A Facile Microwave-Assisted Synthesis of Carbon Dots and Their Application as Sensitizers in Nanocrystalline TiO₂ Solar Cells

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Abstract. Carbon quantum dots (CQDs or CDs) recently have attracted attention due to their unique optical and chemical properties. Herein we demonstrate a facile protocol to synthesize CDs via the microwave-assisted method. In this research, we use citric acid as carbon source and urea as nitrogen source. The UV-vis absorption of CDs show two peaks at 326 and 408 nm respectively correspond to the π→π* transition of C≡C bonds and n→π* transition of C=O or other bonds on the CDs surface. The CDs solution emit green color emission at wavelength 521 nm (λexcitation = 365 nm), which the highest PL intensity is achieved by the CDs heated in microwave for 15 min. Moreover, we also conducted a preliminary study of the CDs as sensitizers in dye-sensitized solar cells (DSSCs) based on TiO₂ nanocrystalline. The power conversion efficiency (η), fill factor (FF) and short-circuit current density (Jsc) of 0.29%, 0.31 and 0.36 mA/cm², respectively, are achieved for the CDs based cell. This research suggests that the CDs have the potential application as sensitizers in DSSCs.

1. Introduction
Dye-sensitized solar cells (DSSCs) have attracted attention due to its simple fabrication process, low fabrication cost, environment-friendly and promising high efficiency. The photosensitizer, as an important component in DSSC, has a key role as energy harvester [1-2]. Nowadays, ruthenium-based dye still dominates photosensitizer market because it has wide absorption and has chemical stability. However, ruthenium is relatively expensive because it was formed by rare materials and very complex chemical structure. On the other hand, natural-based dyes showed low efficiency due to their low charge transport, low absorption in visible-light region and weak binding energy with TiO₂ [3].

Carbon quantum dots (CDs) have potential as photosensitizer for solar cell application because of their facile and low-cost synthesis, abundant raw materials in nature, non-toxic, good stability, high colloidal solubility in polar solvents, high optical absorption, quantum confinement and high endurance towards photobleaching [4]. The CDs synthesis methods generally can be categorized into two main approaches, top-down and bottom-up. The top-down approach consists of laser ablation, arc-discharge, acid dehydration and electrochemical oxidation from carbon source. In contrast, thermal carbonization, microwave-assisted synthesis and ultrasonic treatments from precursors belong to bottom-up approach [5].
Some synthesis methods require delicate instrumentation are tedious in procedures or harmful chemical reagents are unavoidable, making the synthesis technically unfeasible to be performed in general laboratories. Among all the available protocols, a microwave-assisted method is an efficient, time-saving, cost-effective, environment-friendly and narrow size-distributed through the homogeneous heating [6-7]. Therefore, microwave-assisted heating was employed in the synthetic procedure, which was attempted to provide a facile and feasible route of preparing carbon dots without further surface passivation.

Herein we demonstrate a facile method to synthesize CDs via a microwave-assisted method with citric acid as carbon source and urea as nitrogen source. Then, we have used them as sensitizers on the nanocrystalline TiO$_2$ surface. Moreover, ruthenium-dye N719 [cis-di(thiocyanate)bis-(2,20-bipyridyl-4,40-dicarboxylate) ruthenium(II) (bistetramethylammonium)] solution was used as comparison.

2. Method

2.1. Materials
Citric acid and urea were used as precursors without further purification. Fluorine-doped tin oxide (FTO) substrate was used with cut are of 2.5 x 2.5 cm$^2$. Nanocrystalline TiO$_2$ (20 nm, Dyesol, Australia) and platinum paste (Dyesol, Australia) respectively were used as photoanode and counter electrode layers. Electrolyte consist I$_3$/I$^-$(HSE, Dyesol, Australia) was used as the transport mechanism for the redox mediator. Ruthenium-dye N719 (0.3 mM, Dyesol, Australia) solution in a mixture of tert-butanol and acetonitrile was used as comparison sensitizer of CDs.

2.2. CDs synthesis
CDs were synthesized by a microwave-assisted method from previous research reported by Qu et.al. with slight modification [8]. Briefly, 2 g of citric acid and 4 g of urea were dissolved in 60 mL of aquades at 70 °C for 15 min. After that, the solution was sonicated in an ultrasonic bath for 20 min. The solution was moved into the microwave and heated at 450 W. In this condition, there are heating time variations which are 15, 30 and 45 min for each sample. The yellowish-brown product allowed to cool to room temperature naturally then grinded in a mortar to obtain the C-dot powders. Based on the synthesis time (15, 30, and 45 min), the powder named respectively as CD 15, CD 30 and CD 45. After that, the CD powder was dissolved in aquades with the concentration of 0.2 mg/mL.

2.3. The photoanode and counter electrode preparation
The photoanode and counter electrode were prepared by the method reported in our previous research with slight modification [9-10]. Briefly, the TiO$_2$ paste was deposited onto the FTO glass substrate by using the doctor blade method (thickness ~5 μm) with an active area of 1 cm$^2$, then sintered at 500 °C for 45 min. The TiO$_2$ photoanode was immersed into 0.3 mM ruthenium dye N719 and C-dot dye for each sample at ambient environment for 24 h.

To prepare the counter electrode, platinum paste was deposited substrate on a pre-cleaned and drilled FTO glass substrate (hole size 1 mm$^2$ on active area) by the doctor blade method ( thickness ~5) with active area 1 cm$^2$. The Pt electrode was dried at 80 °C, then sintered at 450 °C for 60 min.

2.4. Device assembling
Both the photoanode and the counter electrode were assembled into a sandwich-like structure separated by sealant as a spacer. The I$_3}$/I$^-$ electrolyte was injected through the hole on counter electrode side. Silicon glue was put into the hole to prevent evaporation.

2.5. Characterization
The structural analysis of CDs was characterized by transmission electron microscopy (TEM, JEOL JEM-1400) and fourier transform infrared (FTIR) spectrometer (Alpha Series Bruker, USA). The samples were used for photoluminescence (PL) measurements using Perlin Elmer LS55, the excitation
wavelength was kept at 365 nm. The cell performance was performed by 2602A sourcemeter (Keithley Instrument, USA) under AM 1.5G solar illumination at 100 mW/cm² light intensity.

3. Results and Discussion

Figure 1 shows the TEM image of the CDs prepared at 450 W for 30 min. For CD the average diameter was found to be 10 nm with the perspective of Figure 1. The mean size was obtained by using imageJ software analysis. This result is not much different from the literature reported by Qu et. Al. [8] using a similar method (1-5 nm).

Figure 2. FTIR spectra of CDs with various heating times.

FTIR measurement was done to study the surface functional groups from citric acid. The FTIR spectra (Figure 2) show strong and broad absorption band at 3429 cm⁻¹ and medium absorption band at 3300 cm⁻¹ correspond to O-H and N-H bonds, respectively. The presence of the organic functional groups may improve the solution stability and hydrophilicity of CDs in aqueous phase without further chemical modification [11]. The medium absorption band at 2850 cm⁻¹ corresponds to C-H bond. The strong absorption at 1700 cm⁻¹ corresponds to C-O. The absorption band at 1455 cm⁻¹ corresponding to C-H bond suggests that CDs have methyl and methylene groups on their surface [12]. The absorption band at 1230 cm⁻¹ is ascribed to C-N bond. Other absorption bands below 1230 cm⁻¹ are hard to interpret visually, in this region we have to compare with references to identify specifically.
Figure 3. (a) UV-vis absorption and (b) PL spectra of CDs in aqueous phase. (c) UV-vis absorption (black line) and PL spectra (red line) of CDs aqueous solution. Inset in (c) shows an optical photograph of CDs in aqueous phase under UV light (365 nm). (d) Schematic of PL emission in CDs.

Figure 3(a) shows that UV-vis absorption spectra of CDs in the aqueous phase exhibit less significant effect of heating time. The absorption wavelength of CD 15, CD 30 and CD 45 approximately are 408, 409 and 411 nm, respectively. Figure 3(b) shows that CD 15 has the highest PL emission intensity centering at 521 nm with a full width half maximum (FWHM) of about 88. The emission peak is correlated with green color emission which has the typical wavelength range from 495 to 580 nm. The absorption spectrum of CDs exhibits two optical absorption bands at 326 and 408 nm as shown in Figure 3 (c). The absorption at 326 nm corresponds to the $\pi \rightarrow \pi^*$ transition of C=C bonds. The absorption at 408 nm corresponds to n $\rightarrow \pi^*$ transition of C=O or/and other bonds [13]. The n $\rightarrow \pi^*$ transition happened because the functional groups with electron lone pairs are bonded to aromatic sp$^2$-hybridized carbons. This condition eases electron transitions from the n-states of the functional group to $\pi^*$-states of aromatic rings [14]. The high intensity of $\pi \rightarrow \pi^*$ transition strongly related to the presence of the surface amino group in large number, as shown in IR spectra, resulting in narrowing energy gap [15]. On the other hand, the oxygen functional groups, such as C=O as shown in IR spectra, induce to the domain trap states on CDs surface leading to the red-shift. Therefore, we expect that the green color emission resulted in our research instead blue color emission is induced by red-shifted of PL emission wavelength from 365 to 521 nm as shown in Figure 3(d).
Figure 4 shows the current density-voltage (J-V) characteristics of the DSSCs with various sensitizers were performed under simulated AM 1.5G solar illumination using 100 mW/cm². The power conversion efficiency (PCE) of the DSSCs is determined by short-circuit current density (J_sc), open-circuit potential (V_oc) and the fill factor (FF). The photovoltaic properties of DSSCs with various dyes are listed in Table 1.

Table 1. Photovoltaic properties of the DSSCs with various dyes

| Photoanode + dye          | J_sc (mA.cm⁻²) | V_oc (volt) | FF   | PCE (%) |
|---------------------------|----------------|-------------|------|---------|
| TiO₂ + CD 15              | 0.36           | 1.00        | 0.31 | 0.29    |
| TiO₂ + Ruthenium N719     | 0.53           | 1.00        | 0.49 | 0.52    |

The DSSC with ruthenium N719 dye achieved the highest PCE of 0.52 % with J_sc of 0.53 mA/cm², V_oc of 1.00 volt and FF of 0.49. The CD 15 based cell exhibits slightly lower FF and J_sc but similar V_oc corresponding to lower PCE of 0.29%. The lower current-density of CD 15 based cell is probably caused by the corrosive behavior of I/I₃⁺ on a number of CD sensitizers [16]. Moreover, surface recombination strongly contributed by trap states on CD surface likely leads to the lower current-density [17]. The charge transport of CDs transferred to lowest unoccupied molecular orbital (LUMO) of TiO₂ is still an issue since its inferior to ultrafast-transport of ruthenium N719 dye [18].

Conclusion

The CDs with high colloidal stability and hydrophilicity have been successfully synthesized via microwave-assisted. The further post-synthesis surface passivation is not necessary for this research since citric acid and urea were used as precursors even oxidation still occurred. Additionally, the CDs dissolved in aqueous solution have been applied as sensitizers in DSSCs, achieving PCE of 0.29 % which slightly lower than the PCE of ruthenium N719 based due to low current-density. In summary, the CDs synthesized via microwave-assisted method have potential as alternative sensitizers. However, the further developments are must be conducted to address surface chemistry issues contributing to optical properties, charge transport, and charge recombination.
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References
[1] O'Regan B and Grätzel M 1991 Nature 353 737–740
[2] Nazeeruddin Md K, Baranoff E and Grätzel M 2011 Sol. Energy 85 1172–1178
[3] Shalini S, Prabhu R B, Prasanna S, Mallick T K and Senthilarasu S 2015 Renew. Sustainable Energy Rev. 51 1306–1325
[4] Lim S Y, Shen W and Gao Z 2015 Chem. Soc. Rev. 44 362–81
[5] Wang R, Lu K Q, Tang Z R and Xu Y J 2017 J. Mater. Chem. A 5 3717–34
[6] Mazzier D, Favaro M, Agnoli S, Silvestrini S, Granozzi G, Maggini M, Moretto A 2014 Chem. Commun. 50 6592–95
[7] Wang J, Cheng C, Huang Y, Zheng B, Yuan H, Bo L, Zheng M W, Yang S Y, Guo Y, Xiao D 2014 J. Mater. Chem. C 2 5028–35
[8] Qu S, Wang X, Lu Q, Liu X, Wang L 2012 Angew. Chem. 124 1–5
[9] Prasetio A, Habieb A M, Alkian I, Arifin Z and H Widiyandari 2017 J. Phys.: Conf. Ser. 877 012005
[10] Widiyandari H, Prasetio A, Purwanto A, Subagio A and Hidayat R 2018 Jpn. J. Appl. Phys. 57 68001
[11] Zhang Y, He Y H, Cui P P, Feng X T, Chen L, Yang Y Z and Liu X G 2015 RSC Adv. 5 40393–401
[12] Li H T, Kang Z H, Liu Y and Lee S T 2012 J. Mater. Chem. 22 24230–53
[13] Wang Y and Hu A 2014 J. Materi. Chem. C 2 6921–39
[14] Wang R, Lu K, Tang Z, Xu Y 2017 J. Mater. Chem. A 5 3717–34
[15] Li S, Zhang S, Kulinich S A, Liu Y, Zeng H 2014 Scientific Reports 4 4976
[16] Shalom M, Dor S, Ruhle S, Grinis L and Zaban A 2009 J. Phys. Chem. C 113 3895–98
[17] Zhou J, Booker C, Li R, Zhou X, Sham T, Sun X and Ding Z 2007 J. Am. Chem. Soc. 129 744–45
[18] Mirtchev P, Henderson E J, Soheilnia N, Yip C M and Ozin G A 2012 J. Mater. Chem. 22 1265–69