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Facile synthesis and characterization of carbon quantum dots and photovoltaic applications

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ABSTRACT

In this paper, we report the synthesis and characterization of carbon quantum dots that were easily obtained from citric acid and ethanediamine. The synthesized carbon quantum dots (QDs) had various wavelengths and improved electron extraction. We fabricated photovoltaic cells based on these QDs-integrated in polymer nanocomposite used as an interlayer (electron extraction layer) consisting of carbon QDs dispersed by spin coating on an ethoxylated polyethylenimine. In addition, we investigated the photovoltaic performance of the photovoltaic cells.

1. Introduction

Recently, solution-processing technology has been widely employed to fabricate bistable memory devices [1], field-effect transistors [2], light-emitting diodes [3], and photovoltaic (PV) cells [4] because of their potential applications in next-generation electronic and optoelectronic devices. This technology promises good results in developing low cost, efficient, bright, and large area color displays that are compatible with flexible and bendable substrates. Solution-based nanomaterials have been widely studied as promising opto-electronic materials. Among them, carbon quantum dots (CQDs), a member of opto-electronic nanomaterials, are of increasing importance because they have better properties compared to inorganic quantum dots: They are economical, and they have low toxicity, excellent water dispersibility, and satisfactory biocompatibility. From these outstanding merits, CQDs have proved to be suitable for bioimaging, chemical and optical sensing, photocatalysis (or photo-electrochemical cells), fast energy conversion and so on. [5] These days, CQDs are becoming more attractive materials for many applications because of their potential in next-generation electronic and optoelectronic devices, especially due to their excellent physicochemical stabilities, multi-functionalities, and facile functionalization. Thus, nanocomposites structures, including nanoparticles, have emerged as excellent candidates for promising applications in electronic and optoelectronic devices operating at lower currents, low power consumption, low voltage and higher temperatures [6–12].

In this study, we report the synthesis of CQDs that were easily obtained from citric acid and ethanediamine (EDA). In addition, our characterization of the CQDs investigated the optical, electrical and structural properties with various techniques. To apply the characteristics of CQDs, we fabricated PV cells based on CQD/polyethylenimine ethoxylated (PEIE) composites as an interfacial layer with an electron extraction property on an indium-tin-oxide (ITO)/glass substrate. In addition, we investigated the mechanism and performance of the PV cells.

2. Experimental section

2.1. Synthesis of carbon quantum dots

2.1 g citric acid was slowly added to 30 mL of a distilled water solution containing 1.8 g ethylenediamine. After the clear solution was stirred, it underwent microwave treatment for 8 min in a 750 W microwave oven. Then the resultant product was dissolved in deionized water and centrifuged for 30 min at 5000 rpm before 24 h of dialysis in a disposable biodialyzer (1 kDa molecular weight cut-off, purchased from Millipore-Sigma). The final dialyzed dispersion of CQDs was obtained and freeze-dried for further use.

2.2. Characterization measurements

The morphology and size distribution of the CQDs were determined via transmission electron microscopy (TEM, Philips Tecnai G2 F20 microscope, Netherlands) with an accelerating voltage of 200 kV and atomic force microscopy (AFM, Park Systems NX10). X-ray diffractometry (XRD) patterns were recorded using Cu Kα (λ = 1.540 Å)

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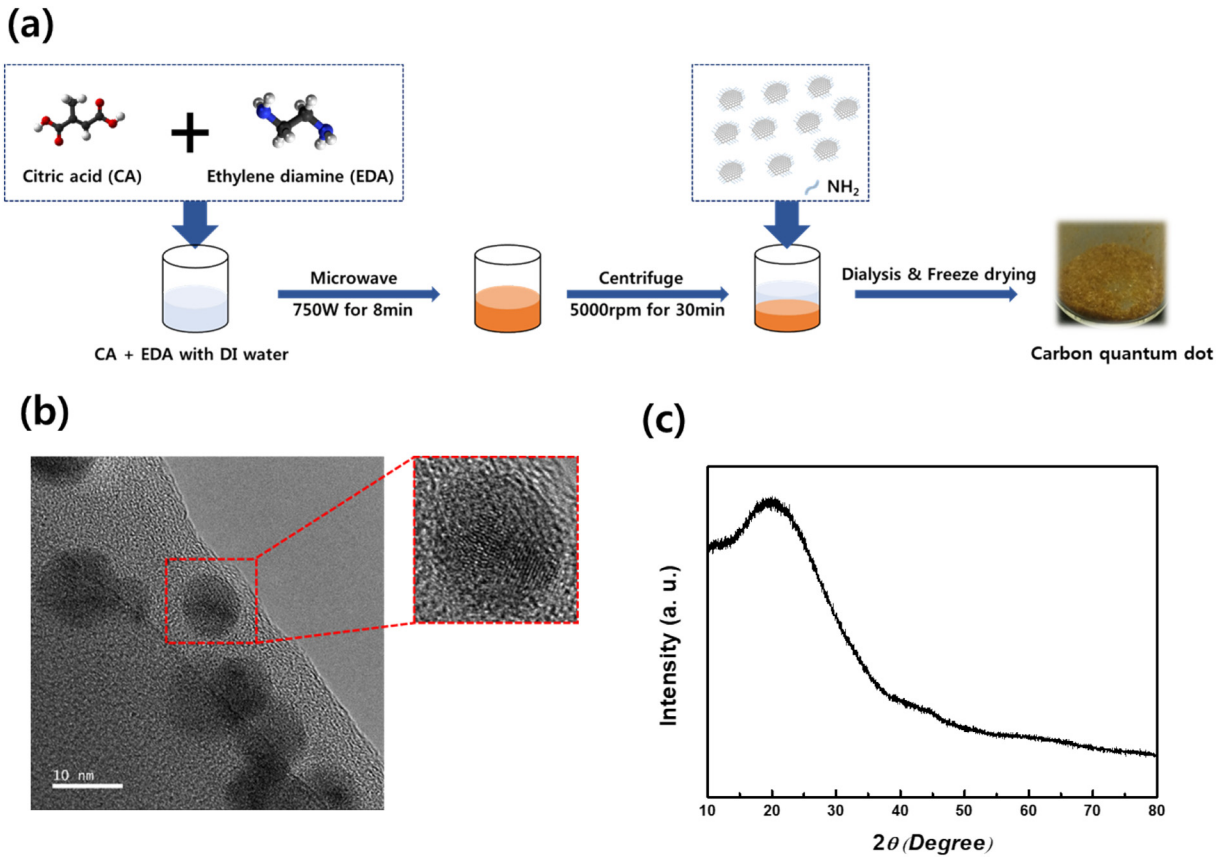

Fig. 1. (a) Schematic of the synthesis method of the CQDs. (b) TEM image of the CQDs. The insert is an enlarged TEM image of the CQDs. (c) XRD patterns of the CQDs.

radiation (max-2500, Rigaku). The chemical structure of the CQDs was measured with a Fourier transform infrared (FT-IR) spectrometer (Frontier, Perkin-Elmer). Ultraviolet-visible (UV–vis) absorption spectra of the CQDs were measured with a UV–vis spectrophotometer (UV-2600) (Shimadzu, Japan). X-ray photoemission spectroscopy (XPS, Thermo Scientific K-alpha) was performed using monochromated Al Kα X-ray photons ($h\nu = 1486.6$ eV).

2.3. Quantum yield measurements

The QY of prepared CQDs was measured by comparing that of the reference quinine sulfate (54% in 0.1 M H_2SO_4). The QY was calculated as follows:

$$Q_x = Q_{st}[I_x/A_x][A_{st}/I_{st}][\eta_x/\eta_{st}]^2$$

where st means the standard reference, x is the sample for test. Q is the quantum yield, and I and A are the integrated emission intensity and optical absorption of the measured sample, respectively. η is the refractive index.

2.4. Characterization of the energy level of carbon dots

Electrochemical cyclic voltammetry was conducted on a ZIVE SP2 electrochemical workstation. The CQDs were dispersed in a 0.5% Nafion solution of isopropanol and dimethylformamide. The solution was dropped on glassy carbon, which was used as the working electrode. A platinum wire and an $Ag/AgNO_3$ electrode in 0.01 M MeCN acetonitrile (MeCN) served as the counter and reference electrode, respectively. A solution of 0.1 M tetrabutylammonium phosphorus hexafluoride ($TBAPF_6$) in anhydrous acetonitrile was used as the electrolyte. Measurement was done at potential scan rates of 100 mV/s and 50 mV/s at room temperature.

2.5. OPV device fabrication

Before making the PV devices, we prepared colloidal CQDs. The concentration of the CQDs solutions was formed by dissolving CQDs (50 wt%) in ethanol in the proper proportions. The ITO glass substrates were cleaned with acetone, ethanol and isopropanol, respectively. The ITO glass was then further treated with O_2 plasma for 40 s. the PEIE layer was coated on the ITO glass at 4000 rpm for 40 s by spin-coating and then annealed with substrates at 110 °C for 10 min. Then the substrates were transferred into a N_2-filled glove box. Immediately afterwards, the CQD solution was spin-coated onto PEIE film substrates at 2000 rpm for 40 s and then the PTB7:$PC_{71}BM$ solution was spin-coated onto the CQDs/PEIE film substrates at 1400 rpm for 10 s. Finally, MoO_3 (10 nm) and Ag (80 nm) were sequentially deposited by thermal evaporation. The substrates were finally annealed at 60 °C for the proper times before use. The solar cells were then tested in air under an AM 1.5G illumination of 100 mW cm^{-2} (Oriel 1 kW solar simulator), which was calibrated with the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc.) for accurate measurement. The external quantum efficiency (EQE) was measured using an Oriel IQE-200 (Newport), a calibrated Si UV detector, and an SR8570 low noise current amplifier.

3. Results and discussion

The chemical synthesis process of CQDs is easily accomplished with citric acid and ethanediamine (EDA) by microwave treatment and further purification, as illustrated in Fig. 1(a). EDA with the amino group (NH^{2+}) is a pharmaceutical ingredient commonly used in large