

## Supporting Information:

### Synthesis of Colloidal Uranium-Dioxide Nanocrystals

Huimeng Wu, Yongan Yang, and Y. Charles Cao\*

Department of Chemistry, University of Florida, Gainesville, FL 32611

Fax: 1-352-392-0588; cao@chem.ufl.edu

#### 1. Chemicals

Uranyl(VI) acetylacetonate (UAA, 99%) was purchased from STREM Chemicals. 1-Octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OAm, 70%), 4-dimethylaminopyridine (DMAP, 99%), *p*-toluenesulfonic acid monohydrate (TA, 98%), and *N,N'*-diisopropyl carbodiimide (DIPC, 99%) were purchased from Aldrich. All the other solvents were purchased from Fisher Scientific International Inc.

#### 2. Synthesis of 5.4-nm UO<sub>2</sub> nanocrystals

UAA (187 mg, 0.4 mmol) was added into a three-neck flask with ODE (1.0 g) and OA (1.0 g). The mixture solution was heated to 150 °C at a rate of 50 °C/min and a brown transparent solution was obtained under stirring. After the solution was cooled to room temperature, OAm (1.0 g) was added. The resulting mixture solution was then degassed at 100 °C for 10 min. Under Ar flow and with stirring, the reaction mixture was heated to 295 °C at a rate of 35 °C/min. The reaction solution was aged at the same temperature for 5 min, and then the solution was cooled to room temperature. Nanocrystals were precipitated from the reaction solution by adding a mixture of hexane and acetone (1:4). The black precipitate was re-dispersed in hexane, and the nanocrystals were further purified by repeated precipitation of hexane solutions with acetone twice. The resulting nanocrystals can be easily dispersed into non-polar organic solvents such as toluene and hexane. The typical reaction yield is about 78%. Without size selective separation, the resulting nanocrystals have a diameter of 5.4 nm with a standard deviation of 2.6%.

#### 3. Reaction-yield determination

The reaction yield of UO<sub>2</sub> nanocrystal synthesis was obtained by Formula 1:

$$Y = \frac{P}{R} \quad \dots\dots \text{Formula 1}$$

(Y: reaction yield, P: moles of UO<sub>2</sub> in the total nanocrystal products, and R: moles of UAA).

The moles of UO<sub>2</sub> units in the total products (P) were calculated using Formula 2.

$$P = \frac{W \times Q}{MW} \quad \dots\dots \text{Formula 2}$$

(W: total weight of product, Q: weight percentage of UO<sub>2</sub> in the nanocrystals, and MW: the

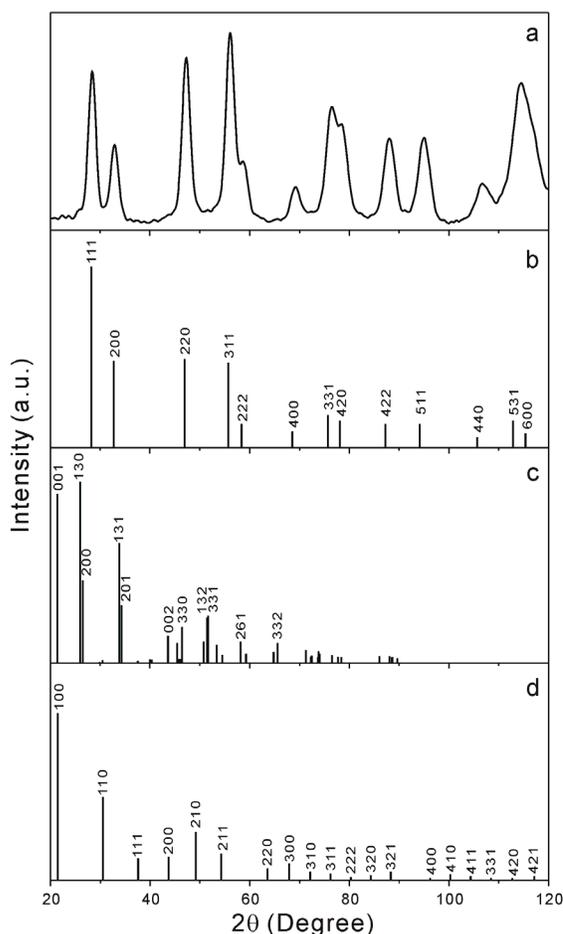
formula weight of  $\text{UO}_2$ ).

The weight percentage of  $\text{UO}_2$  in the nanocrystals (Q) was determined using thermogravimetry analysis (TGA) through measuring the weight change due to loss of organic ligands on the nanocrystal surface.

In the experiments to determine the effect of OA/OAm ratio, we found that the reaction yield was not significantly changed ( $78 \% \pm 5.0 \%$ ) with the change of the OA/OAm ratio from 0.33 to 3.0.

### 3. XRD measurements of $\text{UO}_2$ nanocrystals

Powder X-ray diffraction patterns were measured on a Philips PW 3720 X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation. Approximately 20 mg of nanocrystals were dispersed in 0.5 ml of toluene. Then the solution was deposited onto a low-scattering quartz plate, and toluene was evaporated under air overnight.



**SI-Figure 1.** (Panel a) illustrates XRD pattern of  $\text{UO}_2$  nanocrystals. The standard diffraction peak positions and relative intensities are indicated for the bulk and pure-phased face-centered cubic  $\text{UO}_2$  (panel b),<sup>1</sup> for orthorhombic  $\text{U}_3\text{O}_8$  (panel c),<sup>2</sup> and for primitive cubic  $\text{UO}_3$  (panel d).<sup>3</sup>

The Bragg diffractions of the uranium-oxide nanocrystals can be indexed to nearly all of those of the standard bulk face-centered cubic  $\text{UO}_2$ . These Bragg diffractions are quite distinguishable from those Bragg diffractions of bulk  $\text{UO}_3$  or  $\text{U}_3\text{O}_8$  structures.

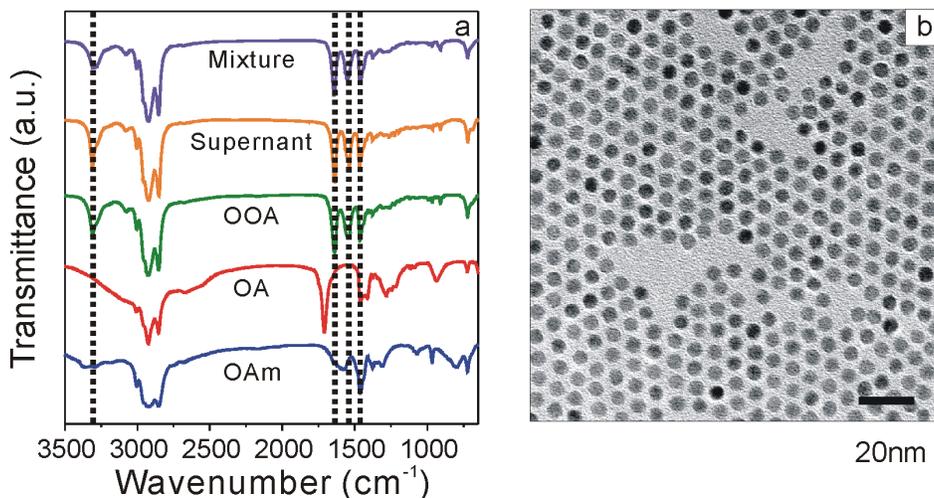
### 4. The effect of additional mixture of OA and OAm with a molar ratio of 1:1

To explore this effect, we carried out a series of syntheses in which various amounts of the OA-OAm mixture were added into a 5.4-nm- $\text{UO}_2$  synthesis (UAA, 0.04 mmol; OA, 1.0g; and OAm, 1.0g). These synthetic experiments were carried out according to the procedure described in the

original synthesis (Page S-1). UAA (187 mg, 0.4 mmol) was added into a three-neck flask with ODE (1.0 g) and OA (1.0 g). The mixture solution was heated to 150 °C at a rate of 50 °C/min and a brown transparent solution was obtained with stirring. After the solution was cooled to room temperature, OAm (1.0 g) and various amounts of the OA/OAm mixture were added into the solution. The resulting solution was then degassed at 100 °C for 10 min. Under Ar flow and with stirring, the reaction mixture was heated to 295 °C at a rate of 35 °C/min. The reaction solution was aged at the same temperature for 5 min, and then the solution was cooled to room temperature. Nanocrystals were precipitated from the reaction solution by adding a mixture of hexane and acetone (1:4).

## 5. IR measurements

IR spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrometer. The specimens were prepared by directly loading hot aliquots (0.1 mL) of a reaction mixture onto a NaCl window, respectively. The IR spectrum of a reaction solution taken at the final stage of the typical synthesis shows two characteristic vibration peaks for alkyl-oleamide: 1645  $\text{cm}^{-1}$  for C=O stretching and 1552  $\text{cm}^{-1}$  for N-H bending (SI-Figure 2a), thus indicating the formation of N-(*cis*-9-octadecenyl)-oleamide (OOA). Note that the amount of  $\text{UO}_2$  nanocrystals is only about 2 % of the amount of the solvent (OA, OAm and ODE), thus the IR signals from  $\text{UO}_2$  nanocrystals were buried in the IR signals from the solvents.



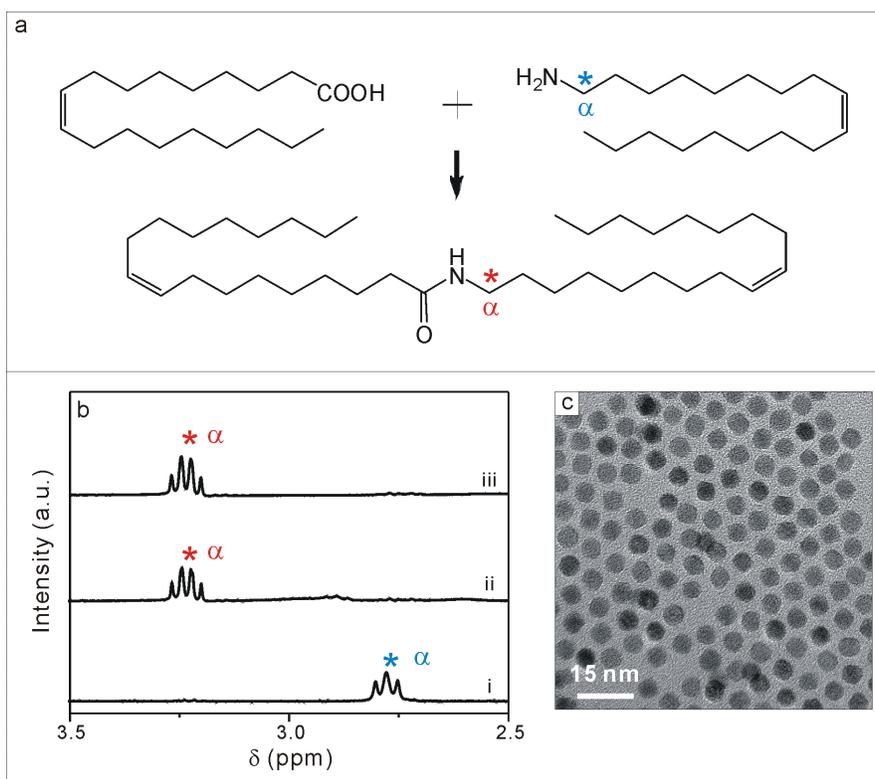
**SI-Figure 2.** (Panel a) IR spectra of a reaction mixture (in violet) and a supernant solution (in orange) from a typical 5.4-nm- $\text{UO}_2$ -nanocrystal synthesis after the reaction solution was aged at 295 °C for 5 min (in red); OOA (in green); OA (in red); and OAm (in blue). (Panel b) A typical TEM image of the  $\text{UO}_2$  nanocrystals separated from the reaction mixture.

## 6. $^1\text{H-NMR}$ measurements

$^1\text{H-NMR}$  spectra were recorded using a Varian Mercury NMR Spectrometer (300 MHz). The samples were prepared by adding aliquots ( $\sim 0.02$  mL) of reaction mixtures into a deuterated solvent ( $\text{CDCl}_3$ ,  $\sim 0.8$  mL).

$^1\text{H-NMR}$  measurements were used to examine the condensation reaction of OA and OAm in a modified 5.4-nm- $\text{UO}_2$  synthesis. The protons ( $\alpha$ ) on OAm molecules were used as a probe to

monitor the condensation reaction (SI-Figure 3a). After the condensation with OA, the chemical shift of these protons appears in a lower field (SI-Figure 3b). In this modified synthesis, the reaction solution was aged at 200 °C for 20 min, and then the solution was heated to 295 °C at a rate of 30 °C/min. After the solution was aged at 295 °C for 5 min, the solution was cooled to room temperature. Interestingly, the size and size distribution of the final product in this modified synthesis are nearly identical to those of the final product in the typical 5.4-nm-UO<sub>2</sub> synthesis (SI-Figure 2b and 3c). In addition, <sup>1</sup>H-NMR measurements show that the condensation of OA and OAm was nearly complete after the reaction solution was aged at 200 °C for 20 min. However, TEM observation shows that no particle was formed at 200 °C. Taken together, these results suggest that the condensation reaction of OA and OAm can be nearly complete before the nucleation stage of UO<sub>2</sub> nanocrystals starts.

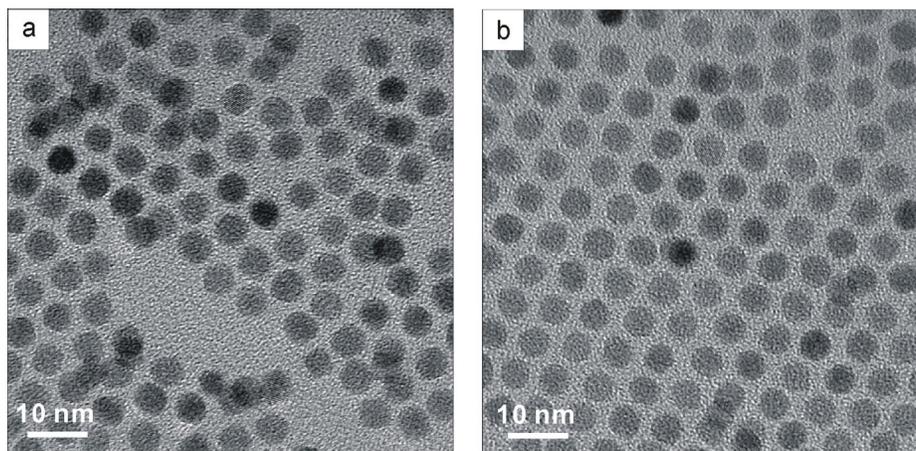


**SI-Figure 3.** (Panel a) illustrates the condensation reaction of OA and OAm. The protons ( $\alpha$ ) are indicated on OAm (in blue), and on OOA (in red). <sup>1</sup>H-NMR spectrum of a reaction mixture was taken from the reaction system when the reaction solution was at 25 °C (panel bi), at 200 °C for 20 min (panel bii), and at 295 °C for 5 min (panel biii). TEM image of the nanocrystals separated from the sample that was taken from the reaction system after the reaction solution was aged at 295 °C for 5 min (panel c).

## 7. The effect of water

To examine the effect of water, a synthesis was carried out according to the protocol described in the 5.4-nm-UO<sub>2</sub> synthesis (Page S-1). In addition, water (1.0 mL) was slowly added into the reaction solution after the temperature of the reaction solution was higher than 200 °C during heating. It took about 10 min to add the water. After the water was added, the reaction

temperature was about 260 °C. Then the reaction solution was continuously heated to 295 °C. Afterward, the solution was further aged at 295 °C for 5 min, and then the solution was cooled to room temperature. A TEM image of the final nanocrystals from this synthesis is shown in SI Figure 4a. The size of the final particles is similar to those made in the typical 5.4-nm-UO<sub>2</sub> synthesis (SI Figure 4b). This result indicates that water does not have significant effect on the nanocrystal formation.



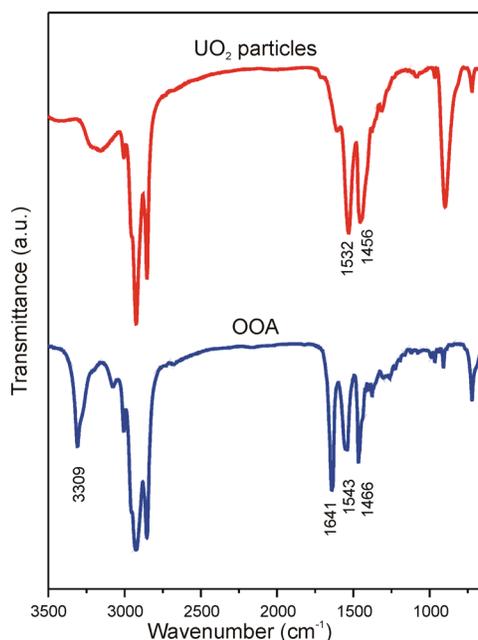
**SI-Figure 4.** TEM images of the particles made in the synthesis with water added (panel a); and in a typical 5.4-nm-UO<sub>2</sub> synthesis (panel b).

### 8. The effect of N-(*cis*-9-octadecenyl)-oleamide (OOA)

To explore this effect, we carried out a series of syntheses in which various amounts of OOA were added into a 5.4-nm-UO<sub>2</sub> synthesis system (UAA, 0.04 mmol; OA, 1.0g and OAm, 1.0g). These synthetic experiments were carried out according to the procedure described in the original synthesis (Page S-1). UAA (187 mg, 0.4 mmol) was added into a three-neck flask with ODE (1.0 g) and OA (1.0 g). The mixture solution was heated to 150 °C at a rate of 50 °C/min, and a brown transparent solution was obtained with stirring. After the solution was cooled to room temperature, OAm (1.0 g) and various amounts of OOA were added into the solution. The resulting solution was then degassed at 100 °C for 10 min. Under Ar flow and with stirring, the reaction mixture was heated to 295 °C at a rate of 35 °C/min. The reaction solution was aged at the same temperature for 5 min, and then the solution was cooled to room temperature. Nanocrystals were precipitated from the reaction solution by adding a mixture of hexane and acetone (1:4).

### 9. IR measurements of purified UO<sub>2</sub> nanocrystals and OOA

IR measurements show that oleate anions were bonded onto the surface of UO<sub>2</sub> nanocrystals (SI-Figure 5). The asymmetric vibration band of C=O was at 1531 cm<sup>-1</sup>, and the symmetric vibration band was at 1456 cm<sup>-1</sup>. The wavenumber separation between the asymmetric and symmetric bands was 75 cm<sup>-1</sup>. Such a small wavenumber separation indicates that oleate anions were bonded onto UO<sub>2</sub> nanocrystals through chelating bidentate interaction.<sup>4,5</sup> Moreover, the IR spectrum of UO<sub>2</sub> nanocrystals was quite distinguishable from the IR spectrum of OOA (SI-Figure 5). This result clearly shows that OOA was not on the surface of UO<sub>2</sub> nanocrystals.

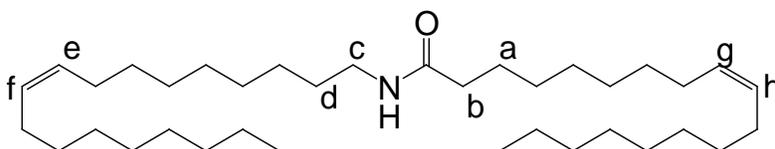


**SI-Figure 5.** IR spectrum of purified UO<sub>2</sub> nanocrystals (in red ) and OOA (in blue).

## 10. Synthesis of OOA

A. 4-(N,N-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared by mixing THF solutions of 4-dimethylaminopyridine (2 M, 50 mL) and p-toluenesulfonic acid monohydrate (2 M, 50 mL) at room temperature under stirring. The resulting precipitate was filtered and dried under vacuum.

B. OA (3.1 g, 0.011 mol), OAm (2.7 g, 0.010 mol), and DPTS (3.7 g, 0.013 mol) were added into a flask with CH<sub>2</sub>Cl<sub>2</sub> (25 mL) at room temperature under stirring. After 10 min, N,N'-diisopropyl cabodiimide (1.9 g, 0.015 mol) was added, and the reaction solution was further stirred for 5 hours. Then the reaction solution was diluted by CH<sub>2</sub>Cl<sub>2</sub> (30 mL), and the reaction solution was extracted by water (50 mL) three times to remove DPTS. The crude product was purified by flash chromatography. Yield: 70%. <sup>1</sup>H-NMR (300-MHz, CDCl<sub>2</sub>): δ 0.887 (t, J=6.6 Hz, 6H), 1.27 (m, 42H), δ<sub>a</sub> 1.49 (m, J=6.6Hz, 2H), δ<sub>d</sub> 1.63 (m, 2H), 2.01(m, 8H), δ<sub>b</sub> 2.15 (t, J=7.5Hz, 2H), δ<sub>c</sub> 3.24 (m, 2H), δ<sub>efgh</sub> 5.35 (m, 4H).



## Reference

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