Supporting Information

Partial aging can counter-intuitively couple with sulfidation to improve the reactive durability of zerovalent iron

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Text S1. Synthesis methods of the AZVI and SZVI samples.

For the synthesis of AZVI, 10.0 g of PZVI was incubated in 0.5 L of distilled water buffered at pH 6.0 ± 0.1 with 0.20 M 2-(N-morpholino)ethanesulfonic acid (MES) for 0.5, 1, and 2 d open to air at 100 rpm with a mechanical stirrer (D2004W, Shanghai Sile Instrument Co., Ltd.). For the synthesis of SZVI, it was carried out in 0.25 L glass serum bottles with deoxygenated distilled water. To obtain SZVI samples at S/Fe molar ratio of 0.1, 2.5 g of PZVI and appropriate amounts of $Na_2S·9H_2O$ were simultaneously added into the bottle shaken at 180 rpm for 12 h in the oscillating box (HZQ-F100, Taicang Huada Experimental Instrument Technology Co., Ltd.). After synthesis, the ZVI samples were filtered, washed with DI water, vacuum-dried and kept in anaerobic sealed bags for subsequent characterization and use.

Text S2. Details of the electrochemical characterization.

To measure the electrochemical parameters, a three-electrode system was employed, which included a clip-on electrode made by the ZVI-prepared samples as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The clip-on electrode based on the three-dimensional foam nickel plate was washed with ethanol three times and dried under vacuum conditions before use. Thereafter, 0.1 g ZVI-prepared sample was dispersed into the 50 μL ethanol mixing with 20 μL 5% Nafion for 5 min. Then the mixture was cast on the surface of the clip-on electrode and dried in vacuum to obtain the working electrode. Finally, the Tafel diagrams were conducted by polarizing the working electrode (200 mV with respect to its open circuit potential at a scan rate of 10 mV/s) in undisturbed solution with 1.0 mM Na_2SO_4 at pH_{ini} 5.0.

Text S3. Details of the XPS analysis.

The distributions of Fe and S species in the ZVI-prepared samples before and after Cr(VI) removal were recorded by XPS with an Al Kα source (spot size 250 μm) for depth profiling. To capture the high-resolution spectra of elements, a pass energy of 50 eV with an energy step size of 0.1 eV were employed. Advantage software (version 5.9921) was used to fit curves of the Fe 2p, S 2p, and Cr 2p spectra to quantify and deconvolute the contribution of Fe, S and Cr species comprised the spectra. The binding energies were calibrated using C 1s peak with a fixed value of 284.8 eV. For determining the optimal spectral baseline and peaks, the Shirley background correction algorithm was accepted to fit the Fe 2p, S 2p and Cr 2p regions. The Fe $2p_{3/2}$ peak positions for Fe^{3+}, Fe^{2+}, and Fe^0 are 711, 709, and 706.7 eV. In addition, The Cr $2p_{3/2}$ peak positions for Cr(III) and Cr(VI) are 576.0 and 579.0 eV, respectively. Moreover, the S $2p_{3/2}$ peak positions for S^{2-}, S_2^{2-}, S_n^{2-}, SO_3^{2-}, and SO_4^{2-} are 161.2, 162.7, 164, 166.5, and 168.2 eV, respectively.

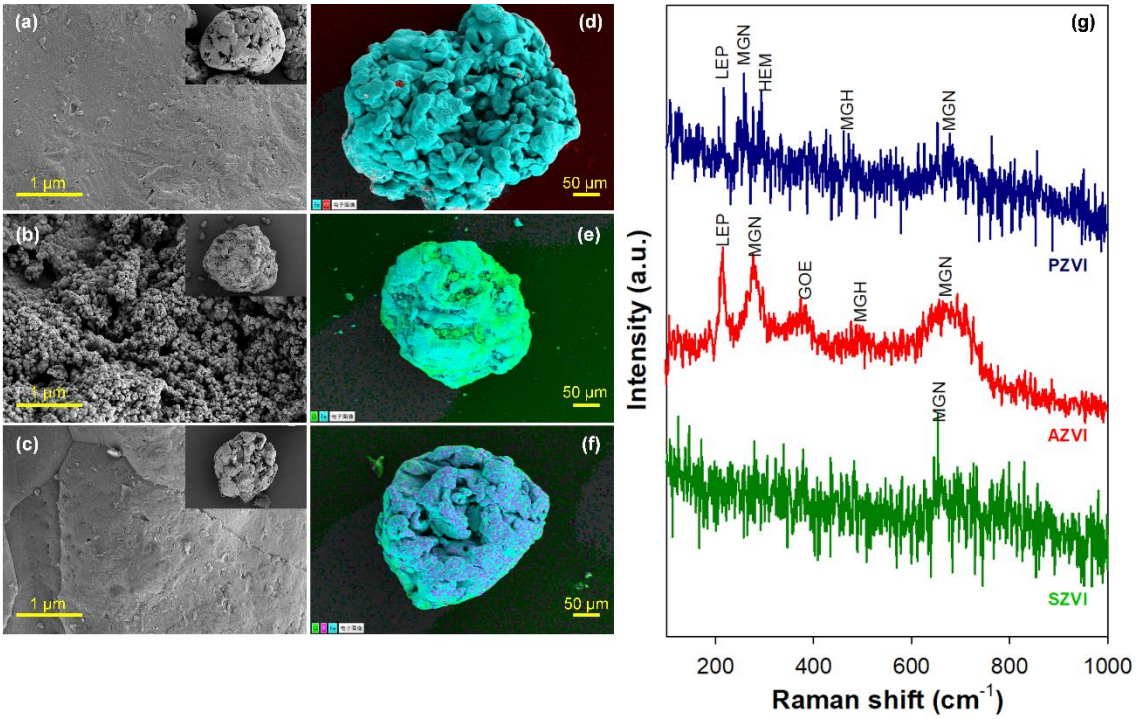

Figure S1. SEM images (a-c) and EDX elemental mappings (d-f) of PZVI (a, d), AZVI (b, e) and SZVI (c, f), along with their Raman spectra (g).

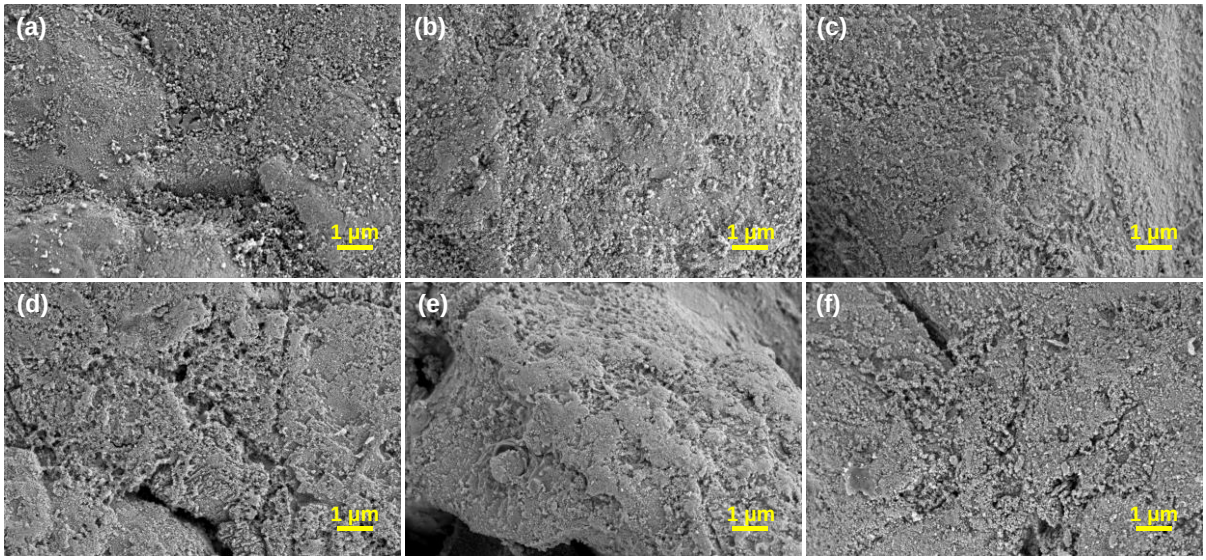

Figure S2. SEM images of ASZVI-0.5 (a), ASZVI-1 (b), ASZVI-2 (c), ASZVI-4 (d), ASZVI-7 (e), and ASZVI-14 (f).

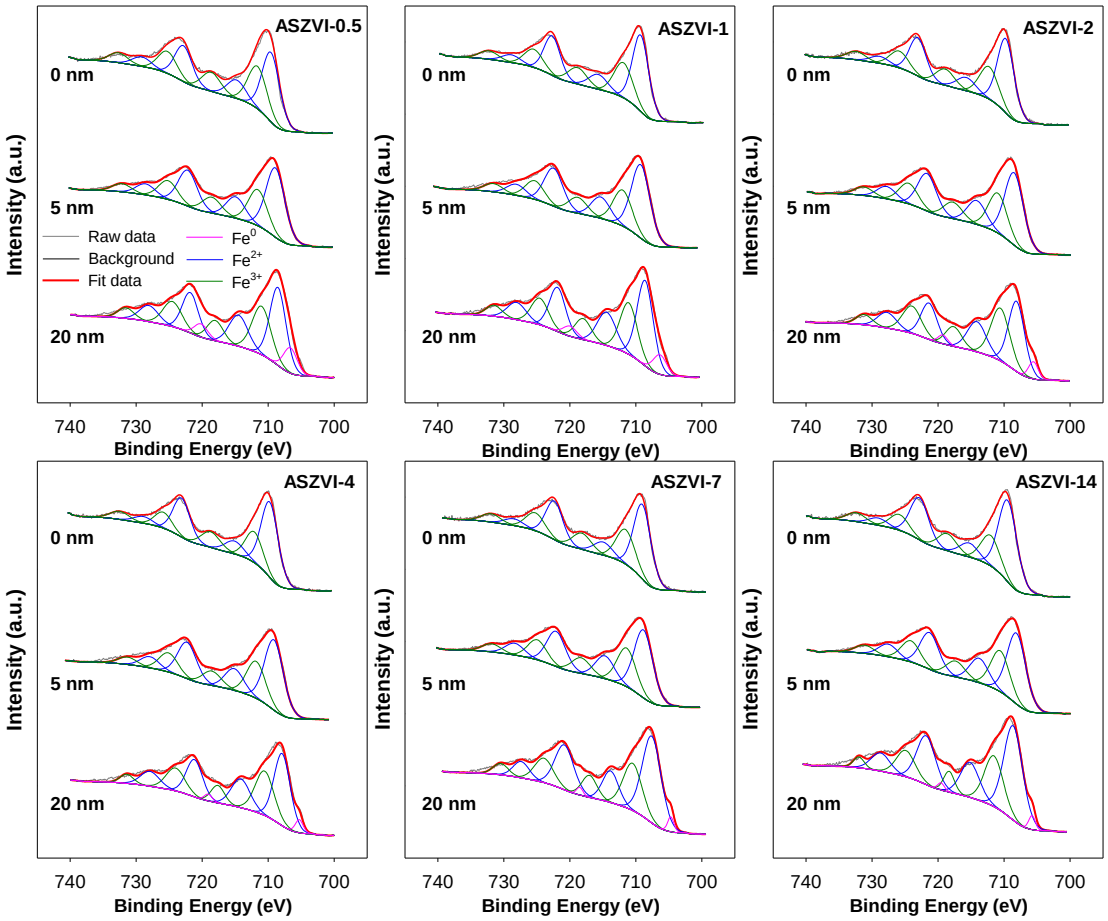

Figure S3. Fe 2p XPS depth profiling spectra of ASZVI samples.

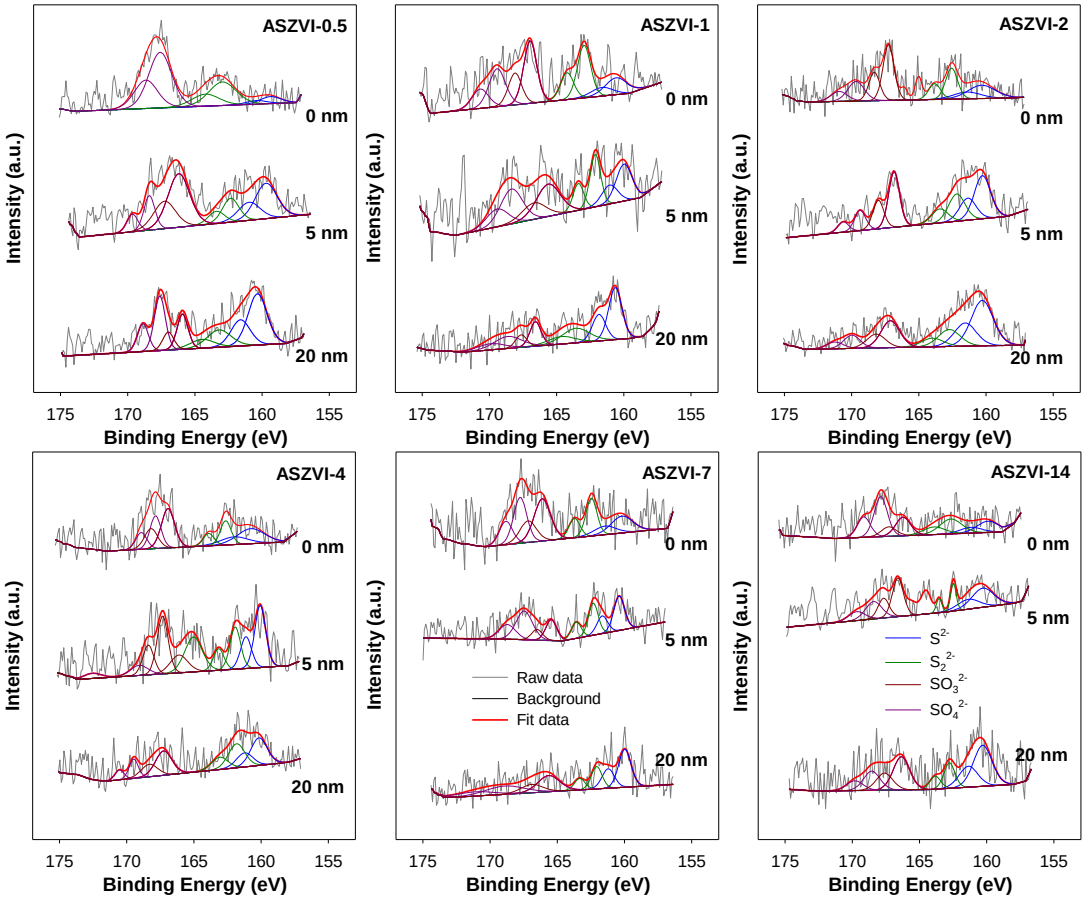

Figure S4. S 2p XPS depth profiling spectra of ASZVI samples.

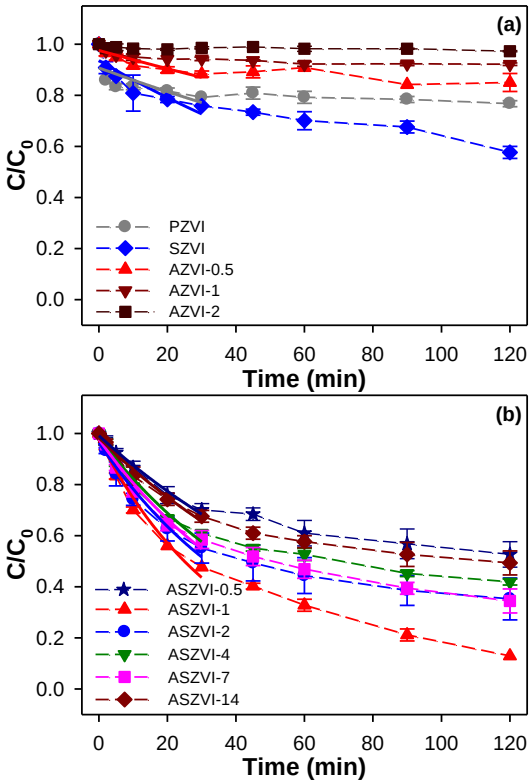

Figure S5. Removal kinetics of Cr(VI) by the PZVI/SZVI/AZVI (a) and ASZVI samples (b). Reaction conditions: $[ZVI]_0$ = 0.5 g/L, $[Cr(VI)]_0$ = 4.0 mg/L, pH_{ini} = 5.0, $[Na_2SO_4]$ = 1.0 mM, T = 25℃.

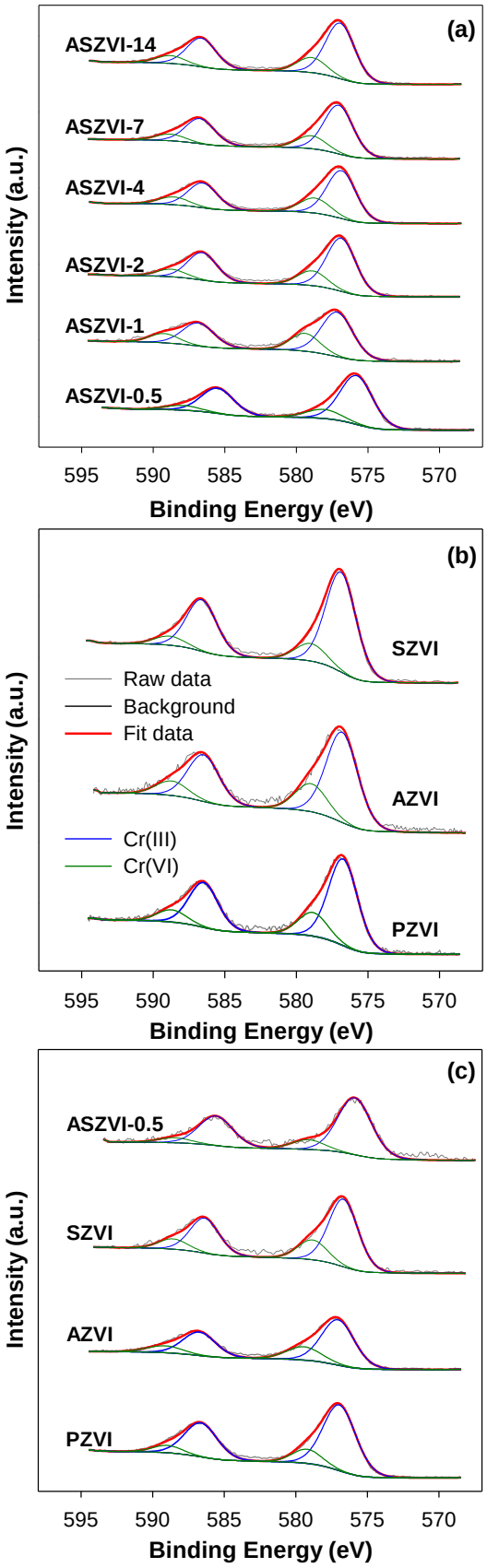

Figure S6. Cr 2p XPS spectra of ASZVI samples (a), PZVI/AZVI/SZVI (b) after reaction with Cr(VI) in batch tests (a-b) and consecutive experiments (c).

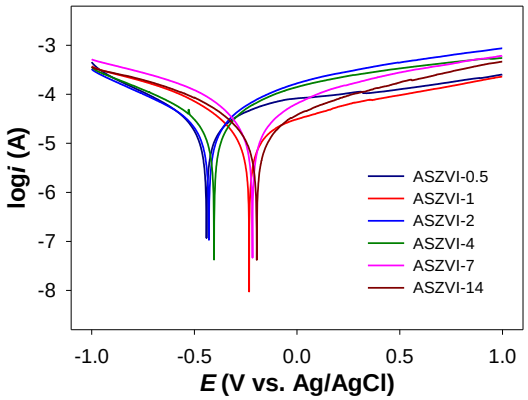

Figure S7. Tafel polarization curves of the ASZVI samples as function of oxic aging time.

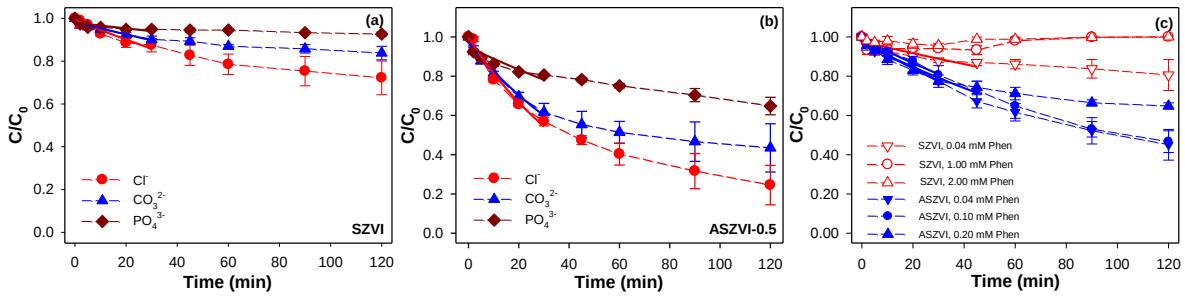

Figure S8. Influence of different anions (a, b) and 1,10-phenanthroline concentrations (c) on the removal kinetics of Cr(VI) by the SZVI and ASZVI-0.5. Reaction conditions: $[ZVI]_0 = 0.5$ g/L, $[Cr(VI)]_0 = 4.0$ mg/L, $pH_{ini} = 5.0$, [Anions] = 1.0 mM, T = 25ºC.

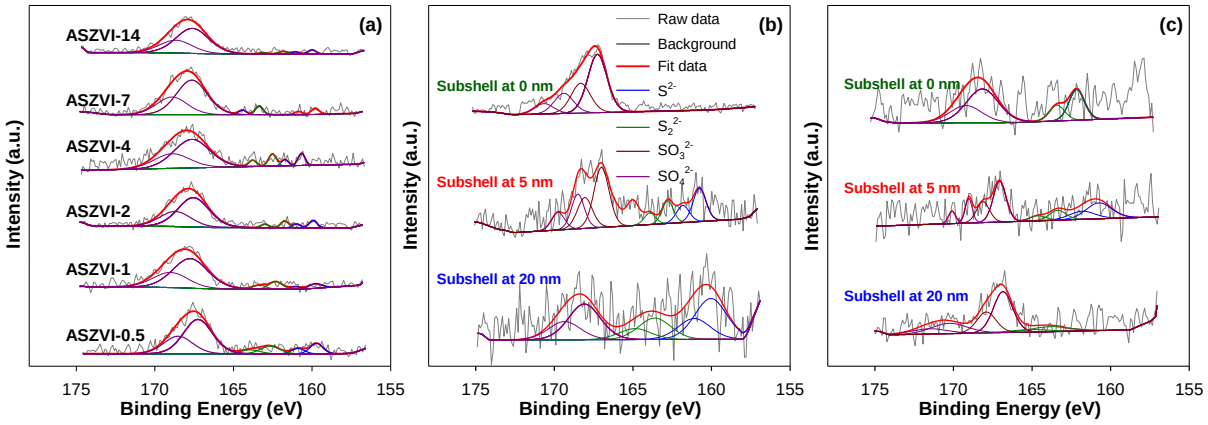

Figure S9. S 2p XPS spectra of ASZVI (a, b) and SZVI (c) samples after reaction with Cr(VI) in batch (a) and consecutive (b, c) experiments.

Table S1. The BET surface area of ASZVI samples.

Samples	BET surface area (m^2/g)
ASZVI-0.5	0.2941
ASZVI-1	1.6174
ASZVI-2	0.8538
ASZVI-4	1.0926
ASZVI-7	1.2816
ASZVI-14	1.6657

Table S2. Fe compositions in the ASZVI samples before their reaction with Cr(VI) calculated from XPS depth spectra.

Samples	Depth (nm)	Normalized Area (CPS. eV)			Relative content (%)			Mass content (%)		
		Fe^0	Fe^{2+}	Fe^{3+}	Fe^0	Fe^{2+}	Fe^{3+}	Fe^0	Fe^{2+}	Fe^{3+}
ASZVI-0.5	0	0	27362.81	20359.27	0	57.28	42.72	0	2.40	1.78
	5	0	44461.04	25507.08	0	63.48	36.52	0	3.38	1.94
	20	4683.93	48590.16	32694.97	9.98	53.77	36.25	0.68	3.68	2.48
ASZVI-1	0	0	31226.18	19866.13	0	61.05	38.95	0	2.60	1.66
	5	0	46454.02	25466.64	0	64.53	35.47	0	3.47	1.91
	20	7107.21	53823.72	32933.61	7.54	57.32	35.14	0.52	3.94	2.41
ASZVI-2	0	0	26290.60	16098.02	0	61.96	38.04	0	2.48	1.53
	5	0	41233.86	24132.95	0	63.02	36.98	0	3.39	1.98
	20	4461.60	45713.42	10875.56	5.21	53.52	41.27	0.37	3.83	2.95
ASZVI-4	0	0	22342.21	12082.83	0	64.83	35.17	0	2.37	1.28
	5	0	39447.71	22008.11	0	64.13	35.87	0	3.39	1.90
	20	2779.66	47830.60	28745.65	3.49	60.24	36.27	0.25	4.31	2.60
ASZVI-7	0	0	26831.37	16790.13	0	61.44	38.56	0	2.47	1.55
	5	0	44491.00	26583.62	0	62.54	37.46	0	3.48	2.08
	20	2502.93	57517.66	32731.90	2.69	61.96	35.35	0.20	4.53	2.59
ASZVI-14	0	0	31005.12	15748.05	0	66.25	33.75	0	2.62	1.34
	5	0	46715.45	27839.56	0	62.60	37.40	0	3.30	1.97
	20	2457.62	65349.87	31660.53	2.46	65.66	31.88	0.17	4.67	2.26

Table S3. S compositions in the ASZVI samples before their reaction with Cr(VI) calculated from XPS depth spectra.

Samples	Depth (nm)	Normalized Area (CPS.eV)				Relative content (%)				Mass content (%)			
		S^{2-}	S_2^{2-}	SO_3^{2-}	SO_4^{2-}	S^{2-}	S_2^{2-}	SO_3^{2-}	SO_4^{2-}	S^{2-}	S_2^{2-}	SO_3^{2-}	SO_4^{2-}
ASZVI-0.5	0	53.86	237.26	0	472.95	7.03	31.01	0	61.96	0.03	0.15	0	0.29
	5	228.69	115.60	345.68	111.44	28.48	14.41	43.18	13.93	0.12	0.06	0.19	0.06
	20	323.66	137.66	128.13	198.51	41.02	17.47	25.24	16.28	0.17	0.07	0.07	0.11
ASZVI-1	0	81.46	153.00	181.61	137.44	14.68	27.61	32.84	24.87	0.05	0.09	0.11	0.08
	5	101.69	95.91	132.07	131.24	22.02	20.79	28.67	28.53	0.05	0.05	0.07	0.07
	20	203.47	117.42	80.83	96.87	40.75	23.55	16.23	19.47	0.11	0.06	0.04	0.05
ASZVI-2	0	106.87	108.67	226.00	94.86	19.86	20.22	42.21	17.71	0.07	0.07	0.15	0.06
	5	200.12	126.56	172.78	62.77	35.55	22.49	30.77	11.19	0.12	0.07	0.10	0.04
	20	384.53	143.76	194.43	84.12	47.59	17.81	24.14	10.46	0.23	0.09	0.12	0.05
ASZVI-4	0	105.92	67.33	133.87	92.84	26.43	16.82	33.51	23.24	0.08	0.05	0.10	0.07
	5	150.64	98.82	275.87	39.25	26.63	17.49	48.91	6.97	0.09	0.06	0.17	0.02
	20	150.46	130.49	132.77	58.35	31.82	27.62	28.17	12.39	0.10	0.08	0.09	0.04
ASZVI-7	0	94.97	107.77	179.14	155.73	17.63	20.03	33.33	29.01	0.06	0.07	0.12	0.10
	5	108.86	92.24	68.04	139.18	26.62	22.57	16.67	34.14	0.06	0.05	0.04	0.08
	20	163.84	83.35	123.99	111.34	33.90	17.26	25.72	23.13	0.09	0.05	0.07	0.06
ASZVI-14	0	90.34	120.36	102.67	194.43	17.75	23.68	20.23	38.34	0.05	0.07	0.06	0.12
	5	100.73	36.81	160.33	68.71	27.43	10.03	43.76	18.78	0.05	0.02	0.08	0.03
	20	196.53	71.99	140.77	81.30	40.00	14.67	28.73	16.61	0.10	0.04	0.07	0.04

Table S4. The rate constants for Cr(VI) removal by ZVI-based samples under different reaction conditions.

Samples	Variables	Reaction conditions	k_{obs} (min^{-1})	k_{SA} ($L\ m^{-2}\ min^{-1}$)
PZVI	-	$[ZVI]_0$ = 0.5 g L^{-1}, $[Cr(VI)]_0$ = 4.0 mg L^{-1}, pH_{ini} = 5.0, $[Na_2SO_4]$ = 1.0 mM, T = 25℃	0.0054	
AZVI-0.5	Aging time = 0.5 d		0.0024	
AZVI-1	Aging time = 1 d		0.0016	
AZVI-2	Aging time = 2 d		0.0003	
SZVI	-		0.0084	
SAZVI-0.5	Aging time = 0.5 d	$[ZVI]_0$ = 0.5 g L^{-1}, $[Cr(VI)]_0$ = 4.0 mg L^{-1}, pH_{ini} = 5.0, $[Na_2SO_4]$ = 1.0 mM, T = 25℃	0.0124	0.0843
ASZVI-1	Aging time = 1 d		0.0269	0.0333
ASZVI-2	Aging time = 2 d		0.0208	0.0487
ASZVI-4	Aging time = 4 d		0.0178	0.0326
ASZVI-7	Aging time = 7 d		0.0193	0.0301
ASZVI-14	Aging time =14 d		0.0135	0.0162

Table S5. Cr compositions on the surface of the ZVI-based samples after their reaction with Cr(VI) calculated from XPS spectra.

Samples	Reaction conditions	Relative content (%)	
		Cr(III)	Cr(VI)
PZVI	$[ZVI]_0$ = 0.5 g L^{-1}, $[Cr(VI)]_0$ = 4.0 mg L^{-1}, pH_{ini} = 5.0, $[Na_2SO_4]$ = 1.0 mM, T = 25℃	78.56	21.44
AZVI-0.5		76.27	23.73
SZVI		85.06	14.94
ASZVI-0.5	$[ZVI]_0$ = 0.5 g L^{-1}, $[Cr(VI)]_0$ = 4.0 mg L^{-1}, pH_{ini} = 5.0, $[Na_2SO_4]$ = 1.0 mM, T = 25℃	83.33	16.67
ASZVI-1		72.87	27.13
ASZVI-2		78.28	21.72
ASZVI-4		75.40	24.60
ASZVI-7		78.97	21.03
ASZVI-14		78.67	21.33
PZVI	$[ZVI]_0$ = 2 g L^{-1}, $[Cr(VI)]_{resplike}$ = 2.0 mg L^{-1}, pH_{ini} = 5.0, [NaCl] = 1.0 mM, T = 25℃	83.86	16.14
AZVI-0.5		76.08	23.92
SZVI		77.25	22.75
ASZVI-0.5		85.81	14.19

Table S6. Parameters of Tafel polarization curves of ASZVI samples.

Samples	E_{corr} (V)	I_{corr} (μA)	i_{corr} (A cm^{-2})	b_a (V dec^{-1})	b_c (V dec^{-1})	R_p (Ω cm^2)
ASZVI-0.5	-0.441	13.74	1.374×10^{-5}	5.097	4.296	3367.6
ASZVI-1	-0.233	8.66	8.662×10^{-6}	5.466	4.158	5215.0
ASZVI-2	-0.429	12.80	1.280×10^{-5}	4.860	5.113	3406.6
ASZVI-4	-0.404	13.13	1.313×10^{-5}	5.093	5.048	3265.9
ASZVI-7	-0.217	12.14	1.214×10^{-5}	5.569	4.900	3420.9
ASZVI-14	-0.196	8.29	8.290×10^{-6}	5.304	5.023	5076.3