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Supporting information

to

Synthesis, physical properties and application of zero-valent iron/titanium dioxide heterocomposite encoding high activity for the sustainable photocalytic removal of hexavalent chromium in water

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Number of pages: 8

Number of figures: 4

Number of tables: 2

Supporting text

Batch experiments for hexavalent chromium removal

The Cr(VI) concentrations in the solutions were determined colorimetrically by using the 1,5-diphenylcarbazide method, which is based on the reaction of Cr(VI) cations with 1,5-diphenylcarbazide molecules leading to the formation of a red−purple chromium 1,5-diphenylcarbazide complex. 0.3 mL of the Cr(VI) solution was mixed with 2.7 mL of distilled water, 120 μL of 1,5-diphenylcarbazide (0.025 g) solution in acetone (10 mL) and 60 μL of H_3PO_4 solution (0.5 mL of H_3PO_4 (85%) in 10 mL of H_2O). The solution was left for 10 min to allow color development, and then the solution concentration was determined spectrophotometrically at 540 nm. Furthermore, the ability of repetitive use of nZVI@TiO_2 nanocomposite has been tested by applying different cycles of reaction with hexavalent chromium. The regeneration of the solid was performed after each three cycles by means of washing and storage for 1 hour in absolute ethanol. Absorption spectra of solutions were measured using a 10 mm optical path quartz cuvette. UV-Vis spectra were recorded on a Shimadzu UV-2401PC two beam spectrophotometer in the range of 350–700 nm, at a step of 0.5 nm, using combination of deuterium and halogen lamps as sources.

Supporting figures

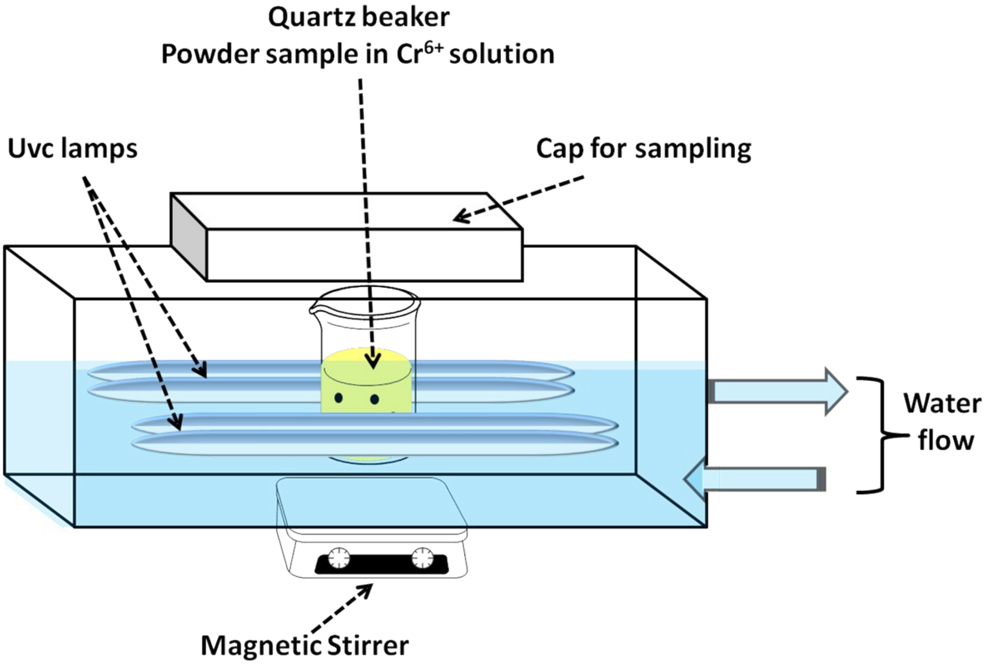

Fig. S1. Schematic illustration of the photoreactor that was used.

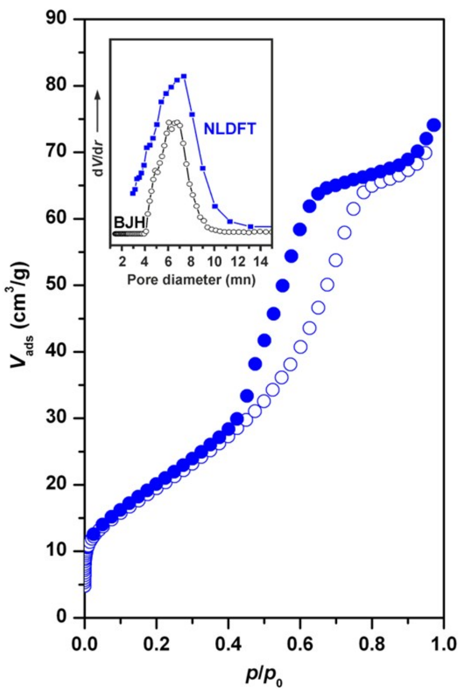

Fig. S2. N_2 adsorption-desorption isotherms of mesoporous pristine TiO_2. Inset: BJH and NLDFT pore size distributions.

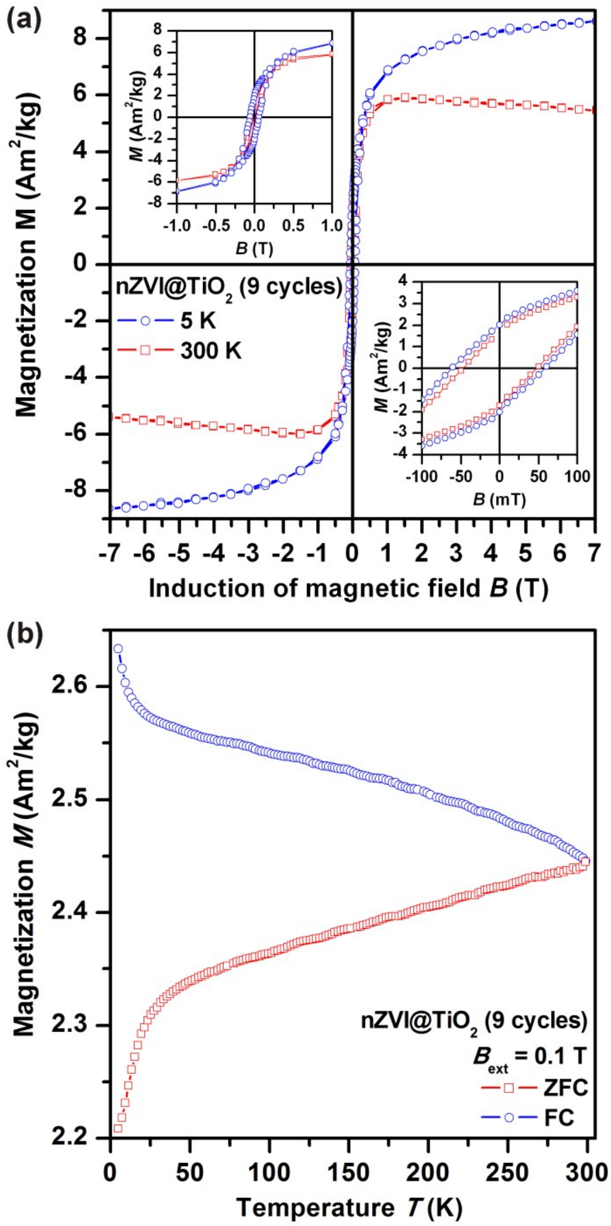

Fig. S3. (a) Magnetic hysteresis loops of the nZVI@TiO_2 photocatalyst after nine (9) reaction cycles with Cr(VI) solutions at 5 and 300 K and (b) ZFC and FC magnetization curves recorded under an applied magnetic field of 0.1 T.

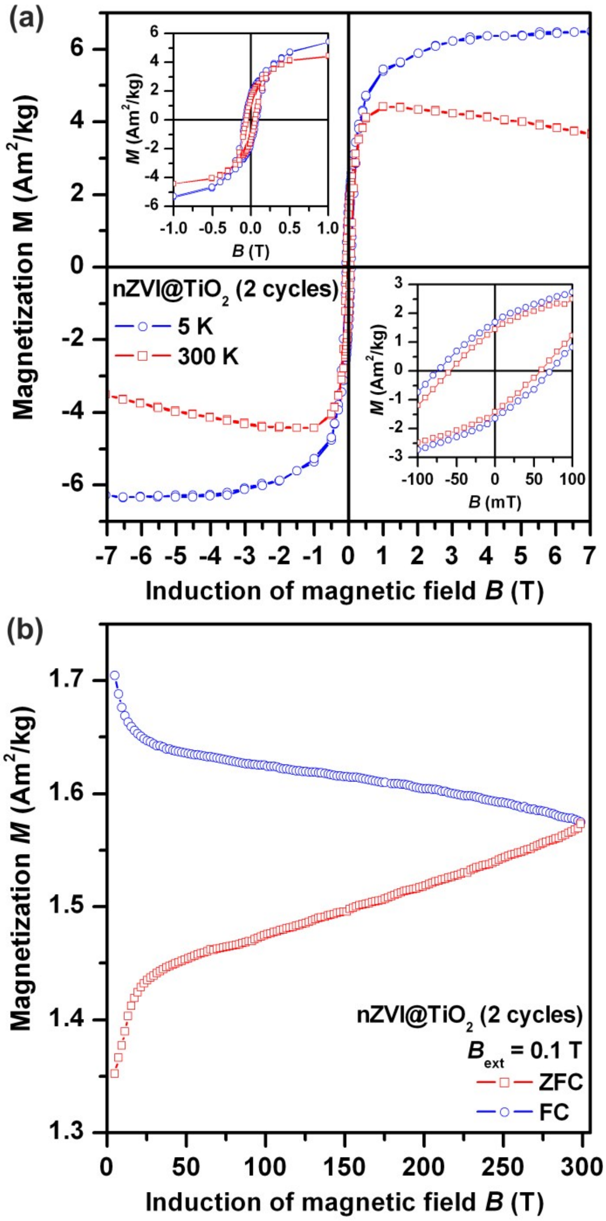

Fig. S4. (a) Magnetic hysteresis loops of the nZVI@TiO_2 photocatalyst after two (2) reaction cycles with Cr(VI) solutions at 5 and 300 K and (b) ZFC and FC magnetization curves recorded under an applied magnetic field of 0.1 T.

Supporting tables

Table S1. Values of hysteresis parameters of the nZVI@TiO_2 samples, derived from the hysteresis loops measured at a temperature of 5 and 300 K, where M_{max+} (7 T) is a maximum magnetization in 7 T, M_{max-} (– 7 T) is a maximum magnetization in – 7 T, B_{C+} is a positive coercivity, B_{C-} is negative coercivity, M_{R+} is a positive remanent magnetization, and M_{R-} is a negative remanent magnetization. (a) denotes the sample before reaction and (b) and (c) denote the samples after reaction with Cr(VI) solution (b – the sample after two reaction cycles without UV-C irradiation, c – the sample after nine reaction cycles under UV-C irradiation).

Conditions/ Number of cycles	T (K)	M_{max+} (7 T) (Am^2/kg)	M_{max-} (– 7 T) (Am^2/kg)	B_{C+} (mT)	B_{C-} (mT)	M_{R+} (Am^2/kg)	M_{R-} (Am^2/kg)
(a) nZVI@TiO_2_0	5	16.17	– 16.17	55.3	– 57.5	4.83	– 4.89
(b) nZVI@TiO_2nZVI without UV-C irradiation/2	5	6.39	– 6.39	71.3	– 74.3	1.68	– 1.64
(c) nZVI@TiO_2nZVI under UV-C irradiation/9	5	8.58	– 8.58	57.6	– 61.2	2.03	– 2.01
(a) nZVI@TiO_2_0	300	13.83	– 13.83	44.7	– 45.2	4.08	– 4.06
(b) nZVI@TiO_2nZVI without UV-C irradiation/2	300	3.60	– 3.60	58.2	– 58.1	1.43	– 1.44
(c) nZVI@TiO_2nZVI under UV-C irradiation/9	300	5.58	– 5.58	47.7	– 47.2	1.74	– 1.73

Table S2. Removal capacities of Cr(VI) with other adsorbents found in literature.

Material	Removal capacity (mg/g)	pH	Ref.
Polyaniline Coated Ethyl Cellulose	38.76	1	1
Polyethylenimine Facilitated Ethyl Cellulose	36.8	3	2
Polyaniline/Carbon Fibers Polyaniline/Ethyl Cellulose	18.1 38.76	1	1
Polyaniline/Fe_3O_4	6.0	3	3
Mesoporous Carbon-Fe_3O_4/Fe	327.5/15.3	1 / 7	4
Mesoporous Carbon-Fe_3O_4/Fe	278.8/22.5	2 / 7	2
ZVI/chitosan	55.8	3	5
γ-Fe_2O_3 nanoparticles	19.2	2.5	6
δ-FeOOH-coated γ-Fe_2O_3	25.8	2	7
Carbon core/ZVI	0.63	NA	8
Polyaniline/Carbon fiber	18.1	1	9
TiO_2	23.8	3	10
TiO_2-Ag	25.7	2	11
nZVI-Fe_3O_4	100-29.4	3-8	12
TiO_2	7.4	4.5	13
Carbon spheres/TiO_2	18.1	2	14
HCB/TiO_2	27.33	2	15
nZVI@TiO_2	**51.6**	**3**	**this work**

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