**High-surface-area and high-nitrogen-content carbon microspheres
prepared by a pre-oxidation and mild KOH activation for superior
supercapacitor**

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Abstract:

KOH activation is a well-accepted approach to develop microporosity for porous carbons, but its severe etching reactions could inevitably destroy the structural integrity and diminish the heteroatomic surface chemistry of the resultant carbons. Herein, we report a method to prepare well-defined micro-spherical, high-surface-area and high-nitrogen-doping carbons via a mild KOH activation. The key to our synthesis relies in the pre-oxidation of the nitrogen-rich polymeric microspheres from resorcinol, formaldehyde and melamine, which could enrich nitrogen heteroatoms into the resultant carbonized framework, resulting in the carbon easily activated by KOH with low surface etching and high residual of nitrogen heteroatoms. The obtained carbons possess high specific surface area of 2234-3121 m²/g, high nitrogen content of 6.1-12.5 wt. % and well-preserved spherical morphology. When used as the electrodes of supercapacitor, these carbon microspheres could deliver high specific capacitance up to 309 F/g, excellent rate performance and high cyclic performance of 96 % after 5000 cycles in H₂SO₄ electrolyte. Furthermore, it is found that nitrogen functionalities could contribute considerable pseudo-capacitance, basically through Faradic reactions of the nitrogen.

1. Introduction

High-surface-area porous carbon materials have attracted widespread interest in energy storage [1, 2], catalysis [3, 4] and adsorption [5-7], owing to their unique characteristics including developed porosity, good electrical conductivity, and excellent thermal and chemical stability in combination with availability. Although a variety of methods such as direct pyrolysis [8, 9], hard template [10, 11] and soft template [12, 13] method have been employed to prepare high-surface-area carbons, carbonization of carbonaceous precursors followed by physical or chemical activation is still most easily accomplished both in research and commercial production, due to its low cost and easy to scale up [14, 15]. In particular, the KOH chemical activation is very promising since it can produce the carbons with huge surface areas up to 3000 m²/g [16]. This method has been successfully commercialized by some companies since 30 years ago [16].

The development of porosity by KOH activation is a very complex and strong chemical process, generally including K-compounds etching of carbon framework, physical activation by as-formed H₂O and CO₂, and carbon lattice expansion by the metallic K intercalation [17-19]. This process could give the carbons with well-developed porosity and plenty of oxygen containing functional groups (~ 10 wt. %), but generally at a cost of macro-structural deficiency and poor heteroatomic surface chemistry. It has been widely reported that the properties of porous carbons depend to a large extent not only on the porosity but also on the heteroatoms that decorate their surface. The most popular heteroatoms such as nitrogen could

alter the electronic and crystalline structures of the carbons, enhancing their chemical stability, surface polarity, electric conductivity, and electron-donor properties [20]. By employing nitrogen-containing precursors, the resulting KOH-activated carbons could inherit partial nitrogen atoms into carbon framework. Unfortunately, the nitrogen doping level is very limited [21-24]. For example, Zhou et al [21] prepared nitrogen-doped carbons by KOH activation of nitrogen-enriched precursors from the polymerization of ethylene diamine and carbon tetrachloride. They found that the porosity and nitrogen content were both depended strongly on the weight ratio of KOH/carbon, and high nitrogen content was always against high surface area. Only 1.1 wt. % nitrogen content could be achieved for the carbons with a high surface area of 1913 m²/g. Similarly, Sevilla et al [22] prepared highly porous N-doped carbons by using polypyrrole as carbon precursor. They concluded that only mild KOH activation could produce the carbons with relatively high nitrogen content (10.14 wt. %) but with an un-developed microporosity. Zhou's group [23] employed KOH activation to prepare N-doped polyaniline-based carbons, which had very high BET surface area but relatively low nitrogen content (<5 at. %). Su et al [24] prepared polypyrrole-derived carbons and found that while the specific surface area of the carbons was up to 1080 m²/g, their nitrogen content dropped below 2.2 %. From the above results, it seems that high surface area and high nitrogen content are two complicating features, which are hard to achieve simultaneously for the porous carbons prepared by KOH activation. This may be due to less stability of nitrogen species, which could be easily decomposed under severe activation process during the creation of highly developed porosity.

In addition to the porosity and surface chemistry, macroscopic morphology is also crucial to

the application properties of porous carbons [25, 26]. Recently, significant research activities have been undertaken to prepare porous carbons with micro-spherical morphology, which could give the carbon extra functionalities such as regular particle size, high packing density and high fluidity [27, 28]. Further development of microporosity into these carbon microspheres by KOH activation is of great importance for extending their applications. Even using well-defined spherical precursors, it is still hard to prepare carbons that could fully inherit morphology of precursors[29, 30], mostly due to the strong surface etching according to KOH activation mechanism. Romero-Anaya et al [29] observed that the strong KOH activation could completely destroy the morphology of hydrothermal-obtained carbon microspheres. In addition, Wickramaratne et al [30] found that KOH activation of polymeric microspheres resulted in structural disintegration with the presence of flake-like morphology. Thus, preserving the well-defined morphology is a challenging task for the porous carbons prepared by KOH activation. This may be succeed via decreasing the activation degree but at the cost of porosity development.

Herein, we developed a mild KOH activation method to prepare the well-defined spherical, high-surface-area and high-nitrogen-content porous carbon materials, having all the above factors in consideration. The preparation starts with the aqueous polymerization of nitrogen-rich polymeric microspheres only using resorcinol, formaldehyde and melamine, followed by pre-oxidation, carbonization and mild KOH activation. The kernel of our method is relied on the pre-oxidation of such polymeric microspheres, which could greatly enrich nitrogen heteroatoms into the resultant carbonized microspheres (up to 28.3 wt. %). During the rebuilding of carbon structures upon consequent KOH activation, such plenty of nitrogen

groups is more reactive with K species, giving the carbons with higher BET surface area, larger pore volume and broader pore size distribution. Under very mild conditions, the obtained carbon microspheres have a well-developed microporosity (2234-3121 cm²/g) without sacrificing the microspherical morphology. And more importantly, the plenty of nitrogen groups enriched by pre-oxidation could provide great opportunity for high-level nitrogen doping, giving the carbons exceptional nitrogen contents of up to 12.5 wt. %. Such value is a highest value among all high-surface-area carbons reported so far. Because of their favorable structural and chemical properties, these materials have been employed as electrodes for supercapacitors yielding a high capacitance, excellent rate capability and outstanding cycling stability. The present work provides a contribution towards the implementation of the KOH activation for the preparation the porous carbon with well-defined morphology, high microporosity and rich surface chemistry, for which numerous applications have been reported within the available literature.

2. Experimental section

2.1 Material preparation

All the chemicals were purchased from Titanchem Co. and without further purification. The polymer microspheres were prepared via a polymerization process using resorcinol (R) and formaldehyde (F) as the carbon source and melamine (M) as the nitrogen source, according to our previous work [31]. In a scale-up preparation, 276.9 g of formaldehyde (F, 37 wt. %, 3.32 mol) and 182.7 g of resorcinol (R, 1.66 mol) were dissolved in 1650 mL distilled water and then stirred at 40 °C for 2 h. Another part of formaldehyde (830.6 g, 9.96

mol) and 418.6 g of melamine (M, 3.32 mol) dissolved in 1650 mL distilled water at 80 °C was then added to the above solution with consecutive agitation. The mixture solution was sealed into a 5 L stainless steel autoclave followed by polymerization at 80 °C for 24 h (see **Fig. S1a**). After air-dried at 80 °C for 12 h, as-prepared nitrogen-rich polymer microspheres were collected and denoted as NPM.

In order to obtain high-surface-area and high-nitrogen-content microporous carbon microspheres, the NPMs were oxidized at 250 °C in air flow for 2 h at the rate of 1 °C/min to obtain the nitrogen-rich polymeric microspheres (O-NPM). The carbonization of O-NPMs was carried out in a tube furnace under flowing nitrogen with a heating rate of 1 °C/min up to 700 °C for 2h. The obtained nitrogen-doped carbon microspheres were denoted as O-NCM.

The KOH activation was performed by placing a nickel boat with O-NCM and KOH under a N₂ flow at 700 °C for 2 h. The obtained materials were liberated by removing inorganic salts using 1 mol/L HCl and washed with deionized water until a neutral pH. The resultant microporous carbon microspheres were denoted as O-ACM-y, where y means the mass ratio of KOH to O-NCM. Taking the activation of O-NCM with the KOH/O-NCM weight ratio of 1 for example, 2 g of O-NCM was impregnated with 10 wt. % KOH solution containing 2 g of KOH, followed by an evaporation step at 80 °C. Then, the impregnated carbons were activated at 700 °C for 2h.

For comparison, the NPMs were directly carbonized at 700 °C for 2h, followed by the same KOH activation with O-NCM. The carbonized and activated samples without pre-oxidation were marked as NCM and ACM-y, corresponding to the O-NCM and O-ACM-y, respectively.

2.2 Characterization

The morphology of the polymer and carbon microspheres were examined by using a Field Emission Scanning Electron Microscope (FE-SEM, Nova NanoSEM450) at 3 kV and a Transmission Electron Microscope (HR-TEM, JEOL2100F) at 200 kV. The solid ^{13}C CP/MAS experiments were performed on a Bruker AVANCE III 400 WB spectrometer operating at 100.62 MHz for ^{13}C . A 4 mm double resonance MAS probe was used for the experiments. The spinning rate was set to 5 kHz. The cross polarization time was 1 ms. The ^{13}C chemical shifts were calibrated using adamantane ($\delta=38.56$ ppm). Elemental analysis was carried out using an Elemental Vario EL III. The carbon (C), hydrogen (H), and nitrogen (N) contents of the carbons were determined directly using the thermal conductivity detector. The porosity of microporous carbon microspheres were determined using nitrogen adsorption-desorption isotherms at 77 K (Micromeritics ASAP 2020). Prior to the measurement, the samples were degassed in vacuum at 473 K for 10 h. The specific surface area was calculated based on the Brunauer–Emmett–Teller (BET) method while the total pore volume was obtained using a single point at a relative pressure of 0.985. The micropore surface area (S_{micro}) and micropore volume (V_{micro}) were calculated using t-plot method. The pore size distributions (PSDs) were determined from the quenched solid-state density functional theory (QSDFT). Axis Ultra DLD X-ray photoelectron spectrometer (XPS) was used to determine the surface elemental composition of microporous carbon microspheres. The XPS spectra of C1s and N1s were all measured at a step size of 0.1 eV. The background of N1s XPS signals were subtract using a Shirley function and the N1s signals were fitted with the mixed Lorentzian-Gaussian curves using XPS peak processing software.

2.3 Electrochemical measurements

The electrodes were fabricated from a blend of 85 wt. % of the as prepared samples, 10 wt. % of carbon black and 5 wt. % of binder polytetrafluoroethylene (PTFE) suspended in ethanol. The slurry was continually stirred to evaporate the ethanol, then rolled into a thin film of uniform thickness, and finally punched into the electrode with a diameter of 12 mm. Each electrode has a thickness of ca. 90 μm with a mass loading of ca. 4 mg/cm^2 . The capacitive performance of as prepared activated carbon microspheres was evaluated with a special-designed Teflon Swagelok-type two-electrode cell together with an Ag/AgCl electrode, which was constructed with two facing carbon electrodes, sandwiched with a separator. Pt plates were used as current collectors and H_2SO_4 (3 mol/L) was employed as the electrolyte.

The cyclic voltammetry (CV) in the voltage range of 0-0.9 V and electrochemical impedance spectroscopy (EIS) in a frequency range from 100 kHz to 10 mHz were performed with an electrochemical working station PCI4/300 (Gamry Instrument). The galvanostatic charge-discharge test and cycle performance were conducted using an Arbin battery cycler (Arbin BT2000). The gravimetric specific capacitance C_g was calculated according to the following equation using the discharge curves:

$$C_g = 2 \times \frac{I \Delta t}{m \Delta V} \quad (1)$$

Where I , t , m and ΔV are discharge (charge) current, discharge time, the mass of active material on one electrode and voltage change during discharge process, respectively.

3. Result and discussion

3.1 Preparation of activated carbon microspheres

Fig. 1 Schematic illustration of the formation process for activated carbon microspheres

Monodispersed nitrogen-rich polymeric microspheres (NPMs) could be obtained by a one-pot co-polymerization of melamine (M), resorcinol (R) and formaldehyde (F) in water, according to our previous work [34]. The co-polymerization of R-M-F could successfully build three-dimensional homogeneous structure with adjusted nitrogen content from 0 to 30.7 wt. % by changing the initial M/R ratio in the precursors [31]. The total synthesis of NPMs is very facile and cost-effective, which have a great potential to be produced on an industrial scale. Herein, the NPMs with the M/F ratio of 2 were prepared in a kilogram-scale by using a 5 L reactor (**Fig. S1a**) for the consequent carbonization and KOH activation study. The obtained NPMs have a very uniform particle size of 2 μm (see SEM image in **Fig. S1b**) and high nitrogen content of 30.7 wt. % (CHN result in **Table 1**). Direct carbonization of these NPMs could produce the carbon microspheres (NCMs) with slightly decreased particle size of 1.5 μm but still a high nitrogen content of 13.9 wt. %. However, while these carbonized microspheres were subsequent to KOH activation even at mild KOH conditions (the mass ratio of $\text{KOH}/\text{NCM} \leq 2$, at 700 $^{\circ}\text{C}$ for 2 h), the resultant activated carbon microspheres have more-or-less morphological deficiency, less-developed microporosity and relatively low

nitrogen content of ≤ 5.4 wt. %. Therefore, to achieve simultaneously well-defined morphology, well-developed microporosity and very-high nitrogen content for the carbons, we develop a modified approach through the pre-oxidation of the NMPs, followed by carbonization and mild KOH activation as illustrated in **Fig. 1**.

Table 1 Chemical composition of as-prepared samples

Sample	C (wt. %)	N (wt. %)	H (wt. %)	O (wt. %)	N/C (at. / at.)
NPM	41.9	30.7	4.7	22.7	0.63
O-NPM	40.5	40.9	3.8	14.8	0.87
NCM	78.8	13.9	1.6	5.7	0.15
O-NCM	65.1	28.3	1.7	4.9	0.37

Fig. 2 FTIR spectra (a) and ^{13}C NMR spectra (b) of NPM and O-NPM

Slow thermal oxidation is a common strategy for some carbon precursors (PAN, pitch) to stabilize their thermoplastic structure prior to further carbonization [32, 33]. By adopting the similar method, however, the thermosetting NPMs had experienced exceptional chemical-structure changes by oxidation at 250 °C. CHN elemental analysis results (**Table 1**) indicate that after the oxidation, only the N content increases remarkably, while the C, O, H contents are all declined. This is apparently different with the oxidative stabilization of nitrogen-rich PAN precursors, which is a definite oxygen-enriched and nitrogen-decreased process [33]. To understand such uncommon change, FTIR and ^{13}C -NMR were used to analyze the structural evolution of NPMs before and after the oxidation. The FTIR spectra (**Fig. 2a**) demonstrate that the adsorption peaks of $-\text{CH}_2$ stretching and scissor vibrations at 2930 and 1480 cm^{-1} [34] disappear, while the peaks of $-\text{CH}_2\text{-O-CH}_2-$ stretching vibration at ca. 1092 cm^{-1} greatly weaken. These results suggest that some of $-\text{CH}_2$ and $-\text{CH}_2\text{-O-CH}_2$ groups of phenolic structure are oxidized to CO_2 and H_2O during the pre-oxidation. Furthermore, ^{13}C NMR spectra (**Fig. 2b**) also show that the $-\text{CH}_2$ peaks at 73, 66, 55, 40.6, 29.8 and 23.6 ppm, which may represent carbons in $-\text{NH}\underline{\text{C}}\text{H}_2\text{OCH}_2\text{NH}-$, aromatic $\underline{\text{C}}\text{H}_2\text{-O-CH}_2\text{OH}$, $-\text{CH}_2\text{-O-}\underline{\text{C}}\text{H}_3$, aromatic- $\underline{\text{C}}\text{H}_2\text{NH}-$, 4,4'- and 2,4'-methylene bridged carbons adjacent to the aromatic ring of resorcinol, respectively [35, 36], disappear after the oxidation. In addition, the vanishing peak at 180 ppm in ^{13}C NMR spectra means the removal of $-\text{C=O}$ groups. On the other hand, after the thermal oxidation, the N containing groups can be well reserved and some of them form new bonds. Aromatic C=N stretching at 1350 and 1558 cm^{-1} in FTIR and the triazine unit peaks at 166 ppm in ^{13}C NMR [37] do not change, which means the triazine structure is stable in the oxidation process. The new peak at ca.

1390 cm^{-1} (C-H bending vibrations in -HN-CH₂-NH-) in FTIR and larger peak at 47 ppm in ¹³C NMR, responding to the formation of methylene bridges between secondary amines (-HN-CH₂-NH-) [36, 38, 39], could be discerned. This might be contributed to the condensation reaction of -NH₂ and -NHCH₂OH groups during the thermal oxidation. Also, a new peak at 1260 cm^{-1} confirms the formation of aromatic C-N bond [40], which may result from the reaction of -NH₂ groups, the -CH or -OH on the benzene ring and O₂ during the thermal oxidation. The result is also corresponding to the disappearance of aromatic carbons connected to -OH and non-substituted aromatic carbons in meta positions at 153, 131 and 103 ppm [34, 35]. Thus, all the above results indicate that the thermal oxidation of NPMs could not only release the thermally-unstable -CH₂, -OH groups, but also enrich the N species such as -HN-CH₂-NH- and aromatic C-N (see possible reaction pathways in **Fig. 1**), giving the ultra-high nitrogen content in the O-NPMs up to 40.9 wt. % (**Table 1**).

While the nitrogen-rich O-NPMs are subsequent to carbonization at 700 °C, as-obtained nitrogen-doped carbon microspheres (labelled as O-NCM) have an ultra-high nitrogen content of 28.3 wt. % (**Table 1**). On the contrast, direct carbonization of NPM could produce the nitrogen-doped carbon microspheres (NCM) with only a nitrogen content of 13.9 wt. %. These two kinds of carbon microspheres, originating from the same polymer precursor but having different pretreatments, were selected as the carbon sources to further prepare activated carbon microspheres (O-ACM and ACM) by mild KOH activation ($\text{KOH/C} \leq 2$, at 700 °C for 2h).

Fig 3. N₂ adsorption/desorption isotherms (a) and pore size distributions (b) of as prepared ACMs and O-ACMs

Table 2. Porosity parameters of as prepared ACMs and O-ACMs

Sample	S_{BET}^a (m ² /g)	S_{Micro} (m ² /g)	$S_{\text{Micro}}/$ S_{BET}	V_{Total}^b (cm ³ /g)	V_{Micro}^c (cm ³ /g)	$V_{\text{Micro}}/$ V_{Total}
ACM-1	1599	1458	0.91	0.76	0.63	0.83
O-ACM-1	2234	1993	0.89	1.10	0.87	0.79
ACM-2	2085	1878	0.9	1.03	0.84	0.81
O-ACM-2	3121	2576	0.82	1.68	1.17	0.70

^a S_{BET} : specific surface area. ^b V_{Total} : total pore volume measured at $P/P_0 = 0.985$. ^c V_{Micro} : micropore volume determined from the t -plot method.

Fig. 3 shows the N₂ adsorption-desorption isotherms and resultant QSDFT pore size distributions of two series of samples. In general, all the samples have a similar type I isotherm with significant adsorption amount below relative pressure P/P_0 of 0.1,

corresponding to the typical microporous structure. But apparently, the O-ACMs experienced by the pre-oxidation have much developed porosity than the ACMs, as shown in **Table 2**. At a low activation condition (KOH/C=1), the O-ACM-1 have a higher BET specific surface area of 2234 m²/g and a higher pore volume of 1.10 cm³/g than these of ACM-1 (1599 m²/g and 0.76 cm³/g, respectively). Increasing the KOH/C ratio to 2 could develop the porosity greatly both for two samples. But similarly, the O-ACM-2 have much larger surface area (up to 3121 m²/g), higher pore volume and broader pore size distribution.

Fig 4 SEM images of ACM-1 (a), ACM-2 (b), O-ACM-1 (c), and O-ACM-2 (d) and TEM images of O-ACM-2 (e and f)

Pre-oxidation has another prime advantage on preserving the micro-spherical morphology. As shown in **Fig. 4**, SEM images well confirm that both O-ACM-1 and ACM-1 exhibit well microspherical morphology with smooth surface under a low KOH/C ratio of 1. However, while KOH/C ratio increases to 2, the O-ACM-2 could reserve the micro-morphology better than the ACM-2. TEM images (**Fig. 4e and f**) further confirm the O-ACM-2 have good spherical morphology with an average particle size of $\sim 1.2 \mu\text{m}$.

The other advantage of pre-oxidation is the capability of enabling high-level nitrogen doping into the well-developed porous carbon framework. As shown in **Table 3**, the ACM series samples have very limited nitrogen content. Even under a very low KOH/C ratio, their nitrogen content is only 5.4 wt. % for ACM-1. On the contrast, the O-ACM series samples have unprecedentedly high nitrogen content, and it is about 12.5 wt. % for O-CAM-1 and 6.1 wt. % for O-CAM-2. As far as we known, such high nitrogen content is rarely reported for the porous carbons, especially for these with very high surface area (up to $2200 \text{ m}^2/\text{g}$) prepared by KOH activation (see comparison in **Table S1**) [41-43].

Table 3 Chemical composition of ACMs and O-ACMs by element analysis and XPS.

Sample	Element Analysis				XPS ^a			
	C	N	O	N/C	C	N	O	N/C
	wt. %	wt. %	wt. %	at./at	at. %	at. %	at. %	at./at
ACM-1	80.8	5.4	12.2	0.06	74.8	10.8	14.4	0.14
O-ACM-1	75.3	12.5	9.3	0.14	61.0	25.2	13.8	0.41
ACM-2	81.4	3.4	12.6	0.04	82.5	5.0	12.5	0.06
O-ACM-2	79.4	6.1	13.3	0.07	80.1	7.9	12.0	0.10

^a: C+N+O=100%

Furthermore, XPS spectra (**Fig. 5**) was employed to compare differences of the chemical composition and surface nitrogen bonding configurations between these samples. The survey spectra show three peaks located at 284.6, 400.0, and 513.4 eV, related to C 1s, N 1s, and O 1s, respectively (**Fig. 5a**). In general, the calculated nitrogen contents from XPS (**Table 3**) are much higher than the corresponding values obtained by elemental analysis. This should be due to the surface specificity of XPS measurements, indicating that the nitrogen atoms are apt to enrich on the surface rather than the bulk of carbon framework.

Fig. 5. XPS survey (a), high-resolution C1s (b) and high-resolution N1s (c) spectra and nitrogen species distributions (d) of ACMs and O-ACMs

The XPS spectra of C1s (**Fig. 5b**) show a very similar asymmetric peak shape. The main peak at 284.6 eV is related to the graphitic carbon, indicating that most of the C atoms are

arranged in a conjugated honeycomb lattice [44]. The N1s spectra (**Fig. 5c**) are further curve-fitted into four peaks with binding energies of 398.7 ± 0.3 , 400.3 ± 0.3 , 401.4 ± 0.5 and 403.6 ± 0.3 eV that corresponded to pyridinic N (N-6), pyrrolic/pyridine N (N-5), quaternary N (N-Q) and pyridine N-oxide (N-X), respectively [45, 46]. It is noteworthy that all the samples show a similar nitrogen species (**Fig. 5d**) and a majority (74%~80%) of nitrogen atoms are located at the edges of graphene layers (N-6, N-5) while nitrogen atoms located at the central region of graphene layers (N-Q) contribute to a minor portion. Therefore, the activated samples have similar nitrogen bonding configurations regardless of the pre-oxidation experience and the nitrogen content of the materials.

From the above results, we could conclude that the pre-oxidation of the NPMs plays an important role on the porosity development, morphology preserving and nitrogen content of the porous carbons prepared by KOH activation. This should be due to the presence of plenty of nitrogen functionalities in the carbon framework induced by pre-oxidation. During the rebuilding of carbon structures upon consequent KOH activation, such nitrogen functionalities are more reactive with K species, giving the carbons with more developed porosity and larger pore size. Meanwhile, more K species could be diffused into the deep body of the carbon through the new-formed microporous channels, thus alleviating the surface etching degree. As a result, the obtained carbon microspheres have a well-developed microporosity without sacrificing the microspherical morphology. Furthermore, the plenty of nitrogen functionalities could provide great opportunity for high-level nitrogen doping even under harsh conditions, giving the carbons simultaneously with exceptional nitrogen content and very high BET surface area.

3.2 Supercapacitor performance of the activated carbon microspheres

Considering the multiple advantages of the O-ACMs, such as high BET surface area, high nitrogen content, regular micro-spherical geometry and suitable particle size, these materials should be good candidates for supercapacitor electrodes with improved electrochemical performance.

Herein, the capacitive performance of the O-ACMs and ACMs were firstly evaluated in symmetrical two-electrode cells in 3 mol/L H₂SO₄ electrolyte. **Fig. 6a and Fig. S2** show the typical CV curves of the samples at a scan rate from 5 to 100 mV/s. For samples with relatively low nitrogen content (≤ 6.1 wt. %), their CV curves in **Fig. 6a** show a typical rectangular shape, conforming the capacitive response majorly coming from the electrical double-layer formation. However, for the O-ACM-1 with 12.5 wt. % nitrogen, its CV demonstrates partially asymmetric shape, possibly due to the contribution of nitrogen functionalities-induced pseudo-capacitive reactions [12]. **Fig. 6b** shows the galvanostatic charge/discharge curves at current density of 0.1 A/g. The specific capacitances are calculated from the discharge curves with values of 233, 309, 249 and 279 F/g for ACM-1, O-ACM-1, ACM-2 and O-ACM-2, respectively. Interestingly, the highest capacitance is achieved for O-ACM-1, which has only mediate BET surface area of 2234 m²/g but highest nitrogen content of 12.5 wt. %. This result indicates that the nitrogen functionalities should contribute considerable pseudo-capacitance on the total capacitance of the material [48].

The charge-discharge curves at current densities and resultant rate performance are plotted in **Fig. S3 and Fig. 6c**, respectively. All the samples have good capacitance retentions in the

range of 72-78 % while the current density increases from 0.1 to 20 A/g. It is noted that the O-ACM-2 has highest capacitance retention, although its capacitance is lower than that of O-ACM-1. This should be ascribed to more developed porosity of O-ACM-2, which can decrease the ion diffusion resistance during charging-discharging process. The EIS testing could well confirm this conclusion as shown in Fig. S4. Furthermore, cycling testing shows that these samples have apparent physical stabilities and good cyclic performance, with ca. 95.7 %, 96.0 %, 96.4 % and 96.9 % of the initial capacitance after 5000 cycles (1 A/g) for ACM-1, O-ACM-1, ACM-2 and O-ACM-2, respectively.

Fig. 6. Electrochemical capacitive behavior of Activated carbon microspheres: cyclic voltammetry (a), galvanostatic charge-discharge curves (b), rate performance (c) and cycling performance (d)

Fig. 7 Potential profiles of the positive and negative electrodes during galvanostatic charge/discharge for ACM-1 (a), O-ACM-A (b), ACM-2 (c) and O-ACM-2 (d), the positive and negative gravimetric capacitances (e) and the difference (ΔC) between the specific capacitance negative and positive electrode (f) of activated carbon microspheres.

Apparently, nitrogen doping does not affect significantly the rate and cyclic performance, but it indeed contributes extra pseudo-capacitance. To further understand such pseudo-capacitive contribution, a special-designed two-electrode cell together with an Ag/AgCl electrode (see illustrated in **Fig. S5**) was used to study the positive electrode and negative electrode simultaneously. In such a cell configuration, the charge/discharge curves of each individual electrode as well as the cell could be recorded separately.

Fig. 7a-d show the typical galvanostatic charge-discharge profiles and potential ranges for each individual electrode and cell at the current density of 0.1 A/g. The potentials of the positive and negative electrodes (right Y-axis) vs Ag/AgCl are automatically recorded corresponding to applied cell voltage (left Y-axis) of 0-0.9 V in H₂SO₄ electrolyte. In principle, the charge stored at the positive and negative electrodes should be equivalent ($Q_+ = Q_-$). The charged stored by each electrode depends on the specific capacitance (C), the potential range (ΔE), and mass of electrode (m) according to

$$Q = C \times m \times \Delta E \quad (2)$$

And then for the positive (+) and negative (-) with the same mass m :

$$C_+ \times \Delta E_+ = C_- \times \Delta E_- \quad (3)$$

For all the samples, the potential range of the positive electrode (ΔE_+) is larger than that of the negative electrode (ΔE_-) (see results in **Table S2**), which means that the capacitance of positive electrode is lower than of the negative one. More importantly, the higher nitrogen content the samples have, the smaller ΔE_- and higher C_- they deliver. For O-ACM-1 with 12.5 wt. % nitrogen, its ΔE_- is only 0.42 V, while for ACM-2 with least nitrogen content (3.4 wt. %) its ΔE_- is 0.44 V (close to the half of work potential, 0.45 V).

According to equation (3), the specific capacitances of positive and negative electrodes at 0.1 A/g are calculated and given in **Fig. 7e**. Obviously, all the cells exhibit an asymmetrical behavior with high capacitance of negative electrode and low capacitance of positive electrode. And such asymmetrical behavior becomes more serious for the sample with higher nitrogen content. For example, the specific capacitance of negative electrode of O-ACM-1 is 330.6 F/g, about 40 F/g higher than that of positive electrode. For comparison, the carbon

microspheres without nitrogen functionalities were prepared using the same method with O-ACM-1, but without melamine in the precursor. As shown in **Fig.S6**, the sample possess the specific surface area of 1101 m²/g and total pore volume of 0.46 cm³/g. The element analysis shows that the oxygen content of the sample is 9.5 wt.%. While used as electrodes for supercapacitor, the sample shows the specific capacitance of 155 F/g. The ΔC of the comparison sample is only 0.7 F/g, which could be ignored. These results may indicate that the nitrogen functionalities play an important role in the total capacitance, especially in negative electrode. This may originate from the fast Faradic reactions between the Lewis basic pyridinic N (N-6), pyrrolic/pyridine N (N-5) and the H⁺ occurred more easily at the material interface of negative electrode [48]. Furthermore, it is found that the difference between the capacitance of negative electrode and the capacitance of positive electrode(ΔC) decreases with the increase of current density (**Fig. 7f**), possibly for nitrogen functionalities-induced redox reaction is limited by the ion diffusion at a high current density[49]. Therefore, the nitrogen functionalities should exhibit an asymmetric pseudo-capacitance contribution between the positive and negative electrodes in H₂SO₄ electrolyte, and the poor capacitance of positive electrode with less pseudo-capacitance contribution should be the key factor that limits the capacitance of whole device.

4. Conclusion

In conclusion, a new method of preparing porous carbons with well-developed microporosity, well-defined morphology and very-high nitrogen content has been developed via pre-oxidation, carbonization and mild KOH activation of nitrogen-rich polymeric microspheres. Pre-oxidation could stabilize and enrich nitrogen heteroatoms into the resultant

carbonized framework for the polymer from resorcinol, formaldehyde and melamine, leading to the carbon easily activated by KOH with low surface etching and high residual of nitrogen heteroatoms. Under a very mild condition of KOH/C=1, the as-prepared carbons exhibit a micro-spherical morphology with a high specific surface area of 2234 m²/g and a high nitrogen content of 12.5 wt. %. While these materials were used as supercapacitor electrodes in 3 mol/L H₂SO₄ electrolyte, they demonstrated good electrochemical performance with high specific capacitances, excellent rate performance and cycling performance. Furthermore, it was found that nitrogen functionalities exhibit an asymmetric pseudo-capacitance contribution between the positive and negative electrodes. Taking these multiple advantages of morphology, microporous structure and enriched surface chemistry, the as-prepared porous carbon microspheres should be extended to many other applications including gas /liquid adsorbents, controlled drugs release and catalyst supports.

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Graphical abstract

High-surface-area and high-nitrogen-content carbon microspheres were prepared by pre-oxidation, carbonization and mild KOH activation of nitrogen-rich polymeric microspheres.