Supporting Information

Large-scale synthesis of N-doped carbon quantum dots and their phosphorescence properties in polyurethane matrix

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Characterization

The transmission electron microscopy (TEM) images were taken by a H800 instrument (Hitachi, Japan). The X-ray diffraction (XRD) pattern was obtained by a Bruker D8 Advance diffractometer (Germany). The X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALAB 250 XPS system (Thermo Electron Corporation, USA). The scanning electron microscope (SEM) image was taken by a Hitachi S-4800 field emission scanning electron microscope (Japan). Fourier Transform infrared spectroscopy (FTIR) was acquired with a Bruker Tensor 27 spectrophotometer (Germany). Raman spectrum was obtained by a Renishaw Raman InVia (Renishaw, UK) by irradiating the samples with the 785 nm line of a Renishaw RL633 laser. The photoluminescence of CQDs and CQDs/PU composites were collected on a Hitachi F-7000 fluorescence spectrophotometer (Japan). The absorbance spectra of N-doped CQDs was performed by a Shimadzu UV-3600 spectrometer (Japan). The time-resolved fluorescence, phosphorescence and decay fluorescence spectra were measured with an Edinburgh FLSP980 fluorescence spectrophotometer (UK). The absolute quantum efficiency was obtained using an integrating sphere connected to an Edinburgh FLSP980 spectrophotometer.

The production yield of CQDs was calculated according to the following equation:

\[
\text{The production yield} = \frac{m}{M} \times 100\%
\]

where \(m\) is the quality of CQDs, \(M\) is the quality of raw material. The Upconverted PL from N-doped CQDs ethanol solution was detected under excitation of a Spectra-Physics Tsunami Ti: Sapphire laser (USA).
**Fig. S1** AFM image and height profile of N-doped CQDs. Height profile is given for the marked white line in the AFM image.

**Fig. S2** Raman spectrum of synthesized N-doped CQDs.
**Fig. S3** Upconverted PL spectra of N-doped CQDs recorded from 740 to 860 nm in 20 nm increments.

**Fig. S4** Digital image (left) of 0.1 mg/mL N-doped CQDs dispersed in isophorone diisocyanate (IPDI), 2,4-tolylene diisocyanate (2,4-TDI), polymethyl methacrylate (PMMA), divinylbenzene (DVB) and styrene (St) and their fluorescent image (right) under UV light excitation (365 nm).

**Fig. S5** FTIR spectrum of CQDs/PU composite.
Fig. S6 SEM image of fractured section of CQDs/PU composite.

Fig. S7 Phosphorescence emission spectra of CQDs/PU composite with extinction wavelength in 375 nm. Magenta line: the phosphorescence spectrum of CQDs/PU composite recorded after exposition under UV light for 2 min; black line and blue line: the phosphorescence spectra of above exposited sample recorded after putting in nitrogen and air for 48 h, respectively; red line: the recovered phosphorescence spectrum of the sample after purging the oxygen media with nitrogen for 12 h.

Table S1 The fluorescence decay components (λ<sub>ex</sub> = 375 nm and λ<sub>em</sub> = 440 nm) of N-doped CQDs. Where α<sub>i</sub>, τ<sub>i</sub> are the amplitude and decay time (ns).

<table>
<thead>
<tr>
<th>Em (nm)</th>
<th>α&lt;sub&gt;1&lt;/sub&gt; (%)</th>
<th>τ&lt;sub&gt;1&lt;/sub&gt; (ns)</th>
<th>α&lt;sub&gt;2&lt;/sub&gt; (%)</th>
<th>τ&lt;sub&gt;2&lt;/sub&gt; (ns)</th>
<th>α&lt;sub&gt;3&lt;/sub&gt; (%)</th>
<th>τ&lt;sub&gt;3&lt;/sub&gt; (ns)</th>
<th>τ&lt;sub&gt;ave&lt;/sub&gt; (ns)</th>
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<tbody>
<tr>
<td>440</td>
<td>15.64</td>
<td>1.34</td>
<td>60.53</td>
<td>3.98</td>
<td>23.83</td>
<td>9.75</td>
<td>6.58</td>
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</table>

The average lifetimes were calculated using the equation:

\[ \tau_{ave} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \]
Table S2 The time resolved phosphorescence and delayed fluorescence decay components (λ_{ex} = 375 nm and λ_{em} = 436 and 500 nm) of CQDs/PU composite. Where α_{i}, τ_{i} are the amplitude and decay time (ms)^{a}.

<table>
<thead>
<tr>
<th>Em (nm)</th>
<th>α_{1} (%)</th>
<th>τ_{1} (ms)</th>
<th>α_{2} (%)</th>
<th>τ_{2} (ms)</th>
<th>α_{3} (%)</th>
<th>τ_{3} (ms)</th>
<th>τ_{ave} (ms)</th>
</tr>
</thead>
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<tr>
<td>436</td>
<td>42.5</td>
<td>0.46</td>
<td>38.39</td>
<td>1.8</td>
<td>19.11</td>
<td>11.58</td>
<td>8.7</td>
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<tr>
<td>500</td>
<td>41.8</td>
<td>0.365</td>
<td>40.94</td>
<td>1.574</td>
<td>17.26</td>
<td>7.32</td>
<td>5.0</td>
</tr>
</tbody>
</table>

^{a} The average lifetimes were calculated using the equation: \( \tau_{ave} = \frac{\sum \alpha_{i} \tau_{i}^{2}}{\sum \alpha_{i} \tau_{i}} \)