

Supporting information

Reduction Kinetics of Nitroaromatic Compounds by Titanium-Substituted Magnetite

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1. XRD analysis

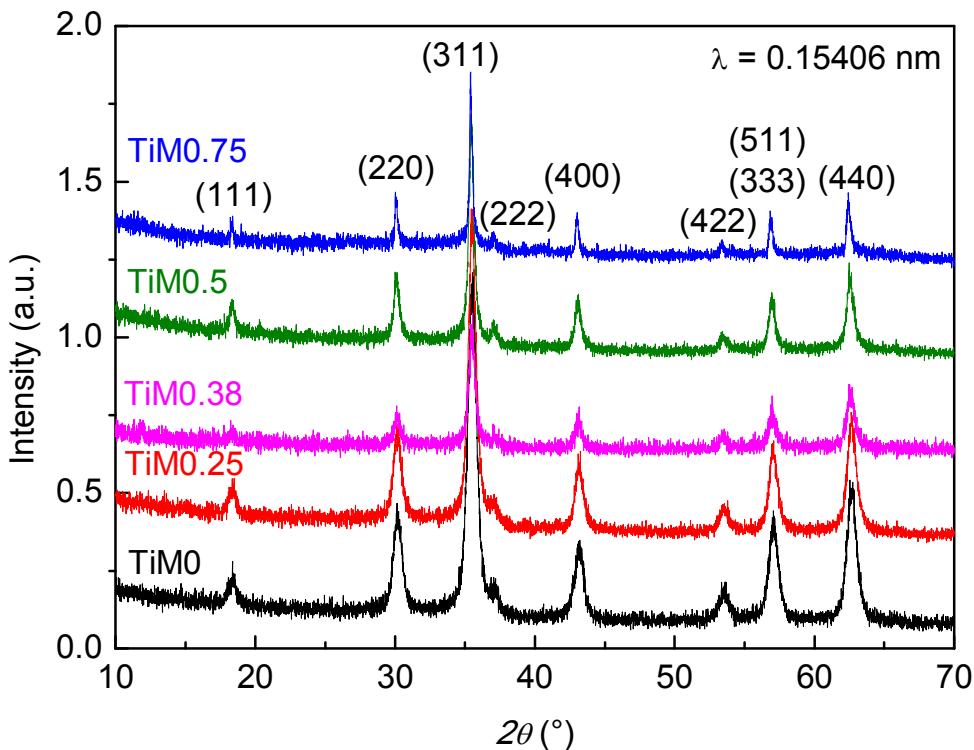
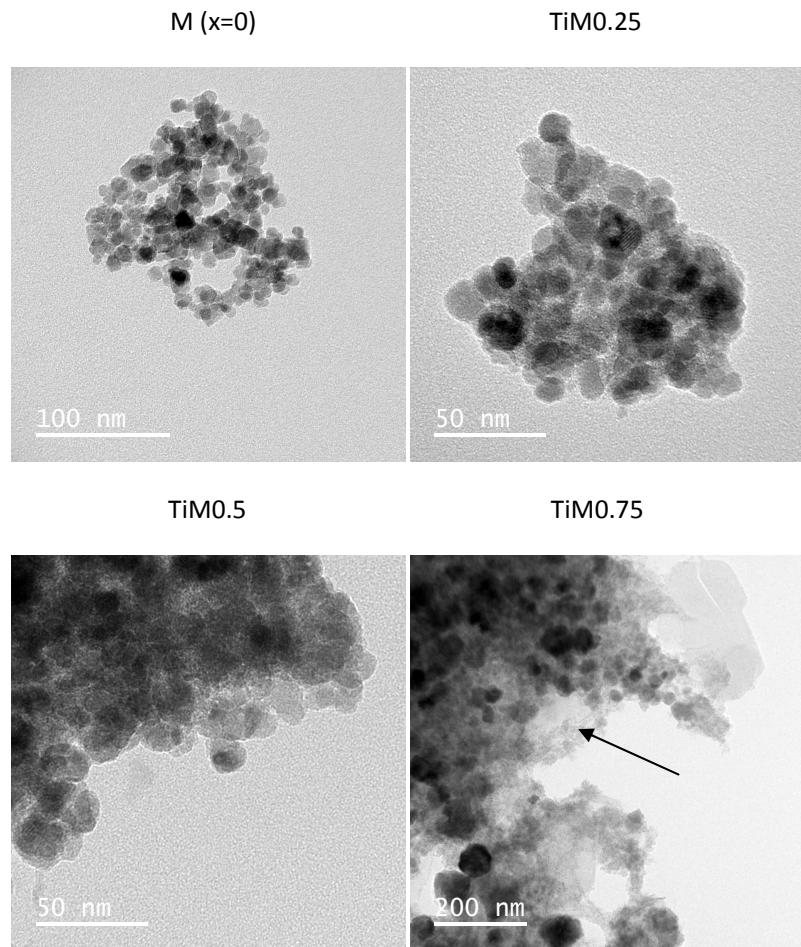


Figure S1. Powder XRD patterns for synthesized titanomagnetites. The Miller indices of the characteristic peaks of magnetite are indicated. For clarity, the patterns have been shifted vertically and the only $10\text{-}70^\circ$ 2θ range is shown.

2. TEM analysis

Figure S2. TEM images for synthesized (titano)magnetites $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$ and (d) $x = 0.75$. Arrow indicate the non-structural Ti(IV)/Fe(II) amorphous phase for $x = 0.75$.



3. Reduction of 4-NP by titanomagnetite ($x = 0.5$) in unbuffered pH system ($\text{pH} \approx 8.3$).

Figure S5 shows [4-NP], [4-AP] and [4-NP]+[4-AP] versus time in presence of 200 mg L^{-1} TiM0.5, at $\text{pH} \approx 8.3$ in the absence of pH buffer. 4-NP follows a consistent trend with experiments conducted in the presence of 50 mM MOPS. Figure S5 also shows the variation in pH, Eh, and dissolved Fe(II) concentration during (1) the reaction of TiM0.5 with water and (2) the transformation of 4-NP in the titanomagnetite suspension. After the addition of TiM0.5 with ultrapure water, $[\text{Fe(II)}]_{\text{aq}}$ increased from 0 to 0.012 mM in 60 min due to the dissolution of TiM0.5. pH remained almost stable at the natural pH of the mother TiM0.5 suspension. Eh decreased because of the reaction of TiM0.5 with water. In addition, the rather slow decrease might also be partially due to the equilibration of the Pt-electrode. After 4-NP addition, $[\text{Fe(II)}]$ dropped below the detection limit (1 μM), consistently with increasing Eh from -443 to -252 mV. pH values do not deviate much from 8.3, probably due to buffering effect of TiM0.5 amphoteric surface groups.

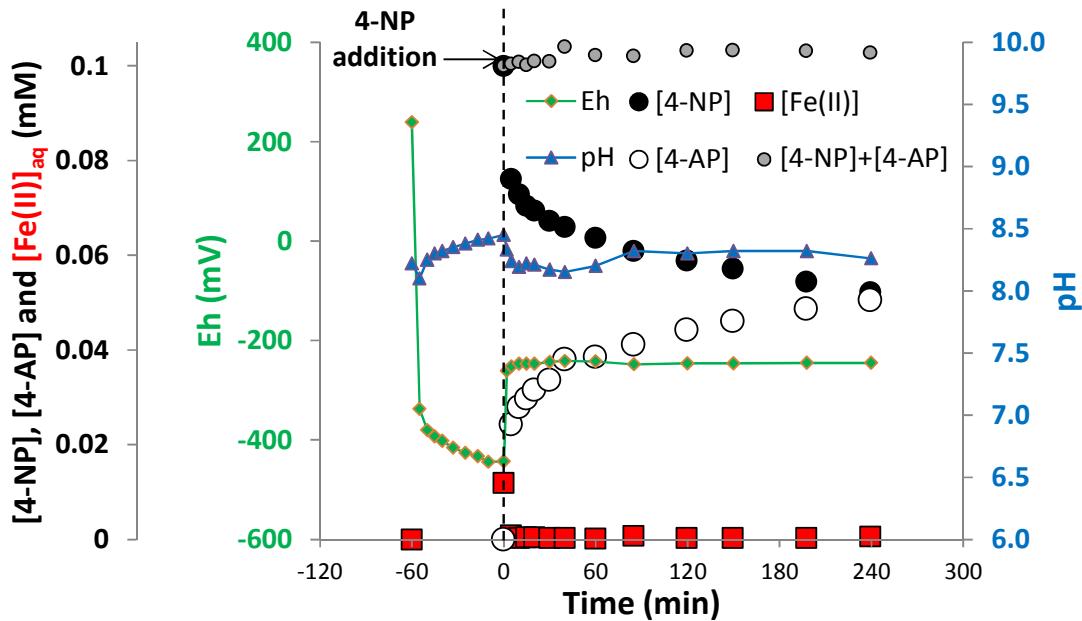


Figure S3. Variations in [4-NP], [4-AP], [4-NP]+[4-AP] and dissolved [Fe(II)], pH and Eh (vs SHE) during the reaction of titanomagnetite (200 mg L^{-1} ; $x = 0.5$; 1.31 mM Fe(II) equivalent) with water (time < 0 min) and during the reduction of 4-NP (0.1 mM) by titanomagnetite (time > 0 min).

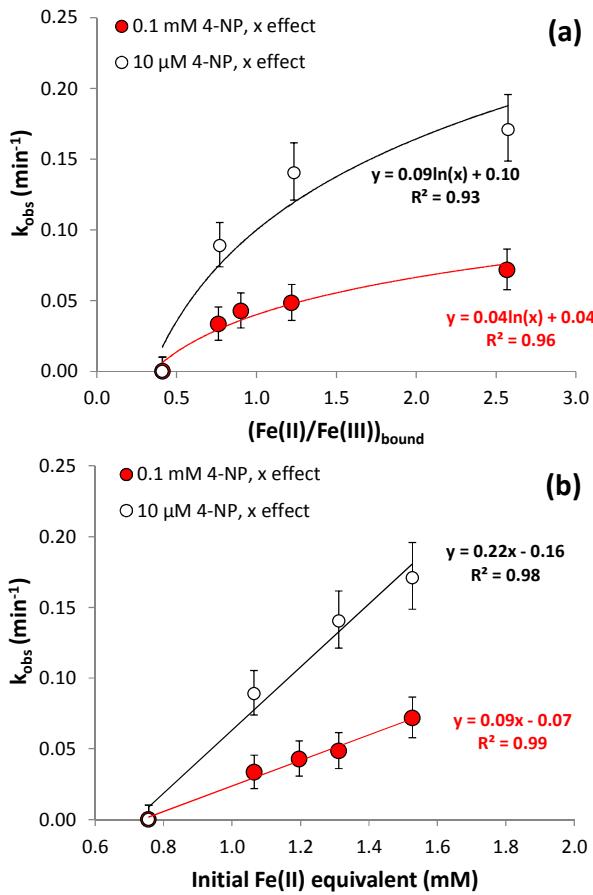


Figure S4. (a) Initial rate constant (k_{obs}) of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($0 < x < 0.75$; 200 mg L⁻¹) versus (a) $(\text{Fe(II)}/\text{Fe(III)})_{\text{bound}}$ and (b) initial Fe(II) equivalent for 4-NP (10 μM and 0.1mM) at pH = 8 (50 mM MOPS).

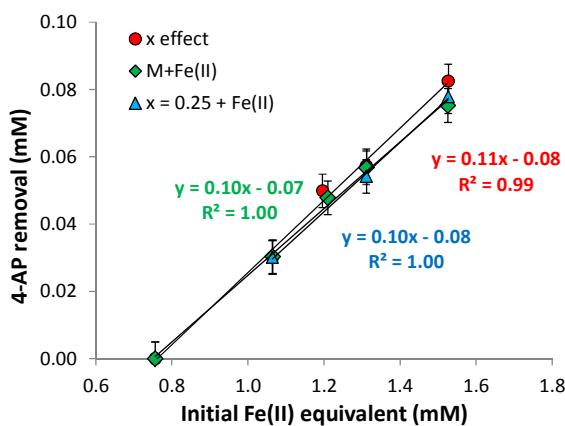


Figure S5. 4-NP removal at the end of the experiment (240 min) versus initial Fe(II) equivalent in the experiments at pH 8 (MOPS) with varying x, Fe(II)-amendment of magnetite or TiM0.25 (0.1 mM 4-NP, 200 mg L⁻¹ solid).

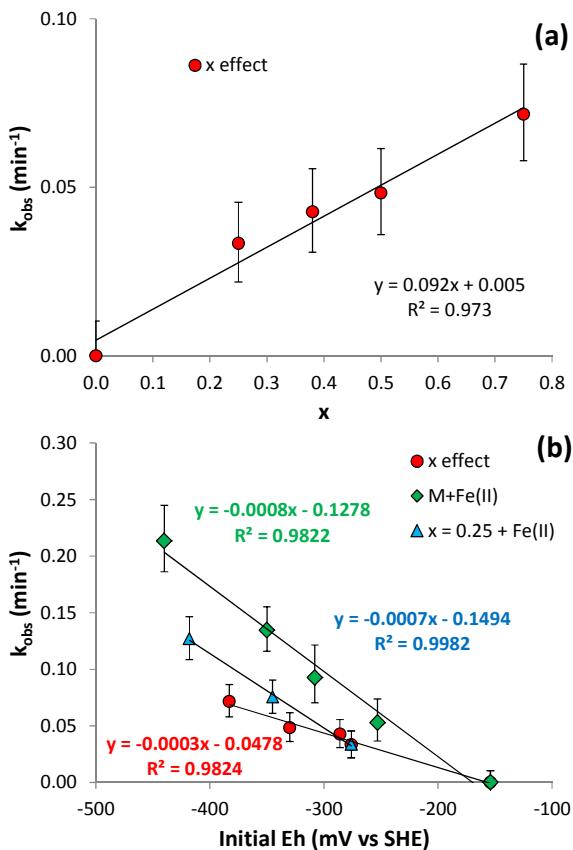


Figure S6. Initial rate constant (k_{obs}) versus (a) x and (b) initial Eh determined for the kinetic data plotted on Figure 1a: experiments at pH 8 (MOPS) with varying x , Fe(II)-amendment of magnetite or TiM0.25 (0.1 mM 4-NP, 200 mg L⁻¹ solid).

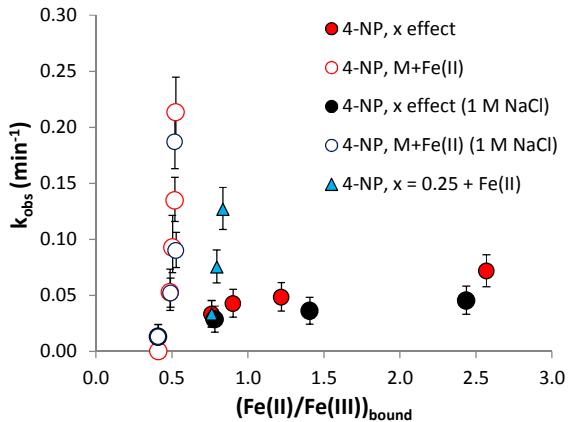


Figure S7. Initial rate constant (k_{obs}) of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($0 < x < 0.75$; 200 mg L^{-1}) or Fe(II)-amendment of magnetite versus $(\text{Fe(II})/\text{Fe(III)})_{\text{bound}}$ for 4-NP (0.1 mM) at $\text{pH} = 8$ (50 mM MOPS), with adding 1 M NaCl and without adding NaCl. Effect of Fe(II)-amendment of TiM0.25 is also shown (without NaCl).

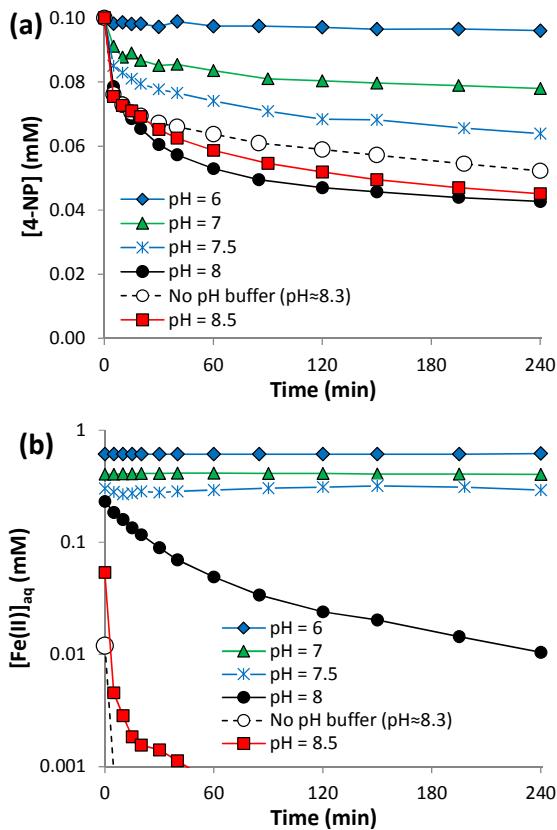


Figure S8. Effect of pH ($6 \leq \text{pH} \leq 8.5$) on the reduction of 0.1 mM 4-NP by 200 mg L^{-1} titanomagnetite ($x = 0.5$) and 200 mg L^{-1} magnetite with 0.56 mM Fe(II) (1.31 mM Fe(II) equivalent in both systems) in buffered pH systems (50 mM MOPS). Unbuffered pH system is also shown for TiM0.5 (see Fig. S3). (a) 4-NP concentration and (b) dissolved Fe(II) concentration versus time.

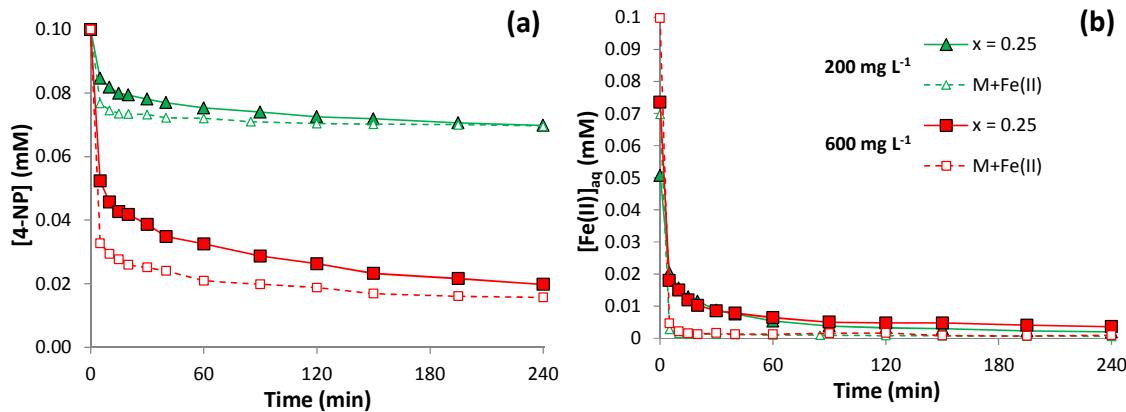


Figure S9. Effect of suspension density (200 or 600 mg L^{-1}) on the reduction of 0.1 mM 4-NP by TiM0.25 and M+Fe(II) (1.06 or 3.18 mM Fe(II) equivalent) at $\text{pH} = 8$ (50 mM MOPS). (a) 4-NP concentration and (b) dissolved Fe(II) concentration versus time.

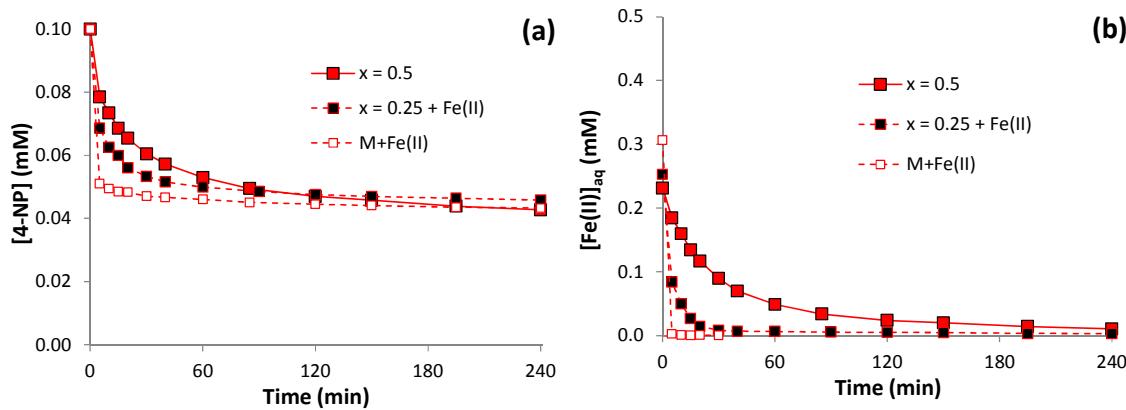


Figure S10. Comparison between reduction of 0.1 mM 4-NP by TiM0.5, TiM0.25+Fe(II) and M+Fe(II) (all for 1.31 mM Fe(II) equivalent) at $\text{pH} = 8$ (50 mM MOPS). (a) 4-NP and (b) dissolved Fe(II) concentrations versus time.

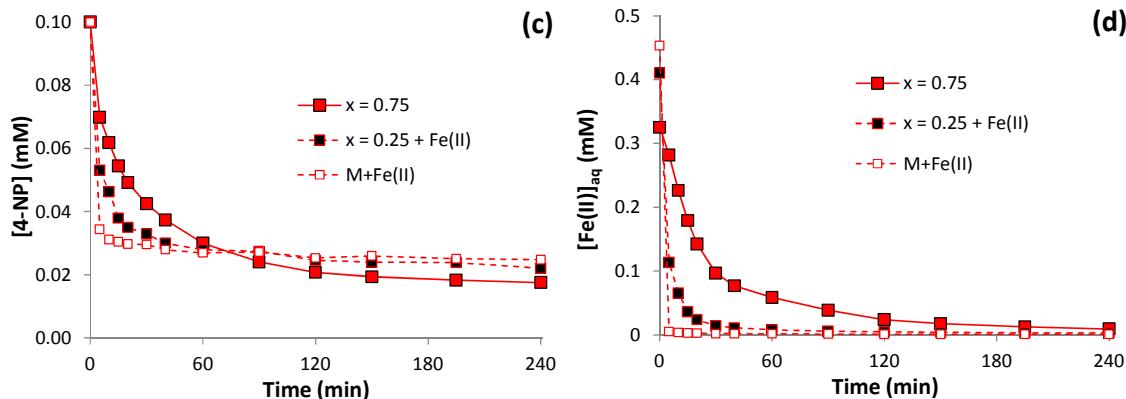


Figure S11. Comparison between reduction of 0.1 mM 4-NP by TiM0.75, TiM0.25+Fe(II) and M+Fe(II) (all for 1.56 mM Fe(II) equivalent) at $\text{pH} = 8$ (50 mM MOPS). (a) 4-NP and (b) dissolved Fe(II) concentrations versus time.

Table S1. Initial [Fe(II)] equivalent, $(\text{Fe(II)}/\text{Fe(III)})_{\text{bound}}$ determined by chemical analysis and Eh values measured before and after reaction. Experimental conditions: 200 mg L⁻¹ (titano)magnetite, 0.1 mM 4-NP, pH = 8 (50 mM MOPS). “nd” means not determined.

Solid / Fe(II) equivalent (mM)	$(\text{Fe(II)}/\text{Fe(III)})_{\text{bound}}$		Eh (mV)	
	Initial	Final	Initial	Final
M / 0.76	0.41	0.41	-154	-145
TiM0.25 / 1.06	0.76	0.58	-276	-181
TiM0.38 / 1.20	0.90	0.63	-286	nd
TiM0.50 / 1.31	1.22	0.78	-330	-218
TiM0.75 / 1.53	2.57	1.06	-383	-240
M+Fe(II) / 1.06	0.49	0.44	-253	-157
M+Fe(II) / 1.20	0.50	0.43	-308	nd
M+Fe(II) / 1.31	0.52	0.45	-351	nd
M+Fe(II) / 1.53	0.53	0.47	-440	-199
TiM0.25+Fe(II) / 1.31	0.79	0.59	-345	nd
TiM0.25+Fe(II) / 1.53	0.84	0.59	-418	nd

Initial: parameters measured in 200 mg L⁻¹ suspension obtained by diluting the mother titanomagnetite suspension.

Final: parameters measured in the same suspension after 240 min reaction with 4-NP.