Supplementary materials

Efficient sequestration of hexavalent chromium on graphene-based nanoscale zerovalent iron composite coupling with ultrasonic pre-treatment

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1. Materials and methods

1.1 Materials

All of the chemicals used in the study were of analytical grade. Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium borohydride ($NaBH_4$), potassium dichromate ($K_2Cr_2O_7$), acetone (CH_3COCH_3), and diphenylcarbazide ($C_6H_5(NH)_2CO(NH)_2C_6H_5$) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Hydrochloric acid (HCl, 36%-38%), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4, 85%), and sulfuric acid (H_2SO_4, 98%) were purchased from Beijing Chemical Works, China. Deionized water was used throughout the experiments.

1.2 preparation of nZVI

nZVI was synthesized with a classic method of chemical reduction, as previously reported [1]. Briefly, 100 mL 0.5 M of a $NaBH_4$ aqueous solution was added dropwise into 200 mL 0.045 M $FeCl_3 \cdot 6H_2O$ aqueous solution by peristaltic pump (revolving speed 20 rpm) at an ambient temperature with strong mechanical agitation. Fe(III) was reduced to Fe(0), according to the following reaction (Equation 1) [2]:

$$Fe(H_2O)_6{}^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 \downarrow + 3B(OH)_3 + 10.5H_2 \quad (1)$$

The process was proceeded by sparking with pure nitrogen (99.99%), which was stopped half an hour after adding the $NaBH_4$ aqueous solution. Afterwards, the mixture was settled for 1 h, and then the precipitate was washed several times by deoxy-deionized water and ethanol. Finally, the solid obtained was dried by vacuum freeze-drying (SiHuan, Beijing, China) and preserved in a seal.

2. Reactivity test

Table S1. PSO kinetic parameters of nZVI/rGO coupled with ultrasonic pre-treatment.

System	Equation	k_{ad} (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
Aerobic	$t/q_t = 0.02606 + 0.01303t$	0.0065	76.75	0.9976
US/aerobic	$t/q_t = 0.00538 + 0.01318t$	0.032	75.87	0.9969
Anaerobic	$t/q_t = 0.0212 + 0.01236t$	0.0072	80.90	0.9959
US/anaerobic	$t/q_t = 0.00415 + 0.01219t$	0.036	82.03	0.9996

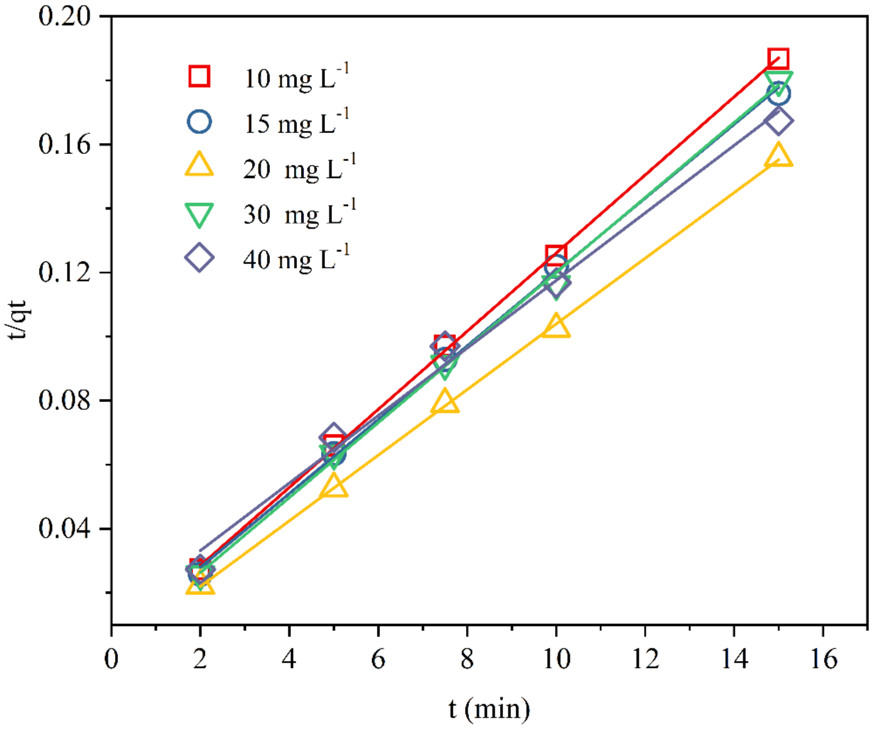

Figure S1. The fitted curves of the PSO model for US-nZVI/rGO system.

Table S2. Parameters obtained from PSO kinetic model for US-nZVI/rGO system.

Initial concentration (mg L^{-1})	Equation	k_{ad} (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
10	$t/q_t = 0.00415 + 0.01219t$	0.036	82.03	0.9996
15	$t/q_t = 0.00495 + 0.01152t$	0.027	86.81	0.9989
20	$t/q_t = 0.00152 + 0.01024t$	0.069	97.66	0.9997
30	$t/q_t = 0.00292 + 0.01171t$	0.047	85.40	0.9985
40	$t/q_t = 0.01212 + 0.01054t$	0.0092	94.88	0.9918

3. Characterization

3.1 EDS

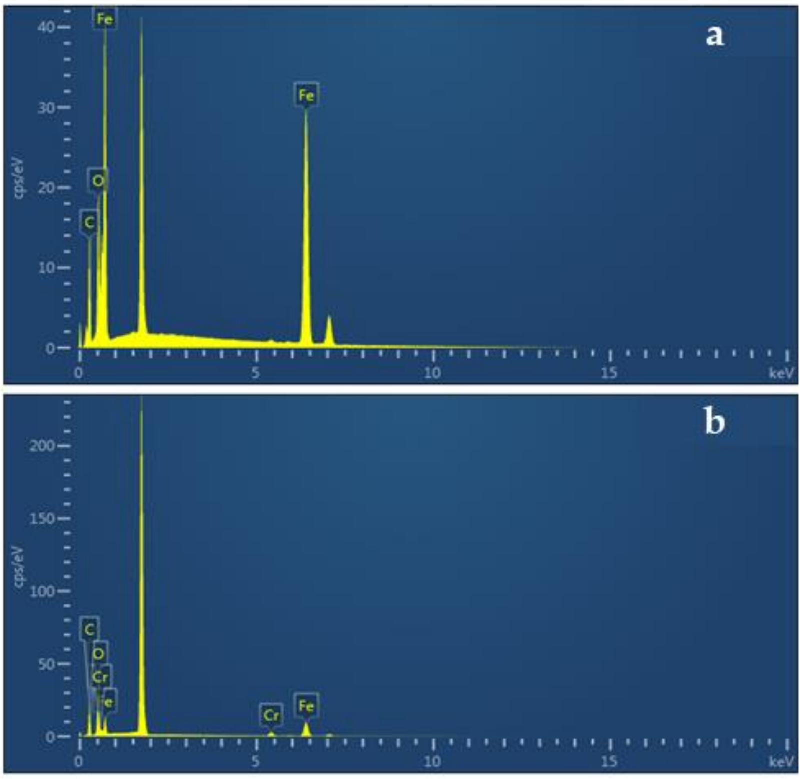

Figure S2. EDS spectra of a) nZVI/rGO and b) nZVI/rGO after reaction.

Table S3. The mass ratio of each element from EDS.

nZVI/rGO		nZVI/rGO after reaction	
elements	*wt%*	elements	*wt%*
C	15.18	**C**	26.22
O	7.20	**O**	28.97
Fe	77.62	**Fe**	39.17
		Cr	5.64
Total	100.00	Total	100.00

3.2 BET

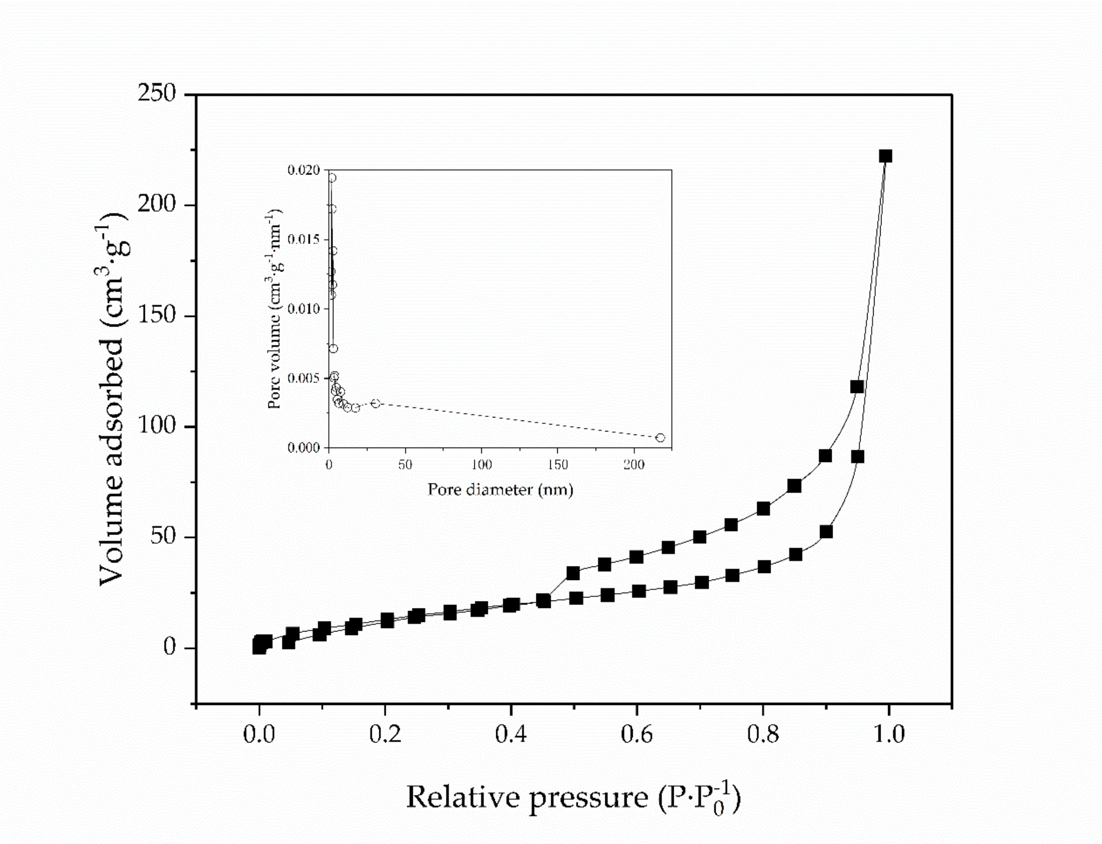

Figure S3. Nitrogen adsorption-desorption isotherms and pore size distribution curve (the insert pattern) for nZVI/rGO.

Table S4. Physical and chemical properties of nanoparticles investigated in this study.

Sample	**S_{BET}（m^2 g^{-1}）**	**Pore size（nm）**	**Pore volume（cm^3 g^{-1}）**	**Reference**
GO	1.23			this study
nZVI	14.56	4.12	0.11	previous study of our group[3]
nZVI/rGO	59.31	2.324	0.345	this study

Table S5. BET specific surface area of nZVI in the provious studies.

material	Synthesis method	Specific surface area (m^2 g^{-1})	Reference
Nano Pd/Fe	$NaBH_4$ reduction	33.5	[2]
nZVI	$NaBH_4$ reduction	24.4	[4]
nZVI	$NaBH_4$ reduction	25	[5]
nZVI	$NaBH_4$ reduction	14.2	[6]

3.3 XPS

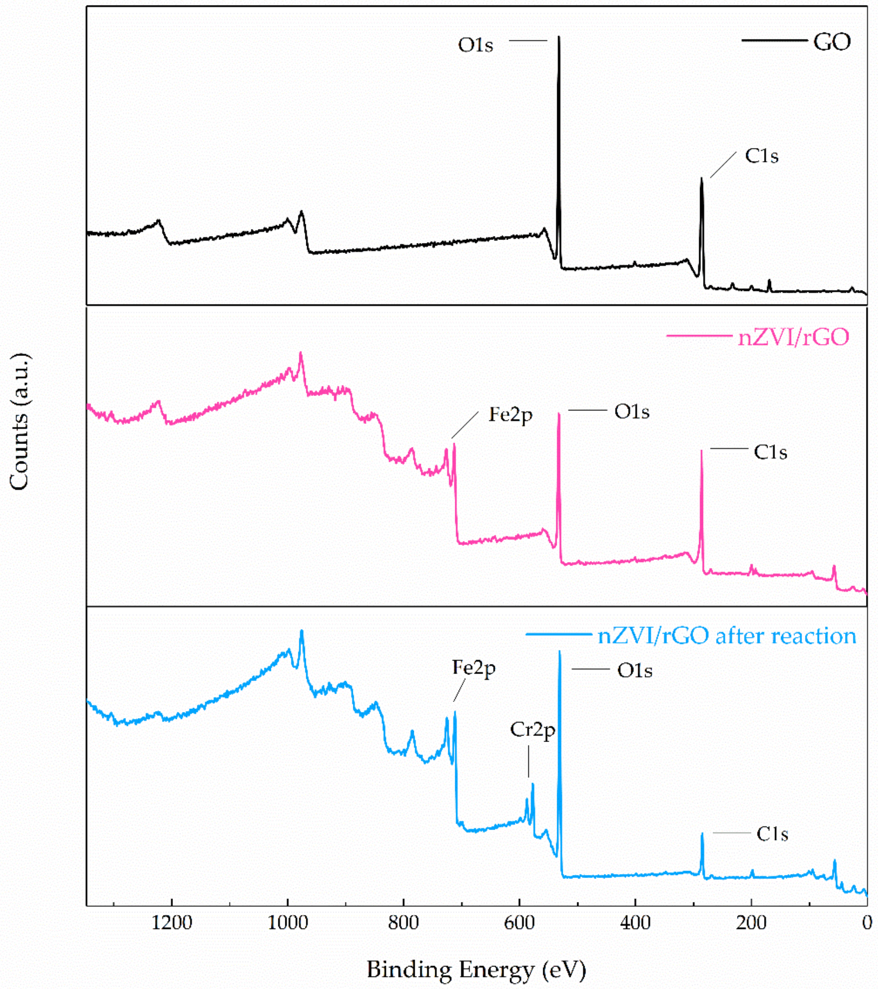

Figure S4. Full survey XPS patterns for nZVI/rGO, nZVI/rGO after reaction, and GO.

Table S6. The peak area fraction of carbon-containing groups.

GO		nZVI/rGO		nZVI/rGO after reaction	
Groups	Percentage (%)	Groups	Percentage (%)	Groups	Percentage (%)
C-C	44.06	C-C	62.45	C-C	63.13
C-O	6.62	C-O	20.76	C-O	20.96
C=O	40.32	C=O	9.15	C=O	4.92
O-C=O	9.00	O-C=O	7.65	O-C=O	10.99

4. Mechanism

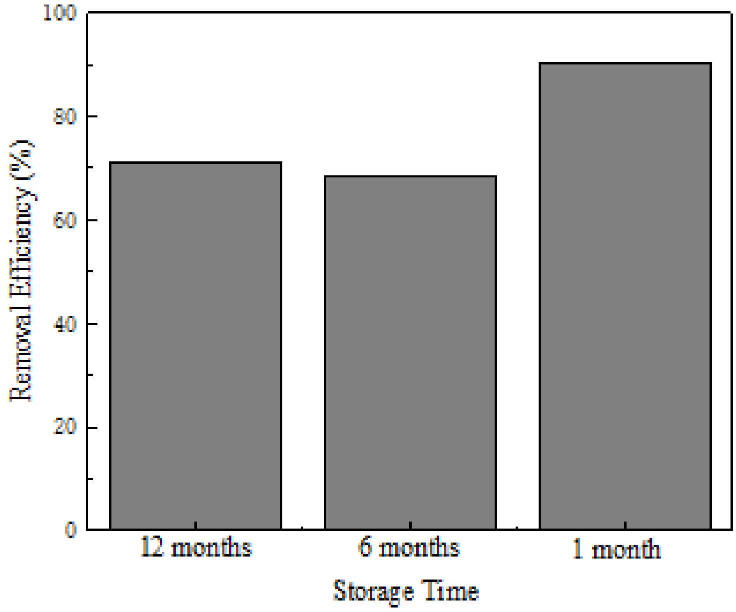

Figure S5. Influence of storage time.

Reference

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