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Blue Electroluminescent Carbon Dots Derived from Victorian Lignite

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ABSTRACT: Carbon dots (CDs) derived from natural products have attracted considerable interest as eco-friendly materials with a wide range of applications, such as bioimaging, sensors, catalysis, and solar energy harvesting. Among these applications, electro-luminescence (EL) is particularly desirable for light-emitting devices in display and lighting technologies. Typically, EL devices incorporating CDs feature a layered structure, where CDs function as the central emissive layer, flanked by charge transport layers and electrodes. Under an applied external bias, electrons and holes are introduced into the active CD layer, resulting in EL through radiative recombination. However, achieving EL with natural product-derived CDs has remained elusive due to challenges such as production difficulties and quenching in the solid state. In this



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study, we present, for the first time, the successful realization of EL from natural product-derived CDs, synthesized using Victorian lignite through a straightforward single-step pyrolysis method. The CDs demonstrated excellent dispersibility in solvents, allowing them to serve as an emissive layer in light-emitting diodes (LEDs). This was achieved by spin-coating a concentrated CD solution between the organic hole and electron transport layers on a glass substrate coated with indium tin oxide. Remarkably, the CDs retained their dispersibility and emissive efficiency both in solution (toluene) and after film formation. Moreover, the resulting LED demonstrated blue EL, characterized by a peak emission at 460 nm and a maximum luminance of 100.4 cd/m^2 . This luminance is comparable to that achieved with CDs synthesized from conventional chemical carbon sources. These results highlight the promise of natural product-derived CDs as sustainable and eco-friendly materials for use in LED applications.

INTRODUCTION

Carbon dots (CDs) have garnered considerable interest due to their stable photoluminescence (PL) and notable benefits, including nontoxicity and environmental compatibility, making them a favorable alternative to traditional heavy metal (Cd/ Pb)-based inorganic semiconductor quantum dots (QDs). Since their discovery by Xu et al.,¹ the photoluminescent (PL) properties of CDs have undergone substantial enhancement.² Notably, the highest reported quantum yield (QY) of 93.3% for blue fluorescent CDs rivals that of top-performing inorganic semiconductor QDs.3 Due to their enhanced properties, CDs are regarded as a promising substitute for traditional semiconductor QDs, sparking significant interest in optoelectronic applications.⁴⁻²² Electroluminescence (EL) has been observed in CDs synthesized from various chemical carbon sources.^{23–40} Recently, CDs derived from natural products have gained significant attention as innovative and eco-friendly materials.⁴⁰⁻⁵¹ In 2020, Dager et al. introduced novel and straightforward methods for synthesizing CDs using fennel seeds⁵² and fenugreek seeds.⁵³

Light-emitting CDs derived from coal as the carbon source are also being actively researched. The synthesis of CDs from coal has been achieved through chemical oxidation methods involving sulfuric acid or nitric acid.^{54,55} However, these approaches entail multiple steps and the use of hazardous oxidants, calling for the development of simpler and safer methods that align with environmentally friendly applications. Solvent extraction from coal has long been employed to investigate the complex chemical composition of this resource.⁵⁶ Previous studies have also reported fluorescence in solutions extracted from coal,⁵⁷ suggesting the possible presence of fluorescent CDs within coal extracts obtained using solvents. Generally, it is not easy to identify the nanostructure of luminescent materials extracted from natural materials. Recently, Inoue et al. reported a one-step extraction method for obtaining blue light-emitting CDs from lignite, a cheap and low-quality grade of coal with a high organic

Received:August 29, 2024Revised:December 18, 2024Accepted:December 20, 2024Published:January 8, 2025







Figure 1. Schematic representation of the synthetic procedure for CDs derived from Victorian lignite by (a) pyrolysis in nitrogen atmosphere with an electric furnace, and (b) extraction of CDs with toluene solvent.

content.⁵⁸ They attempted to identify luminescent materials by examining their luminescent properties that depend on the excitation light wavelength and the choice of extraction solvent.

In this paper, we present the first report of EL from CDs synthesized from Victorian lignite. These CDs exhibited excellent dispersion and emissive properties, both in a toluene solution and within the layered structure of a LED. The lignitederived CDs displayed blue EL with a spectral peak at 460 nm and a maximum luminance of 100 cd m^{-2} , marking a significant advancement in the development of sustainable materials for LED applications. Furthermore, we attempted to identify the light-emitting structure using several analytical methods.

EXPERIMENTAL SECTION

Pyrolysis Process of Victorian Lignite. The CDs derived from Victorian lignite CDs were prepared by pyrolysis in nitrogen at two different temperatures. The synthesis process of the CDs is illustrated schematically in Figure 1. Approximately 3 g of the lignite sample (in diameter < 150 μ m) was weighed and loaded into a quartz boat placed at the middle section of a horizontal quartz tube (50 mm OD \times 44 mm ID \times 600 mm L) and sealed with a flange arrangement. High purity nitrogen was supplied to flush air out of the quartz tube prior to heating up the furnace. Then, the sample was pyrolyzed at a temperature of 300 and 400 °C with a heating rate of 2 °C/min under a nitrogen flow (ca. 100 mL/min). Once the temperature reached the final target temperature, it was held for 2 h to complete the pyrolysis. The lignite reduced in weight by 40-50% after the pyrolysis depending on the pyrolysis temperature employed. The remaining powdery solids containing carbon dots (CD) were collected for further investigation of their respective chemical and luminescence properties, and further processing to validate the blue light emission and to produce the light emitting device.

CD Extraction. The CDs recovered after pyrolysis at 300 °C and at 400 °C were suspended in 15 mL of toluene and dispersed for 15 min in an ultrasonic bath (BRANSON B1500R-DTH). An extract of raw lignite without pyrolysis was also obtained in the same process using toluene solvent. Black and turbid liquids were obtained. The liquid samples were processed in a centrifuge (CLEMENT 2000S) at 3000 rpm for

30 min to separate the solid and liquid phase. The clear yellow liquid phase was then decanted into a sample vial. The transparent solution has a blue light-emission under ultraviolet (UV) light. Figure 2 shows photographs of the extracted

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Figure 2. Photographs of the filtered solution under (a) white light and (b) UV light.

solutions under (a) white light and (b) UV irradiation. The photoluminescence (PL) spectra of the CD solutions were measured using a fluorescence spectrometer (Cary Eclipse, Agilent technologies).

Prototyping EL Devices (Light-Emitting Devices). In preparation for prototyping LEDs, the solution obtained from extraction of the 300 °C pyrolyzed sample in toluene was concentrated by about 100 times by evaporating the solvent. Four mg/L of polyvinyl-carbazole (PVK) was added to this concentrated solution to obtain the final solution for spin coating on the PVK layer.

First, glass substrates with a patterned indium-tin-oxide (ITO) layer were treated for 15 min under UV (Novascan RTS). Poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) was spin-coated as a hole injection layer onto the ITO film at 3000 rpm for 1 min, and baked on a hot plate at 200 °C for 10 min in air. A neat PVK layer was spin-coated from a solution of PVK in toluene (4 mg/mL) on the PEDOT:PSS film at 2000 rpm for 30 s, and baked on a hot plate at 160 °C for 10 min in air. Then, the CDs and PVK mixture layer was spin-coated using the aforementioned toluene solution on the PVK at 1500 rpm for 30 s, and baked on a hot plate at 150 °C for 10 min in air. The electron transport layer of 1,3,5-tri(*m*-pyridin-3-ylphenyl)benzene



Figure 3. (a) Illustration of layered LED device structure and (b) process condition of each layers.

(TmPyPB) with a thickness of 20 nm was deposited in a vacuum chamber (5×10^{-5} Pa) onto the CD/PVK mixture film. The electron injection layer of lithium fluoride (LiF) with a thickness of 1 nm was deposited in a vacuum chamber (5×10^{-5} Pa) onto the TmPyPB film. Finally, the cathode electrode of aluminum (Al) with a thickness of 100 nm was deposited in a vacuum chamber (5×10^{-5} Pa) on the LiF film. The device structure and process conditions are summarized in Figure 3.

The LED device was analyzed by measuring its current– voltage and luminescence characteristics using a Keithley 2400 source measure unit and a Topcon BM-7 luminance colorimeter, respectively. EL spectra were recorded with an ASEQ Instruments LR1 spectrometer.

RESULTS AND DISCUSSION

Photoluminescence (PL) of CDs Solution Extracted from Pyrolyzed Lignite. The raw lignite and carbon materials obtained via the pyrolysis at 300 and 400 °C were used to prepare toluene solutions, and their PL characteristics were compared. As shown in Figure 4, the raw lignite solution



Figure 4. PL spectra of filtered toluene solutions using (a) raw lignite, (b) pyrolyzed CDs on 300 °C, and (c) 400 °C.

has a peak around 380 nm, and the solutions from the 300 and 400 $^{\circ}$ C pyrolysis product have a peak around 408 nm. The strongest PL was observed in the solution with pyrolysis processed CDs at 300 $^{\circ}$ C.

Chemical Characterization of CDs Extracted from Pyrolyzed Lignite. CD toluene solutions extracted from raw and 300 and 400 °C pyrolyzed lignite were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). Given that Fioressi et al.⁵⁹ reported that benzo[a] pyrene has a PL peak at a wavelength of 408 nm, the same as the PL result

shown in Figure 4, our results strongly suggests that the extracted CDs are mainly composed of benzo[a]pyrene or similar aromatic materials. However, as ICP-MS analysis does not detect molecular species, it cannot be definitively concluded that benzo[a]pyrene is the main material of emission, and other unidentified hydrocarbon impurities may be present.

As shown in Table 1, the highest concentration of benzo[a] pyrene were detected remarkably excluding chain

Table 1. Analysis Results of CDs Toluene Solution Extracted from Lignite by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

benzo [a] pyrene TEQ [mg/kg]	
raw lignite/toluene	3.6
pyrolyzed lignite 300 °C/toluene	13.5
pyrolyzed lignite 400 °C/toluene	10.7

hydrocarbons in the CDs toluene solution extracted from 300 °C pyrolyzed lignite, and the lowest concentration of it were detected in the solution extracted from raw lignite. The concentration of benzo[a]pyrene shows the same trend as the PL intensity as shown in Figure 4.

Furthermore, no metal impurities were detected in the ICP-MS analysis. However, as this CD is derived from natural sources, it is plausible that it contains substantial amounts of unidentified hydrocarbon impurities.

Next, we tried to measure the PL lifetime decay of a sample pyrolyzed at 300 °C and extracted with toluene using ps-pulse excitation light with a wavelength of 380 nm to match the UV-vis absorption band. As shown in Figure 5, the PL emission decayed in approximately 50 ns. In model fitting using the exponential function described below, good fitting results were obtained using time constants $\tau_1 = 1.8$ ns, $\tau_2 = 7.0$ ns, and coefficients A = 13.0, $B_1 = 1.5 \times 10^{14}$, $B_2 = 1.2 \times 10^6$.

$$F(t) = A + B_1 \exp\left(-\frac{t}{\tau_1}\right) + B_2 \exp\left(-\frac{t}{\tau_2}\right)$$
(1)

Two time-constants were required for exponential fitting suggesting the existence of at least two emission relaxation processes, which may indicate the presence of species other than benzo[a] pyrene.

We estimated the size of the carbon dots (CDs) using transmission electron microscopy (TEM). The two samples of CD solution were scooped twice with a 3 mm diameter grid (a substrate of TEM) and dried. For the TEM analysis, a solution was prepared by redispersing dried CDs, initially obtained



Figure 5. PL lifetime decay of the CD solution in toluene using CDs synthesized from lignite by pyrolysis at 300 °C.

from a toluene solution, in ethanol to avoid potential contamination of the equipment with toluene. TEM images were subsequently acquired, from which the size of the CDs was measured, and their quantity was counted.

As shown in Figure 6, the average diameters of CDs pyrolyzed at 300 and 400 $^{\circ}$ C were 4.0 nm (standard deviation,



Figure 6. TEM images and size distributions of dried CDs obtained from lignite by pyrolysis at (a) $300 \degree C$ and (b) $400 \degree C$.

 σ = 1.5 nm) and 7.0 nm (σ = 2.9 nm), respectively, with CDs pyrolyzed at 400 °C exhibiting a significantly larger diameter. Additionally, the number of CDs produced at 300 and 400 °C was 554 and 234, respectively, with a higher number observed for the CDs synthesized at 300 °C.

The PL peaks of the CDs pyrolyzed at both 300 and 400 $^{\circ}$ C were both observed at 408 nm, and no strong correlation was found between CD size and PL peak wavelength. This result

suggests that the emission mechanism may be dominated by molecular materials such as benzo[a]pyrene, rather than CD size. However, the higher number of CDs synthesized at 300 °C corresponds to the observed trend in PL intensity.

Additionally, we attempted to obtain TEM images from raw (nonpyrolyzed) CD solutions, but only a very small number of CD particles were obtained. These results indicate a strong relationship between the concentration of CDs and their PL emission intensity.

LED Device Performance. As mentioned above, the CDs solution obtained by pyrolyze at 300 °C had the strongest PL intensity, so we decided to prototype LED devices using this solution.

Figure 7(a) shows the emission spectrum of the prototype EL device. The emission peak was around 461 nm wavelength, and its width was wider than the PL peak. The cause of the wide and red-shifted EL emission peak is thought to be that the particle size of the CDs and the types of functional groups are not uniform, and that impurities remain. Figure 7(b) shows the results of the voltage-current-luminescence (V-I-L) characteristics. The EL device has a turn-on around 7 V and exhibits an emission intensity of 100.4 cd/m² at 12 V. This EL emission using CDs derived from the lignite is a world first result.

The color coordinates on the CIE 1931 color plot of (0.11, 0.31) estimated from the spectral analysis are shown in Figure 7(c). Figure 7(d) shows a photograph of the top view of the light emission on the operating LED device.

During EL operation, carriers are injected from the anode (ITO) and cathode (LiF/Al), which have a work function gap of 1.2 eV (Figure 8(a)), into the CDs. These CDs exhibit a wider energy gap of 2.69 eV (461 nm) under EL compared to the narrower gap observed during PL (3.04 eV, 408 nm) when excited by UV light (4.13 eV, 300 nm), as illustrated in Figure 8(b).

Consequently, the EL emission of the CD-LED is redshifted relative to its PL emission. This result strongly suggests that the emission is obtained from narrower band gap different from benzo[a]pyrene with the main peak at 408 nm of PL.

CONCLUSIONS

We report the first observation of blue electroluminescence (EL) in carbon dots (CDs) derived from Victorian lignite. These CDs were synthesized through a straightforward pyrolysis process. The synthesized CDs exhibited excellent dispersibility in solvents, allowing for their application as an emissive layer in a LED through the spin-coating of a concentrated CD solution. The fabricated LED device displayed blue EL with a spectral peak at 461 nm and a maximum luminance of 100.4 cd/m². Furthermore, a sandwich-structured LED device was constructed using a standard fabrication process that included spin-coating and deposition steps. This process required careful implementation of advanced techniques, including precise control of drying times after spin-coating.

We anticipate that the EL performance can be further enhanced by optimizing the device fabrication process.

Nonetheless, to achieve higher efficiency and narrow-band EL emission, it is essential to purify and standardize the carbon luminescent material. Future research will focus on analyzing the structure of the CDs obtained from lignite and improving their purity.



Figure 7. Device performance of (a) EL spectrum of the LED with pyrolyzed CDs on 300 $^{\circ}$ C as the emission layer. (b) Voltage-currentluminance characteristics of the LED. (c) CIE 1931 color index (0.11, 0.31) of emission from the LED. (d) A top view of blue light emission from the LED.





METHODS

Synthesis of CDs. 3.0 g of ground lignite (in diameter < 150 μ m) were placed in a quartz boat and heated at 2 °C per minute and then held at 300 °C for 3 h in an electric furnace in a nitrogen atmosphere. After cooling to room temperature, the

carbonized powder was dissolved in 115 mL of toluene via sonication for 20 min. The resulting black suspension was centrifuged at 3000 rpm for 30 min to remove any undissolved particles, and the supernatant was subsequently filtered through a 200 nm pore size filter (PALL Acrodisc, Japan). The toluene solution of CDs obtained through this process

was utilized for PL measurements and the fabrication of LED devices. $^{\rm 40}$

Characterization of CDs. The PL spectra of the CD solution were recorded using an excitation wavelength of 300 nm, while PL decay was measured with a 500 kHz UV pulse (320 nm excitation wavelength and 420 nm emission wavelength) using a fluorescence spectrometer (FLS920, EDINBURGH INSTRUMENTS). The TEM images were obtained with a JEM 2100F TEM (JEOL, Japan) operating at an acceleration voltage of 200 kV.⁴⁰

Fabrication of LED Device. For device fabrication, ITOcoated glass substrates were first cleaned with isopropyl alcohol and deionized water in an ultrasonic bath, followed by UVozone treatment in a UV-ozone cleaner (Novascan PSD Pro) to create an oxygen-rich ITO surface, thereby enhancing the work function of ITO. A 40 nm thick layer of PEDOT/PSS (Clevios AI 4083) was then spin-coated as the hole injection layer onto the ITO at 3000 rpm for 1 min and baked at 200 °C for 10 min on a hot plate in air. Next, a 30 nm thick layer of PVK (Lumtec LT-N4077), serving as the hole transport layer, was spin-coated onto the PEDOT/PSS layer at 4000 rpm for 30 s using a solution of PVK in toluene (10 mg/mL) and baked at 150 °C for 10 min in air.

For the emissive layer, a highly concentrated (×100) CD solution in toluene (4.4 mg/L) was prepared by evaporating the solvent, and the concentrated CD solution was spin-coated at 1500 rpm for 30 s onto the PVK layer, followed by baking at 150 °C for 10 min in air. A 30 nm thick BP4mPy (Lumtec LT-N862) electron transport layer was then deposited on the CD layer under high vacuum (approximately 1×10^{-5} Pa). Subsequently, a 1 nm thick LiF layer and a 100 nm thick Al layer were deposited as the cathodes onto the BP4mPy layer under high vacuum. Finally, the device was assembled with encapsulating glass and a desiccant, and sealed with a UV-curable epoxy resin. The glass substrate contained six pixels, each with an area of 2×5 mm^{2.40,60}

Analysis of LED Device. The current-voltage and luminescence-voltage characteristics of the fabricated CD LED were analyzed using a source measure unit (Keithley 2400) and a Topcon BM-7 luminance colorimeter, respectively. The EL spectra were recorded with an LR1 spectrometer (ASEQ Instruments).^{40,60}

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Author Contributions

T.H.: Conceptualization, project administration, supervision, funding acquisition, writing original draft, and editing. D.Y.: Methodology, investigation, data curation, formal analysis, validation, writing review. K.I. and R.S.: Support experimental and characterization. T.M. and K.Y.: TEM image acquisition and analysis. M.T.: Supervision, funding acquisition, writing review. All authors contributed to discussions.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Australian Carbon Innovation (22-A02). This work also was supported by the Japan Society for the Promotion of Science (JSPS) KAK ENHI Grants-in-Aid for Scientific Research (17K06797, 21K04654). We thank Dr. A. Scully of CSIRO for carrying out the PL lifetime decay measurements.

ABBREVIATIONS

BP4mPy, 3,3',5,5'-tetra[(*M*-pyridyl)-phen-3-yl]biphenyl CD, carbon dot CIE 1931, the color space was published by the International Commission on Illumination (CIE) in 1931 EL, electroluminescence ICP-MS, inductively coupled plasma mass spectrometry LED, light-emitting diode PEDOT/PSS, poly(3,4-ethylenedioxythiophene) polystyrenesulfonate PL, photoluminescence PVK, poly(9-vinylcarbazole)

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