Supporting information

Revealing the role of nitrogen dopant in tuning electronic and optical properties of graphene quantum dot from TD-DFT study

Min Yang, †‡ Zan Lian, †‡ Chaowei Si, †‡ and Bo Li*,†

†Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, Liaoning, People’s Republic of China
‡School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, Liaoning, People’s Republic of China
Table S1 Calculated HOMO-LUMO gap and absorption color corresponding to wavelength.

<table>
<thead>
<tr>
<th>GQDs</th>
<th>HOMO-LUMO gap (eV)</th>
<th>color</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>6.80</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>C24</td>
<td>4.04</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>C32</td>
<td>2.93</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>C54</td>
<td>2.82</td>
<td>Violet</td>
</tr>
<tr>
<td>C66</td>
<td>2.06</td>
<td>blue</td>
</tr>
<tr>
<td>C78</td>
<td>1.49</td>
<td>green</td>
</tr>
<tr>
<td>C54-g-1</td>
<td>1.16</td>
<td>blue</td>
</tr>
<tr>
<td>C54-g-2</td>
<td>1.14</td>
<td>blue</td>
</tr>
<tr>
<td>C54-g-3</td>
<td>0.90</td>
<td>red</td>
</tr>
<tr>
<td>C54-g-4</td>
<td>1.09</td>
<td>blue</td>
</tr>
<tr>
<td>C54-g-5</td>
<td>1.42</td>
<td>Infrared</td>
</tr>
<tr>
<td>C54-g-6</td>
<td>3.63</td>
<td>red</td>
</tr>
<tr>
<td>C54-pyd-1</td>
<td>1.39</td>
<td>Violet</td>
</tr>
<tr>
<td>C54-pyd-2</td>
<td>1.64</td>
<td>Violet</td>
</tr>
<tr>
<td>C54-pyd-3</td>
<td>0.91</td>
<td>red</td>
</tr>
<tr>
<td>C54-pyd-4</td>
<td>0.71</td>
<td>green</td>
</tr>
<tr>
<td>C54-pyd-5</td>
<td>1.31</td>
<td>red</td>
</tr>
<tr>
<td>C54-pyd-6</td>
<td>2.15</td>
<td>green</td>
</tr>
<tr>
<td>C42</td>
<td>1.90</td>
<td>red</td>
</tr>
<tr>
<td>C42-pyo-1</td>
<td>1.16</td>
<td>Infrared</td>
</tr>
<tr>
<td>C42-pyo-2</td>
<td>1.14</td>
<td>blue</td>
</tr>
<tr>
<td>C42-pyo-3</td>
<td>0.90</td>
<td>orange</td>
</tr>
<tr>
<td>C42-pyo-4</td>
<td>1.09</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>C42-pyo-5</td>
<td>1.42</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>C42-pyo-6</td>
<td>3.63</td>
<td>ultraviolet</td>
</tr>
</tbody>
</table>
**Table S2** Excitation energies, wavelengths, oscillator strengths, transition coefficients, and associated eigenvalues of the dominated excitation in GQDs.

<table>
<thead>
<tr>
<th>GQDs</th>
<th>Dominant excitation</th>
<th>Excitation energy/eV</th>
<th>Wavelength (nm)</th>
<th>Oscillator strength (f)</th>
<th>Transition coefficients</th>
<th>Transition coefficients</th>
<th>( \lambda_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td></td>
<td>2.90</td>
<td>427.00</td>
<td>0.93</td>
<td>H(-1\rightarrow L+1) 0.48</td>
<td>H(\rightarrow L) 0.48</td>
<td>0.46</td>
</tr>
<tr>
<td>C54</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(-1\rightarrow L) 0.48</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td></td>
<td>2.90</td>
<td>427.00</td>
<td>0.93</td>
<td>H(\rightarrow L+1) -0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S12</td>
<td></td>
<td>2.71</td>
<td>456.97</td>
<td>0.46</td>
<td>H(-1\rightarrow L+1) 0.63</td>
<td>H (\rightarrow L+7) -0.19</td>
<td>0.81</td>
</tr>
<tr>
<td>C54-g-2</td>
<td>S14</td>
<td>2.86</td>
<td>433.67</td>
<td>0.37</td>
<td>H(-1\rightarrow L+3) -0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C54-g-3</td>
<td>S19</td>
<td>1.97</td>
<td>629.24</td>
<td>0.07</td>
<td>aH(-1\rightarrow aH+5) -0.18</td>
<td>aH (\rightarrow aL+4) 0.81</td>
<td>0.48</td>
</tr>
<tr>
<td>C54-g-4</td>
<td>S14</td>
<td>2.54</td>
<td>488.40</td>
<td>0.36</td>
<td>H(-2\rightarrow L) 0.52</td>
<td>H (\rightarrow L+6) -0.37</td>
<td>0.54</td>
</tr>
<tr>
<td>C54-g-5</td>
<td>S14</td>
<td>1.43</td>
<td>869.47</td>
<td>0.04</td>
<td>aH (\rightarrow aL+2) 0.79</td>
<td>aH (\rightarrow aL+4) 0.51</td>
<td>1.29</td>
</tr>
<tr>
<td>S10</td>
<td></td>
<td>2.93</td>
<td>422.59</td>
<td>0.63</td>
<td>L(-1\rightarrow H) 0.66</td>
<td>L (\rightarrow H+1) 0.19</td>
<td>0.88</td>
</tr>
<tr>
<td>C54-pyd-2</td>
<td>S17</td>
<td>3.50</td>
<td>354.47</td>
<td>0.38</td>
<td>H(-3\rightarrow L+1) 0.63</td>
<td>H (\rightarrow L+2) -0.17</td>
<td>0.81</td>
</tr>
<tr>
<td>C54-pyd-3</td>
<td>S10</td>
<td>1.64</td>
<td>758.22</td>
<td>0.17</td>
<td>aH(-1\rightarrow aL+1) 0.59</td>
<td>aH (\rightarrow aL+2) 0.53</td>
<td>0.73</td>
</tr>
<tr>
<td>C54-pyd-4</td>
<td>S11</td>
<td>2.34</td>
<td>529.95</td>
<td>0.58</td>
<td>H(-1\rightarrow L+1) 0.29</td>
<td>H (\rightarrow L+5) 0.56</td>
<td>0.67</td>
</tr>
<tr>
<td>C54-pyd-5</td>
<td>S13</td>
<td>1.87</td>
<td>662.50</td>
<td>0.15</td>
<td>aH(-1\rightarrow aL) 0.211</td>
<td>aH (\rightarrow aL+1) 0.65</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Table S3 Excitation energies, wavelengths, oscillator strengths, transition coefficients, and associated eigenvalues of the dominated excitation in GQDs.

<table>
<thead>
<tr>
<th>GQDs</th>
<th>Dominant excitation</th>
<th>Excitation energy/eV</th>
<th>Wavelength (nm)</th>
<th>Oscillator strength (f)</th>
<th>Transition coefficients</th>
<th>λ_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C42</td>
<td>S15</td>
<td>1.73</td>
<td>715.49</td>
<td>0.16</td>
<td>H→L+1 0.28</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H→L+2 0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S12</td>
<td>2.35</td>
<td>526.68</td>
<td>0.22</td>
<td>H-4→L 0.39</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H-3→L -0.290</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>S14</td>
<td>2.62</td>
<td>473.80</td>
<td>0.23</td>
<td>H-6→H+1 0.60</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H-3→H+1 -0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>αH-6→αL 0.47</td>
<td>0.36</td>
</tr>
<tr>
<td>C42-pyo-2</td>
<td>S15</td>
<td>3.40</td>
<td>364.47</td>
<td>0.33</td>
<td>αH-2→αL -0.32</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>βH-5→βL+1 -0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>βH-2→βL+1 0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S16</td>
<td>3.57</td>
<td>347.65</td>
<td>0.30</td>
<td>H-1→L+2 0.57</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H→L+3 -0.38</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H-1→L+2 0.37</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H→L+3 0.56</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>αH-2→αL 0.29</td>
<td>0.25</td>
</tr>
<tr>
<td>C42-pyo-4</td>
<td>S19</td>
<td>3.44</td>
<td>360.68</td>
<td>0.19</td>
<td>aH-1→αL+2 0.30</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>βH-10 →βL 0.43</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>βH-1→βL+1 0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S20</td>
<td>3.45</td>
<td>359.16</td>
<td>0.21</td>
<td>aH-2→αL+1 0.48</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>aH→αL+2 0.47</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>βH-1→βL+2 -0.32</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>βH→βL+1 0.24</td>
<td></td>
</tr>
</tbody>
</table>
Table S4 The hybridization of nitrogen-bonded carbon of nitrogen doped GQDs and carbon-bonded carbon of pristine GQDs.

<table>
<thead>
<tr>
<th>System</th>
<th>Bond</th>
<th>Number of Carbon Atoms</th>
<th>Hybrids</th>
</tr>
</thead>
<tbody>
<tr>
<td>C54</td>
<td>C 2-C 6</td>
<td>6</td>
<td>s (34.69%) p 1.88(65.28%)</td>
</tr>
<tr>
<td></td>
<td>C 2-C 8</td>
<td>8</td>
<td>s (34.69%) p 1.88(65.28%)</td>
</tr>
<tr>
<td></td>
<td>C 38-C 39</td>
<td>38</td>
<td>s (33.09%) p 2.02(66.87%)</td>
</tr>
<tr>
<td></td>
<td>C 39-C 46</td>
<td>46</td>
<td>s (33.40%) p 1.99(66.56%)</td>
</tr>
<tr>
<td></td>
<td>N 39-C 48</td>
<td>48</td>
<td>s (33.40%) p 1.99(66.56%)</td>
</tr>
<tr>
<td>C42</td>
<td>C 24-C 25</td>
<td>24</td>
<td>s (33.91%) p 1.95(66.05%)</td>
</tr>
<tr>
<td></td>
<td>C 25-C 26</td>
<td>26</td>
<td>s (33.85%) p 1.95(66.10%)</td>
</tr>
<tr>
<td></td>
<td>C 38-N 39</td>
<td>38</td>
<td>s (27.47%) p 2.64(72.42%)</td>
</tr>
<tr>
<td>g-1</td>
<td>N 39-C 46</td>
<td>46</td>
<td>s (26.75%) p 2.73(73.14%)</td>
</tr>
<tr>
<td></td>
<td>N 39-C 48</td>
<td>48</td>
<td>s (26.75%) p 2.73(73.14%)</td>
</tr>
<tr>
<td>pyd-1</td>
<td>N 2-C 7</td>
<td>7</td>
<td>s (27.58%) p 2.62(72.31%)</td>
</tr>
<tr>
<td></td>
<td>N 2-C 9</td>
<td>9</td>
<td>s (27.58%) p 2.62(72.31%)</td>
</tr>
<tr>
<td>pyo-1</td>
<td>C 24-N 25</td>
<td>24</td>
<td>s (27.20%) p 2.67(72.70%)</td>
</tr>
<tr>
<td></td>
<td>N 25-C 26</td>
<td>26</td>
<td>s (26.94%) p 2.71(72.93%)</td>
</tr>
</tbody>
</table>
Fig.S1 The Optimized structure of pristine GQDs with (a) 84 and (b) 138 carbon atoms.

Fig.S2 Orbital delocalization index (ODI) of pristine GQDs with different size. The smaller the value, the higher the degree of delocalization.
Fig. S3 Density of state (DOS) of graphitic N-doped GQDs. At the bottom, the DOS of pristine C54-GQDs are shown. (The vertical dashed lines indicate the position of the HOMO level. The DOS is plotted with a Gaussian width of 0.01 eV).
Fig. S4 Density of state (DOS) of pyridinic N-doped GQDs. At the bottom, the DOS of pristine C54-GQDs are shown. (The vertical dashed lines indicate the position of the HOMO level. The DOS is plotted with a Gaussian width of 0.01 eV).
Fig. S5 Density of state (DOS) of pyrrolic N-doped GQDs. At the bottom, the DOS of pristine C42-GQDs are shown. (The vertical dashed lines indicate the position of the HOMO level. The DOS is plotted with a Gaussian width of 0.01 eV).
Fig.S6 The NTO pairs for the prominent excited states of doped GQDs. For this state the “hole” is below, and the “particle” is on top; the values represent the associated eigenvalue ($\lambda_i$).
Fig. S7 Representation of the electron difference density between the dominant excited state and the ground state for C54 and graphitic nitrogen doping GQDs. At the bottom, the lateral views are shown. (The blue area plots the surface where the value of the difference density is -0.0004, the green area plots the surface where the value of the difference density is +0.0004.)

Fig. S8 Representation of the electron difference density between the dominant excited state and the ground state for pyridinic nitrogen doping GQDs. At the bottom, the lateral views are shown. (The blue area plots the surface where the value of the difference density is -0.0004, the green area plots the surface where the value of the difference density is +0.0004.)
Fig.S9 Representation of the electron difference density between the dominant excited state and the ground state for C42 and pyrrolic nitrogen doping GQDs. At the bottom, the lateral views are shown. (The blue area plots the surface where the value of the difference density is -0.0004, the green area plots the surface where the value of the difference density is +0.0004.)
**Fig.S10** Atomic contributions to HOMO and LUMO. The red circle marks the atom that contributes most to alpha HOMO, the red square marks the atom that contributes most to alpha LUMO; the black circle marks the atom that contributes most to beta HOMO, and the black square marks atoms contributes most to beta LUMO. Atoms in blue represent nitrogen, and atoms in white represent hydrogen, and in yellow represent carbon.

**Fig.S11** The $E^{0-0}$ and $E^{adia}$ of different size of pristine GQDs and nitrogen doping GQDs.
**Fig.S12** The calculated absorption spectra of the C54-GQDs dispersed in gas, water, and toluene.

**Fig.S13** The calculated adsorption spectrum of pristine GQDs with 54 carbon atoms (54C) and the vacancy counterpart with one missing carbon (C54-vac). The inset figure is the optimized structures of ground states. Yellow is carbon and white is hydrogen.