Electronic supplementary information

Carbon dot-based tandem luminescent solar concentrator

Lukáš Zdražil, Sergii Kalytchuk, Kateřina Holá, Martin Petr, Oldřich Zmeškal, Štěpán Kment, Andrey L. Rogach and Radek Zbořil*

Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Palacký University Olomouc, Šlechtitelů 27, 783 71 Olomouc, Czech Republic

Regional Centre of Advanced Technologies and Materials, Department of Experimental Physics, Palacký University Olomouc, Šlechtitelů 27, 783 71 Olomouc, Czech Republic

Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic

Department of Materials Science and Engineering, and Centre for Functional Photonics (CFP), City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong S.A.R.

*Corresponding author’s e-mail: radek.zboril@upol.cz
Table of Contents

1. **Fig. S1** Transmittance spectrum of carbon dot–based tandem LSC  
   S3
2. **Fig. S2** XPS spectra of prepared carbon dots  
   S4
3. **Table S1** XPS results  
   S5
4. **Fig. S3** FTIR spectra of b-CDs, g-CDs, and r-CDs  
   S6
5. **Fig. S4** Raman spectra of b-CDs, g-CDs, and r-CDs  
   S6
6. **Fig. S5** Photostability of blue, green, and red CDs  
   S7
7. **Fig. S6** Optical properties of b-CDs, g-CDs, and r-CDs in polymer matrices  
   S7
8. **Table S2** The fitting parameters of the corresponding PL decay curves  
   S8
9. **Fig. S7** PL QY measurements of blue, green, and red LSC  
   S8
10. **Fig. S8** Experimental setup for electro-optical measurements  
    S9
11. **Fig. S9** Results and specifications of electro-optical measurements  
    S9
12. **Table S3** Overview of literature results for LSCs based on semiconductor QDs, perovskite NCs and CDs  
    S10
Structural characterization of synthesized CDs

The chemical structure of the prepared carbon dots was studied by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy. The composition of the prepared samples as well as the survey scans and high-resolution XPS spectra are presented in Fig. S2. The most intense peak in C 1s high-resolution scans for all three samples appears at 284.6 eV and is related to the C-C (sp$^2$) bonding in b-CDs, g-CDs, and r-CDs. The peak centered at approx. 285.9 eV also occurs in all three samples and corresponds to C-O, C-N bonds, and to C-S bonding state in the case of b-CDs. The typical band for carbonyl groups located around 288.0 eV is also visible in the XPS spectra of the samples. The most significant difference in high resolution C 1s scan of the prepared samples is in the presence of an intense peak at 289.2 eV in r-CDs sample (Fig. S2f). This peak appeared after sodium hydroxide treatment of g-CDs (formation process of r-CDs) and can be assigned to a rise of another electron-rich tautomer form on the surface of the particles according to Yuan et. al. The nitrogen atom in b-CDs is presented mostly in pyrrolic form (400.3 eV) according to the high-resolution N 1s spectra (Fig. S2g), while g-CDs and r-CDs have a mixture of pyrrolic and pyridinic nitrogen in the structure (Fig. S2h–i). It is important to note, that there is no peak above 402.0 eV, which is typical for nitro groups. It suggests that the nitrogenated perylene from the synthesis was fully reacted and is not presented in g-CDs and r-CDs samples (position of the individual peaks as well as their percentage rate is shown in Table S1).

Fig. S1 Transmittance spectrum of carbon dot–based tandem LSC.

S3
Fig. S2 XPS spectra of prepared carbon dots. (a–c) Survey scan, C 1s (d–f), and N 1s (g–i) high-resolution scans of b-CDs, g-CDs, and r-CDs. (j) S 2p high resolution scan of b-CDs.
### Table S1 XPS results.

<table>
<thead>
<tr>
<th>Chemical state</th>
<th>Sample</th>
<th>b-CDs</th>
<th>g-CDs</th>
<th>r-CDs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (eV)</td>
<td>% rate</td>
<td>Position (eV)</td>
<td>% rate</td>
</tr>
<tr>
<td>C-C</td>
<td>284.61</td>
<td>49.0</td>
<td>284.63</td>
<td>50.4</td>
</tr>
<tr>
<td>C-N, C-O, C-S</td>
<td>285.86</td>
<td>25.0</td>
<td>285.94</td>
<td>38.2</td>
</tr>
<tr>
<td>C=O</td>
<td>287.95</td>
<td>26.0</td>
<td>287.85</td>
<td>11.4</td>
</tr>
<tr>
<td>O=C-O'</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pyridinic N</td>
<td>399.58</td>
<td>12.5</td>
<td>399.02</td>
<td>32.6</td>
</tr>
<tr>
<td>Pyrrolic N</td>
<td>400.26</td>
<td>87.5</td>
<td>400.08</td>
<td>67.4</td>
</tr>
<tr>
<td>C-S-C S(_{2p3/2})</td>
<td>163.49</td>
<td>66.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C-S-C S(_{2p1/2})</td>
<td>163.67</td>
<td>33.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

FTIR spectra of b-CDs, g-CDs, and r-CDs are presented in Fig. S3a–c. The measurements confirmed presence of oxygen-, nitrogen-, and sulfur-containing functional groups in b-CDs, which is in the good agreement with previously published protocol\(^2\) and XPS measurements. The FTIR spectrum of b-CDs (Fig. S3a) consists of three dominant regions: very broad peaks at 3040 and 3190 cm\(^{-1}\) typical for N-H and O-H stretching modes; C=O spectral region typical for carboxylic acid salts at 1630 cm\(^{-1}\), 1515 cm\(^{-1}\), and 1428 cm\(^{-1}\); and broader peak at 1583 cm\(^{-1}\) characteristic for aromatic C=C bonding in CDs.\(^3\) The minor bands that occurred in the FTIR spectra at 1210 cm\(^{-1}\) and 1075 cm\(^{-1}\) are typical for C-N/C-S and C-O stretching modes.\(^3\) Similarly, typical peaks for O-H stretching at 3359 cm\(^{-1}\) and for O-H banding mode around 1350 cm\(^{-1}\) are presented in Fig. S3b–c. Absorption around 2900 cm\(^{-1}\) typical for C-H stretching is also visible in the FTIR scan in g-CDs and r-CDs, respectively. The FTIR spectra of r-CDs exhibited very dramatic decrease in intensity of C-O stretching mode at 1044 cm\(^{-1}\) compared to g-CDs. On the other hand, in r-CDs more dominant
peak at region typical for double/aromatic C=C/C=N bonds arises at 1616 cm\(^{-1}\) with an intense carbonyl shoulder at 1675 cm\(^{-1}\). This observation confirms the formation of tautomeric form on the surface of the particles, which may cause the red-shift in PL emission after addition of sodium hydroxide (scheme in Fig. 1a).

**Fig. S3** FTIR spectra of b-CDs, g-CDs, and r-CDs.

Raman spectra of the prepared CDs are presented in Fig. S4. G-band, which is related to the sp\(^2\) bonded carbon in graphite lattice, occurs at 1606 cm\(^{-1}\), 1591 cm\(^{-1}\), and 1586 cm\(^{-1}\) for b-CDs, g-CDs, and r-CDs, respectively. Presence of crystal structure defects or surface/edge bonded states was confirmed by presence of the D band at 1308 cm\(^{-1}\), 1308 cm\(^{-1}\), and 1313 cm\(^{-1}\) for b-CDs, g-CDs, and r-CDs, respectively.\(^4\)

**Fig. S4** Raman spectra of b-CDs, g-CDs, and r-CDs.
**Fig. S5** Photostability of colloidal b-CDs, g-CDs, and r-CDs under 1 mW/cm² monochromatic excitation.

**Fig. S6** Optical properties of b-CDs, g-CDs, and r-CDs in polymer matrices. (a–c) Excitation-emission maps. (d–f) Absorption, PL excitation, and PL emission spectra, (g–i) Time-resolved PL decays and the corresponding single and two-exponential fits.
Table S2 The fitting parameters of the corresponding PL decay curves.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colloidal Solution</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ (ns)</td>
<td>B₁ (%)</td>
</tr>
<tr>
<td>b-CDs</td>
<td>9.8</td>
<td>48.2</td>
</tr>
<tr>
<td>g-CDs</td>
<td>3.9</td>
<td>95.8</td>
</tr>
<tr>
<td>r-CDs</td>
<td>5.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. S7 PL QY measurements of b-LSC (a,b), g-LSC (c,d), and r-LSC (e,f) before and after their edges were masked with a non-transparent black tape.
**Fig. S8** Experimental setup for electro-optical measurements of tandem LSC coupled to the a-Si solar cell.

**Fig. S9** (a) The EQE spectrum of a-Si solar cell is shown compared with AM 1.5G spectrum. (b) $I-V$ measurement of a-Si solar cell and tandem LSC coupled to the same solar cell. (c) Global solar spectrum at air mass 1.5 (highlighted in grey) showing the fraction absorbed by the tandem LSC (highlighted in red).
Table S3 Overview of literature results for LSCs based on semiconductor QDs, perovskite NCs and CDs.

<table>
<thead>
<tr>
<th>Type of LSC</th>
<th>Type of luminophore</th>
<th>Dimensions (cm)</th>
<th>Light source</th>
<th>(\eta_{\text{int}}) (%)</th>
<th>(\eta_{\text{ext}}) (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>single</td>
<td>CdSe/CdS core/shell</td>
<td>2×2×0.2 cm</td>
<td>400 nm</td>
<td>48.0</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>single</td>
<td>CdSe/CdS core/shell</td>
<td>21.5×1.3×0.5 cm</td>
<td>Solar simulator</td>
<td>10.2</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>single</td>
<td>CuInSeS(_2)/In/ZnS core/shell</td>
<td>12×12×0.3 cm</td>
<td>Solar simulator</td>
<td>16.7</td>
<td>3.27</td>
<td>7</td>
</tr>
<tr>
<td>single</td>
<td>Silica-coated CdSe/CdZn(<em>{1-x})S(</em>{1-x}) core/alloyed shell</td>
<td>10×10×0.16 cm</td>
<td>405 nm</td>
<td>24.0</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>single</td>
<td>Silica-coated CdSe/CdZn(<em>{1-x})S(</em>{1-x}) core/alloyed shell</td>
<td>10×10×0.16 cm</td>
<td>sunlight</td>
<td>21.0</td>
<td>1.18</td>
<td>8</td>
</tr>
<tr>
<td>single</td>
<td>PbS/CdS core/shell</td>
<td>10×1.5×0.2 cm</td>
<td>Solar simulator</td>
<td>4.5</td>
<td>1.1</td>
<td>9*</td>
</tr>
<tr>
<td>single</td>
<td>CDs/PLMA CDs/PVP</td>
<td>10×10×0.1 cm</td>
<td>Solar simulator</td>
<td>4.0</td>
<td>0.4</td>
<td>10*</td>
</tr>
<tr>
<td>tandem</td>
<td>CDs/PLMA CDs/PVP</td>
<td>10×10×0.1 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>1.1</td>
<td>10*</td>
</tr>
<tr>
<td>single</td>
<td>N-CDs</td>
<td>2.5×1.6×0.1 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>4.75</td>
<td>11*</td>
</tr>
<tr>
<td>single</td>
<td>Si QDs</td>
<td>12×12×0.26 cm</td>
<td>473 nm</td>
<td>30</td>
<td>2.85</td>
<td>12</td>
</tr>
<tr>
<td>single</td>
<td>Mn(^{2+})-doped perovskite</td>
<td>20×20×0.5 cm</td>
<td>395 nm</td>
<td>7.5</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>tandem</td>
<td>Mn(^{2+})-doped CdSe CISe/ZnS QDs</td>
<td>10×10×0.16 cm</td>
<td>385 nm sunlight</td>
<td>58.0 and 6.4</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>single</td>
<td>N-CDs</td>
<td>2×2×0.2 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>12.23</td>
<td>15*</td>
</tr>
<tr>
<td>Type of LSC</td>
<td>Type of luminophore</td>
<td>Dimensions (cm)</td>
<td>Light source</td>
<td>$\eta_{\text{int}}$ (%)</td>
<td>$\eta_{\text{ext}}$ (%)</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------</td>
<td>---------------------</td>
<td>----------------</td>
<td>--------------</td>
<td>-------------------------</td>
<td>-------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>tandem</td>
<td>CDs</td>
<td>10×10×0.2 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>3.05</td>
<td>16*</td>
</tr>
<tr>
<td></td>
<td>CsPb(I$_{1-x}$Br$_x$)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CsPb(Cl$_{1-x}$Br$_x$)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>single</td>
<td>CNDs</td>
<td>3×3×0.3 cm</td>
<td>354 nm</td>
<td>22.0</td>
<td>12.0</td>
<td>17</td>
</tr>
<tr>
<td>single</td>
<td>CDs</td>
<td>1.8×1.8×0.11 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>5.02</td>
<td>18*</td>
</tr>
<tr>
<td>single</td>
<td>N-CDs</td>
<td>5.0×2.5×0.42 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>4.52</td>
<td>19*</td>
</tr>
<tr>
<td>single</td>
<td>PNPLs</td>
<td>10×10×0.2 cm</td>
<td>sunlight</td>
<td>26.0</td>
<td>0.87</td>
<td>20</td>
</tr>
<tr>
<td>single</td>
<td>CDs</td>
<td>10×10×1 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>0.92</td>
<td>21*</td>
</tr>
<tr>
<td>single</td>
<td>CdSe/CdS QDs</td>
<td>10×10×0.4 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>2.95</td>
<td>22*</td>
</tr>
<tr>
<td>tandem</td>
<td>CDs + AIE molecules</td>
<td>6.5×2.0×0.2 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>1.73 and 2.31</td>
<td>23*</td>
</tr>
<tr>
<td>tandem</td>
<td>CDs + organic dyes</td>
<td>5×5×0.3 cm</td>
<td>Solar simulator</td>
<td>-</td>
<td>4.35 and 11.97</td>
<td>24*</td>
</tr>
<tr>
<td>tandem</td>
<td>CDs</td>
<td>8×8×0.8 cm</td>
<td>Solar simulator</td>
<td>23.6</td>
<td>2.27</td>
<td>This work</td>
</tr>
</tbody>
</table>

Publications marked with and asterisk (*) do not include $Q_{\text{total}}$, $Q_{\text{PL}}$ parameters of used PV cell in formula for optical efficiencies, which may significantly affect the results (In our case, missing $Q_{\text{total}}/Q_{\text{PL}}$ would increase external quantum efficiency from 2.27% to 4.37%)

S11
REFERENCES


21 H. Zhao, *J. Lumin.*, 2019, **211**, 150–156.


Author Contributions

L. Z. and K. H. synthesized the samples. L. Z. and K. H. performed material characterization. L. Z. and S. K. conceived and designed the experiments. L. Z. performed optical characterizations. M. P. performed XPS characterization tests. O. Z. performed electro-optical measurements. R. Z. designed and supervised this study. L. Z., S. K., A. R., and R. Z wrote the manuscript. All authors commented on the manuscript.