

Supporting Information for

A Novel Mesoporous Material for Uranium Extraction, Dihydroimidazole Functionalized SBA-15

Li-Yong Yuan, Ya-Lan Liu[†], Wei-Qun Shi, Zi-jie Li, Jian-Hui Lan, Yi-Xiao Feng, Yu-Liang Zhao,[‡]*

Ya-Li Yuan[†] and Zhi-Fang Chai

Key Laboratory of Nuclear Analytical Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China. (The first two authors contributed equally to this work)

[†] Department of Analytical Chemistry, School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

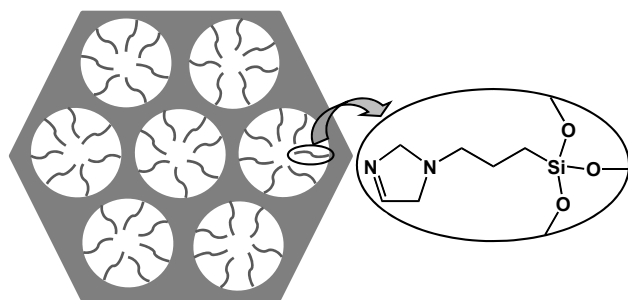
[‡] Key Laboratory for Biomedical Effects of Nanomaterials & Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

* Corresponding author. Fax: 86-10-88235294; Tel: 86-10-88233968; E-mail: shiwq@ihep.ac.cn

SI-1. Chemical Materials

N-(3-triethoxysilylpropyl)-dihydroimidazole (NTSP) was purchased from Meryer, China. Tetraethoxysilane (TEOS) and poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) (P123) were obtained from SCRC, China. Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ACS grade) was purchased from Merck, Germany. All these materials were used as received. Standard stock solution (1.688 g/L) of U(VI) was prepared by dissolving the appropriate amounts of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized water. All the other chemicals were of analytical grade and used without further purification. Deionised water used in all experiments was obtained from the Milli-Q water purification system.

SI-2. The scheme of DIMS



SI-3. Sorption Experiments

In a typical experiment, 4 mg of sorbent was added into 10 mL U(VI) solution in a flask (the solid-liquid ratio is thus 0.4 g/L) stirring for 2 h at room temperature. Then, the suspension was centrifuged at 10000 rpm for 30 minutes. The concentration of U(VI) in the supernatant was determined by Arsenazo III Spectrophotometric Method at wavelength of 656 nm (the detection limit of the method is below 0.1 ppm). Before the determination, the supernatant was diluted 2.5~100 times to make sure that the U(VI) concentration in the dilution is 0.1~5 $\mu\text{g/mL}$, corresponding to the UV absorbance of 0.05~1.0 at 656 nm. To evaluate the adsorptivity of DIMS, the sorption of U(VI) from aqueous solution into DIMS was performed at different conditions of pH,

contact time, initial U(VI) concentration, ionic strength and solid-liquid ratio (m/V). The sorption efficiency (E) and the sorption capacity (q_e) of U(VI) were defined as follows:

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m_{\text{sorbent}}} \times V_{\text{solution}} \quad (2)$$

where C_0 and C_e represent the concentrations of U(VI) in the aqueous phase for the control experiment and the sorption experiment after 2 h stirring, respectively; m_{sorbent} and V_{solution} designate the weight of the DIMS sorbent and the volume of the U(VI) solution used in the sorption experiment, respectively. All values were measured in duplicate with the uncertainty within 5%.

SI-4 Analytical techniques

The DIMS sample was observed with SEM (Hitachi S-4800) at the accelerating voltage of 10.0 kV. The N_2 sorption/desorption isotherm was measured at -196°C with ASAP 2020. High resolution transmission electron microscopy (HRTEM) was performed with a Philips Tecnai F20 microscope operating at 200 kV ($C_s = 1.2$ mm, Point resolution 0.24 nm). Image was recorded using a CCD camera (GATAN 894, 2048×2048 pixels, pixel size 14×14 μm). The small-angle X-ray scattering (SAXS) patterns were taken at the Beijing Synchrotron Radiation Facility (BSRF). The surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The pore size was obtained from the average of the pore size distribution curve calculated by the Barrett–Joyner–Halenda (BJH) method using the sorption branch of the isotherm. The total pore volume was evaluated by the single point method. ^{13}C CP/MAS NMR spectra were measured on a BRUKER AVANCE III 400 spectrometer at 100 MHz and a sample spinning frequency of 3 kHz. The functional group content of DIMS was inspected using a Q50TGA meter at a programmed rate of $10^\circ\text{C}/\text{min}$ in air. The FTIR analysis of the samples was performed by using BRUKER TENSOR27 FTIR spectrometer. Inductively coupled plasma mass spectrograph (ICP-MS, PerkinElmer) was used to determine the residual concentration

of tested ion(s) in supernatants in the selectivity test experiment. The UV absorbance of Arzenazo III–U(VI) complex was recorded in a photometry mode on TU-1901 spectrophotometer with a quartz cuvette of 1 cm path length.

SI-5 The species distribution of U(VI)

The aqueous speciation of U(VI) as a function of pH in the absence of sorbent was calculated according to the thermodynamic data listed in Table S1¹. To clarify whether there is precipitation or not, a solid phase, i.e. the schoepite phase, was also included in the speciation calculation. The distribution of aqueous and solid U(VI) species at different U(VI) concentrations (1.00×10^{-3} mol/L, 5.00×10^{-4} mol/L, 1.00×10^{-4} mol/L, and 5.00×10^{-5} mol/L) were given in Figure S1.

Table S1 U(VI) solution reactions

Species	Reactions	Log <i>K</i> (<i>I</i> =0)
Aqueous species		
UO ₂ ²⁺	UO ₂ ²⁺	—
UO ₂ (OH) ⁺	UO ₂ ²⁺ + H ₂ O = UO ₂ (OH) ⁺ + H ⁺	-5.25
UO ₂ (OH) ₂ ⁰	UO ₂ ²⁺ + 2H ₂ O = UO ₂ (OH) ₂ ⁰ + 2H ⁺	-12.15
UO ₂ (OH) ₃ ⁻	UO ₂ ²⁺ + 3H ₂ O = UO ₂ (OH) ₃ ⁻ + 3H ⁺	-20.25
UO ₂ (OH) ₄ ²⁻	UO ₂ ²⁺ + 4H ₂ O = UO ₂ (OH) ₄ ²⁻ + 4H ⁺	-32.4
(UO ₂) ₂ (OH) ₃ ³⁺	2UO ₂ ²⁺ + H ₂ O = (UO ₂) ₂ (OH) ₃ ³⁺ + H ⁺	-2.7
(UO ₂) ₂ (OH) ₂ ²⁺	2UO ₂ ²⁺ + 2H ₂ O = (UO ₂) ₂ (OH) ₂ ²⁺ + 2H ⁺	-5.62
(UO ₂) ₃ (OH) ₄ ²⁺	3UO ₂ ²⁺ + 4H ₂ O = (UO ₂) ₃ (OH) ₄ ²⁺ + 4H ⁺	-11.90
(UO ₂) ₃ (OH) ₅ ⁺	3UO ₂ ²⁺ + 5H ₂ O = (UO ₂) ₃ (OH) ₅ ⁺ + 5H ⁺	-15.55
(UO ₂) ₃ (OH) ₇ ⁻	3UO ₂ ²⁺ + 7H ₂ O = (UO ₂) ₃ (OH) ₇ ⁻ + 7H ⁺	-32.20
(UO ₂) ₄ (OH) ₇ ⁺	4UO ₂ ²⁺ + 7H ₂ O = (UO ₂) ₄ (OH) ₇ ⁺ + 7H ⁺	-21.90
—	H ₂ O + CO ₂ (g) = H ₂ CO ₃	-1.47
UO ₂ CO ₃ ⁰	UO ₂ ²⁺ + H ₂ CO ₃ = UO ₂ CO ₃ ⁰ + 2H ⁺	-6.74
UO ₂ (CO ₃) ₂ ²⁻	UO ₂ ²⁺ + 2H ₂ CO ₃ = UO ₂ (CO ₃) ₂ ²⁻ + 4H ⁺	-16.75
UO ₂ (CO ₃) ₃ ⁴⁻	UO ₂ ²⁺ + 3H ₂ CO ₃ = UO ₂ (CO ₃) ₃ ⁴⁻ + 6H ⁺	-28.20
(UO ₂) ₂ CO ₃ (OH) ₃ ⁻	2UO ₂ ²⁺ + H ₂ CO ₃ + 3 H ₂ O = (UO ₂) ₂ CO ₃ (OH) ₃ ⁻ + 5H ⁺	-17.55
(UO ₂) ₃ CO ₃ (OH) ₃ ⁺	3UO ₂ ²⁺ + H ₂ CO ₃ + 3 H ₂ O = (UO ₂) ₃ CO ₃ (OH) ₃ ⁺ + 5H ⁺	-16.04
(UO ₂) ₃ (CO ₃) ₆ ⁶⁻	3UO ₂ ²⁺ + 6H ₂ CO ₃ = (UO ₂) ₃ (CO ₃) ₆ ⁶⁻ + 12H ⁺	-46.08
Solid species		
Schoepite	UO ₂ ²⁺ + 3H ₂ O = UO ₃ • 2H ₂ O(cr) + 2H ⁺	-5.9

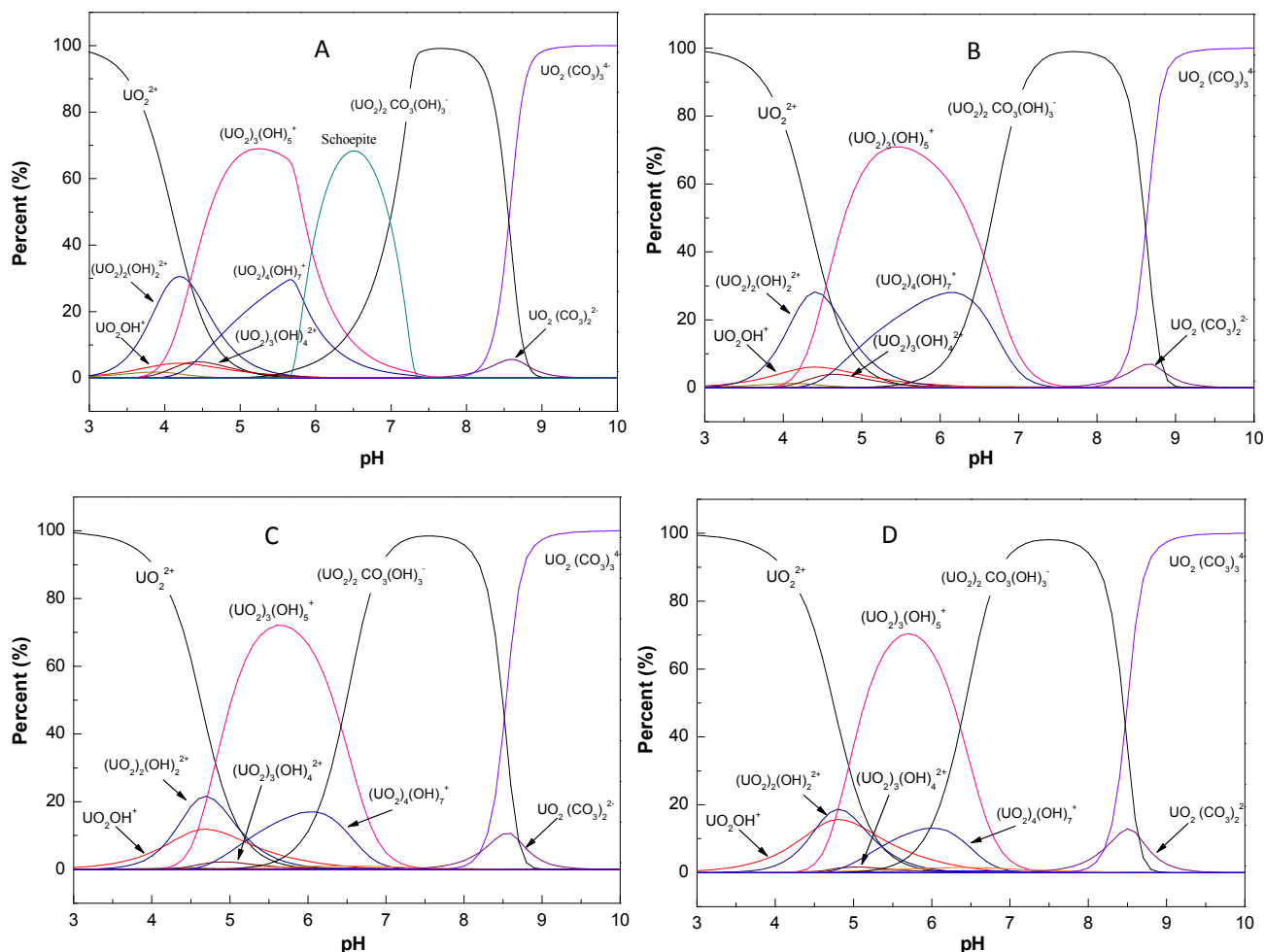


Figure S1. Aqueous speciation of U(VI) in an open system equilibrated with $p(\text{CO}_2) = 10^{-3.5}$ as a function of pH. A, $C[\text{U(VI)}]_{\text{total}} = 1.00 \times 10^{-3}$ mol/L; B, $C[\text{U(VI)}]_{\text{total}} = 5.00 \times 10^{-4}$ mol/L; C, $C[\text{U(VI)}]_{\text{total}} = 1.00 \times 10^{-4}$ mol/L; D, $C[\text{U(VI)}]_{\text{total}} = 5.00 \times 10^{-5}$ mol/L in water solution. (The species less than 1% were not denoted in the figures for clarity)

As can be seen from Figure S1, the distribution of U(VI) species show a dependency on pH values and U(VI) total concentration. At $\text{pH} < 4.5$ and $C[\text{U(VI)}]_{\text{total}} = 5.00 \times 10^{-5}$ mol/L, for example, free uranyl ion (UO_2^{2+}) was the dominant species. With increasing of pH, UO_2^{2+} underwent hydrolysis, and multinuclear hydroxide complexes were the dominant species at $\text{pH} > 5$. The charge of the species is also dependent on the solution pH. The U(VI) hydroxide complexes are mainly positive charge in the pH range of $\sim 5-7$, and mainly negative charge in the pH range above ~ 7 . Besides, schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) precipitates from the solution at $C[\text{U(VI)}]_{\text{total}} = 1.00 \times 10^{-3}$ mol/L and $\text{pH} = 5.7 \sim 7.4$, while no precipitation occurs at other $C[\text{U(VI)}]_{\text{total}}$ and pH.

In this study, the sorption experiments were mainly performed at $\text{pH} 4 \sim 5$ and U(VI) concentration of $5 \sim 8 \times 10^{-4}$ mol/L, in which UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$ are

the dominant species, and no insoluble species were observed during 3 h keeping at room temperature.

SI-6 The desorption of U(VI) from DIMS

In a typical experiment, 4 mg of DIMS was contacted with 10 mL of U(VI) solution (68 μ g/mL) in the optimum conditions of pH (5.0 \pm 0.1) and stirring time (2 h). Then the suspension was centrifuged and 1mL supernatant was removed for U(VI) determination. Subsequently, an appropriate amount of eluting agent, i.e. HNO₃, was added, followed by 30 min stirring at room temperature.

References

- (1) Grenthe I.; Fuger J.; Konings R. J. M.; Lemire R. J.; Muller A. B.; Nguyen-Trung C.; Wanner H. *Chemical Thermodynamics of Uranium*. OECD Nuclear Energy Agency: Amsterdam, North-Holland, 1992.