

## Ultrahigh Affinity and Selectivity Nanotraps for Uranium Extraction from Seawater

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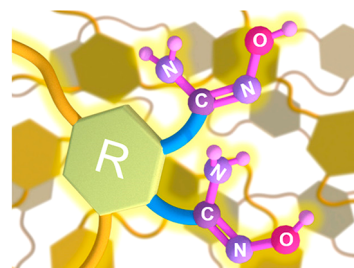
Article Recommendations

Cong-Zhi Wang, Zhi-Fang Chai, and Wei-Qun Shi\*

**Nanotraps with uranyl-specific “hooks” open up a new avenue for the development of efficient adsorbents for extracting uranium from seawater.**

With the increasing demand for nuclear power, mining uranium from seawater is essential to the sustainable development of nuclear energy. However, the very low uranium concentration ( $\sim 3$  ppb), numerous competing metal ions, especially vanadium ions, and microbial accumulation make it extremely difficult to exploit uranium from seawater. Now, in terms of uranium selectivity, Ma and his collaborators proposed a new strategy of nanotraps with uranyl-specific “hooks” that pave the way for overcoming the long-term challenges of competitive adsorption of vanadium in uranium extraction from seawater.<sup>1</sup>

Using highly selective adsorption materials to realize uranium harvesting is necessary for effective extraction of uranium resources in seawater. Since the 1960s, the development of highly efficient uranium adsorbents has been an arduous task. Currently, most well-known adsorbents are usually insufficient to achieve selective recovery of trace uranium in the presence of numerous enriched competing ions, especially vanadium.<sup>2</sup> The design of dedicated chelating sites is a common approach to optimize the selectivity of seawater uranium extraction adsorbents. Various ligands, such as oximes, carboxyl, amines, phosphonates, imidazoles, phenolics, etc., show high coordination affinities toward uranyl ions.<sup>3</sup> Among them, the amidoxime ligand  $[-C(\text{NOH})\text{NH}_2]$  is one of the most attractive ones, which can form tight coordination with uranyl ions. In addition, it can be synthesized economically and efficiently, and it can be easily grafted on the surface of adsorption materials. Since the 1980s, the amidoxime group has been increasingly utilized

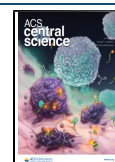


**Figure 1.** Porous frameworks constructed by uranyl-specific ligand “hooks”. Reproduced from ref 1. Copyright 2021 The Authors. Published by American Chemical Society.

to selectively capture uranium from seawater, and it is still a widely employed ligand for adsorbent decoration.<sup>4</sup> However, most amidoxime-based materials also exhibit high adsorption capacity for the vanadium ions in seawater, which represent the main competing ion for uranium extraction. The competitive adsorption of vanadium and uranium greatly limits the application potentials of amidoxime-based materials.<sup>5</sup>

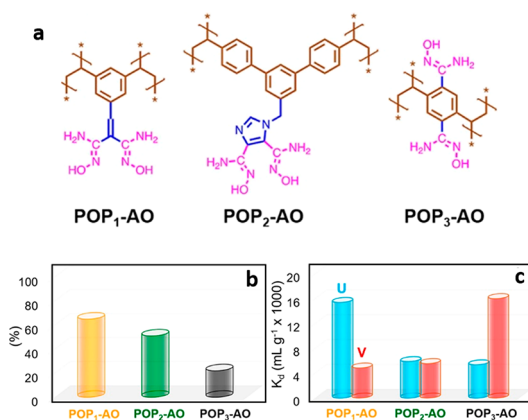
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In recent decades, different types of adsorption materials including artificial materials have been developed for uranium extraction from seawater. In nature, there are already some materials that can selectively identify and chelate specific ions, thus providing inspiration for the design of biomimetic materials to extract uranium from seawater. For example, previous studies<sup>6</sup> have shown that biological proteins exhibit high uranium adsorption properties and have been used in the development of uranium adsorbents. The recently reported bifunctional polymeric peptide hydrogels exhibit high selectivity and strong affinity for uranium in seawater and have significant resistance to biological contamination.<sup>7</sup> The preorganization of the binding site is the basic principle for the design of highly efficient chelating ligands in nature; i.e., the correct spatial arrangement and coordination of the binding site can achieve high-sensitivity identification of specific metal ions, and the collaborative chelation strategy can further improve the interaction. Inspired by this, the previous work<sup>8</sup> from Ma's laboratory showed that by designing the spatial distribution of the binding sites in the adsorbent to promote cooperative binding, the adsorption capacity of the chelating groups in the materials for uranium can be significantly improved.

In their latest work,<sup>1</sup> they improved the strategy of cooperative binding. The uranyl-specific ligand "hooks" were created by precisely manipulating the chelators at the molecular level to enhance uranium selectivity. In this work, they systematically studied a series of smart adsorption materials with uranyl-specific "hooks" through experimental and theoretical analyses, and evaluated the uranium capture performance of these materials and the competitive adsorption of vanadium ions. The amidoxime ligands were selected as chelating sites and porous organic polymers (POPs) as sorbent materials, which have a large specific surface area, flexible structure, and high stability. Accordingly, porous organic polymer uranium nanotraps were constructed, and these nanotraps are decorated with a series of diamidoxime ligands with various R groups as specific "hooks" for uranyl recognition (Figure 1). It was found that manipulating the R groups of amidoxime moieties is beneficial for affording high affinity and selective uranium nanotraps. The created uranyl-specific "hooks" demonstrate ultrahigh affinity and selectivity toward uranium, and the distribution coefficient of uranium is 3-fold higher than that of vanadium (Figure 2). Large-scale adsorption experiments show that over one-third of the uranium in 5 gallons of seawater can be enriched by the optimized nanotrap (2.5 mg) with the enrichment index up to 3836. The uptake capacity and selectivity as well as the enrichment index of uranium are higher than most of the reported representative



**Figure 2.** (a) The corresponding structures of diamidoxime-functionalized POPs. (b) The remaining uranium uptake capacity of various sorbent materials in the presence of equal concentration of vanadium. (c) The distribution coefficient ( $K_d$ ) values for uranium and vanadium over various sorbent materials (cyan, uranium; red, vanadium). Reproduced from ref 1. Copyright 2021 The Authors. Published by American Chemical Society.

adsorbents. In addition to their high selectivity and affinity, these adsorbents are easy to regenerate through mild base treatment. These excellent results set a new benchmark for adsorbents for extracting uranium from seawater and also open up a new avenue for the development of adsorbents for high-efficiency ion recognition in the future.

In this strategy, the amidoxime groups are modified in the appropriate position of the adsorbents to make them synergistically bind in the adsorbents, meanwhile enhancing the density of the adjacent amidoxime groups to achieve the maximum effective coordination, thereby boosting the ability of the adsorbents to selectively recognize uranium ions. Therefore, controlling the modified R groups in the uranium nanotraps to enhance the synergistic effect of the binding site is extremely crucial for enhancing the selective recognition ability of the adsorbents. This strategy provides a reference for establishing the general design principles of high-efficiency adsorbents for uranium extraction from seawater and offers guidance for the development and application of high-performance adsorbents to resources extraction.

These excellent results set a new benchmark for adsorbents for extracting uranium from seawater and also open up a new avenue for the development of adsorbents for high-efficiency ion recognition in the future.

In recent years, with the continuous deepening of research on uranium extraction from seawater, significant progress has been made in improving the adsorption capacity and comprehensive

performance of materials. However, there are still some unresolved issues in extracting uranium from seawater, and its engineering still faces significant challenges. In order to improve the material's adsorption capacity and selectivity for uranium extraction, it is essential to design functional groups with higher selective complexing ability for uranyl ions, and optimize the compositions and microstructures of the adsorption materials to improve the utilization of functional groups. Therefore, it is desirable to fundamentally understand the relationship between the structures of the ligands and the adsorption behaviors, so as to achieve precise control of the structures of the materials. With the rapid development of computer technology and computational science, computational chemistry provides an effective method for the development of materials. At present, density functional theory (DFT) methods including relativistic effects have been applied in designing ligands for extracting uranium from seawater,<sup>9</sup> and multiscale theoretical simulation combined with quantum chemistry and molecular dynamics methods brings the systems closer to reality. In recent years, with the rapid development of computer simulation technology, the application of high-throughput calculations and machine learning methods to material screening<sup>10</sup> has become an inevitable trend in the development of materials for uranium extraction from seawater. In addition, it should be noted that in the characterization of uranium adsorption performance, different studies have been carried out under different experimental conditions making it difficult to compare the adsorption effects of different materials. As there are many factors that affect the extraction of uranium from seawater, changes in any one factor may lead to different experimental results. To compare the ability of different adsorbents to uranium extraction, it is necessary to formulate uniform experimental standards for verification and then to screen out excellent materials. We believe that this is crucial for the development of efficient materials for uranium extraction from seawater.

#### Author Information

##### Corresponding Author

**Wei-Qun Shi** – Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China; [orcid.org/0000-0001-9929-9732](https://orcid.org/0000-0001-9929-9732); Email: [shiwq@ihep.ac.cn](mailto:shiwq@ihep.ac.cn)

##### Authors

**Cong-Zhi Wang** – Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

**Zhi-Fang Chai** – Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China; Engineering Laboratory of Advanced Energy Materials, Ningbo Institute of Industrial Technology, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China

Complete contact information is available at:  
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