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# Uranium fluoride micromaterials: a new frontier in nuclear engineering

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This perspective explores recent advancements in the synthesis and application of uranium fluoride micromaterials, emphasizing their role in the nuclear industry. Uranium micromaterials, including oxides, fluorides, and carbides, are crucial for applications ranging from high-temperature gas-cooled reactors to nuclear forensics and medical isotope production. The perspective highlights a novel chemical transformation process for synthesizing uranium fluoride micromaterials, in which uranium oxides are fluorinated in an autoclave using HF gas (generated from the decomposition of silver bifluoride) or ammonium bifluoride while preserving their original morphologies. This transformation produces various uranium fluoride microstructures, including UF<sub>4</sub>, UO<sub>2</sub>F<sub>2</sub>, and (NH<sub>4</sub>)<sub>3</sub>UO<sub>2</sub>F<sub>5</sub>, in the form of microrods, microplates, and microspheres. The perspective discusses challenges in maintaining controlled morphologies during fluorination and explores future directions, such as the synthesis of actinide fluoride micromaterials and the development of uranium chloride and other uranium compounds. The continued advancement of these materials holds significant potential for innovations in nuclear fuel cycles, actinide material chemistry, and nuclear forensics.

## KEYWORDS

uranium, fluoride, micromaterials, morphology, chemical transformation

## 1 Introduction

Uranium materials with well-defined micro-scale morphologies have diverse applications in the nuclear industry. A key example is their use in high-temperature gas-cooled reactors (HTGRs), where tristructural-isotropic (TRISO) fuel—spherical uranium oxide and/or carbide particles with protective coatings—is molded into rods for prismatic-block designs or dispersed as pebbles in pebble-bed reactors (Ueta et al., 2011).

Historically, the United States operated two prismatic-type HTGRs: Peach Bottom (1967–1974) and Fort Saint Vrain (1979–1989) (Beck and Pincock, 2011). More recently, China has developed two Generation IV pebble-bed HTGRs (HTR-PM), scaled up from the earlier HTR-10 prototype, which remains operational (Beck and Pincock, 2011; IAEA, 2011).

Beyond reactor applications, uranium micromaterials play a critical role in environmental and nuclear forensics monitoring. Reference particles with precisely controlled size and shape are used to validate highly sensitive analytical measurements at nuclear facilities. Techniques such as Large Geometry-Secondary Ion Mass Spectrometry, Thermal Ionization Mass Spectrometry, and Multi-Collector Inductively Coupled Plasma Mass Spectrometry enable precise isotopic characterization (Kegler et al., 2021). In 2022, the

first uranium oxide microparticle reference materials were officially certified, marking a significant milestone in the field (Richter et al., 2022).

The future applications of uranium microstructured materials are extensive. One emerging area is the fluoride Salt-Cooled High-Temperature Reactor (FHR), a next-generation molten salt reactor (MSR) design that utilizes solid TRISO fuel rather than dissolving fuel into the molten salt coolant (Serp et al., 2014; Qualls et al., 2017). In the United States, Kairos Power is leading FHR development (Fluoride Salt-Cooled Reactor, 2023).

Beyond reactor technology, uranium micromaterials have potential applications in medical isotope production (Henry and Saclay, 1959; Passy and Steiger, 1963; Dorhout et al., 2019), space exploration as energy sources (Carmack et al., 2004), and functional materials for information storage, catalysis, sensors, and luminescent devices (Zhang et al., 2005; Kim et al., 2006; Xu et al., 2007; Pradhan et al., 2011).

A promising approach for synthesizing uranium micromaterials is chemical transformation—a process that selectively modifies the chemical composition, crystal structure, or morphology of micro- and nanoscale materials (Moon et al., 2011; Fayette and Robinson, 2014). This technique is widely used in energy applications, such as MoO<sub>3</sub>–MoS<sub>2</sub> nanowires for hydrogen evolution reactions (Chen et al., 2011), Co–CoO nanoparticles for oxygen reduction reactions (Guo et al., 2012), and Cu–Cu<sub>x</sub>S nanotubes for Li-ion battery anodes (Cai et al., 2012).

A recent chemical transformation process for uranium oxide micromaterials was developed (Jang et al., 2023; Jang and Poineau, 2024a; 2024b). This solid-gas reaction replaces oxygen atoms with fluorine atoms while preserving the material's original morphology. The transformation is achieved by generating *in situ* HF gas from bifluoride salts under controlled conditions at mild temperatures (150°C–250°C). Uranium fluorides are essential to the nuclear fuel cycle, particularly as uranium hexafluoride (UF<sub>6</sub>) in enrichment and uranium tetrafluoride (UF<sub>4</sub>) as a primary fuel for MSRs. Developing tailored uranium fluoride micromaterials is crucial for advancing next-generation reactor designs. Additionally, different uranium fluoride micromaterials may exhibit distinct nuclear signatures influenced by particle geometry, which is relevant to nuclear forensics—such as the presence of <sup>22</sup>Na from potential <sup>19</sup>F(α,n)<sup>22</sup>Na reactions (Croft et al., 2019).

Historically, research on uranium microstructures has focused on binary oxides, nitrides, and carbides, while uranium fluoride micromaterials remained largely unexplored. This perspective highlights recent advancements in the field of uranium fluoride micromaterials and their potential implications.

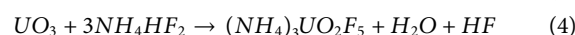
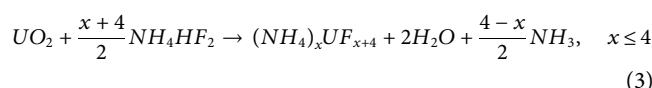
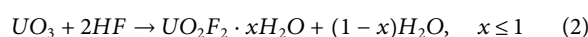
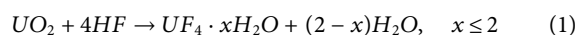
## 2 Fluorination of uranium oxides using HF gas or ammonium bifluoride

The experimental setup for preparing uranium micromaterials has been well documented (Jang et al., 2023; Jang and Poineau, 2024a; Jang and Poineau, 2024b). Uranium oxide microparticles were synthesized hydrothermally and fluorinated using Parr model 4749 general-purpose acid digestion vessels (autoclaves). During fluorination, uranium oxide precursors were placed inside a smaller Teflon vial nested within the Teflon liner of the autoclave, which

contained either silver bifluoride (AgHF<sub>2</sub>, SBF) or ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>, ABF). Upon heating, the gaseous decomposition products of the bifluoride salts—HF gas (HFg) from SBF and HF/NH<sub>4</sub>F/NH<sub>3</sub> from ABF—interacted with the uranium oxide within the inner Teflon vial, enabling controlled fluorination.

Fluorination of uranium oxides with HFg is a straightforward process, primarily dictated by the oxidation state of the starting material. When UO<sub>2</sub> is used, the reaction yields UF<sub>4</sub>, following the standard industrial method. In contrast, fluorination of U<sub>3</sub>O<sub>8</sub> or UO<sub>3</sub> produces UO<sub>2</sub>F<sub>2</sub>, with potential hydration due to water formation as a reaction byproduct (Equations 1, 2, respectively).

Uranium fluorides containing the ammonium cation (NH<sub>4</sub><sup>+</sup>) can be synthesized using ammonium bifluoride. Fluorination of UO<sub>2</sub> yields (NH<sub>4</sub>)<sub>4</sub>UF<sub>8</sub>, whereas U<sub>3</sub>O<sub>8</sub> or UO<sub>3</sub> produces (NH<sub>4</sub>)<sub>3</sub>UO<sub>2</sub>F<sub>5</sub>, both with the possibility of hydration (Equations 3, 4, respectively). In all cases, the presence of water can induce side reactions, necessitating careful control.



## 3 Reported uranium fluoride materials

### 3.1 Microstructures of UO<sub>2</sub>F<sub>2</sub>·xH<sub>2</sub>O (x = 0, 1.5)

Recent studies have reported various microstructures of anhydrous and hydrated UO<sub>2</sub>F<sub>2</sub>, including microspheres (ms), microrods (mr), and microplates (mp) (Jang et al., 2023; Jang and Poineau, 2024a; Jang and Poineau, 2024b). These materials were synthesized by reacting hydrothermally precipitated UO<sub>3</sub> or U<sub>3</sub>O<sub>8</sub> with *in situ* generated HF gas. Results indicate that temperature plays a crucial role in hydration: reactions conducted at 200°C–250°C consistently produced anhydrous UO<sub>2</sub>F<sub>2</sub> across all microstructures (Figures 1a–c). In contrast, lower-temperature reactions initially formed hydrated UO<sub>2</sub>F<sub>2</sub>, which subsequently converted to its anhydrous form upon heating to 250°C (Figure 1d). The release of bound water at around 250°C is a classical behavior commonly exhibited in oxyhydroxides (Lee et al., 1980; Frolova, 2021).

### 3.2 Microstructures of UF<sub>4</sub>·xH<sub>2</sub>O (x = 0, 1.5, 2, 2.5)

Microspheres of anhydrous UF<sub>4</sub> (~20 μm) are commercially available from International Bio-Analytical Industries, with several SEM characterizations reported in the literature (Plaue, 2013; Villa-Aleman and Wellons, 2016; Christian et al., 2021; Foley et al., 2022). These UF<sub>4</sub> microspheres were reportedly produced via anhydrous hydrofluorination reactions with HF (Foley et al., 2022).

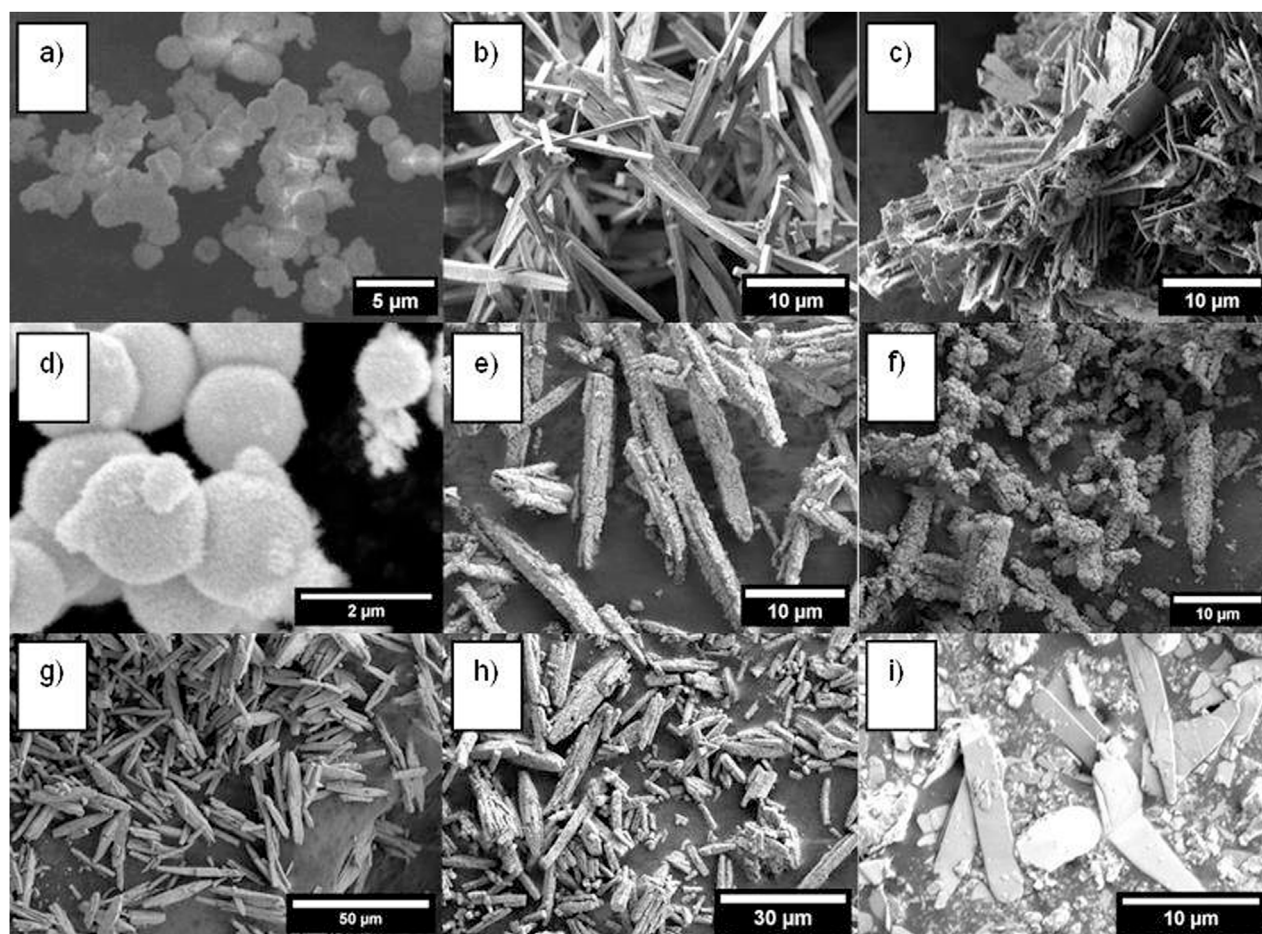


FIGURE 1

Uranium fluoride microstructures prepared: (a)  $\text{UO}_2\text{F}_2$  ms obtained from the reaction between  $\text{UO}_3$  ms and SBF at  $200^\circ\text{C}$  for 24 h (b)  $\text{UO}_2\text{F}_2$  mr obtained from the reaction between  $\text{U}_3\text{O}_8$  mr and SBF at  $250^\circ\text{C}$  for 24 h (c)  $\text{UO}_2\text{F}_2$  mp from the reaction between  $\text{U}_3\text{O}_8$  mp and SBF at  $250^\circ\text{C}$  for 24 h (d)  $\text{UO}_2\text{F}_2$  ms obtained from the treatment of  $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$  ms at  $250^\circ\text{C}$  for 5 days (e)  $\text{UF}_4/\text{UF}_4 \cdot 2\text{H}_2\text{O}$  mr obtained from the reaction between  $\text{UO}_2$  mr and SBF for 24 h at  $250^\circ\text{C}$  (f)  $\text{UF}_4/\text{UF}_4 \cdot x\text{H}_2\text{O}$  mr obtained from the reaction between  $\text{UO}_2$  mr and SBF for 24 h at  $250^\circ\text{C}$  prepared under  $\text{N}_2$  atmosphere (g)  $\text{UF}_4 \cdot 1.5\text{H}_2\text{O}$  mr obtained from the reaction between  $\text{UO}_2$  mr and SBF for 24 h at  $150^\circ\text{C}$ . (h)  $\text{UF}_4$  mr obtained from the treatment of  $\text{UF}_4$  mr (Figure 1e) at  $600^\circ\text{C}$  under argon atmosphere, (i)  $\text{UF}_4$  mp obtained from the reaction of  $\text{UO}_2$  mp and SBF at  $250^\circ\text{C}$ .

Additionally, the room-temperature hydrolysis of  $\text{UF}_4$  microspheres has been shown to yield  $\text{UF}_4(\text{H}_2\text{O})_{2.5}$  microrods (Christian et al., 2021).

Microrods and microplates of both anhydrous and hydrated  $\text{UF}_4$  have been synthesized via chemical transformation reactions. A study investigating the influence of experimental parameters on morphology found that reactions between  $\text{UO}_2$  microrods and SBF at  $250^\circ\text{C}$  resulted in mixed phases of anhydrous and hydrated  $\text{UF}_4$  microrods when conducted in air (Figure 1e) and under a nitrogen atmosphere (Figure 1f), with the latter exhibiting a notably rougher surface morphology. In contrast, reactions at  $150^\circ\text{C}$  produced  $\text{UF}_4 \cdot 1.5\text{H}_2\text{O}$  microrods as a single phase with a smooth morphology (Figure 1g). The anhydrous  $\text{UF}_4$  microrods shown in Figure 1e were further converted through thermal treatment at  $600^\circ\text{C}$  under an argon atmosphere (Figure 1h).

Additionally, reactions between  $\text{UO}_2$  microplates and SBF at  $250^\circ\text{C}$  directly yielded anhydrous  $\text{UF}_4$  microplates (Figure 1i). A summary of uranium fluoride microstructures prepared via chemical transformation is presented in Table 1.

### 3.3 Microstructures obtained from fluorination with ammonium bifluoride

The chemical transformation of uranium oxide microstructures using ammonium bifluoride as the fluorinating agent has been investigated. In most cases, morphological preservation was not achieved. For instance, reactions between ABF and  $\text{UO}_2$  microspheres (ms) yielded coalesced particles of  $(\text{NH}_4)_2\text{UF}_6$  ms, while transformations involving  $\text{U}_3\text{O}_8$  microrods (mr) and  $\text{U}_3\text{O}_8$  microplates (mp) produced deformed  $(\text{NH}_4)_3\text{UO}_2\text{F}_5$  mr and large pebble-like clusters of  $(\text{NH}_4)_3\text{UO}_2\text{F}_5$ , respectively. In these reactions, the  $\text{NH}_3$  generated as a decomposition product significantly altered the material's morphology.

The only successful reaction that maintained the original morphology was observed between  $\text{U}_3\text{O}_8$  microspheres and ABF, resulting in  $(\text{NH}_4)_3\text{UO}_2\text{F}_5$  ms. This product was further decomposed at  $300^\circ\text{C}$ , forming textured  $\text{UO}_2\text{F}_2$  ms (Jang and Poineau, 2024b).



TABLE 1 Reported shape, size, and preparation method of uranium fluorides materials. (ms: microsphere, mr: microrod, mp: microplate).

Material	Shape	Size	Preparation method Fluorinating agent: (Precursor) - additional steps	Reference
UO <sub>2</sub> F <sub>2</sub>	ms	1–2 μm	SBF: (UO <sub>3</sub> or U <sub>3</sub> O <sub>8</sub> ms)	Jang et al. (2023), Jang and Poineau (2024b)
			ABF: (U <sub>3</sub> O <sub>8</sub> ms) -decomposition of (NH <sub>4</sub> ) <sub>3</sub> UO <sub>2</sub> F <sub>5</sub> ms	Jang and Poineau (2024b)
	mr	3–20 μm length	SBF: (U <sub>3</sub> O <sub>8</sub> mr)	Jang and Poineau (2024b)
	mp	1–7.5 μm length	SBF: (U <sub>3</sub> O <sub>8</sub> mp)	Jang and Poineau (2024b)
UF <sub>4</sub> ·xH <sub>2</sub> O	mr	7–30 μm length	SBF: (UO <sub>2</sub> mr)	Jang and Poineau (2024a)
UF <sub>4</sub> ·2.5H <sub>2</sub> O	mr	<20 μm length	HF: (UO <sub>2</sub> ms) - hydrolysis of UF <sub>4</sub> ms	Christian et al. (2021)
UF <sub>4</sub>	ms	~20 μm	HF: (UO <sub>2</sub> ms)	Plau (2013), Villa-Aleman and Wellons (2016), Christian et al. (2021), Foley et al. (2022)
	mr	5–25 μm length	SBF: (UO <sub>2</sub> ) - dehydration of UF <sub>4</sub> ·xH <sub>2</sub> O	Jang and Poineau (2024a)
	mp	2–15 μm length	SBF: (UO <sub>2</sub> )	Jang (2024)
(NH <sub>4</sub> ) <sub>3</sub> UO <sub>2</sub> F <sub>5</sub>	ms	2–4 μm	ABF: (U <sub>3</sub> O <sub>8</sub> ms)	Jang and Poineau (2024a)
3UF <sub>4</sub> ·H <sub>2</sub> O·HF	ns	250–350 nm	SBF: (UO <sub>2</sub> ns)	Jang (2024)

## 4 Future directions

One promising direction is the development of actinide tetrafluoride micromaterials, such as AnF<sub>4</sub> microspheres (An = Th, Np, Pu) from the fluorination of AnO<sub>2</sub> microspheres. Thorium oxide (ThO<sub>2</sub>) and plutonium oxide (PuO<sub>2</sub>) microspheres are already used in high-temperature reactors (HTRs) (Lloyd and Haire, 1968; Ganguly and Hegde, 1997; Brandau, 2002), and both react with HFg to produce the tetrafluoride (Dawson et al., 1954; Fisher, 1958; Souček et al., 2017). Additionally, ThO<sub>2</sub>, NpO<sub>2</sub>, and PuO<sub>2</sub> react with ABF to form ThF<sub>4</sub>, NpF<sub>4</sub>, and PuF<sub>4</sub>/PuF<sub>3</sub>, respectively (Wani et al., 1989; Silva et al., 2012; Che Zainul Bahri et al., 2019; Tosolin et al., 2021). The controlled morphologies of these actinide oxides have been well studied (Nkou Bouala et al., 2017; Clavier et al., 2019; Clavier et al., 2023; Clavier et al., 2024; Trillaud et al., 2019; Asplanato et al., 2023) as well as for cerium oxides (Wang et al., 2007; Ta et al., 2013) that could be used as surrogate material. While transplutonic oxides may exhibit similar chemistries, it remains uncertain whether their oxide precursors can be morphologically controlled.

Beyond hydrothermal precipitation, template materials have also been used to prepare uranium micromaterials with controlled morphologies. uranium (IV) microspheres (>100 μm) were prepared by sorbing U(VI) ions onto fumarated polystyrene microspheres (Elsalamouny et al., 2017).

The chemical transformation of uranium oxide nanospheres (UO<sub>x</sub> ns) represents a viable approach. Methods for preparing UO<sub>x</sub> nanospheres are already known, and reactions such as those for UO<sub>2</sub>F<sub>2</sub> and UF<sub>4</sub> could be successfully replicated with these materials, potentially achieving higher reactivity due to their larger surface areas. Preliminary work involving UO<sub>2</sub> ns hydrothermally

precipitated in acetone/NH<sub>4</sub>OH (Yan et al., 2019) yielded some success, producing 3UF<sub>4</sub>·H<sub>2</sub>O·HF ns. However, UO<sub>2</sub> ns precipitated from ionic liquids (Yang et al., 2019) were too small (1–2 nm) to be properly resolved by SEM.

The development of uranium chloride micromaterials is an exciting and promising field. Uranium chloride chemistry is well-established, with several methods to prepare UCl<sub>4</sub> and UO<sub>2</sub>Cl<sub>2</sub> using chlorinating agents such as carbon tetrachloride, hexachloropropene, and thionyl chloride (Yoshimura et al., 1971). Additionally, *in situ* preparation of HCl gas (potentially via MgOHCl) (Ozcan and Dincer, 2016; Asal et al., 2024) is a promising alternative. Due to the high hygroscopicity of uranium chlorides, the retention of morphology is challenging process. Preliminary attempts using similar experimental setups, presented above, with chlorinating agents resulted in coalesced uranium or uranyl chloride materials, with some samples hydrolyzing rapidly prior to SEM analysis.

Uranium micromaterials, including metal, bromides, and sulfides, can be synthesized via chemical transformation. While uranium metal is challenging to produce at the laboratory scale through chemical transformation (Jang et al., 2022), it is a widely used precursor for the preparation of various uranium compounds (Grenthe et al., 2006). Successful transformations could open new pathways for uranium micromaterials. For example, uranium metal can be obtained by treating UO<sub>2</sub> with lithium gas (Usami et al., 2002). Uranium disulfide (US<sub>2</sub>) and monosulfide (US) can be synthesized by reacting uranium metal (Flöter et al., 1980) or uranium tetrachloride (UCl<sub>4</sub>) (Yoshihara et al., 1967) with hydrogen sulfide (H<sub>2</sub>S) (Van Lierde and Bressers, 1966). Uranium bromides (UBr<sub>x</sub>, x = 1–5) can be produced by reacting uranium metal (Morss et al., 2011) or uranium carbide (UC) (Lau and Hildenbrand, 1987) with bromine gas.

## 5 Conclusion

Uranium fluoride micromaterials play a crucial role in the nuclear industry, serving as fuel, reference materials, and fission target materials. They also contribute to nuclear forensics and actinide material chemistry. While research on uranium micromaterials has historically focused on uranium microspheres—particularly oxides, nitrides, and carbides—studies on halide-based microstructures remained limited until recently.

In recent years, several studies have expanded this field by developing diverse uranium fluoride micromaterials. Chemical transformation methods using sublimed bifluoride and ammonium bifluoride have opened new pathways for synthesizing various uranium fluoride microstructures, including microspheres, microrods, and microplates. These methods have enabled the preparation of previously unreported micromaterials, such as  $\text{UO}_2\text{F}_2$  and  $\text{UF}_4$  microspheres/microrods/microplates, and  $(\text{NH}_4)_3\text{UO}_2\text{F}_5$  microspheres. Continued advancements in the chemical transformation of uranium are expected to yield novel materials with controlled morphologies, driving further progress in this field.

## Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

## Author contributions

HJ: Conceptualization, Investigation, Methodology, Validation, Visualization, Writing—original draft. FP: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing—review and editing.

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