Nitrogen doped hierarchically structured porous carbon nanofibers with ultrahigh specific surface area for removal of organic dyes

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Synthesis of BA-a

The BA-a monomer (2,2-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane was synthesized *via* a Mannich reaction using bisphenol-A, paraformaldehyde and aniline. Typically, 30 g of bisphenol-A, 15.78 g of paraformaldehyde and 24.48 g of aniline were added into a three necked flask with continuous stirring for 30 min. The resultant homogeneous solution was then gradually increased to 110 °C in 30 min and kept for 4 h with continuous stirring under N_2 protection, following cooling down to room temperature. Then the obtained yellow product was dissolved in 150 mL of dichloromethane and washed by 2 wt% of NaOH solution and pure water at least three times, respectvely. The resultant yellow product was treated with anhydrous calcium chloride to remove the residual water, finally dried at 85 ^oC for 24 h.
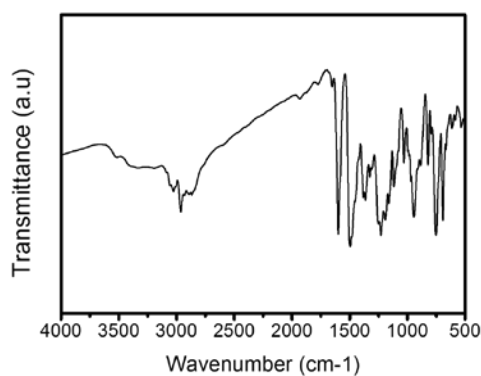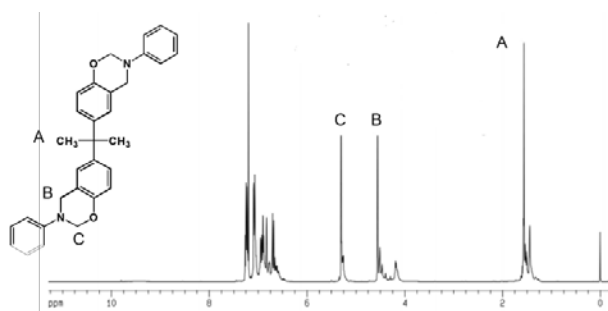

Fig. S1 FTIR spectrum of BA-a.

Fig. S2 ^{1}HNMR spectrograph of BA-a.

FTIR and ^{1}HNMR are used to confirm the chemical structures of BA-a. FTIR spectrum displayed the characteristic absorptions at 1230-1236 cm^{-1} (the asymmetric stretching of C-O-C), at 1028-1036 cm^{-1} (symmetric stretching of C-O-C), at 1327-1340 cm^{-1} (CH$_3$ wagging), and at 920-950 (trisubstituted benzene ring) for BA-a, respectively. The ^{1}HNMR spectrum shown in Fig. S2 further confirmed the structure of BA-a. The characteristic peaks at 1.44-1.60 ppm with a multiplet peaks was corresponded to –CH$_3$. The characteristic peaks at 4.58 and 5.33 ppm were corresponded to N-CH$_2$-Ph and N-CH$_2$-O, respectively. In addition, the characteristic peaks between 6.67-7.25 ppm was attributed to the Ph-H. Both the characterization of FTIR and ^{1}HNMR confirmed the successfully synthesis of BA-a.

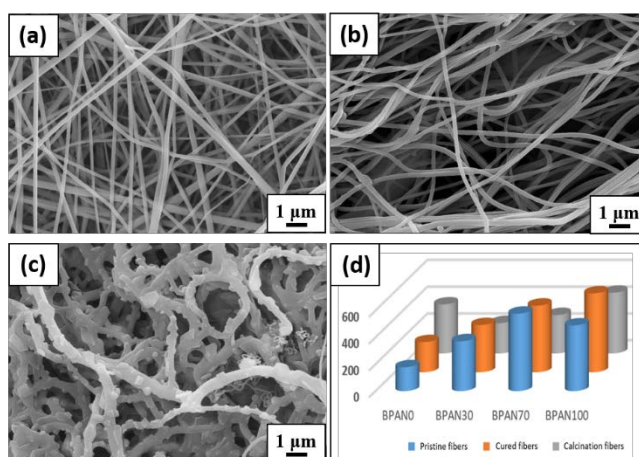Fig. S3 FE-SEM images of (a) pure PAN fibers, (b) pre-treatment of PAN fibers at 280 ^{o}C in hot N$_2$ atmosphere and (c) directly carbonized at 1000 ^{o}C in N$_2$ atmosphere. (d) Showing the average diameters of relevant fibers.
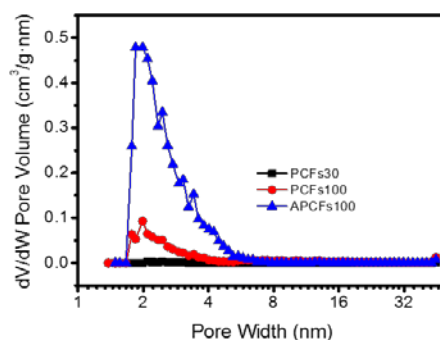

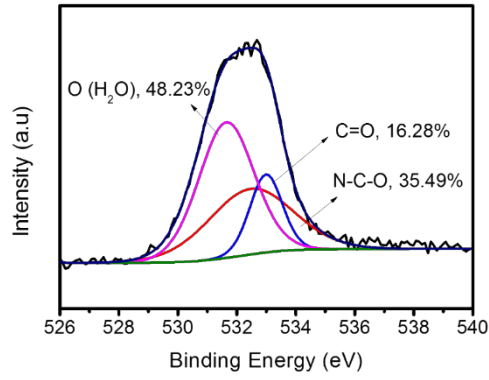Fig. S4 Pore size distributions of relevant carbon fibers.
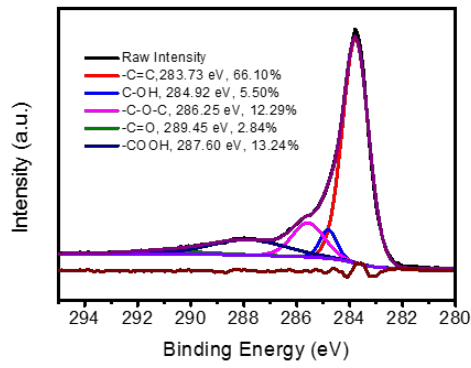
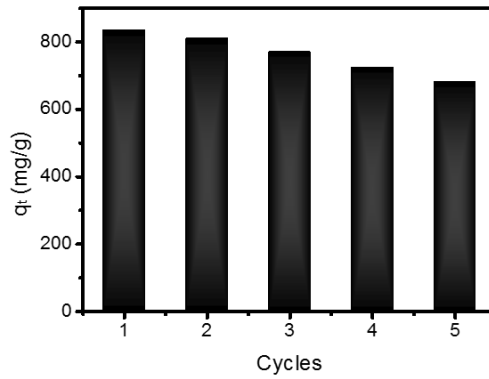Fig. S5 O1s spectra of APCFs100.

Fig. S6 C1s spectra of APCFs100.

Fig. S7 Recyclability of APCFs100 for MeB adsorption in five cycles. ([adsorbent dosage] =10 mg, [adsorption time] =120 min, pH =7, T =20 ℃).
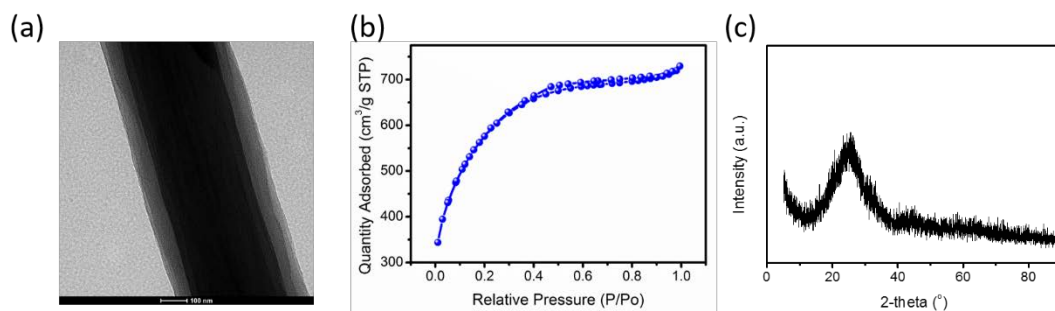
Fig. S8 (a) TEM image, (b) N_2 ad/desorption isotherm and (c) XRD pattern of APCFs100 after 5 cycles of adsorption-desorption.
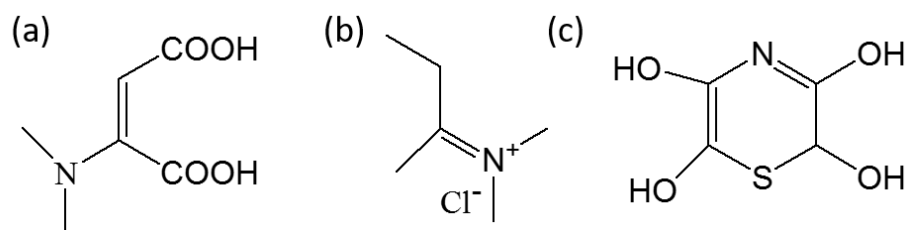

Fig. S9. (a) The degraded intermediate products of MeB.

The degraded byproducts of MeB were also identified using a UHPLC coupled triple quadrupole mass spectrometer. By the analysis of mass spectra, three degradation products of MeB have been identified, as shown in Fig. S9. According to these results, the degradation processes may attributed as follows: Firstly, the PMS would be adsorbed on the surface of nanostructured APCFs100. Secondly, the PMS would be activated by nitrogen doped APCFs100 to generate highly reactive oxygen radicals. Thirdly, the strong oxidative capacity of reactive oxygen radicals would break the benzene ring to form the carbon-bear free radicals and undergo electrophilic addition reaction, resulting in the formation of intermediates with hydroxyl groups. After that, the carbon-bear free radicals were further oxidized by reactive oxygen groups, then rearranged to form the benzoquinone structure. Subsequently, the benzoquinone would also be oxidized to form the intermediates like 2-dimethylamino-1,4-butenedioic acid. Finally, the intermediates would be further oxidized completely to generate carbon dioxides and water.

Table S1. Structure parameters of relevant hierarchical porous carbon fibers.

Samples	S_{BET}[a] (m^2/g)	S_{micro}[b] (m^2/g)	V_{total}[c] (cm^3/g)	V_{micro}[d] (cm^3/g)
PCFs30	125.22	25.52	0.13	0.01
PCFs100	692.35	525.49	0.45	0.23
APCFs100	2337.16	1190.02	1.21	0.57

[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 calculated at $P/P_0=0.99$. [d] Vmicro was calculated by the Horvath-Kawazoe (HK) method.

Table S2. Comparison of the adsorption capacity of MeB by different adsorbents.

Adsorbents	q_m (mg/g)	Reference
Bamboo based activated carbon	452	[1]
Oxidized graphene oxide	600	[2]
Polysaccharides-modified graphene oxide	780	[3]
Sodium hydroxide activated carbon	1030	[4]
Activated carbon	588	[5]
Commercial activated carbon	200	[6]
Covalent organic frameworks	1691	[7]
Triptycene-based 3D polymer	560	[8]
Agar/graphene oxide composite aerogel	578	[9]
Activated hierarchical carbon fiber	2020	This study

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