Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Electronic Supplementary Information

Probing pollutants reactions at the iron surface:

A case study of selenite reactions with nanoscale zero-valent iron

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The Electronic Supplementary Information contains 11 pages, including 1 Table and 4 Figures.

1. Materials

The main materials and reagents of experimental are as follows: $FeCl_3 \cdot 6H_2O$, $NaBH_4$, Na_2SeO_3 (AR, Sigma Aldrich (Shanghai) Trading Co., LTD).

The analysis of pure drugs does not require further purification treatment, directly used for the preparation of the reserve solution. Except for special instructions, the reserve solutions were prepared with deionized water and diluted to the appropriate concentration for the experiment on the day. The glassware used for the experiment was soaked in 5% nitric acid solution for 24 hours, then rinsed with deionized water and dried in an air-drying oven for later use[1,2].

2. Equipments

The main instruments and equipment used in this study are shown as follows: X ray photoelectron spectrometer (XPS, PHI Versa Probe 5000, Japan-USA Nanometer Surface Analysis Instrument Co. LTD); pH/ORP analyzer (pHS-4S, Shanghai Electronic Scientific Instrument Co., LTD); Vacuum freeze dryer (FD-1A-50, Shanghai Bilang Instrument Manufacturing Co., LTD). In addition to the instruments and equipment mentioned, nitrogen cylinders, microporous filter head, multi-mouth flask and other common laboratory glass instruments are also used in the experiment[3].

3. Preparation methods

The nano zero-valent iron (nZVI) was prepared by sodium borohydride liquid-phase reduction ferric chloride method[4], the reaction equation is shown below:

$$4Fe^{3+} + 3BH_4^{-} + 9H_2O \rightarrow 4Fe^{0}\downarrow + 3H_2BO_3^{-} + 12H^{+} + 6H_2\uparrow \quad (1)$$

The synthesis steps are as follows: Ferric chloride ($FeCl_3$) solution of a certain volume of 0.05 M and sodium borohydride ($NaBH_4$) solution of the same volume of 0.2 M were prepared. $FeCl_3$ solution was added to $NaBH_4$ solution drop by drop under nitrogen (N_2, purity > 99.9%) conditions, and the mixture was fully mixed by mechanical agitation. After the reaction was completed, the synthesized nZVI was collected by vacuum filtration, washed repeatedly with a large amount of deionized water and anhydrous ethanol, and then stored in anhydrous ethanol at 4°C for later use[4-7].

Added the synthesized nZVI to the 500 mL Se(IV) solution with a concentration of 1.3 mM, and made the concentration of nZVI to be 1.0 g L^{-1}. Under nitrogen (N_2, purity > 99.9%) conditions, the mixture was fully mixed by mechanical agitation. The initial pH was 5.00. Sampling 1.0-5.0 mL every once in a while, and at the same time recorded the solution pH and ORP, then made up to 10 mL with deionized water and diluted nitric acid. All samples were filtered with 0.22 μm (Millipore) filter and repeated 3 times[8]. The adsorption capacity of Se(IV) by nZVI was measured by inductively coupled plasma optical emission spectrometer.

The concentration of total Fe and total Se in the water was determined. After the reaction, the remaining solution was centrifuged at high speed. Flush repeatedly with a large number of deionized water and ethanol, and then placed in vacuum freezing dryer freeze-drying 24 h, saved in the glove box filled with nitrogen for further analysis. Considering the practical wastewater treatment systems are not buffer system, so the experiment did not join the buffer to change the pH of the fixed solution.

4. Inductively coupled plasma optical emission spectrometer (ICP-OES)

This study used ICP-OES to analyze the water phase element content[4]. During the measurement, the sample was brought into the atomization system by carrier gas (Argon, Ar). After atomization, the sample entered the axial channel of plasma in the form of aerosol. The content of the corresponding element was determined by the strength of the characteristic spectral line. The operating conditions of the instrument for sample determination were: cooler pressure:55 psi; Argon and nitrogen pressure: 80 psi; Plasma gas flow rate: 17 L min^{-1}; Auxiliary gas flow: 0.2 L min^{-1}; Atomization gas flow rate: 0.8 L min^{-1}; Peristaltic pump injection rate: 2.0 mL min^{-1}. ICP-OES were able to accurately and rapidly measure various elements in aqueous solution such as selenium (Se), iron (Fe), etc[1,3,9].

5. High-resolution X-ray photoelectron spectroscopy (HR-XPS) analysis

The instrument was equipped with Al Kα X-ray source, energy hv = 1486.6 eV, operation power was 3.8 kW, scanning range of 0-1100 eV. Binding energy calibration was performed by adjusting the C 1s peak to 284.8 eV[10].

Table S1 The kinetics equation and particle dispersion model parameters for Se(IV).

Pseudo-first order			Pseudo-second order		
Q_e	k_1	R^2	Q_e	k_2	R^2
105.535	0.059	0.655	106.383	0.015	0.999

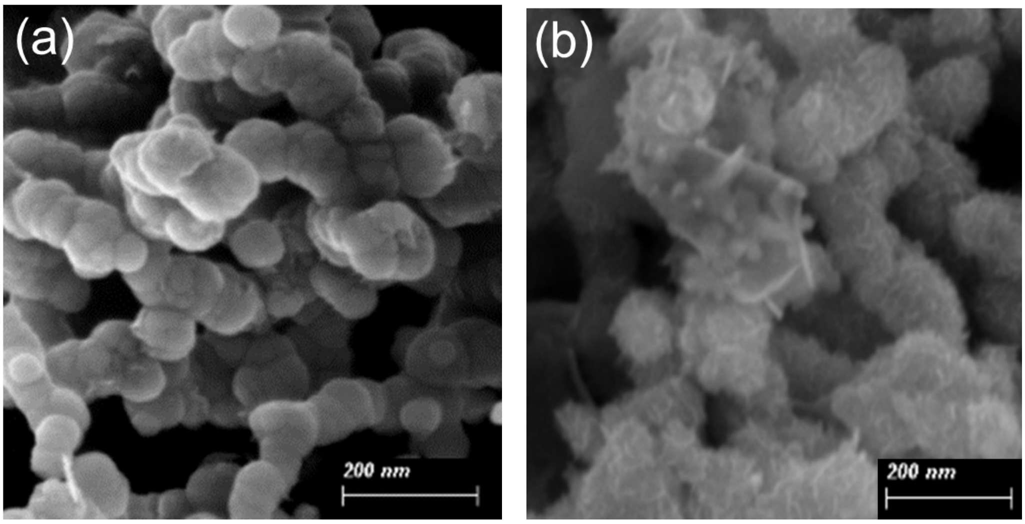

Fig. S1 Scanning electron microscope (SEM) of nZVI. (a) Fresh nZVI; (b) Spent nZVI after the reactions with partial sodium selenate solution (Se(IV))

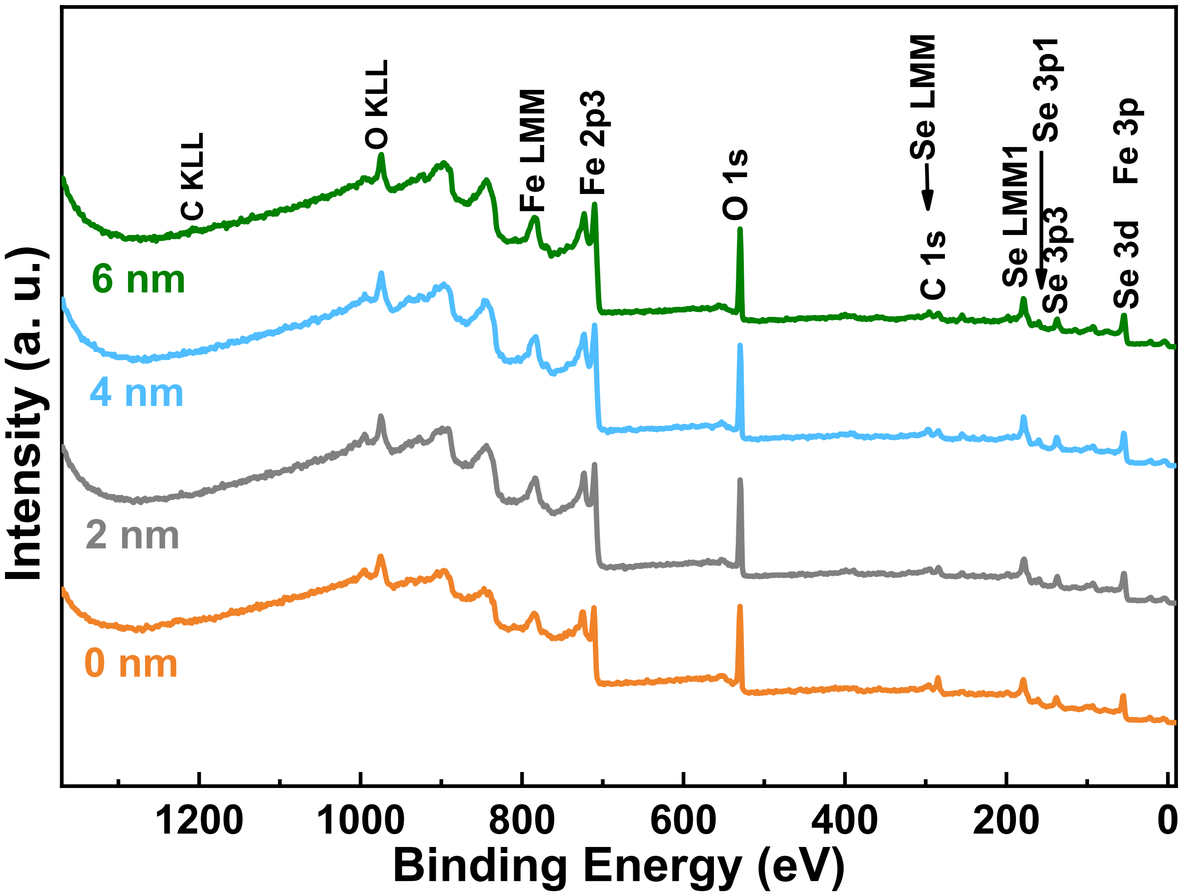

Fig. S2 Full spectrum of HR-XPS spectra of Se-nZVI. $[Se(IV)]_{initial}$ = 1.3 mM; the nZVI dose is 1.0 g L^{-1}, the $pH_{initial}$ is 5.0, and the reaction time is 24 h.

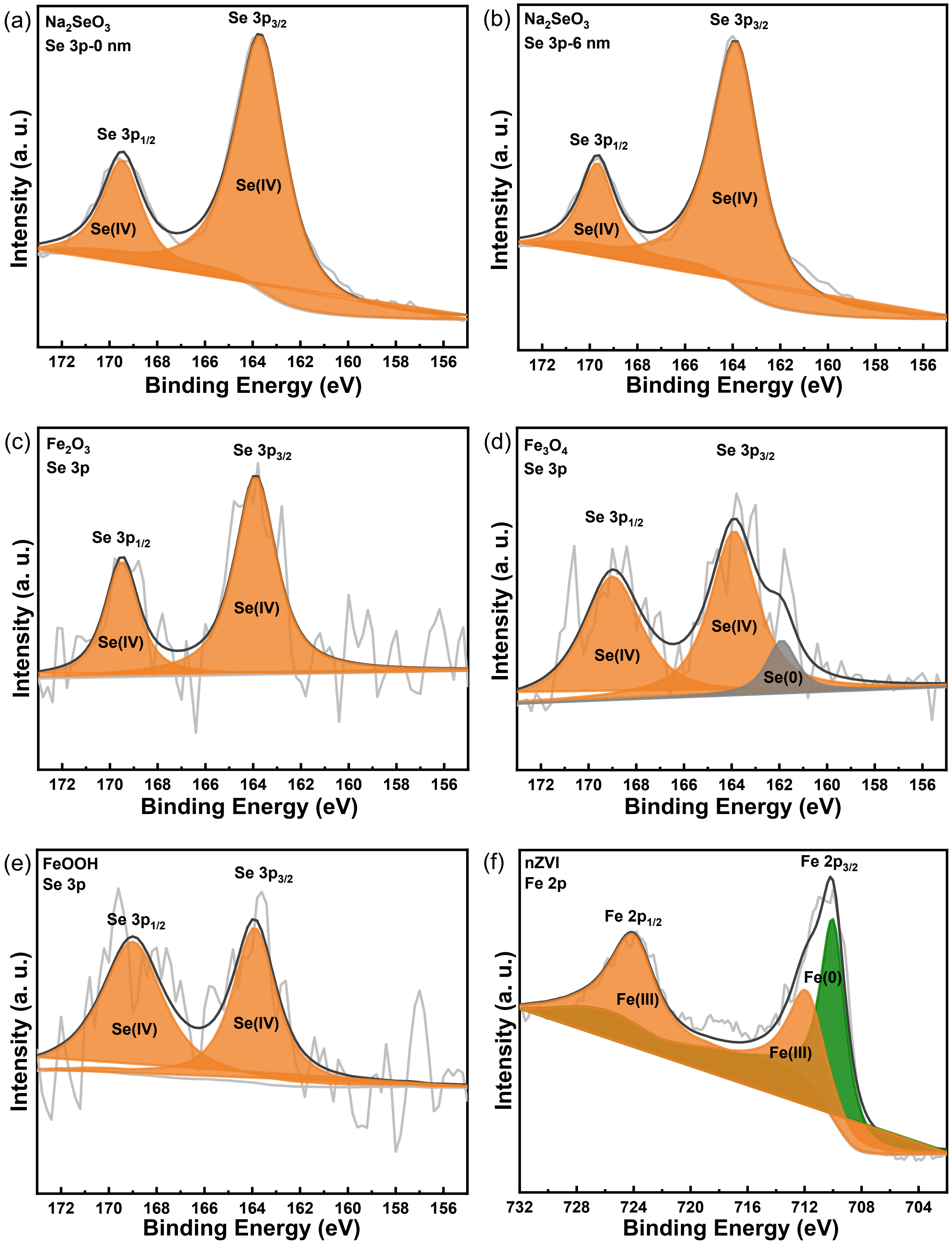
(a)
Na_2SeO_3
Se 3p-0 nm
Se $3p_{3/2}$
Se $3p_{1/2}$
Se(IV)
Se(IV)
Intensity (a. u.)
172 170 168 166 164 162 160 158 156
Binding Energy (eV)
(b)
Na_2SeO_3
Se 3p-6 nm
Se $3p_{3/2}$
Se $3p_{1/2}$
Se(IV)
Se(IV)
Intensity (a. u.)
172 170 168 166 164 162 160 158 156
Binding Energy (eV)
(c)
Fe_2O_3
Se 3p
Se $3p_{3/2}$
Se $3p_{1/2}$
Se(IV)
Se(IV)
Intensity (a. u.)
172 170 168 166 164 162 160 158 156
Binding Energy (eV)
(d)
Fe_3O_4
Se 3p
Se $3p_{3/2}$
Se $3p_{1/2}$
Se(IV)
Se(IV)
Se(0)
Intensity (a. u.)
172 170 168 166 164 162 160 158 156
Binding Energy (eV)
(e)
FeOOH
Se 3p
Se $3p_{3/2}$
Se $3p_{1/2}$
Se(IV)
Se(IV)
Intensity (a. u.)
172 170 168 166 164 162 160 158 156
Binding Energy (eV)
(f)
nZVI
Fe 2p
Fe $2p_{3/2}$
Fe $2p_{1/2}$
Fe(III)
Fe(0)
Fe(III)
Intensity (a. u.)
732 728 724 720 716 712 708 704
Binding Energy (eV)

Fig. S3 HR-XPS spectra of Se 3p and Fe 2p species at oxide layer. (a) XPS spectra of Se 3p element in 0 nm of Na_2SeO_3; (b) XPS spectra of Se 3p element in 6 nm of Na_2SeO_3; (c) XPS spectra of Se 3p element in Fe_2O_3-Se(IV); (d) XPS spectra of Se 3p element in Fe_3O_4-Se(IV); (e) XPS spectra of Se 3p element in FeOOH-Se(IV); (f) XPS spectra of Fe 2p species in fresh nZVI. $[Se(IV)]_{initial}$ = 1.3 mM, the nZVI dose is 1.0 g L^{-1}, the $pH_{initial}$ is 5.0, and the reaction time is 24 h.

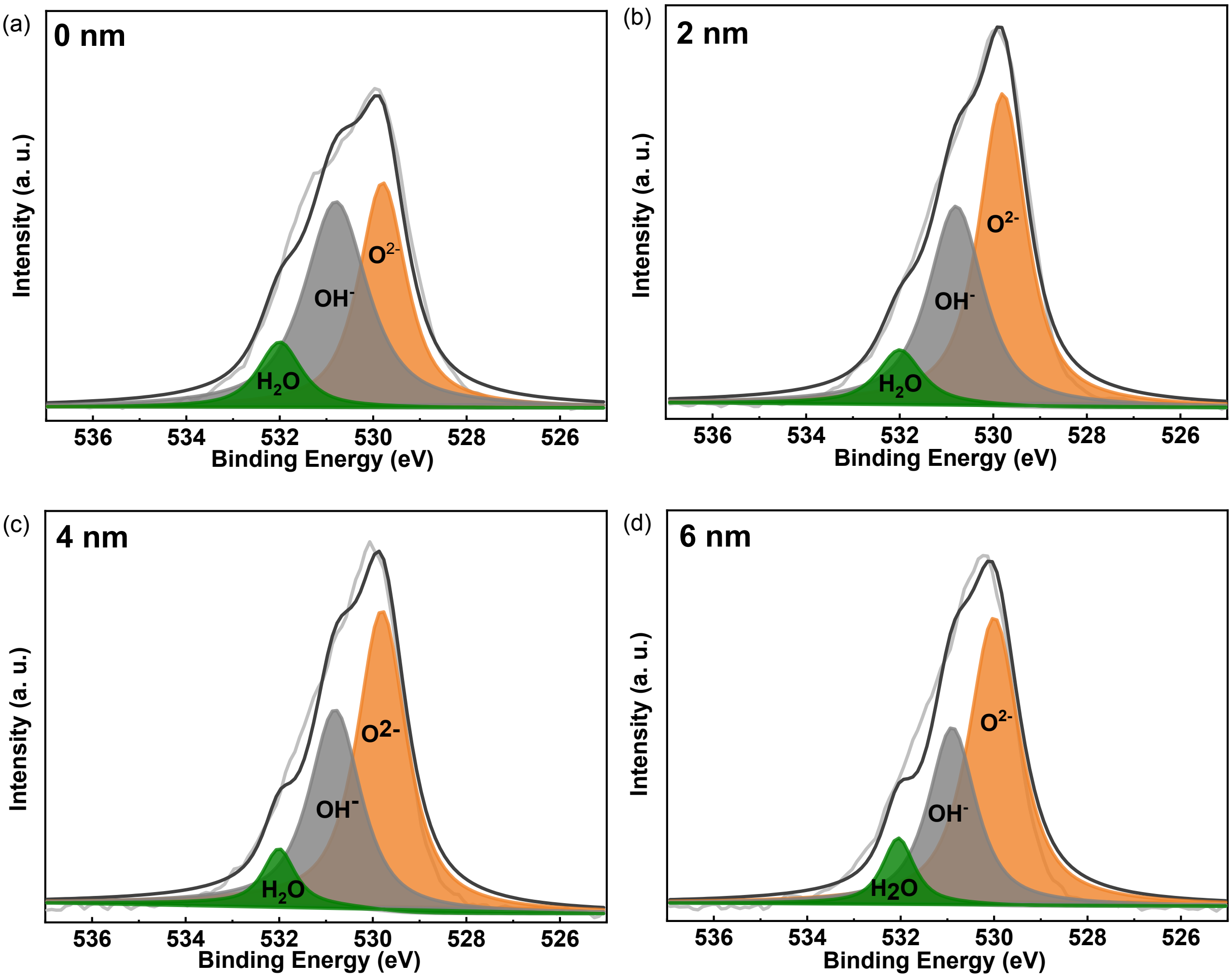

Fig. S4 HR-XPS spectra of Fe 2p species at selected depth. (a) 0 nm; (b) 2 nm; (c) 4 nm; (d) 6 nm. $[Se(IV)]_{initial}$ = 1.3 mM; the nZVI dose is 1.0 g L^{-1}, the $pH_{initial}$ is 5.0, and the reaction time is 24 h.

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