Fe_3O_4@N-doped carbon derived from dye wastewater flocculates as heterogeneous catalyst for degradation of methylene blue

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Experimental

2.1 Materials

Iron pieces (2 × 55 × 50 mm^3) were received from Feiyue Metal Products Co., Ltd., which was used as anode and cathode materials. Sigma-Aldrich provided all chemical reagents without further purification. The simulated dye wastewater contains 2.7 mM Malachite Green (MG) dye and 10 mM Na_2SO_4.

2.2 Characterizations

X-ray diffraction (XRD) measurements were carried out using an X-ray powder diffractometer (Smart Lab 9KW, Japan). The morphology of the sample was recorded via scanning electron microscopy (SEM, SU8220, Japan) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20,). X-ray photoelectron spectroscopy (XPS) patterns were collected using a non-monochromatic Al Kα X-ray source and a hemispherical energy analyzer (ESCALAB Xi+, English). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a STA PT1600 system in a nitrogen atmosphere with a heating rate of 0 °C min^{-1} in the temperature range of 30 −1000 °C. N_2 adsorption-desorption isotherms were recorded using an automated gas sorption analyzer (BET, Autosorb-iQ-C, USA). EPR signals were recorded using a Bruker E500 spectro-meter. The settings for the EPR spectrometer were as follows: center field, 3502 G; sweep width, 100 G; power, 6.325mW. Ultraviolet-visible (UV-vis) spectra were recorded using the Shimadzu spectrophotometer (UV-3600 Plus, Japan).Magnetic hysteresis loops at room temperature were obtained using a VSM (LAKESHORE-7404, USA, ±2T/MH) at room temperature. The iron content of the sample obtained by microwave-digested samples and the iron concentration were determined using inductively coupled plasma (ICP-MS, NexION 300D).

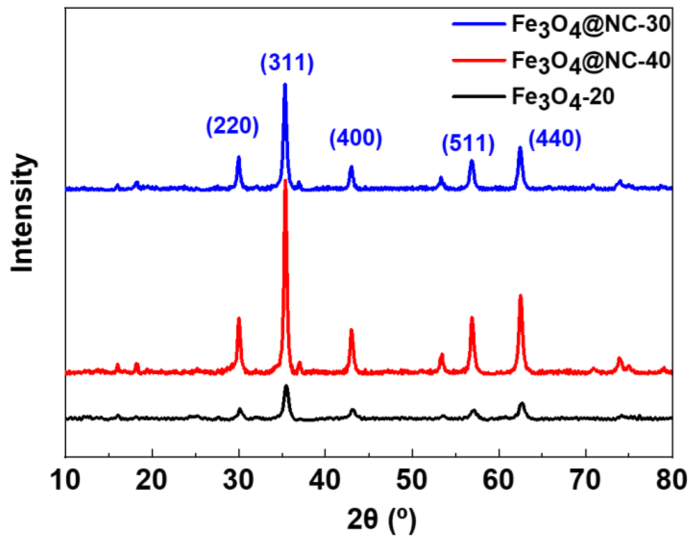

Figure S1. The XRD pattern of Fe_3O_4@NC-30, Fe_3O_4@NC-40 and Fe_3O_4-20.

Table S1. The removal efficiency of MG dye with different electrolysis time.

method	Electrolysis time	Removal efficiency	Concentrations (mg/L)
EC	5 min	95.37%	46.3
	10 min	99.08%	9.2
	20 min	100%	undetected
	30 min	100%	undetected
	40 min	100%	undetected

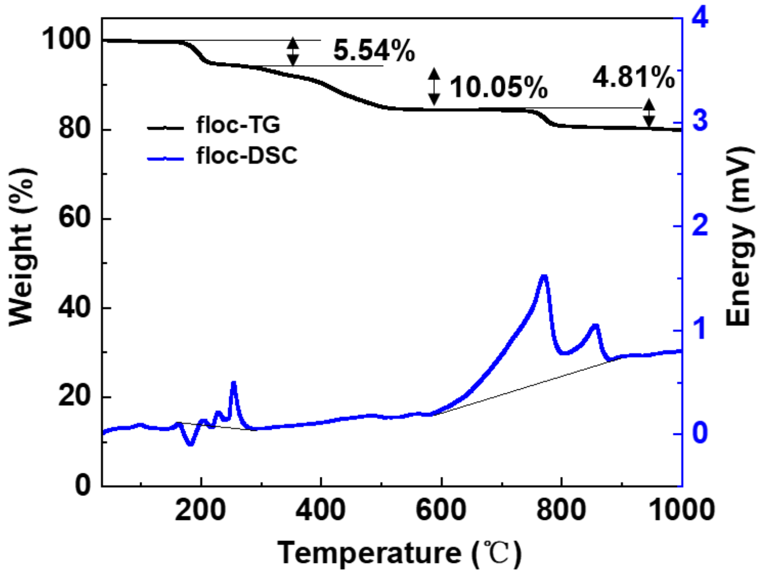

Figure S2. TGA and DSC curve of MG dye molecular.

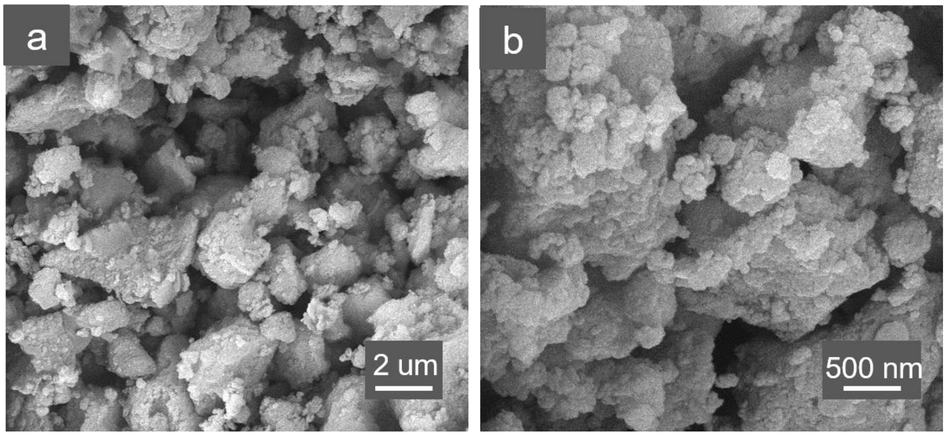

Figure S3. SEM images of the sample floc-20-r (Fe_3O_4-20 precursor).

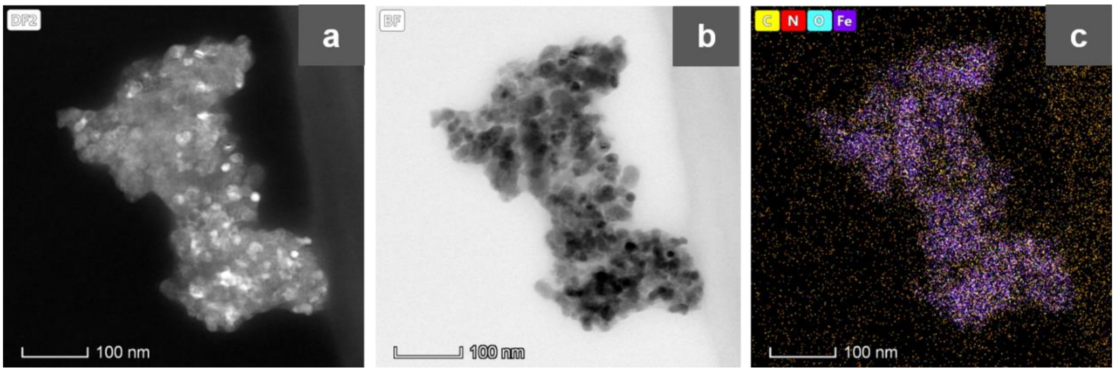

Figure S4. (a, b) the HAADF-STEM images; (c) the EDX elemental mapping image

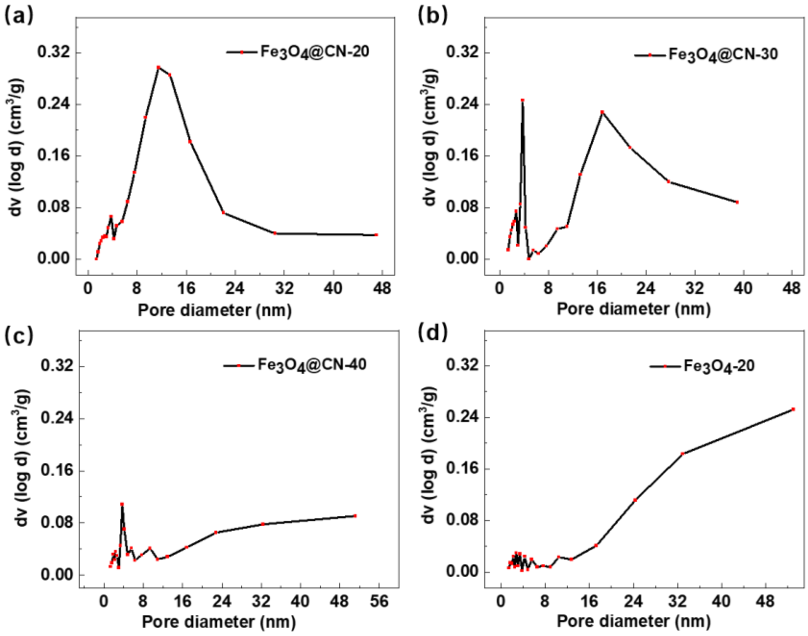

Figure S5. the BJH pore size distribution of Fe_3O_4@NC-20, Fe_3O_4@NC-30, Fe_3O_4@NC-40 and Fe_3O_4-20.

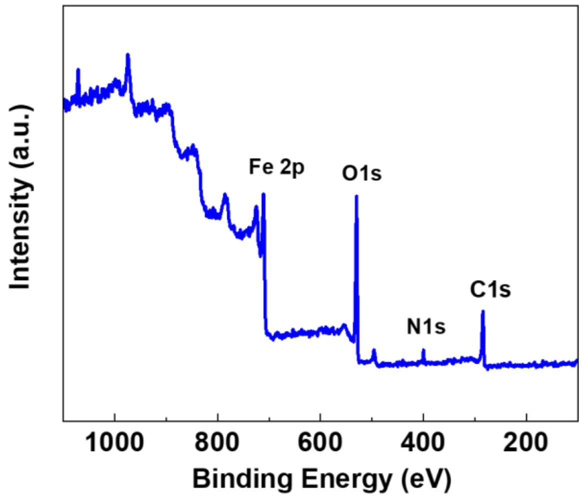

Figure S6. XPS spectra of Fe_3O_4@NC-20.

Table S2. Comparison of catalytic ability between Fe_3O_4@NC-20 and other reported Fe-based heterogeneous Fenton catalysts.

Sample	catalyst dosage(g/L)	MB (ppm) /Volume	H_2O_2 (mmol/L)	Time (min)	TOC (%) /MB (%)	leaching Fe (ppm)	References
Fe_3O_4@C	2.0	40 (10 ml)	16	40	68/100	0.5	[1]
Fe_3O_4@C	2.0	60 (20 ml)	293	300	65/90	-	[2]
$Fe_3O_4/SiO_2/C$	1.0	50 (20 ml)	440	15	96/68[a]	-	[3]
$Fe_3O_4/FeMnO_x$	0.5	25 (200ml)	743	250	-/98	1	[4]
Fe_3O_4/TiO_2	50	1600 (1ml)	990	5	-/99	-	[5]
Fe_3O_4@PDA-MnO_2	0.17	40 (25ml)	1650	240	97.36	-	[6]
MoS_2-Fe_3O_4	0.5	20 (100ml)	50	20	-/100	-	[7]
Fe_3O_4@MAFCC	0.6	50 (50 ml)	59.4	20	37.2/100	<2	[8]
Fe_3O_4/usGO	0.0029	5 (50 ml)	10	120	-/100	0.03	[9]
Fe_3O_4@NC-20	0.75	50 (20 ml)	239	50	64/100	0.435	This work

(-) Iron ions leaching is not reported. [a] COD removal (%).

Table S3. Magnetic Properties and Iron Content of Fe_3O_4@NC-20, Fe_3O_4@NC-30, Fe_3O_4@NC-40 and Fe_3O_4-20.

Sample	Fe_3O_4 (wt%)	Magnetic properties		
		Ms(emu/g)	Hc(Oe)	M_r(emu/g)
Fe_3O_4@NC-20	55.02%	63.1	113.1	5.8
Fe_3O_4@NC-30	66.21%	69.3	122.5	7.6
Fe_3O_4@NC-40	73.47%	72.3	133.6	6.1
Fe_3O_4-20	95.03%	76.2	142.3	5.3

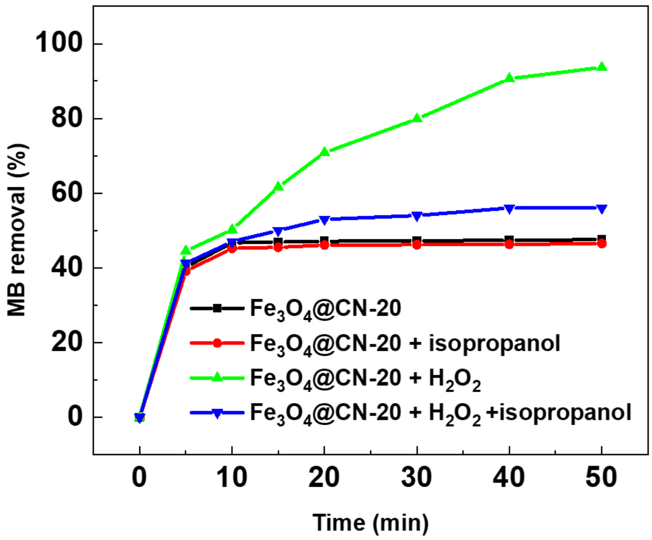

Figure S7. Removal efficiency of MB dye. Reaction conditions: catalyst, 0.75 g L^{-1}; H_2O_2, 239 mmol L^{-1}; MB, 50 mg L^{-1}; pH, 5.0.

References

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