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# Calibrations on the basic strength of the nitrogen groups on the nanostructured carbon materials<sup>†</sup>

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**The basicity of the graphitic, pyridine, and pyrrole nitrogens groups on the graphene and single-walled carbon nanotubes are evaluated and compared in terms of both Brønsted base and Lewis base. It turns out that the pyridine group is the most strong basic site, while the graphitic nitrogen does not bring any improvements over the undoped one.**

The solid base catalysts have an unique role in the catalysis for both the scientific research and the industrial applications.<sup>1,2</sup> The acid-base property is one of the most important characters of the catalysts. A few useful principles in catalysis are directly derived from the acid-base property such as HSAB theory.<sup>3</sup> Furthermore several industrial chemical reactions are propelled by employing the base catalyst such as aldol-type conversions, ketonization, transesterification *et al.* The metal oxides like alkali metal and alkali earth metal are the most common solid base catalysts. Recently, the nanostructured carbon materials modified by the nitrogen show the great potential as a new class of the solid base catalyst. In 2006, Bitter and his co-workers demonstrated that the nitrogen doped carbon nanotube is an effective solid base catalyst in the Knoevenagel condensation and the catalytic performance is comparable with the conventional base catalysts.<sup>4</sup> Since then, the various nitrogen doped carbon materials have been examined as the base catalyst in several reactions including the Knoevenagel condensation,<sup>5,6</sup> the transesterification of triglycerides,<sup>7,8</sup> the hydrolysis of ethyl acetate<sup>9</sup> *et al.* Moreover the basic strength of the nitrogen doped carbon catalysts can be adjusted by varying the synthesis method, temperature, and the precursors.<sup>10,11</sup> It can be envisioned that the metal-free nanostructured carbon materials as the base catalysts will have profound impacts in the environmental protections and the economical savings.

The nitrogen species is quite diverse on the doped carbon catalysts including graphitic nitrogen, pyridine, pyrrole, and

oxidized nitrogen.<sup>12</sup> It is still a challenge to synthesize the doped carbon catalyst with the certain kind or number of the nitrogen groups. It is generally assumed that the pyridine group contributes the most basicity of the nitrogen doped carbon catalysts although there is still absent of the solid evidence to support this statement.<sup>4,10,13</sup> Moreover the basicity from the other nitrogen groups remains elusive. Montes-Morán and his co-workers have calculated the basicity in water of a series model compounds which contain the pyridine nitrogens by using DFT method.<sup>14,15</sup> They use the  $H_3O^+$  as the probe molecule to calibrate the strength of the basic site in the model compound. We are not aware any computational works have done so far for the basicity of the nitrogen groups on the nanostructured carbon catalysts.

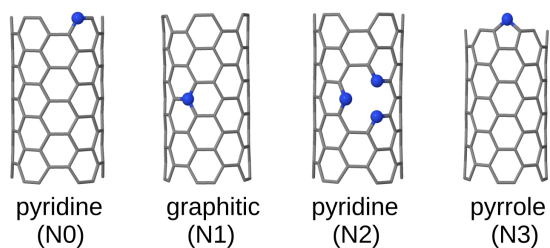
In current study, we aim to carry out a thorough study on the basicity of the nitrogen groups on the nanostructured carbon catalysts by employing DFT calculations. Two purposes are attempted to achieve: (1) the basicity of the nitrogen groups which include the pyridine, graphitic nitrogen, and pyrrole respectively is evaluated at the same footing. As aforementioned, there are various nitrogen species on the doped carbon catalysts, and these nitrogen groups are the most often observed ones. It is important to be able to describe their individual basicity and the corresponding contributions to the overall basicity. On the other hand, the basicity of the nitrogen group is also studied on the different nanostructured carbon catalysts including graphene and single-walled carbon nanotube (SWCNT). This will probably shed light on the relationship between the geometrical structure and the basicity. It also serves for the predictions of the basicity of the nitrogen groups on the other nanostructured carbon materials. (2) The basicities from both the Brønsted base and the Lewis base are calculated for the nitrogen groups. For the Brønsted base evaluation, both the proton affinity and the  $pK_a$  are calculated to probe the performance from the different nitrogen groups. For the Lewis base evaluation, the local Fukui Function is employed to measure the donating electron ability. In our previous work, the nucleophilicity of the oxygen functional groups on the nanostructured carbon catalysts is obtained.<sup>16</sup> The similar procedure will apply to the nitrogen groups in order to

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calibrate their Lewis basicity.

The basicity of the four different nitrogen species as shown in Fig. 1 are calculated and compared on the graphene and SWCNTs ((5,5), (9,0) and (11,0)). Here the pyridine group which has a single nitrogen is designated as N0; the graphitic nitrogen is designated as N1; the pyridine group which has



**Fig. 1** The schematic illustrations of the four different nitrogen groups on (5,5) SWCNT. The N0 group represents the pyridine group with a single nitrogen atom; the N1 group represents the graphitic nitrogen; the N2 group represents the pyridine group with three nitrogen atoms and the N3 group represents the pyrrole group. The labels of N0-N3 have the same meaning throughout the paper.

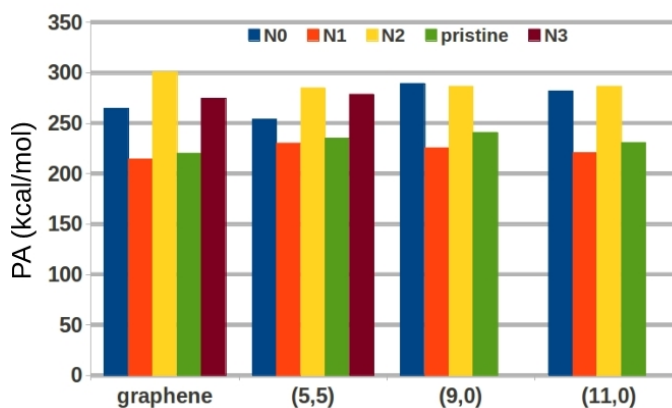
three nitrogens is designated as N2 and the pyrrole group is designated as N3. These symbols bear the same meaning throughout the paper. Before carrying out the basicity calculations, the geometric structure and atomic charge of the nitrogen groups are obtained. The coordinates of the optimized structures are included in the supporting information. The average values of the nitrogen-carbon bond distances are in the ranges of 1.35-1.38 Å and 1.42-1.44 Å for N0, N2 and N1, N3 respectively as listed in Table 1. The differences observed from the nitrogen-carbon bond distance reflect the different hybridization degree in the bonding orbital. Although the investigated nitrogen groups are all attributed as  $sp^2$  hybridization, the  $p$  orbital contributions from the nitrogen are varying for the different groups. The bonding orbitals in the N1 and N3 groups have more  $p$  orbital contributions than the N0 and N2 groups as show in Table S1 in the supporting informations. For the N1 and N3 groups, the  $p$  orbital contributions is slightly over 66.67% which is for the standard  $sp^2$  hybridization, while it is below 66.67% for the N0 and N2 groups.

The previous computational studies reveal that the charges transfer from the carbon to the nitrogen after the nitrogen modifications onto the graphene and carbon nanotubes due to their electronegativity difference.<sup>17-19</sup> This phenomena is important as it creates the active site which is often used to explain the good reactivity of ORR reaction on the nitrogen doped carbon catalysts.<sup>17</sup> Similar to the previous studies, the charge transfer is also witnessed in the current calculations. The charges obtained by nitrogen are listed in Table S2 in the supporting information. From the NBO analysis, the amount of charges obtained by the nitrogen in the N1 group is the smallest one

**Table 1** The average bond distance (in Å) of the nitrogen with its bonded carbon atoms. The calculations are done for the graphene and SWCNTs including (5,5), (9,0) and (11,0) respectively. The meaning of N0-N3 groups is shown in Fig. 1

groups	graphene	(5,5)	(9,0)	(11,0)
N0	1.35	1.36	1.38	1.37
N1	1.42	1.42	1.43	1.42
N2	1.36	1.36	1.36	1.35
N3	1.44	1.42		

among the studied groups for both graphene and SWCNTs. The pyrrole and pyridine groups both acquire more charges than the graphitic nitrogen. This finding is very informative as the graphitic nitrogen is deemed as the active center in several important reactions such as the activation of oxygen molecule, halogenation of acetylene, oxidative dehydrogenation reaction,<sup>20</sup> and selective oxidation.<sup>21</sup> From the charge analysis, it is not unreasonable to pay the equivalent attentions to the other nitrogen groups together with the graphitic nitrogen in future studies.



**Fig. 2** The calculated proton affinity (PA) of the various nitrogen functional groups (N0-N3) on the graphene and SWCNTs including (5,5), (9,0) and (11,0).

The proton affinity (PA) is often invoked to characterize the Brønsted basicity in gas phase and defined as the negative of the free energy change after a basic site to bind a proton.<sup>22-24</sup> The calculated gas phase PA is shown in Fig. 2. It is interesting to observe that the PA of the graphitic nitrogen is comparable with the pristine one which does not contain any nitrogen atoms. This seems to suggest that the inclusion of the graphitic nitrogen will not improve the basicity. In contrast, the pyridine and pyrrole groups significantly increase the PA and indeed show a potential to be a basic site. On the other hand, the PAs of the different nitrogen groups do not

significantly change from the graphene to the SWCNTs. This implies that the basicity might not have a strong relationship with the curvatures of the different carbon materials, at least for the investigated ones.

Unlike the gas phase PA calculations, the acid dissociation constant ( $pK_a$ ) describe the deprotonation of the base in the aqueous phase. Its value gives another way to measure the basicity. Many common acids and bases have tabulated  $pK_a$  in chemistry handbook. Based on the thermodynamic cycle as shown in Figure S1 in the supporting information, the  $pK_a$  is readily obtained from the equations below. In the equation, the A represents the graphene or SWCNTs containing nitrogen groups.

$$pK_a = \Delta G_{aq} / 2.303RT \quad (1)$$

$$\Delta G_{aq} = G_{gas}(A) + G_{gas}(H^+) - G_{gas}(AH^+) + \Delta G_{sol}(A) + \Delta G_{sol}(H^+) - \Delta G_{sol}(AH^+) \quad (2)$$

Furthermore, the relative  $pK_a$  calculation is suggested to be more reliable to pursue.<sup>23,25</sup> To perform this calculation, the molecule with the known  $pK_a$  is taken as the reference. The 1,8-bis(dimethyl amino) naphthalene (DMAN) molecule is chosen as the reference in current work and the  $pK_a$  of DMAN in water is 12.1. The relative  $pK_a$  is thus obtained as the following,

$$pK_a = (\Delta G_{aq}(BH) - \Delta G_{aq}(AH)) / 2.303RT \quad (3)$$

The calculated  $pK_a$  in water is listed in Table 2. The graphitic nitrogen, N1, again has the lowest basicity compared with the others as its  $pK_a$  turns out to be negative. The pyridine group, N2, is not only the most basic site but also shows a better basic ability than the reference molecule DMAN. Overall, the predictions from the  $pK_a$  calculations is in a good agreement with the PA results. These calculations suggest that the pyridine nitrogen (N2 group) is indeed the most Brønsted basic site either in gas phase or in water.

**Table 2** The calculated  $pK_a$  for the various nitrogen groups (N0-N3) on the graphene and SWCNTs including (5,5), (9,0), and (11,0). The calculation procedure is outlined in Eq. 1-3.

groups	graphene	(5,5)	(9,0)	(11,0)
N0	4.74	1.83	21.75	21.73
N1	-29.46	-17.59	-19.71	-25.13
N2	28.57	15.69	19.73	17.66
N3	17.93	16.50		

Besides Brønsted base, the Lewis base is another definition for the basicity. The Lewis basicity is related with the ability

of the donating electron. In our previous work, we have employed Fukui Function to calculate the nucleophilicity of the oxygen functional groups on the nanostructured carbon materials.<sup>16</sup> In current work, the Lewis basicity of the nitrogen functional groups are obtained by using the same method. The local softness ( $s^-$ ) is used to examine the donating electron ability of the nitrogen groups and the larger value means the better capability to give electrons. The computed local softness is listed in Table 3. The graphitic nitrogen group (N1) delivers the least ability to donating electrons which means its Lewis basicity is weaker than the others. On the other hand, the pyridine group (N2) owns the largest  $s^-$  except for graphene. This indicates that it also has very strong Lewis base. Overall, a quantitatively description of the Lewis base is obtained for the nitrogen groups and the comparison suggests that the pyridine group has the strongest donating electrons ability.

**Table 3** The calculated local softness ( $s^-$ ) of the nitrogen groups (N0-N3) on the graphene and SWCNTs including (5,5), (9,0) and (11,0).

groups	graphene	(5,5)	(9,0)	(11,0)
N0	0.0066	0.0636	0.0012	0.0244
N1	0.0051	0.002	0.0008	0.0046
N2	0.0212	0.1704	0.0045	0.1084
N3	0.2818	0.0023		

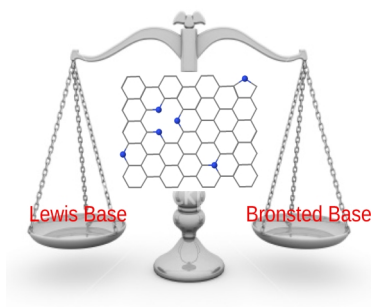
The nitrogen doping becomes an effective way to tailor the properties of the nanostructured carbon materials. Not only it can induce the charge transfer which could create the active site but also the basicity is modified after doping. Both effects are analyzed in current work. The various nitrogen groups have very different contributions to the basicity. From a series calculations on the proton affinity,  $pK_a$ , and the local softness, the results indicate that the graphitic nitrogen does has the lowest basicity, and will not enhance the basicity of the host after doping. In contrast, the pyridine groups show a strong basicity in terms of both Brønsted and Lewis bases definitions. Moreover, the quantitatively comparison between the four different nitrogen groups are performed for both graphene and a series SWCNTs. The comparison establishes the foundation for the future application of the nitrogen doped carbon materials as the base catalysts. In the end, it is recommended to increase the basicity of the carbon catalysts by introducing the pyridine nitrogens.

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Weighting the basicity of nitrogen groups.