Insight into the structure-property relation of UO$_2$ nanoparticles

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Experimental

![UV-vis spectra of 0.1M uranium solution in 0.5M before and after reduction.](https://example.com/uv-vis-spectra.png)

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, UO$_2$ and U$_4$O$_9$ 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 M⁴ HERFD experimental data. The increase of the peak asymmetry is notable.

Calculations of HERFD spectra:
The calculations of the U(IV) M₄ 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 literature¹,² 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 3d¹⁰⁵f², 3d⁸⁵f⁴ and 4f¹⁵⁵f³ configurations, respectively. To simulate different U(IV) environment in terms of varying U coordination number (CN), the calculations were done in tetrahedral (Td), octahedral (O₆⁶), cubic (O₈⁸) and icosahedral (I₉) symmetry for CN equal to 4, 6, 8 and 12, respectively. The Wybourne’s crystal field parameters in the calculations were set to Td: $B_{40}^0 = -0.30$ eV, $B_{60}^0 = -0.70$ eV; O₆⁶: $B_{40}^0 = 0.93$ eV, $B_{50}^0 = 0.35$ eV; $B_{40}^0$: $B_{40}^0 = -0.93$ eV, $B_{50}^0 = 0.35$ eV; I₉: $B_{40}^0 = 0.65$ (-0.65) eV. For I₉ symmetry both positive and negative values of the $B_{40}^0$ parameter were used which produce different results. The abovementioned choice of values was based on already established values for UO₂³⁺ and relative changes of parameter values for different symmetries discussed in literature.⁴,⁵
Fig. S6. Mo HERFD spectra calculated for the U(IV) ion in environments with different coordination number (CN).

**EXAFS results:**

![EXAFS spectra](image)

Fig. S7. U L₃ EXAFS results. a) U L₃ 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 L₂₃ EXAFS spectra with U-O, U-U shells, (k range of 2.0-11.5 Å⁻¹).

| Sample | First coordination shell | Second coordination shell | $\Delta E_0$ [eV] | R-factor, % |
|--------|---------------------------|---------------------------|-------------------|-------------|
|        | CN | R [Å] | $\sigma^2$ [Å²] | CN | R [Å] | $\sigma^2$ [Å²] |        |
| 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 |
| UO₂ 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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