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Supplementary Material

Effects of Geochemical Conditions, Surface Modification, and Arsenic (As) Loadings on As Release from the As-loaded Nano Zero-valent Iron in Simulated Groundwater

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Synthesis of nZVI

The synthesis of pristine nZVI was prepared as follows: 0.05 M $FeCl_3$ was prepared, followed by dropwise dripping 0.02 M $NaBH_4$ in 250 mL 3-mouth flask (v/v=1) with continuously N_2 sparging and mechanically stirring. Afterwards, an additional 30 min of agitation was provided for the complete reaction between the $FeCl_3$ and $NaBH_4$, as well as in assisting the formation of homogeneous nZVI products. The precipitate was collected by centrifugation (3000 rpm, 15 min) of the suspension and was then washed three times by degassed ultrapure water and ethanol.

For the synthesis of chitosan modified-nZVI, 0.25 g of chitosan was dissolved into 50 mL of acetic acid solution (0.05 M), and the mixture was then stirred at room temperature for 2 h to make it homogenous. This was followed by adding 2.08 g of $FeCl_3 \cdot 6H_2O$ into the chitosan solution, and the mixture was stirred under a N_2 atmosphere overnight. Freshly prepared 2% borohydride solution was then added drop-wise to the mixture, followed by an additional 90 min of stirring. The precipitate was centrifuged (3000 rpm, 15 min) and washed two times by deoxygenated ultrapure water, and then was then vacuum freeze-dried before use.

Polyaniline (PANI)-nZVI was synthesized from dissolved Fe(III) by the redox reaction with sodium borohydride in the presence of PANI nanofiber precursor, which was prepared by aniline monomer. Aniline (0.8 mL) was syringed to a 250 mL 3-mouth flask containing 80 mL of 6 g $FeCl_3$ solution. It was magnetically stirred at 600 rpm for 5 min. Afterwards, the mixture was kept for 2 days without stirring. Then, the freshly prepared 100 mL 1 M $NaBH_4$ solution was added drop-wise to the mixture with continuously N_2 sparging and mechanically stirring. Afterwards, an additional 20 min of stirring was provided for the complete reaction between the $FeCl_3$ and $NaBH_4$ and for assisting in the formation of homogeneous nZVI products. Finally, the black products were centrifugated at 3000 rpm for 15 min and were washed three times by deoxygenated ultrapure water and ethanol.

All obtained nZVI samples were dried and stored in a vacuum freezing dryer. All freshly synthesized nZVI was used within one week to limit any potential interference caused by aging effects. All the ultrapure water used during the experiment was degassed for 30 min before use.

As adsorption

All adsorption experiments were conducted with 150 mg/L nZVI (pristine nZVI, chitosan-modified nZVI, and PANI-modified nZVI) in the synthetic groundwater. The synthetic groundwater was prepared based our previous method [1]: 10 mM Na^+, 0.8 mM Ca^{2+}, 1.6 mM Cl^-, 3 Mm HCO_3^-, and 1 mM SO_4^{2-}. First, experiments of adsorption kinetics were carried out using 150 mg/L nZVI suspension and 20 mg/L As(V) in synthetic groundwater at pH 7. Supernatants were collected by using 0.45-mm pore size cellulose nitrate filters, and were acidified by nitrate acid, diluted by deionized ultrapure water and analyzed by a Graphite Furnace-Atomic Absorption Spectrophotometer (GF-AAS) (Hitachi, Z-8200) for the total As concentration measurement. The results are shown in Fig. S1 that the equilibrium time for As(V) adsorption by pristine nZVI, chitosan-modified nZVI and PANI-nZVI are reached in about 120 min, 180 min and 60 min respectively. The equilibrium time was comparable to the related studies, which As(V) adsorption by pristine nZVI was determined to be 90 min[1], by chitosan-modified nZVI was 180 min[2], and by PANI-nZVI was 30 min[3].

Experiments of isotherm adsorption were conducted with aqueous As(V) concentrations ranging from 1 to 50 mg/L (1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L) in the synthetic groundwater. After equilibrium time, the suspensions were filtered through 0.45 μm pore size cellulose nitrate filters. The filtrates were then acidified by concentrated HNO_3 (0.1 mL), diluted (if needed) before measurement by the GF-AAS for total As concentration. The adsorbed amount of As(V) per mass of nZVI (g) was calculated according to As(v) mass balance before and after adsorption:

$$q_e = \frac{C_i - C_e}{m} \cdot V \tag{1}$$

where c_i and c_e are initial and equilibrium concentrations of As(V) (mg/L), q_e is the amount of As adsorbed on per gram of the nZVI at equilibrium (mg/g), m is the dry mass of nZVI (g) and V is the volume of the solution (L). Langmuir model[4] was employed to fit the adsorption isotherm results

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} \cdot b} \tag{2}$$

where q_e (mg/g) is the amount of As adsorbed onto nZVI at equilibrium, C_e (mg/L) is the equilibrium concentration of As in the solution, q_{max} (mg/g) is the maximum As sorption capacity, and b (L/mg) is the Langmuir constant related to the affinity of binding sites for As.

Fig. S2 shows that the maximum adsorption capacities of pristine nZVI, chitosan-modified nZVI, and PANI-nZVI are 131.6 mg/g, 149.3 mg/g, and 217.4 mg/g, respectively. Since the three types of nZVI show different maximum adsorption capacities, and especially pristine nZVI has the lowest adsorption capacity (131.6 mg/g), it is better ensure that all types of nZVI have high and even the same adsorption capacities toward As. Thus, 130 mg/g was selected as the high As loading. The value of 30 mg/g as the low As loading was selected due to the significant gap with the high loading. This low loading can be also obtained by the three types of nZVI at the same initial As concentration. To obtain the same high loading of As on three types of nZVI, the initial As concentrations were selected at 50 mg/L for pristine nZVI, at 30 mg/L for chitosan-modified nZVI, and at 20 mg/L for PANI-modified nZVI. For low As loading, the initial As concentrations were selected at 5 mg/L for all nZVI.

Kinetics of As release

The kinetics of As release was then conducted to determine the As release equilibrium time from As-loaded nZVI. The As-loaded nZVI (pristine nZVI, chitosan-modified nZVI, and PANI-modified nZVI) were filtered from the solution after reaching their adsorption equilibrium. The filters with the As-loaded nZVI were immediately transferred into a vial with 40 mL of synthetic groundwater. The vials were capped and were hand shaken to detach the As-loaded nZVI from filters.

Afterwards, the filters were removed from solution by tweezers, and the vials were shaken in an end-over-end rotator at 26 rpm, at room temperature (23°C). The supernatants were collected at different time intervals and were then acidified for the analysis of As release. Fig. S3 shows that the equilibrium times of As release for the As-loaded pristine, chitosan- and PANI-modified nZVI are 18 h, 18 h and 14 h, respectively. To unify the release equilibrium time, 18 h was selected for the experiments of As release.

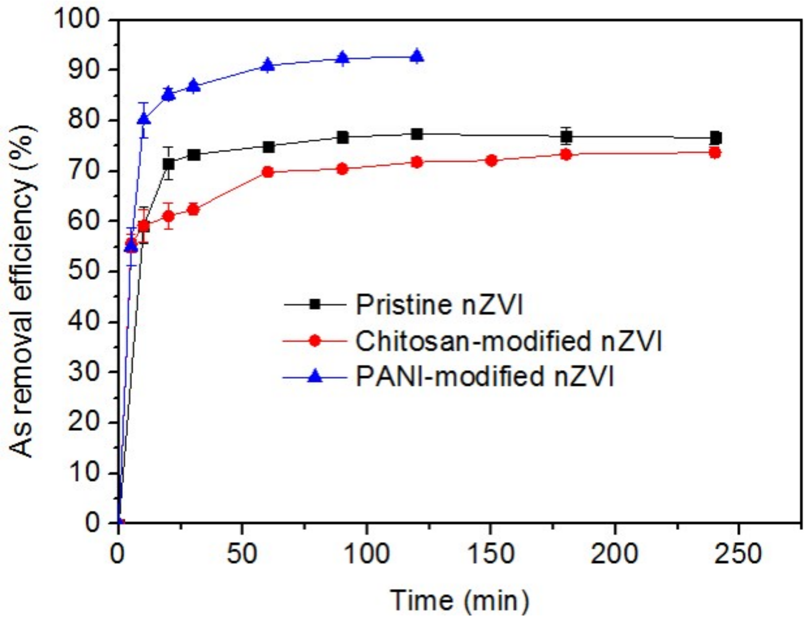

Fig. S1 Adsorption kinetics of the three types of nZVI toward As (dose: 150 mg/L, initial As concentration: 20 mg/L). All samples were prepared in the synthetic groundwater at pH=7±0.1, Ca^{2+}=32 mg/L, and HA=0 mg/L. The error bars represent standard deviation.

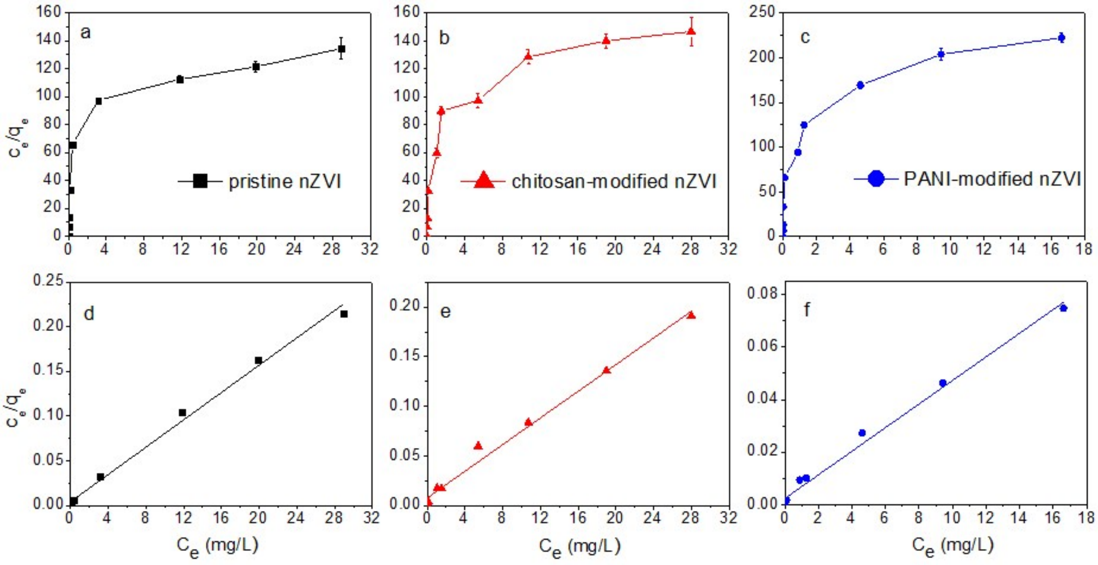

Fig. S2 Adsorption isotherm plots for the As(V) adsorption by (a) pristine nZVI, (b) chitosan-modified nZVI and (c) PANI-modified nZVI, and (d, e, f) their Langmuir adsorption plots, respectively. The experiments were conducted in the synthetic groundwater at pH=7±0.1, Ca^{2+}=32 mg/L, and HA=0 mg/L. The error bars represent standard deviation.

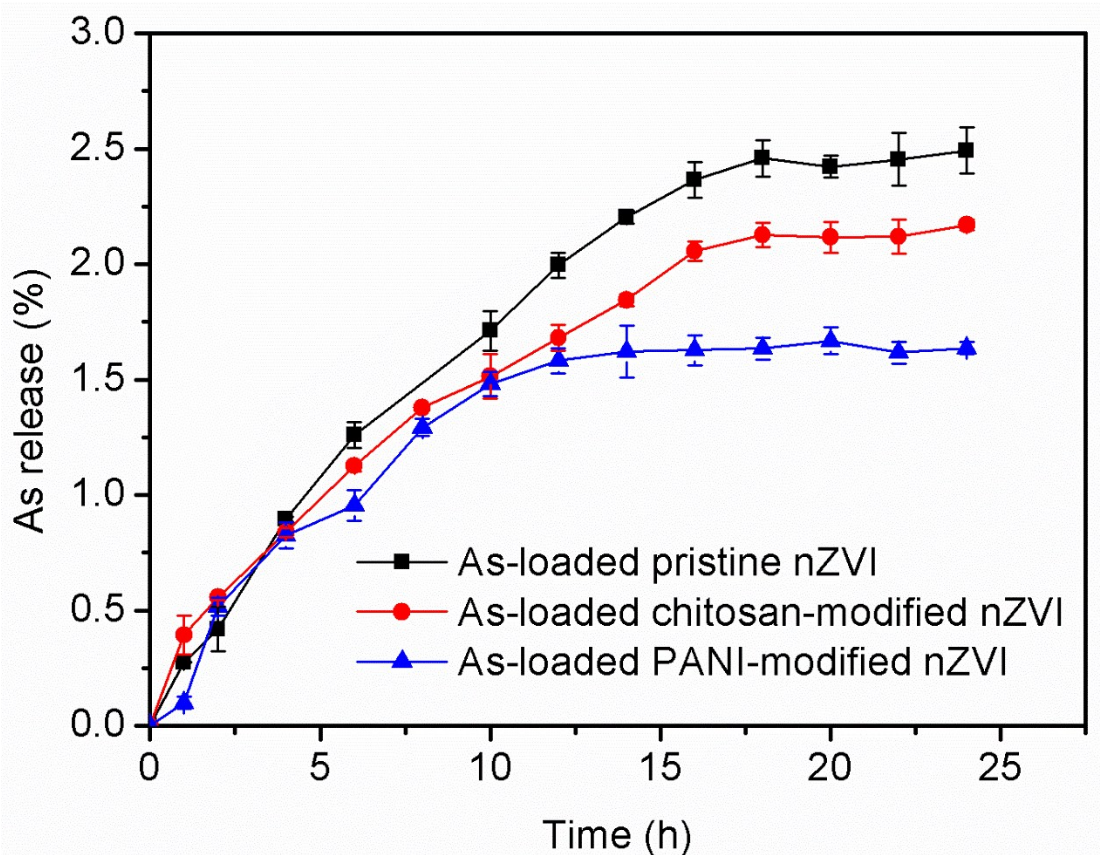

Fig. S3 Kinetics of As release from the three types of As-loaded nZVI in the synthetic groundwater. The amounts of As loading on pristine, chitosan-modified, and PANI-modified nZVI were 115.01 mg/g, 124.54 mg/g, and 130.33 mg/g respectively, which were determined from adsorption experiments. The solution pH was fixed at 7.0. The error bars represent standard deviation.

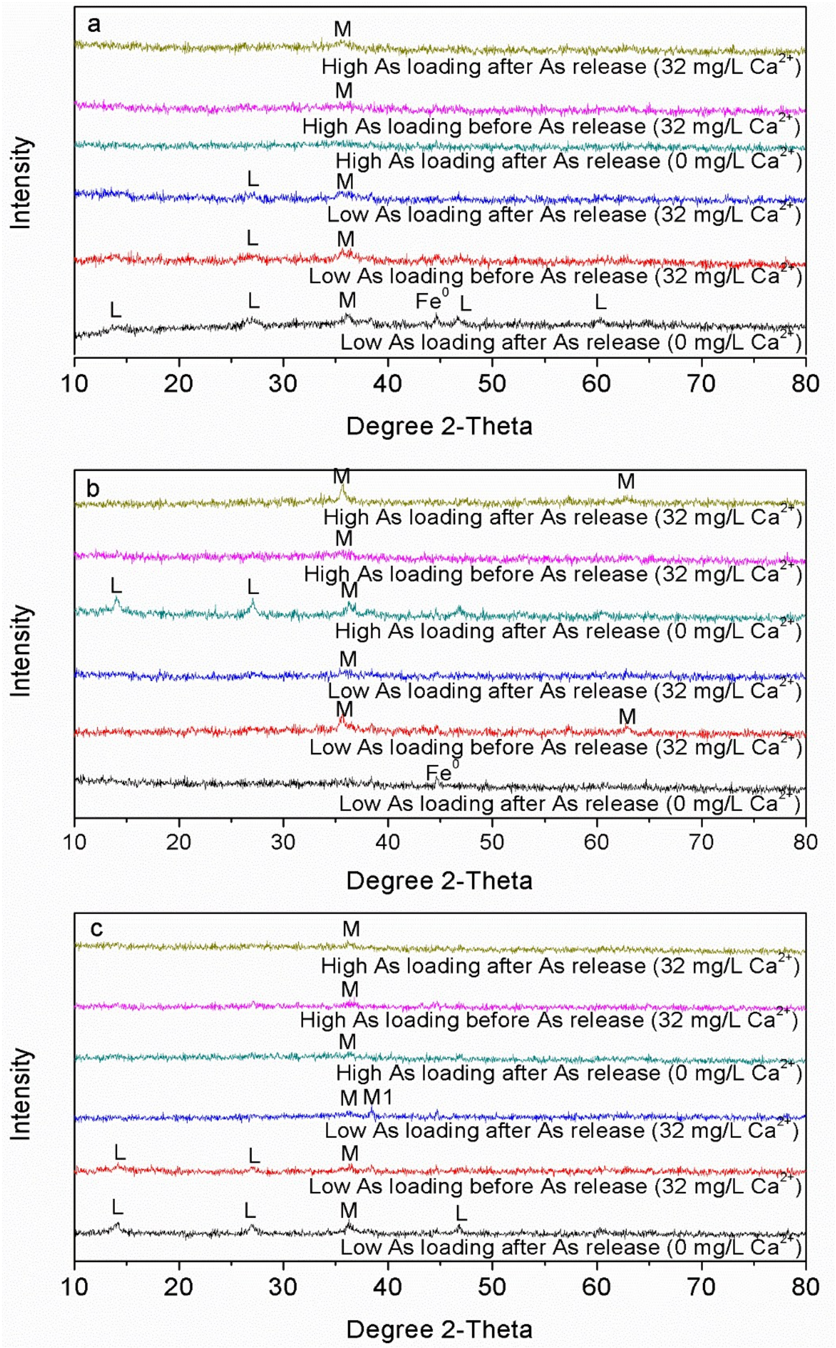

Fig. S4 XRD analysis of (a) As-loaded pristine nZVI, (b) As-loaded chitosan-modified nZVI, and (c) As-loaded PANI-modified nZVI at low and high As loadings. The measurements were taken before and after As release at two Ca^{2+} concentrations (0 and 32 mg/L). The marked peaks are referred to maghemite/magnetite (M), maghemite (M1), lepidocrocite (L), and nZVI (Fe^0).

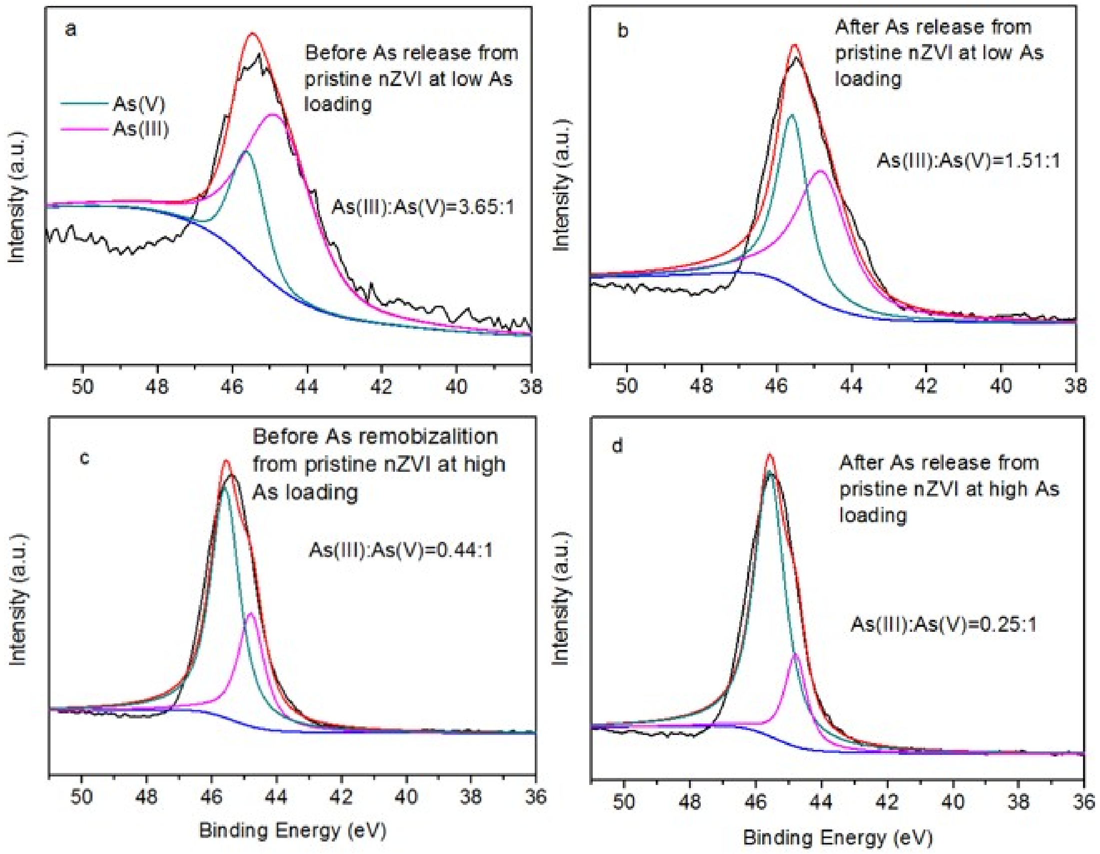

Fig. S5 XPS spectra in As 3d region of As-loaded pristine nZVI (a) before and (b) after As release at low As loading, as well as (c) before and (d) after As release at high As loading. Two distinct peaks of As species (As(V) and As(III)) were observed after curve fitting, and the ratio of As(III)/As(V) was calculated based on their peak areas. All samples were prepared at pH 7±0.1, 32 mg/L Ca^{2+}, and 0 mg/L HA.

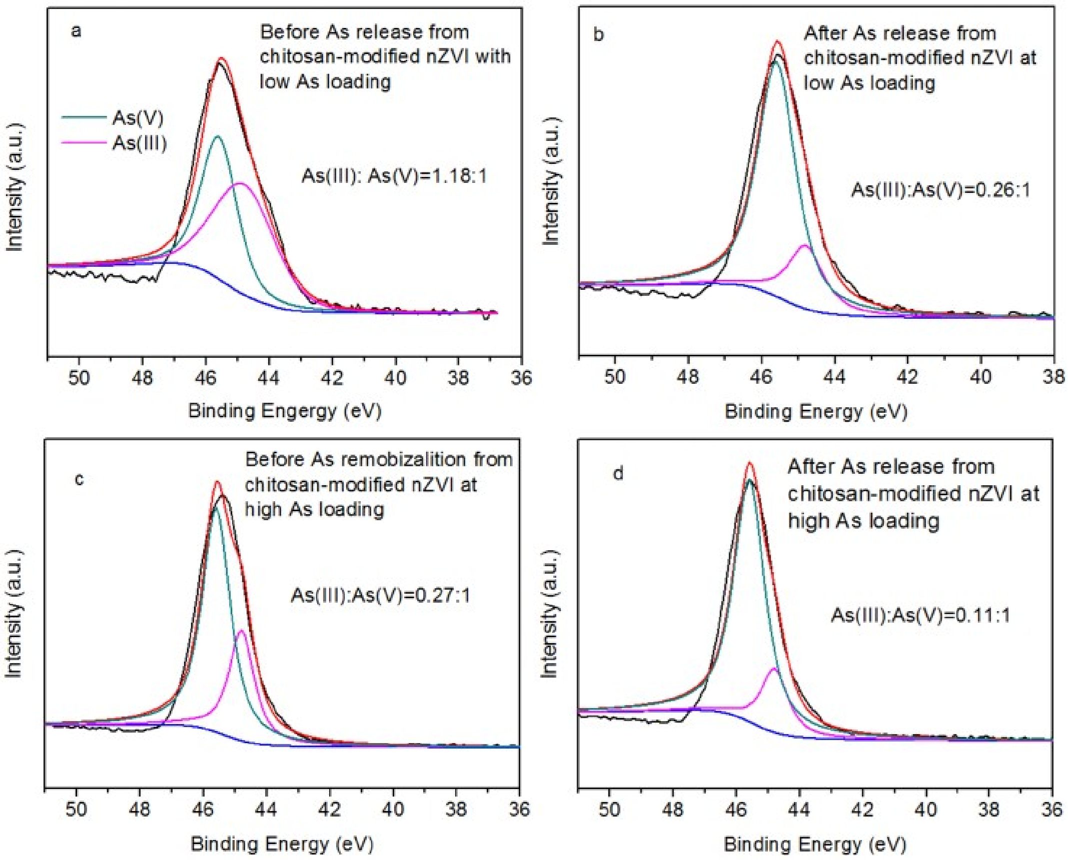

Fig. S6 XPS spectra in As 3d region of As-loaded chitosan-modified nZVI (a) before and (b) after As release at low As loading, as well as (c) before and (d) after As release at high As loading. Two distinct peaks of As species (As(V) and As(III)) were observed after curve fitting, and the ratio of As(III)/As(V) was calculated based on their peak areas. All samples were prepared at pH 7±0.1, 32 mg/L Ca^{2+}, and 0 mg/L HA.

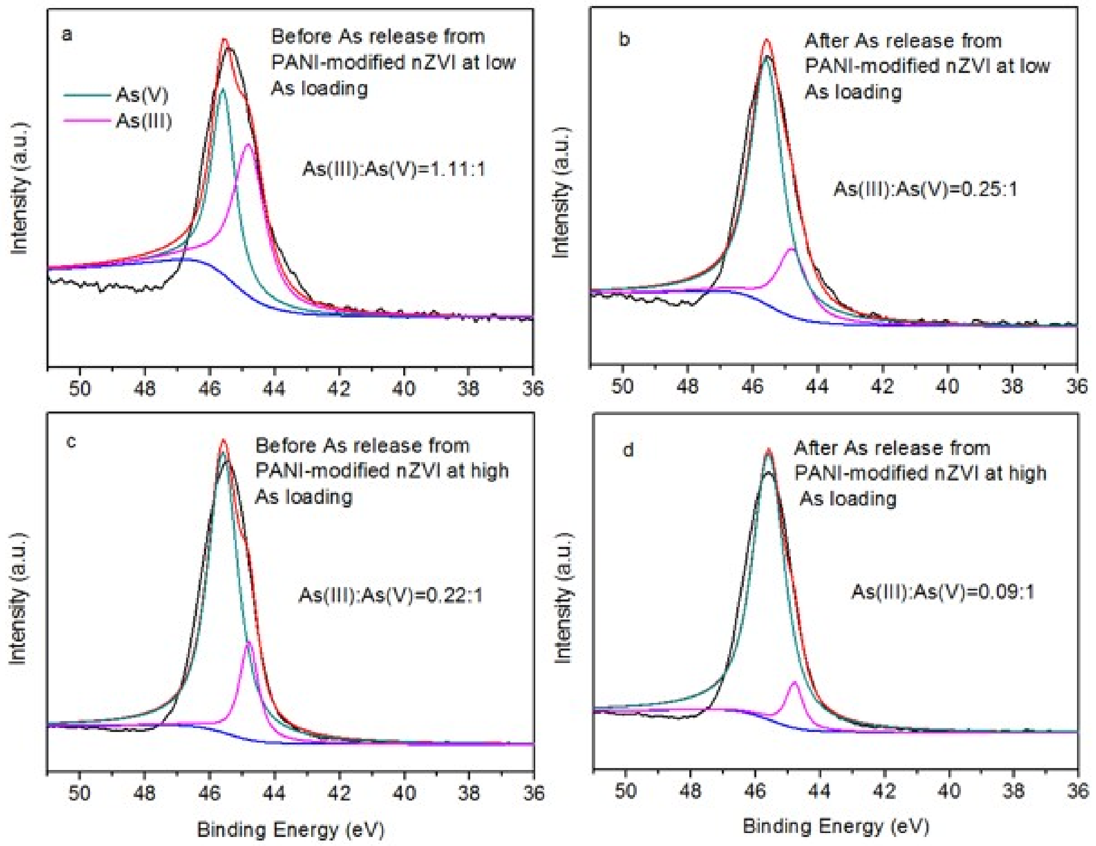

Fig. S7 XPS spectra in As 3d region of As-loaded PANI-modified nZVI (a) before and (b) after As release at low As loading, as well as (c) before and (d) after As release at high As loading. Two distinct peaks of As species (As(V) and As(III)) were observed after curve fitting, and the ratio of As(III)/As(V) was calculated based on their peak areas. All samples were prepared at pH 7±0.1, 32 mg/L Ca^{2+}, and 0 mg/L HA.

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