



Fluorescent carbon quantum dots synthesized by chemical vapor deposition: An alternative candidate for electron acceptor in polymer solar cells



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ABSTRACT

Excitation-wavelength-dependent blue-greenish fluorescent carbon quantum dots (CQDs) with graphite structure were synthesized by chemical vapor deposition (CVD) method. In comparison with those synthesized by hydrothermal method (named H-CQDs), C-CQDs have less hydrophilic terminal groups, showing good solubility in common organic solvents. Furthermore, these synthesized C-CQDs show a low LUMO energy level (LUMO = -3.84 eV), which is close to that of phenyl- C_{61} -butyric acid methyl ester (PC₆₁BM, LUMO = -4.01 eV), the most widely used electron acceptor in polymer solar cells. Photoluminescence quenching of the poly(3-hexylthiophene-2,5-diyl):C-CQDs blended film (P3HT:C-CQDs) indicated that a photo-induced charge transfer between P3HT and C-CQDs occurs in such a composite film. Bulk heterojunction solar cells using C-CQDs as electron acceptors or doping materials were fabricated and tested. High fill factors were achieved for these C-CQDs based polymer solar cells, demonstrating that CQDs synthesized by CVD could be alternative to the fullerene derivatives for applying in polymer solar cells.

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1. Introduction

As a novel type of carbon nanomaterials, carbon dots (CDs) have attracted increasing interests after being obtained during purification of single-walled carbon nanotubes in 2004 [1]. CDs comprise discrete, quasi-spherical nanoparticles with sizes less than 10 nm [2]. There are two major types of CDs, graphene quantum dots (GQDs) and carbon quantum dots (CQDs). GQDs are sheet-like

materials consisting of single or few graphene layers, and usually show anisotropic charge transport properties in lateral dimension better than the vertical dimension. GQDs exhibit tunable fluorescence emission or electronic properties and low charge transfer resistance [3,4]. Generally, GQDs are obtained by two-step cutting routes from different carbon resources, such as carbon fiber [3], carbon nanotube [1] or graphene sheets [5,6]. Relatively complicated procedures and long synthesis periods would result in high cost of GQDs. As a zero-dimension nanocarbon materials, CQDs are usually spherical and have crystal graphite lattice [7,8]. CQDs can be synthesized by hydrothermal processes [9], ultrasonics- [10] or microwave-assistant [11,12] hydrothermal processes from cheap carbon sources. These hydrothermally synthesized CQDs (H-CQDs) usually contain multiple hydrophilic groups at the periphery, and have excellent solubility in polar solvent. In addition, H-CQDs

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possess advantages of excellent chemical and thermal stability, low toxicity, intensive photoluminescence performances [7], low photobleaching and good biocompatibility [13], and have been applied to fields of bioimaging [14,15] and labeling [16], drug delivery [17,18], sensing [14], fluorescent ink [19], photocatalysis [20,21] and light-emitting diode [22].

Recently, applications of CQDs in solar cells were also reported [23–25]. For example, Choi et al. [26] prepared carbon-dot-supported silver nanoparticles as the electrode in polymer solar cells. Such a composite electrode takes the surface plasmon resonance effect of metal particles, and power conversion efficiency enhancement was achieved. Narayanan et al. [27] and Liu et al. [28] reported the use of CQDs as an additive in quantum dot and organic solar cells, respectively. In these reports, charge transport as well as device performance was improved by cooperation with CQDs. Huang et al. reported the use of CQDs as a luminescent down-shifting layer on organic solar cells. Enhanced incident photon-to-current efficiency (IPCE) was observed over 350–450 nm, leading to a device performance enhancement [29]. Furthermore, Zhang et al. [30] and Briscoe et al. [31] reported the use of CQDs as a sensitizer in traditional liquid electrolyte and solid state dye-sensitized solar cells (DSSCs) respectively. Although all these CQD-based DSSCs showed low performance, these results confirmed that CQDs are promising optical active materials for use in DSSCs.

High photovoltaic performance of polymer solar cells based on CQD-doped photoactive layer has been reported in the literatures [32,33]. However, only few papers have reported the use of hydrothermally synthesized CQDs as a single electron acceptor in solution processed polymer solar cells. In 2014, Kwon et al. firstly reported the use of CQDs as electron acceptors in P3HT based solar cells, and a power conversion efficiency of 0.23% was reached [34]. Dhawan et al. reported the use of CQDs and ZnO:CQD composite as an electron acceptor in polymer solar cells, and high efficiency of more than 2% was achieved when they were blended with a large band-gap polymer [35]. It is worth to note that CQDs used in these polymer solar cells were synthesized by hydrothermal methods, which usually contain multiple hydrophilic terminal groups or with long alkyl side chains, which might hinder the charge transport in the blended film. Therefore, development of more controllable CQDs with less hydrophilic terminal groups is highly interesting for solution processed organic solar cells, since CQDs should have advantages of easy of large-scale preparation and low cost.

Knowing chemical vapor deposition (CVD) is an excellent alternative method to synthesize CQD with better property control and less hydrophilic groups, this paper report the synthesis of high quality CQDs via a simple and fast CVD method (named C-CQDs). Optical and electronic properties, as well as the use of C-CQDs in polymer solar cells were carefully investigated. The results showed that C-CQDs are applicable in polymer solar cells, promoting the development of high performance carbon based materials for polymer solar cells.

2. Experimental

2.1. Materials

Highly pure C_2H_2 and Ar (>99.99%) were purchased from Leap Gas Co. Ltd. N,N-Dimethylformamide (DMF) was purchased from Tianjin Fuchen Chemical Reagents Factory. N-Hexane and cyclohexane were supplied by Tianjin Guangfu Technology Development Co. Ltd. Regioregular poly(3-hexylthiophene) was purchased from Solarmer Energy, Inc. (Beijing). ZnO was synthesized by so-gel method [36]. H-CQDs were synthesized by hydrothermal method [37].

2.2. Preparation of C-CQDs

C-CQDs were synthesized by CVD in Ar atmosphere using C_2H_2 as carbon source [38]. The preparation was conducted in a quartz tube (32 mm i.d. and 1 m long), which was mounted in a horizontal tubular furnace. At the beginning of synthesis, the quartz tube was heated to 1000 °C in Ar atmosphere. Then a mixture of C_2H_2 /Ar was introduced into the reactor at a rate of 70/700 mL min^{-1} for 2 h. After the reaction, the quartz tube was cooled to room temperature under the protection of flowing Ar. The crude product was collected in a receiving flask, and dissolved in 200 mL of DMF by sonication for 30 min. The DMF solution was filtered through a filter paper (in middle speed) and a syringe filter (PTFE, 0.45 μm). The organic solvents were removed under vacuum to give C-CQDs.

2.3. Preparation of solar cell

Photovoltaic devices were fabricated on commercial glass slides coated with patterned ITO. The substrates were cleaned in an ultrasonic bath using detergent, deionized water, acetone and isopropanol in sequence. Immediately prior to device fabrication, the substrates were treated in a UV-ozone oven for 30 min. ZnO (10 mg/mL in acetone) was spin-coated on the cleaned and patterned ITO substrates at 2300 rpm for 60 s. The samples were subsequently annealed at 120 °C for 10 min on a hot plate. A solution of 10 mg/mL poly(3-hexylthiophene-2,5-diyl) (P3HT) in 1,2-dichlorobenzene with different CQDs contents (0, 2.5, 5 and 10 wt.% vs. P3HT) was spin-coated onto the top of the ZnO layer at 1000 rpm for 60 s and subsequently annealed at 120 °C for 10 min in order to fabricate P3HT:C-CQDs solar cells. For P3HT:C-CQDs:PC₆₁BM solar cells, the P3HT and PC₆₁BM were first dissolved in 1,2-dichlorobenzene at a weight ratio of 1:1 (with a total concentration of 40 mg/mL) doping with different ratio of C-CQDs (0, 0.025, 0.05, 0.075 and 0.1 wt vs. P3HT:PC₆₁BM). The wet P3HT:PC₆₁BM blend films were then put into covered Petri dishes for 1.5 h. The samples were subsequently heated at 120 °C for 10 min. Finally, MoO₃ (20 nm) and Al (100 nm) were sequentially vacuum-deposited on the top of the active layer as the hole-extracting layer and the anode, respectively. The effective area of the devices was 0.09 cm².

2.4. Characterization

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images of the C-CQDs were taken from an FEI Tecani G2 F20 S-Twin 200 kV microscope. Fourier transformation infrared spectra of C-CQDs and H-CQDs were characterized by a Tenor 27 FTIR spectrometer. The U-3900 ultraviolet–visible spectrophotometer (UV–Vis) and Fluoromax-4 photoluminescence (PL) spectrometer were used to characterize the optical property of the composite. Cyclic voltammetry (CV) curves are obtained in a tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 mol L⁻¹) supported DMF solution at room temperature using a RST3000 electrochemical workstation operated at a scanning rate of 100 mV s⁻¹, in which a Pt wire ($\phi = 1$ mm) embedded in Teflon column was used as the working electrode, and a Pt sheet and Ag/AgCl electrodes were served as the counter and reference electrodes, respectively, and a ferrocene/ferrocenium was used as the internal reference to calibrate the redox potentials. The current density–voltage (J – V) characteristics are measured in a N₂-filled glove box using a Keithley 2400 source meter under an AM 1.5G filter (100 mW cm²) generated by white light from a halogen tungsten lamp, filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter. External quantum efficiency (EQE) was measured under simulated one sun operation condition using bias light from a 532 nm solid state laser. Light from a 150 W

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