Emerging technologies for uranium extraction from seawater

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The use of enriched uranium (^{235}U) in nuclear fission reactors allows electricity generation with negligible CO_2 emissions. Thus, nuclear energy is expected to play an important role in global efforts to decarbonize the energy sector [1]. To meet the energy needs of future societies and achieve zero-emissions targets, more nuclear reactors will be needed, which increases demand for uranium fuel. Although extensive research on actinide chemistry is essential for the safe disposal of nuclear waste and promotes the development of nuclear fuel recycling [2], the increasing demand for uranium now requires further production of natural uranium. In recent years, the extraction of uranium from seawater has attracted researchers' attention, owing to the limited reserves of uranium ore on land [3]. However, capturing uranium from seawater is extremely challenging due to the very low natural uranium concentration (approximately 3.3 ppb), the coexistence of a variety of other metal ions, and the potential for marine biofouling of adsorbents.

Traditional adsorbents, such as functionalized carbon [4], silica composites [5], and layered inorganic materials [6], have been extensively investigated for uranium extraction from seawater, but have limitations such as poor selectivity, slow adsorption kinetics, or limited uranium uptake capacities. Organic-based materials, including porous organic polymers (POPs) [7], metal-organic frameworks (MOFs) [8], biomass-based materials [9,10], and covalent organic frameworks (COFs) [11], are promising candidates for selective uranium extraction from seawater [12]. However, these adsorbents also have drawbacks, including (i) poor stabilities in seawater; (ii) disordered structures in the case of POPs that reduce the availability of U adsorption sites; (iii) pore blocking by uranium that hinders uranium recovery and adsorbent reuse; (iv) susceptibility to biofouling caused by marine bacteria and algae; and (v) high cost of adsorbent development. Novel adsorbents, featuring high uranium selectivity, fast uptake of uranium under high ionic strength conditions, and high uranium adsorption capacities must be discovered. Further, the captured uranium must be in a form that is easily recovered.

Recently, researchers have discovered that amidoxime-functionalized adsorbents show good performance for uranium extraction from seawater, due to the strong interaction between amidoxime groups and uranyl ions (UO_2^{2+}), enabling both high adsorption capacities and fast kinetics (Figure 1) [13,14]. However, amidoxime groups also have modest affinities for vanadium and copper ions present in seawater, which represents an obstacle to uranium extraction. The post-capture separation of U, V and Cu ions is undesirable, increasing the overall cost of uranium extraction from seawater.

In an exciting breakthrough, Liu *et al*. [15] reported a novel physicochemical adsorption and electrochemical deposition method for mining uranium from spiked seawater. U (VI) in the form of UO_2^{2+} was selectively adsorbed on an

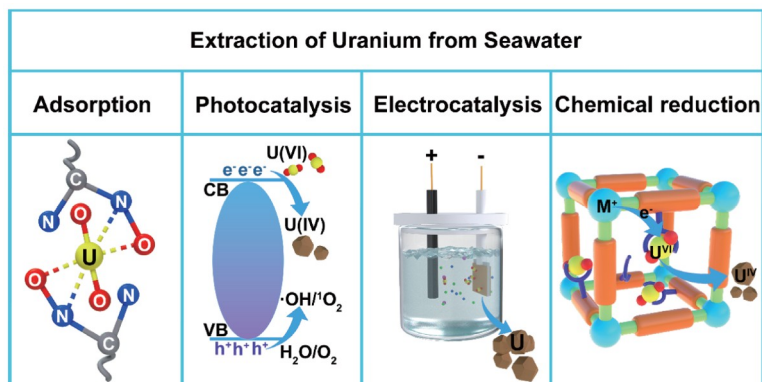*Corresponding author (email: xkwang@ncepu.edu.cn)

Figure 1 Schematic illustration of the emerging technologies for uranium extraction from seawater (color online).

amidoxime-functionalized adsorbent-electrocatalyst, after which a half-wave rectified alternating current electrochemical method was used to reduce the U(VI) to insoluble UO_2 (containing U(IV)) onto the electrode surface at voltages of -5 to 0 V. Inspired by this pioneering work, our team has recently developed novel metal-nitrogen-carbon adsorption-electrocatalysis materials (Fe-N_x-C-R and In-N_x-C-R) with enhanced performance for uranium extraction from seawater (Figure 1). The Fe-N_x-C-R and In-N_x-C-R adsorbent-electrocatalysts, containing Fe and In single atom sites dispersed on N-doped carbon supports modified by amidoxime (R) groups, displayed remarkable uranyl affinities and extremely rapid uranium uptake kinetics in seawater [16,17]. The FeN_x and InN_x sites enabled rapid electrocatalytic conversion of the adsorbed U(VI) ions to solid $Na_2O(UO_3 \cdot H_2O)_x$ precipitates through a reversible $U^{6+} \leftrightarrow U^{5+}$ redox pathway, thus allowing facile uranium product collection. Wang *et al*. [18] recently developed an ion pathway method for electrochemical uranium extraction from seawater, incorporating conductive chains into the porous channels of porous aromatic frameworks (MISS-PAF-1). The developed system offered uranium uptake kinetics 2 to 3 orders of magnitude faster than conventional polymer adsorbents using physical diffusion. The efficiency of the electrochemical uranium extraction method was further improved by the same group using conductive graphene-based PAFs as electrocatalysts [19].

In addition to electrochemical systems, adsorption-photocatalysis systems also show promise for efficiently and selectively extracting uranium from seawater (Figure 1) [20,21]. By incorporating photo-active groups in the nanopores of COFs and supporting amidoxime groups for uranyl binding, uranium extraction capacities as high as 4.62 mg U/g adsorbent/day have been achieved under visible light irradiation [20]. This method of converging cooperative functions in COFs offers significant advantages over conventional adsorbents or photocatalytic systems for uranium mining from seawater.

Although great progress related to the development of materials and processes for uranium extraction from seawater has been made in recent years, step-change improvements in extraction efficiencies should be possible through synergistic optimization of adsorption kinetics, adsorption capacity, and adsorbent durability, whilst also harnessing advanced redox processes to deliver easy collected solid uranium-containing products. Besides electrocatalytic reduction and photocatalytic reduction, chemical reduction is also considered as a promising technology for uranium extraction. The chemical reduction process of adsorbed U(VI) to insoluble U(IV) can promote the regeneration of the active site (Figure 1) [22]. Therefore, the design of redox active site is of great significance for improving the performance of uranium uptake materials. It is particularly important to deeply understand the structure of adsorbent/catalyst and the mechanism(s) of uranium capture at the molecular level. *In situ* characterization techniques such as Raman spectroscopy and X-ray absorption spectroscopies (XANES/EXAFS) are especially valuable in this regard. Further, more consideration needs to be given to uranium extraction systems that can be deployed cost-effectively at scale. Currently, most studies exploring uranium extraction from seawater have used uranium-spiked seawater, with experiments being conducted on a laboratory-scale and using less than 1 gram of adsorbent. To make uranium extraction economically viable, practical uranium extraction systems would need to use kilograms to tonnes of adsorbent (depending on the size of the extraction system) with high seawater throughputs necessary compensate for the extremely low concentration of uranium in natural seawater. To date, the large-scale synthesis of cost-effective adsorbents or catalysts for uranium capture remains challenging, especially for adsorbent-electrocatalyst or adsorbent-photocatalyst systems that harness cooperative functions to boost uranium extraction efficiencies.

To summarize, increasing global demand for electricity continues to drive new fundamental research in the area of

uranium extraction from seawater. Successful mining of uranium from our oceans will demand the active cooperation of chemists, materials scientists, and engineers. Recently, a number of novel strategies that allow the selective capture of uranium over vanadium and copper in seawater (in lab studies) have been developed. These pioneering studies are laying the roadmap towards practical systems for uranium extraction from seawater, potentially allowing nuclear energy to remain a key part of the global energy mix for the next few hundred years.

Conflict of interest   The authors declare no conflict of interest.

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