Supporting information

Colloids and interfaces

Rapid hydrolysis of organophosphates induced by U(IV) nanoparticles: A kinetic and mechanistic study using spectroscopic analysis

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Figure S1. UV-Vis absorption spectra; (a) before and after the synthesis of U(IV)_{NPs} from 1 mM U(IV) solution at pH 2.3; (b) a comparison of U(IV)_{NPs} spectra with ionic U(IV) species $(U^{4+}(aq) \text{ at pH } \sim 0 \text{ and } U(OH)^{3+}(aq) \text{ at pH } \sim 2, [U(IV)] = 6.3 \text{ mM}).$



Figure S2. Particle size distribution obtained from DLS analysis of U(IV)_{NPs} prepared in an aqueous solution containing 0.1 M NaClO₄ ([U]_{total}, 1 mM).



Figure S3. Particle size and zeta-potential measurements of 1 mM $U(IV)_{NPs}$ in 0.1 M NaClO₄ at a wide range of pH by DLS.

*Note that the data were represented using the average values of three measurements and the size and zeta-potential were measured at r.t. in 1 h preparation of samples, after which the pH was measured.



Figure S4. Absorption spectra collected during the initial reaction of the NPP-U(IV) mixture (black) (50 μ M NPP, 0.1 M NaClO₄, pH 7.5); (a) with 100 μ M U(IV)_{NPs} at 25 °C for initial 600 s and after 0.5 h (thick red); (b) with 100 μ M U(IV)-OH(am) at 50 °C for initial 600 s. *Note that in (a) dashed lines (arrow a) exhibit the initial transition between two intermediates adsorbed on the surfaces of U(IV)_{NPs}, and in (b) such an initial transition is absent.



Figure S5. UV-Vis absorption spectra of 5–50 μ M NPP (left column) and NP (right column) at (a) pH 3, (b) pH 7, and (c) pH 9.



Figure S6. Initial rate monitoring for hydrolysis of 25, 50, and 100 μ M NPP with 0.5 mM U(IV)_{NPs} at 50 °C and pH 7.5 ± 0.2. Linear fitting curves are added for each reaction to calculate the rates of hydrolysis.

*Note that the equations for the rate constant (k_{obs}) calculation are below.

$$[NPP] + [U] \rightarrow [NP]$$
$$r = k[NPP][U] = k_{obs}[NPP] = -\frac{d[NPP]}{dt}$$

**Note that in the above equations [U] indicates the concentration of U(IV)_{NPs}.



Figure S7. ATR-FTIR spectra of reaction mixture; (a) for 0.1 mM NPP without $U(IV)_{NPs}$ (dashed) and from the addition of 0.1–2 mM $U(IV)_{NPs}$ to 0.1 mM NPP (solid, pH 3.2–2.0); (b) for 5 mM NPP without $U(IV)_{NPs}$ (red, pH 5.2) and from the addition of 2 mM $U(IV)_{NPs}$ to 0.1 mM NPP (black, pH 6.1).



Figure S8. (a) ATR-FTIR spectra of various reaction mixtures; one for 5 mM NPP without $U(IV)_{NPs}$ (black-dashed, pH 5.2); the others by increasing NPP concentration from 0.5 to 10 mM with 1 mM $U(IV)_{NPs}$ (solid, pH 3.2–5.2); (b) plots of peak intensities at 1350 cm⁻¹ of ATR-FTIR spectra obtained by increasing the concentration of NPP; one with 1 mM $U(IV)_{NPs}$ (square dots); the other without $U(IV)_{NPs}$ (circle dots).



Figure S9. ReactLab KINETICS fitting results of the NPP hydrolysis mediated by U(IV)_{NPs} at 50 °C and pH 6.2 for 100 s; calculated values are $k_1 = 2.9 \times 10^{-2}$ and $k_2 = 4.8 \times 10^{-4}$; a) concentrations of species over time and molar coefficient spectra of colored species, and b) UV-Vis spectra obtained by experiment and simulated by the ReactLab program with residual spectra.

*Note that the equations for the rate constant (kobs) calculation are below.

$$[I2] + [U] \xrightarrow{k_2} [NP] + [U]$$

$$r = k_2[I2][U] = k_{obs}[I2]$$

**Note that in the above equations [U] indicates the concentration of U(IV)_{NPs}.



Figure S10. ReactLab KINETICS fitting results of the NPP hydrolysis mediated by $U(IV)_{NPs}$ at 50 °C and pH 7.5 for 100 s; calculated values are $k_1 = 5.5 \times 10^{-2}$ and $k_2 = 1.2 \times 10^{-3}$; a) concentrations of species over time and molar coefficient spectra of colored species, and b) UV-Vis spectra obtained by experiment and simulated by the ReactLab program with residual spectra.



Figure S11. ReactLab KINETICS fitting results of the NPP hydrolysis mediated by $U(IV)_{NPs}$ at 50 °C and pH 9.3 for 100 s; calculated values are $k_1 = 3.3 \times 10^{-1}$ and $k_2 = 7.4 \times 10^{-4}$; a) concentrations of species over time and molar coefficient spectra of colored species, and b) UV-Vis spectra obtained by experiment and simulated by the ReactLab program with residual spectra.