Supporting Information for

Zero-Valent Iron Nanoparticle with Sustained High Reductive Activity for Carbon Tetrachloride Dechlorination

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1   **1 Supplementary materials and methods**

2   **1.1 Chemicals.**

3   Chemicals used in the experiment were carbon tetrachloride (CT) (99.5%, Sigma),

4   chloroform (CF) (99.9%, Sigma), dichloromethane (DCM) (99 %, Sigma),

5   perchloroethylene (PCE) (Aladdin) and $FeCl_2 \cdot 4H_2O$ (99%, DAMAO).

6   $FeSO_4 \cdot 7H_2O$ (99%), NaOH (96%), HCl (36%~38%) and $NaBH_4$ (98%) were

7   purchased from Sinopharm Chemical Reagent Co. Ltd., China. Methane standard gas

8   was used for the analysis of non-chlorinated transformation product. Methanol (99.9%,

9   Fisher) for preparation of CT stock solution was HPLC grade. All experiments were

10 prepared by deaerated deionized water (DDW) which was prepared using Minipore

11 ultrapure water (18MΩ•cm) and purged with N_2 for 30 min.

12

13 **1.2 Synthesis of nZVI.**

14 nZVI was synthesized following previous method [1] with slight modification: 100 mL

15 DDW was adjusted to pH=2 with H_2SO_4 (acidic-DDW) and then 0.3 mol/L of

16 $FeSO_4 \cdot 7H_2O$ (solution A) was prepared using the acidic-DDW. Another 100 mL

17 DDW was used to prepare 0.6 mol/L of $NaBH_4$ solution (solution B). In a typical

18 synthesis process, solution B was dropped into solution A with a rate of 20 mL/min at

19 N_2 atmosphere. During the addition of solution B, the solution was fully mixed with

20 magnetic stirring. The black precipitates appeared and scattered equably in the

21 solution. After the addition, the Fe precipitates were settled for 30 min followed by

22 filtration with sand core funnel (G3) and then washed with DDW for three times and

23 ethanol for twice. Then the filtrated nZVI was vacuum-dried for 12 hours, grinded and

24 saved for use.

25

26 **1.3 Characterization of Materials.**

27 For SEM-EDS, XRD and XPS analysis, Fe suspension was collected from the serum

28 bottle after several cycles of reductive dechlorination and immediately washed with

29 DDW for 3 times and ethanol for 2 times in the anaerobic chamber. Then, the

30 suspension was filtrated and the retenate was dried for 12 h using vacuum drier.

31

32 The changes in particle morphology of nZVI and Fe precipitates were identified by

33 scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

34 which were performed on a Quanta FEG250 scanning electron microscope.

35

36 Oxidation of Fe surface and formation of Fe oxides/hydroxides were identified on a

37 Bruker D8 Advance X-ray diffractometer with Cu Ka radiation (λ = 1.54178 Å). Fe(0)

38 particles were collected in an anaerobic chamber after each reaction cycle and dried

39 for 12 h. The samples were scanned between 10° to 70° 2θ. XRD patterns of samples

40 were analyzed by comparing to those in the Joint Committee on Powder Diffraction

41 Standards (JCPDS) diffraction data files (JADE 6).

42

43 X-ray photoelectron spectroscopy (XPS) analysis was recorded with a Thermo

44 ESCALAB 250 X-ray photoelectron spectroscope equipped with a standard and

45 monochromatic Al kα X-ray (1486.6 eV) source operated at 150 W. The binding

46 energies obtained in the XPS analysis were corrected for specimen charging with C 1s

47 peak at 284.8 eV as a reference. Shirley baseline and a Gaussian-Lorentzian peak

48 shape were used to fit the data.

49

50 **1.4 Analytical Methods.**

51 The samples of CT and chlorinated products (CF and DCM) in headspace were

52 measured by an Agilent 6890 gas chromatograph (GC) equipped with an electron

53 capture detector, a HP-5 column was used to separate the organic compounds and

54 with ultra-high purity nitrogen (>99.9995%) as the carrier gas. The oven temperature

55 was programmed as follows: 5 min at 50 °C, ramping to 65 °C at a rate of 5 °C/min,

56 and 1 min at 65 °C and temperatures of the injector and detector were maintained at

57 200 and 250 °C. Methane was measured by a FuLi 9790 GC equipped with a thermal

58 conductivity detector and a Molecular Sieve 5A packed column. The temperature of

59 the injector and detector was set at 50 and 80 °C, respectively and oven temperature

60 was isothermally maintained at 40 °C. For a typical measurement, the test bottles

61 were taken out of the orbital shaker at each sampling time and samples were collected

62 by withdrawing 50 μL of gas in headspace using a gastight syringe (100 uL, SGE).

63 The headspace sample was immediately injected into the injection port for analysis.

64

65　The production of ferrous ion in serum bottles during the reductive dechlorination of

66　CT were investigated by measuring the concentration of aqueous Fe(II) by the 1,10-

67　Phenanthroline spectrophotometry method at the wavelength of 510 nm using a UV-

68　vis spectrometer (Shimadzu UV-1800) . In a typical process, the supernatant was

69　filtered by 0.45 μm PTFE membrane filter to remove particles and was immediately

70　acidified with 3 M HCl and mixed vigorously. Then colorimetric tubes (10 mL) were

71　added with 1mL acetate-ammonium acetate buffer (40 g ammonium acetate and 50

72　mL acetate and then diluted to 100mL with DDW), 1mL diluted aqueous sample and

73　200 uL 0.5% 1,10-phenanthroline (m/V) and then were diluted to scale with DDW.

74　The absorbance of Fe-Phenanthroline complex was measured after 15 min coloration

75　reaction.

## 2 Supplementary Results and Discussion
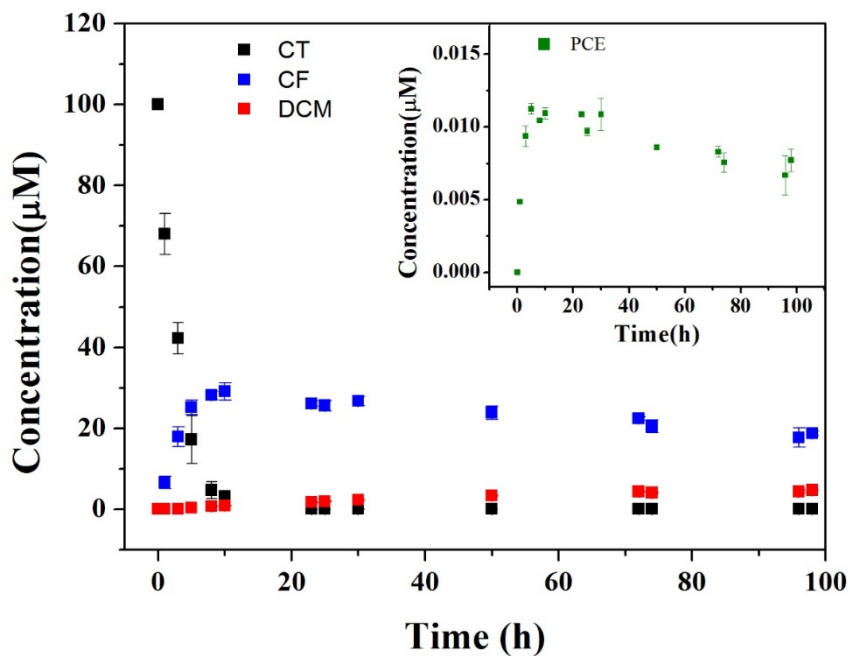
Fig. S1. Concentrations of CT and its chlorinated products vs. time. The initial CT concentration was 100 μM. Error bars are the ranges of duplicate samples. Inserted showing the formation of PCE. CT depleted completely and CF began to be degraded accompanied with the increased concentration of DCM. The concentration of PCE changed with the same trend as CF.
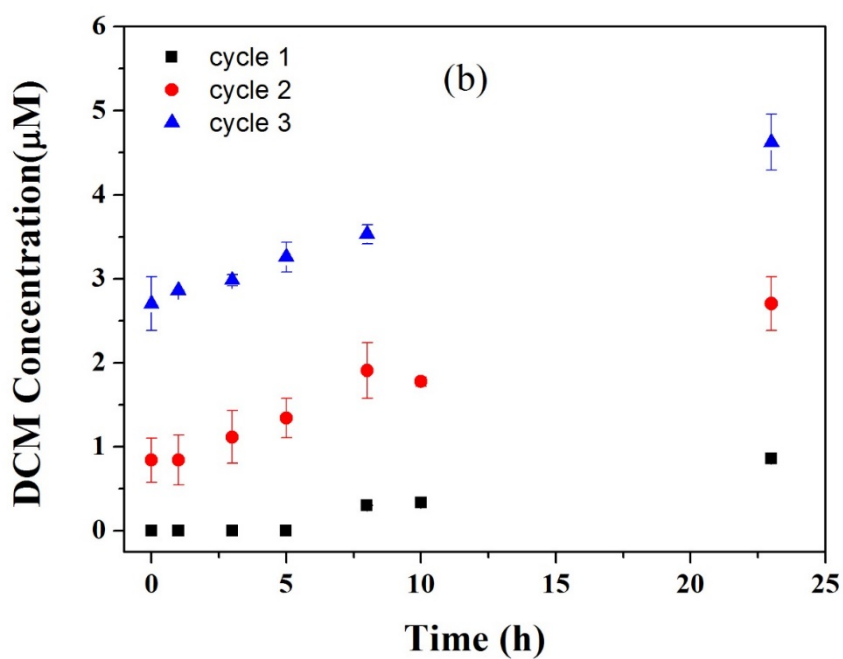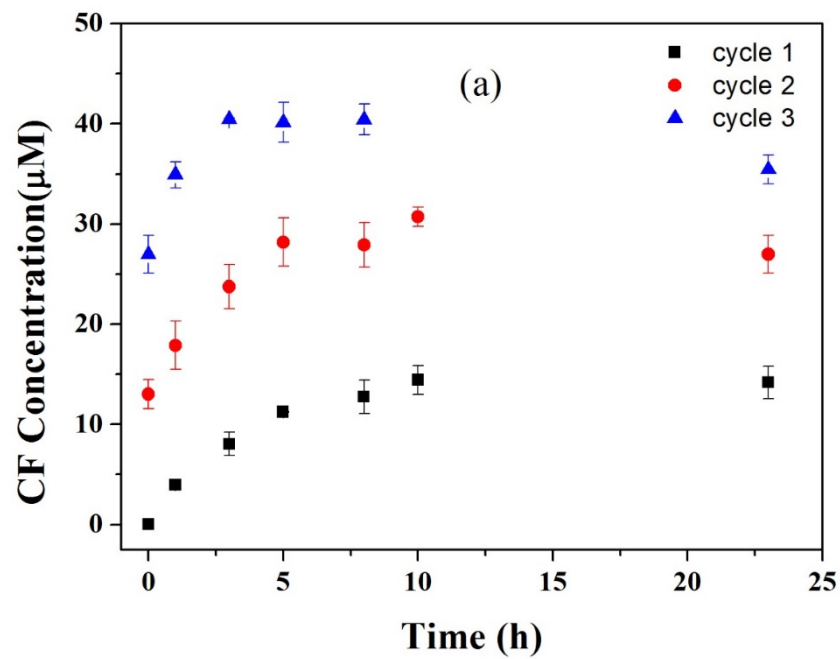
Fig. S2. Concentrations of dechlorinated products (a) CF and (b) DCM versus time in Cycles 1-3. Error bars are the ranges of duplicate samples
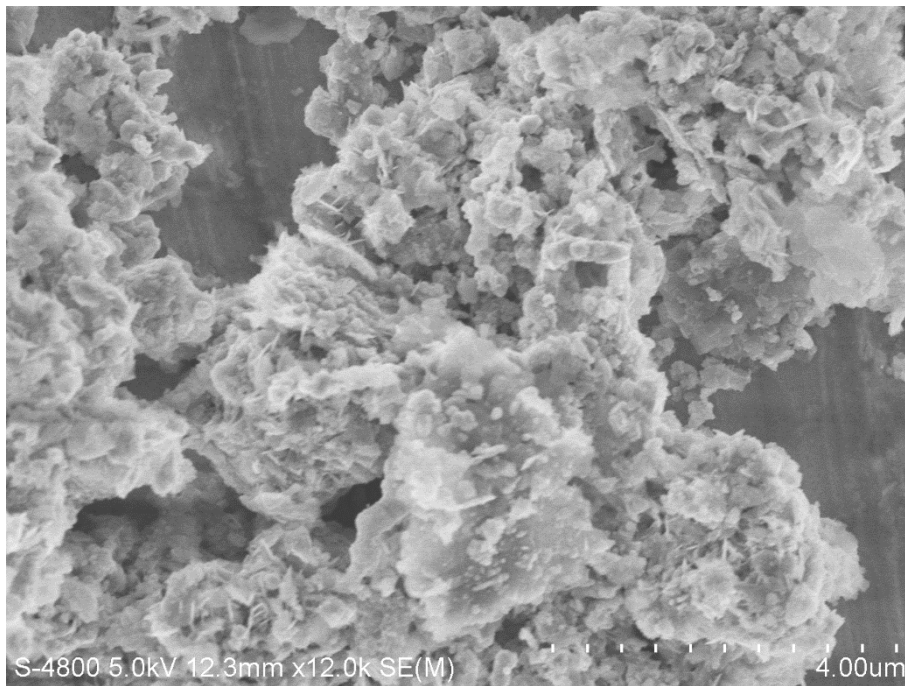
Fig. S3. SEM image of Aged-nZVI at the end of the experiment.
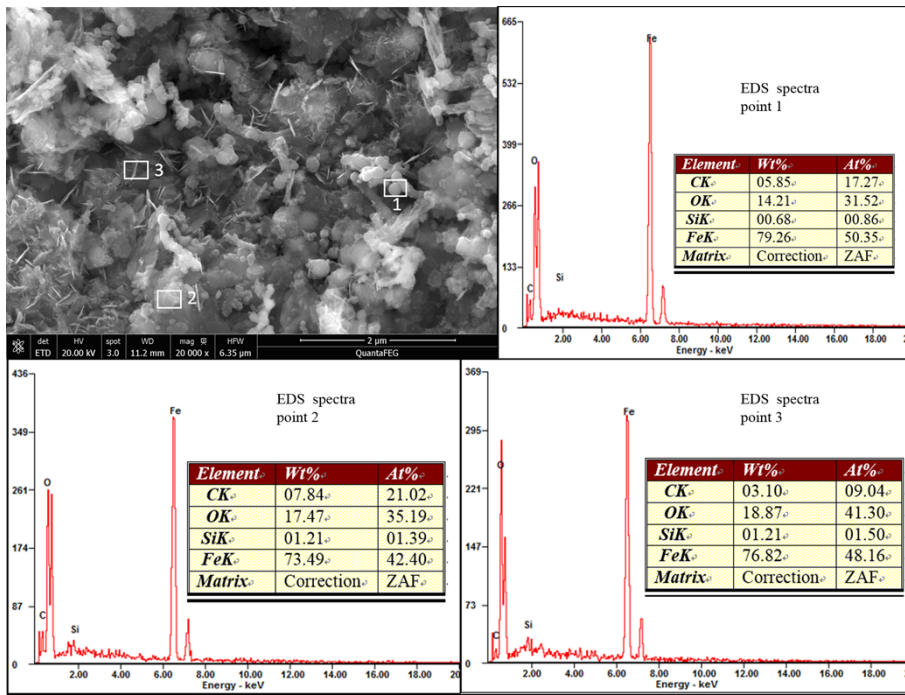
Compared to the SEM image after Cycle 3, the laminated-Fe decreased while the bulk-structured Fe minerals increased, which indicates that the species of Fe oxides or oxyhydroxides changed during the consecutive cycles of dechlorination. The morphologies of the Fe materials were similar to the magnetite and hematite formed during nitrate reduction by Fe(0) nanoparticles [2].

(a)

Element	Wt%	At%
CK	05.01	17.56
OK	05.73	15.09
FeK	89.26	67.35
Matrix	Correction	ZAF

EDS spectra point 1

Element	Wt%	At%
CK	05.88	19.82
OK	06.62	16.75
FeK	87.50	63.43
Matrix	Correction	ZAF

EDS spectra point 2

(b)

EDS spectra point 1

Element	Wt%	At%
CK	05.85	17.27
OK	14.21	31.52
SiK	00.68	00.86
FeK	79.26	50.35
Matrix	Correction	ZAF

EDS spectra point 2

Element	Wt%	At%
CK	07.84	21.02
OK	17.47	35.19
SiK	01.21	01.39
FeK	73.49	42.40
Matrix	Correction	ZAF

EDS spectra point 3

Element	Wt%	At%
CK	03.10	09.04
OK	18.87	41.30
SiK	01.21	01.50
FeK	76.82	48.16
Matrix	Correction	ZAF

(c)

Element	Wt%	At%
CK	09.60	24.83
OK	16.64	32.31
SiK	03.34	03.70
FeK	70.42	39.16
Matrix	Correction	ZAF

EDS spectra point 1

Element	Wt%	At%
CK	07.42	19.94
OK	17.49	35.30
SiK	02.34	02.69
FeK	72.76	42.07
Matrix	Correction	ZAF

EDS spectra point 2

Element	Wt%	At%
CK	13.29	34.59
OK	11.46	22.39
SiK	01.60	01.78
FeK	73.66	41.24
Matrix	Correction	ZAF

EDS spectra point 3
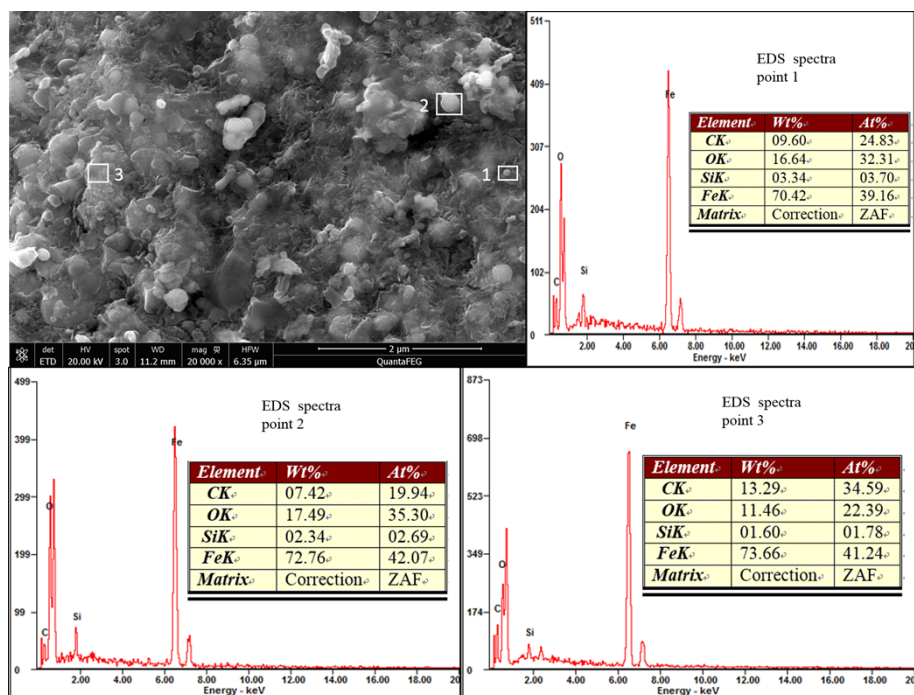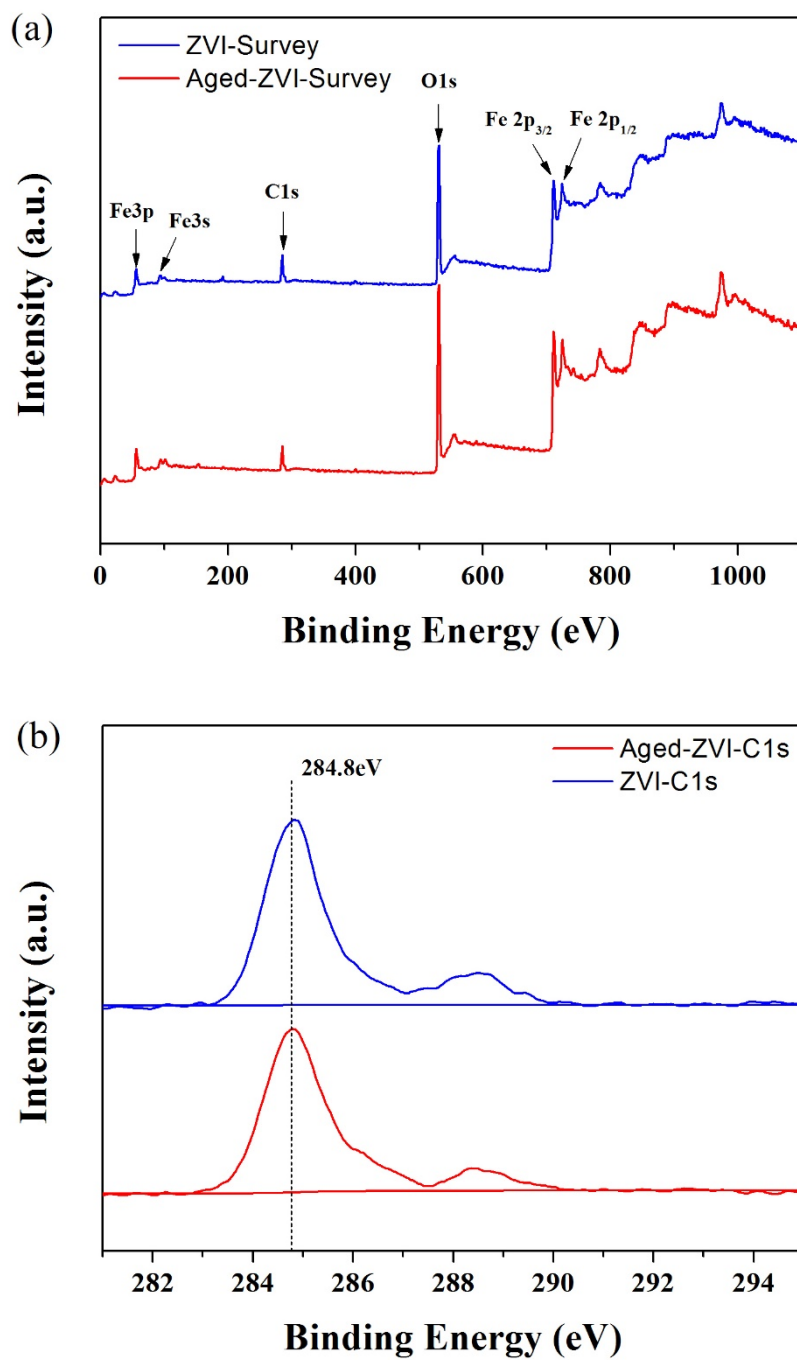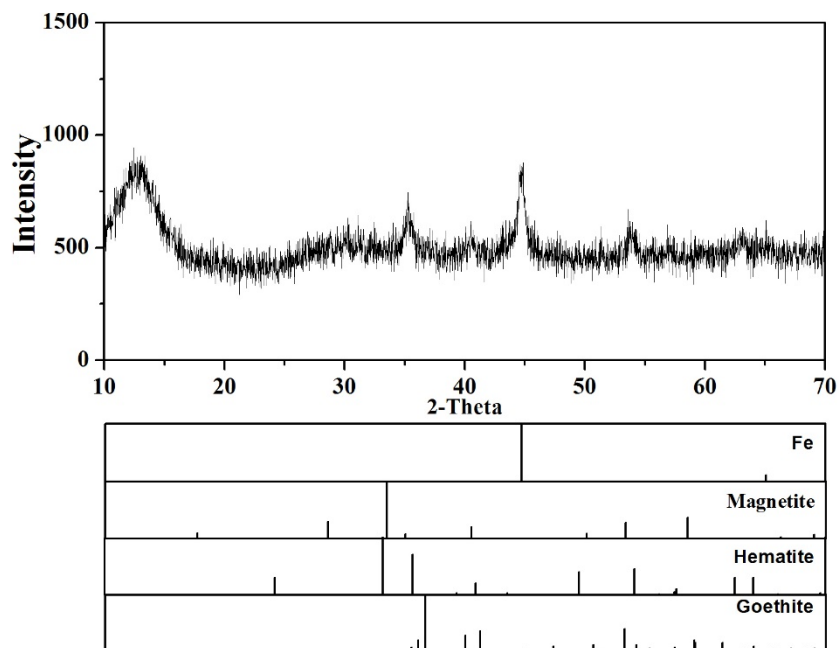
Fig. S4. SEM image and EDS spectra of (a) initial nZVI; (b) solids after 3-day dechlorination reaction; (c) after 14-d dechlorination.

Fig. S5. (a) XPS Survey spectra; (b) High resolution C 1s XPS spectra.

Fig. S6. XRD analysis of Aged-nZVI at the end of the experiment.

References

1. C.-B. Wang and W.-X. Zhang, *Environ. Sci. Technol.*, 1997, **31**, 2154-2156.
2. K. Sohn, S. W. Kang, S. Ahn, M. Woo and S.-K. Yang, *Environ. Sci. Technol.*, 2006, **40**, 5514-5519.