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## Revealing uranium tetrafluoride microrods†

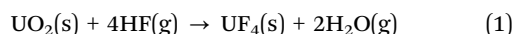
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Anhydrous and hydrated UF<sub>4</sub> microrods (5–25 μm) were prepared from the reactions of UO<sub>2</sub> microrods (5–15 μm) with HF(g), produced from the decomposition of silver bifluoride (AgHF<sub>2</sub>, SBF). In order to optimize the preparation of UF<sub>4</sub> mr, several experimental parameters including atmosphere (air or N<sub>2</sub>), temperature (150 or 250 °C) and amount of SBF were evaluated. In all reactions, rodlike morphologies were retained. At 250 °C, the reaction products always consist of an anhydrous UF<sub>4</sub>/hydrated UF<sub>4</sub> mixture, while at 150 °C only hydrated UF<sub>4</sub> was detected. Anhydrous UF<sub>4</sub> microrods were obtained by dehydration of the anhydrous UF<sub>4</sub>/hydrated UF<sub>4</sub> mixture using TGA-DSC. Changing the atmosphere from air to N<sub>2</sub> or reducing the amount of SBF by half did not affect the nature of the reaction products.

## Introduction

At the nano- and microscale, materials can exhibit properties (e.g., optical, catalytic, electronic, mechanical, thermal, magnetic)<sup>1–3</sup> that are not observed at the macroscale. The common applications of micro- and nano- materials (e.g. gas sensors, electrochromic devices, solar cells, batteries) are shared between many metal oxides (e.g. Ti,<sup>4</sup> Co,<sup>1,5,6</sup> Ni,<sup>2,7</sup> Zn,<sup>8–10</sup> Mo,<sup>11–15</sup> and In<sup>16,17</sup>). The rod-morphology is one of the most studied and examples of microrods and nanorods respectively include In<sub>1–x</sub>Ga<sub>x</sub>P,<sup>18</sup> MnOOH,<sup>19</sup> Bi<sub>2</sub>S<sub>3</sub>,<sup>20</sup> and Ga<sub>2</sub>O<sub>3</sub>.<sup>21</sup>

One element whose material chemistry of micro- and nanorods has been poorly studied is uranium. Research on uranium has primarily focused on the study of spherical particles of binary oxides, nitrides, carbides, and fluorides.<sup>22–28</sup> Uranium microstructures can find applications as targets for medical isotope production,<sup>29–31</sup> fuels for nuclear reactors,<sup>32–34</sup> standards for nuclear forensics,<sup>35–37</sup> and energy sources for space exploration.<sup>38</sup> Morphological studies of uranium materials are also relevant to the field of nuclear forensics.<sup>39,40</sup> One critical material for the nuclear industry is UF<sub>4</sub>, which is produced from the reaction of UO<sub>2</sub> with HF gas at elevated temperatures (eqn (1)).



Besides serving as an intermediate in UF<sub>6</sub> production,<sup>41,42</sup> UF<sub>4</sub> has also found applications as targets for heavy ion production<sup>43</sup> and the primary precursor material for U metal production.<sup>44</sup> It is also proposed as a fuel for molten salt

reactors.<sup>45</sup> Anhydrous UF<sub>4</sub>, a green solid with low solubility in water,<sup>46</sup> exhibits several hydrated forms (i.e., UF<sub>4</sub>·xH<sub>2</sub>O, x = 0.5, 0.7, 0.75, 1.2, 1.3, 1.5, 2.0, 2.5)<sup>47–49</sup> which are formed upon reactions of the material with water (eqn (2)).



As water is ubiquitous in the uranium industry, it is important to address environmental and industrial concerns pertaining to the hydrolytic behaviors of UF<sub>4</sub>.<sup>48</sup> Though the physico-chemical properties of UF<sub>4</sub> and its hydrates are well characterized at the macroscale,<sup>47–64</sup> there is a lack of knowledge concerning their preparations and characterizations at the microscale. As the applications of UF<sub>4</sub> expand, it is essential that information and accessibility to UF<sub>4</sub> materials at the microscale become more readily available.

So far, the only UF<sub>4</sub> morphology that can be prepared and controlled at the microscale is the spherical one. UF<sub>4</sub> microspheres (ms) have already been produced and are commercially available,<sup>27,49,54,65</sup> and although details on their production remain proprietary, high temperature hydrofluorination of UO<sub>2</sub> was mentioned.<sup>66</sup> Other UF<sub>4</sub> morphologies such as microrods (mr) or microplates (mp) have not yet been prepared in a controlled manner.

Previously, we have reported on the preparation of UO<sub>2</sub>F<sub>2</sub> microspheres, microrods and microplates using chemical transformation.<sup>28,67</sup> In these works, uranium oxide micromaterials (UO<sub>3</sub>, U<sub>3</sub>O<sub>8</sub>) were fluorinated in an autoclave with HF(g) produced from the thermal decomposition of silver bifluoride (AgHF<sub>2</sub>, SBF). Scanning electron microscope (SEM) results concerning the morphology and particle size distribution of UO<sub>2</sub>F<sub>2</sub> mp have shown high variance, whereas SEM results relating to UO<sub>2</sub>F<sub>2</sub> mr have been consistent. As a continuation, investigating U(IV) fluoride micromaterials was a natural

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progression and microrods were selected as the primary microstructure.

Here, we report on the preparation of anhydrous and hydrated  $\text{UF}_4$  microrods. The materials were prepared by chemical transformation from the reaction of  $\text{UO}_2$  mr with SBF in autoclaves and were characterized by scanning electron microscopy and powder X-ray diffraction (PXRD).

## Experimental

**Caution!** Uranium-238 is an  $\alpha$  emitter ( $E_{\text{max}} = 4.26$  MeV). All manipulations were performed in a designed radiochemistry laboratory equipped with HEPA filter hoods and by following approved radioisotope handling and monitoring procedures.

### Materials and methods

Silver bifluoride ( $\geq 99\%$ , Alfa Aesar), glycerol ( $\geq 99.5\%$ , Sigma-Aldrich), and urea ( $\geq 98\%$ , Sigma-Aldrich) were used as received.  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (UNH) was prepared from the treatment of uranium metal dissolved in hot nitric acid followed by recrystallization. Fluorination and hydrothermal reactions were conducted within a Parr model 4749 autoclave placed in a Thermo Scientific Thermolyne Benchtop muffle furnace (model FB1315M). Fluorinations were conducted at  $150$ – $250$  °C for 6–24 hours in the setup reported previously.<sup>67</sup> For dry reactions,  $\text{N}_2$  was regarded as inert as it does not react with reactants at these temperatures.  $\text{HF(g)}$ , the gaseous decomposition product of SBF, provides the source of fluorine for the reactions. In these reactions, SBF in excess molar quantity was placed on the Teflon liner of the vessel, while the uranium oxide material was placed in a 15 mL Teflon vial above the SBF.<sup>67</sup>

Powder X-ray diffraction measurements were performed at room temperature on a Bruker D8 Advanced diffractometer equipped with  $\text{Cu K}\alpha$  X-rays ( $\lambda = 1.5406$  Å) and a solid-state Si detector. Imaging was performed on the JEOL Tescan CLARA field emission scanning electron microscope, and samples were mounted on carbon tape without coating. TGA-DSC measurements were conducted with a TA instruments SDT 650 Discovery series TGA-DSC from  $50$ – $600$  °C with a heating rate of  $10$  °C  $\text{min}^{-1}$ . The measurements were performed in alumina crucibles under flowing argon gas with a sample and balance flow rate of approximately  $100$  mL  $\text{min}^{-1}$ . Particle sizes were measured using ImageJ, and particle size distribution figures were generated using SciDAVis.

### Sample preparation

**Preparation of  $\text{UO}_2$  mr.**  $3\text{UO}_3 \cdot \text{NH}_3 \cdot 5\text{H}_2\text{O}$  mr (234.1 mg, 0.244 mmol), prepared using the reported method,<sup>68</sup> was

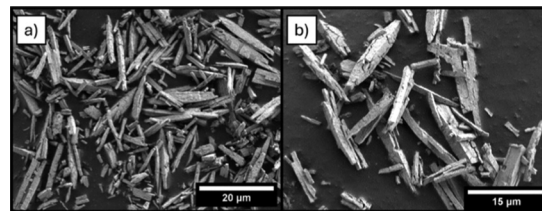


Fig. 1 SEM images of  $\text{UO}_2$  mr at (a)  $4790\times$  and (b)  $6640\times$ .

placed in an alumina boat and treated at  $600$  °C for 3 hours under air. The resulting  $\text{U}_3\text{O}_8$  product (172.3 mg, 0.205 mmol) was then heated to  $600$  °C for 5 hours under flowing 5%  $\text{H}_2/95\%$  Ar gas.<sup>69</sup> The resulting  $\text{UO}_2$  mr (159 mg, 0.589 mmol, 80.6% yield from  $3\text{UO}_3 \cdot \text{NH}_3 \cdot 5\text{H}_2\text{O}$ ) was characterized by SEM (Fig. 1) and PXRD (Fig. S1, ESI†) (Table 1).

## Results and discussion

Here, the reactions were set up identically to previous  $\text{UO}_2\text{F}_2$  microrod works except that the starting material (*i.e.*,  $\text{U}_3\text{O}_8$  mr) was replaced with  $\text{UO}_2$  mr.

Various experimental parameters have been evaluated (atmosphere, temperature, amount of SBF). A total of four reactions were investigated. In each reaction,  $\text{UO}_2$  was weighed and placed in a Teflon vial and then placed in the Teflon liner of the autoclave containing SBF. The autoclave was sealed either in air (reaction 1, 3, and 4) or under  $\text{N}_2$  atmosphere (reaction 2) and thermally treated for 24 hours at  $150$  or  $250$  °C. Following the reaction, the autoclave was cooled for 2 hours to room temperature and opened, and the resulting product was weighed and characterized by PXRD and SEM. The conditions, reaction products, and yields for the four reactions are presented in Table 1, and the effects of atmosphere, temperature, and amount of SBF on the nature of the reaction products are discussed in the following sections.

### Baseline reaction

Reaction 1 follows the same procedure as the one applied for the preparation of  $\text{UO}_2\text{F}_2$  (24 hours at  $250$  °C using  $\sim 300$  mg SBF [ $\text{U}:\text{HF} = \sim 3$ – $5$ ] prepared in air). Here the reaction of  $\text{UO}_2$  and  $\text{HF(g)}$  led to a mixture of anhydrous and hydrated  $\text{UF}_4$  (Fig. S2a, ESI†). The presence of hydrated  $\text{UF}_4$  in the reaction product is probably due to the reaction of  $\text{UF}_4$  and water (eqn (2)) that was formed as a byproduct (eqn (1)).

Morphologically, the rodlike particles remained intact and experienced some visible surface roughing (Fig. 2a–c). Particle

Table 1 Experimental conditions and reaction products for the fluorination of  $\text{UO}_2$  mr with SBF

Reaction #	Mass of $\text{UO}_2$ (mg)	Mass of SBF (mg)	$T$ (°C)	Time (h)	Atmosphere	Yield (mg, %)	Reaction product
1	50.8	303.9	250	24	Air	57.9 (98.0%)	$\text{UF}_4/\text{UF}_4 \cdot 2\text{H}_2\text{O}$
2	30.1	400.0	250	24	$\text{N}_2$	29.5 (82.3%)	$\text{UF}_4/\text{UF}_4 \cdot x\text{H}_2\text{O}$
3	31.5	301.6	150	24	Air	35.0 (86.0%)	$\text{UF}_4 \cdot 1.5\text{H}_2\text{O}$
4	33.8	155.8	250	24	Air	35.2 (89.6%)	$\text{UF}_4/\text{UF}_4 \cdot 2\text{H}_2\text{O}$



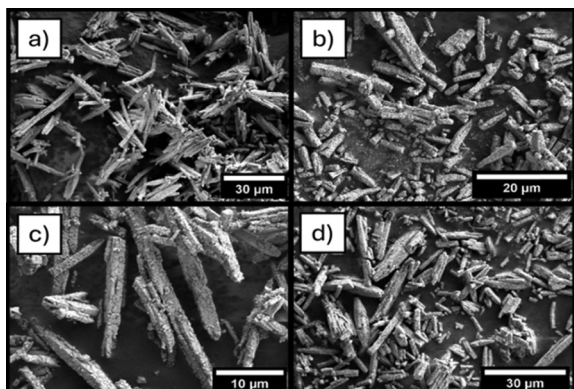


Fig. 2 SEM images of the reaction products of reaction 1 at (a) 2000 $\times$ , (b) 4450 $\times$ , (c) 6650 $\times$ , and (d) after TGA-DSC at 2650 $\times$ .

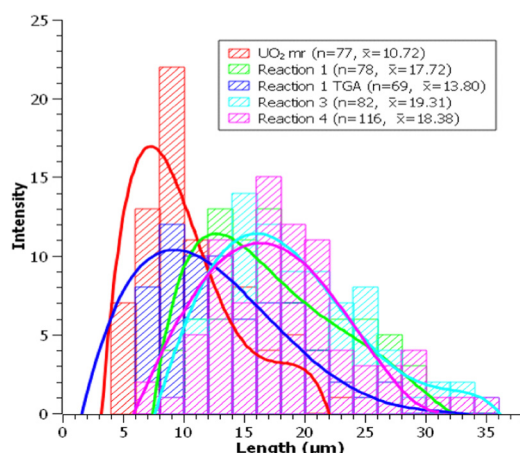


Fig. 3 Particle size distribution of  $\text{UO}_2$  mr and particles from reaction 1, 3, and 4.

size distribution (PSD) analysis (Fig. 3) shows the average length of these particles have increased by  $\sim 7 \mu\text{m}$ .

Treatment of the reaction product (16.94 mg) by TGA-DSC up to 600  $^\circ\text{C}$  (ramp rate of 10  $^\circ\text{C min}^{-1}$ ) under argon converted the  $\text{UF}_4/\text{UF}_4 \cdot 2\text{H}_2\text{O}$  mixture to anhydrous  $\text{UF}_4$ . The TGA-DSC curves (Fig. S3, ESI $^\dagger$ ) show a steady mass decrease followed by a plateau at  $\sim 380^\circ\text{C}$ , indicating the point of complete dehydration to anhydrous  $\text{UF}_4$ . Following TGA-DSC, the sample was characterized by SEM (Fig. 2d) and PXRD (Fig. S2b, ESI $^\dagger$ ). SEM

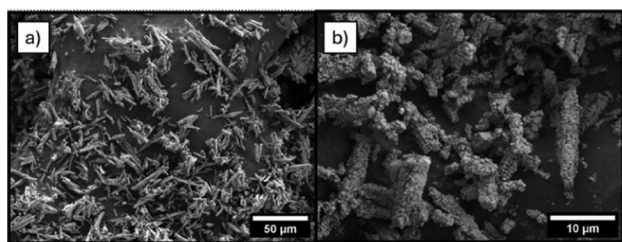


Fig. 4 SEM images of the reaction products of reaction 2 at (a) 1260 $\times$  and (b) 7360 $\times$ .

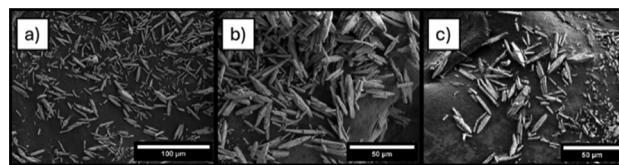


Fig. 5 SEM images of the reaction products of reaction 3 at (a) 1950 $\times$  and (b) 3510 $\times$ , and reaction 4 at (c) 3080 $\times$ .

analysis shows no morphological changes to the particles, and PSD analysis showed a decrease in average particle length by  $\sim 4 \mu\text{m}$ . The dehydration of  $\text{UF}_4/\text{UF}_4$  hydrate proved efficient for the preparation of anhydrous  $\text{UF}_4$  mr and could be transposed to other morphologies of  $\text{UF}_4$  hydrates.

### Effect of atmosphere

The effect of atmosphere on the reaction product was investigated in reaction 2. Treatment of  $\text{UO}_2$  with  $\text{HF(g)}$  under  $\text{N}_2$  atmosphere at 250  $^\circ\text{C}$  for 24 hours yielded a mixture of anhydrous  $\text{UF}_4$  and hydrated  $\text{UF}_4$  (PXRD in Fig. S2c, ESI $^\dagger$ ). SEM shows the rods to exhibit rough surfaces that were not observed in the  $\text{UO}_2$  mr precursor (Fig. 4), and PXRD shows less hydrated  $\text{UF}_4$  than from the one from reaction 1 (Fig. S2c, ESI $^\dagger$ ).

### Effect of temperature

Reaction 3 was performed at 150  $^\circ\text{C}$ , while the other parameters (atmosphere, reaction time, and amount of SBF) were identical to the baseline reaction. Following the reaction, PXRD analysis (Fig. S2d, ESI $^\dagger$ ) shows the presence of  $\text{UF}_4 \cdot 1.5\text{H}_2\text{O}$  as a single phase.

SEM analysis (Fig. 5a and b) shows the  $\text{UF}_4 \cdot 1.5\text{H}_2\text{O}$  mr to exhibit smoother surfaces than the reaction products from reactions 1 and 2. The particle size distributions (Fig. 3) showed no size disparities between  $\text{UF}_4 \cdot 1.5\text{H}_2\text{O}$  mr and that of  $\text{UF}_4/\text{UF}_4 \cdot 2\text{H}_2\text{O}$  mr (reaction 1).

The absence of anhydrous  $\text{UF}_4$  at 150  $^\circ\text{C}$  indicated that the hydrate was initially formed near this temperature and that the increase in temperature to 250  $^\circ\text{C}$  would initiate dehydration leading to the partially hydrated mixture. We hypothesized that the reaction at 400  $^\circ\text{C}$  should lead exclusively to anhydrous  $\text{UF}_4$ .

### Effect of SBF

In reaction 4, about half the amount of  $\text{AgHF}_2$  was used (155.8 mg, 1.061 mmol). Calculations indicated that at 250  $^\circ\text{C}$ , decreasing the amount of SBF by half would decrease the partial pressure of  $\text{HF(g)}$  in the autoclave from  $\sim 4$  atm to  $\sim 2$  atm ( $\sim 5$  atm to  $\sim 3$  atm total pressure). PXRD analysis showed the presence of a  $\text{UF}_4/\text{UF}_4 \cdot 2\text{H}_2\text{O}$  mixture (Fig. S2e, ESI $^\dagger$ ) while SEM (Fig. 5c) indicated the presence of microrods. PSD observations (Fig. 4) were consistent with the results of reactions 1 and 3. Overall, decreasing the amount of SBF does not fundamentally change the nature of the reaction products as anhydrous  $\text{UF}_4$  and hydrated  $\text{UF}_4$  were obtained.





## Conclusions

For the first time, uranium tetrafluoride microrods were prepared by chemical transformation. The reactions of  $\text{UO}_2$  microrods (5–15  $\mu\text{m}$ ) with  $\text{HF(g)}$ , produced from the decomposition of SBF, were investigated in autoclaves. Several experimental parameters including atmosphere, temperature, and amount of SBF were tested. In all reactions, rodlike morphologies were retained. At 250  $^{\circ}\text{C}$ , the reaction products always consist of an anhydrous  $\text{UF}_4$ /hydrated  $\text{UF}_4$  mixture, while at 150  $^{\circ}\text{C}$  only the presence of hydrated  $\text{UF}_4$  was detected. Anhydrous  $\text{UF}_4$  microrods were obtained by dehydration of the anhydrous  $\text{UF}_4$ /hydrated  $\text{UF}_4$  mixture *via* thermal treatment using TGA-DSC. Changing the atmosphere from air to  $\text{N}_2$  or reducing the amount of SBF by half did not fundamentally affect the nature of the reaction products. Using experimental set-up to 250  $^{\circ}\text{C}$  for the highest operational temperature indicated that the preparation of single phase hydrated  $\text{UF}_4$  or anhydrous  $\text{UF}_4$  is respectively a one-step (hydrofluorination) and two-step process (hydrofluorination and dehydration). The preparation of anhydrous  $\text{UF}_4$  in a single step process would require hydrofluorination in an autoclave at  $T > 250$   $^{\circ}\text{C}$ .

Currently, the preparation of  $\text{UF}_4$  nanospheres and microplates using the method presented here is under progress and results will be reported in due course. Finally, successful fluorinations of uranium oxide micromaterials will lay the groundwork for the development of other f-element fluoride micromaterials.

## Author contributions

The manuscript was written through contributions of all authors. H. J.: investigation, methodology, validation, visualization, and writing – original draft. F. P.: conceptualization, funding acquisition, project administration, resources, supervision, and writing – review & editing.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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