

Electronic Supplementary Information (ESI) for Molecular–Scale Structures of Uranyl Surface Complexes on Hematite Facets

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Text S1. Preparation of Hematite Nanocrystals. The hematite nanoplates (HNPs), nanocubes (HNCs) and nanorods (HNRs) were synthesized following the hydrothermal or/and solvothermal methods reported previously.³³⁻³⁵ For the synthesis of HNPs,³³ 1.09 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 40.0 mL of ethanol, 2.8 mL of deionized water and 3.2 g of sodium acetate were mixed thoroughly by stirring at room temperature. Then, the mixture was stirred at room temperature until the complete formation of homogeneous solution. The solution was sealed in a Teflon-lined stainless steel autoclave (100mL) and heated in an oven at 180 °C for 12 hours. The precipitation was collected and washed thoroughly with deionized water and ethanol, and finally dried in a desiccator at 40 °C for 12 hours. As for the synthesis of HNCs,³⁴ 2.08 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to the solution which was composed of 6.93 g sodium oleate, 35 mL ethanol and 4.3 mL oleic acid and then stirred for 2 hours. The resulting homogeneous solution was transferred into 100 mL Teflon-lined stainless steel autoclave, and heated at 180 °C for 12 hours. The resulting hematite precipitation was collected, rinsed with water and ethanol and finally dried at 40 °C for 12 hours. As for the synthesis of HNRs,³⁵ 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to 77 mL of NH_4Cl aqueous solution (0.16 mol/L) and then stirred until the complete formation of homogeneous solution. The resulting homogeneous solution was sealed in a Teflon-lined stainless steel autoclave (100 mL), and heated at 120 °C for 12 hours. The resulting FeOOH precipitation was collected and washed thoroughly with deionized water and ethanol, and finally dried in a desiccator at 40 °C for 12 hours. The FeOOH sample was calcined at 520 °C for 2 hours with a heating rate of 10 °C/min in air to obtain the HNRs for use.

Text S2. Calculation of Adsorbed Uranyl Site Densities on Hematite Facets. If the adsorbed uranyl site densities (Q , #U/nm²) on the {001} and {110} facets of hematite were estimated as follows.

$$\text{As } Q_{\text{HNPs}} = 84.3\% \times Q_{\{001\}} + 15.7\% \times Q_{\{012\}} \approx 84.3\% \times Q_{\{001\}} \quad (\text{S1})$$

$$\begin{aligned} Q_{\text{HNRs}} &= 47.1\% \times Q_{\{001\}} + 47.1\% \times Q_{\{110\}} + 2.9\% \times Q_{\{120\}} + 2.9\% \times Q_{\{210\}} \\ &\approx 47.1\% \times Q_{\{001\}} + 47.1\% \times Q_{\{110\}} \end{aligned} \quad (\text{S2})$$

where, Q_{HNPs} and Q_{HNRs} are uranyl site densities for HNPs and HNRs, respectively.

Thus $Q_{\{001\}} = 0.18$, $Q_{\{110\}} = 0.32$

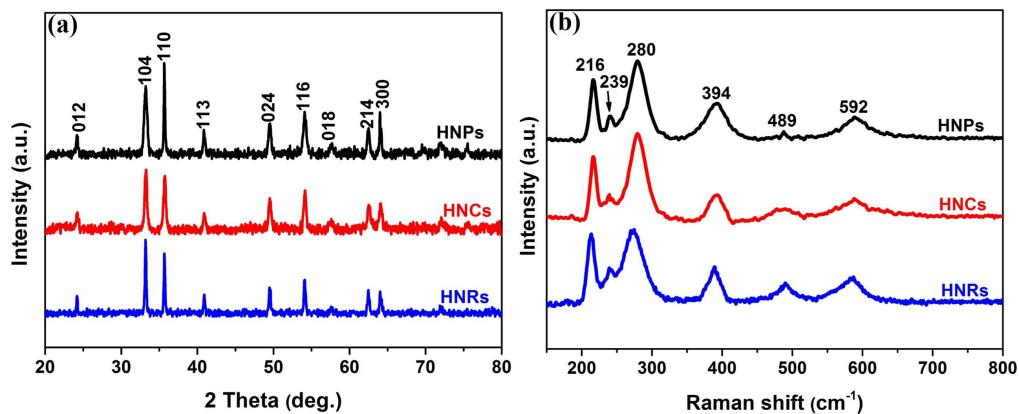


Figure S1. (a) Powder XRD patterns of the different hematite nanocrystals. (b) Raman spectra of the different hematite nanocrystals.

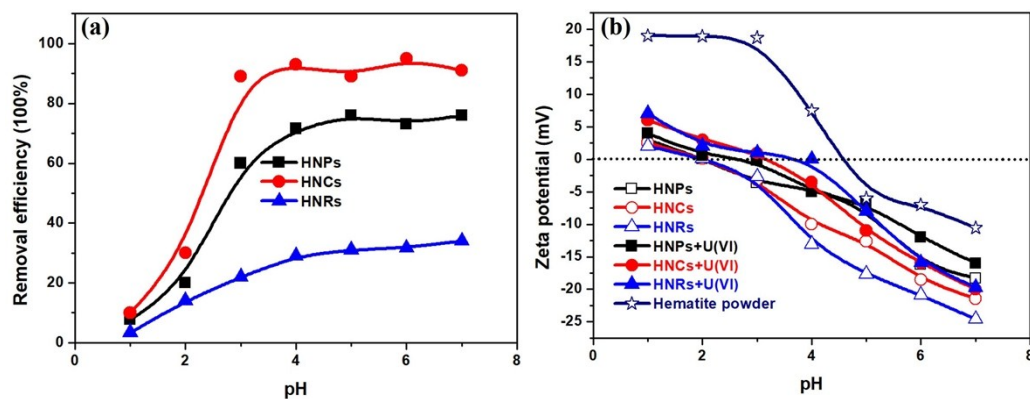


Figure S2. (a) Effect of initial pH on the removal of U(VI) ions by the different hematite nanocrystals. (b) Relation between zeta potential and pH for the different hematite nanocrystals in the absence and presence of U(VI) ions.

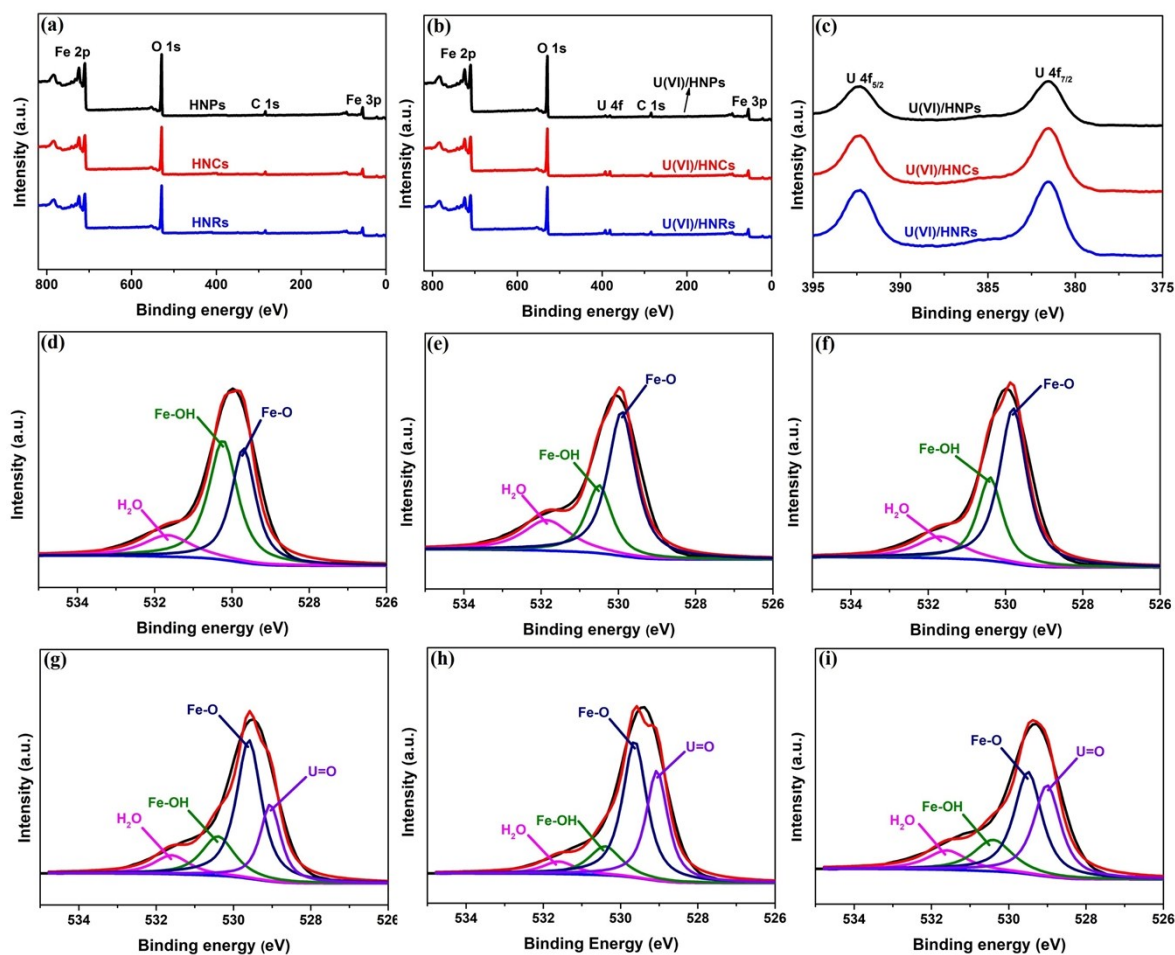


Figure S3. XPS spectrum of different hematite nanocrystals before and after U(VI) adsorption. (a) Full-range XPS spectra of different hematite nanocrystals. (b) Full-range XPS spectra of different hematite nanocrystals after U(VI) adsorption. (c) U 4f XPS spectrum of different hematite nanocrystals after U(VI) adsorption. (d) O 1s XPS spectrum of HNPs. (e) O 1s XPS spectrum of HNCs. (f) O 1s XPS spectrum of HNRs. (g) O 1s XPS spectrum of HNPs after U(VI) adsorption. (h) O 1s XPS spectrum of HNCs after U(VI) adsorption. (i) O 1s XPS spectrum of HNRs after U(VI) adsorption.

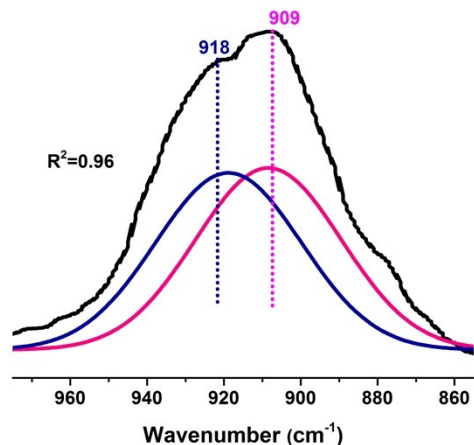


Figure S4. The peak positions were held constant for the fitting of the spectra.

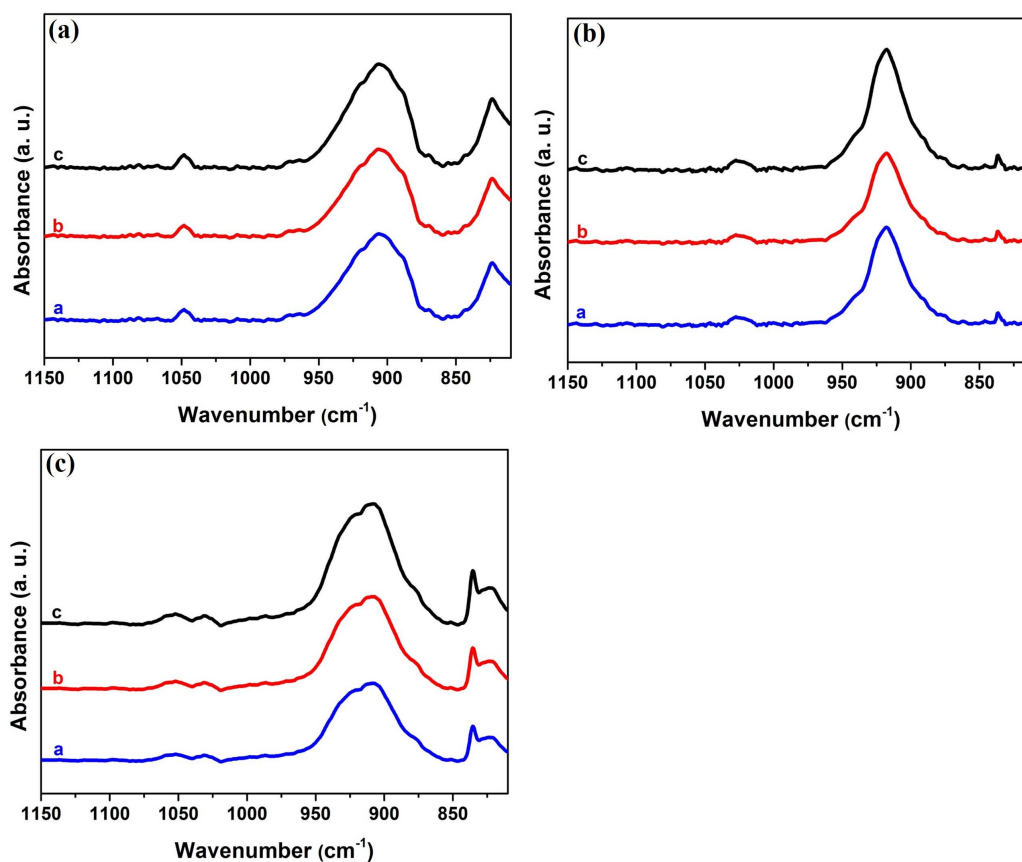


Figure S5. Effect of ionic strength on U(VI) ions adsorption. (a) ATR–FTIR spectra of U(VI) ions adsorption on HNPs as a function of NaCl solution. (b) ATR–FTIR spectra of U(VI) ions adsorption on HNCs as a function of NaCl solution. (c) ATR–FTIR spectra of U(VI) ions adsorption on HNRs as a function of NaCl solution. The NaCl concentration (bottom to top) were 0.1, 0.5, and 1.0 mol/L, respectively.

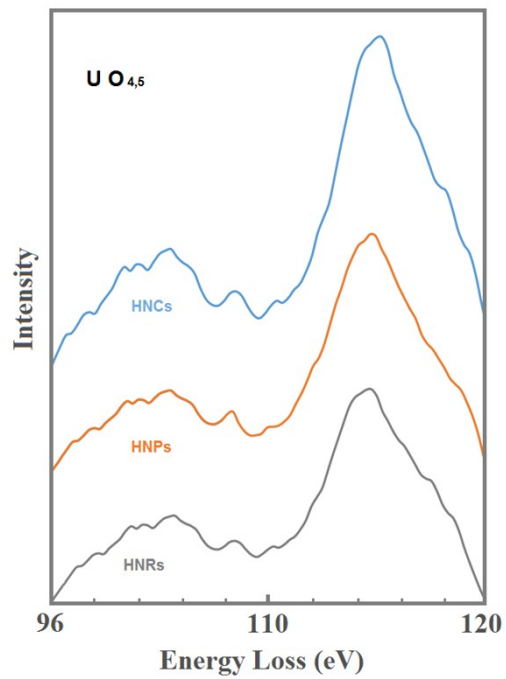


Figure S6. The O_{4,5} edges of U(VI) adsorption on hematite nanocrystals (Gray curve for HNRs, orange for HNPs and blue for HNCs).

Table S1. The different adsorption configuration parameters and theoretical frequencies of U(VI) adsorbed on hematite facets.

| Configuration | E_{ads} (kJ/mol) | $R_{\text{U=O}}$ (Å) | $R_{\text{U-O}}$ (Å) | $R_{\text{U-Fe}}$ (Å) | Frequencies (cm ⁻¹) |
|----------------------|---------------------------|----------------------|----------------------|-----------------------|---------------------------------|
| ² E-{001} | - 57.6 | 1.85 | 2.34 | 3.40 | 1040, 912, 811 |
| ² C-{001} | - 26.3 | 1.85 | 2.34 | 4.05, 4.20 | 1030, 925, 843 |
| ² E-{012} | - 67.1 | 1.85 | 2.34 | 3.82 | 1045, 907, 816 |
| ² C-{012} | - 76.0 | 1.85 | 2.34 | 4.02, 4.24 | 1026, 920, 841 |
| ² E-{110} | 14.9 | 1.85 | 2.34 | 3.68 | 1052, 907, 809 |
| ² C-{110} | - 64.0 | 1.85 | 2.34 | 4.10, 3.98 | 1031, 922, 840 |

Table S2. Parameters defining local coordination environment of U(VI) adsorbed on hematite nanostructures as determined by EXAFS spectroscopy.

| entry | shell | CN | R (Å) | σ^2 (Å ²) |
|-------|-------------------|------|-------|------------------------------|
| HNPs | U=O _{ax} | 2.0 | 1.80 | 0.0021 |
| | U-O _{eq} | 5.3 | 2.32 | 0.0043 |
| | U-Fe | 0.9 | 3.43 | 0.0054 |
| HNCs | U=O _{ax} | 2.0 | 1.80 | 0.0017 |
| | U-O _{eq} | 5.5 | 2.41 | 0.0033 |
| | U-Fe | 1.46 | 4.06 | 0.0047 |
| HNRs | U=O _{ax} | 2.0 | 1.80 | 0.0029 |
| | U-O _{eq} | 5.2 | 2.30 | 0.0042 |
| | U-Fe | 0.9 | 3.41 | 0.0060 |
| | | 0.75 | 4.11 | 0.0053 |

Table S3. IR vibrations of aqueous and coordinated uranyl ions on the surface of hematite.

| | species | type | infrared band positions (cm ⁻¹) | | | | ref |
|-----------------|---|-----------------------------------|---|---------|-----|-----|------------|
| | | | 1000 | 900 | 800 | | |
| aqueous | UO ₂ ²⁺ | | 961 | | 870 | | 56 |
| | UO ₂ ²⁺ | | 962 | | 870 | | 57 |
| | (UO ₂) ₂ (OH) ₂ ²⁺ | | | 943 | | 853 | 57 |
| | (UO ₂) ₃ (OH) ₅ ⁺ | | | 923 | | 835 | 57 |
| | UO ₂ ²⁺ | | | 961 | | | this study |
| adsorbed uranyl | hematite | | | | 906 | | 57 |
| | hematite | | | 919/925 | | | 58 |
| | HNPs | ² E | 1048 | | 909 | 823 | |
| | HNCs | ² C | | 1027 | 918 | 835 | this study |
| | HNRs | ² E and ² C | 1051 | 1031 | 918 | 909 | 835 |

Table S4. Correlation between theoretical and experimental frequencies of uranyl surface complexes on HNPs–{001}.

| Models | Experimental frequencies (cm ⁻¹) | | Theoretical frequencies (cm ⁻¹) | |
|----------------------|--|--|---|----------------------|
| | U(VI)/HNPs–{001} | | ² E–{001} | ² C–{001} |
| v(U–O) | 1048 | | 1040 (–8)* | 1030 (–18) |
| v ₃ (U=O) | 909 | | 912 (3) | 925 (–16) |
| v(U–O–Fe) | 823 | | 811 (–12) | 843 (20) |
| R ² | NA | | 0.99 | 0.99 |
| Slope | NA | | 1.01 | 0.82 |
| Intercept | NA | | – 13.59 | 169.19 |
| Standard deviation | NA | | 10.42 | 22.14 |

*The numbers in parenthesis = theoretical frequencies - experimental frequencies.

Table S5. Correlation between theoretical and experimental frequencies of uranyl surface complexes on HNCs–{012}.

| Models | Experimental frequencies (cm ⁻¹) | Theoretical frequencies (cm ⁻¹) | |
|----------------------|--|---|----------------------|
| | U(VI)/HNCs–{012} | ² E–{012} | ² C–{012} |
| $\nu(\text{U-O})$ | 1027 | 1045 (18)* | 1026 (-1) |
| $\nu_3(\text{U=O})$ | 918 | 907 (-11) | 920 (2) |
| $\nu(\text{U-O-Fe})$ | 835 | 816 (-13) | 841 (6) |
| R ² | NA | 1.00 | 1.00 |
| Slope | NA | 1.20 | 0.98 |
| Intercept | NA | - 186.03 | 35.69 |
| Standard deviation | NA | 17.52 | 4.53 |

*The numbers in parenthesis = theoretical frequencies - experimental frequencies.

Table S6. Correlation between theoretical and experimental frequencies of uranyl surface complexes on HNRs–{110}.

| Models | Experimental frequencies (cm ⁻¹) | Theoretical frequencies (cm ⁻¹) | |
|----------------------|--|---|----------------------|
| | U(VI)/HNRs–{110} | ² E–{110} | ² C–{110} |
| v(U–O) | 1031 | 1052 (21)* | 1031 (0) |
| v ₃ (U=O) | 918 | 907 (–11) | 922 (4) |
| v(U–O–Fe) | 835 | 809 (–26) | 840 (5) |
| R ² | NA | 1.00 | 1.00 |
| Slope | NA | 1.24 | 0.98 |
| Intercept | NA | – 230.2 | 27.21 |
| Standard deviation | NA | 24.88 | 4.53 |

*The numbers in parenthesis = theoretical frequencies - experimental frequencies.

Table S7. Kinetics parameters of uranyl ions adsorption onto hematite nanocrystals.

| Samples | SSA (m ² /g) | q _e (mg/m ²) | k ₂ (m ² /(mg min)) | R ² |
|---------|-------------------------|-------------------------------------|---|----------------|
| HNPs | 20.92 | 0.0724 | 0.6066 | 0.98 |
| HNCs | 20.41 | 0.1208 | 0.8874 | 0.99 |
| HNRs | 2.59 | 0.0928 | 0.5329 | 0.92 |