Synthesis and Preservation of Graphene-Supported Uranium Dioxide Nanocrystals

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Abstract

Graphene-supported uranium dioxide (UO_2) nanocrystals are potentially important fuel materials. Here, we investigate the possibility of synthesizing graphene-supported UO_2 nanocrystals in polar ethylene glycol compounds by the polyol reduction of uranyl acetylacetonate under boiling reflux, thereby enabling the use of an inexpensive graphene precursor graphene oxide into a one-pot process. We show that triethylene glycol is the most suitable solvent with an appropriate reduction potential for producing nanometer-sized UO_2 crystals compared to monoethylene glycol, diethylene glycol, and polyethylene glycol. Graphene-supported UO_2 nanocrystals synthesized with triethylene glycol show evidence of heteroepitaxy, which can be beneficial for facilitating heat transfer in nuclear fuel particles. Furthermore, we show that graphene-supported UO_2 nanocrystals synthesized by polyol reduction can be readily stored in alcohols, impeding oxidation from the prevalent oxygen in air. Together, these methods provide a facile approach for preparing and storing graphene-supported UO_2 nanocrystals for further investigation and development under ambient conditions.

1. Introduction

Many consider further development of nuclear power to be essential for the sustained development of our society using low-carbon baseload energy supplies [1, 2]. Currently, there are 71 reactors under construction in the world. Future nuclear reactors are expected to be more accident-tolerant, modularized for rapid assembly and mobility, and operated with fuels that are easy to disassemble for reprocessing (i.e., removal of radioactive fission products and extraction of fissile materials) [3]. To provide designers of future reactors with fuel options superior to conventional bulk uranium dioxide (UO_2), research has begun to focus on UO_2 nanocrystals for potential benefits that include a lowered sintering temperature [4] thanks to melting-point suppression and the increased kinetics of UO_2 dissolution in reprocessing [5] thanks to the increase of specific surface area. In addition, using UO_2 nanocrystals presents a new opportunity for blending UO_2 with highly conductive nanomaterials to provide novel solutions for the long-standing issue regarding uranium dioxide's low thermal conductivity [6, 7]. Recent simulations have shown that blending UO_2 with 10% of graphene by volume can increase the thermal conductivity of fuel particles by more than 30%, which can not only increase the rate of energy extraction but also improve reactor safety by lowering the fuel operating temperature [8].

A well-established route for synthesizing graphene-supported metal and metal oxide nanocrystals uses graphene oxide as a graphene precursor [9-11]. Graphene oxide can be prepared as single-layer carbon sheets from natural graphite by chemical exfoliation that breaks apart π - π stacking [12-15]. Because of the use of strong acids and oxidants in chemical exfoliation, graphene oxide contains a rich number of hydroxyl, carboxyl, and epoxyl surface groups, making it hydrophilic and dispersible in polar solutions [16, 17]. The majority of the oxygen-containing functional groups can be removed upon reduction, which converts

carboxylate, hydroxyl, and epoxyl groups back to sp^2 carbon, creating graphene sheets (formally known as reduced graphene oxide to be distinguished from graphene prepared from bottom-up synthesis) [18, 19]. The reduction of graphene oxide can be incorporated into the synthesis of nanocrystals in a one-pot process when polar solvents are used to accommodate the dispersion of graphene oxide, producing graphene-supported nanocrystals [10, 20, 21].

Previously, UO_2 nanocrystals having a nominal diameter of 10 nm or less have been made by employing ferrous [22], amine-assisted [23-25], radiolytic [4, 26], electrochemical [27], and microbial mediated reduction of U(VI) salts [28-30]. Among the existing methods, the thermal reduction of uranyl acetylacetonate ($UO_2(C_5H_7O_2)_2$) by oleylamine is a scalable chemical method carried out in nonpolar solvents such as octadecene, which offers good control of nanocrystal structure, size, and morphology [23, 25]. Because UO_2 nanocrystals, like most oxide nanoparticles, are hydrophilic, synthesis in nonpolar solvents requires the use of capping agents such as oleic acid to give the nanocrystals a hydrophobic surface in order to stabilize them against aggregation in nonpolar solvents. In principle, it is possible to switch nanocrystal surface wettability from being hydrophobic to being hydrophilic through ligand exchange so that they can be dispersed in polar solvents [31]; however, successful experimental protocols are not yet available for UO_2 nanocrystals. Obviously, using graphene oxide as the precursor for preparing graphene-supported UO_2 requires a synthetic route performed in polar solvents.

A widely used synthetic method for preparing metal oxide nanocrystals, such as those made of iron oxide and copper oxide, is polyol reduction in ethylene glycols (EGs; $(CH_2)_{2n}O_{n-1}(OH)_2$, $n = 1, 2, 3, 4 \dots$) [32-34]. EG compounds are mild reductants that can be oxidized to aldehydes, then carboxylic acids, and eventually carbon dioxide and protons [35-37]. They have sufficient reducing potential to transform graphene oxide to graphene [9-11]; however, whether

the polyol reduction method can be used to prepare graphene-supported UO_2 nanocrystals has not been investigated. One of the two objectives of this study is, therefore, to determine the possibility of and conditions for preparing graphene-supported UO_2 nanocrystals by polyol reduction in a one-pot operation. The second objective of this study is to determine how to handle the resulting graphene-supported UO_2 nanocrystals under ambient conditions so that they can be stored and studied before U(IV) is oxidized back to U(VI) .

2. Material and Methods

All chemicals of reagent grade were purchased from Sigma Aldrich except as otherwise specified. Deionized (DI) water was generated on site using a Millipore system.

Synthesis of Uranyl Acetylacetonate. 3.26 g $\text{UO}_2(\text{NO}_3) \cdot 2\text{H}_2\text{O}$ (depleted uranium) was first dissolved into 12.5 mL DI water. Under stirring, 25 mL water, 1.35 g acetylacetonate, and 13.5 mL NaOH aqueous solution (0.54 mol mL^{-1}) were added to the solution. The mixture was heated to 60°C and held at this temperature for 5 min. After the solution was cooled to the ambient temperature, yellow-colored precipitates were collected with a filter paper, washed with water three times, and dried in a vacuumed desiccator. The yield of $\text{UO}_2(\text{acac})_2$ from uranium nitrate precursor was approximately 85%.

Synthesis of UO_2 Nanocrystals. 0.1 mmol uranyl acetylacetonate was first dissolved in 4 mL ethylene glycol. Four different EG solvents with different chain lengths were investigated as solvent and reducing agent including monoethylene glycol (MEG, $\text{C}_2\text{H}_6\text{O}_2$), diethylene glycol (DEG, $\text{C}_4\text{H}_{10}\text{O}_3$), triethylene glycol (TEG, $\text{C}_6\text{H}_{14}\text{O}_4$), and polyethylene glycol (PEG, $\text{C}_8\text{H}_{18}\text{O}_5$). The mixture was heated to 140°C for 20 minutes under vacuum for degassing. The temperature was then ramped to the boiling point (197°C for MEG, 244°C for DEG, 285°C for TEG, and 330°C for PEG) [38] within 20 min under argon protection. The mixture was refluxed for 20

min. After the mixture was cooled to the ambient temperature, the product was precipitated with acetone and purified with a mixture of water and acetone (4:1 volume ratio) or a mixture of ethanol and hexane (3:1 volume ratio) and then re-dispersed in either water or ethanol. The product was then washed and re-dispersed in cyclohexene. To stabilize UO_2 nanocrystals against aggregation in microscopic analysis, 0.5 mmol polyvinylpyrrolidone ($(\text{C}_6\text{H}_9\text{NO})_{257}$, PVP), citric acid, or ascorbic acid was added to the mixture as capping agent. Nanocrystals stabilized with oleic acid were prepared similarly by adding 0.5 mmol oleic acid. To examine the effect of water, 100 μL of IGEPAL (octylphenoxy poly(ethyleneoxy)ethanol) was added to 5 mL cyclohexene suspension with 5 mL DI water.

Synthesis of Graphene-Supported UO_2 . Single-layer graphene oxide sheets were prepared by the chemical exfoliation of natural graphite powder according to the modified Hummers' method [39]. To do so, 1-g graphite was mixed with 1-g sodium nitrate, 46-mL sulfuric acid, and 6-g potassium permanganate in an ice bath. The mixture was then transferred to a water bath maintained at 35 $^\circ\text{C}$ and stirred for 30 min. DI water was added into the mixture to raise the temperature to 98 $^\circ\text{C}$. After 40 min of reaction, hydrogen peroxide was added to the mixture to stop the reaction. Graphene oxide was then collected by centrifugation, washed repeatedly with water, and dried under vacuum at 60 $^\circ\text{C}$ for 3 days. To synthesize graphene-supported UO_2 , graphene oxide powder was first dispersed into water to create a 10 mg mL^{-1} solution, 200 μL of which was then added to the TEG solution with $\text{UO}_2(\text{acac})_2$ before performing boiling reflux (i.e., except the addition of graphene oxide, other conditions are the same as those used to synthesize unsupported UO_2 nanocrystals).

Material Characterization. UO_2 nanocrystals were characterized using a variety of microscopic and spectroscopic techniques. The morphologies and sizes of UO_2 nanocrystals and

their oxidation products were examined using transmission electron microscopy (TEM; FEI Titan 80-300), scanning electron microscope (FEI Magellan 400), atomic force microscope (Park XE-70), powder X-ray diffraction (XRD; Bruker D8 Advance Davinci), and X-ray photoelectron spectroscopy (PHI VersaProbe II). High-resolution TEM (HRTEM) images were taken with UO_2 nanocrystals to elucidate shape and crystallinity. Molecular models of nanocrystals were created using the commercial software CrystalMarker[®].

3. Results

3.1. Synthesis of Graphene-Supported UO_2

The most important condition for synthesizing graphene-supported UO_2 is the selection of an ethylene glycol compound with an appropriate chain length. We investigate the selection of EG chain length in the absence of graphene oxide. Unsupported UO_2 nanocrystals are synthesized by the reduction of uranyl acetylacetonate in the EG solution heated to boiling reflux. As outlined in Figure 1, the synthesis protocol includes two main steps. First, uranyl (UO_2^{2+}) nitrate aqueous solution is mixed with acetylacetonate to produce $\text{UO}_2(\text{acac})_2$, which is collected by precipitation [40, 41]. Second, $\text{UO}_2(\text{acac})_2$ is dissolved in an ethylene glycol solvent in a one-pot operation. The reactive solution is heated to boiling reflux under argon protection. The boiling point of the EG solvent increases with the chain length [38].

Figure 2 shows the synthetic products prepared with the four EG solvents. As the aliphatic chain of ethylene glycol increases in length, the color of the product solution changes from orange to yellow, black, and then grey (Figure 2a – d). The yellow-to-black color transition is a well-known characteristic associated with the U(VI)-to-U(IV) reduction. The observation of

the gradual color change with the increasing EG chain length indicates that the reduction of U(VI) is incomplete with MEG and DEG but complete with TEG and PEG. Close examination using transmission electron microscopy shows that nanowires are formed with MEG (Figure 2e) while nanoparticles are formed with DEG, TEG, and PEG (Figure 2f – h). Further analysis using powder X-ray diffraction indicates that the nanowires produced by MEG are ianthinite ($\text{U}(\text{UO}_3)_5\text{O}_7 \cdot 10\text{H}_2\text{O}$) [42], a U(VI) oxide hydrate (Figure 2i). For the sample synthesized with DEG, the characteristic diffraction maxima for UO_2 become prominent, confirming the formation of UO_2 nanocrystals. However, the presence of equally prominent reflections from ianthinite (e.g., 004 at 12°) indicates the existence of a significant amount of ianthinite as an impurity. The reflections for ianthinite become indiscernible for the TEG product, suggesting that the amount of U(VI) impurity has become negligible (Figure 2j). The XRD patterns for the nanocrystals match well with those for bulk UO_2 (i.e., uraninite) [43], although the peaks are broadened in the synthetic sample due to diminished particle size (as expected). Compared to the product synthesized using TEG, the sample obtained from PEG shows broad reflections with barely discernible peaks, suggesting that the sample lacks long-range ordering and thus is amorphous in nature. The formation of amorphous materials is an indication that the reducing power of PEG is too potent, which creates a high level of supersaturation favouring instantaneous nucleation without much crystal growth [21]. These results suggest that TEG is the most appropriate solvent and reducing agent for producing UO_2 nanoparticles (see Discussion for further explanation).

Under TEM, nanocrystals made with TEG are identifiable as particles around 3 nm in diameter (Figure 2g). The lattice fringes of the nanocrystals, although visible, are not sharp, which suggests the presence of a relatively high percentage of defects. The defect concentration

can be greatly reduced by adding PVP and preheating TEG to reflux temperature, which provides an improved temperature control. As shown in Figure 3a, nanocrystals synthesized with preheated TEG have sharp lattice fringes. Nanocrystals shown in Figure 2g and 3a are slightly aggregated when they are deposited on the TEM grid. The aggregation of nanoparticles often occurs during sample preparation because the evaporation of solvent creates capillary force that pulls nanocrystals together. Evaporation-induced aggregation can be prevented by replacing PVP with either citrate or ascorbate, which provides improved steric repulsion that can resist capillary pulling [44]. Citric acid is thermally stable at the synthesis temperature [45], while ascorbic acid likely decomposes into products containing carboxylate formed by opening the lactone ring [46]. As shown in Figure 3b and c, citrate and ascorbate-capped nanocrystals exhibit a more uniform and isolated distribution on TEM grids, which offers the opportunity for accurately measuring the sizes of the nanocrystals. According to measurements made with 228 isolated nanocrystals, their nominal diameter is $d_{\text{TEM}} = 2.8(\pm 0.3)$ nm by fitting the histogram with a Gaussian function, as shown in Figure 3d. This value agrees well with the value estimated from XRD peak broadening. According to Scherrer's Equation, $d = 0.89 \lambda \beta^{-1} \cos^{-1} \theta$ where Cu K α X-ray wavelength $\lambda = 1.54$ Å.[47] For the {111} peak with diffraction angle $\theta = 14.00(\pm 0.03)$ deg and broadening at half the maximum intensity $\beta = 0.050(\pm 0.004)$ radian, $d_{\text{XRD}} = 2.85(\pm 0.23)$ nm. According to these estimates, the coefficient of variation is computed at 8 – 10%, suggesting the nanocrystal population has a near mono-dispersed size distribution [48-50].

To synthesize graphene-supported UO₂, single-layer graphene oxide is added to TEG with uranyl acetylacetonate. Under boiling reflux, TEG reduces both uranyl acetylacetonate and graphene oxide. As shown in Figure 4a, nano-sized UO₂ deposits are formed uniformly on graphene sheets, suggesting a switch of crystallization mechanism from homogenous to

heterogeneous nucleation. As expected, reduction removes a significant amount of oxygen functional groups on graphene oxide (61% $\rightarrow$ 34%; Figure S1) without changing the overall sheet thickness (i.e., 1.7 nm; Figure S2).[51] XRD confirms that the deposits are UO_2 , as shown in Figure 4b. Compared to the XRD patterns shown in Figure 2k, UO_2 deposited on graphene shows an intensified (002) reflection. The lack of a distinctive peak at $2\theta = 26.6^\circ$ corresponding to the 002 reflection of graphite[52] confirms that graphene sheets are made of single layers of carbon without a significant amount of multi-layer sheets consisting of π - π stacking. The lack of peaks around $2\theta = 11^\circ$ suggests that there is also no stacking of graphene oxide sheets through water intercalation. As shown in Figure 4c, high resolution TEM reveals that UO_2 on graphene has a shape of parallelogram. Statistical analysis estimates that the parallelograms have a nominal diameter of $2.49(\pm 0.46)$ nm, as illustrated in Figure 4d.

3.2. Preservation of Graphene-Supported UO_2

An important challenge of synthesizing, handling, and storing uranium dioxide is the oxidation of UO_2 by the omnipresence of ambient oxygen (O_2). Compared to bulk materials, the oxidative transformation of UO_2 is particularly rapid for nanocrystals having high surface-to-volume ratios that can promote surface reaction with O_2 . As shown in Figure 5a – c, freshly prepared UO_2 nanocrystals dispersed in water and exposed to air are transformed to nanowires in two days even without stirring. The nanowires are further oxidized into micrometre-sized disks in approximately a week, with the latter morphology typical for schoepite and other uranyl oxide hydrates. The physical transformation is accompanied by the color change of the aqueous suspension: from the characteristic dark grey of U(IV) to the bright yellow of U(VI). XRD reveals that the nanowires and microdisks are both crystalline materials with almost identical diffraction patterns, as shown in Figure 5g and h. Based on the shapes of these crystals, we

identify the structure of nanowires as ianthinite and that of microdisks as schoepite($(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}\cdot 12\text{H}_2\text{O}$) [53]. The same oxidative transformation is also observed for UO_2 deposited on graphene sheets (Figure S3).

Structures of uraninite, ianthinite, and schoepite are shown in Figure 5i. Uraninite has a fluorite structure, in which each U(IV) cation is bonded to 8 neighbouring oxygen atoms as a result of the hybridization of one $6d$ and three $5f$ orbitals. As oxidation occurs, a portion of the 8-coordinated U(IV) atoms in uraninite is transformed into 10-coordinated U(VI) atoms, forming ianthinite. Ianthinite has a layered structure, in which a layer completely consisting of decahedral U(VI) alternates with a layer consisting of a 5:1 mixture of decahedral U(VI) and octahedral U(IV). The layers are stacked together with the intercalation of water molecules. All U(IV) atoms are oxidized to U(VI) in schoepite with further addition of intercalated water. Compared to uraninite, ianthinite and schoepite are in themselves not good choices for nuclear fuel material because of the reduced mass fraction of uranium and the presence of large amounts of water; however, a simple thermal treatment to 450 °C can convert both materials to uranium trioxide (UO_3), a common UO_2 precursor [54].

The fact that intercalated water is an essential structural component in both ianthinite and schoepite suggests that disrupting contact with water can be a potentially effective strategy for preventing UO_2 nanocrystals from being oxidized in the presence of ambient oxygen. To test this hypothesis, we prepare oleic acid-capped UO_2 nanocrystals and disperse them in cyclohexene, which is immiscible with water. The resulting suspension has a black color, as shown in Figure 6a. Pure oxygen gas is then bubbled into the suspension for 9 h. As shown in Figure 6b, the color of the suspension remains black, indicating the lack of significant UO_2 oxidation. We then mix half of the suspension with an equal volume of water. Due to the density difference between the

two liquids, the UO_2 suspension floats on top of the water, as shown in Figure 6c. After 10 days of exposure to air, the color of the suspension remains black, confirming an insignificant degree of oxidation of UO_2 . The surfactant IGEPAL is then added to facilitate the dispersion of water as microscopic droplets into cyclohexene upon shaking. After 5 days, the suspension turned yellowish and opaque, as shown in Figure 6d. XRD confirms the formation of schoepite, as shown in Figure 6e.

The experiments described above verify that water is a required reactant for UO_2 oxidation in our systems over the timeframe of our experiments. This result encourages us to examine whether graphene-supported UO_2 nanocrystals dispersed in alcohols such as methanol, ethanol, and propanol have longevity in storage. As shown in Figure 7a – c, graphene-supported UO_2 stored in ethanol shows the same XRD pattern as nano-sized UO_2 after 8 days in contact with air. The preservation of UO_2 nanocrystals can be attributed to limiting access to water rather than reducing the concentration of dissolved oxygen because the solubility of oxygen in ethanol is greater than that in water.[55] After extended storage of 5 months, the X-ray diffraction pattern contains a new peak at $2\theta = 22.8(\pm 2.4)^\circ$, as shown in Figure 7d. This peak may be attributed to the 001 reflection of triuranium octoxide ($\alpha\text{-U}_3\text{O}_8$) [56], suggesting that oxidation has proceeded through a different reaction pathway in the absence of water. As shown by the inset of Figure 7, $\alpha\text{-U}_3\text{O}_8$ contains both U(VI) and U(IV) with a 2:1 molar ratio. Normally, the oxidation of UO_2 to U_3O_8 through intermediates such as U_4O_9 and U_3O_7 requires elevated temperatures (e.g., 250 °C) [56], which should be sluggish at ambient temperatures.

4. Discussion

4.1. Reduction Potential of EG Compounds

In the process of developing the polyol reduction method for graphene- UO_2 synthesis, we have shown that the selection of an appropriate EG chain length is important for success (cf. Figure 2). Although EG compounds have been widely used to prepare metallic and oxide nanoparticles, the selection of the appropriate chain length and synthetic conditions is usually made through trial and error. To understand the dependence of reductive potential on the EG chain length, we now compare our results with those from reports describing the synthesis of other metallic and oxide nanocrystals using polyol reduction at or near reflux conditions and in the absence of promoter chemicals such as sodium hydroxide.

Figure 8 plots the standard reduction potentials of nanocrystal synthesis reactions against the EG chain length [32-34, 57-61]. Here, the reduction potentials have been adjusted from the values at the standard condition to those at the temperatures under which synthesis is performed (see Table S1 for literature data). It is not surprising that nanocrystals of noble metals such as iridium (Ir; purple) [57], platinum (Pt; pink) [57], gold (Au; brown) [57], palladium (Pd; red) [57], silver (Ag; blue) [58], and ruthenium (Ru; lime) [57, 59], because of their high reduction potentials, are readily synthesized using the least reactive MEG. Even for transition metals such as iron (Fe; green), all EG compounds can reduce ferric iron (Fe^{3+}) to magnetite (Fe_3O_4) containing a mixture of ferric and ferrous iron [32, 33]. The reduction of copper (Cu; cyan) from its divalent cation (Cu^{2+}) to copper oxide (Cu_2O) with MEG has also been reported [34]. For nickel (Ni; grey), which has a negative reduction potential, the synthesis of metallic nanocrystals can only be performed using TEG and PEG [60, 61]. This is similar to the reduction of uranium (yellow) observed in our experiments, which has a potential near zero in the weakly acidic EGs

($pK_a = 15$) [62]. A quantitative relationship may be obtained through the regression between the lowest potential of the synthesis reaction and the EG chain length (i.e., the highest point for each n value), giving an approximate maximum reduction potential of $1.30(\pm 0.77)$ V for MEG and a decrease of $0.40(\pm 0.28)$ V for the increase of every ethylene unit.

4.2. Heteroepitaxy of UO_2 on Graphene

Further analyses of the lattice structures of unsupported and graphene-supported UO_2 suggest that heteroepitaxy is likely the mechanism responsible for UO_2 growth on graphene. An unsupported UO_2 nanocrystal synthesized in TEG is visualized using high resolution TEM (HRTEM) in Figure 9a. The HRTEM image shows that the nanocrystal has a face-centred close (FCC) packing structure and is seated with the (110) plane facing upward and almost perfectly perpendicular to the electron beam. The orientation of the nanocrystal is determined by comparing the Fast Fourier transform (FFT) of the HRTEM image, as presented in Figure 9b, with the electron diffraction pattern of a UO_2 standard [43]. Using CrystalMaker[®], we have identified the prominent electron diffraction spots of the nanocrystal, several of which are marked in Figure 9c.

The individual nanocrystal in Figure 9a is further analyzed with the assistance of a molecular model. As shown in Figure 9c, the molecule, which is terminated with oxygen atoms on the surface, has the shape of a truncated octahedron. The molecule consists of 281 uranium atoms and 792 oxygen atoms and has a mass $m = 132 \times 10^{-21}$ g. According to the uraninite density $\rho = 1.01 \times 10^7$ g m⁻³, [43] the model molecule has a volume of 1.3×10^{-26} m³ and a nominal diameter of 2.8 nm. To aid comparison, we have marked the distinctive patterns of seven uranium atoms in the centre of the (110) plane on both the HRTEM image and the molecular model in Figures 9a and c, which match perfectly. We have also marked the edge of

the model molecule in the HRTEM image with dashed lines in Figure 9a. These results suggest that UO_2 nanocrystals suspended in alcohols are likely in the shape of a truncated octahedron, as illustrated in Figure 9d. Several uranium atoms of the nanocrystal are located outside the model boundary, suggesting that the nanocrystal surface can be rugged on the atomic level.

A close examination of UO_2 nanocrystals deposited on graphene, as shown in Figure 10a, indicates a preferred orientation and thus possible heteroepitaxy. FFT performed on representative crystals show that the nanocrystals still have the FCC structure but that they are always seated with the $[110]$ zone axis perpendicular to the underlying graphene sheet. As shown in Figure 10b – d, the diffraction spots of individual crystals (see Figure S4 for the diffraction pattern of the entire field) are formed by the reflections of $\{111\}$ and $\{002\}$ planes. Three types of rotational transformations are found among the nanocrystals, consistent with the 3-fold symmetry of graphene, as demonstrated in the HRTEM of Figure 10e, which shows UO_2 nanocrystals as hexagons with clear lattice fringes. An alternative explanation of the orientation is due to the formation of a network of UO_2 nanocrystals, which connect with one another through specific planes. However, such an explanation is inconsistent with the presence of isolated islands of UO_2 crystals on graphene (cf. Figure 4a and b).

The epitaxial interface between graphene and UO_2 is further modelled in Figure 10f, with U and O atoms on top of the center of the six-member carbon rings. The distance between U and O is 2.37 Å and that between O and O is 2.73 Å. The angles of the hexagonal UO_2 are 109° and 125° , which are identical with the angles shown in the model. Because the distance between two adjacent six-member carbon rings is 2.46 Å and the angles for the six-member carbon rings beneath the hexagonal UO_2 are 120° , the structures of UO_2 and graphene have mismatch on the atomic level, which may have constrained the size of the nanocrystals. Epitaxial linkages with

similar degrees of mismatch have been observed at the interfaces of graphene with ruthenium [63], copper [64], molybdenum sulfide (MoS_2) [65], bismuth selenide (Bi_2Se_3) [66], and gold cyanide (AuCN) [67]. Density functional theory calculations suggest that the interfaces are likely formed by graphene donating π electrons to the overgrowing phases [67]. A distinctive feature of the weak van der Waals bond, compared to the much stronger covalent [68] and ionic [69] bonds, is the preferred formation of islands and nanowires instead of continuous films [70]. This is consistent with the UO_2 islands over graphene observed in our experiments, as shown in Figure 10a. However, the estimation of the size of the mismatch zone at the interface is beyond the scope of this study.

In theory, the hypothesized heteroepitaxial growth mechanism can be validated by comparing the lattice of UO_2 and that of the underlying graphene. To achieve the atomic resolution of a single-layer graphene or graphene oxide, the observation requires a transmission electron aberration-corrected microscope operated under a low beam energy [71]. Although a beam of electrons accelerated at tens to hundreds of kilovolts can provide atomic resolutions in TEM, the actual resolution is restricted by spherical and chromatic aberrations [72]. In addition, single-layer graphene is fragile and can be readily damage by electrons having an energy above 85 keV [73, 74]. In our experiments, the lattice structure of single-layer graphene is not resolved because our instrument is operated energy of 300 keV and not equipped with aberration correction.

5. Conclusions

We have successfully synthesized graphene-supported UO_2 nanocrystals using triethylene glycol as solvent and reductant. We show that UO_2 nanocrystals grow on graphene through heteroepitaxy by forming chemical bonds at the interface, which can be beneficial for facilitating

heat transfer in nuclear fuel particles. We also show that graphene-supported UO_2 nanocrystals can be dispersed in alcohols under ambient conditions to prevent oxidation, providing a convenient strategy for storing and handling reduced uranium nanomaterials in laboratory. Although detrimental to the storage of UO_2 , the oxidative transformation of nanocrystals, in both the presence and absence of graphene support, to ianthinite nanowires and schoepite microdisks may be utilized to offer morphological controls on the microscopic level as precursor materials. Provided the reduced form of uranium is desirable, the oxidized form can be readily reduced by hydrogen to UO_2 or simply by carbon in the graphene support to uranium carbide, both of which are well established chemical processing routes for bulk fuel materials [75, 76].

The solution-based synthetic method described here represents a bottom-up molecular approach, which may prove useful for preparing mixed oxide fuel (MOX) containing both uranium and plutonium oxides. Currently, MOX fuel particles are typically produced by ball-milling of the oxide powders, which tends to result in fuels with heterogeneous microstructures dominated by the occurrence of plutonium-rich clumps in a UO_2 matrix [77]. Increasing the microscopic homogeneity of MOX is known to promote fuel burn-up (i.e., energy extracted from a unit mass of metal) [78]. Therefore, producing a truly homogeneous fuel pellet may lead to better and more predictable thermal characteristics, less overall deterioration of the material during reactor operation, and possibly easier reprocessing. Although the redox chemistry of plutonium is very different from uranium, the combination of uranyl and plutonyl in a solvent followed by the production of mixed nanocrystals in a one-pot reaction appears to warrant further study.

Although the focus of this study is directed toward common fuel materials for nuclear reactors, targeted synthesis of radiological nanomaterials such as UO_2 nanocrystals may also

356 contribute to the development of neutron detectors for nonproliferation monitoring and
357 radioisotope electrical generators for space exploration [79, 80].

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Figure Captions

Figure 1. Polyol reduction process investigated for the synthesis of uranium dioxide nanocrystals.

Figure 2. Reduction of uranyl acetylacetonate by (a, e, i) ethylene glycol, (b, f, j) diethylene glycol, (c, g, k) triethylene glycol, (d, h, l) polyethylene glycol. (a – d) Digital graphs. (e – h) Transmission electron micrographs. Scale bars: *e*, 1 μm ; *f*–*g*, 5 nm. (i – l) Powder X-ray diffraction. Vertical lines mark reflections from ianthinite (JCPDS 12-272; dash lines) and uraninite (JCPDS 65-285; solid lines).

Figure 3. Uranium dioxide nanocrystals synthesized with (a) pre-heated triethylene glycol as well as (b) citrate or (c) ascorbate capping. (d) Statistical analysis of nominal diameter of nanocrystals in *b* and *c*. Scale bar: 5 nm.

Figure 4. Uranium dioxide nanocrystals decorated on graphene sheets. (a) Transmission electron micrograph (TEM). (b) Powder X-ray diffraction. (c) High resolution TEM. (d) Statistical analysis of nanocrystal size. Scale bars: *a*, 20 nm; *c*, 5 nm.

Figure 5. Oxidation of uranium dioxide nanocrystals in water and exposed to air. (a, b) Transmission electron micrographs taken at the beginning of the experiment and after 2 days. (c) Scanning electron micrograph taken after 1 week. (d, e, f) Photographs of the aqueous suspensions imaged in *a*, *b*, and *c*, respectively. (g, h) powder X-ray diffraction patterns of *b* and *c*, with prominent reflection peaks marked for ianthinite (JCPDS 12-272) and schoepite (JCPDS 13-241). (i) Oxidative transformation of uraninite to ianthinite and then to schoepite. In ianthinite and schoepite, oxygen atoms not bonded with hydrogen, which are located at the apexes of the polyhedrons, are not shown for the simplicity of presentation. For the same

reason, all hydrogen atoms are not shown. Colors: U(IV), grey; U(VI), yellow; O, red; O in H₂O and OH, cyan. Scale bars: *a*, 10 nm; *b*, 150 nm; *c*, 1.5 μ m.

Figure 6. Digital photographs of oleic acid-capped UO₂ nanocrystals dispersed in cyclohexene (a) before the bubbling of pure oxygen, (b) after bubbling oxygen for 9 h, (c) 10 days after mixing with water (clear liquid underneath the suspension), and (d) 5 days after mixing with water and IGEPAL. (e) Powder X-ray diffraction pattern of *d*, with prominent reflection peaks marked for schoepite (JCPDS 13-241).

Figure 7. Powder X-ray diffraction patterns of graphene-supported UO₂ nanocrystals stored in ethanol for (a) 1 day, (b) 5 days, (c) 8 days, (d) 5 months. Most of the diffraction patterns are consist with the reflections of uraninite (JCPDS 65-285) except the 001 reflection of triuranium octoxide marked by the vertical line. Inset: Crystal structure of triuranium octoxide with U(VI) in yellow and U(IV) in grey. Oxygen atoms located at the apexes of the polyhedrons are omitted for clarity of presentation.

Figure 8. Reduction potential of different ethylene glycol compounds. Colors: green, $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$; silver, $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$; blue, $\text{Ag}^+ + e^- \rightarrow \text{Ag}$; cyan, $\text{Cu}^{2+} + e^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$; purple, $\text{IrCl}_6^{2-} + 4e^- \rightarrow \text{Ir} + 6\text{Cl}^-$; pink, $\text{PtCl}_6^{2-} + 4e^- \rightarrow \text{Pt} + 6\text{Cl}^-$; brown, $\text{AuCl}_4^- + 3e^- \rightarrow \text{Au} + 4\text{Cl}^-$; red, $\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$; lime, $\text{Ru}^{3+} + 3e^- \rightarrow \text{Ru}$; yellow, $\text{UO}_2^{2+} + 2e^- \rightarrow \text{UO}_2$. See Table S1 for the literature data used to plot the figure. Curves: solid, linear regression; dash, standard deviations.

Figure 9. Structure and morphology of suspended UO₂ nanocrystals. (a) High resolution transmission electron micrograph of a single UO₂ nanocrystal. To compare with the molecular model in *c*, the near surface uranium atoms are connected by yellow dash

lines and the distinctive pattern of uranium atoms in the (110) planes are marked with seven yellow dots. (b) Fast Fourier transform of b , showing electron diffraction spots. (c) A model molecule of truncated UO_2 nanocrystal $\text{U}_{281}\text{O}_{792}$ viewed from the [110] direction. Seven black circles are used to illustrate the pattern marked by the seven yellow dots in a . (d) A model of truncated octahedron. Atoms in color: U, yellow; O, red. Scale bars: a , 5 Å; b , 5 nm^{-1} .

Figure 10. Heteroepitaxy of UO_2 nanocrystals deposited on graphene. (a) Transmission electron micrograph (TEM) showing nanocrystals with equivalent orientations. (b, c, d) Fast Fourier transform of nanocrystals in a with 0° , 60° , and 120° rotations, respectively. (e) High resolution TEM showing the sharp edges of nanocrystals. (f) Molecular model showing heteroepitaxy. Atoms in color: U, yellow; O, red. Scale bars: a , 10 nm; $b - d$, 5 nm^{-1} ; e , 2 nm.

Figure 1

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