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Electronic Supplementary Information

# Adsorption-intensified degradation of organic pollutants over bifunctional α-Fe@carbon nanofibres

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## Experimental

### *Materials*

Polyacrylonitrile (PAN *Mw*=80,000) was used as received from Jilin Carbon Group, China. *N,N*-dimethylacetamide (DMAc), iron chloride ($FeCl_3$), peroxymonosulfate (PMS), metheylene blue (MeB), methyl orange (MO), Cango red (CR) and phenol were purchased from Aladdin Chemical Reagent Co., Ltd., China. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purhased from Xilong Chemical Co., Ltd. All chemicals were of analytical grade and were used as received without further purification.

### *Preparation of activated composite nanofibers*

PAN/$FeCl_3$ hybrid nanofibers were fabricated with co-electrospinning of polymer with iron precursors. Various concentration of $Fe^{3+}$ were added into the electrospinning solution, the weigt ratio of $FeCl_3$ /PAN was fixed at 0:10, 1:9, 1:3 and 1:1. Take 1:1 as a example, $FeCl_3$ (3.0 g) was added into 47.0 g DMAc with vigorous stirring for 30 min with a rate of 200 r/min (MYP11-2, Shanghai Mei Yingpu Instrument and Meter Manufacturing Co,. Ltd), followed by adding 3.0 g of PAN powder stirred at room temperature with additional 12 h to get homogeneous solution. The electrospinning processes were performed at a fixed positive voltage of 12 kV and a fixed feed rate of 0.25 mL $h^{-1}$ with a distance of 10 cm between the needle tip to the round collector. All the chamber temperature and relative humidity during electrospinning were 23±2 $^{o}$C and 42±3 %. Finally, the electrospun $FeCl_3$/PAN nanofiber membrane were collected on a aluminum foil then calcined at 700 $^{o}$C, 900

$^{o}$C and 1100 $^{o}$C in $N_2$ flow with a heating rate of 2 $^{o}$C/min. The carbon nanofibers calcined at different temerature are referred to Fe@CNF700, Fe@CNF900 and Fe@CNF1100. Subsequently, the obtained Fe@CNF1100 was immersed into the KOH aqueous solution (30 wt%) with slightly stirring for 6 h, following dried at 60 $^{o}$C under vacuum for 3 h. Finally, the activated Fe@CNF1100 was carbonized at 900 $^{o}$C for 30 min in $N_2$ flow, and washed with 0.1 M HCl at least 3 times, the black activated Fe@CNF1100 were obtained.

*Oxidative degradation*

For the organic dyes degradation tests, methylene blue (MeB) was chosen as the model contaminant. In general, A-Fe@CNF1100 (10 mg) and PMS (25 g/L of 2 mL) were mixed in MeB solution (10 mg/L, 100 mL) with vigorous stirring at room temperature in light. For the purpose of comparison, the degradation performance of Fe@CNF1100 or PMS alone, as well as the combinations of Fe@CNF700+ PMS, Fe@CNF900+ PMS and Fe@CNF1100+ PMS were also tested under the same conditions. For the degradation of MO, CR and phenol, the pollutant concentration and reaction conditions are the same as MeB. The dye concentration in the solution after filtered by cellulose acetate membrane with a pore size of 0.45 μm was monitored by UV-vis spectra (Shimadzu UV spectrophotometer, UV-1800) with an interval of 1-10 min. The concentration of phenol was analyzed using a Varian high performance liquid-chromatography (HPLC) with a UV detector set at 270 nm. AC-18 column was used to separate the organics while the mobile phase made of 30% $CH_3CN$ and 70% water was at a flow rate of 1 mL/min.

During the reusability of catalyst, an external magnet wrapped by aluminum foil was employed to collect A-Fe@CNF1100 from liquid. Then the catalyst was reloaded to the fresh MeB solution by remove the magnet from aluminum foil. Each reaction time is 15 min.

*Characterizations*

The morphology of CNFs was measured by a scanning electron microscope (SEM, Zeiss SUPRA 55 SAPPHIRE). TEM, HRTEM, EDS mapping and selected-area electron diffraction patterns were observed by transmission electron microscope (JEM-2100F, JEOL Ltd.) at an acceleration voltage of 200 kV. Crystal structure of samples were measured by X-ray diffractometer (XRD, Rigku, ultima IV) using a Cu K$\alpha$ (0.1504 nm) radiation under the conditions of 40 mA and 40 kV. The surface area and pore size distribution of the samples were derived from $N_2$ sorption measurements using an automatic micropore physisorption analyzer (Tristar 3020, USA). Before measurement, the samples were degassed at 300 $^{o}$C for at least 10 h under 0.133 Pascal pressure. Magnetic properties were measured with a vibrating sample magnetometer (VSM, Lake Shore 7304). The near-surface chemical information of materials were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Al K$\alpha$ radiation, 1486.6 eV, 12 kV, 3 mA). Raman spectrum was obtained by using a micro-Raman spectroscopy system (inVia-Reflex, Renishaw, Co., UK). The EPR spectra was analyzed and exported by Bruker Xeon software. The DMPO radical adducts were identified by hyperfine splitting constants of DMPO-OH ($\square_N$=14.8, $\alpha_H$=14.8) and DMPO-SO$_4$ ($\alpha_N$=13.2,$\alpha_N$=14.8, $\alpha_H$=14.8 and $\alpha_H$=0.78).

**Figures**

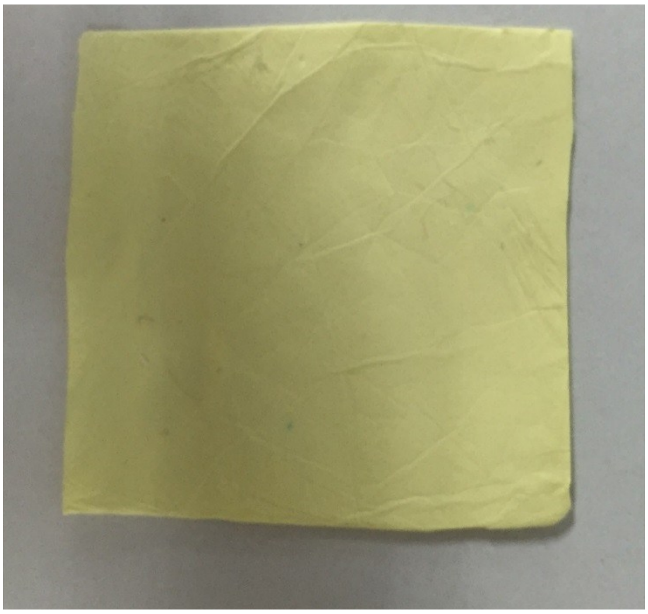


Fig. S1 Photograph of as-prepared PAN/$FeCl_3$ hybrid nanofibers with weight ratio of 1:1

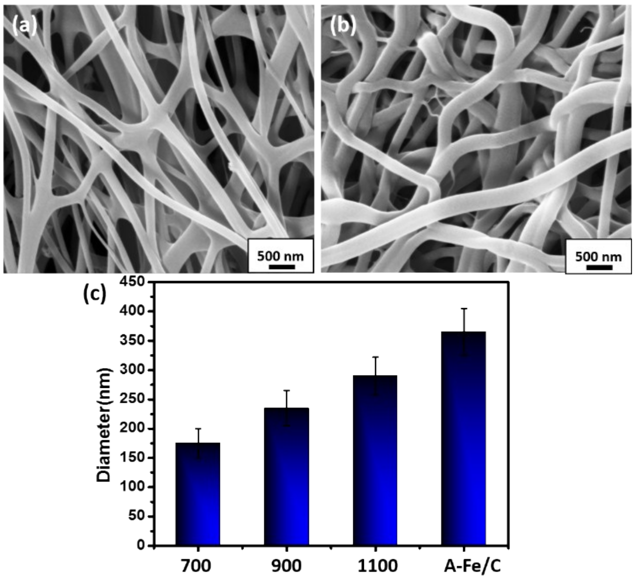


Fig. S2 SEM images of PAN/$FeCl_3$ nanofibers calcined at various temperature, (a) 700$^o$C, (b) 900$^o$C. (c) The average nanofiber diameter of different calcination temperature.

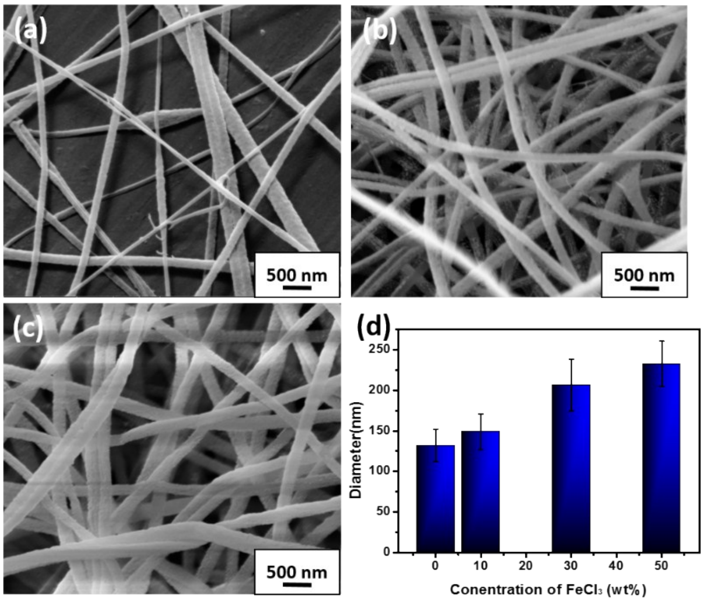


Fig. S3 SEM images of PAN/$FeCl_3$ nanofibers fabricated from various $FeCl_3$ content, (a) pristine PAN nanofiber, (b) 10 wt% and (c) 30 wt% $FeCl_3$. (d) The average nanofiber diameter of relevant nanofibers.

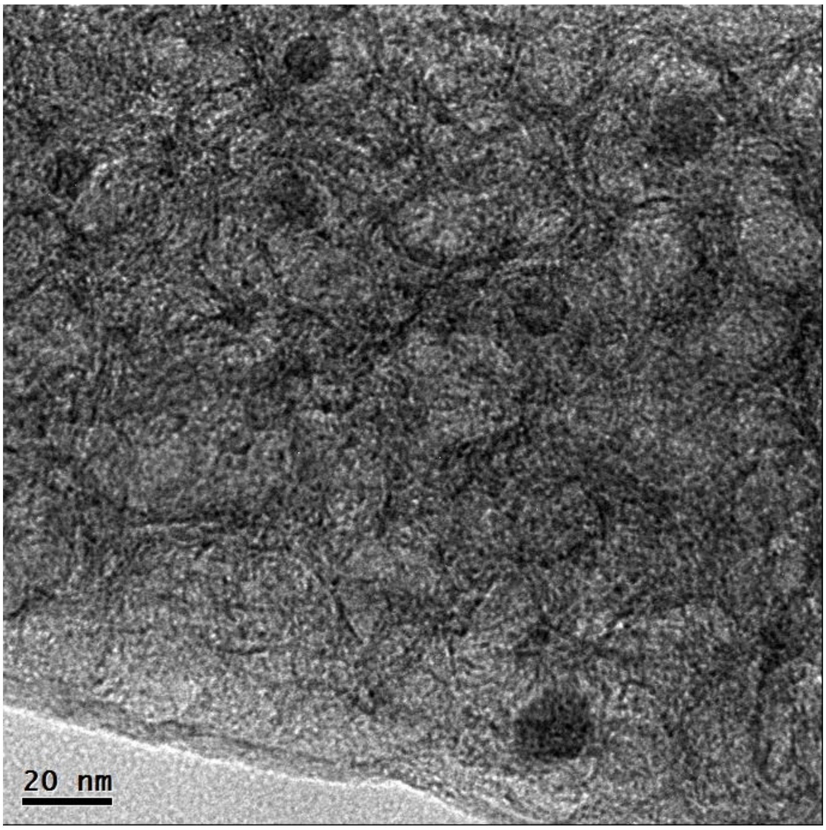


Fig. S4 TEM image of single fiber of Fe@CNF1100.

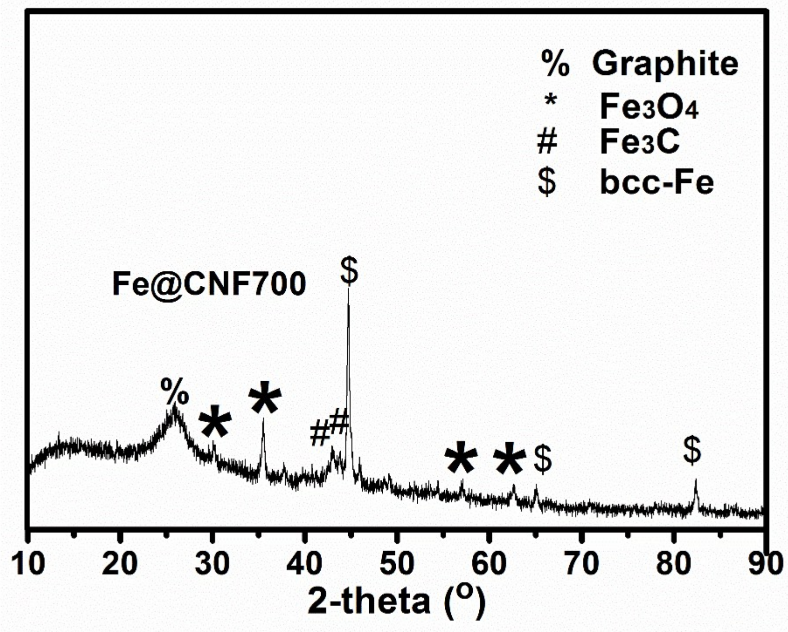
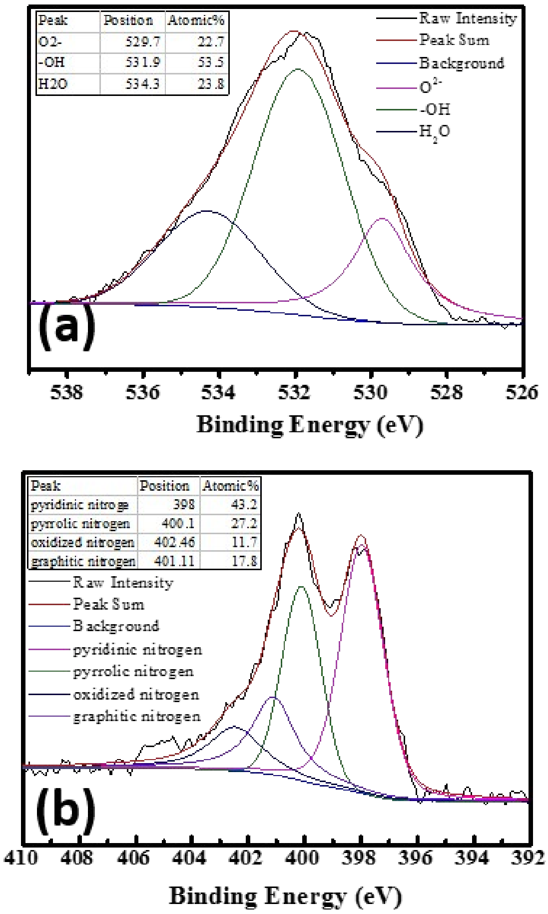


Fig. S5 X-ray diffraction (XRD) patterns of PAN/$FeCl_3$ calcined at 700 °C.



| Peak | Position | Atomic% |
|---|---|---|
| O2- | 529.7 | 22.7 |
| -OH | 531.9 | 53.5 |
| H2O | 534.3 | 23.8 |

| Peak | Position | Atomic% |
|---|---|---|
| pyridinic nitroge | 398 | 43.2 |
| pyrrolic nitrogen | 400.1 | 27.2 |
| oxidized nitrogen | 402.46 | 11.7 |
| graphitic nitrogen | 401.11 | 17.8 |

Fig. S6 XPS survey spectra of O 1s and N 1s of A-Fe@CNF1100.

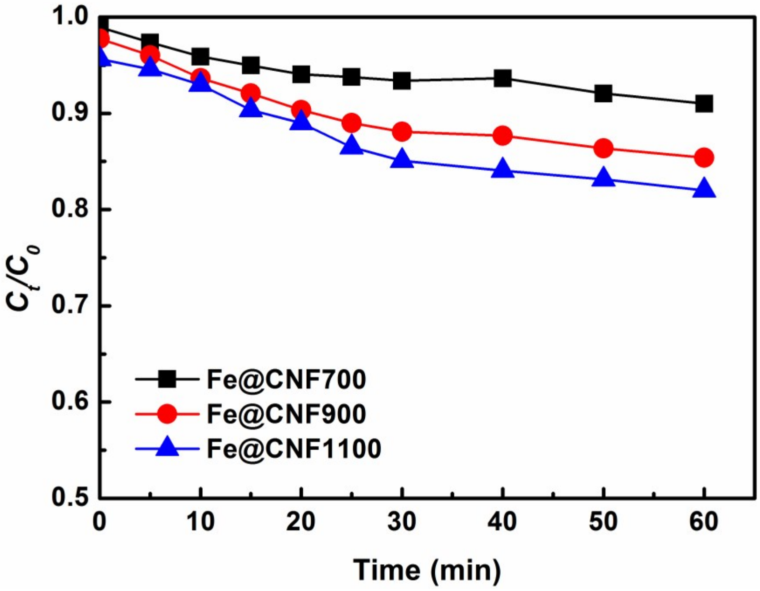


Fig. S7 MeB adsorption rates through Fe@CNF700, Fe@CNF900 and Fe@CNF1100.

Table S1 The summary of pore structure parameters of Fe@CNFs.

| Samples | $S_{BET}$[a] ($m^2g^{-1}$) | $S_{micro}$[b] ($m^2g^{-1}$) | $SF_{micro}$[c] (%) | $V_{total}$[d] ($m^3g^{-1}$) | $V_{micro}$[e] ($m^3g^{-1}$) |
|---|---|---|---|---|---|
| Fe@CNF700 | 85.76 | 16.31 | 19.01 | 0.122 | 0.007 |
| Fe@CNF 900 | 353.43 | 230.48 | 65.21 | 0.356 | 0.103 |
| Fe@CNF 1100 | 506.26 | 451.94 | 89.27 | 0.456 | 0.181 |
| A- Fe@CNF1100 | 853.15 | 727.52 | 125.63 | 0.756 | 0.292 |

[a] Total surface area was calculated by the Brunauer-Emmett- Teller (BET) method. [b] Microporous surface area was calculated by the Bareet, Joyner and Halenda (BJH) method. [c] $SF_{micro}$ indicates the surface area fraction of microporous. [d] the total pore volume was estimated was calculated at $P/P_0$=0.99. [d] Vmicro was calculated by the BJH method.

Table S2 The intensities of D band and G band and of $I_D/I_G$ ratio of Fe@CNFs.

| Samples | $\boldsymbol{I_D}$ | $\boldsymbol{I_G}$ | $\boldsymbol{I_D/I_G}$ |
|---|---|---|---|
| Fe@CNF700 | 2595.25 | 2320.14 | 1.12 |
| Fe@CNF900 | 2601.45 | 2402.56 | 1.08 |
| Fe@CNF1100 | 2588.86 | 2442.27 | 1.06 |
| A-Fe@CNF1100 | 2481.60 | 2465.16 | 1.01 |

Table S3 Comparison of the properties of A-Fe/CNF1100 with the literature results.

| PMS activator | Pollutant | Concentration of pollutant (mg/L) | Activator in solution (g/L) | Concentration of PMS (g/L) | T ($^{o}$C) | Time (min) | Conv. (%) | Ref |
|---|---|---|---|---|---|---|---|---|
| $MnFe_2O_4$-rGO | MB | 20 | 0.05 | 0.5 | 25 | 40 | ~100 | [1] |
| OMS-2 | MB | 20 | 0.25 | 0.25 | - | 15 | ~100 | [2] |
| rGO900 | MB | 10 | 0.2 | 0.61 | - | 10 | ~100 | [3] |
| CNT | Phenol | 9.4 | 0.1 | 1.14 | - | 60 | ~92 | [4] |
| α-$MnO_2$ | Phenol | 25 | 0.4 | 2 | 25 | 30 | ~100 | [5] |
| $Fe^0/Fe_3C$@CS | Phenol | 20 | 0.1 | 2 | 25 | 30 | ~100 | [6] |
| A-Fe@CNF1100 | MB | 10 | 0.1 | 0.5 | 25 | 15 | ~100 | This study |
| A-Fe@CNF1100 | Phenol | 10 | 0.1 | 0.5 | 25 | 15 | ~100 | This study |

## Reference

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