

Synthesis of porous carbon fibers with strong anion exchange functional groups

EXPERIMENTAL

Materials

Unless specified, all chemicals were purchased from Sigma-Aldrich and used as received. Polyacrylonitrile (PAN) ((C₃H₃N)_n, M_w ~ 150,000) and zinc chloride (ZnCl₂) were used for the synthesis of an activated carbon coating on a substrate fiber (Crane 230). Iodomethane (CH₃I), chloromethane (CH₃Cl, SJ Smith), dimethyl sulfate (DMS), and 1-bromobutane (Br-Bu) were used for the methylation reaction. Ethanol (Decon, 200 proof), dimethylformamide (DMF) (Fisher Scientific), dimethyl sulfoxide (DMSO, Fisher Scientific), and acetonitrile (MeCN, Fisher Scientific) were used as solvent. Potassium dichromate was used as a stock solution of hexavalent chromium, and 1,5-diphenylcarbazide (DPC) was used as the color reagent. Methanol (Fisher Scientific) was HPLC grade for dissolving color reagent. Reagents used for Boehm titration wet chemistry include NaOH, NaHCO₃ (Fisher Scientific) and Na₂CO₃ (Fisher Scientific) and HCl (Macron).

Synthesis

There were two steps in this synthesis procedure: first, synthesis of porous carbonaceous precursor that is rich in nitrogen; second, alkylation reaction onto nitrogen to introduce anion exchange functional group.

Precursor, namely polyacrylonitrile based activated carbon fibers (PANCAF), was prepared using a patented approach developed in Economy's Group with minor modifications¹. Polyacrylonitrile (PAN) was dissolved in DMF at 70 °C, and then add ZnCl₂ to make a viscous solution. Weight ratio of PAN: ZnCl₂: DMF is 6.5:19:174. After ZnCl₂ was dissolved, a glass fiber mat (Crane 230, Crane Co) was dip-coated into the above mixture. Then dip wash the coated fiber in 5%_wt ZnCl₂ aqueous solution to make a uniform coating without losing ZnCl₂. After dried the samples in a fume hood overnight, put them into a furnace at 200°C for 10 hours in air to stabilize the coatings. Afterwards, put the samples in flowing N₂ by increasing heating temperature ~ 30°C/min to the preset temperature in-between 350 °C and 550 °C and then held isothermed for 30 mins. After cooling down in flowing N₂ for ~10 hrs, sample was taken out and washed with 0.5 M HCl, DI Water, 0.5M NaOH and DIW in sequence. The sample was first dried in the hood overnight, and then vacuum dried at 110 °C overnight to remove residual moisture.

During alkylating reactions to synthesize hybrid anion exchange activated carbon fibers (HACAX), four different alkylation reagents were evaluated, including methyl iodide, dimethyl sulfate, 1-bromobutane, and methyl chloride. Alkylation reaction conditions are summarized in Table S 1. After reaction, the solid samples were washed with ethanol and DI water to remove

the residual chemicals and solvents attached on the fiber. The sample was then dried and stored for further tests and characterization.

Table S 1 Methylation reaction conditions

Methylation Reagent	Solvent and/or Catalyst	Temperature (°C)
CH ₃ Cl	MeCN	80
1-Br-Butane	MeCN	80
(CH ₃) ₂ SO ₄	Water/KHCO ₃	0-80
CH ₃ I	EtOH, MeCN or NMP	25-80

Ion exchange properties

Ion exchange capacity was measured through classical ion exchange reactions at natural pH (as shown in Fig.S 1). In the measurement, 50 mg HACAX samples (PANCAF as comparison) were each soaked in 30 ml of a 1M NaNO₃ solution and shaken for overnight. Then measure the iodide ions concentration in solution by an iodide selective electrode (Cole-Parmer). In the current study, instead of studying the typical ion exchange between NO₃⁻ and Cl⁻, the exchange of I⁻-NO₃⁻ is employed to avoid errors on chloride electrode reading introduced by residual iodide ions.

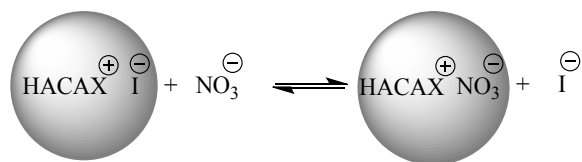


Fig.S 1 Ion Exchange of Iodide vs. NO₃⁻

Ion exchange regeneration performance was also tested. HACAX was soaked in 1M NaNO₃ and 1M NaI solutions periodically and rinsed with DIW several times in-between. Exhausted NaNO₃ solution with iodide ions were collected and measured with iodide ISE.

Cr(VI) adsorption performance

Hexavalent chromium stock solution was prepared by dissolving 0.5658 g potassium dichromate (K₂Cr₂O₇) in 200 ml DI water, giving a 1000 ppm Cr(VI). All other test solutions and standard solutions were made by diluting the 1000 ppm stock solution.

The concentration of Cr(VI) was measured by UV-Vis Spectroscopy at λ=540 nm via photometric diphenylcarbohydrazide method^{2, 3}. Color indicator was prepared by dissolving 125 mg of 1,5-diphenylcarbohydrazide (DPC) into 25 ml HPLC-grade methanol, then 125 ml 5.5% H₂SO₄ was added and diluted into 250 ml solution with DI water. Before UV-Vis measurement, a 3ml sample solution (or diluted sample) and 1 ml color indicator was mixed and put into 3.5 ml

polystyrene cuvette. Standard solutions were prepared at concentrations of 0, 5, 10, 20, 40, 80, 120, 400, 600, 800, 1000 ppb for calibration with $R^2 > 0.9998$. After mixing with color indicator, the sample was measured in a timely way to ensure a precise result.

Adsorption kinetics was studied in aqueous solution at room temperature in a 250 ml flask with magnetic stirring. During the test, 150 mg sample was put into 200 ml solution with initial Cr(VI) concentration at 4 ppm. The solution was sampled at pre-set time points and stored awaiting further measurements.

Characterizations

SEM images were obtained using a Hitachi S-4700 with mixed field emission with a 10 kV - 15 kV accelerating voltage. Samples were attached on an aluminum sample holder using a carbon tape. The samples were coated with a thin layer of metals to improve conductivity using a gold palladium plasma spray.

Surface areas and pore size analysis were obtained using a Quantachrome Autosorb-1 pore surface analyzer. All samples were first dried at 110 °C under vacuum before measurement. These samples were degassed at 150 – 200 °C until the outgassing pressure change was below 5 $\mu\text{m Hg/min}$ before analysis. N_2 was used to measure the surface area and pore volume at 77 K. BET equation was used to calculate the surface area using P/P_0 range from 0.05 to 0.3; The Dubinin-Radushkevitch (DR) equation was used to determine micropore (< 2 nm) volumes. The total pore volume was estimated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$. Mesopore volume was calculated by the difference of total pore volume and micropore volume.

Coating content and thermal stability of samples were measured by TGA (Hi-Res TA Instruments 2950 Thermogravimetric Analyzer). The coating content of HACAX was measured by burning off the carbon coating at 800°C in air. Sample's coating content was calculated by the following equation:

$$\text{Coating Content \%} = \frac{\text{Weight loss \% (from } \sim 110 \text{ }^\circ\text{C to } 800 \text{ }^\circ\text{C)}}{1 - \text{moisture content \% (weight loss from RT to } \sim 110 \text{ }^\circ\text{C)}}$$

Elemental analysis was used to quantify carbon, hydrogen, nitrogen and other heteroatoms presents in the carbon matrix. Chemical composition (C, H, and N) of samples was determined using a Model CE440 Elemental Analyzer. The detection limit for each element was 0.10% with errors 0.06%. Additionally, zinc (Zn) content was determined by ICP/MS with detection limits on the level of ppb or even ppt. Oxygen content was determined indirectly using principles of mass balance, as estimated using the following equation:

$$w[\text{O}] = w[\text{coating content\%}] - w[\text{C}] - w[\text{H}] - w[\text{N}] - w[\text{Zn}]$$

The zeta potential (ζ) of PANCAF and HACAX was measured at different equilibrium pH using Zetasizer Nano ZS (Malvern Instruments) to identify the isoelectric point (IEP). Samples (~ 10 mg) were grounded into powder, and mixed with 15 ml aqueous solution with pH between 2 and

12. pH of solution was adjusted by adding 0.5M HCl or NaOH. After shaking for 24 hrs, the zeta potential of adsorbent and final pH of suspension was measured.

The pH isotherm was measured to identify point of zero charge pH (PZC), which is the pH when the activated carbon materials have zero net charge as total; Above which, the carbon is negatively charged and vice versa. This method is based on the work by Lopez-Raman et al.⁴ with minor modifications. Samples (~ 10 mg) were ground into powder, and mixed with 15 ml aqueous solution with pH between 2 and 12. pH of solution was adjusted by adding 0.5M HCl or NaOH and measured by pH electrode (Cole-Parmer, Cat. EW-59001-70). After shaking for 24 hrs, pH of the final suspension was measured by pH electrode. The pH at which $pH_{\text{final}} = pH_{\text{initial}}$ or plateau is determined as PZC.

Thermo Nicolet Nexus 670 FTIR was used to obtain infrared spectrum of the samples and to identify chemical functional groups. As activated carbon samples are intrinsic absorbers, traditional transmission format does not produce a usable spectrum. DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) mode is applied to maximize signal intensity. Fibrous samples were directly measured without KBr addition. Data acquisition was performed by Omnic[®] software with 32 scans at a resolution of 4 cm^{-1} .

Boehm titration was employed to identify surface functional groups within activated carbon. In this method, three bases (NaHCO_3 ($pK_a=6.37$), Na_2CO_3 ($pK_a = 10.25$), NaOH ($pK_a = 15.74$))⁵ with different pK_a and HCl were used to titrate activated carbon. Traditional Boehm titration assumes only surface oxygen functional groups present on the surface. In order to apply this technique in current system, a hypothesis was made here: the surface functional groups are categorized into: carboxylic acid, lactonic, phenolic, pyridinium, pyridine and pyrrolic groups. Amount of pyridine could be identified by acid consumption; pyrrolic groups are relatively stable which won't react with any acid/base; in all functional groups, pyridinium is very unique due to its anion exchange properties. Upon soaking in base solution, pyridinium on surface can exchange iodide with OH^- and/or CO_3^{2-} and/or HCO_3^- , which are perceived as partial consumption of base by acid-base titration. Each base or acid can reacts with different acidic functional groups spectrum as shown in Table S 2.

Table S 2 Titration with proposed different model compounds

Titrants	NaOH	Na₂CO₃	NaHCO₃	HCl	Calculated or Perceived as
Surface Groups	a	b	c	d	
Carboxylic Acid	Yes	Yes	Yes	No	c
Lactonic	Yes	Yes	No	No	b-c
Phenolic	Yes	No	No	No	a-b
Pyridinium	Partially	Partially	Partially	No	Partially of a, or b, or c
Pyridine	No	No	No	Yes	d
Pyrrolic	No	No	No	No	

This technique was originally developed by Boehm⁶ more than 40 yrs ago. Traditional Boehm titration is under dispute due to the error caused by dissolved CO₂. Combined with recent development⁷⁻⁹, plus author's new technique by introducing blank comparison, this technique is more applicable and less interference by dissolved CO₂. The procedure is as follows:

Weigh four pieces of samples with each ~ 0.23 g; and then cut into small pieces and placed in glass vials containing 15 ml 0.025M NaOH, Na₂CO₃, NaHCO₃, HCl, respectively. A parallel set of blank solution without samples were also prepared and treated using the same procedure. All solutions were sealed and shaken for 24 hrs. Afterwards, solutions with or without samples were both filtered by syringe and membrane filters (Nylon 0.45 μm) to remove solids. Then 5 ml of filtered solutions were transferred to another container and added over amount of 0.05M HCl (10 ml HCl for NaHCO₃ or NaOH solution, 15 ml HCl for Na₂CO₃, or 0 ml HCl for HCl solutions). Solutions were then degassed by nitrogen for 2 hrs to remove dissolved CO₂. Lastly, solutions were titrated by traditional acid/base titration method using phenolphthalein as indicator⁵ and microburette for improved resolutions (0.004 ml/drop compared with 0.05 ml/drop for traditional burette). During titration, the solution was kept degassing by N₂ to prevent dissolution of CO₂.

RESULTS

Elemental analysis

Table S 3 Elemental analysis of PANCAF and HACAX

	Weight %				Atomic Ratio		
	C	H	N	Coating ^a	C/N	H/N	O/N
PANCAF	22.5%	1.0%	7.7%	39%	3.4	1.8	0.9
HACAX	25.0%	1.2%	7.8%	42%	3.8	2.2	0.9

Note: Coating content was measured by TGA. Oxygen content was calculated between the differences of coating content and C, H, N, Zn elements.

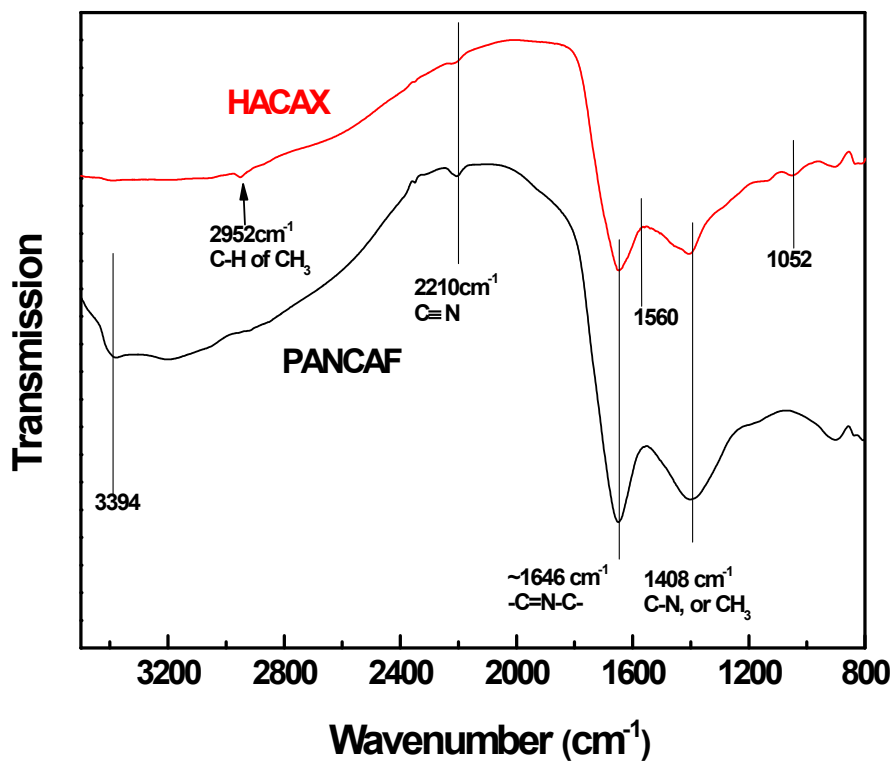


Fig.S 2 FTIR spectrum for PANCAF and HACAX

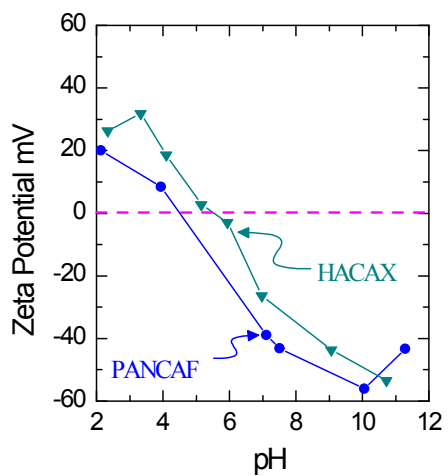


Fig.S 3 Zeta Potential of PANCAF and HACAX

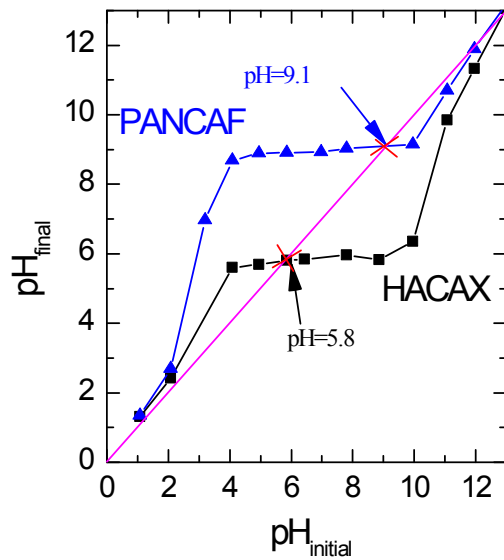


Fig.S 4 Illustration of pH isotherm for PANCAF and HACAX

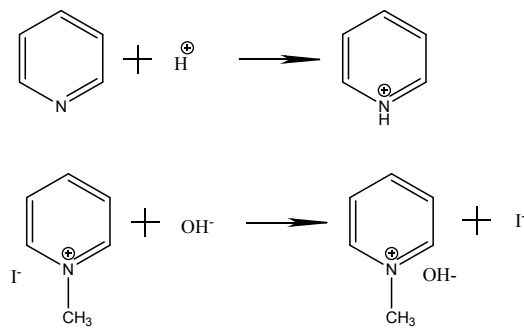


Fig.S 5 Possible mechanism and chemistry for pH isotherm between PANCAF and HACAX

Small molecule probes - Boehm titration

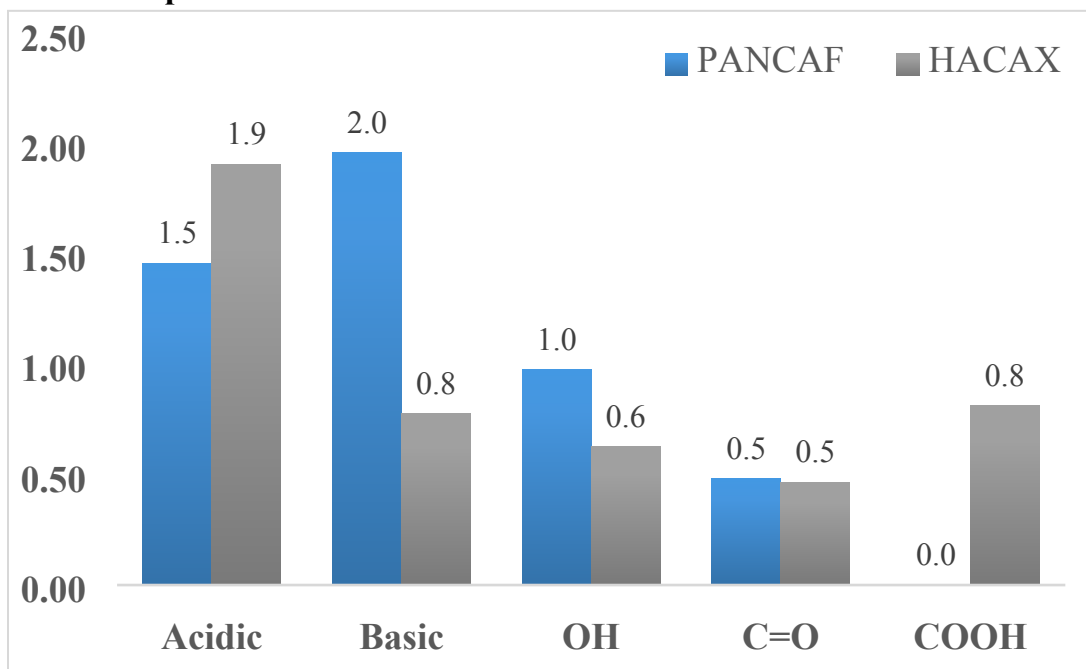


Fig.S 6 Boehm titration of PANCAF and HACAX, and perceived functional groups.

Physical structure

Table S 4 Surface area and pore volumes of PANCAF and HACAX ¹⁰

Sample	Surface Area ^a	Volume		Volume Ratio	
	BET	DR Micropore	Mesopore	Micropore	Mesopore
	m ² /g	ml/g	ml/g	%	%
PANCAF	982	0.51	0.036	93%	7%
HACAX	1045	0.49	0.59	46%	54%

^aNote: all data are normalized based on the coating by TGA measurement.

Ion exchange properties

Table S 5 Ion Exchange Capacity (IXC) of HACAX by different methylation

Methylation Reagent	Solvent and/or Catalyst	Temperature	Time	Max. IXC
		(°C)		mmol/gC
CH ₃ Cl	MeCN	81	1-24 hr	1.1
1-Br-Butane	MeCN	81	1-7 day	0.6
(CH ₃) ₂ SO ₄	Water/KHCO ₃	0-80	1-24 hr	2.1*
CH ₃ I	EtOH, MeCN, NMP, DMSO	25-80	1-24 hr	1.4-1.8

Note: * DMS was not used later on due to its extreme toxicity; IXC (ion exchange capacity) is based on carbon coating.

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