

Americium/lanthanide separation enabled by a distinct polyoxometalate cluster

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Nuclear energy is viewed as a low carbon-emission electricity-generating technology with high-energy density, which has attracted extensive attention and shown broad development prospects [1]. However, to ensure sustainability and cleanability in the development of nuclear energy, one crucial challenge is to exploit efficient and economical technologies to simultaneously recover fissionable nuclides from nuclear waste and separate long-lived toxic fission products [2].

Americium (Am) is a long-lived radionuclide, and mainly exists as the Am(III), representing one of major sources for the long-term radioactive hazard of nuclear wastes. Due to the similar structures and properties between Am(III) and coexisting lanthanides (Ln(III)), it is very difficult to selectively separate and remove Am(III) from the nuclear waste. A frontier research target for the separation of americium from lanthanides is to oxidize Am(III) to its higher oxidation states existing as linear dioxo actinyl ions such as Am(VI)O₂²⁺ and Am(V)O₂⁺ [3]. Subsequently, the Am(VI)O₂²⁺ or Am(V)O₂⁺ could be isolated through solvent extraction, precipitation, and ion-exchange chromatography [4,5]. However, Am(V)/Am(VI) can be reduced to Am(III) in a few seconds when contacting with organic extractants/solvents or passing through a chromatographic column. Therefore, techniques for selectively isolating americium from lanthanides are highly sought after, particularly under extreme conditions, but present a challenge. In a recent

Nature contribution by Wang and co-workers, a nanoscale polyoxometalate (POM, Se₆W₄₅) cluster was developed for the selective separation of Am(VI)O₂²⁺ from Ln(III) ions in the absence of any organic components (Figure 1) [6]. The presence of vacant equatorial donor sites in the {Se₆W₄₅} offered suitable binding sites for actinyl ion (AnO₂²⁺, An = Am, U, Np, Pu), whilst not suitable for binding Ln(III) ions. Remarkably, such an Se₆W₄₅ cluster stabilized Am(VI) to an unmatched level with negligible reduction occurring over 24 h.

Based on host-guest interactions, the tested absorption bands of NpO₂²⁺, PuO₂²⁺, and AmO₂²⁺ shifted to higher wavenumbers when adding the {Se₆W₄₅}, suggesting strong complexation between AnO₂²⁺ ions and the {Se₆W₄₅} clusters. These were confirmed by a spectrophotometric titration of the AmO₂²⁺-{Se₆W₄₅} system, *ab initio* molecular dynamics (AIMD) simulations, and electrochemical redox measurements. Ln(III)-{Se₆W₄₅} demonstrated much weaker binding affinities under similar conditions. Taken together, these experimental, structural characterization, and computation results reveal valuable information about their newly developed strategy that the vacancy site in {Se₆W₄₅} POM precisely matches the coordination geometry of actinyl (VI) ions and is unsuitable for binding Ln(III) ions.

On the basis of the above results, the authors proposed a protocol for the separation of Am-POM nanoclusters from lanthanide ions-containing nitric acid solution, relying on a commercially available ultrafiltration technique. This whole separation procedure does not involve any organic compo-

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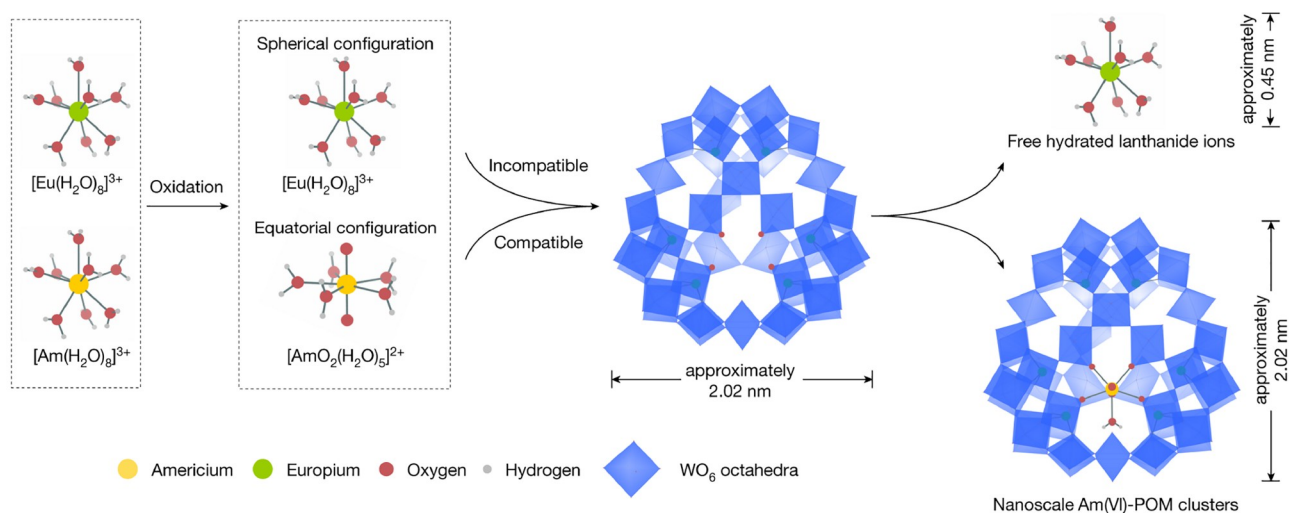


Figure 1 Schematic illustration of the frame of the ultrafiltration separation of nanoscale Am(VI)-POM clusters from lanthanides [5] (color online).

nents, reducing the amount of secondary radioactive waste. In addition, the purified Am(VI)-POM can be further reduced to obtain Am(III) products, and the released POM clusters can be recyclable again by ultrafiltration for the next separation cycle.

In conclusion, this pioneering work proposes a new technique for separating americium from lanthanides in aqueous solutions that are not easily accessible using traditional methods. We expect that this work can be extended to the separation of actinide families from fission products during the reprocessing of used nuclear fuel.

Conflict of interest The authors declare no conflict of interest.

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