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Original article

One-step synthesis of hollow UO_2 nanospheres *via* radiolytic reduction of ammonium uranyl tricarbonate

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ABSTRACT

Black precipitates were successfully obtained by radiolytic reduction of ammonium uranyl tricarbonate in the aqueous solution of $HCOONH_4$ by one step. TEM, SAED, EDS, and XRD analysis indicated that the precipitates consist of hollow UO_2 nanospheres (ϕ: 30–50 nm, wall thickness: 8–15 nm, and cavity diameter: 10–20 nm). The effect of $HCOONH_4$ concentration, irradiation time and dose rate on the morphology, and size of nanospheres was investigated. Then, a gas-bubble template mechanism was proposed.

1. Introduction

Uranium oxides, including UO_2, UO_3, U_3O_8, 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 UO_2 nanoparticles [5–7], flower-like U_3O_8 nanostructures [8], U_3O_8 nanorods [5,9], U_3O_8 nanotubes [10], hierarchical uranium oxides nano/microspheres [8,11] were obtained by thermochemical and electrochemical methods. Besides, ionizing irradiation was applied to prepare UO_2 nanoparticles using $UO_2(NO_3)_2$ 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 Ni_n-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 syntheses of nanoparticles and nanostructures, and obtained mesoporous $BaSO_4$ microspheres, octahedron Cu_2O nanocrystals, solid and hollow Cu_2O nanocubes, and prismatic $PbSO_4$ microcrystals [20–22]. Herein, hollow UO_2 nanospheres are prepared by the radiolytic reduction of alkaline $(NH_4)_4UO_2(CO_3)_3$. 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 $mmol \cdot L^{-1}$ AUC, 100 $mmol \cdot L^{-1}$ $HCOONH_4$, and 15 $mmol \cdot L^{-1}$ Na_2CO_3 was prepared, where $Na_2CO_3$was used as stabilizer. After bubbling with ultrapure N_2 for 20 min, the solution at room temperature was irradiated in the Gamma Irradiation Facility of Peking University using ^{60}Co 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.

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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 Tacnai G2 T20 microscope operated at 200 kV. Energy dispersive X-ray spectrum (EDS) was obtained on a FEI NanoSEM 430 microscope operated at 15 keV. 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 $HCOONH_4$ 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.

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 UO_2 (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 UO_2 nanospheres. In the relevant XRD pattern (Fig. 1C), three broaden (111), (220), and (311) diffraction peaks corresponding to cubic phase UO_2 (JCPDS No. 41–1422) are observed, further validating the generation of UO_2. 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 UO_2 within experimental error. Therefore, the as-prepared product is UO_2 hollow nanospheres.

Fig. 2 exhibits the TEM images of the products prepared at different $HCOONH_4$ concentrations with a dose rate of 40 Gy·min^{-1} and an irradiation time of 900 min. The products synthesized at a lower $HCOONH_4$ concentration are solid nanospheres (Fig. 2A and B). A higher $HCOONH_4$ concentration favors the generation of hollow UO_2nanospheres (Fig. 2C and D).

Besides the concentration of $HCOONH_4$, the irradiation time could also affect the morphology of the UO_2 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

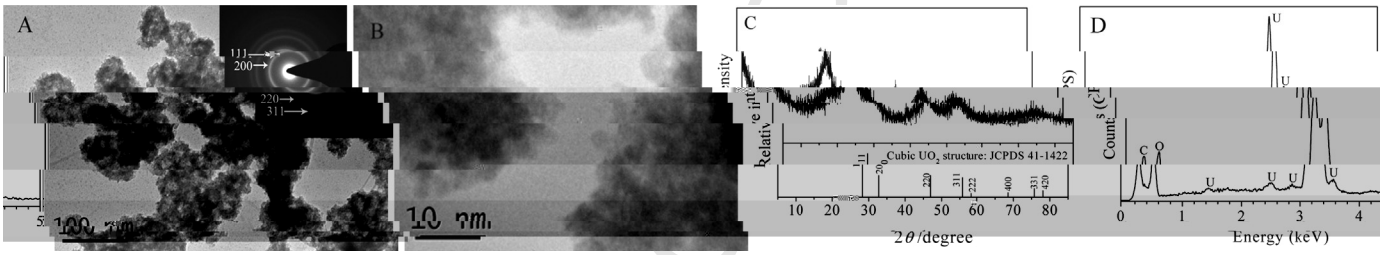

Fig. 1. TEM images (A and B), XRD pattern (C) and EDS spectrum (D) of the product. The inset in (A) shows the SAED pattern of the corresponding product. The concentration of $HCOONH_4$ is 100 mmol·L^{-1}, the dose rate is 40 Gy·min^{-1}, and the irradiation time is 900 min.

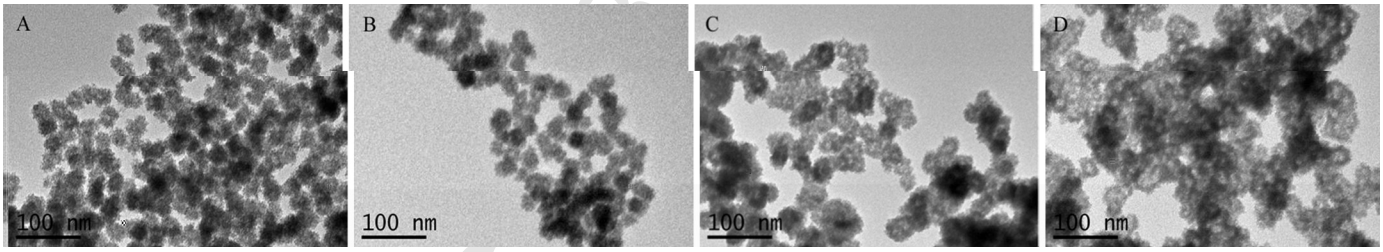

Fig. 2. TEM images of the products prepared at different $HCOONH_4$ concentrations.$HCOONH_4$ concentration: (A) 30 mmol·L^{-1}, (B) 50 mmol·L^{-1}, (C) 80 mmol·L^{-1}, and (D) 120 mmol·L^{-1}. The dose rate is 40 Gy·min^{-1}, and the irradiation time of 900 min.

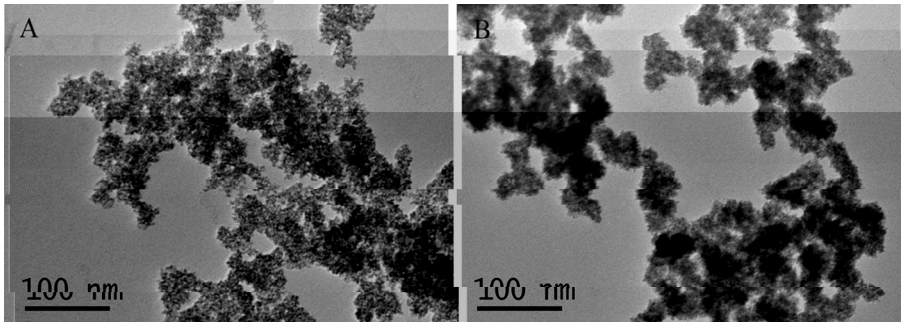

Fig. 3. TEM images of the products prepared with different irradiation time. Irradiation time: (A) 100 min and (B) 200 min. The dose rate is 40 Gy·min^{-1}.

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some incompact and irregular aggregates of nanoparticles. When the irradiation time increased to 200 min, the obtained sample was still colloid solution. The related TEM image (Fig. 3B) exhibits that there appear hollow nanospheres with a diameter of 20–30 nm, a wall thickness of 4–8 nm and a cavity diameter of 10–15 nm, besides a few incompact and irregular aggregates. As the irradiation time extended to 900 min, the incompact and irregular aggregates disappeared, and the hollow nanospheres were precipitated, whose diameter and wall thickness increase to 30–50 nm and 8–15 nm, respectively. It is worth noting that the cavity diameter is in the range of 10–20 nm, close to that of the sample obtained at the irradiation time of 200 min. Moreover, the change of dose rate does not affect the hollow structure of nanospheres (Fig. S1 in Supporting information).

In our experiment, when the aqueous solution was irradiated by γ-rays, the water molecules absorbed most of the irradiation energy and generated many reactive species, such as hydrated electrons (e_{aq}^-),·H and ·OH, and so on (Eq. 1) [24].

$$H_2O \xrightarrow{\text{irradiated}} e_{aq}^-, \cdot H, \cdot OH, H_2, H_2O_2, H_3O^+ \cdots\cdots \quad (1)$$

Then, the oxidative ·OH and the reductive ·H were eliminated by $HCOO^-$ with the rate constants of 3.2×10^9 and 2.1×10^8 L·mol^{-1}·s^{-1}, respectively (Eq. 2) [24].

$$HCOO^- + \cdot OH(\cdot H) \rightarrow \cdot CO_2^- + H_2O(H_2) \quad (2)$$

The reducing species, *e.g.*, e_{aq}^-, reduced the precursors $UO_2(CO_3)_3^{4-}$ ions to U(IV) ions. Whereafter, $U(OH)_4$ was generated in the basic aqueous solution, which was transformed to UO_2 via dehydration (Eq. 3).(3)$UO_2(CO_3)_3^{4-} \xrightarrow{e_{aq}^-} U(IV) \xrightarrow{OH^-} U(OH)_4 \xrightarrow{-H_2O} UO_2(s)$

It may be the low solubility of $U(OH)_4$ ($pK_{sp} = 52$) [25] that leads to the quick formation of colloidal nanoparticles and the following aggregates.

In the literature, hollow spheres were always synthesized with the assistance of hard templates (*e.g.*, silica spheres and polystyrene spheres) and soft templates (*e.g.*, normal micelles, block copolymer micelles, and (micro) emulsion droplets) [15]. However, in our experiments, no normal additive or template was added. It is noteworthy that H_2 molecules are generated by the radiolysis of water (Eq. 1) and the hydrogen abstraction reaction between ·H and $HCOO^-$ (Eq. 2) in the irradiation course. A higher $HCOONH_4$ concentration and the extending of irradiation time favor the generation of H_2. Because the diameter and wall thickness increase continuously and the cavity diameter does not change obviously with the prolonging of irradiation after the formation of hollow nanospheres, Ostwald ripening may play a minor role if any. Therefore, it can be assumed that the hollow nanospheres are a result of the assemblies of nanoparticles around the gas-water interface of the nano-sized H_2 gas bubbles generated *in situ* [18,19], which is shown in Scheme 1.

4. Conclusion

Hollow nanospheres (ϕ: 30–50 nm, wall thickness: 8–15 nm, and cavity diameter: 10–20 nm), consisted of UO_2 nanoparticles (ϕ: 3–5 nm), were successfully obtained by the radiolytic reduction of AUC in the $HCOONH_4$ aqueous solution. A higher $HCOONH_4$ 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 UO_2 nanoparticles around the gas-water interface of the nano-sized H_2 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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