Citation
Guo, X. and Zhang, H. and Sun, H. and Tade, M. and Wang, S. 2017. Green Synthesis of Carbon Quantum Dots for Sensitized Solar Cells. Chemphotochem. 1 (4): pp. 116-119. http://doi.org/10.1002/cptc.201600038

Author Manuscript

Title: Green Synthesis of Carbon Quantum Dots for Sensitized Solar Cells

Authors: Xiaochen Guo; Huayang Zhang; Hongqi SUN; Moses O Tade; Shaobin Wang

To be cited as: 10.1002/cptc.201600038

Link to VoR: https://doi.org/10.1002/cptc.201600038

Green Synthesis of Carbon Quantum Dots for Sensitized Solar Cells

Xiaochen Guo[a], Huayang Zhang[a], Hongqi Sun*[b], Moses O. Tade[a], and Shaobin Wang*[a]

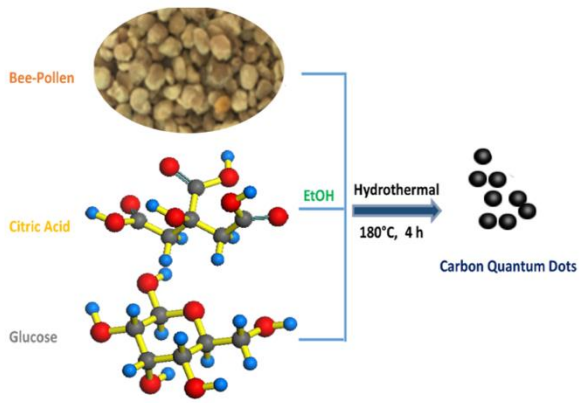
Abstract: Carbon quantum dots (CQDs) have attracted tremendous interests owing to their applications in bio-imaging, sensors, medicine and catalysis. Herein, CQDs were prepared from several carbon sources as sensitizers for solar cells and bee pollens based CQDs (B-CQDs) have achieved the highest power conversion efficiency of 0.11% under one Sun illumination (AM 1.5).

Carbon quantum dots (CQDs) were first discovered during the study on single-walled carbon nanotubes in 2006.[1] Since then, CQDs have been investigated widely as a new member of semiconductor quantum dots family.[2] Compared with other metal-based semiconductor QDs, CQDs exhibit competitive merits owing to the features of metal-free, low toxicity, low cost, high biocompatibility, eco-friendliness and strong photoluminescence (PL).[3] A variety of applications in biosensors,[4] bio-imaging,[5] elemental sensors,[6] medical use[7] as well as catalysts[8] have been demonstrated.

The synthesis of CQDs is still challenging and two strategies, e.g. top-down and bottom-up, were developed.[3] Top-down route focuses on breaking the bigger carbon structures down into tiny fragments. Up to now, different top-down approaches have been developed to prepare CQDs, including laser ablation,[9] electrochemical exfoliation,[10] pyrolysis,[11] microwave passivation,[12] and plasma treatment.[13] Bottom-up method, on the contrary, emphasizes the formation of CQDs based on the chemical precursors. With comprehensive comparison, the bottom-up protocol attracts the preference because of the extensive smaller-carbon-structure-containing sources, simple and environmentally benign procedure, especially suitable for biomass precursors. The bottom-up methods mainly introduce hydrothermal treatment.[14] Among them, hydrothermal synthesis is considered to be simple, repeatable and cost-effective.[15] Besides, hydrothermal method can be applied to most of the carbon sources, which makes it universal.[16]

Up to now, a dye-sensitized solar cell (DSSC) usually employs ruthenium-based dyes or semiconductor QDs like PbS or CdSe to convert solar energy.[17] Though these heavy metals and dyes can contribute to energy innovation, they might produce harmful effects on the environment.[18] Besides, preparation of these QDs requires complicated processing steps.[19] In consideration of the environment and cost, coupled with its broad absorption spectra, great absorption coefficient, and good compatibility, CQDs can be regarded as a promising alternative for energy converting application. Mirtchev reported a nanocrystalline-TiO_2 based solar cell sensitized with CQDs via carbonization synthesis, realizing 0.13% efficiency.[20] All-solid-state solar cells using CQDs were assembled by Briscoe with biomass as a carbon source via hydrothermal treatment, achieving the highest efficiency at 0.077%.[17a] Furthermore, other carbon-dots-based materials by heteroatom modifications have been studied and successfully applied for solar cells.[21]

In this study, carbon QDs were synthesized from three different carbon sources, bee pollens (B-CQDs), citric acid (C-CQDs) and glucose (G-CQDs), through a hydrothermal route (Scheme 1). The prepared CQDs were applied as a green sensitizer to fabricate mesoporous titanium dioxide based solar cells.



Scheme 1. Preparation of carbon quantum dots (CQDs).

[a] Mr X.C.Guo, Mr H.Y.Zhang, Prof M.O.Tade, Prof S.B.Wang
Department of Chemical Engineering
Curtin University
GPO Box U1987, Perth, WA 6845, Australia
E-mail: shaobin.wang@curtin.edu.au
[b] Prof H.Q.Sun
School of Engineering
Edith Cowan University
270 Joondalup Dr, Joondalup WA 6027, Australia
E-mail: h.sun@ecu.edu.au

Supporting information for this article is given via a link at the end of the document.

Figure 1 shows TEM images of the synthesized CQDs. The three CQDs were well dispersed and showed spherical morphologies. Average particle sizes of B-CQDs, C-CQDs and G-CQDs were calculated to be 2.4, 2.4 and 5.2 nm, respectively via size distribution measurements (ESI, Figure S1). It can be seen that the precursor would determine the particle size of the derived CQDs. The size difference was probably caused by the Maillard reactions between the compounds formed during the hydrothermal treatment because of the existence of varied functional groups on the surface of CQDs.[22] The interplanar spacing of the lattice fringes of the CQDs was 0.21 nm, matching the (100) spacing reported for graphitic carbon.[23]

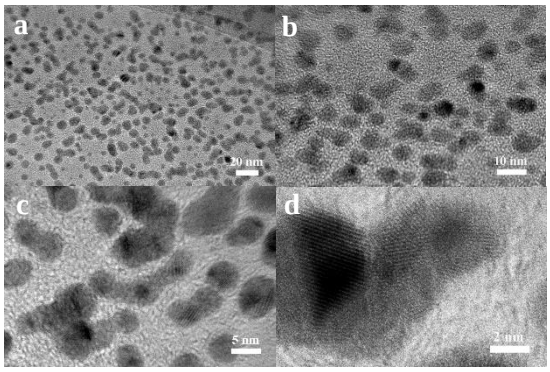


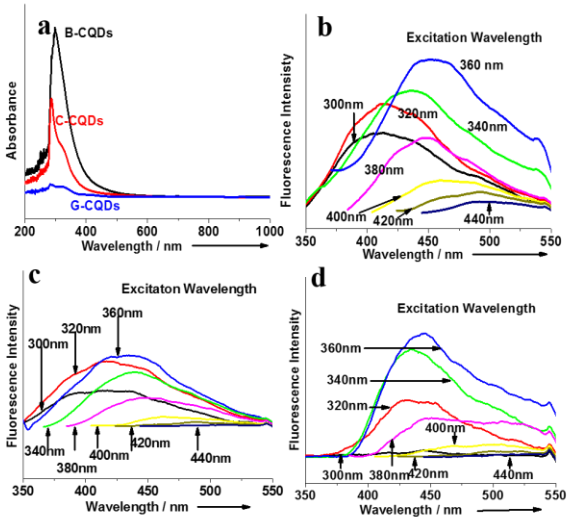
Figure 1. TEM and high-resolution TEM images of a), b) B-CQDs, c) C-CQDs, and d) G-CQDs.

The compositional information and functional groups were investigated with both XPS (Table 1 and Figure S2) and FTIR (Figure S3). Two types of nitrogen species were revealed by C-N-C (399.3 -399.4 eV) and N-H (400.1 -401.4 eV), which can also be found in FTIR spectra. It was also demonstrated that carbon existed in three types, C-C, C-OH/C-N and C=O. To be noticeably, varying ratios of each bonding were observed, which explained the precursor's influence on CQDs.

Table 1. XPS results of three carbon quantum dots.

Sample	Element	Peak	Binding energy/ eV	Functional Groups
B-CQDs	C 1s	1	284.2	C-C
	C 1s	2	285.8	C-OH/C-N
	C 1s	3	287.9	C=O
	N 1s	1	399.3	C-N-C
	N 1s	2	402.1	N-H
C-CQDs	C 1s	1	284.6	C-C
	C 1s	2	286.2	C-OH/C-O-C
	C 1s	3	288.5	C=O
	N 1s	1	399.3	C-N-C
	N 1s	2	400.1	N-H
G-CQDs	C 1s	1	284.2	C-C
	C 1s	2	285.6	C-OH/C-N
	C 1s	3	288.0	C=O
	N 1s	1	399.4	C-N-C
	N 1s	2	401.4	N-H

Figure 2 showed UV-visible absorption and



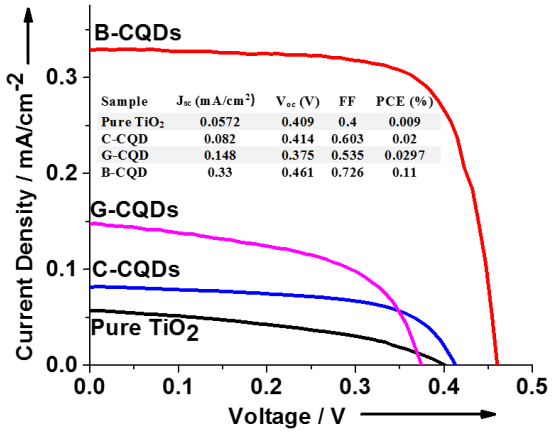
photoluminescence (PL) spectra of the B-CQDs, C-CQDs and G-CQDs. The as-prepared CQDs demonstrated the optimal absorption at around 280 nm (Figure 2a), which was ascribed to the descriptive absorption of π–π* transition of aromatic carbons.[2] As the PL spectra of CQDs solutions under varied excitation wavelengths presented (Figure 2b, c and d), strong and wide peaks emerged and centered at 450 nm. This result was consistent with the color difference of CQDs solutions under daylight and ultraviolet light, as the photographs shown in Figure S4.

Figure 2. (a) UV/Visible absorption spectra of three CQDs and photoluminescence spectra of (b) B-CQDs (c) C-CQDs and (d) G-CQDs.

Moreover, peaks shifted towards longer wavelengths as the excitation wavelength increased. The excitation-dependent emission behavior is attributed to multiple electronic transitions which were caused by the diverse functional groups on the surface of CQDs (carboxylic groups, hydroxyl groups, amines, and amides).[17a] Due to the presence of a series of functional groups on the surface, plentiful trapping states with energy levels in the energy gap were introduced.[14, 24] The corresponding electronic transitions modes would dominate under different excitations. Thus, different emission wavelengths were obtained. The fluorescence quantum yields (QYs) of CQDs were calculated to be 6.7% for B-CQDs, 4.0% for C-CQDs and 2.2% for G-CQDs, respectively, which were slightly below the reported data with a similar method.[17a] This may be caused by the diverse functional groups on the surface of the carbon sources. These groups bring in different defects to the CQD surface, eventually affecting the fluorescence performance.[25]

The current-voltage curves of sensitized solar cells with CQDs solutions are exhibited in Figure 3 along with relevant parameters as compared with the uncoated device (pure TiO_2). It could be seen that the three kinds of CQDs succeeded in enhancing the photoelectric conversion efficiency. The highest

power conversion efficiency at 0.11% was witnessed on the solar cells sensitized with B-CQDs, on account of the highest



Sample	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Pure TiO_2	0.0572	0.409	0.4	0.009
C-CQD	0.082	0.414	0.603	0.02
G-CQD	0.148	0.375	0.535	0.0297
B-CQD	0.33	0.461	0.726	0.11

open-circuit voltage (Voc) and short-circuit current density (Jsc). The best performance parameters of reported and prepared solar cells have been listed in Table S1 as comparison. While our self-made mesoporous TiO_2/CQDs solar cells possess compatible current density with nanocrystalline TiO_2/CQD, a higher open circuit voltage and a filling factor were obtained with a comparable efficiency. Besides, the hydrothermal treatment has great advantages over this reported carbonization method on account of its use of strong sulfuric acid. [20]

Figure 3. Curves of Voltage-Current of CQDs sensitized solar cells.

The higher power conversion efficiency of B-CQDs sensitized solar cells than the others was attributed to the higher open circuit voltage and short-circuit current density. The higher V_{OC} was related to the smaller size of B-CQDs. This phenomenon is on account of the quantum size effect that the heterojunction barrier governing the hole transportation increases with the decrease of particle size, resulting in the increase of V_{OC}. [21c] Higher J_{SC} was a result of the broad and strong light absorption and the outstanding electron transfer of B-CQDs. Despite of a similar particle size, solar cells sensitized with C-CQDs showed an unsatisfactory performance in energy conversion. It was assumed to be related to the surface defects and internal recombination because the photo-generated electrons failed to transfer outbound to the counter electrode.

Photoluminescence spectra of pure TiO_2, three CQDs solutions and CQDs/TiO_2 mixture were obtained to determine the sensitizing effect of CQDs on TiO_2 (Figure S5). Evidently, three CQDs solutions displayed detectable peaks, while pure TiO_2 showed no photoluminescence property. With the addition of TiO_2 into CQDs solutions, emission of CQDs decreased but still presented visible peaks compared with pure TiO_2. Normally, pure CQDs solutions would display PL performance if being irradiated under a certain excitation light. When CQDs are adsorbed on TiO_2 and cover the surface, part of electrons generated by photons would transfer to the conduction band of TiO_2. The injected electrons would accomplish the current circle. Therefore, some electrons did not participate in the light emission, making the CQDs/TiO_2 solutions present weak PL. These findings proved that a portion of the photo-generated electrons inside CQDs could be transferred into TiO_2 instead of recombining with holes, leading to emission.

In conclusion, carbon quantum dots derived from green carbon sources, bee pollens, citric acid and glucose, were successfully synthesized in a simple route. The prepared CQDs were used in the sensitized solar cells and the highest power conversion efficiency at 0.11% was achieved on solar cells using CQDs derived from bee pollens. The CQDs derived from such a simple and green method provide us a new perspective towards their versatile applications. Undeniably, the efficiency accomplished now is not satisfying. It can be improved potentially by further refining the particle size and functional groups on the surface.

Experimental Section

Synthesis of Carbon Quantum Dots: Bee pollens, citric acid and d-(+)-glucose were used as precursors to synthesize carbon quantum dots (CQDs). The precursors (2 g) were dissolved in deionized (DI) water (20 mL) separately and placed in a Teflon-lined, stainless steel autoclave, which underwent treatment at 180 ℃ for 4 h. The obtained dark brown solution was centrifuged at 13000 rpm for 10 min. The supernatant was filtered using standard 0.2 μm syringe filters. Then the solution of CQDs was purified by putting into DI water via hydrolysis membrane (3500 Dolton) at -4 ℃ for 24 h.

Fabrication of CQDs sensitized solar cells: For solar cell fabrication, aqueous TiO_2 paste (25% w/w P25 TiO_2, 10% w/w polyethylene glycol (MW 20000)) was doctor bladed onto FTO substrates. The films were then calcined at 450 °C for 30 min. After cooling down, TiO_2 films were coated with carbon quantum dots (CQDs) by soaking the substrates in three CQD solutions for 24 h before removing and rinsing with clean ethanol to remove any poorly adhered QDs. Sandwich cells were prepared using platinum coated FTO as the counter electrode. Triiodide/iodide (I_3^-/I^-) (MS005615, Dyesol) was injected into the space between the two electrodes as an electrolyte. The two electrodes were sealed by melting a thin transparent film of polymer gasket at 80 °C on a hot plate.

Characterization: Field-emission scanning electron microscopy (FIBSEM, Zeiss Neon 40EsB), transmission electron microscopy (TEM, Titan G2 80-200), high-resolution transmission electron microscopy (HRTEM) were used to investigate the morphology of CQDs. Ultraviolet-visible (UV−Vis) absorption spectra of the CQDs solutions were recorded using a JASCO V-670 UV−Vis/NIR spectrophotometer. Fluorescence spectra was obtained using PerkinElmer LS 55 Fluorescence spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos AXIS Ultra DLD machine with a monochromatic Al Kα X-ray gun. Fourier transform-infrared spectra (FT-IR) were performed by using a PerkinElmer Spectrum 100 FTIR Spectrometer. The current-voltage characteristics of the solar cells were recorded by an electrochemical workstation (Zahner Zennium and XPOT) under simulated AM 1.5 G illumination (100 mW/cm^2) provided by a solar simulator (TriSOL, OAI). The incident light intensity was calibrated using a reference Si solar cell.

Acknowledgements

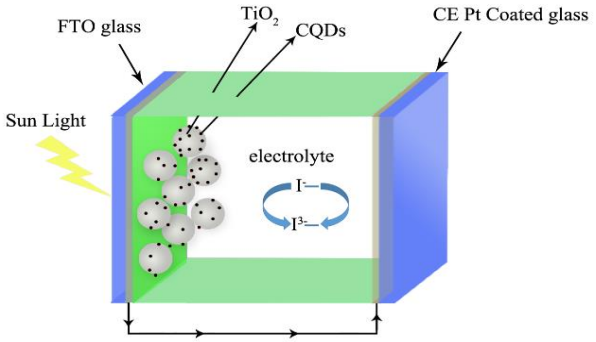
This work is supported by Australian Research Council under project DP150103026.

Keywords: carbon quantum dots • sensitized solar cell • energy conversion

[1] a) X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker, W. A. Scrivens, *J. Am. Chem. Soc.* **2004**, *126*, 12736-12737; b) Y.-P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. Wang, P. G. Luo, H. Yang, M. E. Kose,B. Chen, L. M. Veca, S.-Y. Xie, *J. Am. Chem. Soc.* **2006**, *128*, 7756-7757.
[2] J. Zhang, Y. Yuan, G. Liang, S.-H. Yu, *Adv. Sci.* **2015**, *2*, 1500002.
[3] [3] S. Y. Lim, W. Shen, Z. Gao, *Chem. Soc. Rev.* **2015**, *44*, 362-381.
[4] R. Ye, C. Xiang, J. Lin, Z. Peng, K. Huang, Z. Yan, N. P. Cook, E. L. G. Samuel, C.-C. Hwang, G. Ruan, G. Ceriotti, A.-R. O. Raji, A. A. Marti, J. M.Tour, *Nat.Commun.* **2015**, *6*.
[5] P. G. Luo, S. Sahu, S.-T. Yang, S. K. Sonkar, J. Wang, H. Wang, G. E.LeCroy, L. Cao, Y.-P. Sun, *J. Mater. Chem. B.* **2013**, *1*, 2116.
[6] F. Yan, Y. Zou, M. Wang, X. Mu, N. Yang, L. Chen, *Sens. Actuators, B.* **2014**, *192*, 488-495.
[7] Q. Wang, X. Huang, Y. Long, X. Wang, H. Zhang, R. Zhu, L. Liang, P.Teng, H. Zheng, *Carbon.* **2013**, *59*, 192-199.
[8] A. Prasannan, T. Imae, *Ind. Eng. Chem. Res.* **2013**, *52*, 15673-15678.
[9] L. Cao, X. Wang, M. J. Meziani, F. Lu, H. Wang, P. G. Luo, Y. Lin, B. A. Harruff, L. M. Veca, D. Murray, S.-Y. Xie, Y.-P. Sun, *J.Am.Chem.Soc.* **2007**, *129*, 11318-11319.
[10] B. Kong, J. Tang, Y. Zhang, T. Jiang, X. Gong, C. Peng, J. Wei, J. Yang, Y. Wang, X. Wang, G. Zheng, C. Selomulya, D. Zhao, *Nat. Chem.* **2016**, *8*, 171-178.
[11] X. Li, J. Chang, F. Xu, X. Wang, Y. Lang, Z. Gao, D. Wu, K. Jiang, *Res. Chem. Intermed.* **2013**, *41*, 813-819.
[12] Q. Wang, H. Zheng, Y. Long, L. Zhang, M. Gao, W. Bai, *Carbon.* **2011**, *49*, 3134-3140.
[13] J. Wang, C.-F. Wang, S. Chen, *Angew. Chem. Int. Ed.* **2012**, *124*, 9431-9435.
[14] S. Sahu, B. Behera, T. K. Maiti, S. Mohapatra, *Chem. Commun (Camb).* **2012**, *48*, 8835-8837.
[15] M.-M. Titirici, M. Antonietti, N. Baccile, *Green Chem.* **2008**, *10*, 1204-1212.
[16] S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang, B. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3953-3957.
[17] a) J. Briscoe, A. Marinovic, M. Sevilla, S. Dunn, M. Titirici, *Angew. Chem. Int. Ed.* **2015**, *54*, 4463-4468; b) W. Wang, M. O. Tade, Z. Shao, *Chem. Soc. Rev.* **2015**, *44*, 5371-5408.
[18] Q. Liang, W. Ma, Y. Shi, Z. Li, X. Yang, *Carbon.* **2013**, *60*, 421 -428.
[19] Y.-L. Lee, Y.-S. Lo, *Adv. Funct. Mater.* **2009**, *19*, 604-609.
[20] P. Mirtchev, E. J. Henderson, N. Soheilnia, C. M. Yip, G. A. Ozin, *J. Mater. Chem.* **2012**, *22*, 1265-1269.
[21] a) Y. Q. Zhang, D. K. Ma, Y. G. Zhang, W. Chen, S. M. Huang, *Nano. Energy.* **2013**, *2,* 545–552; b) H. Wang, P. Sun, S. Cong, J. Wu, L. Gao, Y. Wang, X. Dai, Q. Yi, G. Zou, *Nanoscale Res. Lett.* **2016**, *11*, 27-33; c) X.Li, M.Rui, J. Song, Z. Shen, H. Zeng, *Adv. Funct. Mater*. **2015**, *25*: 4929-4947.
[22] N. Baccile, G. Laurent, C. Coelho, F. Babonneau, L. Zhao, M.-M. Titirici, *J. Phys. Chem. C.* **2011**, *115*, 8976-8982.
[23] K. Linehan, H. Doyle, *RSC Adv.* **2014**, *4*, 12094-12097.
[24] a) J. Zhou, C. Booker, R. Li, X. Zhou, T.-K. Sham, X. Sun, Z. Ding, *J. Am. Chem. Soc.* **2007**, *129*, 744-745; b) X.Li, S.Zhang, S. A. Kulinich, Y. Liu, H.Zeng, *Sci. Rep.* **2014**, *4*, 4976-4983
[25] a) Y. Yang, J. Cui, M. Zheng, C. Hu, S. Tan, Y. Xiao, Q. Yang, Y. Liu, *Chem. Commun.* **2012**, *48*, 380-382; b) X.Li, Y.Liu, X. Song, H.Wang, H.Gu, H.Zeng, *Angew. Chem. Int. Ed*. **2015**, *54* , 1759-1764.

COMMUNICATION

Carbon quantum dots were synthesized from common materials in a green way and applied on sensitized solar cells.



Xiaochen Guo, Huayang Zhang, Hongqi Sun, Moses O. Tade and Shaobin Wang**

Page No. 1 – Page No.4

Green Synthesis of Carbon Quantum Dots for Sensitized Solar Cells