One-step synthesis of hollow UO₂ nanospheres via radiolytic reduction of ammonium uranyl tricarbonate

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Original article

ABSTRACT

Black precipitates were successfully obtained by radiolytic reduction of ammonium uranyl tricarbonate in the aqueous solution of HCOONH₄ by one step. TEM, SAED, EDS, and XRD analysis indicated that the precipitates consist of hollow UO₂ nanospheres (d: 30–50 nm, wall thickness: 8–15 nm, and cavity diameter: 10–20 nm). The effect of HCOONH₄ concentration, irradiation time and dose rate on the morphology, and size of nanospheres was investigated. Then, a gas-bubble template mechanism was proposed.

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1. Introduction

Uranium oxides, including UO₂, UO₂-, U₃O₈, and so on, are not only a class of key nuclear materials, but also a kind of important catalysts [1–3]. In the last decade, some nano-sized uranium oxides were found to have a much better catalytic performance [4,5]. Thus, uranium oxide nanomaterials have attracted much attention. By far, quasi-spherical UO₂ nanoparticles [5–7], flower-like U₃O₈ nanostuctures [8], U₁₋₂O₈ nanorods [5,9], U₁₋₂O₈ nanotubes [10], hierarchical uranum oxides nano/microspheres [8,11] were obtained by thermochemical and electrochemical methods. Besides, ionizing irradiation was applied to prepare UO₂ nanoparticles using UO₂(NO₃)₂ as precursor in acidic solution [12–14]. In the fields of catalysis, gas-storage, and so on, uniform hollow structures within nanometer-to-micrometer dimensions have been of intense interest for their tailored structural, mechanical, surface, and penetration properties [15–17]. And many preparation methods were developed, including templates (i.e., hard templates and soft templates) methods, and template-free processes based on Kirkendall effect, Ostwald ripening or galvanic replacement [15,16]. Meanwhile, as a kind of soft templates, gas bubbles were used to synthesize hollow ZnS nanospheres [18] and Ni₆p-QD nanospheres [19] free away from impurities. However, to the best of our knowledge, there have been no any reports about the formation of hollow uranium oxides structures. Therefore, there exists a great challenge.

In the last decade, we tried our best to control the radiolytic synthesis of nanoparticles and nanostructures, and obtained mesoporous BaSO₄ microspheres, octahedron Cu₂O nanocrystals, solid and hollow Cu₂O nanocubes, and prismatic PbSO₄ microcrystals [20–22]. Herein, hollow UO₂ nanospheres are prepared by the radiolytic reduction of alkaline (NH₄)₂UO₂(CO₃)₂. Then, the mechanism based on gas bubble template is proposed.

2. Experimental

Ammonium uranyl tricarbonate (AUC) crystal was prepared according to Ref.[23] (Supporting information). A typical solution containing 5 mmol L⁻¹ AUC, 100 mmol L⁻¹ HCOONH₄ and 15 mmol L⁻¹ Na₂CO₃ was prepared, where Na₂CO₃ was used as stabilizer. After bubbling with ultrapure N₂ for 20 min, the solution at room temperature was irradiated in the Gamma Irradiation Facility of Peking University using ⁶⁰Co γ-ray source for a fixed time at a special location whose dose rate was determined by a ferrous sulfate dosimeter. After irradiation, black colloid solution or precipitates were obtained. The pH values of the solution before and after irradiation were measured to be 8.75 and 8.86, respectively.
The black precipitates were collected by centrifugation immediately and thoroughly washed by water, dried in a vacuum oven overnight at room temperature, and then black powders were achieved. The well washed powders were dispersed in water, and were dropped onto a carbon-coated copper grid. After the solvent was evaporated at room temperature, transmission electron microscopy (TEM) images, and selected area electron diffraction (SAED) were carried out on a FEI Tecnai G2 T20 microscope operated at 200 kV. Energy dispersive X-ray spectrum (EDS) was obtained on a FEI NanoSEM 430 microscope operated at 15 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax-2000 diffractometer with Cu Kα radiation (λ = 0.15418 nm).

3. Results and discussion

Fig. 1A shows the TEM image of the precipitate prepared with a dose rate of 40 Gy min⁻¹ and an irradiation time of 900 min at the HCOONH₄ concentration of 100 mmol L⁻¹. It can be seen that the product is composed of nanospheres with a diameter of 30–50 nm. It is noteworthy that the brightness of the edge is different from that of the center, indicating their hollow nature. The wall thickness and cavity diameter are estimated to be 8–15 nm and 10–20 nm, respectively. Besides, the margin of the particles is quite coarse. From the related TEM image in a higher magnification (Fig. 1B), it could be clearly found that they are composed of some smaller nanoparticles, with a diameter ranging from 2 to 5 nm.

![Fig. 1](image1.png)

Fig. 1. TEM images (A and B), XRD pattern (C) and EDS spectrum (D) of the product. The inset in (A) shows the SAED pattern of the corresponding product. The concentration of HCOONH₄ is 100 mmol L⁻¹, the dose rate is 40 Gy min⁻¹, and the irradiation time is 900 min.

The related SAED pattern (inset, Fig. 1A) exhibits four diffraction rings with plane distance of 0.320, 0.281, 0.198, and 0.168 nm, consistent with the cubic phase UO₂ (111), (200), (220), and (311) plane distances of 0.3153, 0.2733, 0.1933, and 0.1647 nm (JCPDS No. 41–1422). This confirms the formation of polycrystalline UO₂ nanospheres. In the relevant XRD pattern (Fig. 1C), three broadened (111), (220), and (311) diffraction peaks corresponding to cubic phase UO₂ (JCPDS No. 41–1422) are observed, further validating the generation of UO₂. Moreover, based on the (111) diffraction peak, the average size is estimated to be about 3 nm by using Scherrer’s formula, consistent with the result of the TEM image in a higher magnification. According to the EDS analysis (Fig. 1D), the presence of U and O in a ratio of 1:00:1.98, close to the stoichiometry of UO₂ within experimental error. Therefore, the as-prepared product is UO₂ hollow nanospheres.

Fig. 2 exhibits the TEM images of the products prepared at different HCOONH₄ concentrations with a dose rate of 40 Gy min⁻¹ and an irradiation time of 900 min. The products synthesized at a lower HCOONH₄ concentration are solid nanospheres (Fig. 2A and B). A higher HCOONH₄ concentration favors the generation of hollow UO₂ nanospheres (Fig. 2C and D).

Besides the concentration of HCOONH₄, the irradiation time could also affect the morphology of the UO₂ nanospheres. In this work, the dose rate was fixed at 40 Gy min⁻¹. At an irradiation time of 100 min, only colloid solution was generated. In the corresponding TEM image (Fig. 3A), it is found that the product consists of

![Fig. 2](image2.png)

Fig. 2. TEM images of the products prepared at different HCOONH₄ concentrations. HCOONH₄ concentration: (A) 30 mmol L⁻¹, (B) 50 mmol L⁻¹, (C) 80 mmol L⁻¹, and (D) 120 mmol L⁻¹. The dose rate is 40 Gy min⁻¹, and the irradiation time of 900 min.

![Fig. 3](image3.png)

Fig. 3. TEM images of the products prepared with different irradiation time. Irradiation time: (A) 100 min and (B) 200 min. The dose rate is 40 Gy min⁻¹.
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obtained by the radiolytic reduction of AUC in the HCOONa aqueous solution. A higher HCOONa concentration and the extending of irradiation time favored the formation of hollow nanospheres, while the effect of dose rate was inconspicuous. The results suggested that the assemblies of UO2 nanoparticles around the gas-water interface of the nano-sized H2 gas bubbles generated in situ lead to the formation of hollow nanospheres. To the best of our knowledge, this is the first report about the hollow uranium oxides nano-/microspheres. It is believed that the results reported herein will not only make the morphologies of uranium oxides more abundant, but also favor the exploration in the field of catalysis with uranium oxides as catalyst.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2016.06.035.

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