PDAN[24] was treated with $NH_2OH{\cdot}HCl$ for 72 h. Due to the five-fold

ISSN 2616-5880 Vol. 4, Issue 7: 8-12, DOI: 10.25236/AJMC.2023.040702

penetration dia topology of the 3D COFs, the material has excellent stability, and PXRD measurements and structural simulations show that its morphology structure is well maintained during chemical modification. Qiu's group carried out kinetic experiments in uranium-containing seawater, in which TFFM-PDAN-AO exhibited a rapid uptrend at 60 min, and its 3D porous structure promoted the rapid migration of uranium. In addition, the adsorbent utilizes the C=C bond connection, so it has better chemical and photoelectrical properties and radiation stability than other dynamic covalent bond-connected COFs. Due to the irreversibility of the C=C bond, this may result in TFFM-PDAN-AO showing good thermal stability. At the same time, the team confirmed the interaction between the amidoxime group and uranium using XPS spectroscopy[25], where the O=U and N=U bonds indicate that the U(VI) is successfully coordinated with the amidoxime group.

3. Conclusion

This paper mainly reviews the latest progress of sp^2C covalent organic framework materials in extracting uranium from seawater, such as COFs material enhanced uranium adsorption, and on-line monitoring and efficient extraction of U(VI). Through the design and synthesis of sp^2C-COF, improving the adsorption capacity and affinity of uranyl ions and synthesize the porous -C=C- linked two-dimensional COFs. The U(VI) embed into COF was reduced to U(IV) to make it have high anti-biological pollution activity to marine organisms. The application prospect of sp^2C covalent organic framework is demonstrated.

At present, the adsorption and extraction of radionuclides by COF materials is still standing at the laboratory stage, but the application in the real marine environment still needs to be further improved, such as the ability to resist seawater erosion and biological pollution needs to be improved, and there is still a distance from the actual application to the real marine environment. At the same time, the synthetic cost of COFs materials is still high, and industrial synthesis and large-scale production cannot be achieved at present, which limits its practical application. But these research advances also provide a new idea for sp^2 carbon covalent organic framework materials and expand their application and development field. With the development of material science, the prospect of large-scale, industrial production and application of COFs materials is no doubt, and shortly, COFs materials will attract more attention and research interest in radionuclides, providing a feasible research direction for uranium extraction from seawater, spent fuel recycling and sustainable development of nuclear energy.

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