Preparation of ultrafine fibrous uranium dioxide by electrospinning

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1. Introduction

Uranium oxides attract attention since the dawn of nuclear technology. The current effort is focused on the production of nanosized uranium oxides due to their good properties in low-temperature sintering [1–4] and spark plasma sintering [5]. Nanocrystalline UO₂ is also studied in connection with the high burnup structures (HBS) in nuclear fuel pellets. In this regard, nanocrystalline uranium oxide phases possess favorable physical and chemical characteristics, such as high retention of fissile gases, mechanical stability owing to plasticity and low susceptibility to radiation damage as compared to conventional microcrystalline nuclear fuel [6]. Uranium oxides also found application in heterogeneous catalysis and electrocatalysis [7–10]. Synthetic methods applied in the field of nanostructural uranium oxide preparation provided various morphologies, which included nanoparticles [11], hollow nanospheres [12], thin films [13,14], mesoporous materials [15,16], microspheres with urchin-like nanoneedles [17] and also nanowires and nanoribbons [10]. The range of synthetic techniques is very broad and they include sol-gel reactions [18], precipitation [19], hydrothermal reaction [20], solvothermal reaction [21], radiolytic reduction by gamma irradiation [12], UV photolysis [22], electrodeposition [23,24], polymer assisted deposition [13], citrate gel combustion [25–28], microwave-assisted thermal decomposition of U(IV) complexes [29], non-aqueous synthesis in oleylamine [30–32], and thermal decomposition of oxalates [33].

All listed methods have their advantages and disadvantages considering the economy, applicability/continuity of production, safety, and of course, shape and size control of nanostructures. By considering results of previous works and properties of various synthetic techniques, it could be seen that there is still a need for the preparation of nanofibers of uranium oxides via electrospinning.

Electrospinning [34] is nowadays a widely used laboratory and even industrial technique with a broad range of produced fibers of different chemical, structural, and material types. Electrospun fibers could be prepared in various diameters from several nanometers to micrometers. Industrial production of nanofibers is mainly focused on polymeric nonwovens used in filtration and textile industry while production of inorganic nanofibers is still in a mainly academic domain with several exceptions. Technology, however, for the production of polymeric fibers is the same as for inorganic ones (Fig. 1). The fabrication of ceramic nanofibers is a multi-step process where electrospinning of polymer-inorganic composite is the first task [35]. The composite usually contains
inorganic precursor and supporting organic polymer, which plays the role of a fiber-forming agent and also controls viscosity and other parameters of the electrospinning solution. All components are dissolved in a suitable solvent and introduced to a syringe or an electrospinning machine. To the tip of the needle or the electrode with fiber-forming solution, positive high voltage is applied, and fibers are drawn from the surface of the solution towards a grounded or negatively charged collector. During the flight between electrodes, the solvent evaporates, and fibers solidify and are collected in the form of a nonwoven textile mat.

The second step of the production of inorganic fibers is calcination of the green composite. During high temperature curing in various atmospheres, the organic component is usually burned out, but the fibrous shape is preserved. The process of calcination is a critical step where the key factors are applied temperature, heating rate and time, and used atmosphere. Resulting inorganic structures are polycrystalline or amorphous depending on their chemical composition and heat treatment conditions. Electrospinning, as a method for the preparation of nanofibers, has been used for many types of materials, such as binary oxides, metals, spinels, perovskites, nitrides, carbides, carbon and many more [36]. Despite these efforts, preparations of uranium and other actinide oxide fine fibers have not been described at industrial or laboratory scale preparations of uranium oxide nano fibers with submicron to nanometer range of diameters could easily produce large quantities of fine fibers with a stable diameter, morphology, and a relatively high surface area. Since 1996 when Taylor introduced uranium oxide as a catalyst that can effectively destroy volatile organic compounds containing chlorine [37], there have been many studies on this topic [38–48]. The whole area of interest is covered in a 2013 review [7]. Uranium oxides were also studied as a semiconductor in electronics [49] and widely used in the nuclear energy field [50].

Here we report for the first time the preparation of uranium oxide nanofibers with submicron to nanometer range of diameters by the electrospinning method. The properties of uranyl acetylactonate solutions in ethanol/acetone were optimized, and the effects of collector material on the properties of the fiber mat were examined. Reduction of the UO₂ fibres in H₂/N₂ atmosphere provided UO₂ as the final crystalline phase.

2. Experimental

2.1. General

Polyvinylpyrrolidone (PVP, Mₘ = 360 kDa) was purchased from Sigma Aldrich and used as received. Uranyl acetylactonate hydrate was synthesized according to the literature [51]. In a typical procedure, uranyl nitrate hexahydrate (3.94 g, 10.0 mmol) was dissolved in 50 cm³ of demineralized water at approx. 343 K together with acetylactone (2.10 g, 21.0 mmol). The mixture was stirred and kept warm till a homogenous orange solution was formed. A solution of NaOH (0.84 g, 21 mmol) in demineralized water (10 cm³) was added dropwise and the whole mixture was stirred and let cool down to ambient temperature. An orange amorphous precipitate was filtered, washed several times with cold demineralized water, dried in air and used for further work. Acetic acid and ethanol were used in 99 wt% and 96 wt% concentration, respectively. Forming gas with a composition of 5 vol% of H₂ in N₂ (<20 ppm of H₂O and O₂) was used for reductions.

2.2. Preparation of solutions and electrospinning

Uranyl acetylactonate hydrate and PVP were dissolved in a mixture of acetic acid and ethanol in various mass ratios (solutions A–C, Table 1). The solution was stirred for 2 h, characterized, transferred to a syringe and electrospun. The three solutions were prepared based on different ratios of the inorganic precursor and polymer and amount of ethanol and acetic acid. The actual compositions and corresponding chemical and physical characteristics of electrospinning solutions are shown in Table 1.

The process was conducted on a home-build set-up based on two high-voltage power sources capable of an output of 0 to +25 kV and 0 to −15 kV and on a New Era Scientific syringe pump. The syringe with a blunt-tip needle of 1 mm diameter was used as a carrier of the spinning solution. A negative-charge source was connected to the collector electrode which was a circular metal plate with a diameter of 110 mm. Fibers were collected directly on the counterelectrode, or the collector plate was covered with printer paper, ashless paper, or three types of aluminum foil with a thickness of 10, 25, and 50 μm. Experiments were performed in an air-conditioned laboratory with a fixed temperature of 296 ± 2 K and relative humidity of 40 ± 10%. Electrospinning parameters are presented in Table 2.

2.3. Calcination and reduction treatment

After electrospinning process, in which a green composite of uranyl acetylactonate and PVP polymer is formed, the calcination step is performed to obtain purely inorganic oxide fibers. For oxidative treatment, a muffle oven set to four different temperatures (673, 873, 1073, and 1273 K) with an ambient air atmosphere. In cases where an aluminum foil was used as the collector material, the maximum temperature was set to 873 K. Green fibers were

| Table 1 Electrospinning solution compositions and properties. |
|---|
| Solution parameter | A | B | C |
| UO₂(acac)₂ H₂O [g] | 1.0 | 1.0 | 1.0 |
| PVP [g] | 1.6 | 1.3 | 1.3 |
| EOH [g] | 55.3 | 40.0 | 26.5 |
| Acetic acid [g] | 6.1 | 2.9 | 2.9 |
| Dynamic viscosity [mPa s] | 24.6 ± 0.6 | 32.3 ± 2.3 | 75.5 ± 1.6 |
| Conductivity [μS cm⁻¹] | 53.4 ± 1.1 | 65.8 ± 3.1 | 79.6 ± 8.5 |
| Surface tension [mN m⁻¹] | 25.0 ± 0.1 | 24.9 ± 0.2 | 25.9 ± 0.1 |
calcinated on different collector materials (ashless paper, printer paper, aluminum foil), or they were peeled off from the collector. In all cases, the heating rate was set to 4 h to achieve the maximum calcination temperature then followed by another 4 h at a constant temperature and finished by spontaneous cooling down to ambient temperature. After heat treatments, calcined materials were collected and analyzed. For reduction treatment, a horizontal tube furnace equipped with a quartz tube was used and forming gas was delivered from a gas cylinder. The same maximum temperatures and heating program were used as in the case of calcination.

2.4. Characterization

Prepared electrospinning solutions were characterized by conductometry, viscosimetry, and surface tension measurements. The electrical conductivity of solutions was obtained on a Cond51 conductometer from XS Instrument. Viscosity measurements were performed on an Alpha Fungilab rotational viscosimeter. Surface tension was obtained by measurements on a Sigma 700 tensiometer with a Wilhelmy probe. Obtained characterization data are mentioned in Table 1, together with solution compositions.

Prepared micro- and nanofibrous materials were characterized by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) on an FEI Magellan 400 XHR microscope. Images were analyzed by the imageJ software for fiber diameter and size distribution. The fibrous materials were also studied with the focused ion beam technique on a FIB-SEM TESCAN Lyra3 XMH system. Thermogravimetric analysis and simultaneous differential scanning calorimetry (TG/DSC) were performed on a Netzsch Jupiter STA 449 instrument with a heating rate of 10 K min\(^{-1}\) and the maximum temperature of 1273 K. Synthetic air (70 cm\(^3\) min\(^{-1}\)) was used as atmosphere to simulate ambient conditions. Powder X-ray diffraction (PXRD) measurements were performed on Rigaku Smart Lab and GNR Europe 600 diffractometers equipped with Cu (\(\lambda_{\text{Cu}} = 0.154060\) nm, \(\lambda_{\text{Ko2}} = 0.154443\) nm) and Co (\(\lambda_{\text{Ko1}} = 0.178901\) nm, \(\lambda_{\text{Ko2}} = 0.179290\) nm) X-ray lamps, respectively.

Table 2

| Property                        | Value  |
|--------------------------------|--------|
| High voltage (+) [kV]           | 15.0 ± 0.1 |
| High voltage (−) [kV]           | −10 ± 0.1  |
| Flow rate [µl min\(^{-1}\)]     | 50      |
| Electrode distance [cm]         | 15 (20°) |

* - in case of electrospinning of solution B, a different electrode distance was used.

3. Results and discussion

Properties of the precursor solution A were optimized for electrospinning with respect to spinnability. Several electrospinning experiments were conducted to test which concentration of components is suitable for the fiber-forming process. At low concentrations of PVP and uranyl precursor, electrospinning occurred but with visible droplets and flooding on the collector surface. However, upon increasing the concentration, the fibers were visible on the collector, and after a few minutes of continuous spinning, 3D microfibrous structures were obtained. An orange slightly viscous solution of PVP and uranyl acetylacetonate in acetic acid and ethanol forms a uniform yellowish layer of homogeneous fibers. Ashless paper was used for these initial experiments as the collector material to assemble fiber mats. Morphology of the as-obtained fiber mat was characterized by electron microscopy. The SEM image of the green fibrous composite is shown in Fig. 2. An average diameter of the fibers was 273 ± 102 nm (Histogram 1 in Supplementary material). It is evident that fibers have a broad distribution of diameters.

The prepared green composite fibers were scraped from the ashless paper support and examined by thermal analysis (TG/DSC) in the synthetic air atmosphere to establish an optimal calcination temperature (Fig. 3). It was found that the main burning process was very fast, and an abrupt mass loss started around 556 K (onset) with a strong exothermic effect at 562 K (peak). A stable mass was achieved at a temperature range from 823 to 873 K.

According to the TG/DSC analysis results, we have directed calcination in the air as the next step. The composite fibers were calcined in a muffle oven at four different temperatures (673, 873, 1073, and 1273 K) to observe the development of their morphology and phase composition. Products of calcination were left to cool down and analyzed by the STEM technique (Fig. 4) and PXRD measurements (Fig. 5). According to obtained diffractograms, all samples consisted of U\(_3\)O\(_8\) phase. When the lowest calcination temperature was used, the fibers displayed smooth surface morphology without signs of polycrystallinity, and in their diffractogram, there are broad peaks of nanosized of amorphous phase overlapped with diffractions of uranium oxide U\(_3\)O\(_8\) (COD no. 2310811). From the TG/DSC analysis, it is clear that the temperature of 673 K is insufficient to achieve a chemically and phase pure structure. The fibers formed at 873 K are more porous and show a low degree of material sintering. When a higher temperature (1073 K) is used, a polycrystalline structure without porosity is visible, and the thickness of fibers increased. The highest temperature of 1273 K resulted in the sintered microstructure, therefore the average diameter or corresponding histogram were not obtained. Average diameters of fabricated structures are shown together with the STEM images in Fig. 4. Corresponding histograms (2, 3, and 4) are attached in Supplementary material.

After initial experiments with ashless paper, we tested the influence of different supporting materials at the collector plate, such as aluminum foils with a thickness of 10, 25, and 50 µm and standard printer paper, on the thickness of the calcined fibers. To compare the results, we have also used support-free calcination of as-prepared green fibrous composites, which were scraped from the aluminum foil surface before high-temperature treatment. Electrospinning conditions were the same as in previous experiments. The temperature of calcination was set to 873 K. After burning off the organic supporting polymer, the sample was left to
cool down to laboratory temperature and imaged with SEM (Fig. 6). Uranium oxide prepared by calcination of fibers without any support was found in an aggregated bulk form (Fig. 6A). The material prepared on printer paper appeared like a scrolled bilayer sandwich with a dark green material inside and a white crust of calcined paper residue on the outside. The fibers appeared thick and non-uniform (Fig. 6B), which corresponds with an average diameter in the sub-micrometer range (127 ± 42 nm, histograms 5 in Supplementary material). In case of aluminum foil used as collector material, there was a brightly golden layer on the foil surface which could be easily scraped off. The mean diameters of fibers attached to the aluminum foil surface was 52 ± 21 (Fig. 6C), 28 ± 12 (not shown) and 20 ± 5 (Fig. 6D) nm for aluminum foils of 10, 25, and 50 μm thickness, respectively. Thus, the thicker aluminum foil provided thinner fibers. Corresponding histograms (6, 7, and 8) are attached in Supplementary material.

After these experiments, we have focused on the mechanism of binding of calcined uranium oxide nanofibers to the aluminum foil.
with the Focused Ion Beam-SEM method (Fig. 7). A precise cut through the layers of nanofibers and the aluminum foil support was produced. The imaging was performed in backscattered electrons (BSE) mode, which produces elemental contrast. Acceleration high voltage was set to 10 kV. From Fig. 7, it is possible to observe that the calcined nanofibers of U3O8 lie on the surface of aluminum foil. Some of them apparently form an adhesive bond by ceramic-ceramic interface with oxidized aluminum surface. This adhesion could lead to an explanation of different diameters of fibers on aluminum foils with different thickness. We suggest that during the calcination process, the fibers contract and bending of the thinner foil possibly leads to thicker diameters of fibers. The thicker aluminum foil is more rigid, does not bend and exerts some tension force on fibers; therefore, we suppose the resulting fibers are thinner.

During the SEM measurements, we have also noticed that nanofibers appear to be hollow, and therefore, TEM images were acquired to prove that fact (Fig. 8). Previously described methods of hollow fiber preparation rely mostly on coaxial electrospinning where inner and outer needle-in-needle system is used with different feeding solutions resulting in the composite structures which are converted into core-shell or hollow fibers. However, a single needle system was used in the presented system, therefore observed cavities must be formed during electrospinning or calcination processes. There are several studies concerning this phenomenon. The formation of hollow fibers is observed during drying at 333–353 K from two-solvent system of DMF and ethanol [52]. According to another study [53] the cavities are formed at elevated temperatures by decomposition of inorganic precursor. In both cases the formation of fully hollow structures was achieved; in contrast, in the present study only partly hollow fibers are formed. It was not determined which mechanism is involved.

To confirm the reproducibility of our initial findings of differences in average diameter and their dependence on different types of supporting material, we repeated experiments several times, measured a more significant number of samples and calculated average diameters which confirmed our conclusions.

The solution A was used in the first study to gain an overall view of the process. After the first analysis, we have prepared different solutions (B and C) to see the differences in the electrospinning process and the influence of the supporting materials. All samples were spun at the same conditions from the same solution batch. After electrospinning, three small samples with dimension 1 × 6 cm were cut from each fiber-covered foil, and all strips were calcined together in a muffle oven at 873 K with a 4 h ramp followed by a dwell time of 4 h. After cooling down, photos were taken (Fig. 9), and SEM images were made at five different sites on each sample (examples of SEM measurements are attached in Supplementary material as Figs. 15–95). Average diameters of hundred or more individual fibers were then calculated by the imageJ software (Table 3, the histograms 6–14 in Supplementary material).

From photographs in Fig. 9, the effect of temperature treatment on the aluminum foil is clearly visible. While the thickest collector material maintains its shape upon calcination, the thinnest foil becomes crumpled. Differences between the electrospinning solutions are also visible. The solution C, which is more concentrated, produces thicker fibers and in Fig. 9G–I one can observe macroscopic clumps formed from the fibers. In the case of solution B, especially on the thickest aluminum foil, it is evident that fibers stayed attached to the surface and formed the goldish color of the sample. In case of 25 μm aluminum foil, all samples are bent, and in case of solution B, prepared fibers are not attached to the surface but peeled off, which is probably the reason why the average diameter is high. Taking those observations together with measured differences in average diameters, the thickness of the aluminum foil is most probably the reason why the fiber diameters are different. In the case of thicker fibers (solution C), we can see the difference in the order of units of percent however when
solution B is used the effect is much more evident, and the change from 10 \( \mu \text{m} \) to 50 \( \mu \text{m} \) collector material corresponds with the change of the average fiber diameter of 40\% of original thickness. From these results, it is possible to conclude that while green fibers are unaffected by the used collector material, the average diameter of calcined uranium oxide nanofibers is dependent on aluminum foil thickness. However, the phenomenon is less evident where the concentrated solution for electrospinning is used.

For further reduction study, we have selected \( \text{U}_3\text{O}_8 \) fibers

Fig. 6. Nanofibrous composites after calcination at 873 K on different supporting materials (A — without supporting material, B — printer paper, C — aluminum foil of 10 \( \mu \text{m} \) thickness, D — aluminum foil of 50 \( \mu \text{m} \) thickness).

Fig. 7. SEM image (BSE) of the FIB-produced cut through the layer of uranium oxide nanofibers bonded to the aluminum foil (bottom).

Fig. 8. TEM images of hollow uranium oxide nanofibers.
Electrospun from solution C on the 50 μm aluminum foil and calcined them at 873 K because of easier manipulation with thick fibers. Pealed-off fibers were loaded into the tube furnace and reduced with forming gas at 673, 873, 1073, and 1273 K. After cooling down, dark black samples were collected and further studied by the SEM analysis (Fig. 10) and PXRD technique (Fig. 11). Corresponding histograms are attached in Supplementary material.

It is evident from obtained diffractograms that the temperature of 673 K is not sufficient for a complete reduction however measured micrographs display a radical decrease in the fiber average diameter from 187 ± 56 nm for unreduced U₃O₈ to 85 ± 60 nm for the sample treated at 673 K. It is due to the contractions connected to change of oxidation state, density increase corresponding with net volume decrease [54]. Also, diffractions corresponding to UO₂ (COD no. 1541665) are already present next to the UO₃ ones (COD no. 1527743) and U₃O₈ (COD no. 2310811) according to the Rietveld refinement (Table 1S in Supplementary material). However, when a higher temperature of 873 K is applied, a complete reduction to UO₂ is already observed. Further temperature increase results in narrowing of diffractions. Crystallite size and phase composition were computed by the Rietveld method based on COD models (Table 1S in Supplementary material). According to these results, we can observe the phase transformation from the mixed composition at 673 K where three phases are present (UO₂, U₃O₈, and U₃O₆) into the pure uraninite phase. From the morphology point of view, after contraction, another phenomenon is present. When reduction is performed at 873 K, UO₂ fibers have a higher average diameter than at 673 K, and a mixture of thicker and ultrathin fibers is formed. However, at 873 K, thin fibers are breaking and when even higher temperature 1073 K is applied only thicker fibers remain and consequently a higher average diameter with a lower standard deviation is found. Fiber thickness and diameter dispersity are similar for the two highest temperatures. We assume that high temperatures lead to thickening of fibers by material transport from thin fibers towards fibrous structures with high diameter. Dependence of average diameter and its standard deviation on reduction temperature is depicted in Fig. 12.

Electrospinning started as a laboratory method and its simple set up facilitated wide dispersal to many materials chemistry laboratories. The method itself has also been successfully transformed into industrial processes [55–57]. Therefore, the electrospinning step of the uranium oxide nanofiber production may readily be scaled up as the overall process is robust and stable in longer period of time.

4. Conclusion

For the first time, we have prepared polycrystalline uranium oxide-based nanofibers and microfibers by a simple needle electrospinning method followed by calcination in air and further reduction treatment in forming gas. Their phase composition was identified as triuranium octaoxide as the final oxidized form and uranium dioxide the product of the reduction process. The internal structure of the calcined fibers was shown in TEM images as partially hollow. We have found that the role of the collector material during heat treatment, together with precise solution composition is crucial for the preparation of ultrafine fibers. As the most important result of this study, we can consider the observation of differences in average diameters among different collector

| Solution | 10 μm | 25 μm | 50 μm |
|----------|-------|-------|-------|
| A        | 52 ± 21 | 28 ± 12 | 20 ± 5  |
| B        | 67 ± 29 | 48 ± 26 | 39 ± 14 |
| C        | 247 ± 62 | 215 ± 68 | 187 ± 56 |

Table 3: Average diameter [nm] of calcined U₃O₈ nanofibers.

Fig. 9. Photos of calcined uranium oxide fibers on different aluminum foils: 10 μm (A, D, G), 25 μm (B, E, H), and 50 μm (C, F, I) prepared from electrospinning solutions A (A–C), B (D–F) and C (G–I).
Fig. 10. SEM images of reduced uranium oxide nanofibers.

Fig. 11. PXRD analysis of reduced uranium oxide nanofibers.
developed method for the UO2 safety standards of nuclear materials manipulation and provide the species due to a very low mass-to-volume ratio and a relatively high crystallites they are composed of and bulk properties of agglomerates due to a very low mass-to-volume ratio and a relatively high crystalline factors for the preparation of ultra and its rigidity during calcination were con bers have simultaneously nanoscopic properties of crystalline fibers in avoiding handling issues typical for particulate materials.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jnucmat.2019.151877.

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Fig. 12. Dependence of average thickness on reduction temperature (273 K – before reduction).
