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Uniform formation of uranium oxide nanocrystals inside ordered mesoporous hosts and their potential applications as oxidative catalysts†

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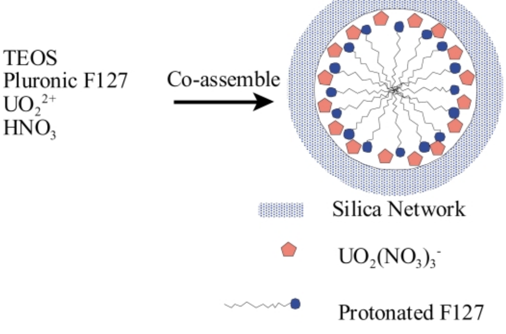
Received (in Purdue, IN, USA) 27th May 2002, Accepted 7th August 2002
First published as an Advance Article on the web 23rd September 2002

Highly dispersed uranium oxide nanocrystals supported on ordered mesoporous silica matrixes with large surface areas and porosities have been synthesized *via* a co-assembly methodology; the preliminary catalysis tests showed that these materials have a high catalytic activity for the thermal oxidation of volatile organic compounds (VOCs).

Volatile organic compounds (VOCs) released from various industrial operations are contaminating our environment because of their stability against degradation by microorganisms and their persistence in environmental media. Accordingly, it is important to establish effective chemical means to convert VOCs to benign compounds before their release.[1] Hutchings and coworkers have shown that uranium oxides (especially U_3O_8) have high efficiency and long-term catalytic stability in the destruction of VOCs as compared with some of the commercial catalysts, such as precious metals, TiO_2 and Co_3O_4.[2,3] The potential application of uranium oxides as catalysts may provide ways to re-utilize enormous quantities of depleted uranium, which has resulted from enrichment production.[2–4] The key factors limiting further enhancement of the catalytic activities for uranium oxides prepared by the conventional methods are low *surface area* and limited *pore size*.[4] To overcome these limitations, we report here the synthesis of uranium oxide nanocrystals dispersed on ordered mesoporous silica hosts (SBA-15) through a co-assembly synthesis. Mesoporous materials possessing very high surface areas with tailored pore sizes are ideal for hosting and dispersing active catalysts.[5–11] Unlike microporous hosts, which can interact with reactants only on outer surfaces, mesoporous materials have larger pore openings, which allow for access to the inner pore surfaces. This enhanced interaction should result in a much higher catalytic efficiency for catalysts supported on the mesoporous materials.[11] Moreover, because of their unique mesoporous pore diameters (20–300 Å), the mass transport of organic vapors in these materials is far more efficient than in conventional microporous catalysts, such as crystalline zeolites.

The co-assembly approach used in our synthesis is based on the I^+ M^- S^+ scheme for the synthesis of mesoporous supports in an acid medium.[6,12] The positively charged surfactant molecules (S^+), such as protonated block copolymers, interact with positively charged inorganic oxide precursors (I^+) through a negatively charged mediator M^-. Nitric acid was used in our synthesis to enhance the solubility of uranyl nitrate in the sol–gel precursor solution. Accordingly, the mediator (M^-) in this case can be both nitrate ions and the anionic complexes of uranyl. The nitrate complexes of uranyl ions are known to be very stable and dominant species under high nitrate concentration in several different solvent systems.[13] Their preferential location at the interface between silica and surfactants may prevent excessive disruption of the silica wall during the formation of the mesostructure. The overall reaction is shown schematically in Scheme 1. The surfactant template can be removed by calcination. The uranium oxide nanoparticles are expected to be gradually phase separated or breed out from the amorphous mesoscopic SiO_2 host *via* a space-confined crystallization. In the mesoporous materials obtained in such way, the mesopores would be embedded with the uranium oxide nanoparticles. In a typical synthesis, the transparent mesostructured silica-block copolymer composite doped with UO_2^{2+} was prepared by mixing HNO_3 (0.05 M) with tetraethoxysilane (TEOS) and $UO_2(NO_3)_2{\cdot}6H_2O$. The mixture was added to a solution of Pluronic F127 (BASF), butanol, and cyclohexane. The initial mass ratio was F127 (0.75) : butanol (0.17) : cyclohexane (0.30) : HNO_3/H_2O (2.00) : TEOS (1.87) : $UO_2(NO_3)_2{\cdot}6H_2O$ (0.19). A monolithic mesoscopic gel formed after 1 week of condensation and gelation. The mesoporous silica material incorporating U_3O_8 nanoparticles was obtained by calcination, first at 350 °C for 4 h and then at 800 °C for 2–5 h.

Fig. 1 shows the electronic absorption spectrum of the as-synthesized mesoscopic monolithic gel. The uranyl characteristic bands between 420 and 500 nm match well with those expected for the uranyl trinitrate complex.[13] This observation agrees with our proposed synthesis mechanism and location of uranyl ions. Fig. 2 shows scanning transmission electron microscopy (STEM) images of the calcined periodic mesopor-



Scheme 1

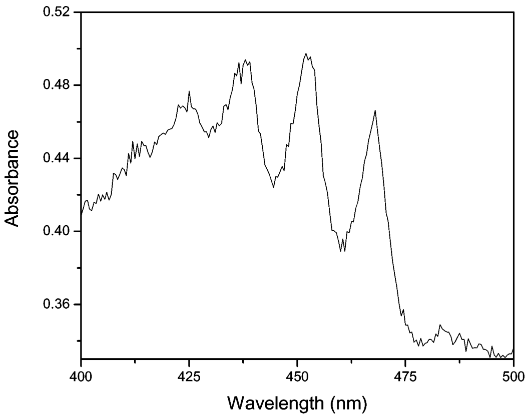


Fig. 1 Electronic absorption spectrum of the uranyl trinitrate anion complex in the as-synthesized monolithic gel.

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† Electronic supplementary information (ESI) available: nitrogen adsorption–desorption isotherms. See http://www.rsc.org/suppdata/cc/b2/b204987b/

DOI: 10.1039/b204987b

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ous silica doped with uranium oxide nanoparticles. As seen in the figure, the hexagonal porous silica structure was retained during calcination, despite the high loading of the uranium oxide nanocrystals. The sizes of the nanocrystals are below 10 nm, and the dispersion of the nanocrystals is highly uniform. The uranium oxide nanocrystals are more visible as the bright nanodomains in the dark-field (*Z*-contrast) image (Fig. 2(b)) because of the extremely large atomic number of uranium. The principle behind the high-annular dark-field imaging is that the intensity of the Rutherford scattered beams is directly proportional to Z^2, where Z is the atomic number of the element.[14] Although there are many reports on the incorporation of nanoparticles into ordered mesoporous materials through wet or gas-phase impregnation,[15–17] few nanocrystals have been co-assembled into the mesoporous hosts without destruction of the ordered mesopores. The crystallization process during calcination leads to the phase separation of amorphous silica and nanocrystal domains, which usually destroys the silica ordered mesostructures. The retention of the ordered mesopores during crystallization of uranium oxide nanocrystals is very surprising.

Fig. 3 shows the X-ray diffraction (XRD) pattern of the mesoporous silica embedded with the uranium oxide nanocrystals. This XRD pattern agrees well with a crystalline phase of U_3O_8 assigned to an orthorhombic structure.[18,19] Accordingly, the redox reaction has been induced during the calcination treatment of the precursor gel. The nitrogen adsorption–desoportion isotherm (see ESI†) of the U_3O_8-incorporated mesoporous material shows type IV adsorption isotherm behaviour with a type H1 hysteresis loop with the surface area as high as 250 $m^2\ g^{-1}$ and a pore volume of 0.31 $cm^3\ g^{-1}$. The narrow pore distribution centered around 6.1 nm was calculated from the adsorption isotherm, which is consistent with the direct observation by STEM. The catalytic activity of the U_3O_8-incorporated mesoporous material for the thermal oxidation of toluene into CO_2 and H_2O was tested under conditions similar to those reported in the literature.[2,3] The products were analysed using gas chromatography. A catalytic conversion yield as high as 99.2% at 375 °C was observed, while the pure U_3O_8 only has 28.0% conversion yield under the same conditions.

In conclusion, we have demonstrated a co-assembly method to synthesize U_3O_8 nanocrystals in the periodic mesoporous silica. The U_3O_8 nanocrystals were highly dispersed with very uniform size below 10 nm. The U_3O_8-incorporated mesoporous material has a high surface area and retains cylindrical pores. Preliminary tests show good catalytic activity for the destruction of VOCs.

This work was supported by the office of Science and the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

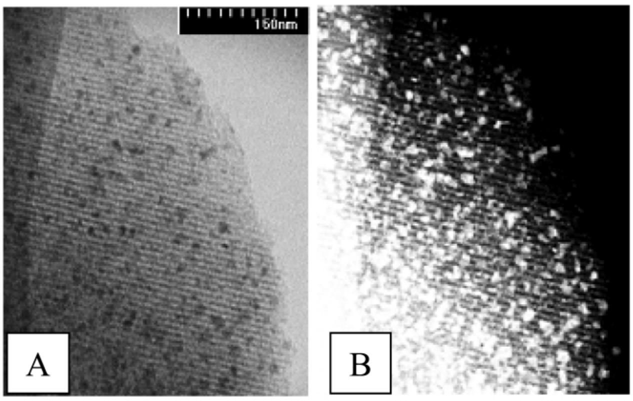

Fig. 2 Bright field (A) and dark field (B) TEM images of U_3O_8-incorporated ordered mesoporous materials recorded in the same region.

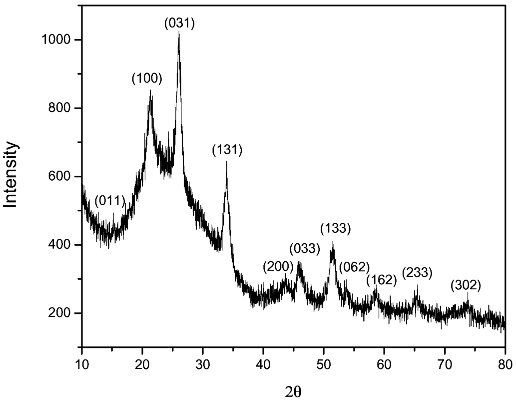

Fig. 3 XRD pattern of U_3O_8-incorporated mesoporous materials.

Notes and references

1 J. J. Brown, M. D. Erickson and N. J. Beskid, *Hazard. Waste Hazard. Mater.*, 1993, **10**, 335.
2 G. J. Hutchings, C. S. Heneghan, I. D. Hudson and S. H. Taylor, *Nature*, 1996, **384**, 341.
3 S. H. Taylor, C. S. Heneghan, G. J. Hutchings and I. D. Hudson, *Catal. Today*, 2000, **59**, 249.
4 K. Vidya, S. E. Dapurkar, P. Selvam, S. K. Badamali, D. Kumar and N. M. Gupta, *J. Mol. Catal*, 2002, **181**, 91.
5 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
6 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
7 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152.
8 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.
9 M. Kruk, V. Antochshuk, J. R. Matos, L. P. Mercuri and M. Jaroniec, *J. Am. Chem. Soc.*, 2002, **124**, 768.
10 J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed.*, 1999, **38**, 56.
11 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
12 Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, M. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
13 E. Rabinowitch and R. L. Belford, *"Spectroscopy and Photochemistry of Uranyl Compounds"*, Pergamon Press Book, New York, 1964.
14 S. J. Pennycook, D. E. Jesson, A. J. McGibbon and P. D. Nellist, *J. Electron Microsc.*, 1996, **45**, 36.
15 Z. T. Zhang, S. Dai, X. D. Fan, D. A. Blom, S. J. Pennycook and Y. Wei, *J. Phys. Chem. B*, 2001, **105**, 6755.
16 L. Zhang, G. C. Papaefthymiou and J. Y. Ying, *J. Phys. Chem. B,*, 2001, **105**, 7414.
17 W. H. Zhang, J. L. Shi, L. Z. Wang and D. S. Yan, *Chem. Mater.*, 2000, **12**, 1408.
18 B. O. Loopstra, *Acta Crystallogr.*, 1964, **17**, 651.
19 R. J. Ackermann, A. T. Chang and C. A. Scorrell, *J. Inorg. Nucl. Chem.*, 1977, **39**, 75.