

Bifunctional PDDA-stabilized β -Fe₂O₃ nanocluster for improved photoelectrocatalytic and magnetic field enhancing photocatalytic applications

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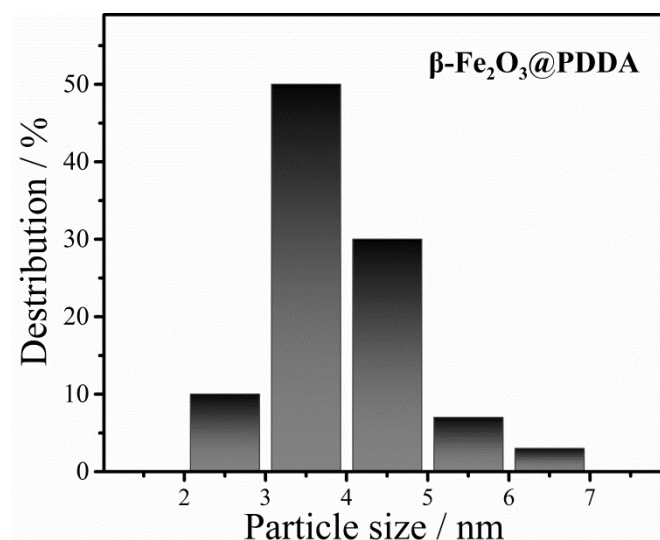


Figure S1. Particle size distribution of $\beta\text{-Fe}_2\text{O}_3\text{@PDDA}$.

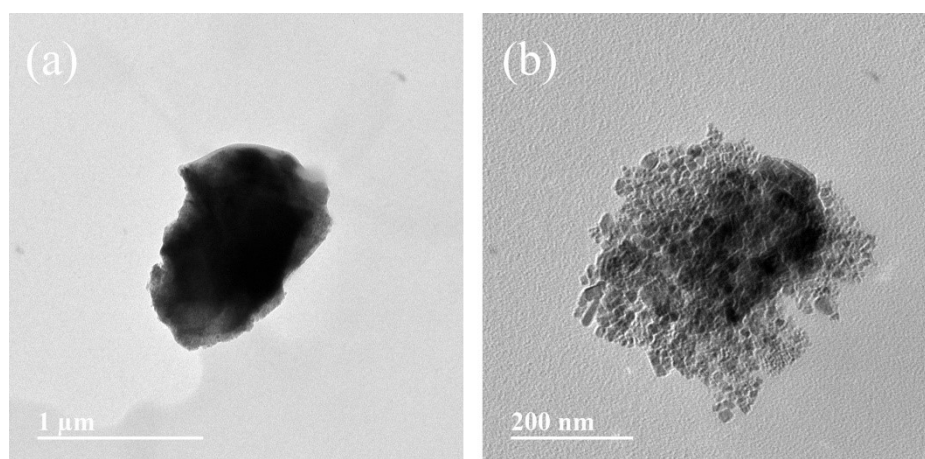


Figure S2. TEM image of bulk $\alpha\text{-Fe}_2\text{O}_3$ (a); TEM image of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticle (b).

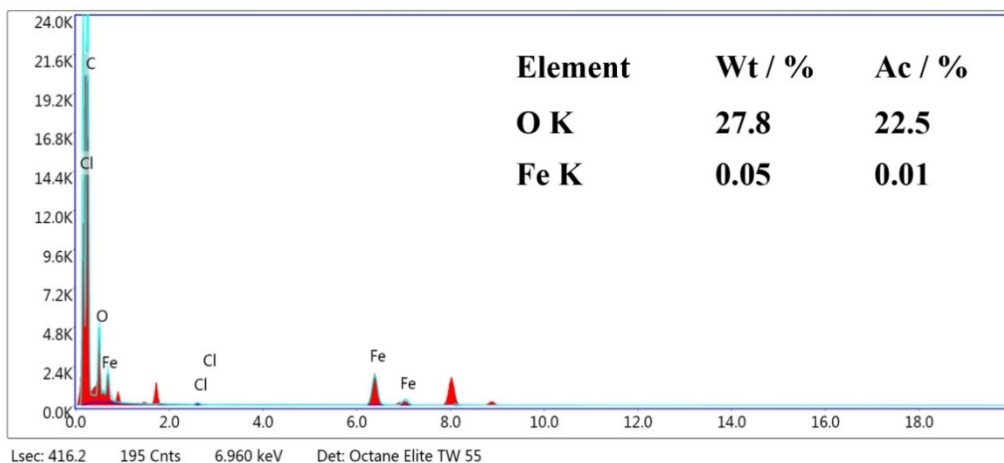


Figure S3. EDS spectrum of $\beta\text{-Fe}_2\text{O}_3\text{@PDDA}$.

Table S1. The crystal plane spacing of $\beta\text{-Fe}_2\text{O}_3\text{@PDDA}$ sample and PDF standard value.

Planes–crystal structure	d-Spacing (Å) PDF#76-1821	crystal plane spacing of $\beta\text{-Fe}_2\text{O}_3\text{@PDDA}$ sample (nm)	Ratio(%)
(0 0 4)	5.6375	0.56	3
(1 0 0)	4.8151	0.48~0.49	13.8
(1 0 6)	2.9627	0.29~0.32	20.7
(1 1 -1)	2.7591	0.27~0.28	24.1
(1 1 3)	2.6074	0.26~0.27	37.9

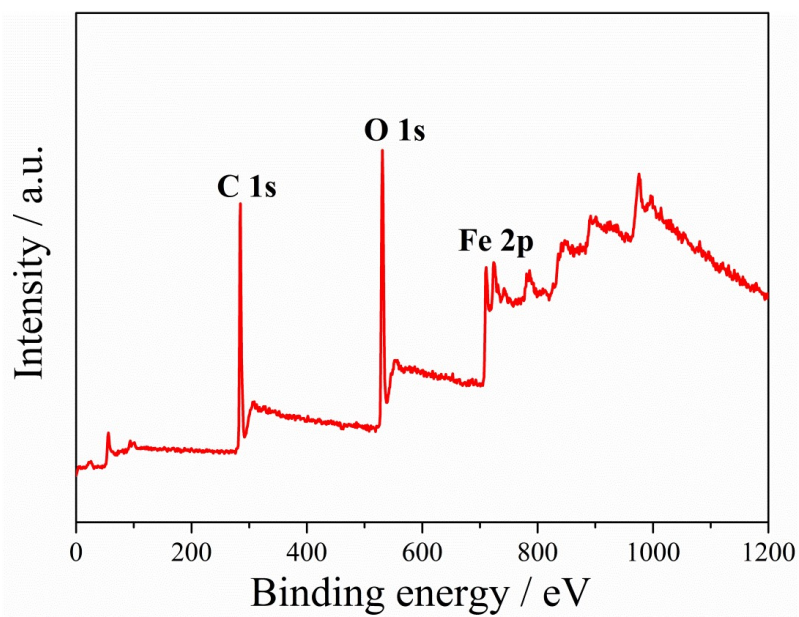


Figure S4. XPS spectra of β -Fe₂O₃@PDDA nanocluster.

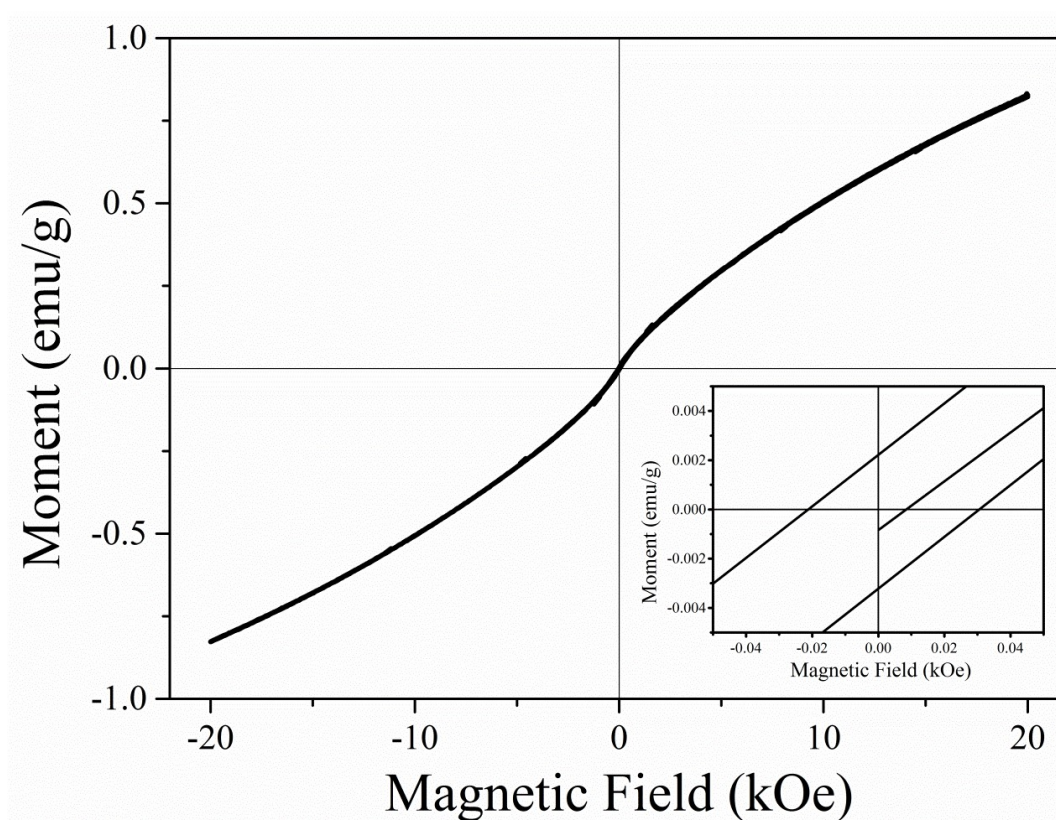


Figure S5. Magnetic hysteresis curve of β -Fe₂O₃@PDDA nanocluster.

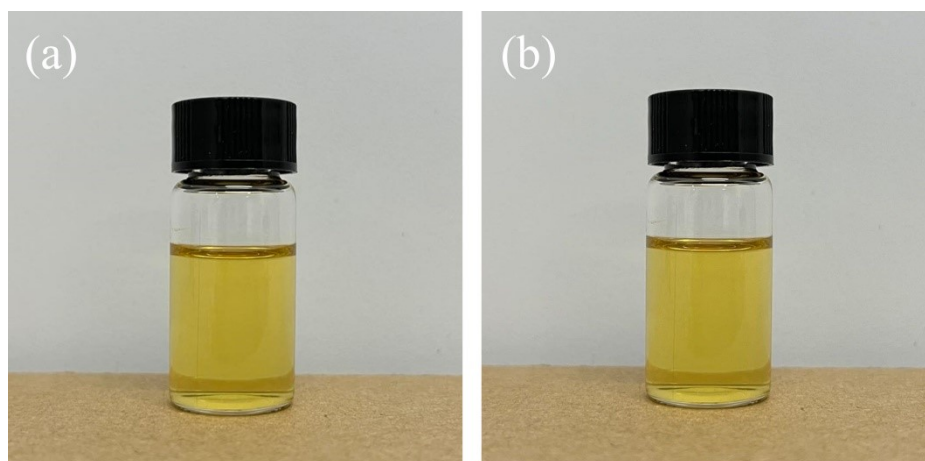


Figure S6. β - Fe_2O_3 @PDDA nanocluster samples are uniformly dispersed in aqueous solution(a), and let the solution sit for 10 d(b).

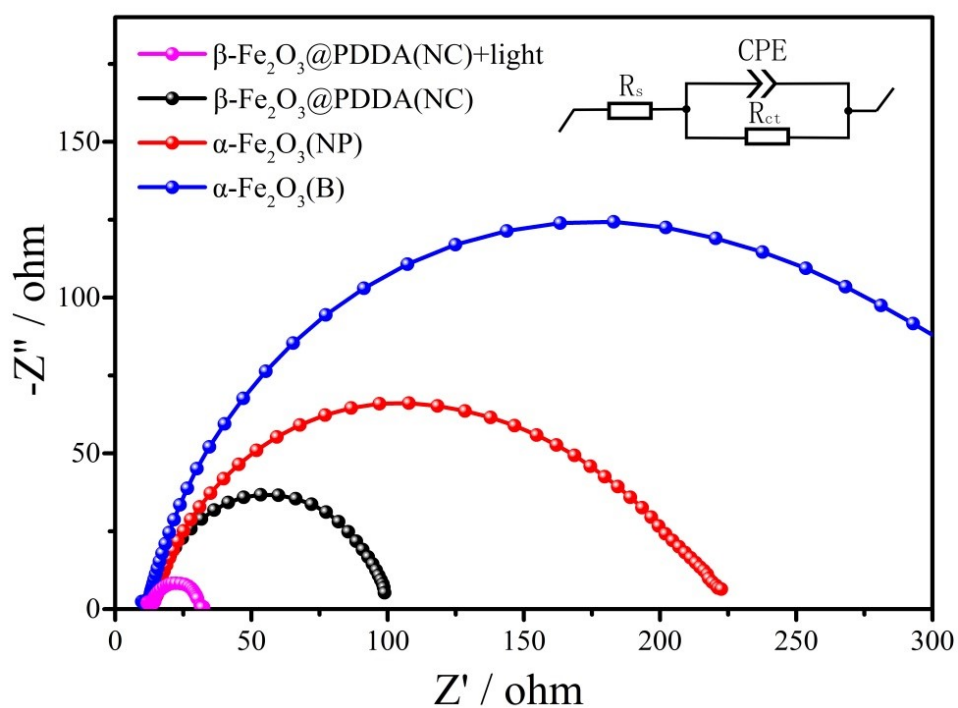


Figure S7. Electrocatalytic impedance spectra (EIS) Nyquist plots(inset:Equivalent circuits of Nyquist plots of materials consisting of three elements: R_s , R_{ct} , and CPE.)

S1. Mass activity and specific activity Calculation.

Mass activities (mA mg^{-1}) of catalysts are calculated based on the catalyst loading (0.25 mg cm^{-2}) and the achieved current density j (mA cm^{-2}) at an η of 520 mV. The corresponding equation is

$$\text{Mass activity (mA mg}^{-1}\text{)} = \frac{\text{Achieved current density (mA cm}^{-2}\text{)}}{\text{Catalyst loading (mg cm}^{-2}\text{)}}$$

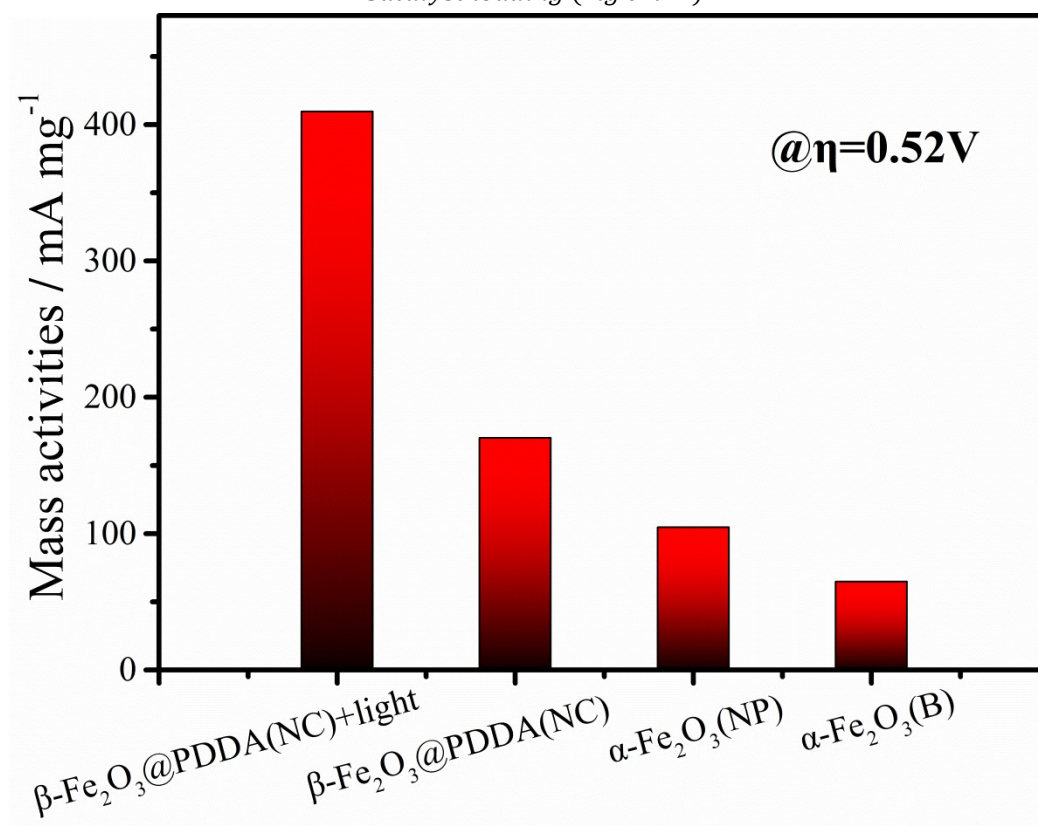


Figure S8. Mass activity (MA) of bulk $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$ nanoparticle, $\beta\text{-Fe}_2\text{O}_3\text{@PDDA}$ nanocluster and $\beta\text{-Fe}_2\text{O}_3\text{@PDDA}$ nanocluster under an additional light for OER at an η of 520 mV.

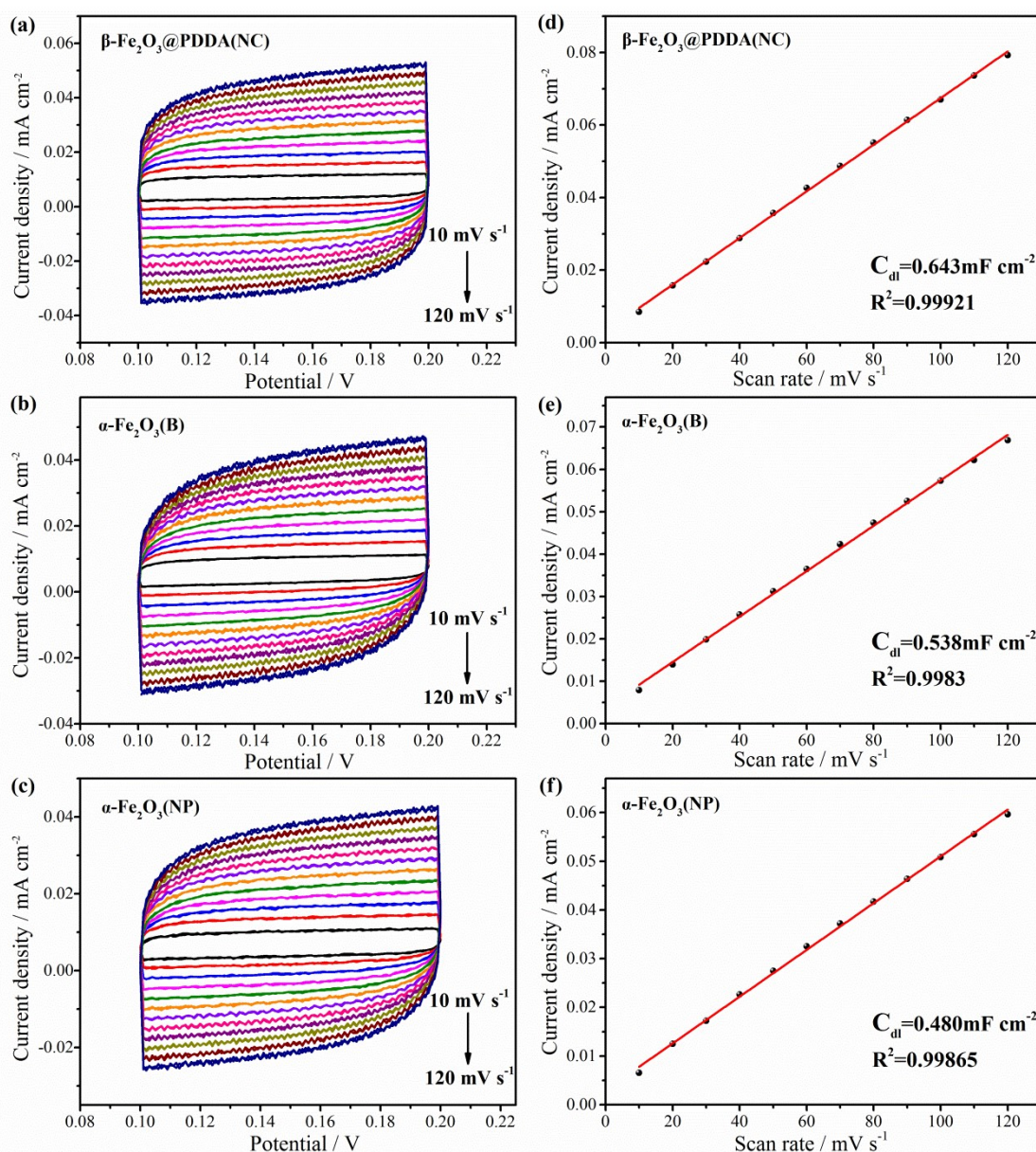


Figure S9. CV curves for (a) β -Fe₂O₃@PDDA nanocluster; (b) bulk α -Fe₂O₃; (c) α -Fe₂O₃ nanoparticle in the region of 0.10~0.20 V vs. Ag/AgCl with various scan rates (10~120 mV s⁻¹) for OER; Fitting curves for of scanning rate and current density for (d) β -Fe₂O₃@PDDA nanocluster; (e) bulk α -Fe₂O₃; (f) α -Fe₂O₃ nanoparticle.

Table S2. Comparison of the OER activity for several recently reported active transition metal-based electrocatalysts.

Electrocatalysts	Overpotential (mV) $j=10 \text{ mA cm}^{-2}$	Tafel slope (mV dec ⁻¹)	Electrolyte (pH)	Reference
$\beta\text{-Fe}_2\text{O}_3\text{@PDDA NC}$ (PEC-OER)	300	45	1.0 M KOH	This work
$\beta\text{-Fe}_2\text{O}_3\text{@PDDA NC}$	370	77	1.0 M KOH	This work
$\alpha\text{-Fe}_2\text{O}_3$ NP	430	107	1.0 M KOH	This work
$\alpha\text{-Fe}_2\text{O}_3$ B	460	129	1.0 M KOH	This work
$\alpha\text{-Fe}_2\text{O}_3\text{@g-C}_3\text{N}_4$	425	280	0.5 M KOH	1
$\gamma\text{-Fe}_2\text{O}_3$ NWs	650	~	1.0 M KOH	2
$\alpha\text{-Fe}_2\text{O}_3$	310	272	0.1 M KOH	3
Fe_2O_3	440	134	1.0 M KOH	4
Ni- Fe_2O_3	277	68	1.0 M KOH	4
$\gamma\text{-FeOOH}$	550	~	1.0 M KOH	5
FeTiO_3 hollow spheres	420	~	1.0 M KOH	6
NiO	~	242	1.0 M KOH	7
NiOOH	360	111	1.0 M KOH	8
Co_3O_4 Mesoporous	636	~	0.1 M KOH	9
Co_3O_4 Mesoporous	476	~	1.0 M KOH	9
Co_2CrO_4	400	87	1.0 M KOH	10
Co_2CrO_4	370	56	1.0 M KOH	10
IrO_2	481	238	1.0 M HClO ₄	11
Pt	420	~	1.0 M KOH	12

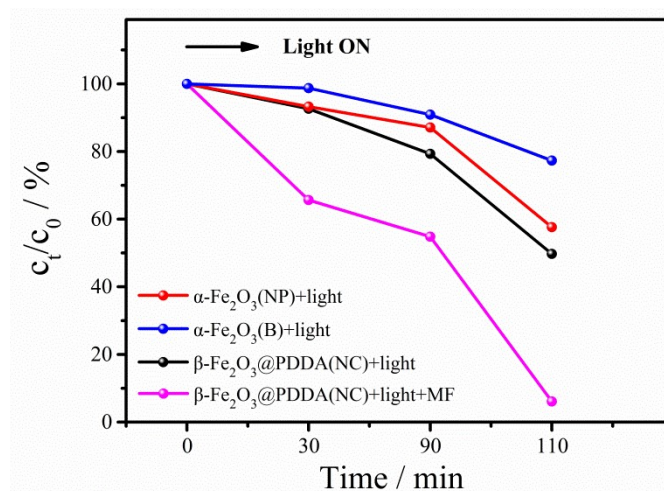


Figure S10. Line chart of RhB concentration (C/C_0) changing with irradiation time.

Table S3. Comparison of several iron oxide based photocatalysis for RhB degradation reported in recent years.

Photocatalysts	Degradation time (min)	Degradation percentage of the RhB dye (%)	Reference.
β -Fe ₂ O ₃ @PDDA NC (magnetic-field-enhanced)	110	94	This work
β -Fe ₂ O ₃ @PDDA NC	110	50	This work
α -Fe ₂ O ₃ NP	110	42	This work
α -Fe ₂ O ₃ B	110	23	This work
pure α -Fe ₂ O ₃	120	56	¹³
PANI/ α -Fe ₂ O ₃ /FeOOH	120	91	¹³
α -Fe ₂ O ₃	100	60	¹⁴
α -Fe ₂ O ₃ /RT(0 mM)	100	76	¹⁴
α -Fe ₂ O ₃ /RT(0.025 mM)	100	93	¹⁴

References

1. O. Alduhaish, M. Ubaidullah, A. M. Al-Enizi, N. Alhokbany, S. M. Alshehri and J. Ahmed, *Sci Rep*, 2019, **9**, 14139.
2. S. Arumugam, Y. Toku and Y. Ju, *Sci Rep*, 2020, **10**, 5407.
3. U. Farooq, P. Chaudhary, P. P. Ingole, A. Kalam and T. Ahmad, *ACS Omega*, 2020, **5**, 20491-20505.
4. A. Samanta, S. Das and S. Jana, *ACS Sustain. Chem. Eng.*, 2019, **7**, 12117-12124.
5. D. Friebe, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M. J. Cheng, D. Sokaras, T. C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Norskov, A. Nilsson and A. T. Bell, *J Am Chem Soc*, 2015, **137**, 1305-1313.

6. T. Han, Y. Chen, G. Tian, J. Q. Wang, Z. Ren, W. Zhou and H. Fu, *Nanoscale*, 2015, **7**, 15924-15934.
7. Y. Zhao, X. Jia, G. Chen, L. Shang, G. I. Waterhouse, L. Z. Wu, C. H. Tung, D. O'Hare and T. Zhang, *J Am Chem Soc*, 2016, **138**, 6517-6524.
8. H.-Y. Wang, Y.-Y. Hsu, R. Chen, T.-S. Chan, H. M. Chen and B. Liu, *Adv. Energy Mater.*, 2015, **5**, 1500091.
9. H. Tüysüz, Y. J. Hwang, S. B. Khan, A. M. Asiri and P. Yang, *Nano Res.*, 2012, **6**, 47-54.
10. C.-C. Lin and C. C. L. McCrory, *ACS Catal.*, 2016, **7**, 443-451.
11. L. Ouattara, S. Fierro, O. Frey, M. Koudelka and C. Comninellis, *J Appl Electrochem*, 2009, **39**, 1361-1367.
12. C. K. Ranaweera, C. Zhang, S. Bhoyate, P. K. Kahol, M. Ghimire, S. R. Mishra, F. Perez, B. K. Gupta and R. K. Gupta, *Mater. Chem. Front.*, 2017, **1**, 1580-1584.
13. R. Qin, L. Hao and J. Li, *J. Inorg. Organomet. Polym. Mater*, 2020, **30**, 4452-4458.
14. Z. Zhou, H. Yin, Y. Zhao, J. Zhang, Y. Li, J. Yuan, J. Tang and F. Wang, *Catalysts*, 2021, **11**, 396.