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## Supporting information for

### Unveil mechanism of electron transfer facilitated regeneration of active Fe<sup>2+</sup> by nano-dispersed iron/graphene catalyst for phenol removal

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**The synthesis of GO.**

GO were synthesized from graphite powder according to reported procedure.<sup>1, 2</sup> Typically, the mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> (H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> = 360:40 by volume) was added to 1000 mL round bottom flask. Then, the mixture of graphite powder (3.0 g, 1 wt equiv) and KMnO<sub>4</sub> (18.0 g, 6 wt equiv) were added slowly to the flask while the temperature was kept below 10 °C. The mixture was stirred for 12 h at 50 °C, cooled down to room temperature and poured onto ice cold water (400 mL), then H<sub>2</sub>O<sub>2</sub> (30%) aqueous solution was added to the resultant suspension until the color of the suspension changed to bright yellow. The suspension was repeatedly centrifuged and washed first with HCl (30%) solution then with deionized water until the *pH* value of the supernatant was neutral. The collected precipitates were vacuum-dried overnight at room temperature. The resultant products were graphite oxide flake. Finally, GO were obtained via ultrasonic treatment of the graphite oxide flakes.

**Methods and sample analysis.**

The concentrations of phenol were analyzed via high performance liquid chromatography (Ultimate 3000, Dionex) equipped with UV absorbance detector and C18 column (4.6 mm × 250 mm). The mobile phase was methanol and water (50:50, v/v) at a flow rate of 0.50 mL min<sup>-1</sup> with column temperature of 30 °C, and the analytical wavelength was 270 nm.

H<sub>2</sub>O<sub>2</sub> concentration was analyzed by iodometric method.<sup>3</sup> 2.0 mL sample solution was diluted with deionized water to 20 mL. In the following step, 1.0 mL 20% H<sub>2</sub>SO<sub>4</sub>, 200 μL 10% KI and one drop ammonium molybdate solution were added. The mixture was then titrated with 0.01 mol L<sup>-1</sup> sodium thiosulfate until end point indicated by a faint yellow color. After that, 2.0 mL starch indicator was added and titration was continued until disappearing of blue color.

Chemical Oxygen Demand (COD) was determined by a known procedure.<sup>3</sup> In general, Na<sub>2</sub>CO<sub>3</sub> powder was added to 3.0 mL sample until the concentration of

$\text{Na}_2\text{CO}_3$  reached  $20 \text{ g L}^{-1}$ . Then the sample was covered to minimize evaporation losses and heated in a water bath at  $90 \text{ }^\circ\text{C}$  for 90 min. Finally COD was measured using a COD measurement kit (Hach, United States) by the  $\text{K}_2\text{Cr}_2\text{O}_7$ -oxidation method with 0-150 ppm COD digestion solution, a Hach DRB 200 digestion chamber and a Hach DR1010 COD calorimeter. The concentration of total dissolved iron was measured with 1,10-phenanthroline after adding hydroxylamine hydrochloride at 510 nm on a UV/Vis spectrophotometer.<sup>4,5</sup>

### Electron paramagnetic resonance (EPR) studies.

5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was used as spin-trapping agent. 25 mg of catalyst was added to 25 mL of  $50 \text{ mg L}^{-1}$  phenol solution with pH adjusted to 3 by addition of  $\text{H}_2\text{SO}_4$  in a conical flask.  $13 \text{ } \mu\text{L}$  of  $\text{H}_2\text{O}_2$  (35%) was added to the solution to initiate the reaction. After 5 min, 1 mL suspension was drawn, immediately mixed with  $200 \text{ } \mu\text{L}$   $0.2 \text{ mol L}^{-1}$  DMPO to form DMPO–radical adduct. The EPR spectra were obtained on a Bruker E500 spectrometer with a microwave bridge at room temperature.

### Zeta potential of $\text{Fe}_3\text{O}_4$ -RGO

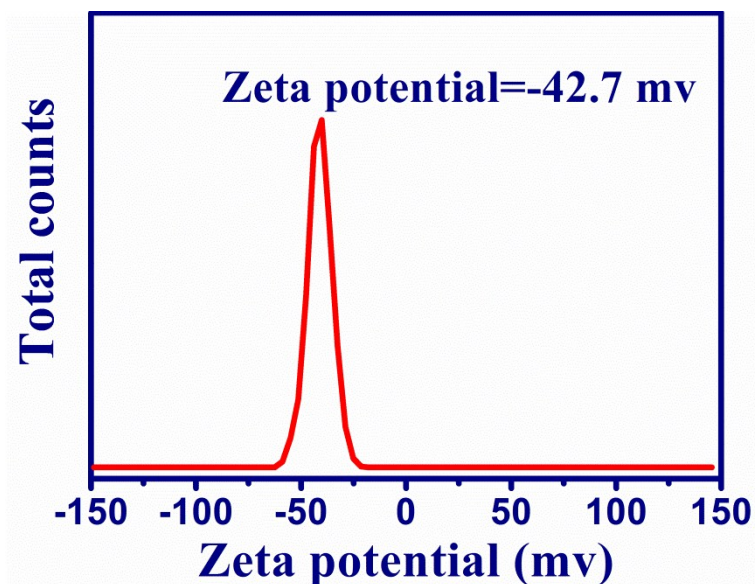
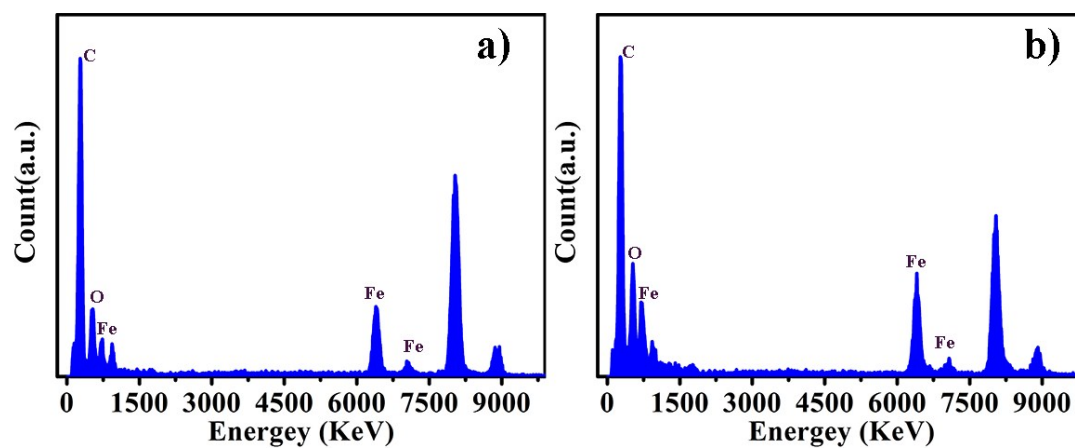


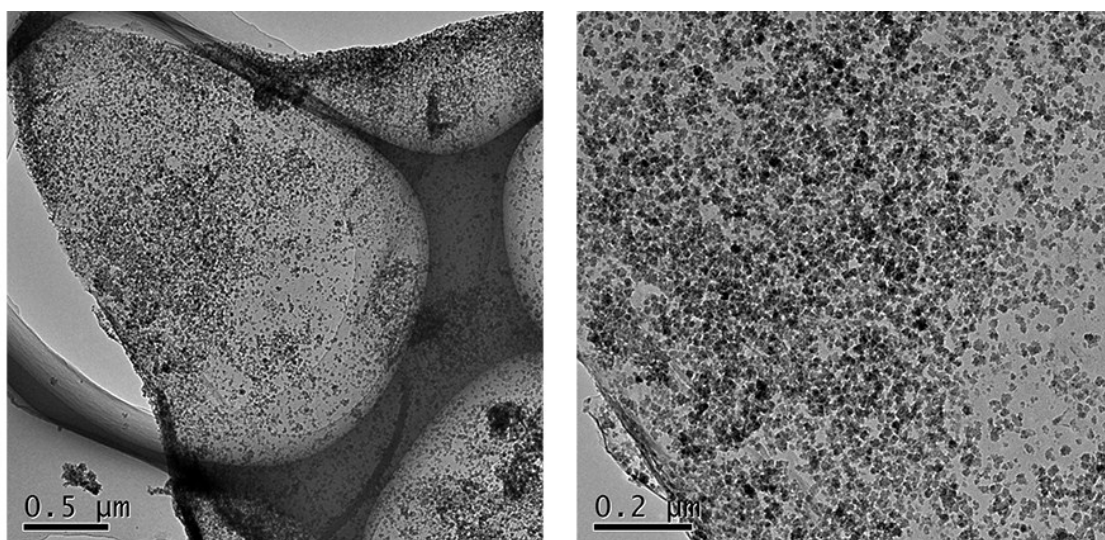
Fig S1 Zeta potential of  $\text{Fe}_3\text{O}_4$ -RGO

### The EDX spectrum of catalyst



**Fig S2** the EDX analysis showing the presence of C, Fe, and O for a)  $\text{Fe}_3\text{O}_4$ -RGO and b)  $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO

### The TEM images of catalyst



**Fig S3** Different resolution TEM images of  $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO

## Comparison of catalytic activity for different Fenton catalysts

**Table S1** Comparison of different Fenton-like catalysts for phenol removing.

Catalyst	Catalyst dose (g L <sup>-1</sup> )	[phenol] <sub>0</sub> mM	[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> mM	pH	T (°C)	Degradation (%)	Reaction time (h)	Ref.
Fe <sub>3</sub> O <sub>4</sub>	5	1	1200	N/A <sup>a</sup>	RT <sup>a</sup>	95	6	6
Au/HO-npD	NA <sup>a</sup>	1.06	5.88	4	RT <sup>a</sup>	93	24	7
Fe/AC	0.5	1.06	15	3	50	100	4	8
Fe-ZSM-5.	1.5	0.691	90	3.5	70	81	3	9
FeAlSi-ox]	3	0.500	50	6.9	RT <sup>a</sup>	32	8	4
FeSi-ox	3	0.500	50	6.9	RT <sup>a</sup>	44	8	4
Magnetite (Fe <sub>3</sub> O <sub>4</sub> )	3	0.266	150	7	RT <sup>a</sup>	42	24	10
Fe-Al-pillared clay	0.6	0.213	4	4	28	100	2.5	11
Fe <sup>0</sup> /Fe <sub>3</sub> O <sub>4</sub> -RGO	1	0.531	5	3	25	100	0.5	<b>This work</b>

<sup>a</sup> Data not available. <sup>b</sup> Room temperature

## References

1. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS nano*, 2010, 4, 4806-4814.
2. P. Wang, X. Zhou, Y. Zhang, L. Wang, K. Zhi and Y. Jiang, *Rsc Adv*, 2016, 6, 102348-102358.
3. T. Wu and J. D. Englehardt, *Environmental science & technology*, 2012, 46, 2291-2298.
4. A. L. T. Pham, C. Lee, F. M. Doyle and D. L. Sedlak, *Environmental science & technology*, 2009, 43, 8930-8935.
5. H. Tamura, K. Goto, T. Yotsuyanagi and M. Nagayama, *Talanta*, 1974, 21, 314-318.
6. S. Zhang, X. Zhao, H. Niu, Y. Shi, Y. Cai and G. Jiang, *Journal of Hazardous Materials*, 2009, 167, 560-566.
7. S. Navalon, R. Martin, M. Alvaro and H. Garcia, *Angew Chem Int Edit*, 2010, 49, 8403-8407.
8. J. A. Zazo, J. A. Casas, A. F. Mohedano and J. J. Rodríguez, *Applied Catalysis B: Environmental*, 2006, 65, 261-268.
9. K. Fajerwerg and H. Debellefontaine, *Applied Catalysis B-Environmental*, 1996, 10, L229-L235.

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10. K. Rusevova, F.-D. Kopinke and A. Georgi, *Journal of Hazardous Materials*, 2012, 241–242, 433-440.
  11. M. Luo, D. Bowden and P. Brimblecombe, *Applied Catalysis B: Environmental*, 2009, 85, 201-206.