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Nitrogen-doped arch and hollow shaped nanocarbons for CO₂ adsorption[†]

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We report arch and hollow nanocarbons with high nitrogen content and appreciable surface area that are highly capable of adsorbing CO₂ (4.23 mmol g⁻¹), are selective (CO₂/N₂: ~13%) and have high facile regeneration properties (98%) under ambient conditions, respectively.

Inefficient CO₂ sequestration during post- and pre-combustion processes in the energy sector causes venting of CO₂ into the atmosphere and increases the concentration of CO2 in the atmosphere, which directly impacts on global warming, a serious concern for our civilization.1 The conventional state-ofthe-art CO₂ sorbent (alkanolamine solution) used in power plants has critical issues, including corrosion control and additional energy consumption for sorbent regeneration.² Alternatively, various promising porous sorbents such as metalorganic frameworks (MOFs), microporous zeolites and activated carbons have been reported.3-5 Owing to stringent industrial requirements, the practical use of the majority of MOFs and zeolites could be restricted due to the complex and expensive synthesis approaches involved, despite them having better CO₂ sorbent characteristics. So, the development of an alternate porous sorbent with good CO₂ selective adsorption and regeneration for industrial realization is needed, but is still a major task.

In recent decades, porous carbon materials, a class of nanocarbons, have found potential applications in energy storage, gas adsorption, molecular separation, catalysis, and so on due to their tunable structural texture, adjustable surface functionality, chemical stability, low price and easy availability in versatile forms such as fibers, powders, sheets, foams, composites and tubes, *etc.*⁶⁻¹⁰ Porous carbons with surface

functionalized groups that have high surface area are the most desirable for obtaining high electro-sorption and gas sorption properties.11 Nitrogen functionalized carbon materials have drawn much attention for CO₂ adsorption, as N-doping generates basic groups that promote the adsorption of acidic CO₂ gas.12 Mostly, N-doped porous carbons are prepared by two common approaches: post heat treatment synthesis using high surface area carbon materials under a N-source, and an in situ synthesis approach, *i.e.*, a hard and soft template approach.¹³⁻¹⁶ However, the former approach results in low N-content, and in the latter approach complicated microphase separation, expensive templates for synthesis, toxic chemicals for etching and a time consuming tedious carbonization process are required.17 Alternatively, by using electrospinning, a high Ncontent can be obtained using N-source polymers.18 However, the N-doped carbon materials obtained using this approach often have limited surface area due to their cylindrical fibrous morphology. Thus, a post activation process using KOH treatment (physical or chemical activation) was adopted to increase the surface area, but at the cost of the high N-content.¹⁹ Thus, a facile and cost-effective method to fabricate N-doped nanocarbons with high surface area for CO₂ adsorption is also necessary for use in CO₂ capture applications.

Herein, we meticulously designed a new class of carbon material with a high level of N-doping and appreciable surface area. Porous carbon nanostructures with different morphologies were fabricated *via* a co-axial electrospinning approach, followed by leaching of sacrificial material using hot de-ionized water and a subsequent carbonization under inert atmosphere. Thus, two different N-doped carbon nanostructures, hollow (HCNR) and arch (ACNR) shaped morphologies, were obtained. The developed N-doped ACNR materials exhibit good textural properties along with a high N-content under ambient conditions, 298 K and 1 bar. In CO₂ capture studies, a maximum CO₂ adsorption of 4.23 mmol g⁻¹, a good CO₂ selectivity of ~13%, and a regenerative capability of 98%, were obtained.

The fabricated N-doped porous HCNR and ACNR are illustrated in Scheme 1. The co-axially prepared electro-spun fibrous

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Scheme 1 Schematic representation of HCNR and ACNR synthesis steps.

membranes of the HCNR and ACNR samples display average diameters of 270 and 330 nm, respectively. During the leaching process, the hydrophilic PVP core material was leached out completely from the electro-spun HCNR and ACNR membranes. Finally, carbonization of the HCNR material results in a hollow structure with a core diameter of 40 to 70 nm, while the carbonized ACNR material has an arch-shaped or semi hollow carbon nanostructure. Furthermore, during the carbonization, the diameters of the HCNR and ACNR decrease to 180 and 155 nm, respectively (Fig. 1(b) and (d)).

The FE-TEM images in Fig. 1(e) and (f) confirm the morphologies of the HCNR and ACNR samples. For comparison, carbon nanorods (CNRs) were fabricated using a single spinneret electrospinning approach and carbonized using the same parameters as used for the ACNR and HCNR samples. The carbonized CNRs display a typical cylindrical rod shaped morphology as shown in Fig. S1(a)–(d).†

The XRD spectra reveal that all the carbonized samples were turbostatic carbon in nature (Fig. S2†). Through CHNS elemental analysis, the N-contents were found to be 8.51, 7.53 and 8.07 weight% for the CNR, HCNR and ACNR samples, respectively. The XPS spectra of the N-doped carbon nano-structures show strong signals for carbon, nitrogen and oxygen. The deconvoluted N 1s spectra of all the samples show the existence of pyridinic-N and quaternary-N (Fig. S3†). It is noted that the nitrogen functionalities act as Lewis base sites, which are active for CO₂ sequestration.²⁰ The peak deconvolution

analysis shows that the amounts of pyridinic (N1) in the CNR, HCNR and ACNR samples were found to be 30, 37 and 35%, respectively.

Brunauer–Emmett–Teller (BET) measurements (Fig. S4 and Table S2†) reveal that the ACNR, HCNR and CNR samples exhibit BET surface areas (S_{BET}) of 619, 557 and 484 m² g⁻¹, respectively. The *t*-plot micropore surface areas for ACNR, HCNR and CNR are 432, 417 and 334 m² g⁻¹, indicating 70–74% microporosity in all the samples (Table S2†). The total pore volumes from NL-DFT studies for the ACNR, HCNR and CNR samples are 0.6589, 0.5681 and 0.4803 cm³ g⁻¹, respectively. The ACNR and HCNR samples exhibit high surface area, pore volume and micro-pore area, which means they could be highly suitable for gas sorption applications, such as H₂, CH₄, or CO₂ capture.

To counter a major greenhouse gas component, CO₂, our Ndoped porous carbon materials were employed for CO₂ sequestration and their performance was measured. Fig. 2(a)shows the CO₂ and N₂ adsorption isotherms of ACNR, HCNR and CNR at 298 K, which show that a maximum CO₂ adsorption of 4.23 mmol g^{-1} at 1 bar was observed for ACNR, higher than that of the other materials. Also, at 273 K, ACNR exhibits a high adsorption of 6.53 mmol g^{-1} at 1 bar (Fig. S5(a)[†] and Table 1). The high CO₂ adsorption of ACNR is due to its high surface area (619 m² g⁻¹), high pore volume (0.6589 cm³ g⁻¹) and high Ncontent (8.70 wt%). Also, the N-species from pyridinic groups, which as explained in the XPS studies exist in all N-doped carbon nanostructures and act as Lewis base sites for CO₂ adsorption, play a vital role, particularly in low pressure regions.20 In addition, the ACNR and HCNR samples display no saturation limit for CO₂ at 1 bar in comparison to the CNRs, which indicates that high CO2 adsorption could be possible at elevated pressures. The same phenomenon of CO₂ capture was even observed at various temperatures, including 273 K, 293 K and 303 K (Fig. S5(a)-(c)), and the obtained results are listed in Table 1. In comparison, the cylindrical CNR sample shows poor CO₂ adsorption because of its low surface area, despite it having a high N-content.



Fig. 1 HCNR sample FE-SEM (a and b) and FE-TEM (e) images. ACNR sample FE-SEM (c and d) and FE-TEM (f) images.



Comparison with the CO2 capture of various N-doped and N-

free state-of-the-art carbon sorbents suggests that higher and comparable CO_2 adsorption capacities for the ACNR and HCNR samples were achieved (Table S3[†]). It is clear from this

Fig. 2 (a) CO_2 adsorption and CO_2/N_2 selectivity tests conducted at 298 K for all samples. (b) CO_2 regenerative test for ACNR at 298 K using high purity CO_2 gas.

Table 1 \mbox{CO}_2 adsorption/separation performances of the N-doped ACNR, HCNR and CNR samples

	CO ₂ capture at 1 bar, at:				CO ₂ /N ₂ selectivity at 298 K, at:		
Sample	273 K	293 K	298 K	303 K	0.15 bar	0.85 bar	$\rm CO_2/N_2^{a}$
ACNR	6.53	4.49	4.23	3.95	1.51	0.63	13.53
HCNR	6.00	4.16	3.75	3.58	1.00	0.59	9.63
CNR	2.72	2.58	1.98	1.75	0.84	0.51	8.87
^a From I	AST at a	$CO_2: N$	I_2 ratio o	of 0.15 :	0.85 bar at	298 K.	

comparison that N-doped ACNR could be considered amongst the potential N-doped carbon materials for $\rm CO_2$ adsorption applications.

In addition to CO_2 adsorption evaluation, the selectivity for CO_2 over other flue gas components, predominately N_2 gas (70–80%), is crucial for power plants during the post combustion process. It is also to be expected that the presence of N-content could result in the preferential adsorption of CO_2 over N_2 .²¹ Thus the ideal adsorption solution theory (IAST) was used to evaluate the selectivity for CO_2/N_2 of all the samples. As shown in Fig. 2(a), the selectivities for CO_2 over N_2 gas at 298 K for ACNR, HCNR and CNR were found to be 13.53, 9.63, and 8.87%, respectively, which reveals that the ACNR sorbent has good selectivity for CO_2 gas. Also, ACNR selectivity is higher than that of other porous materials, such as MOF-253, which possesses a selectivity of 12%.²²

For industrial CO₂ capture applications, the adsorbents should possesses the critical criteria of high cyclic stability towards CO₂ adsorption. To ascertain this, a CO₂ regenerative/ cycle test for the best CO₂ adsorption sample, ACNR, was tested by performing ten subsequent adsorption–desorption processes at 298 K under vacuum evacuation, and monitoring each cycle (Fig. 2(b)). This revealed that ACNR has 98% CO₂ retention after 10 cycles. Thus, the ACNR sample with high CO₂ adsorption, good selectivity and regenerative capability characteristics is impressive for industrial applications.

Also, to determine the strength of interaction between CO_2 and our N-doped carbon materials the isosteric heat of adsorption (Q_{st}) was calculated using the Clausius-Clapeyron equation for CO₂ isotherms performed at 273, 293, 298 and 303 K (Fig. S5(d)[†]). The Q_{st} evaluated for all samples indicate the physisorption nature of an absorbent, i.e., weak van der Waals forces. Also, it was found that N-content in all the samples could substantially improve the isosteric heat of adsorption at low coverage, but the micropores play a vital role in high coverage, which overshadows the N-content role. From the results, ACNR had the highest Q_{st} value, 36.27 kJ mol⁻¹; HCNR and CNR had lower $Q_{\rm st}$ values of 20.80 kJ mol⁻¹ and 7.8 kJ mol⁻¹, respectively. In general, the high $Q_{\rm st}$ is a necessary criteria for flue gas separation, owing to the high CO₂ uptake at very low pressure. At the same time, too high a Q_{st} , which would result in chemisorption, would cause difficulty in the regeneration of the sorbents.²³ Notably, ACNR with a $Q_{\rm st}$ of 36.27 kJ mol⁻¹ is highly suitable for flue gas separations.

In summary, we have successfully developed high N-content and appreciable surface area of arch and hollow nanocarbons, by using a simple co-axial electrospinning technique. Their CO_2 uptake properties were demonstrated to be superior in all aspects, including higher CO_2 uptake amounts, selectivity of CO_2 at low pressure, regenerative capability and much higher Q_{st} . Nanocarbons enabling such cost effective and appreciable CO_2 sequestration could possibly meet the criteria of commercial CO_2 sorbents. Further, we hope that these unique N-doped nanocarbon structures will open new opportunities in applications related to H_2 adsorption, electrocatalysts for CO_2 reduction, energy storage, separation, and medicine.

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