doi:10.1017/S143192761300980X
Microsc. Microanal. 19 (Suppl 2), 2013

In-situ Growth of Uranyl Clusters Inside Mesoporous Silica SBA-15

Yi Liu[1], Laurent Jouffret[2], Jennifer E. S. Szymanowski[2], Sergei Rouvimov[3], Ginger Sigmon[2], and Peter C. Burns[1,2]*

[1.] Department of Chemistry and Biochemistry, [2.] Department of Civil & Environmental Engineering & Earth Sciences, and [3.] Notre Dame Integrated Imaging Facility, University of Notre Dame, Notre Dame, IN 46556, USA.

Introduction: Nuclear energy is an important contributor to the world's energy supply, and will likely grow in importance over the coming decades. Methods of immobilizing radionuclides, including the actinides, in durable matrices are important for safe disposal. Encapsulation in mesoporous silica has been investigated because the large surface area and pore volume of the mesoporous materials provides several immobilization options. To achieve high loading amounts of uranium, for example, functionalization of the inner surface of the mesoporous silica by organic phosphorus ligands can provide adsorption sites for the uranium species. Uranium in such a system is immobilized as a single molecular layer on the inner surface of the mesopores. To achieve higher loading with uranium, we propose sequestration of uranium in mesoporous silica SBA-15 as nanoscale uranyl cage clusters. By this approach, uranium will be immobilized as a three-dimensional cluster instead of a two-dimensional layer inside the mesopores of SBA-15, without employing phosphorus ligands. In this work, we sequestrate uranium in SBA-15 by the in situ growth of U60 clusters inside the pores of SBA-15. The resulting materials were characterized by Raman spectra, N_2 adsorption and desorption, and transmission electron microscopy (TEM).

Experimental details: SBA-15 was synthesized based on reference [1]. The SBA-15 was added into the mother solution of U60 clusters [2]. After standing under ambient condition for seven days, the materials were filtered and dried under ambient condition for further characterization.

Results and discussion: Raman spectra (Fig. 1) show two bands centered at 839 and 810 cm^{-1}, which correspond to O-O stretching vibrations of bridging peroxo ligands and symmetric stretching vibration of the U=O bonds in the uranyl groups in U60, respectively. This result is consistent with the Raman spectra of pure U60 solids, consistent with the formation of U60 clusters in SBA-15. To understand the location of the U60 clusters in U60-SBA-15, TEM and N_2 adsorption and desorption experiments were conducted. TEM images in Fig. 2(a) show the existence of crystallized nanoparticles inside the pores of SBA-15, and energy dispersive spectra (EDS) in Fig. 2(b) indicate the major elemental composition of the U60-SBA-15 are U, Si, and O. These results indicate uranium is entrapped inside the mesopores of SBA-15, which is consistent with the results of N_2 adsorption and desorption (Table 1). Both the pore volume and specific surface area significantly decreased after U60 clusters formed in the materials, as the consequence of pore blocking by U60 clusters.

Conclusions: These results indicate that U60 clusters formed inside the mesopores of SBA-15 via in situ growth of the clusters. The loading amount of uranium in the SBA-15 will be tested by Inductively Coupled Plasma Optical Emission Spectrometry. Additional research will focus on selectively immobilizing uranium from waste streams in mesoporous silica.

References:

[1] D. Y. Zhao, *et al.*, Chem. Mater. **12** (2000), p. 275-279.
[2] G. E. Sigmon, *et al.*, Angew. Chem., Int. Ed. **48** (2009), p. 2737–2740.
[3] The authors acknowledge funding by the Office of Basic Energy Sciences of the U.S. Department of Energy as part of the Materials Science of Actinides Energy Frontier Research Center (DE-SC0001089).

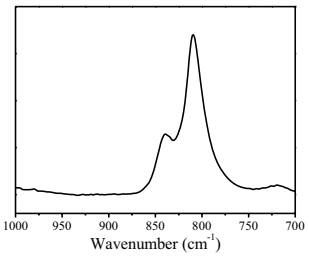

Figure 1. Raman spectra of U60-SBA-15.

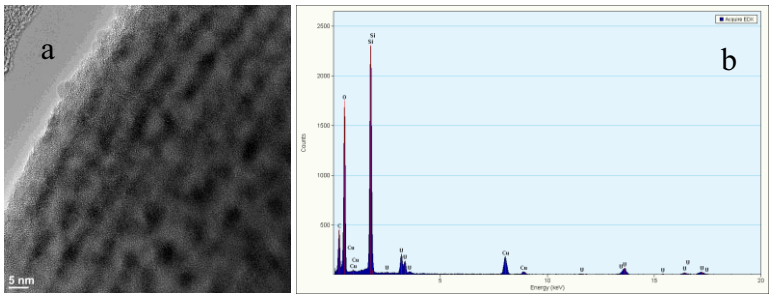

Figure 2. (a) TEM image and (b) EDS spectra of U60-SBA-15.

Table 1. Pore volume and surface area of SBA-15 and U60-SBA-15 by N_2 adsorption and desorption experiment.

Sample	Pore volume (cm^3/g)	BET surface area (m^2/g)
SBA-15	0.92	740
U60-SBA-15	0.31	157

https://doi.org/10.1017/S143192761300980X Published online by Cambridge University Press