Chemical state of nitrogen in carbon aerogels issued from phenol–melamine–formaldehyde gels

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ABSTRACT

Chemical states of nitrogen in the carbon aerogels synthesized from phenol-melamine-formaldehyde were investigated by elemental analysis, X-ray photoelectron spectroscopy and nitrogen adsorption. It is found that the carbon aerogels are rich in mesopores and the nitrogen content of the carbon aerogels increases from 1.6 to 3.1 wt. % with increasing melamine to phenol ratios. Over two-thirds of nitrogen are on periphery of graphene layers (pyridinic-N, pyrrolic-N and/or pyridonic-N, pyridine N-oxide) and less than one-third in central position of graphene layers (quaternary-N). Polymerisation at low pH might cause a preferred location of nitrogen on periphery of graphene layer.

Carbon aerogels prepared from resorcinol and formaldehyde (RF) have attracted a lot of attention in aspect of micro-structure control at nanometer scale [1,2] and of applications in catalyst supports and electrode materials for supercapacitors, fuel cells and capacitive deionization [3–5]. Other precursors were also employed to prepare carbon aerogels, such as phenolic novolak-furfural [6], polyvinyl chloride [7] and phenolic resole-melamine-formaldehyde [8]. In the case of carbon aerogels synthesized from nitrogen containing precursors, nitrogen was integrated in carbon aerogels. Nitrogen atoms can be inserted on periphery and in central positions of graphene layers [9]. The basic nitrogen groups have pseudocapacitive effect in acidic electrolyte as electrodes of supercapacitors [10]. The pyrrolic and pyridinic nitrogen groups are known to chelate metals in aqueous solution [11]. Nitrogen doping can lower band gap of the doped carbons. The band gap reduction is dependent on the chemical state of nitrogen and important in electron transfer reactions [12]. And mass transport of substances is related to the pore size and its distribution in porous carbons [13]. Therefore, it is of great importance to investigate deeply the chemical states of nitrogen in N-doped carbon aerogels.

In this paper, nitrogen doped carbon aerogels were synthesized from phenol, melamine and formaldehyde (PMF). The nitrogen chemical states and porous properties of the carbon aerogels are reported.

Phenol and formaldehyde were dissolved in NaOH (basification agent) solution at 70 °C for 40 min with stirring. Melamine and another part of formaldehyde were added to the above solution with consecutive agitation until the solution became clear. Finally, the solution was diluted with deionized water. The diluted solution was sealed and placed in a water bath at 85 °C for 5 days. The as-formed wet organic gels were immersed in a methanol bath at 45 °C for 3 days, which was displaced by fresh methanol every day. Then the gels were placed in an autoclave to carry out supercritical petroleum ether (boiling range 30–60 °C) drying at 240 °C and 7.0 MPa for 1 h. Organic aerogels were pyrolyzed at 800 °C for 3 h under nitrogen to obtain carbon aerogels. In this work, the molar ratio of melamine to phenol (M/P) and the molar ratio of melamine and phenol to basification agent ((M + P)/B) were varied from 0.2 to 0.8 and 4.4 to 44, respectively while the molar ratios of formaldehyde to phenol, formaldehyde to melamine and water to reactants were kept at 2, 3 and 16, respectively. Through this article, the samples are named directly by the values of M/P and (M + P)/B with a solidus in-between.

Elemental analysis were performed using an Elemental Vario EL III to obtain global content and N/C ratios of carbon aerogels.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the nitrogen chemical state and the surface atom composition of the carbon aerogels. The data were
collected by an ESCALab 220i-XL electron spectrometer from VG Scientific using non-monochromatized (300 W) Al K X radiation (1486.6 eV). Prior to the measurements, all carbon aerogels were dried at 100 °C for 2 h. The base pressure was about 3 × 10⁻⁷ Pa. There were four peaks identified in the XPS spectra, corresponding to C1s, N1s, O1s and Na1s. Their positions were calibrated by the binding energy of C1s as reference of 284.8 eV before calculation of surface N/C ratios. High resolution part of N1s spectra are shown in Fig. 1. Deconvolution of the spectra provided the ratios of the four forms of nitrogen, pyridinic-N (N-6) at 398.7 ± 0.3 eV, pyrrolic-N in five-membered ring and/or pyridonic-N (N-5) at 400.3 ± 0.3 eV, quaternary-N (N-Q) at 401.4 ± 0.5 eV and pyridine-N-oxide (N-X) at 402–405 eV [14]. Curve fitting was performed by assuming a mixed Gaussian/Lorenzian peak until an acceptable fit was obtained. The elemental analysis and XPS results are compiled in Table 1.

For a better understanding of nitrogen evolution from precursors to carbon aerogels, the fraction of nitrogen retained in carbon aerogels was calculated by mass balance (the product of the nitrogen content in carbon aerogels by elemental analysis, yield of organic aerogels and conversion of organic aerogels to carbon aerogels was divided by nitrogen content in precursors). The results are tabulated together with nitrogen contents in precursors in Table 1.

Adsorption and desorption isotherms (Fig. 2) of carbon aerogels were determined by N2 adsorption, using an ASAP 2020M analyzer (Micromeritics, USA). Samples were degassed under vacuum pressure of 25 Pa at 200 °C for 12 h before adsorption. The specific surface areas (S_BET) were analyzed by the Brunauer–Emmett–Teller method. Micropore volumes (V_mic) were obtained by the t-plot method. Mesopore volumes (V_mes) and average mesopore sizes (D_m) were obtained by using the Barrett–Joyner–Halenda (BJH) model. The porous properties are listed in Table 2.

Although the amount of nitrogen contained in the precursors increases with M/P, the nitrogen content of carbon aerogels, calculated by mass balance, decreases. This could be caused by pyrolysis during which organic precursors are converted into carbon-rich graphitic-like structures by a preferred release of non-carbon atoms. The fact that the mass loss of organic aerogels during pyrolysis increases with M/P also supports this assumption too. Although the nitrogen amount contained in the precursors is constant at constant M/P (13.9 wt.% when M/P = 0.4) and independent of (M + P)/B, the nitrogen retained in carbon aerogels decreases slightly with (M + P)/B. Indeed, increasing (M + P)/B from 4.4 to 43.7 leads to decreasing the nitrogen retained (NR) from 9.3 to 8.5 wt.% (Table 1). This could be due to a more homogeneous polymerization of phenol and melamine at high catalyst concentration, i.e. at lower (M + P)/B value. The contents of nitrogen in carbon aerogels was a compromised result of the percent of nitrogen contained in precursors and the fraction of nitrogen retained in carbon aerogels (Table 1).

Results of Table 1 show that over two-thirds of the nitrogen are located in the six-membered ring (N-6 and N-Q), over two-thirds of the nitrogen are on periphery (N-6, N-5 and N-X) and less than one-third is in central positions of graphene layers. The small part of nitrogen in central positions can be ascribed to a high energy state for a centrally doped graphene layer. The decreasing of N-Q nitrogen was compensated by the increasing of N-6 nitrogen. This could be explained by a lower activation energy required for the conversion of nitrogen from N-Q to N-6 than from N-Q to N-5. The percentage

Fig. 1 – High resolution fitted XPS spectra of N1s for samples with different (a) M/P ratios and (b) (M + P)/B ratios.
of N-Q nitrogen for the carbon aerogel prepared under the highest (M + P)/B (the lowest pH value) was the lowest. This could be caused by an inhomogeneous polymerization of phenol and melamine because low pH favors condensation reaction of phenolic resole. As the carbon aerogels were formed under non-oxidative conditions, the N-X fraction is low. Normally, XPS measurement provides surface compositions while elemental analysis gives global atom compositions of carbon aerogels. As X-ray can transmit through mesopores in carbon aerogels, the sampling of a XPS is from the surface to inner of carbon nano-network, not from the surface of monolithic carbon aerogels. The similarity of N/C from elemental analysis and XPS for each sample implies that the sampling depth for a XPS measurement for carbon aerogels be close to the size of carbon nano-network for carbon aerogels.

The density of the carbon aerogels is low (0.3–0.71 cm³/g). Their isotherms exhibit a type IV isotherm with a H2 hysteresis loop, indicative of mesoporous characteristics. The size and volume of mesopores range from 0.80 to 2.86 cm³/g and 8 to 24 nm, respectively. The modification of the porous properties of carbon aerogels with (M + P)/B in PMF system were quite similar to that observed in RF system, in which increasing basification ratios or lowering pH led to an increased mesoporosity [1,2]. The intermolecular interaction of the polymers that formed carbon aerogels increases with M/P, which should be unfavorable for coarsening in sol–gel, supercritical drying and pyrolysis and lead to an increased mesoporosity with M/P.

**Table 1 – Elemental compositions and nitrogen forms of carbon aerogels**

<table>
<thead>
<tr>
<th>Samples</th>
<th>pH</th>
<th>N</th>
<th>NR</th>
<th>ML</th>
<th>N</th>
<th>N/C CHN</th>
<th>N/C XPS</th>
<th>N-6</th>
<th>N-5</th>
<th>N-Q</th>
<th>N-X</th>
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<tr>
<td></td>
<td>±0.01</td>
<td>±0.1</td>
<td>±0.1</td>
<td>±0.2</td>
<td>±0.002</td>
<td>±0.002</td>
<td>N-X</td>
<td>±3</td>
<td>±3</td>
<td>±3</td>
<td>±1</td>
</tr>
<tr>
<td>0.2/8.7</td>
<td>9.42</td>
<td>8.0</td>
<td>10.5</td>
<td>44.3</td>
<td>1.6</td>
<td>0.015</td>
<td>0.017</td>
<td>37</td>
<td>30</td>
<td>27</td>
<td>6</td>
</tr>
<tr>
<td>0.4/8.7</td>
<td>9.44</td>
<td>13.9</td>
<td>8.9</td>
<td>48.1</td>
<td>2.4</td>
<td>0.024</td>
<td>0.027</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>4</td>
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<tr>
<td>0.6/8.7</td>
<td>9.45</td>
<td>17.7</td>
<td>7.9</td>
<td>49.6</td>
<td>2.8</td>
<td>0.029</td>
<td>0.032</td>
<td>33</td>
<td>23</td>
<td>35</td>
<td>9</td>
</tr>
<tr>
<td>0.8/8.7</td>
<td>9.49</td>
<td>20.5</td>
<td>7.3</td>
<td>51.3</td>
<td>3.1</td>
<td>0.032</td>
<td>0.033</td>
<td>43</td>
<td>26</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td>0.8/43.7</td>
<td>8.7</td>
<td>13.9</td>
<td>8.5</td>
<td>48.2</td>
<td>2.3</td>
<td>0.024</td>
<td>0.025</td>
<td>53</td>
<td>26</td>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>0.4/17.5</td>
<td>9.03</td>
<td>13.9</td>
<td>8.8</td>
<td>48.5</td>
<td>2.4</td>
<td>0.024</td>
<td>0.027</td>
<td>29</td>
<td>33</td>
<td>32</td>
<td>6</td>
</tr>
<tr>
<td>0.4/4.4</td>
<td>9.67</td>
<td>13.9</td>
<td>9.3</td>
<td>48.0</td>
<td>2.5</td>
<td>0.025</td>
<td>0.028</td>
<td>30</td>
<td>33</td>
<td>34</td>
<td>3</td>
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**Table 2 – Porous properties of carbon aerogels**

<table>
<thead>
<tr>
<th>Samples</th>
<th>ρCA</th>
<th>S BET</th>
<th>V mes</th>
<th>V mic</th>
<th>D m</th>
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</thead>
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<tr>
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<td>±0.02</td>
<td>±10</td>
<td>±0.02</td>
<td>±0.02</td>
<td>±1</td>
</tr>
<tr>
<td>0.2/8.7</td>
<td>0.69</td>
<td>620</td>
<td>0.98</td>
<td>0.11</td>
<td>8</td>
</tr>
<tr>
<td>0.4/8.7</td>
<td>0.51</td>
<td>675</td>
<td>1.63</td>
<td>0.10</td>
<td>12</td>
</tr>
<tr>
<td>0.6/8.7</td>
<td>0.40</td>
<td>650</td>
<td>2.21</td>
<td>0.13</td>
<td>18</td>
</tr>
<tr>
<td>0.8/8.7</td>
<td>0.30</td>
<td>610</td>
<td>2.86</td>
<td>0.09</td>
<td>24</td>
</tr>
<tr>
<td>0.4/43.7</td>
<td>0.44</td>
<td>685</td>
<td>2.06</td>
<td>0.11</td>
<td>15</td>
</tr>
<tr>
<td>0.4/17.5</td>
<td>0.50</td>
<td>620</td>
<td>1.75</td>
<td>0.07</td>
<td>13</td>
</tr>
<tr>
<td>0.4/4.4</td>
<td>0.71</td>
<td>525</td>
<td>0.80</td>
<td>0.11</td>
<td>9</td>
</tr>
</tbody>
</table>

Note: aThe bulk densities of carbon aerogels by measuring the dimensions and mass of each cylindrical sample. bBy assuming cylindrical pore geometry using BJH model.

![Fig. 2 – Adsorption and desorption isotherms of carbon aerogels under (a) different M/P and (b) different (M + P)/B.](image-url)
The nitrogen contents of carbon aerogels increased from 1.6 to 3.1 wt.% with M/P. The nitrogen in graphene layers of carbon aerogels are located preferentially at lower energy positions of the graphene layers, i.e. N-6, N-5 and N-Q. Finally, polymerisation at low pH might cause a preferred location of nitrogen on periphery of graphene layer.

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REFERENCES


Pyroelectric temperature sensitization of multi-wall carbon nanotube papers

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ABSTRACT

This study explores the possibility of converting a self-supporting, randomly aligned, low impedance multi-wall carbon nanotube (MWCNT) paper into a resistive temperature measurement unit working at ambient pressure in air in the 25–70 °C range. Thermosensitization was achieved by decorating the surface of the films with pyroelectric CsNO$_3$ or LiNbO$_3$ crystals. Assuming a linear temperature response, temperature coefficient of resistance values of −0.158% °C$^{-1}$ and −0.246% °C$^{-1}$ were calculated for CsNO$_3$ and LiNbO$_3$ doped films, respectively. The corresponding temperature measurement accuracies (2.2 °C and