

ARTICLE

Insight into the structure-property relation of UO_2 nanoparticles

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Supplementary information

Experimental

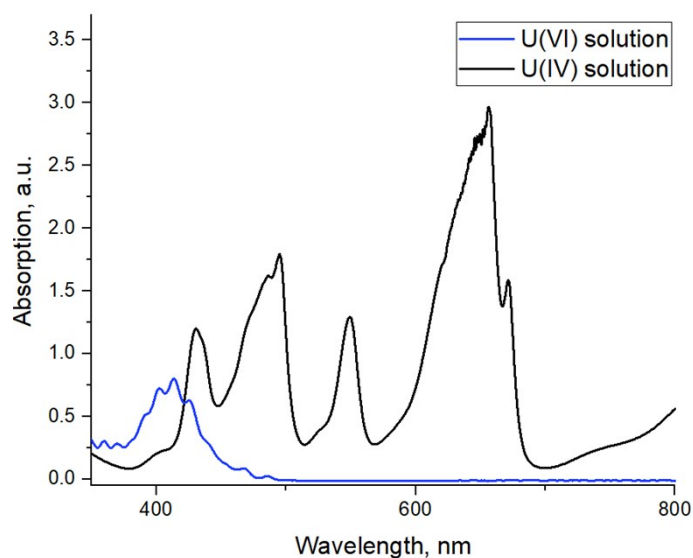


Fig. S1. UV-vis spectra of 0.1M uranium solution in 0.5M before and after reduction.

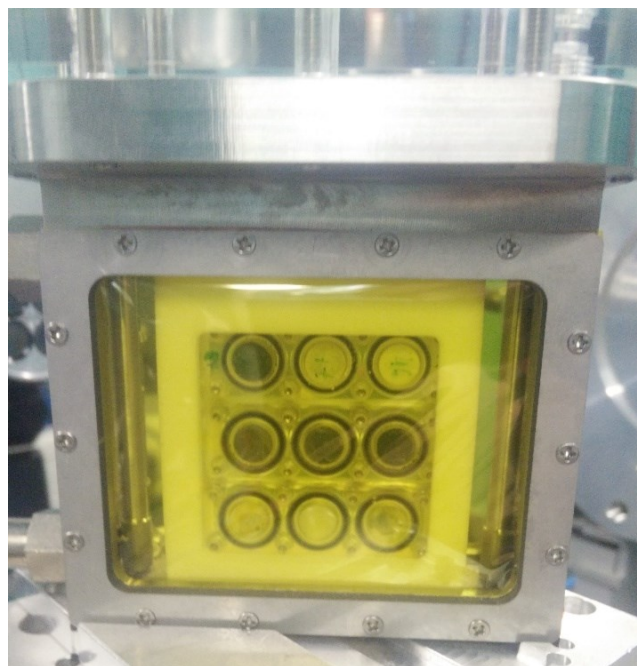


Fig. S2. Photo of the sample cell, including triple holders.

Table S1. pH and Eh values after the end of the reactions.

Sample	pH	Eh, mV
0.01 M U(IV) pH 8	8.0	-272
0.01 M U(IV) pH >11	11.6	-287
0.1 M U(IV) pH 8	8.0	-84
0.1 M U(IV) pH >11	10.9	-482

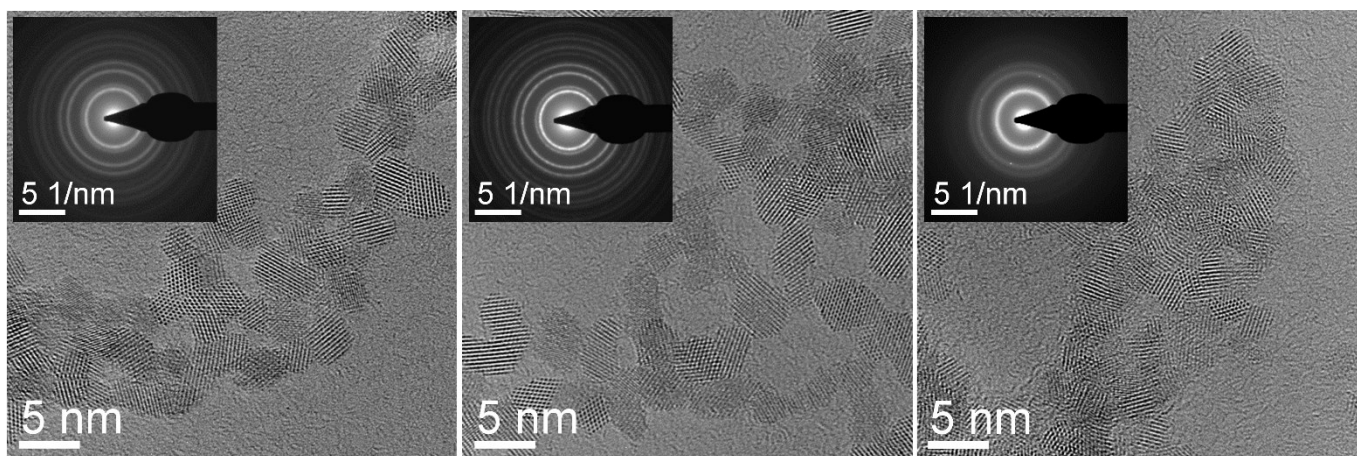


Fig. S3. HRTEM images of NPs and corresponding SAED patterns (inset): a) 0.01M U(IV) pH >11, b) 0.1M U(IV) pH 8, c) 0.1M U(IV) pH >11.

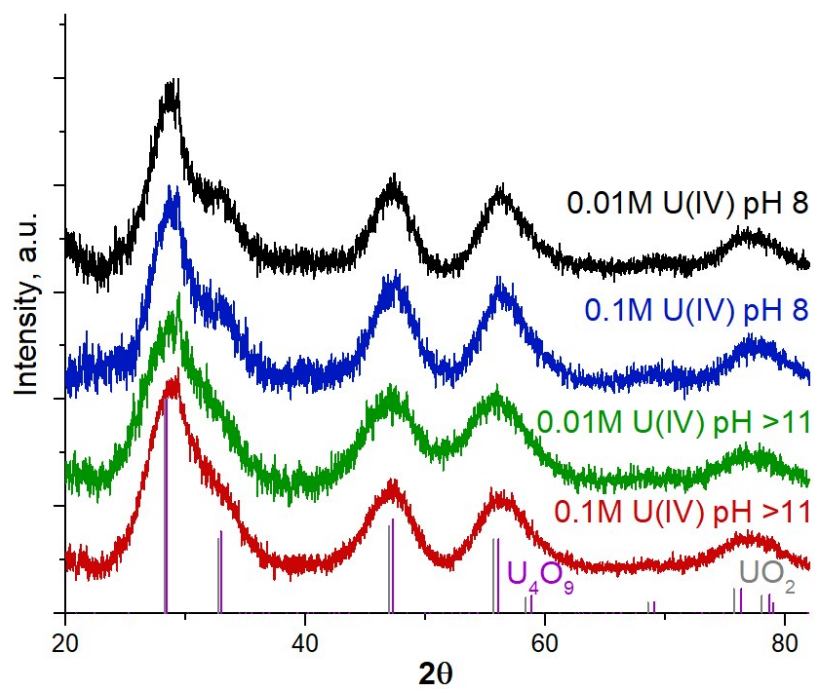


Fig. S4. XRD patterns of the precipitates from U(IV) with different pH and concentrations, UO₂ and U₄O₉ references.

Table S2. Particle size estimation of the samples by XRD and HRTEM.

Sample	Size, nm (XRD)	Size, nm (HRTEM)
0.01 M U(IV) pH 8	2.5±0.6	2.7±0.8
0.01 M U(IV) pH >11	1.7 (one peak)	3.1±0.7
0.1 M U(IV) pH 8	2.5±0.5	3.8±0.9
0.1 M U(IV) pH >11	1.8±0.3	2.7±0.8
0.1 M U(IV) pH 8 aged	6.0±0.2	6±1
0.1 M U(IV) pH >11 aged	4.8±0.1	6±1

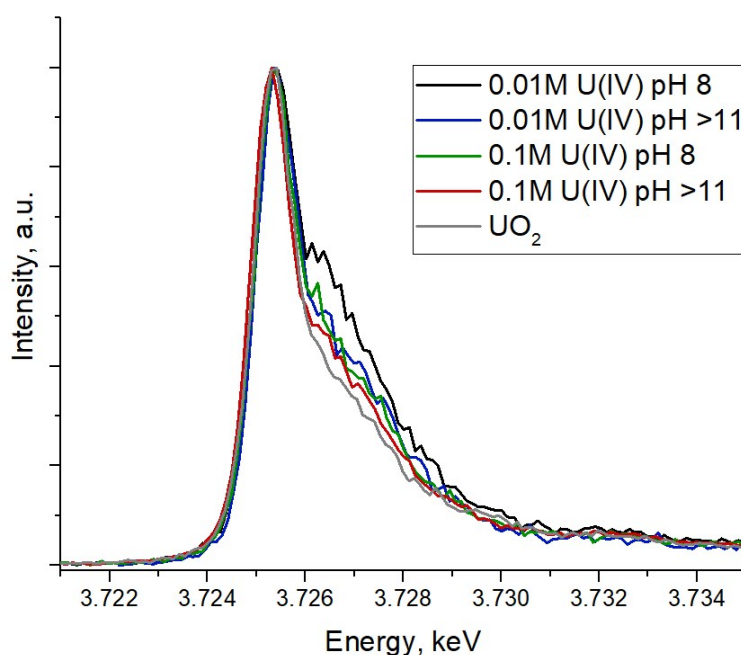


Fig. S5. $U M_4$ HERFD experimental data. The increase of the peak asymmetry is notable.

Calculations of HERFD spectra:

The calculations of the U(IV) M_4 HERFD spectra were performed using crystal field theory. To obtain the HERFD spectra, the core-to core (3d-4f) resonant inelastic x-ray scattering (RIXS) intensity maps were calculated on the emission versus incident photon energy scales and a cut at the constant emission energy, corresponding to the maximum of the RIXS intensity was made along the incident photon energy axis. The RIXS maps were calculated in a manner described in literature^{1,2} by taking into account the full multiplet structure due to intra-atomic and crystal field interactions. The Slater integrals $F^k(5f,5f)$, $F^k(3d,5f)$, $F^k(4f,5f)$ as well as $G^k(3d,5f)$ and $G^k(4f,5f)$ calculated for the U(IV) ion were scaled down to 80 % of their *ab-initio* Hartree-Fock values. The ground, intermediate and final states of the spectroscopic process were represented by the $3d^{10}5f^2$, $3d^95f^3$ and $4f^{13}5f^3$ configurations, respectively. To simulate different U(IV) environment in terms of varying U coordination number (CN), the calculations were done in tetrahedral (T_d), octahedral (O_h^6), cubic (O_h^8) and icosahedral (I_h) symmetry for CN equal to 4, 6, 8 and 12, respectively. The Wybourne's crystal field parameters in the calculations were set to T_d : $B^4_0 = -0.30$ eV, $B^6_0 = -0.70$ eV; O_h^6 : $B^4_0 = 0.93$ eV, $B^6_0 = 0.35$ eV; O_h^8 : $B^4_0 = -0.93$ eV, $B^6_0 = 0.35$ eV; I_h : $B^6_0 = 0.65$ (-0.65) eV. For I_h symmetry both positive and negative values of the B^6_0 parameter were used which produce different results. The abovementioned choice of values was based on already established values for UO_2 ³ and relative changes of parameter values for different symmetries discussed in literature.^{4,5}

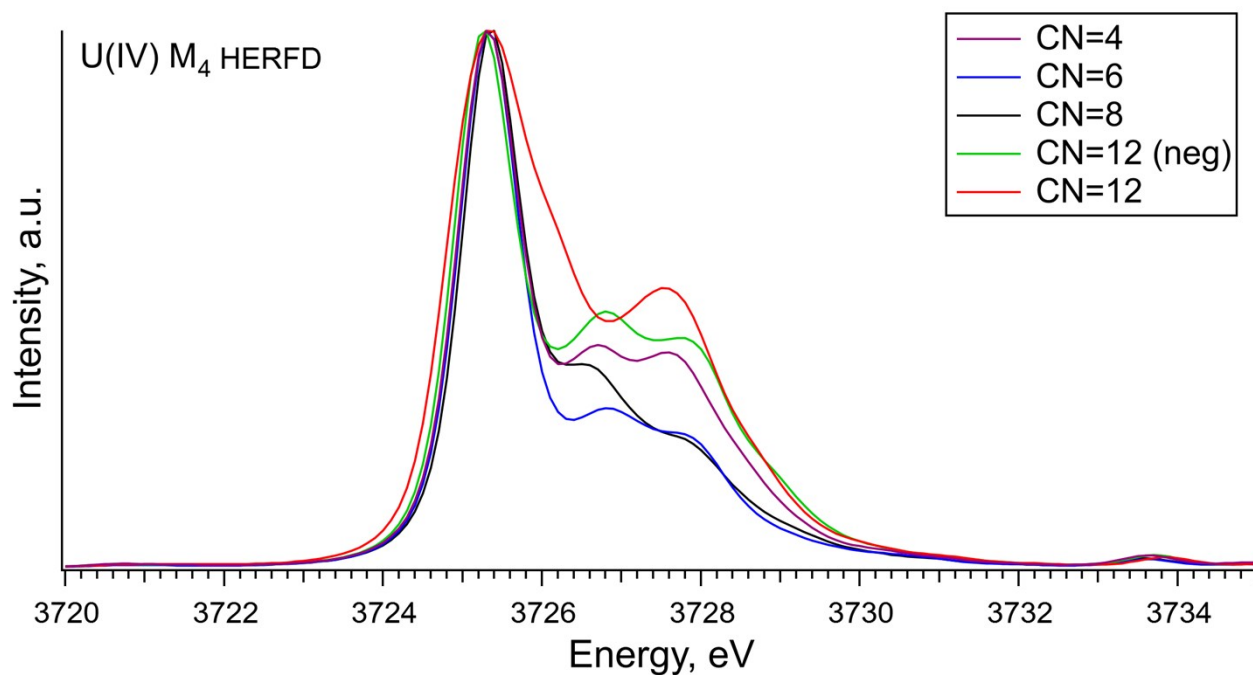


Fig. S6. M_4 HERFD spectra calculated for the U(IV) ion in environments with different coordination number (CN).

EXAFS results:

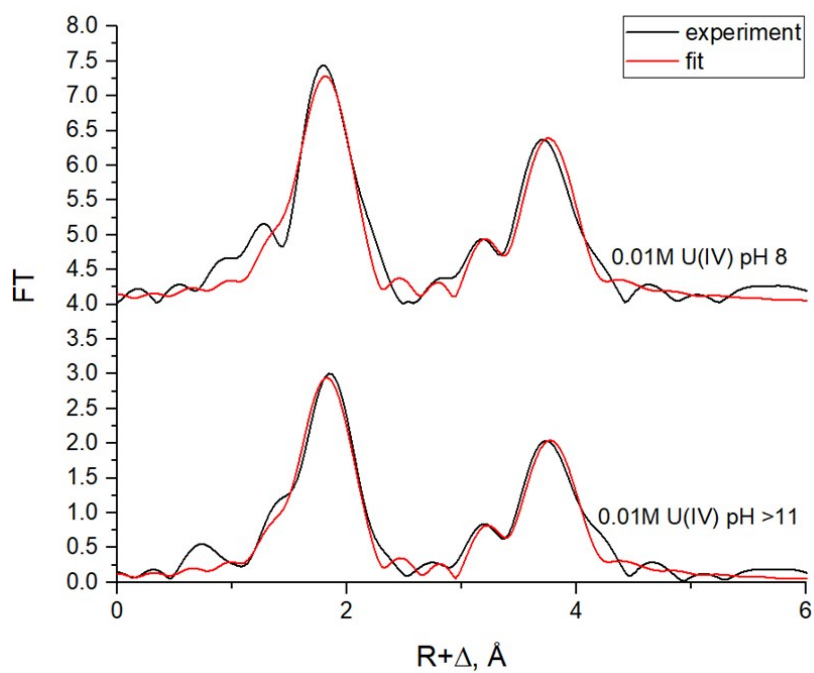


Fig. S7. U L_3 -EXAFS results. a) U L_3 -EXAFS spectra $\chi(R)$ fit results, Fourier transform (FT) magnitude of experimental EXAFS data (black) and shell fit (red) with U-O, U-U shells.

Table S3. Metric parameters extracted by least-squares fit analysis of U L₃ EXAFS spectra with U-O, U-U shells, (k range of 2.0-11.5 Å⁻¹).

Sample	First coordination shell			Second coordination shell			ΔE_0 [eV]	R-factor, %
	CN	R [Å]	σ^2 [Å ²]	CN	R [Å]	σ^2 [Å ²]		
0.01M U(IV) pH 8	4.9(0.6) O	2.33(0.01)	0.011	3.6(1.0) U	3.855(0.008)	0.005	5.9	3.1
0.01M U(IV) pH >11	4.2 O (0.5)	2.33(0.01)	0.011	2.9 U(0.8)	3.861(0.007)	0.004	7.0	2.6
UO ₂ structure	8 O	2.3677		12 U	3.8665 U			

Reactivity of the NPs

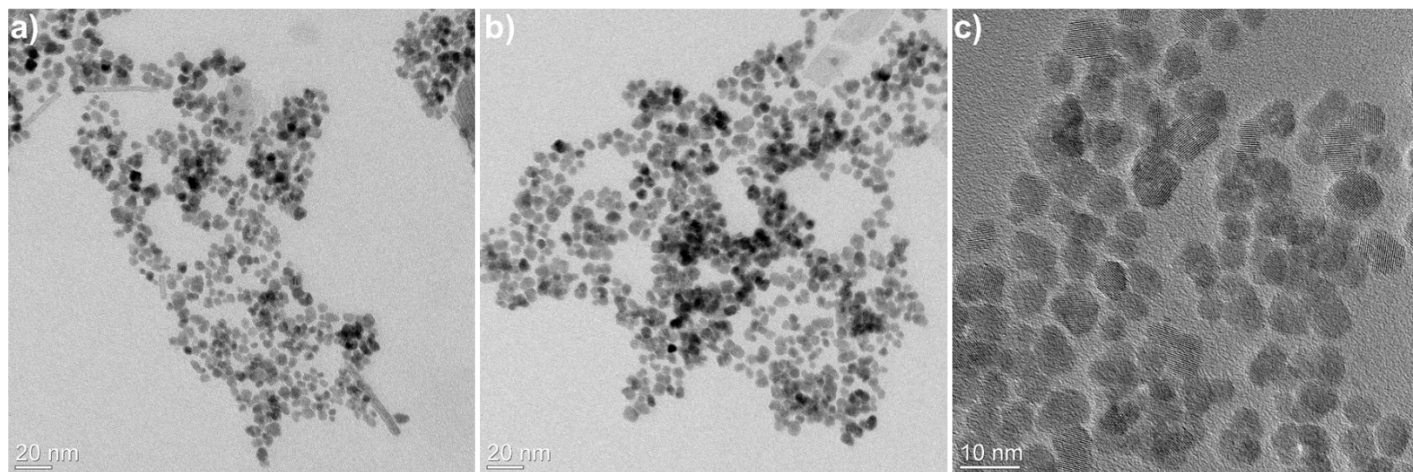


Fig. S8. HRTEM images of the one-year-old 0.1 M U(IV) pH >11 sample at different scales: a), b) scale bar 20 nm, different analysis regions, c) scale bar 10 nm.

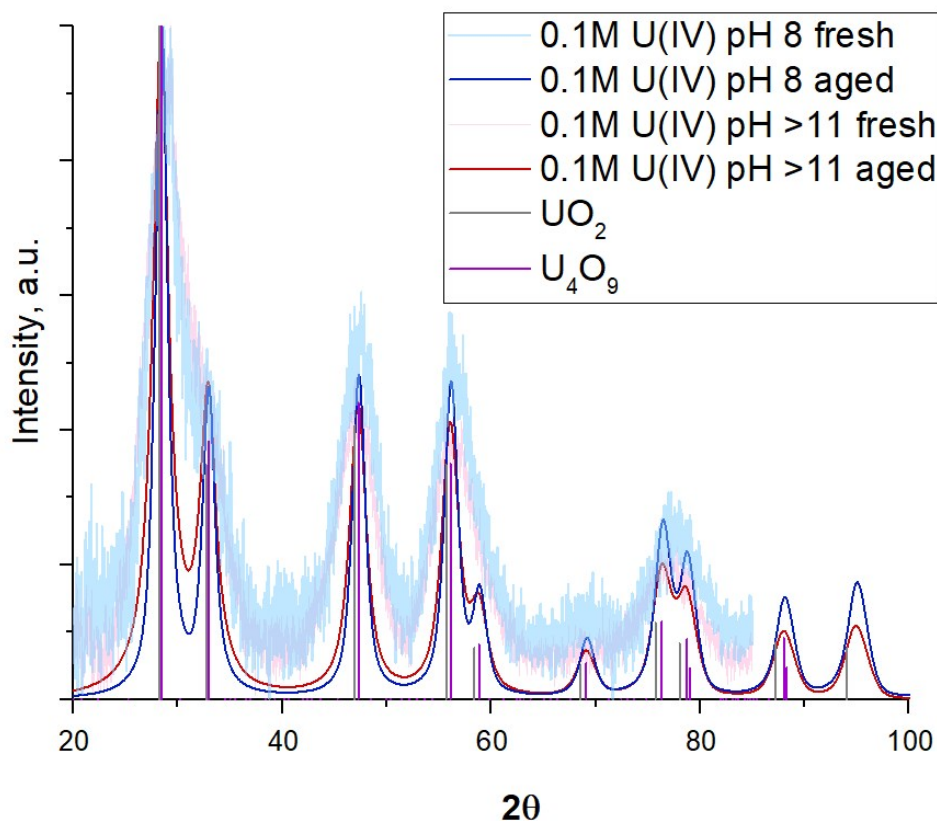


Fig. S9. X-ray diffraction patterns measured from fresh and 1-year old samples.

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