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From fish scales to highly porous N-doped carbon: a low cost material solution for CO₂ capture

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This article reports a strategy to treat fish scales as raw materials for synthesizing CO₂ capture materials. The synthesis employs thermal treatment and chemical treatment to convert fish scales to N-rich porous carbons. The proteins in fish scales were the major source for carbon and nitrogen. By varying the reaction conditions, the porosity and N content can be controlled in the produced porous carbons. It was found that the porosity increases first and then drops upon the increase of thermal treatment temperature. The N content drops along with the increase of the temperature. The capture capacity of the as-synthesized carbon (NFPC-750) for CO₂ can be up to 171 mg/g at 25 °C, 1 bar. This high capacity is attributable to its porous structure with a high specific surface area (up to 3206 m²/g) and large pore volume (micropore volume up to 0.76 cm³/g and total pore volume up to 2.29 cm³/g). More attractively, quaternary nitrogen was effectively preserved at the same time (2.90% N), which should be another contributor for enhancing CO₂ capture capacity through the chemical adsorption between nitrogen groups and CO₂. In addition, the sorbent preliminarily exhibits high cycle stability with retention of 91.8% of its initial CO₂ capacity after 10 cycles. This highly porous N-doped porous carbon obtained from fish scales is thus considered a promising material for CO₂ capture.

1. Introduction

Carbon dioxide (CO₂) is one of major greenhouse gases. Its amount in atmosphere has been found increasing in recent decades and this has been believed as the major factor resulting in global warming. To reduce the CO₂, efforts have been made in reducing emission at resources like power plants as well as developing new techniques to capture and then reuse this small molecule. In recent years, various solid sorbents have been developed. Popular materials include zeolite, hydrotalcite-like compounds, and carbon-based sorbents such as carbon nanotubes and porous carbons.¹⁻⁹ The CO₂ capture capacities of these sorbents are mainly originated from their high specific surface area. To further increase the capture capacity, basic sites are introduced into the sorbents to enhance the affinity of CO₂ to the surface.^{10,11}

Nitrogen-containing groups have been reported to act as basic sites in porous carbons for CO₂ adsorption.¹²⁻¹⁷ Hence, one of research interests is to develop approaches to

introduce N into porous carbons. The early reported methods were grafting some N-rich molecules onto the surface of carbons.^{13,14} Afterwards, some researchers selected carbon precursors with abundance of nitrogen-containing compounds to facilitate the synthesis of efficient sorbents.^{2,18-20}

In this work, we report for the first time that fish scales can be an excellent raw material to synthesize highly porous N-doped carbon for CO₂ adsorption, which shows the following advantages. First, the protein is the main component of fish scales containing both carbon and nitrogen. Second, hydroxyapatite, which exists in fish scale in nanoscale, could be used as a natural template for porous carbon synthesis. Third, fish scales are inexpensive as a byproduct of food processing industry.²¹ The result shows that the as-synthesized carbon gave a very high specific surface area of 3206 m²/g and large pore volume (total pore volume up to 2.29 cm³/g). More important thing is that this carbon exhibited strong capture capacity for CO₂ up to 171 mg/g at 25 °C, 1 bar, and it would be a promising adsorbent for CO₂ capture.

2. Experimental method

2.1 Materials preparation

Tilapia fish scales were obtained from Dali, Yunnan province. Clean and dry fish scale was precarbonized at 330 °C for 3h in a N₂ atmosphere. The precarbonized fish scales were then blended with KOH (as an activating agent) in a weight ratio of

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1:1 and ground to powder. The powder was heated in a N₂ atmosphere at different temperatures (at the range of 600 to 900 °C) for 1h. For comparison, some precarbonized fish scale powder was directly heated at the same temperatures without KOH. All the activated and not activated products were first washed with 1M HCl and then washed and filtered with hot deionized water until the electrical conductivity of filtered liquid is equal to that of pure water. The products were then dried at 100 °C for 24 h to obtain N-doped fish-scale-based porous carbons. In this paper, the carbon materials with and without KOH activation were denoted as NFPC-T and NFPC-T-NA, respectively, where "T" represents the carbonization temperature of the material and "NA" implies no activation.

2.2 Materials characteristics

The porous texture of the samples was examined by N₂/77 K adsorption/desorption isotherms (Quantachrome NOVA 1200). The surface areas were calculated using the Brunauer-Emmett-Teller (BET) method based on N₂ adsorption on the sample. The total pore volumes were estimated to be the volumes of liquid nitrogen adsorbed at $P/P_0=0.99$. The micropore volumes were determined by the t-plot method. The pore size distribution plots were extracted from the adsorption branch of the isotherm based on density functional theory. Scanning electron microscopy (SEM, HITACHI S-4700) was used to observe the microstructure of the samples. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific USA ESCALAB-250) was carried out to determine N contents of the samples. Fourier transform infrared spectroscopy (FTIR, Thermo Fisher Scientific USA, Nicolet iS5) was measured to demonstrate the functional groups of different samples.

2.3 Carbon dioxide adsorption

A CO₂ adsorption test was carried out under pure CO₂ at 1 bar using thermo gravimetric analyzer (TGA, Hengjiu China). In the experiment, samples at the range of 3 mg to 5 mg were loaded into the TGA. Prior to the measurement, the samples were all degassed to remove the impurity under N₂ at 200 °C for 1h. After cooling the sample to the analysis temperature (25 or 50 °C), the test began and CO₂ was instilled for 1h to make the TGA full of CO₂. After adsorption test, materials were desorbed under N₂ at 200 °C for 1 h. Desorbed materials could be used in cycle test of the CO₂ adsorption. Cycle test was under the same condition as the adsorption/desorption test. Adsorption capacity can be calculated from the result of the TGA by transferring the gross increasing mass into per gram of increasing mass. Selectivity and isosteric heat of adsorption were measured by N₂ and CO₂ adsorption isotherms at 0 °C and 25 °C (Quantachrome Autosorb-1).

3. Results and discussion

3.1 Composition of the synthesized carbons

The precarbonized material (heated to 330 °C) has high N content up to 13.02% and hence could be a potential raw material for N-rich carbons. The nitrogen contents of the as-synthesized materials are listed in Table 1. The nitrogen content of the samples decrease as the temperature increased, irrespective of whether the sample was activated or not. This is probably because nitrogen is less stable than carbon at high temperatures. In addition, each NFPC-T-NA sample shows a higher N content than the NFPC-T sample treated at the same temperature. It indicates that KOH activation accelerates the N removal. This is consistent with the literatures and such an activation has been ascribed to an oxidization effect of KOH to N groups.¹⁹

The N 1s core-level spectra of the samples are shown in Fig. 1 (a) and 1 (b). In these two figures, three peaks at 398.7 eV, 400 eV and 400.7 eV are corresponding to pyridinic nitrogen, pyrolic nitrogen/pyridonic nitrogen, and quaternary nitrogen, respectively.²² It should be noted that pyrolic N and pyridonic N cannot be distinguished by XPS.¹⁹ Owing to the oxidization of KOH, the 400 eV peak corresponds to pyridonic N in the Fig. 1 (a). Besides, the pyrolic N/pyridonic N peak shows the lowest stability among the three N species under pyrolytic conditions (Fig. 1 (b)), which suggests that the 400 eV is more likely to be pyridonic N. In addition, the peak due to the pyridinic N is diminished to the maximum extent because of KOH activation. The pyridinic N peak diminishes significantly from 600 °C to 750 °C (Fig. 1 (a)). However, under pyrolytic conditions, there is no significant removal of the pyridinic N until the temperature reaches 900 °C. These results confirm the KOH's oxidization effect. As seen in both figures, the quaternary N finally becomes the most stable N species at very high temperature.

The deducing of XPS result can be attested via FTIR. As Fig. 2 shows, the peak at 3420 cm⁻¹ is corresponding to N-H stretching vibration, but it overlaps with O-H stretching vibration, making identification difficult. The weak peaks at

Table 1 N content of as-synthesized carbons

Synthesis temperature (°C)	N content (wt %)	
	Activated samples	No activated samples
600	7.49	10.80
750	2.90	9.23
900	1.50	3.79

*The N content of the precarbonized Tilapia fish scales (heated to 330 °C) is 13.02 wt%.

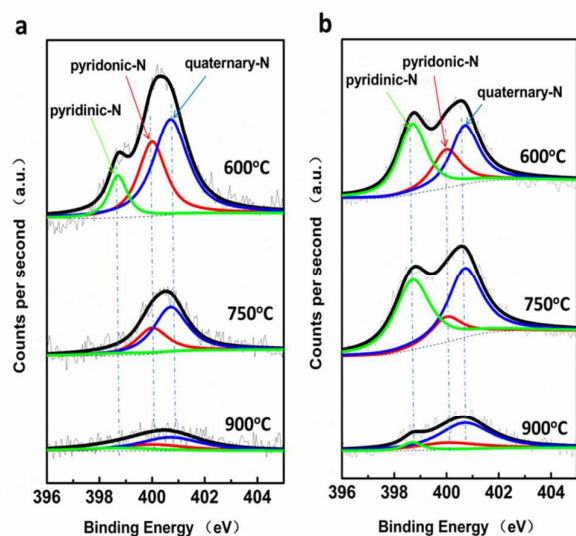


Fig. 1 N 1s core-level spectra of samples (a) NFPC-Ts and (b) NFPC-T-NAs.

1720 cm^{-1} corresponds to C=O stretching vibration. This peak becomes weaker with activation temperature rising up, demonstrating gradual disappearance of C=O. The bands at $1400\sim 1610\text{ cm}^{-1}$ are ascribed to existence of ring structures that contain N group. The band at 1250 cm^{-1} is attributed to C-N stretching vibration. These bands all decrease with temperature rising up, which reveals to removal of N. The information mentioned above point to removal of N-containing group.

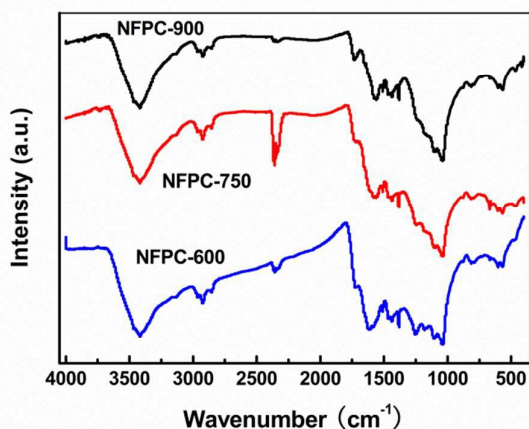


Fig. 2 FTIR spectra of NFPC-900, NFPC-750, and NFPC-600.

3.2 Pore structures of the synthesized carbons

Fig.3 shows the typical SEM images of samples. Sample NFPC-600 exhibits a lamellar structure with fewer pores and offers a large interfacial area for activation reaction with KOH. This morphology could be preserved well through activation at $750\text{ }^{\circ}\text{C}$. Fig 3 (b) shows that more pores appeared at $750\text{ }^{\circ}\text{C}$ and the foam-like structure begin to emerge, which represents intense KOH activation. Some of the pores are interconnected, indicative of over-activation; this phenomenon becomes more pronounced in Fig 3 (c). Over-activation diminished the specific surface area, which is confirmed in the nitrogen adsorption/desorption isotherms shown in Fig.4. Compared with NFPC-750, NFPC-750-NA still shows a lamellar structure but much fewer pores (Fig. 3 (d)), because of no KOH activation. The only pores in NFPC-750-NA can be attributed to hydroxyapatite that is washed away.

The nitrogen adsorption/desorption isotherms and corresponding PSDs (pore-size distributions) of major samples are illustrated in Fig. 4. The major structural property data for these samples are displayed in Table 2. With increasing temperature, the specific surface area and total pore volume of the NFPC-T-NAs increase, but the micropore volume remains constant at $0.06\text{ cm}^3/\text{g}$. This result shows that only mesopores and macropores are formed during carbonation. No apparent hysteresis loop occurs in the curves for NFPC-600-NA. This result suggests that macropores are the main pore type existing in NFPC-600-NA and that these pores were formed by washed hydroxyapatite. At a temperature of $900\text{ }^{\circ}\text{C}$, a mesopore hysteresis loop begins to appear. Interestingly, the pyridinic N would decrease substantially when the temperature

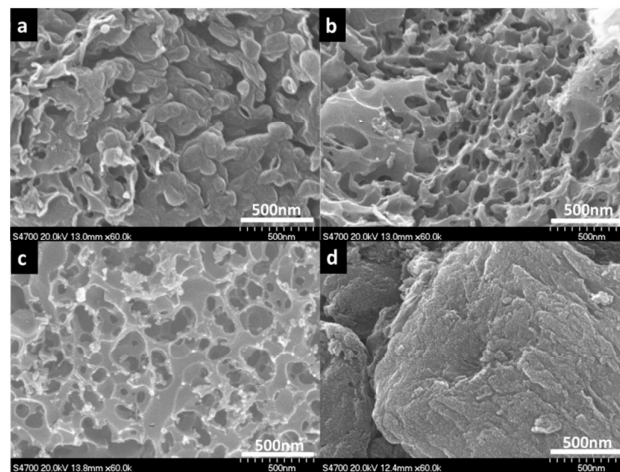


Fig. 3 SEM images of samples (a) NFPC-600, (b) NFPC-750, (c) NFPC-900, and (d) NFPC-750-NA.

Table 2 Structure properties of the carbons synthesized.

Samples	Structural properties			
	^a $S_{\text{BET}}(\text{m}^2/\text{g})$	^b $V_p(\text{cm}^3/\text{g})$	^c $V_{\text{micro}}(\text{cm}^3/\text{g})$	^d $D_p(\text{nm})$
NFPC-600	1479	0.88	0.54	2.4
NFPC-750	3206	2.29	0.76	2.9
NFPC-900	2712	2.73	0.66	4.0
NFPC-600-NA	317	0.19	0.06	2.4
NFPC-750-NA	586	0.40	0.06	2.7
NFPC-900-NA	731	1.03	0.06	5.6

^a S_{BET} : specific surface area. ^b V_p : total pore volume. ^c V_{micro} : micropore volume. ^d D_p : average pore diameter.

Increased from 750 °C to 900 °C, suggesting that pyridinic N removal is correlated to the formation of mesopores. In contrast, the specific surface area of the NFPC-Ts shows a peak value of to 3206 m²/g at the activation temperature of 750 °C. At this point, the micropore volume is 0.76 cm³/g, much larger than the micropore volume of NFPC-750-NA. It implies that KOH activation forms micropores. NFPC-900 has a lower micropore volume and specific surface area because of over-activation. It has been reported that micropores can benefit for CO₂ capture.²³ That is to say, NFPC-750 would have large advantage in CO₂ capture.

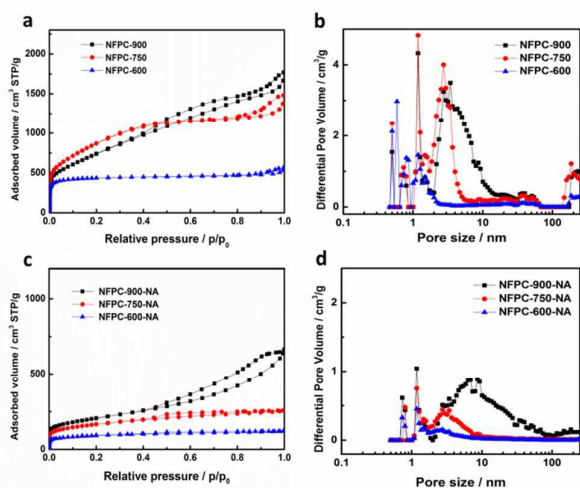


Fig. 4 (a) N₂ adsorption/desorption isotherms of NFPC-Ts and (b) PSDs of NFPC-Ts; (c) N₂ adsorption/desorption isotherms of NFPC-T-NAs and (d) PSDs of NFPC-T-NAs.

3.3 Carbon dioxide capture capacity

Table 3 displays the summary of the CO₂ capture capacities of the samples. Each adsorbent shows higher CO₂ capture capacity at 25 °C than that at 50 °C, which suggests that these materials tend to adsorb CO₂ at low temperature. In addition, the NFPC-Ts exhibit higher CO₂ capture capacity than that of NFPC-T-NAs, which can be attributed to their favourable pore structure, especially the large micropore volume and specific surface area. However, this advantageous pore structure was obtained at the cost of the nitrogen content. Moreover, the capture capacity of the NFPC-T-NAs decreased with increasing temperature. It can be concluded that, if the material lacks of micropores, N content would be a more dominant factor influencing capture capacity. NFPC-900 shows a higher capacity at 25 °C than NFPC-600, but a lower capacity at 50 °C. This result demonstrates that N content would contribute more at higher temperature. Among all the samples, NFPC-750 exhibits the highest CO₂ capture capacity (171 mg/g at 25 °C). It is because NFPC-750 has the highest specific surface area and micropore volume among all the synthesized carbons and the quaternary N was preserved in this sample, owing to the proper activation temperature. This material shows capacity of 107 mg/g at 50 °C, also the highest capacity at this temperature.

To further investigate the interaction strength between CO₂ and NFPC-Ts, the isosteric heat of adsorption (Q) is calculated from CO₂ adsorption isotherms (Fig. 5 (a)) measured at two temperatures (0 and 25 °C) by means of Clausius-Clapeyron equation: $(T_2 - T_1) \cdot Q / (RT_1 T_2) = \ln(p_2/p_1)$, where T₂ and T₁ are 0 °C and 25 °C, respectively; p₂ and p₁ are pressure values of CO₂; and R is universal gas constant. The result (Fig 5 (b)) shows that the initial isosteric heat of adsorption of NFPC-600 is about 59 kJ/mol, which is higher than that of NFPC-750 (42 kJ/mol) and much higher than that of NFPC-900 (25 kJ/mol). High Q value indicates strong interaction between CO₂ and the material. Given that N

Table 3 CO₂ capture capacity of the carbon synthesized.

T (°C)	Capacity at 25°C (mg/g)		Capacity at 50°C (mg/g)	
	NFPC-T	NFPC-T-NA	NFPC-T	NFPC-T-NA
600	123	81	104	58
750	171	74	107	45
900	150	56	93	43

*The adsorptions were all under 1 atm.

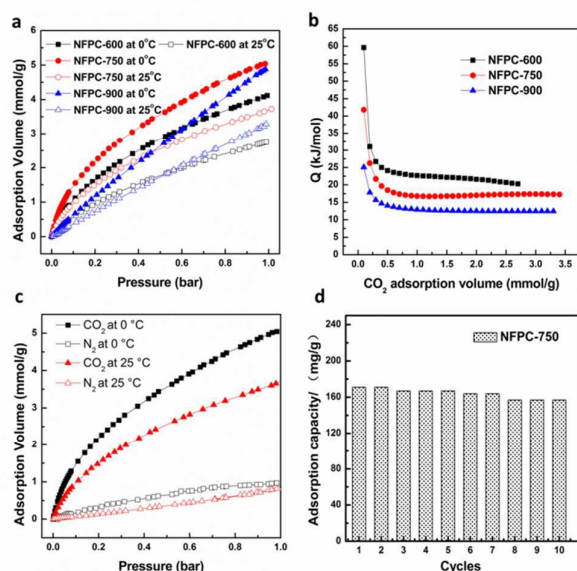


Fig. 5 (a) N₂ and CO₂ adsorption isotherms of NFPC-750 at 25 °C and 0 °C, respectively; (b) CO₂ adsorption isotherms of NFPC-Ts at 25 °C and 0 °C; (c) isosteric heat of CO₂ adsorption of NFPC-Ts as a function of CO₂ adsorption; and (d) CO₂ adsorption cycles of NFPC-750 at 25 °C.

contents of NFPC-Ts also decrease as the increase of T, the reduction of the interaction between CO₂ and NFPC-Ts corresponds to the removal of nitrogen groups. That is to say, N groups of NFPC-Ts play key roles in CO₂ adsorption. The high value of isosteric heat of adsorption of NFPC-750 (42 kJ/mol) demonstrates that its N groups are strong enough to act as basic sites. Q value obviously decreases with the increase of CO₂ adsorption volume, which suggests that the interaction becomes weaker with basic sites.^{19,24} The Q value of NFPC-750 finally remains stable at about 17 kJ/mol which means high affinity of this adsorbent to CO₂ even at high relative pressure.

Except for high capacity, adsorption selectivity between CO₂ and N₂ is also important for the sorbent. We examined the CO₂/N₂ selectivity of NFPC-750 at 25 °C and 0 °C (Fig. 5 (c)), respectively. It is found that the volume of adsorbed N₂ is much lower than that of adsorbed CO₂. At 1 bar and 25 °C, the volume of adsorbed N₂ (0.81 mmol/g) is 21.7% of adsorbed CO₂ (3.73 mmol/g). At 1 bar and 0 °C, the volume of adsorbed N₂ increases to 0.97 mmol/g, which is 19.2% of

adsorbed CO₂ (5.04 mmol/g). It indicates that NFPC-750 may perform better at lower temperature for CO₂ capture. The high CO₂/N₂ selectivity (at the ratio of 5.21 at 0 °C) suggests that NFPC-750 can be a selective sorbent for CO₂ over N₂.

The regeneration capacity of NFPC-750 was investigated via cycling adsorption and desorption. It was found that NFPC-750 showed good regeneration performance (Fig. 5 (d)). The CO₂ capture capacity retains high up to 157 mg/g after 10 cycles. It is about 91.8% of the initial capacity. The well regeneration performance of NFPC-750 makes it a promising sorbent that can be reused.

4. Conclusion

In summary, we have demonstrated a strategy to use fish scales to produce highly porous N-doped carbon for CO₂ capture. Upon optimization of the pore structure and N content (up to 2.90%), the CO₂ capture capacity of the carbon sorbent can be 171 mg/g at 25 °C. The N species on the carbon could be tuned by varying the thermal treatment temperature and KOH activation conditions. Quaternary N, but not pyridonic N and pyridinic N, showed higher stability during KOH activation. Interestingly, the peak value of specific surface area (up to 3206 m²/g) and micropore volume (up to 0.760 cm³/g) were obtained with KOH activation at 750 °C, and meanwhile quaternary N species were remained unchanged. In addition, NFPC-750 showed high affinity to CO₂ (isosteric heat of adsorption is 17 kJ/mol), high selectivity for CO₂ over N₂ (at the ratio of 5.21 at 0 °C), and good regeneration performance (up to 91.8% of the initial capacity after 10 cycles). All these outstanding characteristics indicate that fish scales can be a promising raw material for producing efficient CO₂ sorbent materials.

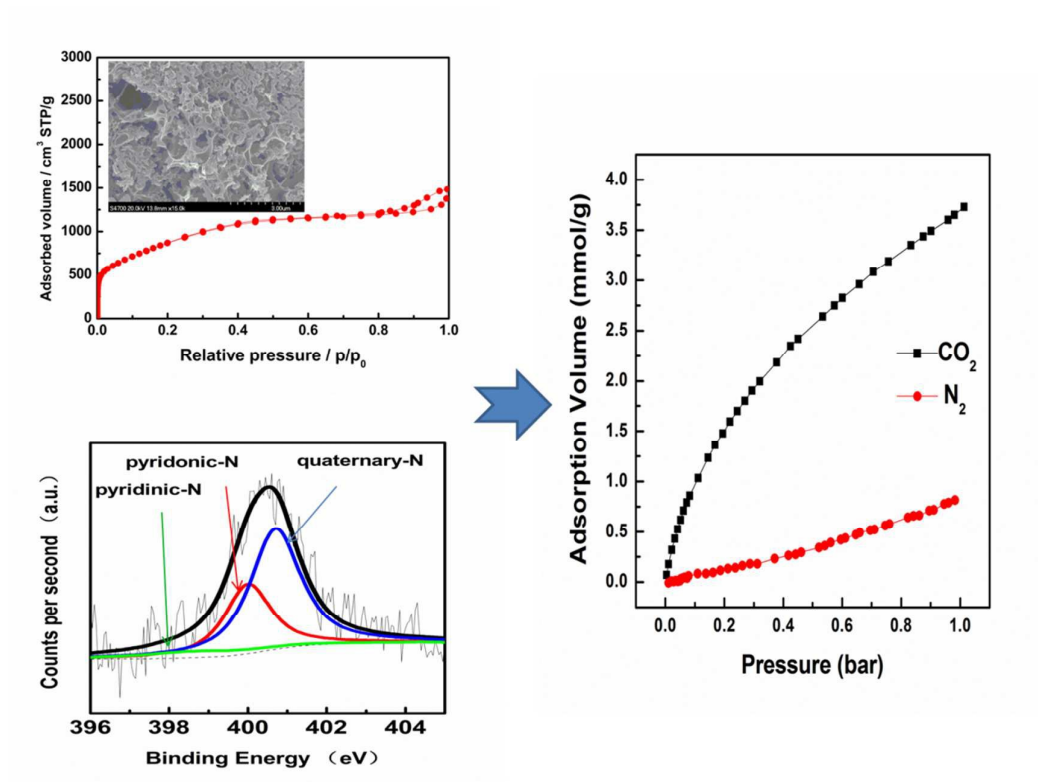
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Quaternary nitrogen effectively preserved and highly porous structure of the carbon lead to high CO₂ capacity.