Supporting Information

Structures of Multinuclear U(VI) Species on Hydroxylated α-SiO_2 (001) Surface: Insights from DFT Calculations

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Table S1. Structural parameters (in Å), binging energies (in eV), and bond/dihedral angles of surface complexes of $(UO_2)_2(OH)^{3+}$ and $(UO_2)_2(OH)_2^{2+}$ at ≡SiOHO(H)-SiOHO(H), ≡SiOHO(H) and ≡SiOHSiO(H) sites.

Bind mode	Adsorbate	Surface site	U-O_s	U-U	U-Si	H_w-O_s	H_s-O_{yl}	H_b-O_s	∠UO(O)U[a]	ΔE_{bind}
End-on	$(UO_2)_2(OH)^{3+}$	≡SiOHO	2.20, 2.84	4.69	3.22	2.07, 2.22	-	-	165.57 (158.20)	-3.61
	$(UO_2)_2(OH)_2^{2+}$	≡SiOHO	2.22, 2.63	3.68	3.10	-	-	-	154..25 (164.46)	-2.75
	$(UO_2)_2(OH)^{3+}$	≡SiOHOH	2.60, 2.69	4.61	3.42	1.65	-	-	153.66 (158.20)	-1.50
	$(UO_2)_2(OH)_2^{2+}$	≡SiOHOH	2.56, 2.70	3.70	3.38	-	-	-	155.02 (164.46)	-1.26
	$(UO_2)_2(OH)^{3+}$	≡SiOHSiO	2.16, 2.58	4.67	3.58, 4.00	2.05	-	-	166.35 (158.20)	-4.21
	$(UO_2)_2(OH)_2^{2+}$	≡SiOHSiO	2.11, 2.49	3.76	3.60, 3.93	1.82	-	-	158.78 (164.46)	-3.48
	$(UO_2)_2(OH)^{3+}$	≡SiOHSiOH	2.51, 2.69	4.74	3.94, 4.02	1.88, 2.26	-	-	166.31 (158.20)	-1.56
	$(UO_2)_2(OH)_2^{2+}$	≡SiOHSiOH	2.52, 2.54	3.71	3.91, 4.08	1.65	-		158.41 (164.46)	-1.50
Side-on	$(UO_2)_2(OH)^{3+}$	≡SiOHO-SiOHO	2.43, 2.43, 2.53, 2.77	4.43	3.34, 3.22	1.97	-	-	142.28 (158.20)	-5.66
	$(UO_2)_2(OH)^{3+}$	≡SiOHOH-SiOHOH	2.54, 2.60, 2.75, 2.79	4.58	3.45, 3.46	2.01	-	-	154.21 (158.20)	-2.73
	$(UO_2)_2(OH)_2^{2+}$	≡SiOHvSiO	2.22, 3.05	3.92	3.83, 4.48	1.70	1.63	2.01	164.10 (164.46)	-2.62
	$(UO_2)_2(OH)_2^{2+}$	≡SiOHvSiOH	2.59, 3.10	3.85	4.17, 4.53	1.80, 1.94	1.68	1.75	157.91 (164.46)	-1.33

[a] The values in brackets are the angles of the corresponding molecules.

Table S2. U-U distances measured by EXAFS for different U(VI) adsorption systems[1–5]

System	U(VI) initial concentration (μM)	pH	U-U distance(Å)
U(VI)-Silica	41.5	6.46	3.97
U(VI)-Alumina	41.8/1000	6.50/9.00	4.01/3.91
U(VI)-Gibbsite	10	5.60/9.70	4.30/3.92
U(VI)- Hematite	12-133	6.39-8.49	3.85-3.92
U(VI)-Al hydroxide	1.26-960	3.00-6.90	3.91-3.93

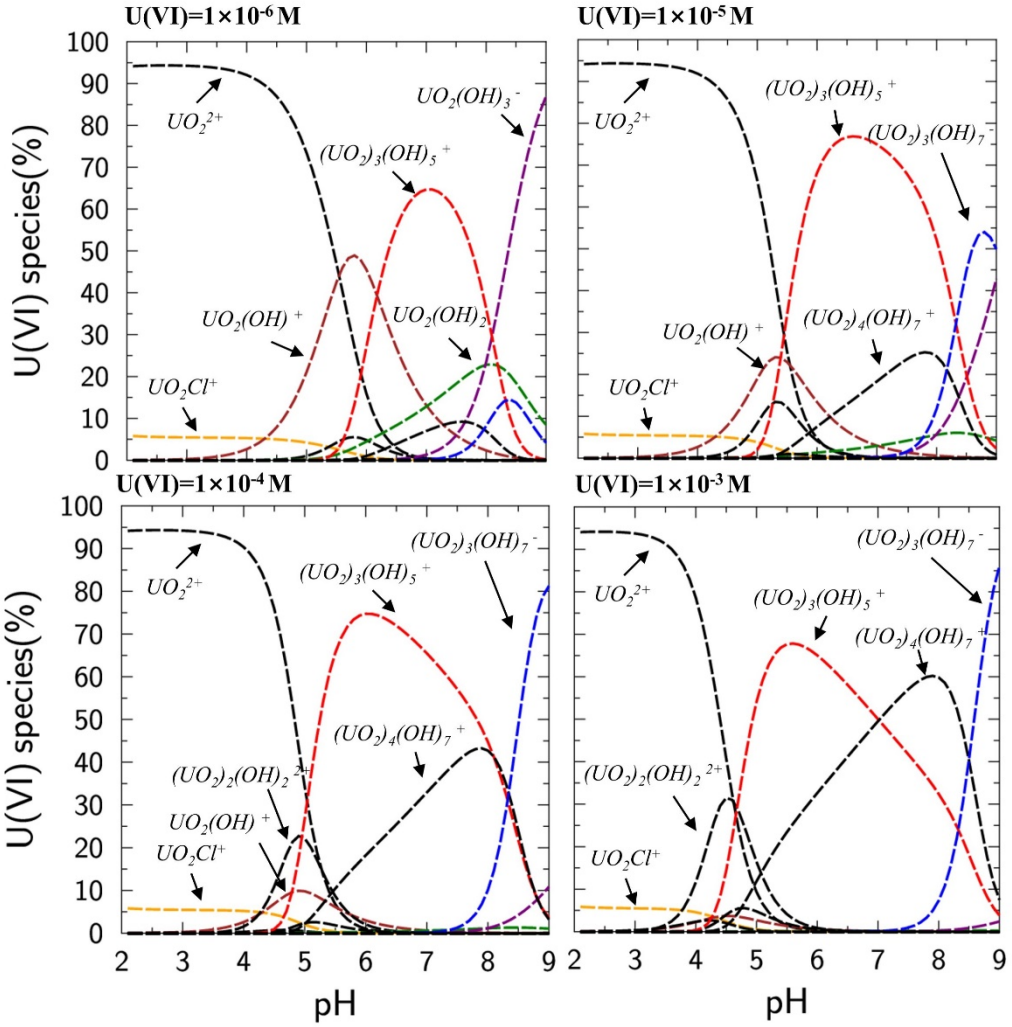

Fig. S1. U(VI) speciation at concentrations of 10^{-6}-10^{-3} M in 0.1mol/L NaCl solution at 25°C. The PHREEQC code with THERMOCHIMIE v.11a thermodynamic database was used in speciation calculations.[6]

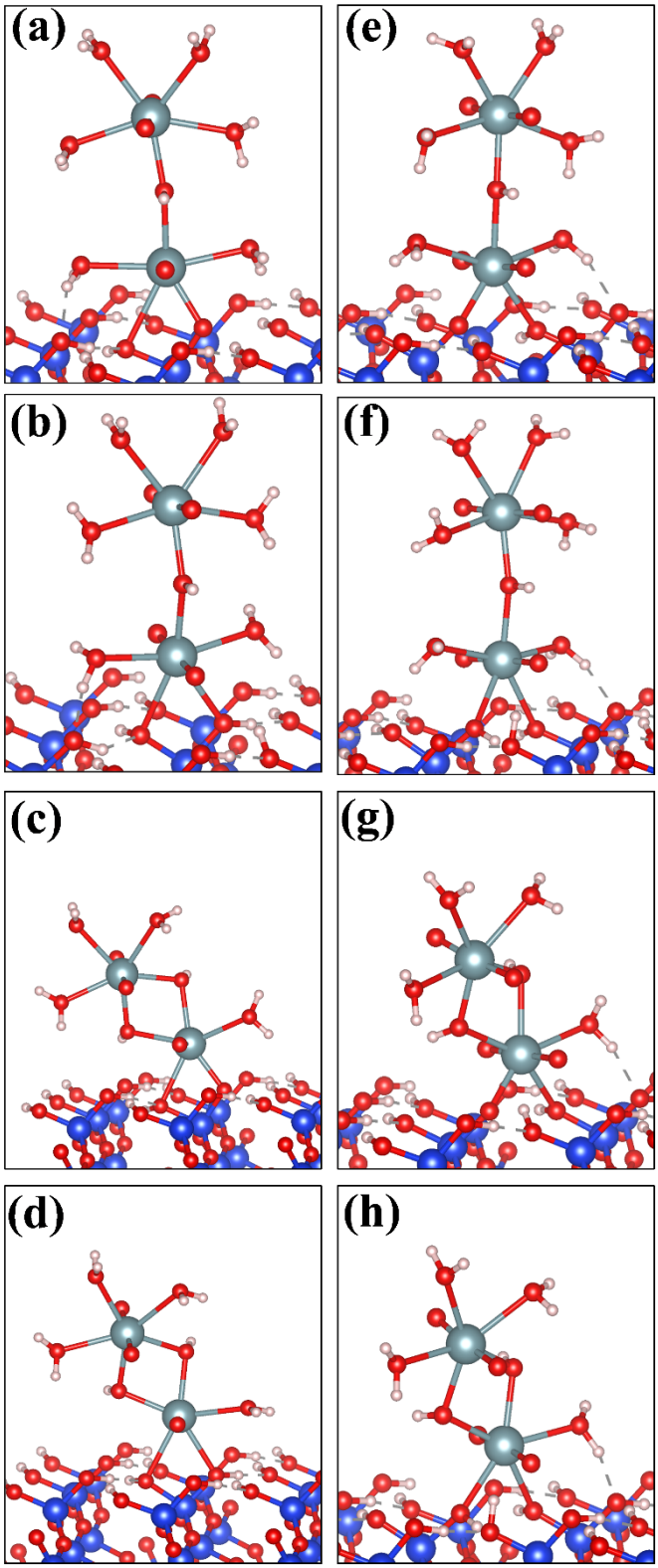

Fig. S2. Configurations of the end-on surface complexes of $(UO_2)_2(\mu\text{-}OH)(H_2O)_8^{3+}$ and $(UO_2)_2(\mu\text{-}OH)_2(H_2O)_6^{2+}$ at (a)-(d) ≡SiOHO(H) and (e)-(h) ≡SiOHSiO(H).

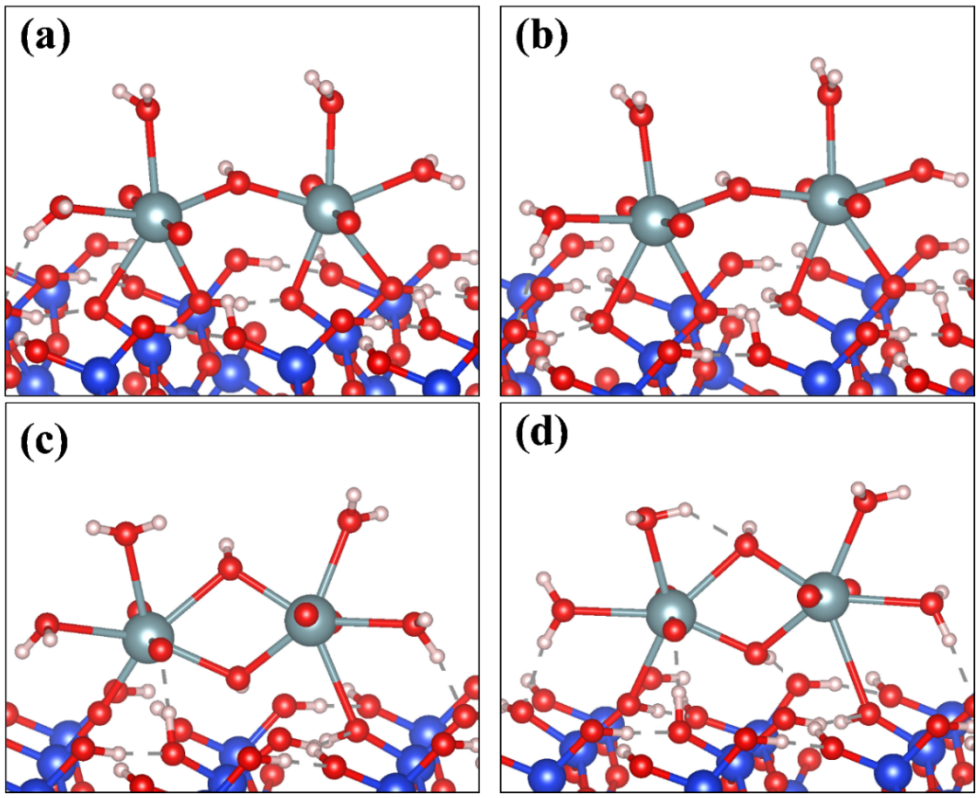

Fig. S3. Configurations of the side-on surface complexes of (a)-(b) $(UO_2)_2(\mu\text{-}OH)(H_2O)_8^{3+}$ at ≡SiOHO(H)-SiOHO(H) and those of (c)-(d) $(UO_2)_2(\mu\text{-}OH)_2(H_2O)_6^{2+}$ at ≡SiOH*v*SiO(H).

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