

Iron and Sulfur Precursors Affect Crystalline Structure, Speciation, and Reactivity of Sulfidized Nanoscale Zerovalent Iron

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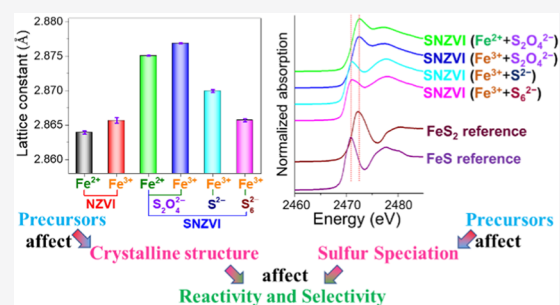


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ABSTRACT: The reactivity of sulfidized nanoscale zerovalent iron (SNZVI) is affected by the amount and species of sulfur in the materials. Here, we assess the impact of the Fe (Fe^{2+} and Fe^{3+}) and S ($\text{S}_2\text{O}_4^{2-}$, S^{2-} , and S_6^{2-}) precursors used to synthesize both NZVI and SNZVI on the resulting physicochemical properties and reactivity and selectivity with water and trichloroethene (TCE). X-ray diffraction indicated that the Fe precursors altered the crystalline structure of both NZVI and SNZVI. The materials made from the Fe^{3+} precursor had an expanded lattice in the Fe^0 body-centered-cubic (BCC) structure and lower electron-transfer resistance, providing higher reactivity with water (~ 2 – 3 fold) and TCE (~ 5 – 13 fold) than those made from an Fe^{2+} precursor. The choice of the S precursor controlled the S speciation in the SNZVI particles, as indicated by X-ray absorption spectroscopy. Iron disulfide (FeS_2) was the main S species of SNZVI made from $\text{S}_2\text{O}_4^{2-}$, whereas iron sulfide (FeS) was the main S species of SNZVI made from $\text{S}^{2-}/\text{S}_6^{2-}$. The former SNZVI was more hydrophobic, reactive with, and selective for TCE compared to the latter SNZVI. These results suggest that the Fe and S precursors can be used to select the conditions of the synthesis process and provide selected physicochemical properties (e.g., S speciation, hydrophobicity, and crystalline structure), reactivity, and selectivity of the SNZVI materials.



1. INTRODUCTION

Nanoscale zerovalent iron (NZVI) has been studied as an in situ groundwater remediation technology for more than two decades.^{1–12} More recently, sulfidation of NZVI (SNZVI) has been proposed as a promising modification to greatly improve the reactivity, selectivity, and longevity of NZVI, decreasing the undesirable side reaction between Fe^0 and water (H_2 evolution).^{13–25} The electron efficiency or selectivity of SNZVI for contaminants can be described as the fraction of electron equivalents from Fe^0 that is used for the reduction of the target contaminant.^{19,26} The electron efficiency for the reduction of trichloroethene (TCE) in water is ~ 25 – 400 -fold higher for SNZVI compared to NZVI.^{18,19,27–29}

Various sulfidation methods and S precursors have been proposed to synthesize SNZVI. A typical co-sulfidation method uses $\text{Na}_2\text{S}_2\text{O}_4$ as the sulfur precursor, which is mixed with a NaBH_4 solution and then dropwise added into an aqueous solution of either Fe^{2+} or Fe^{3+} .^{13,30–34} Alternatively, a typical postsulfidation method uses Na_2S as the sulfur precursor to sulfidize as-prepared NZVI particles.^{14,35–40} Other approaches have also been reported, e.g., using Na_2S as a co-sulfidation reagent, using $\text{Na}_2\text{S}_2\text{O}_4$ or thiosulfate as a postsulfidation reagent.^{41–44} Few studies measured and reported the actual amount of S in the synthesized particles. Our recent studies have demonstrated that the actual S amount in the particles can be much lower than the dosed amount, and

that co-sulfidation incorporates more S into the materials than postsulfidation.^{27,28,44} However, the impact of the type of Fe and S precursors on the S content of SNZVI is unknown.

Besides the S content, the S speciation is another important factor that controls the physicochemical properties of SNZVI.²⁸ In the literature, the S speciation is mainly studied using X-ray photoelectron spectroscopy (XPS), which detects S oxidation states primarily on the surface (< 10 nm). This can lead to artifacts because the surface of the materials is inevitably oxidized during sample preparation for the XPS measurement. Although the reduction of the contaminants by NZVI is generally considered a surface reaction, the overall electron-transfer efficiency from the Fe^0 -rich core to the reactive surface will likely be controlled by the FeS_x speciation in or on the surface of the particles, due to the different band gaps of FeS_x , e.g., $\text{FeS} = 0.10$ eV, $\text{FeS}_2 = 0.95$ eV, and $\text{Fe}_3\text{S}_4 = 0.00$ eV.⁴⁵ It is widely reported that an FeS (iron monosulfide) phase is either coated onto or mixed with the Fe^0 phase for particles made from either co-sulfidation by $\text{Na}_2\text{S}_2\text{O}_4$ or

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postsulfidation by Na_2S , mostly according to the S 2p XPS spectra and/or transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (TEM-EDX) analysis.^{13,41} A recent study-used synchrotron-based pair distribution function (PDF) analysis found an FeS shell on the $\text{Na}_2\text{S}_2\text{O}_4$ co-sulfidized SNZVI.⁴⁶ X-ray absorption spectroscopy (XAS), which provides an average S speciation in the particles (surface and interior), confirmed the predominance of FeS in the SNZVI particles made by co-sulfidation using $\text{Na}_2\text{S}_2\text{O}_4$.^{28,47} However, FeS_2 was recently found in the SNZVI particles with higher S content.²⁸ There is a limited understanding of whether or not different S and Fe precursors would affect the speciation of S in the SNZVI particles.

The commonly used Fe precursors (Fe^{2+} or Fe^{3+}) for NZVI or SNZVI synthesis have not been reported to impact the properties and reactivity of the resulting particles. Differences in the reactivity of NZVI or SNZVI reported from individual research groups are most often attributed to batch-to-batch variations in the surface oxidation/passivation, Fe^0 content, S content, and the available surface area. However, florfenicol was only poorly reactive after 2 h with NZVI synthesized using an Fe^{2+} precursor,^{16,17} but it was reactive with NZVI synthesized using an Fe^{3+} precursor (Figure S1). The surface-area-normalized rate of florfenicol removal by NZVI and SNZVI synthesized using an Fe^{3+} precursor was 12 and 17 times higher than that using an Fe^{2+} precursor, respectively, under exactly the same synthesis and reaction conditions. The reasons for such a big difference in the reactivity are unclear, assuming that the surface oxidation state and Fe^0 content were similar because they were synthesized under the exact same conditions using excess NaBH_4 . It is unclear if different Fe precursors will affect the nucleation process, crystalline structure, and other properties (e.g., electron transfer, S content, and hydrophobicity) of NZVI or SNZVI, and how these properties affect the reactivity.

Several studies on NZVI or SNZVI using different precursors reported widely divergent reactivity, which is in need of clarification. In this work, NZVI and SNZVI with different Fe precursors (Fe^{3+} and Fe^{2+}) and S precursors ($\text{S}_2\text{O}_4^{2-}$, S^{2-} , and S_6^{2-}) were synthesized and characterized to determine how different Fe and S precursors influence the physicochemical properties of NZVI or SNZVI (crystalline structure, S amount/distribution/speciation, hydrophobicity, and electron-transfer resistance) and their reactivity with water and a groundwater contaminant (TCE). This understanding helps to resolve apparent discrepancies in the reported reactivity and provides the knowledge to guide (i.e., selecting the precursors) the synthesis of SNZVI with the desired properties and reactivity.

2. EXPERIMENTAL SECTION

2.1. Materials. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (98%), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (98%) NaBH_4 (98%), Na_2S (90%), and TCE ($\geq 99.5\%$) were purchased from Fisher Scientific. FeCl_3 (97%) and potassium polysulfide ($\geq 42\%$ K_2S basis, which is close to K_2S_6) were obtained from Sigma-Aldrich. $\text{Na}_2\text{S}_2\text{O}_4$ ($\geq 88\%$) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. The measured trace metals in the precursor chemicals and the resulting NZVI and SNZVI materials are shown in Figure S2. Deoxygenated deionized water was used in all experiments.

2.2. Synthesis of NZVI and SNZVI. The NZVI and SNZVI particles were synthesized according to the previously reported methods.^{1,13,19,21,48,49} Briefly, the NZVI particles with

different Fe precursors were synthesized by dropwise addition ($\sim 7 \text{ mL min}^{-1}$) of 200 mL of 34 g L^{-1} NaBH_4 solution into a continuously stirred (600 rpm) 200 mL vessel containing 10 g L^{-1} Fe^{2+} or Fe^{3+} solution under N_2 purging, followed by 10 min of stirring. The SNZVI particles with different Fe or S precursors were synthesized by dropwise addition of 200 mL of 34 g L^{-1} NaBH_4 and 2.2 g L^{-1} $\text{Na}_2\text{S}_2\text{O}_4$ (or 2.0 g L^{-1} Na_2S or 1.1 g L^{-1} K_2S_6) solution into 200 mL of a 10 g L^{-1} Fe^{2+} or Fe^{3+} solution while mixing under nitrogen purging. In all cases of SNZVI, the solution volumes and concentrations theoretically provide a 0.14 S/Fe molar ratio. The resulting NZVI or SNZVI suspensions were washed three times with deoxygenated DI water and then dried in a vacuum oven at 60°C for 8 h. The vacuum was slowly released by air over 3 h to stabilize the particles, which were subsequently ground and stored in sealed vials in an anaerobic glovebox prior to use.

2.3. Batch Experiments. Batch reactivity studies were conducted in 160 mL serum bottles containing 100 mL of deoxygenated DI water (pH ~ 5.0) or TCE solution and 60 mL of headspace. The bottles were capped by Teflon Mininert valves. In all experiments, the bottles were rotated on an end-over-end rotator at 30 rpm at $25 \pm 2^\circ\text{C}$. The reactivity of each NZVI and SNZVI (1 g L^{-1}) with water was determined over 80 days reaction. The reactivity of each NZVI and SNZVI (1 g L^{-1}) with TCE ($70 \mu\text{M}$) was also determined over 8 days to assess the application potential for remediation of TCE-contaminated groundwater.

2.4. Analytical Methods. The H_2 , TCE, and its main products (C_2H_2 , C_2H_4 , and C_2H_6) in the headspace were quantified using an Agilent 6850 GC-TCD system and an HP 6890 GC-FID system. The detailed methods of GC measurement, calculations of the total amount of TCE and its products in the reactor, calculations of electron selectivity (defined as the fraction of electron equivalents from Fe^0 that is used for TCE) have been described in our previous studies.^{19,50} The Fe^0 content in the particles was determined by measuring the H_2 in the headspace after acidification assay using a 37% HCl solution ($\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2(\text{g})$). The actual S/Fe of each material was determined via the measurement of the total S and Fe by ICP-OES (PerkinElmer Optima 8300DV) after acidification using aqua regia solution.⁴¹ The details of various characteristic techniques, including transmission electron microscopy and energy-dispersive X-ray (TEM-EDX) analysis, surface area, determination of hydrophobicity (measuring the water contact angle of the pellets made from each material), and electrochemical impedance spectroscopy (EIS) analysis, have been described in our previous studies.^{19,27} Since cobalt radiation has a much higher sensitivity and yields higher quality diffractograms than copper radiation for iron containing materials,⁵¹ X-ray diffraction (XRD) analysis was carried out on PANalytical X'pert PRO MPD with a cobalt source to make phase identification unambiguous.

The S speciation of SNZVI with different S precursors was determined by examining the X-ray absorption near edge structure (XANES) features at the S K-edge at 2.47 keV. The vacuum-dried samples were grounded in an inert environment and thinly deposited on sulfur-free tape. XANES data were collected on beamline 4-3 (SSRL, SLAC synchrotron) using a Si(111) monochromator, under an inert He atmosphere laminar flux at ambient temperature. The samples and reference standards were prepared, as described earlier.²⁸ Energy was calibrated at 2472.02 eV for each spectrum by recording the sodium thiosulfate spectra between the samples.

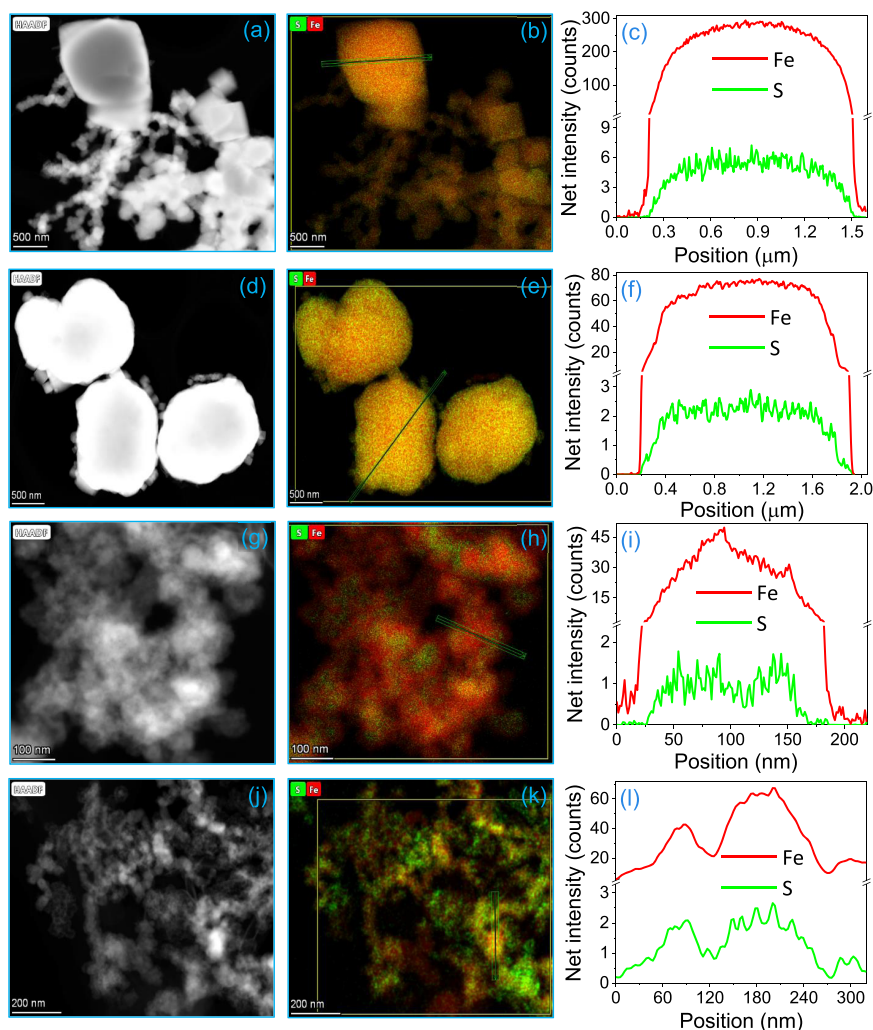


Figure 1. High-angle annular dark-field (HAADF) images and elemental distributions of SNZVI made from (a–c) Fe^{2+} and $\text{S}_2\text{O}_4^{2-}$ precursors, (d–f) Fe^{3+} and $\text{S}_2\text{O}_4^{2-}$ precursors, (g–i) Fe^{3+} and S^{2-} precursors, and (j–l) Fe^{3+} and S_6^{2-} precursors.

The XANES spectra were recorded using a lytle detector for the samples and a 4-element Si–Li Vortex detector for the references. Self-absorption was considered to be insignificant since the sample mass was <10 mg,⁵² and no beam damage was detected in successive scans.

All of the materials used in this paper were prepared and handled identically for experiments and characterizations. We used the experimental protocols to limit the exposure of materials to the air, e.g., N_2 purging during the synthesis process, drying the materials in a vacuum oven, grinding–storing–grabbing the materials in an anaerobic glovebox, sealing the materials under a N_2 atmosphere during transportation to the characterization facilities, and preparing the samples in an anaerobic glovebox on the site for TEM-EDX and XAS measurements. However, some brief exposure to air is inevitable. Specifically, for Fe^0 content, S content, XRD, and XPS measurements, the samples were exposed to the air for ~ 1 min during the preparation. The results of TEM-EDX, water contact angle, and XPS, XRD, and XAS analyses of NZVI synthesized by FeCl_3 and SNZVI synthesized by FeCl_3 and Na_2SO_4 were both close to the results from our previous studies,^{19,28} suggesting high reproducibility of the synthesis and of the analysis. Regardless, the differences in reactivity relate back to the initial properties of the materials and they do

so in a way that is consistent with expectation based on those properties, as discussed below.

Density functional theory (DFT) calculations were performed to study the impact of the lattice constant on water and H adsorption on the Fe(110) surfaces with or without sulfur incorporation into the Fe body-centered-cubic (BCC) structure. The Fe surfaces were modeled as four-layer, (3×3) , (110) slabs, with the bottom two layers constrained in bulk positions. The S-in-Fe(110) surfaces were modeled by replacing one surface Fe atom with a S atom. Hydrogen is adsorbed in the hollow sites after DFT optimizations, while the water molecule is adsorbed at the top position of Fe or S. Details of the computational methods are described in our previous study.²⁸

3. RESULTS AND DISCUSSION

3.1. Fe and S Precursors Affect the Morphology, Elemental Distribution, S Content, and Fe^0 Content of NZVI and SNZVI. Since the FeCl_2 chemical was not pure (primarily FeCl_2 , but some yellowing indicated partial oxidation of FeCl_2 to FeCl_3), we did not include the results of NZVI and SNZVI synthesized by FeCl_2 into the main discussion. However, the measured crystalline domain size, lattice spacing, lattice constant, electron-transfer resistance, and

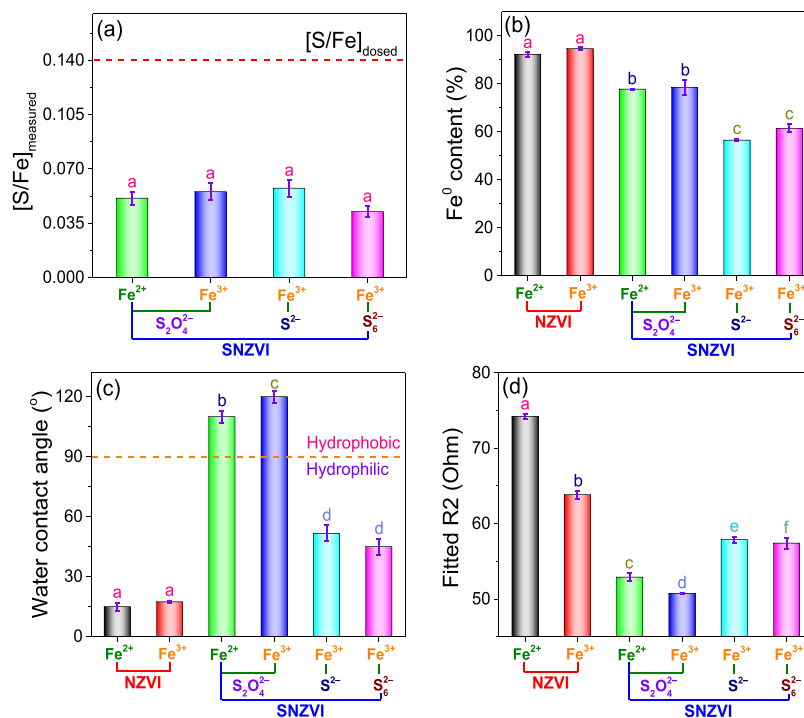


Figure 2. (a) $[S/Fe]_{\text{measured}}$, (b) Fe^0 content, (c) water contact angle and of pellets made from NZVI and SNZVI with different Fe or S precursors, and (d) fitted resistance from electrochemical impedance spectroscopy. Different letters indicate significantly different values of the Fe^0 content, $[S/Fe]_{\text{measured}}$, fitted resistance, and water contact angle between NZVI and SNZVI with different Fe and S precursors ($\alpha = 0.05$; one-way analysis of variance (ANOVA)).

the reactivity with TCE for NZVI and SNZVI made from FeCl_2 (Table S1 and Figure S4) were all between the materials synthesized using FeSO_4 and FeCl_3 , but closer to that of the FeSO_4 . This was consistent with the fact that the FeCl_2 chemical was likely a mixture of FeCl_2 and FeCl_3 , but primarily FeCl_2 . These results suggest that the anions (SO_4^{2-} and Cl^-) do not greatly affect the properties and reactivity of NZVI and SNZVI, which is mainly attributed to the Fe ion precursors. In the following discussion, the Fe^{2+} and Fe^{3+} represent the FeSO_4 precursor and FeCl_3 precursor, respectively.

The initial pH of 10 g L⁻¹ of Fe^{2+} solution and Fe^{3+} solution was 3.6 and 1.9, respectively. Particle nucleation and crystal growth are essential steps to obtaining nanoparticles. The black and magnetic particles were observed immediately upon adding a NaBH_4 solution or a $\text{NaBH}_4 + \text{Na}_2\text{S}_2\text{O}_4$ solution into the Fe^{2+} precursor solution (Figure S3a), indicating that nucleation of $\text{NZVI}_{\text{Fe}^{2+}}$ and $\text{SNZVI}_{\text{Fe}^{2+}}$ occurs at the beginning of the synthesis process when pH ~ 3.6 . However, the observation of particles was delayed for the Fe^{3+} precursors (Figure S3a,b). The formed particles (likely Fe^0) are dissolved at the lower pH ($\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$) and in the presence of Fe^{3+} ($2\text{Fe}^{3+} + \text{Fe}^0 \rightarrow 3\text{Fe}^{2+}$). Observable magnetic particles began to accumulate after ~ 2 min (pH ~ 1.5) for the synthesis of $\text{NZVI}_{\text{Fe}^{3+}}$, while it took ~ 5 min (pH ~ 6.5) for the synthesis of $\text{SNZVI}_{\text{Fe}^{3+}}$, consistent with a previous study that investigated the nucleation of $\text{NZVI}_{\text{Fe}^{3+}}$ and $\text{SNZVI}_{\text{Fe}^{3+}}$.⁵³ In addition to the difference in pH for the initial conditions of the reaction, two other factors may influence the resulting particle properties and reactivity. First, there was Fe^{3+} in the solution when $\text{NZVI}_{\text{Fe}^{3+}}$ or $\text{SNZVI}_{\text{Fe}^{3+}}$ began to nucleate.⁵³ This is not the case for the use of Fe^{2+} as a precursor. Second, the replacement of a water molecule from the first coordination

shell represents an important step in complex-formation reactions of metal cations and in many redox processes. The water exchange rate of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ($4.4 \times 10^6 \text{ s}^{-1}$) is much faster than for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ($1.6 \times 10^2 \text{ s}^{-1}$),⁵⁴ so the nucleation of Fe^{2+} may be faster than Fe^{3+} . While complicated, the synthesis procedures used here resulted in materials with very different reactivity, as discussed later.

Both iron precursors (Fe^{2+} and Fe^{3+}) resulted in the same typical chain-like structures and comparable elemental distributions of the NaBH_4 -reduced NZVI particles (Figures S5 and S6), indicating that the differences in reactivity between $\text{NZVI}_{\text{Fe}^{2+}}$ and $\text{NZVI}_{\text{Fe}^{3+}}$ discussed later were not related to differences in the morphology or the elemental distribution. Sulfur was clearly identified on the EDX spectra after the sulfidation of NZVI, regardless of the sulfur precursor used (Figures S7–S10). NZVI sulfidation by dithionite resulted in larger particles as compared with the unsulfidized NZVI particles (Figure 1a,d). Both the elemental distribution maps and the intensity profiles across both the smaller and larger individual particles revealed an even distribution of S and Fe in the SNZVI particles synthesized from the $\text{S}_2\text{O}_4^{2-}$ precursor (Figures 1b,c,e,f, and S11), regardless of the valence state of the Fe precursor. This suggests that these two particle types were similar. In contrast, the SNZVI particles made from the sulfide or polysulfide were much smaller, and their morphology and elemental distribution were different from NZVI and SNZVI made from the $\text{S}_2\text{O}_4^{2-}$ precursor (Figure 1g–l). These HAADF images and elemental maps suggest that the S precursors, and the different reactivity of the S precursors with Fe, resulted in differences in the morphology and elemental distribution of SNZVI, which would also affect the S speciation and crystallinity of the SNZVI particles, as discussed later. The differences in the primary particle size also led to a different

N₂-Brunauer–Emmett–Teller (BET) specific surface area (Figure S12).

The measured S/Fe molar ratio ($[S/Fe]_{\text{measured}}$) in the particles was ~ 0.05 using a dose of 0.14 S/Fe molar ratio in the synthesis (Figure 2a), indicating that the Fe and S precursors did not vary the S/Fe ratio. The amount of incorporated S was therefore not considered in the following discussion of the impacts of the Fe and S precursors. No S or SO₄²⁻ was detected by the XPS analysis of NZVI_{Fe²⁺} and NZVI_{Fe³⁺} (Figure S13), suggesting that there is no sulfur in the NZVI structures, i.e., the SO₄²⁻ precursor was not reduced to sulfides or adsorbed to the surface, and there is no S contamination from the chemicals besides the S precursors. The S 2p narrow spectra of SNZVI were also quite similar. These results indicate that the contributions of shell differences to the reactivity are likely less important than the differences in the Fe⁰ core.

The Fe⁰ content of the particles (Figure 2b) represents their potential to degrade contaminants through chemical reduction. The Fe⁰ content of NZVI with the Fe²⁺ precursor ($\sim 92\%$) was close to that of NZVI with the Fe³⁺ precursor ($\sim 95\%$), suggesting that the Fe precursor did not affect the Fe⁰ content of NZVI that was synthesized using excess reductant (NaBH₄). The Fe⁰ content of SNZVI ($\sim 78\%$) made using dithionite was slightly lower than that of NZVI due to the incorporation of S.²⁹ The Fe precursor did not affect the Fe⁰ content of SNZVI. However, using sulfide or polysulfide as a sulfur source led to SNZVI with statistically significantly lower amounts of Fe⁰, suggesting that the choice of sulfur species used in the synthesis affected the Fe⁰ content of the resulting particles. This lower Fe⁰ content is consistent with the differences in sulfur speciation in the particles, considering that there is a similar amount of S in the materials (Figure 1a). More Fe is present as FeS in SNZVI synthesized with the S²⁻ and S₆²⁻ precursors (as shown by the S K-edge XANES spectra in Figure 3 below) than for SNZVI made using S₂O₄²⁻ as a

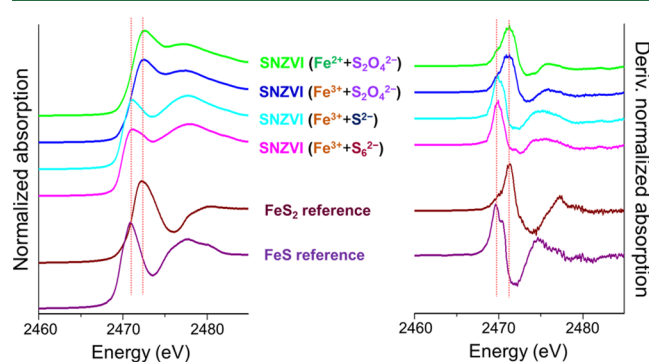


Figure 3. S K-edge XANES of SNZVI synthesized using different Fe and S precursors and their derivative spectra in comparison to pyrite (FeS₂) and mackinawite (FeS) reference samples features.

precursor, where the Fe species are mainly FeS₂. In addition, there is an iron oxide (maghemite, Fe₂O₃) peak observed in the XRD patterns of SNZVI with the S²⁻ and S₆²⁻ precursors (Figure S14e,f). This observation is consistent with the lower Fe⁰ content of these two materials than other materials without iron oxide peaks in the XRD patterns (present as amorphous phase and/or below the detection limit of XRD, ~ 5 wt %).

3.2. S Precursors Control S speciation, while Fe Precursors Alter Crystalline Structure. XANES analysis at

the S K-edge was performed to determine if the Fe and S precursors affected the S speciation in the resulting SNZVI. The dotted lines in Figure 3 show the positions of the S K-edge XANES spectra for the iron monosulfide (FeS) structure at 2470.9 eV and iron disulfide (FeS₂) structure at 2472.3 eV.^{55,56} FeS₂ was the main S species of SNZVI prepared by S₂O₄²⁻ regardless of the Fe²⁺ or Fe³⁺ precursor, and the XANES spectra contained very minor (or no) contribution of FeS features. In contrast, FeS was the major S species of SNZVI prepared by S²⁻ or S₆²⁻. This indicates that the S speciation in synthesized SNZVI can be controlled by the S precursors used, since the S content in these materials was quite close, as shown in Figure 1a. While a previous study suggested that the amount of S incorporated into the Fe⁰ BCC structure affects the S speciation,²⁸ the results of this study indicate that altering the S precursor allows tuning the S speciation in SNZVI.

These S speciation results are consistent with the water contact angle (hydrophobicity) of the resulting particles (Figure 2c). The water contact angles of NZVI with Fe²⁺ or Fe³⁺ precursors were $\sim 15^\circ$, suggesting that the Fe precursors did not significantly affect the hydrophobicity of NZVI. After the co-sulfidation with S₂O₄²⁻, the hydrophobicity of SNZVI was greatly increased ($>100^\circ$). However, the water contact angle of SNZVI with the S²⁻ and S₆²⁻ precursors (mainly FeS) was only ~ 50 and 45° , respectively, which was much lower than that of SNZVI with the S₂O₄²⁻ precursor (mainly FeS₂). This was consistent with reported DFT calculations that sulfur makes the Fe surfaces more hydrophobic and pyrite is more hydrophobic than mackinawite.^{28,57}

We also compared the effect of the Fe precursor on the resulting crystalline properties of NZVI and SNZVI. Different intensities and positions of the Fe peaks were observed in the XRD patterns (Figure S14); profile fitting and refinement (Rietveld) (Figure S15) were carried out to obtain precise values of the lattice constant (*a*), crystalline domain size (*D*), and lattice spacing (*d*) (Figure S16).⁵⁸ Specifically, the Fe(110) peak observed for NZVI_{Fe³⁺} has a lower intensity and is shifted compared to the spectra of NZVI_{Fe²⁺} (Figure 4a). Generally, the lower/broader peak is attributed to either the smaller domain size or to poorer crystallinity. Since the crystalline domain size (*D*) of the Fe(110) plane of NZVI_{Fe³⁺} was similar to that of NZVI_{Fe²⁺} (Figure S16a), the higher intensity of NZVI_{Fe²⁺} indicates that it was more crystalline than NZVI_{Fe³⁺}. The lattice spacing (*d*) and lattice constant (*a*) of the Fe(110) plane of NZVI_{Fe³⁺} were larger than those of NZVI_{Fe²⁺} (Figure S16d). A similar shift was observed between the Fe(110) peaks of SNZVI with the Fe²⁺ and Fe³⁺ precursors (Figure 4b). The higher peak intensity and *D* values of SNZVI than those of NZVI indicate that sulfidation improved the crystallinity and had a higher impact on the crystallinity than the Fe precursor. For different S precursors, there is a slight shift between SNZVI with the S₆²⁻ and S²⁻ precursors, while a larger shift and a more intense peak were observed for the SNZVI with the S₂O₄²⁻ precursor (Figure 4c). Similar results were observed for Fe(200) and Fe(211) planes (Figure S14c,d). The choice of the sulfur precursors caused more pronounced shifts than that of the Fe precursors, indicating that the BCC lattice structure of Fe⁰ was distorted, especially when dithionite is used.²⁸ This is probably because new phases (i.e., FeS or FeS₂) were formed as suggested by the S K-edge XANES results (Figure 3). The distorted lattice constants (larger lattice constant tends to facilitate the electron transfer)

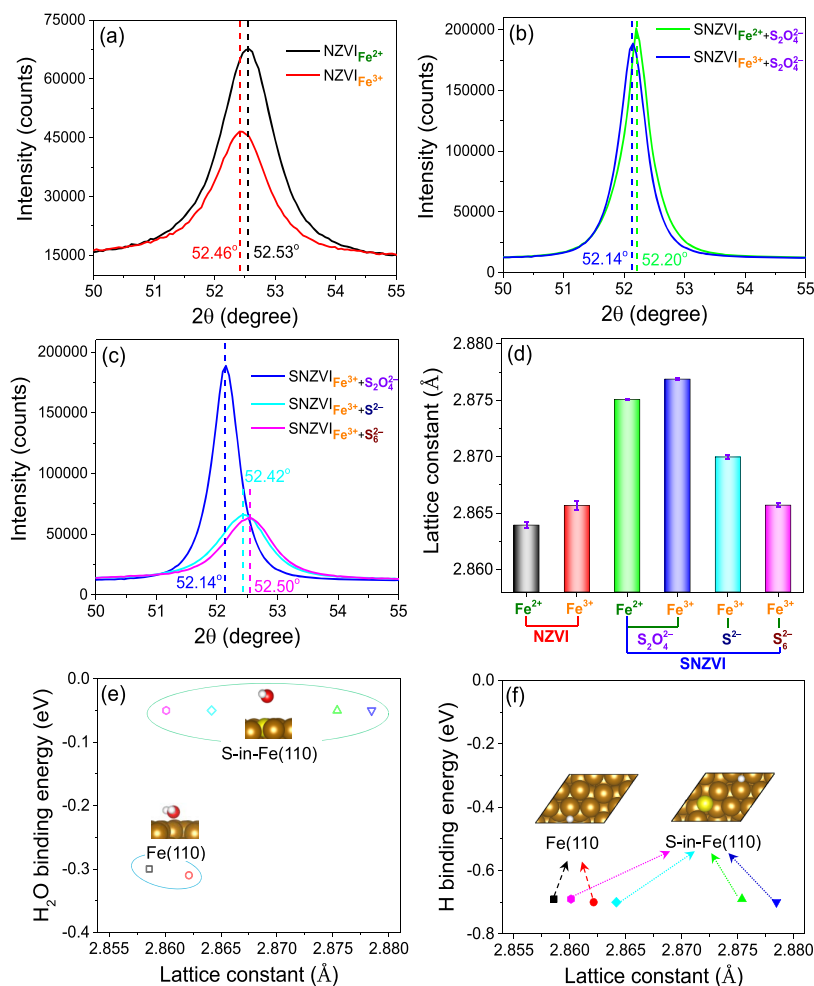


Figure 4. XRD patterns of Fe(110) of (a) NZVI and (b) SNZVI made from different Fe precursors and (c) SNZVI made from different S precursors. (d) Lattice constants of the Fe BCC structure according to the XRD Rietveld refinement. Different letters indicate significantly different values of the lattice constant between NZVI and SNZVI with different Fe and S precursors ($\alpha = 0.05$; one-way ANOVA). Impact of the lattice constant on the DFT-calculated (e) H_2O and (f) H binding energies at Fe(110) and S-doped Fe(110) surfaces. The insets show the H_2O and H adsorption geometries after DFT structural relaxations.

and the presence of iron sulfides would significantly alter the electron-transfer resistance due to the lower band gap of iron sulfides compared to iron oxides (Fe_2O_3), which is consistent with the measurements of electron-transfer resistance (Figure 2d).

Note that there was no shift between the XRD patterns of the SNZVI used in this study and SNZVI that had been synthesized and analyzed five months prior with the same Fe and S precursors (Figure S17a,b). This indicates good reproducibility of the XRD analysis and indicates that the shifts observed in this study were from the samples and not from the instrument. The values of the shift in 2θ from Fe^{3+} to Fe^{2+} increased with increasing of 2θ (Figure S17c), which also indicates that the shifts were from the samples. In addition, the XRD analysis was performed immediately after the instrument calibration, which also limits the impact of instrument conditions on the 2θ values of the Fe peaks. The average lattice constants of the (110), (200), and (211) planes of NZVI and SNZVI with the Fe^{3+} precursor were significantly larger than those with the Fe^{2+} precursor, respectively, and the average lattice constant of SNZVI made from the $\text{S}_2\text{O}_4^{2-}$ precursor was significantly larger than that with the S^{2-} or S_6^{2-} precursor (Figure 4d). These results indicate that the choice of

the Fe and S precursors affect the crystalline structure, including the crystallinity, crystalline domain size, lattice spacing, and lattice constant, which would further affect their physicochemical and reactive properties, e.g., electron transfer.

The charge-transfer resistance of NZVI and SNZVI with different precursors was probed by electrochemical impedance spectroscopy (EIS) (Figure S18). Since all samples were pelleted with the same pressure (~ 5 tons) and weight (~ 40 mg), it is assumed that the contact resistance between the pellet and Ti mesh is similar, and the differences in the fitted resistance (R2) from the EIS results reflect their differences in the electron-transfer resistance. The fitted R2 of NZVI $_{\text{Fe}^{3+}}$ was lower than that of NZVI $_{\text{Fe}^{2+}}$ (Figure 2d), suggesting its lower resistance to electron transfer. The NZVI $_{\text{Fe}^{2+}}$ had a smaller lattice constant, that is, the smaller interatomic distance, and the valence electrons require more energy to be released upon oxidation. As a rule of thumb, the band energy gap is inversely proportional to the interatomic distance.^{60,61} Thus, the NZVI $_{\text{Fe}^{3+}}$ and SNZVI $_{\text{Fe}^{3+}}$ with larger lattice constants (Figure 4d) had a lower resistance to electron transfer than NZVI $_{\text{Fe}^{2+}}$ and SNZVI $_{\text{Fe}^{2+}}$, respectively (Figure 2d). In addition, the electron-transfer resistance of SNZVI synthesized by S^{2-} and S_6^{2-} was higher than those made by the $\text{S}_2\text{O}_4^{2-}$ precursor.

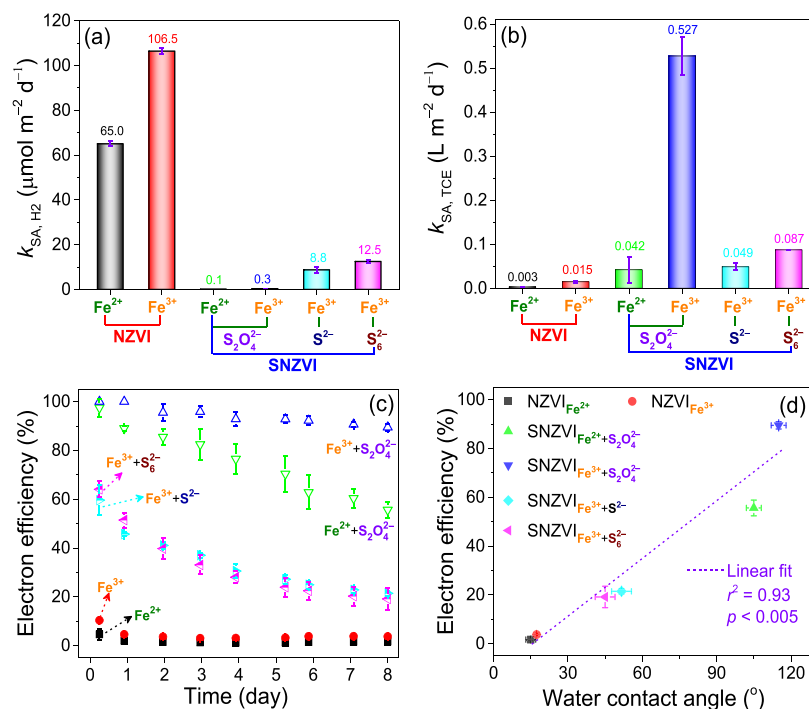


Figure 5. Impact of different Fe and S precursors on the reactivity of NZVI and SNZVI with water and TCE. (a) k_{SA,H_2} without TCE (calculated from the first 8 days of reaction); (b) $k_{SA,TCE}$; (c) electron efficiency for TCE degradation as a function of reaction time; (d) correlation between electron efficiency and hydrophobicity. Linear correlation lines with r^2 and p values were calculated using R (initial pH = 5.0, $T = 25 \pm 2$ °C, initial TCE = 70 μM , NZVI or SNZVI = 1.0 g L^{-1}).

Besides the lattice constant, the higher resistance of SNZVI made by the S²⁻ or S₆²⁻ precursors was also consistent with their lower Fe⁰ (conductive metal) content (Figure 2b) and higher Fe₂O₃ (insulator) content (Figure S14e,f). The Fe₂O₃ with a high band gap (2.20 eV) was expected to have a higher resistance than Fe⁰ (0.00 eV), FeS (0.10 eV), and FeS₂ (0.95 eV).⁴⁵ Alloying oxygen with iron sulfides would also increase the band gap of FeS, increasing the resistance for electron transfer.^{45,59}

The impact of the lattice constant of NZVI and SNZVI on their affinity toward H₂O (Figure 4e) and H (Figure 4f) was further investigated by DFT calculations. The lattice constants do not significantly affect the binding energies of H₂O onto the surface for NZVI and SNZVI, respectively (Figure 4e). Regardless of the lattice constant, the bindings of H₂O onto the SNZVI surfaces are much weaker (i.e., more positive) than those onto the NZVI surfaces. Note that S significantly hinders the H adsorption, and H migrates from the S to the Fe site upon optimization. The varied lattice constants of NZVI and SNZVI do not significantly affect the binding energies of H (Figure 4f) onto their Fe surfaces after DFT structural relaxations. These results suggest that the impact of the lattice constant on the hydrophobicity of SNZVI could be ruled out, and the S speciation controls the hydrophobicity of SNZVI.

3.3. Fe and S Precursors Affect the Corrosion of NZVI and SNZVI by Water. The Fe and S precursors resulted in differences in the reactivity of NZVI and SNZVI with water (without TCE), according to the H₂ evolution measured during their aging in water over 80 days (Figure S19). For comparison, the initial rates of H₂ evolution (first 8 days) for different NZVI and SNZVI in water (without TCE) were described as a surface-area-normalized zero-order rate constant (Figure 5a). The k_{SA,H_2} of NZVI_{Fe³⁺} was approximately two

times higher than that of NZVI_{Fe²⁺}, although their Fe⁰ content (Figure 2b), hydrophobicity (Figure 2c), oxidation state, and morphology (Figures S5 and S6) were quite similar. This is consistent with the increased lattice constant (Figure 4d) and decreased charge-transfer resistance (Figure 2d) of NZVI_{Fe³⁺} as compared with NZVI_{Fe²⁺}, promoting the electron transfer from Fe⁰ to water. For similar reasons, the H₂ evolution by SNZVI_{Fe³⁺} was approximately three times faster than that by SNZVI_{Fe²⁺}. Sulfidation of NZVI greatly inhibited the H₂ evolution as expected,^{19,20} and almost no H₂ was detected by SNZVI with the S₂O₄²⁻ precursor within the initial 4 days (Figure S19a), probably aided by the high hydrophobicity (Figure 2c).

The S precursors (S₂O₄²⁻, S²⁻, and S₆²⁻) also greatly affected the reactivity of SNZVI (Fe³⁺ precursor) with water (Figure 5a). The k_{SA,H_2} of SNZVI with the S²⁻ and S₆²⁻ precursors was ~30 and ~40 times higher than that with S₂O₄²⁻, respectively, though their S contents were similar (Figure 2a) and the charge-transfer resistances of SNZVI made from the S²⁻ and S₆²⁻ precursors were higher than that made from S₂O₄²⁻ (Figure 2d). This is because the SNZVI with the S²⁻ or S₆²⁻ precursors was hydrophilic, while the SNZVI with the S₂O₄²⁻ precursor was hydrophobic (Figure 2c). Iron monosulfide (FeS) as the main species of the SNZVI with the S²⁻ or S₆²⁻ precursors (Figure 3) is more favorable to water adsorption and to H adsorption than iron disulfide (FeS₂), the main species of the SNZVI made from the S₂O₄²⁻ precursor.²⁸ Interestingly, the accumulated H₂ (%) by SNZVI made using the S²⁻ or S₆²⁻ precursors was close to that of NZVI made using the Fe²⁺ precursor (Figure S19b). Thus, it cannot be generalized that all SNZVI is less reactive with water than NZVI. Rather, the reactivity with water depends on the specific physicochemical properties of materials of the resulting

materials (e.g., hydrophobicity, S speciation, charger transfer), which is affected by the Fe and S precursors used for the synthesis.

3.4. Fe and S Precursors Affect the Reactivity and Selectivity of NZVI and SNZVI With TCE. The reactivity of NZVI and SNZVI with different Fe and S precursors for TCE was evaluated (Figure S20). The choice of the Fe and S precursor did not change the degradation products from TCE reduction by NZVI or SNZVI. However, both the Fe and S precursors affected the reaction rate of TCE with NZVI or SNZVI. The surface area-normalized first-order kinetic rate constant of TCE removal ($k_{SA,TCE}$) by NZVI or SNZVI made from the Fe^{3+} precursor was ~ 5 and 13 times higher than the Fe^{2+} precursor, respectively (Figure 5b), and the $k_{SA,TCE}$ of SNZVI using the $S_2O_4^{2-}$ precursor was ~ 11 -fold and 6-fold higher than that using the S^{2-} or S_6^{2-} precursors (Figure 5b), respectively. These results were consistent with the expanded lattice (lower energy gap) (Figure 4d), lower charge-transfer resistance (facilitated electron transfer) (Figure 2d), and higher hydrophobicity (Figure 2c) of the materials using the Fe^{3+} and $S_2O_4^{2-}$ precursors compared to the other precursors. In addition, the higher reactivity of $SNZVI_{Fe^{3+}}$ than $SNZVI_{Fe^{2+}}$ with similar $[S/Fe]_{measured}$ also appears to be true for the S^{2-} precursor. The $k_{SA,TCE}$ ($0.049\text{ L m}^{-2}\text{ d}^{-1}$) by the SNZVI synthesized by the Fe^{3+} and S^{2-} precursors in this work was ~ 3.6 – 5.5 times higher than those (~ 0.009 – $0.015\text{ L m}^{-2}\text{ d}^{-1}$) in a previous study,⁴¹ where the SNZVI was synthesized by the Fe^{2+} and S^{2-} precursors when the $[S/Fe]_{measured}$ (0.035 or 0.05) was similar to this study.

The electron efficiency of TCE degradation by NZVI or SNZVI made from different precursors as a function of the reaction time is shown in Figure 5c. For all of the materials, the electron efficiency gradually decreased as the reaction proceeded. This is because the concentration of TCE decreases and the fraction of electrons from Fe oxidation going to TCE decreases relative to the stable reaction with water (Figure S21).²⁶ Since SNZVI cannot activate and use the H_2 for TCE reduction,¹⁸ the increasing discrepancy between the electrons for H_2 evolution and TCE reduction resulted in the decreasing electron efficiency. Therefore, the electron efficiency would be affected by the ratio of Fe/TCE, as was previously shown for NZVI and SNZVI.^{27,50} These data suggest that using the Fe^{3+} and $S_2O_4^{2-}$ precursors to synthesize NZVI or SNZVI (for 0.05 $[S/Fe]_{measured}$ materials) rather than other precursors would reduce the amount of NZVI or SNZVI material required and provide greater reactivity with TCE.

The electron efficiency of the materials for TCE degradation after 8 days of reaction tended to positively correlate with the hydrophobicity ($r^2 = 0.93$, $p < 0.01$) (Figure 5d), no matter what Fe and S precursor was used. Note that the correlation between electron efficiency and hydrophobicity was maintained during the reaction ($r^2 > 0.88$, $p < 0.005$) (Figure S22), despite having the electron efficiency decrease over time. These results suggest that tuning the hydrophobicity of SNZVI via different S precursors may allow maximizing the electron efficiency for TCE degradation. This correlation also suggests that the electron efficiency of the more hydrophilic SNZVI is mainly attributed to the inhibition of H_2 evolution, while for the more hydrophobic SNZVI, other factors (e.g., electron transfer or TCE reactivity) further determine the electron efficiency for TCE degradation since the H_2 evolution is already largely inhibited.

4. ENVIRONMENTAL IMPLICATIONS

The results of this study indicate that different Fe and S precursors can affect the physicochemical properties of NZVI and SNZVI, including the crystalline structure, lattice constant, charge-transfer resistance, hydrophobicity, and S speciation, which largely determine the reactivity and selectivity of NZVI and SNZVI. The information on these properties will allow better comparisons and prediction of the reactivity/selectivity of NZVI and SNZVI with the same or different precursors. The Fe precursors can affect the lattice constant of Fe body-centered cubic structure and result in varied electron transfer, while the S precursors can control the S speciation (FeS vs FeS_2) in SNZVI and result in varied hydrophobicity. As an important index of a remediation agent, the electron efficiency of SNZVI is strongly correlated with the hydrophobicity of SNZVI. The results of electron efficiency evaluations suggest that tuning the physicochemical properties of SNZVI by selecting appropriate precursors can be a feasible way to improve the reactivity and selectivity for the reduction of contaminants over the reduction of water. Besides improving our understanding of the batch-to-batch reactivities of synthesized SNZVI in different labs, these findings can also guide the rational synthesis of commercial ZVI, NZVI, and SNZVI particles (e.g., selecting appropriate precursors) and benefit the investigation of these commercial particles' reactivity for environmental remediation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c03879>.

Dechlorination rate of antibiotic florfenicol by NZVI and SNZVI with Fe^{2+} or Fe^{3+} precursors, properties and reactivity of NZVI and SNZVI made from $FeCl_2$, TEM images and elemental distribution of NZVI and SNZVI; surface area, XRD patterns and Rietveld refinement, XPS analysis, EIS analysis, accumulated H_2 with or without TCE, TCE and its main degradation products of NZVI and SNZVI with different precursors (PDF)

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Notes

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