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Synthesis and preservation of graphene-supported uranium dioxide nanocrystals

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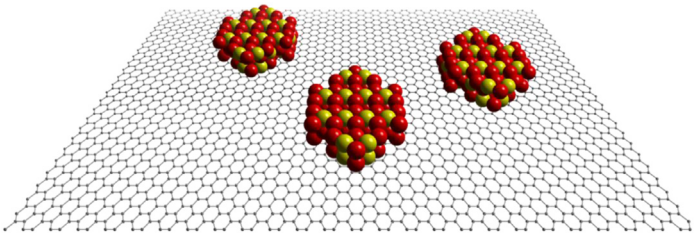
HIGHLIGHTS

- UO_2 nanocrystals are synthesized using polyol reduction method.
- Triethylene glycol is the best reducing agent for nano-sized UO_2 crystals.
- UO_2 nanocrystals grow on graphene through heteroepitaxy.
- Graphene-supported UO_2 nanocrystals can be stored in alcohols to prevent oxidation.

GRAPHICAL ABSTRACT



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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 acetylacetone 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

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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 ($UO_2(acac)_2$ or $UO_2(C_5H_7O_2)_2$) 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; $(CH_2)_{2n}O_{n-1}(OH)_2$, $n = 1, 2, 3, 4 \ldots$) [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.

2.1. Synthesis of uranyl acetylacetone

3.26 g $UO_2(NO_3)_2 \cdot 6H_2O$ (depleted uranium) was first dissolved into 12.5 mL DI water. Under stirring, 25 mL water, 1.35 g acetylacetone, 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 $UO_2(acac)_2$ from uranium nitrate precursor was approximately 85%.

2.2. Synthesis of UO_2 nanocrystals

0.1 mmol uranyl acetylacetone 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, $C_2H_6O_2$), diethylene glycol (DEG, $C_4H_{10}O_3$), triethylene glycol (TEG, $C_6H_{14}O_4$), and polyethylene glycol (PEG, $C_8H_{18}O_5$). The mixture was heated to 140 °C for 20 min 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 ($(C_6H_9NO)_{257}$, 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 octylphenoxy poly(ethyleneoxy)ethanol (IGEPAL) was added to 5 mL cyclohexene suspension with 5 mL DI water.

2.3. 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 °C and stirred for 30 min. DI water was added into the mixture to raise the temperature to 98 °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 °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 $UO_2(acac)_2$ before performing boiling reflux (i.e., except the