**Blue Light-Emitting Carbon Dots from Victorian Brown Coal**

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**Abstract.** Carbon dots (CDs) are innovative fluorescent carbon nanomaterials with sizes smaller than 10 nm. However, the practical applications of CDs have been hindered by the relatively high cost of precursors, which limits their large-scale production. Coal is known to be the most abundant with low cost and broadly distributed natural resource on the Earth. It is an organic matter mainly composed of carbon, hydrogen, and oxygen. Thus, coal is an attractive precursor for synthesizing CDs with a large-scaled production. In this study, we demonstrate a one-step extraction method for obtaining blue light-emitting CDs from Victorian brown coal in Australia, which is low cost and has an abundant reserve over the world. The extraction of certain substances from the brown coal was achieved using ethanol as a solvent. Subsequently, the solution of the extracted substances exhibited blue luminescence when exposed to ultraviolet irradiation. Transmission electron microscopy images revealed nanoparticles with an average size of 4.0 nm. The photoluminescence spectrum displayed a broad peak with a full width at half maximum of 116 nm, centered around 448 nm, when excited at 360 nm. Remarkably, these characteristic features closely resemble those observed in fluorescent CDs obtained from high-cost precursors using multi-step procedures such as pyrolysis decomposition, chemical oxidation, microwave-assisted synthesis, ultrasonic synthesis, and laser ablation synthesis. These results demonstrate the successful extraction of fluorescent substances or CDs from the brown coal using a simple one step extraction method. Furthermore, we suggest that fluorescent substances or CDs may naturally be present in Victorian brown coals.

# INTRODUCTION

Carbon dots (CDs) are a novel class of fluorescent carbon nanomaterials characterized by their sub-10 nm size. Compared to traditional semiconductor quantum dots, CDs offer several advantages, including high photostability, excellent aqueous solubility, robust chemical inertness, and easy modifiability [1]. They have been successfully synthesized from a variety of carbon-containing materials such as graphite [2], graphene [3], and organic molecules like citric acid [4, 5]. In recent years, there has been a growing interest in utilizing natural resources as precursors for CDs due to their eco-friendliness, low cost, and abundance [6]. Notably, facile, and effective methods for synthesizing CDs from plant seeds have been developed with an application in LED technology [7-9].

Coal is known to be the low cost and one of the most abundant natural resources distributed across the globe [10]. It is a plant based organic matter mainly composed of carbon, hydrogen, and oxygen with nitrogen, sulfur and chlorine being minor elements. Therefore, coal, as a natural resource, is attractive for a precursor for synthesizing CDs with a large-scaled production. Generally, coal is classified into four main types including anthracite, bituminous, subbituminous, and brown coal [11]. Among coals, brown coal, also known as lignite, is classified as low rank coal which contains the least fixed carbon and the most volatile matter (organic components). Brown coal is generally considered to be a low-cost resource. Australia is known to have abundant reserves of brown coal resources with a total estimated reserve of 430 billion tonnes (a total production of 57.8 million tonnes in 2013-2014) [12]. Most of the brown coal resources are located in the state of Victoria, with an approximate 65 billion tonnes of the resources confirmed in the Latrobe Valley (southeast of Victoria), which is equivalent to 25% of the world confirmed brown coal reserve.

There are some studies on the synthesis of CDs from coal [13], as well the synthesis of other nanocarbons such as carbon nanotubes [14] and graphene [15]. CDs derived from coal have mainly been synthesized by chemical oxidation methods utilizing sulfuric acid [16] and nitric acid [17]. However, these methods require multi-step procedures with the usage of toxic oxidants. Thus, a simpler and safer method is desired as a more environmentally friendly approach. An extraction method is one of the simplest methods for the synthesis of CDs [18]. To date, extraction methods have been employed to extract CDs from some sources such as man-made carbon black [19], coffee [20], and beer [21]. However, to the best of our knowledge, there have been no reports on the extraction of CDs from coal using a solvent extraction method. Solvent extraction has long been used to examine the complex chemical compositions of coal [22]. Additionally, some solutions extracted from coal have been reported to exhibit fluorescence [23]. Thus, it is expected that fluorescent CDs may be present in solvent extracts from coal. Based on the aforementioned discussions regarding the starting materials and methodology to extract carbon-based nanomaterials, we conceived the original idea of extracting CDs from brown coal as a starting material, using a simpler and more environmentally

friendly methodology.

In this paper, we utilized one of the Victorian brown coals and report a novel one-step extraction method for obtaining blue light-emitting CDs from the brown coal.

# MATERIAL AND METHOD

**Extraction with Ethanol**

Yallourn brown coal, one of the several Victorian brown coals, was used as a starting source material. A total of

0.2 g of the brown coal was dissolved in 5 mL of ethanol through sonication at room temperature for 10 minutes. Ethanol (99.5%, KANTO CHEMICAL CO., INC.) was used in its as-received state. Subsequently, the resulting mixture, appearing black in color, was subjected to centrifugation at 15,000 rcf for 12 minutes to remove any undissolved particles. The supernatant was then filtered using a 0.1 µm-pore size filter (PALL ACRO DISC, Japan). The filtered solution, referred to as the ethanol-extracted sample, underwent various optical and structural characterizations to determine their properties. Additionally, water-extracted samples were prepared for comparative analysis.

# Refluxing with Ethylenediamine

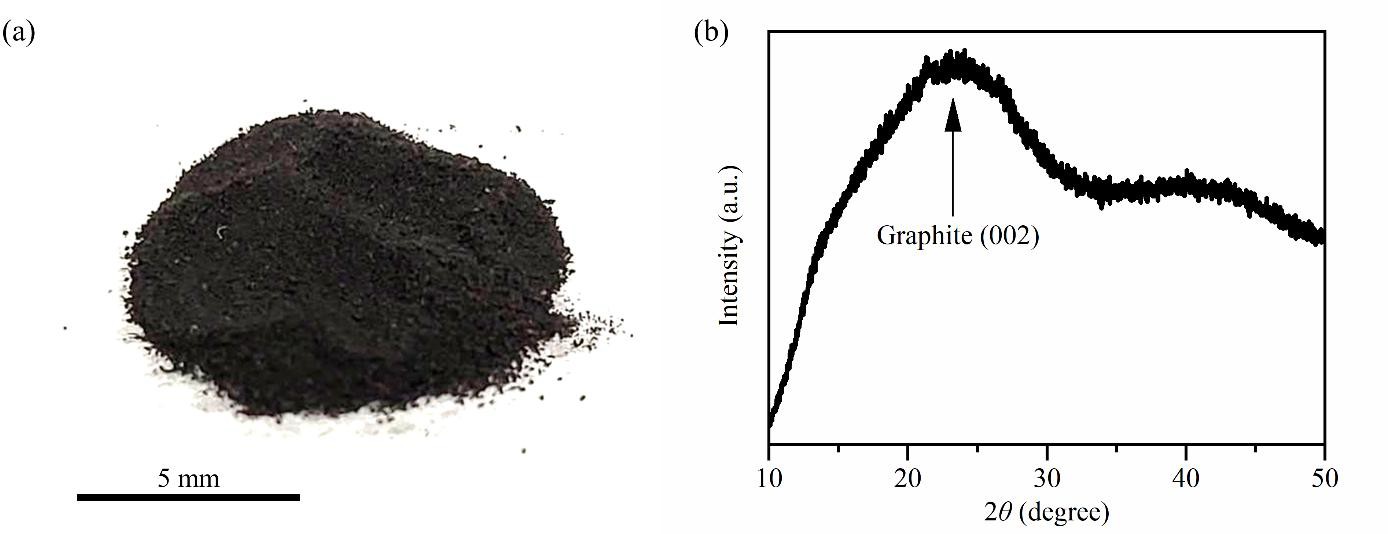
0.4 g of the brown coal was added to 20 mL of a 5% ethylenediamine (EDA) solution, diluted with water. The mixture was refluxed at 100 °C for 12 hours. After refluxing, the resulting suspension was heated at 200 °C, and the solvent was evaporated to obtain a solid residue. Subsequently, the solid residue was immersed into 5 mL of ethanol, and it was sonicated for 10 minutes at room temperature. The resulting blackish mixture was centrifugated at 15,000 rcf for 12 minutes to separate undissolved solid particles from the supernatant. Then, the supernatant was filtered using a 0.1 µm-pore size filter (PALL ACRO DISC, Japan). The filtered solution, referred to as the EDA-refluxed sample, underwent various optical and structural characterizations to assess their properties.

# CHARACTERIZATION

The structural characterization of brown coal and the ethanol-extracted sample was performed using an X-ray diffractometer (D8-ADVANCE, BRUKER) with a Cu Kα radiation (a wavelength of 1.5418 Å). To gain insight into the detailed structure of the ethanol-extracted CDs and EDA-refluxed CDs, transmission electron microscopy (JEM- 2100F, JEOL) was employed. Furthermore, the composition and elemental analysis of all the samples were conducted using a Fourier-transform infrared spectrometer (FT/IR-4100, JASCO) and an X-ray photoelectron spectrometer (Quantera-SXM, ULVAC-PHI, INC), respectively. The optical properties of the ethanol-extracted samples containing CDs and EDA-refluxed sample were investigated through photoluminescence spectroscopy (FP-8500, JASCO, Japan) and ultraviolet-visible absorption spectroscopy (V-730, JASCO, Japan). Additionally, the quantum yield for the PL emission was determined using a fluorescence spectrometer (FP-8500, JASCO).

# RESULTS AND DISUCUSSION

**Characterization of the Brown Coal**



**FIGURE 1.** (a) Photograph of Yallourn brown coal used in this work. (b) XRD pattern of brown coal.

**TABLE 1. Proximate and ultimate analyses of the Yallourn coal sample used in this work [24].**

Proximate analysis [wt%, dry basis] Ultimate analysis [wt%, dry ash free basis]

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Fixed carbon | Volatile matter | Ash | C | H | O (by difference) | N | S |
| 48.05 | 49.25 | 2.15 | 65.75 | 4.30 | 29.25 | 0.45 | 0.25 |

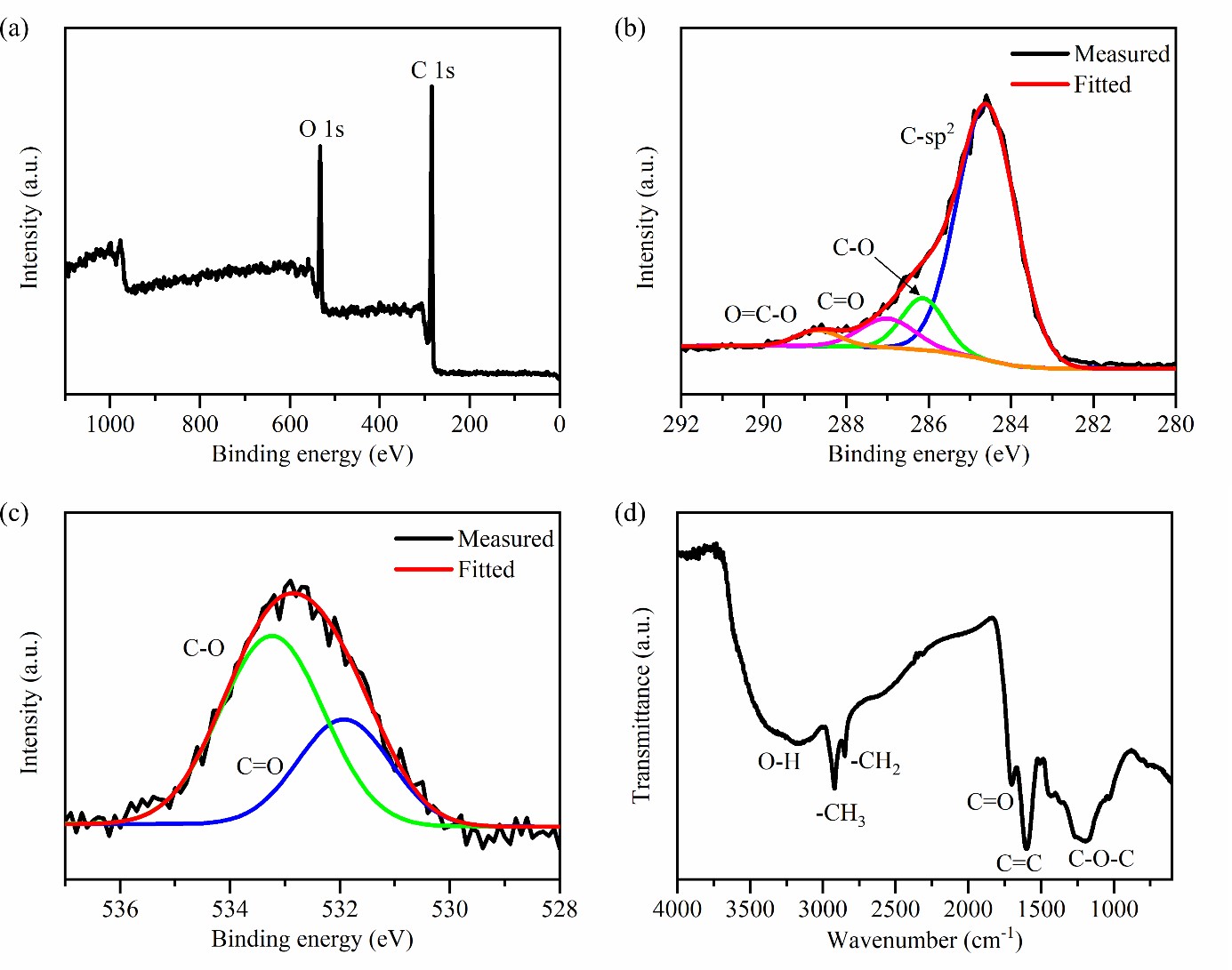
**TABLE 2. Ash analysis of the Yallourn coal sample used in this work [24].**

|  |  |
| --- | --- |
| Minerals and Inorganics | Composition [wt%] |
| SiO2 | 5.3-15 |
| Al2O3 | 3-5 |
| Fe2O3 | 34.1-40.4 |
| TiO2 | 0.1-0.44 |
| K2O | 0.3-1.0 |
| MgO | 14.2-17.2 |
| Na2O | 4.8-6.0 |
| CaO | 6.3-8.3 |
| SO3 | 13.7-17 |

The photograph of the Yallourn brown coal used in this work is depicted in Figure 1(a). The proximate and ultimate analyses, and ash analysis of the Yallourn brown coal are shown in in Tables 1 and 2, respectively [24]. The coal has the carbon content of 65.75 wt% with a relatively high volatile matters (49.25 wt%) which is consistent with the classification of the low rank coal.

The X-ray diffraction (XRD) pattern of the powdered brown coal is presented in Figure 1(b). The pattern reveals a broad peak centered around 23.7°, corresponding to the (002) reflection of graphite. Notably, the lattice spacing of

0.38 nm observed in the brown coal sample is slightly larger than that of graphite (d = 0.34 nm) [25]. This observation suggests the presence of disordered graphite or amorphous carbon in the brown coal structure.



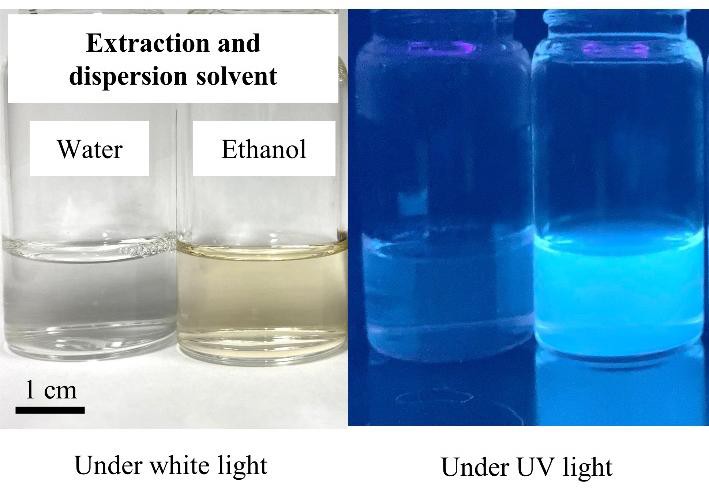
**FIGURE 2.** XPS spectra of brown coal. (a) Survey scan. (b) C 1s. (c) O 1s narrow scan. (d) FT-IR spectra of brown coal.

Figure 2(a-c) shows the X-ray photoelectron spectroscopy (XPS) spectra of brown coal, both in wide and narrow scans. The wide scan XPS spectrum reveals the presence of carbon (C) with a composition of 78.60 at%, oxygen (O) with a composition of 20.58 at%, and nitrogen (N) with a composition of 0.75 at%.

The C 1s XPS spectrum exhibits four distinct components at binding energies of 284.6, 286.2, 287.7, and 288.7 eV, which are attributed to C-sp2, C-O, C=O, and O=C-O, respectively [26] (Figure 2(b)). Additionally, the O 1s spectrum displays two prominent components at binding energies of 531.9 and 533.2 eV, corresponding to C=O and C-O, respectively [26] (Figure 2(c)).

The presence of diverse chemical components in the brown coal sample was confirmed through Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectrum showed characteristic peaks at 1194, 1600, 1702, 2850, 2920, and 3169 cm-1, which can be attributed to specific functional groups: C-O-C, C=C, C=O, CH2, CH3, and O-H, respectively (Figure 2(d)). It is worth noting that the observed FT-IR spectrum aligns well with those reported previously [27].

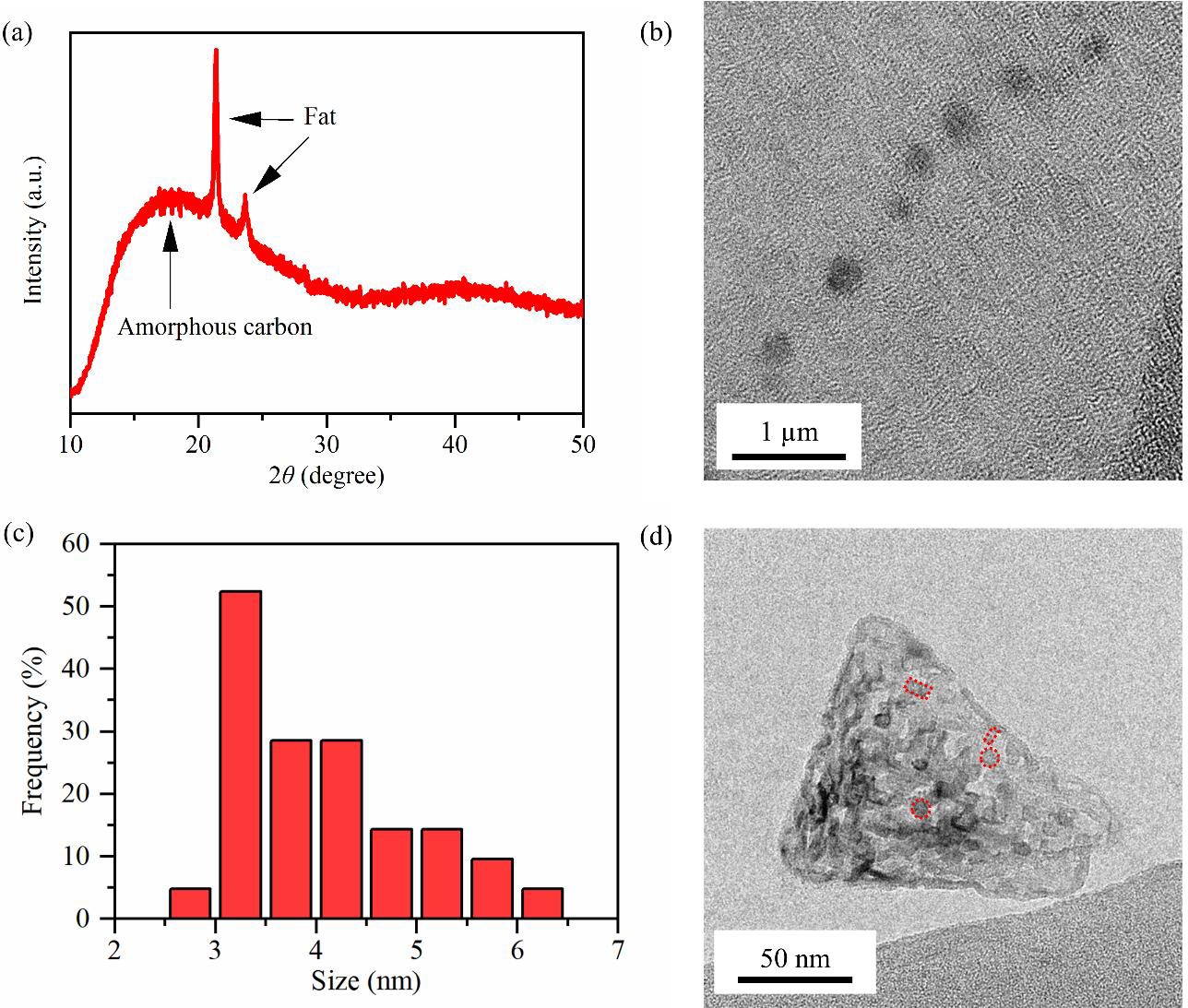
# Ethanol-Extracted CDs from Brown Coal



**FIGURE 3.** Photographs of extracted solution from brown coal.

The extracted solutions from the brown coal were prepared using water and ethanol as solvents. Figure 3 presents photographs of these extracted solutions under white light and UV irradiation. The water-extracted solution appears nearly transparent under white light, while the ethanol-extracted solution exhibits a light brownish colour. Notably, the ethanol-extracted solution displays strong blue luminescence when exposed to 365 nm UV irradiation, whereas no fluorescence is observed in the water-extracted solution. These findings suggest the presence of fluorescent substances or CDs within the brown coal sample.

Furthermore, the difference in fluorescence intensity between the water- and ethanol-extracted solutions may be attributed to the varying amounts of fluorescent substances or CDs extracted from the brown coal. This discrepancy is consistent with the visual contrast in colour observed under white light. Similar trends have been reported in previous studies regarding the extraction rate or amount of fluorescent substances or CDs from brown coal using solvents such as ethanol, EDA, water, and pyridine [22]. Hence, ethanol demonstrates higher efficacy in extracting fluorescent substances or CDs from brown coal compared to water.



**FIGURE 4.** (a) XRD pattern of ethanol-extracted substances or CDs. (b) TEM image of isolated particles of ethanol- extracted CDs. (c) Distribution of the diameters of the isolated particles. (d) TEM image of aggregates of carbon particles (some

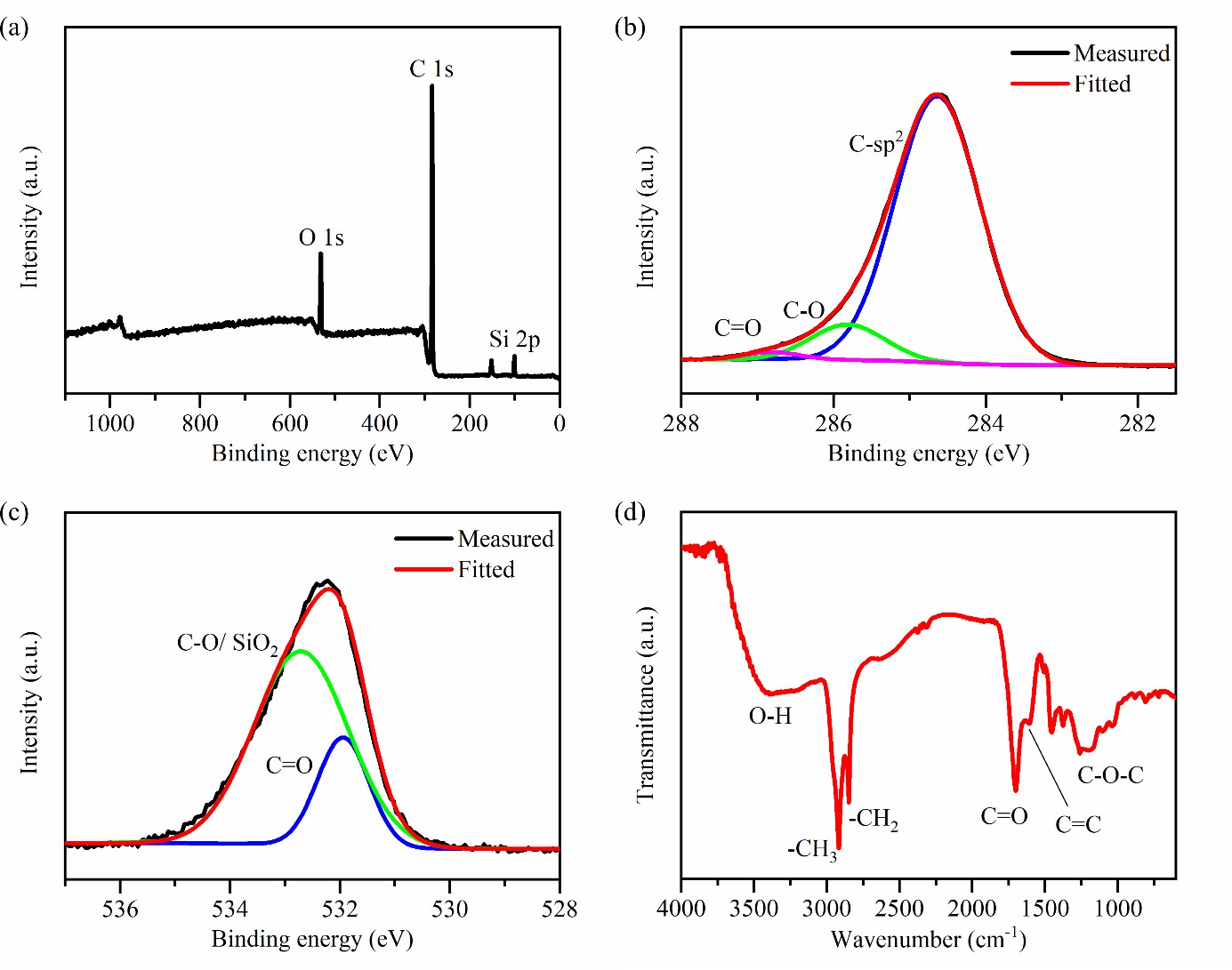
of the round and polygonal shaped particles are marked in red).

To clarify the average structure of the ethanol-extracted substances or CDs, XRD measurements were conducted. Figure 4(a) shows the XRD pattern obtained from the ethanol-extracted sample. The pattern exhibits a broad peak centered around 18.8°, accompanied by two unexpected sharp peaks at 21.4° and 23.6°.

The broad peak corresponds to the characteristic amorphous carbon phase, which has been commonly observed in various CDs reported in the literature [28, 29]. This broad peak can be attributed to the small size and amorphous nature of the CDs present in the ethanol-extracted sample. Additionally, the two sharp peaks at 21.4° and 23.6° can be assigned to the presence of fatty components [30]. It is hypothesized that the brown coal naturally contains fat, which is in line with the high levels of moisture and impurities observed in the brown coal sample (Table 1). Consequently, it is plausible that the observed crystalline peaks associated with fat in the XRD pattern resulted from the crystallization of fat during the drying process of the extracted solution in preparation for XRD measurements.

Figure 4(b-d) shows transmission electron microscopy (TEM) images and the size distribution of the particles of the ethanol-extracted CDs. Figure 4(b) reveals the presence of isolated particles, although clear lattice fringes are not discernible in these particles. This means that observed particles have non-crystalline or amorphous structure. Multiple TEM images were analysed to determine the size distribution of the particles, as shown in Figure 4(c). The average diameter was determined to be 4.0 nm. The observed shape and size of the particles align with those reported for other CDs in the literature [9,31,32]. Consequently, it is reasonable to conclude that the observed particles correspond to fluorescent CDs exhibiting a disordered graphite or amorphous structure, which are inherently present in brown coal. Furthermore, aggregates with dimensions of approximately 100 nm were frequently observed, as depicted in Figure 4(d). As evident in the TEM image, the aggregate appears to comprise two distinct types of particles exhibiting round and polygonal shapes. This observation suggests the coexistence of two types of CDs within the brown coal. Moreover,

it is worth noting that CD aggregation occurs not only in the dried state but also in solution. Such aggregation can significantly influence the optical properties of the CDs.

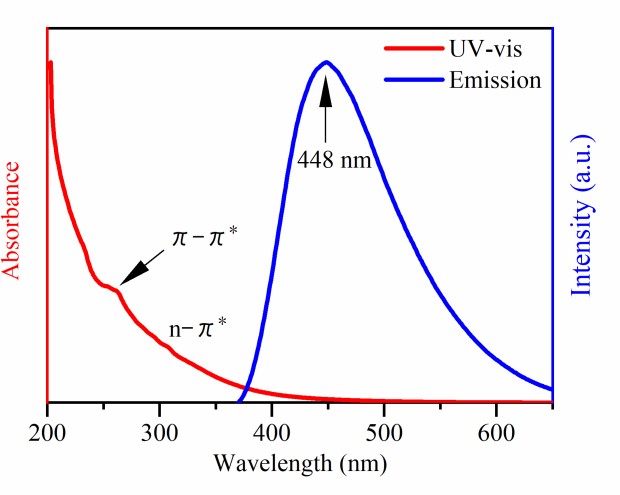


**FIGURE 5.** XPS spectra of ethanol-extracted substances or CDs. (a) Survey scan. (b) C 1s. (c) O 1s narrow scan. (d) FT-IR spectrum of ethanol-extracted substances or CDs.

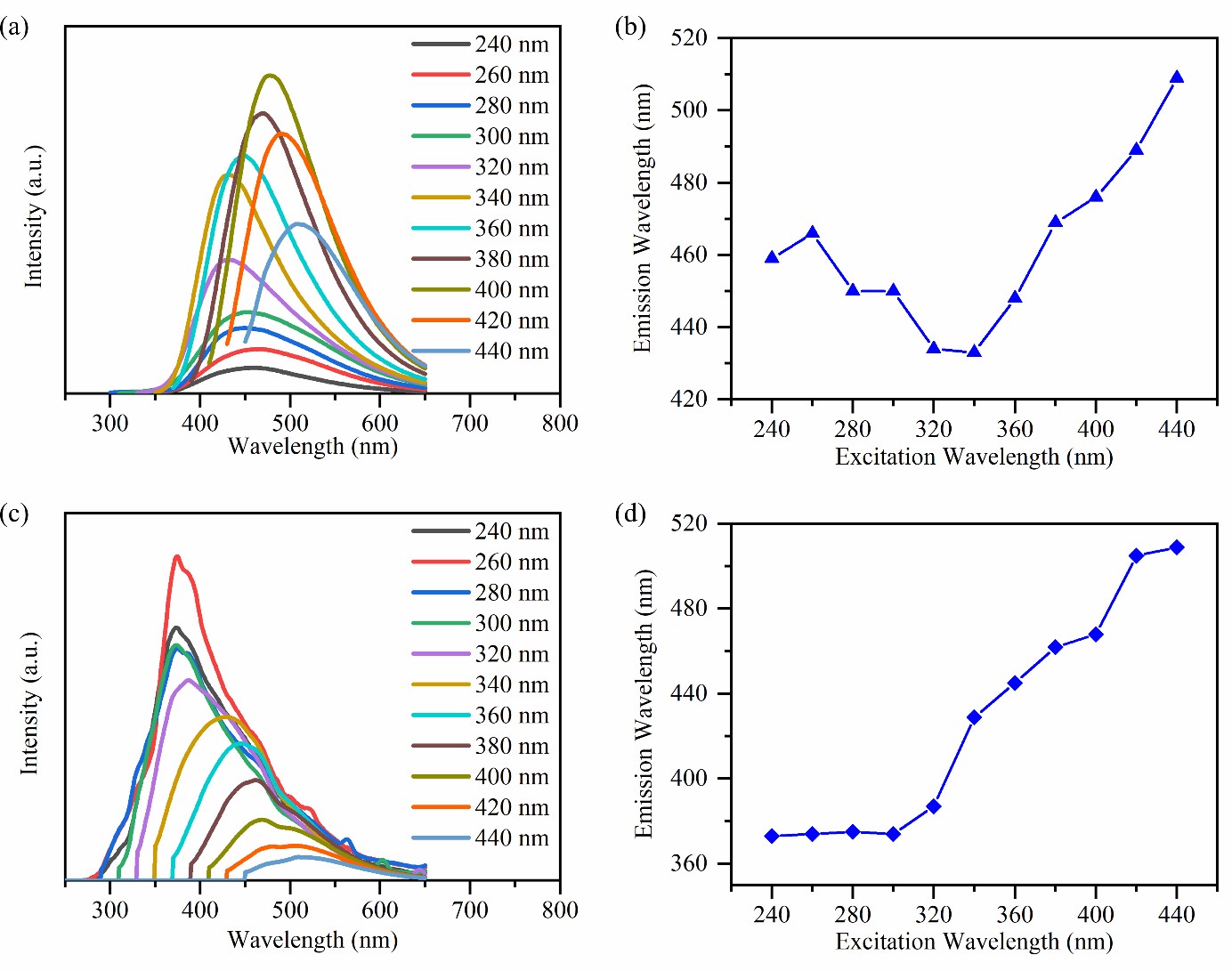
XPS was employed to conduct elemental analysis of the ethanol-extracted substances or CDs. Figure 5(a-c) shows the XPS spectra obtained from wide and narrow scans. The wide scan spectrum demonstrates the presence of C (83.39 at%), O (12.21 at%), and Si (4.40 at%). Notably, no nitrogen (N) atom was detected in the extracted substances, despite the presence of N in the raw brown coal. It should be noted that the relatively elevated Si concentration is likely attributed to Si contamination originating from the glass container used during sample preparation, rather than being derived from the brown coal itself.

The C 1s XPS spectra exhibit three distinctive components at 284.6, 285.8, and 286.8 eV, which can be assigned to C-sp2, C-O, and C=O, respectively [33] (Figure 5(b)). Meanwhile, the O 1s XPS spectra display three components at 531.9 and 532.7 eV, corresponding to C=O and C-O/ SiO2, respectively [33, 34] (Figure 5(c)).

To clarify the chemical composition of the ethanol-extracted substances or CDs, FT-IR spectra were obtained. Figure 5(d) shows the FT-IR spectrum of the CDs, revealing characteristic peaks at 1170-1250, 1608, 1702, 2849, 2917, and 3394 cm-1. These peaks can be assigned to specific functional groups, namely C-O-C, C=C, C=O, CH2, CH3, and O-H, respectively [35]. Notably, these FT-IR results align with the findings from the XPS analysis, reinforcing the consistency of the compositional characterization of the CDs.



**FIGURE 6.** UV-vis spectrum (red) and PL spectrum (blue) of ethanol-extracted solution containing CDs.



**FIGURE 7.** (a) PL spectra of the ethanol-extracted CDs solution, taken with different excitation wavelengths. (b) Correlation between excitation wavelength and emission wavelength. (c) PL spectra of the solution diluted 30-fold, taken with different

excitation wavelengths. (b) Correlation between excitation wavelength and emission wavelength of the solution diluted 30-fold.

Figure 6 shows the Ultraviolet-visible (UV-vis) absorption spectrum (red line) and photoluminescence (PL) spectrum (blue line) of the ethanol-extracted solution containing CDs. The UV-vis spectrum exhibits characteristics similar to those reported for fluorescent CDs. Notably, a prominent absorption peak is observed at 262 nm, attributed

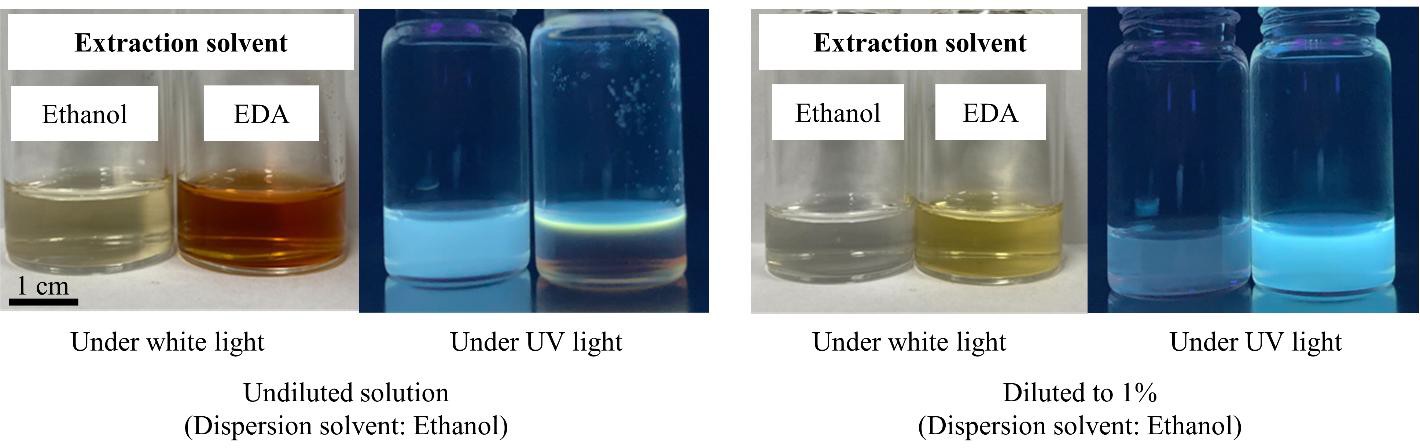
to the π-π\* transitions of aromatic C-C bonds. Additionally, a shoulder peak appears around 310 nm, which can be ascribed to the n-π\* transition of C=O bonds or other associated groups with lone pair electrons.

Moving on to the PL spectrum, a broad peak with a full width at half maximum (FWHM) of 116 nm is observed at approximately 448 nm, utilizing an excitation wavelength of 360 nm. The photoluminescence quantum yield (QY) was determined to be 2.4%.

PL spectra of the ethanol-extracted CDs solution were measured at various excitation wavelengths, ranging from 240 to 440 nm, as shown in Figure 7(a). The peak emission wavelength of the PL was plotted as a function of the excitation wavelength (Figure 7(b)). The PL spectra exhibit a notable dependence on the excitation wavelength. Specifically, the peak emission wavelength of the PL undergoes a blue-shift when the excitation wavelength increases from 260 to 340 nm, and a red-shift when the excitation wavelength increases from 340 to 440 nm. The maximum PL intensity is observed at an excitation wavelength of 400 nm. The QY value at 400 nm excitation is expected to be higher than that at 360 nm excitation as mentioned above. This excitation-wavelength dependence aligns with findings reported for many other CDs [8, 36, 37].

Moreover, the excitation-wavelength dependence is also observed for the extracted solution diluted 30-fold, as shown in Figure 7(c). However, the behavior of the excitation dependence differs from that of the solution before dilution, as demonstrated in Figure 7(d). This distinction can be attributed to the concentration and aggregation of fluorescent substances or CDs. Such concentration or aggregation-dependent PL behavior can provide valuable insights for understanding the PL mechanism.

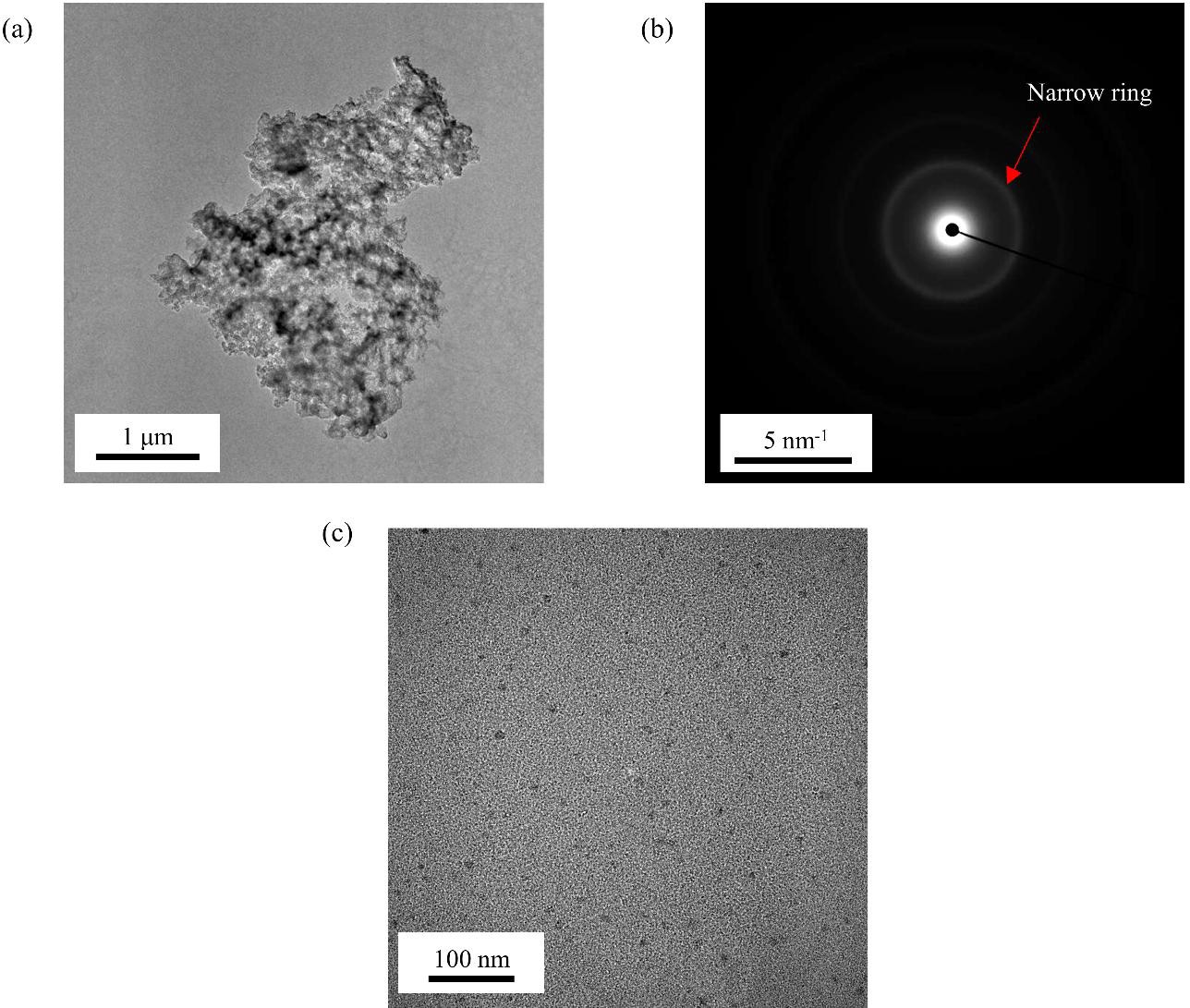
# Ethylenediamine-Refluxed N-CDs from Brown Coal



**FIGURE 8.** Photographs of ethanol-extracted, and EDA-extracted/ refluxed solution.

Amination is a well-known method for enhancing the PL properties of fluorescent CDs. Hydrothermal synthesis and reflux treatment in nitrogenous solvents are commonly employed for amination. EDA and ammonia liquor are examples of solvents used in this process. Previous research has demonstrated the effectiveness of EDA in the extraction of substances from coal, surpassing other solvents such as ethanol and water [22].

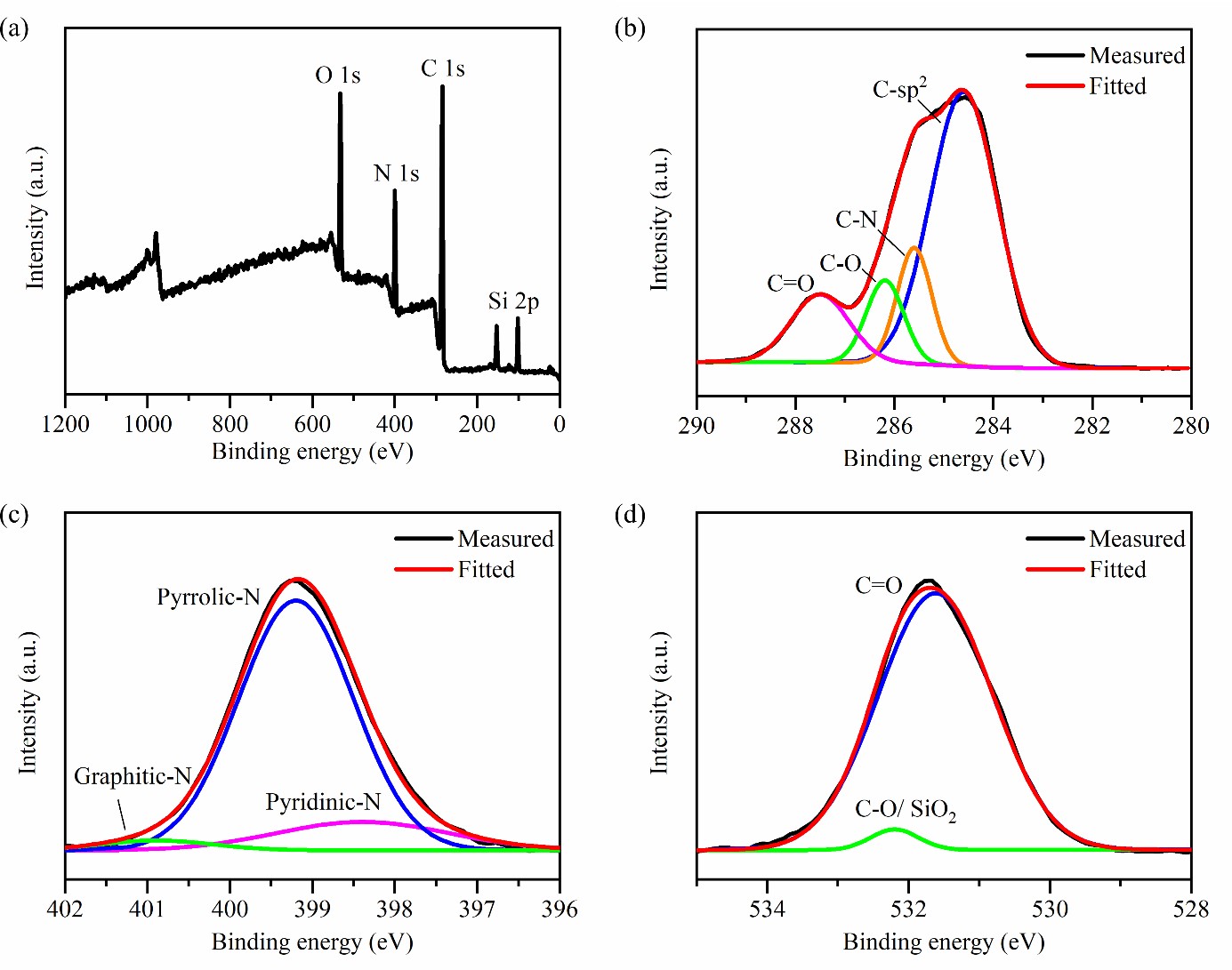
In this study, the extraction and amination of CDs from brown coal were performed using EDA, resulting in the formation of N-CDs. Figure 8 shows photographs of the EDA-refluxed solution obtained from brown coal, with the ethanol-extracted solution provided for comparison. The EDA-refluxed and ethanol-extracted samples are referred to as N-CD and CD, respectively. The photographs show the solutions under white light and UV irradiation. Both solutions exhibit blue luminescence under UV irradiation, but notably, the EDA-refluxed solution demonstrates strong blue luminescence. This enhanced luminescence can be attributed to the greater extraction of fluorescent substances or CDs and the amination process facilitated by EDA.



**FIGURE 9.** TEM images of EDA-refluxed substances or N-CDs. (a) Aggregated N-CDs. (b) Electron diffraction pattern of

aggregated N-CDs. (c) Isolated N-CDs.

TEM images of EDA-refluxed substances or N-CDs are shown in Figure 9. A typical aggregate larger than 1 μm in size is shown in Figure 9(a), where components of the aggregate are various particles with different sizes and shapes. The electron diffraction pattern obtained from the aggregate is shown in Figure 9(b). Because the narrow ring is observed in the diffraction pattern, the components of the aggregate are basically in the nanocrystal state. Note that the diameter of the ring corresponds to the lattice spacing of about 0.35 nm, which is in good agreement with (002) lattice spacing of graphite. This suggests that the aggregates are composed of graphite-like particles. A bright-field image of some isolated particles of about 10 nm in diameter are shown in Figure 9(c). In the image, the particles exhibit the dark diffraction contrast, which indicates that the particles are in the nanocrystal state. These results show that EDA-refluxed N-CDs have graphite-like structure, similar to ethanol-extracted CDs.



**FIGURE 10.** XPS spectra of EDA-refluxed substances or N-CDs. (a) Survey scan. (b) C 1s. (c) N 1s. (d) O 1s narrow scan.

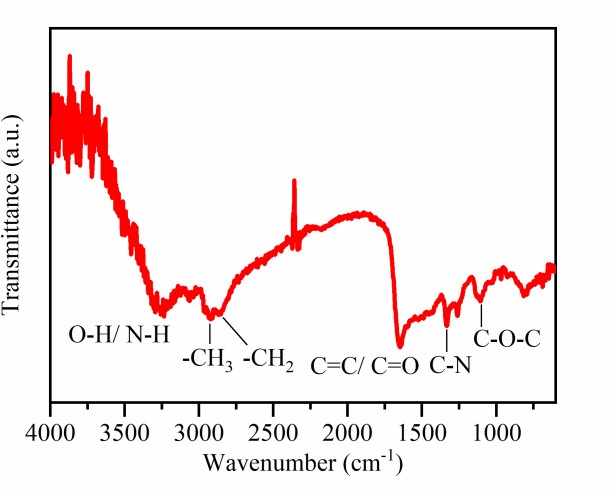
**TABLE 3. Elemental compositions of brown coal, ethanol-extracted CDs, and EDA refluxed N-CDs.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | | | at% |  |
|  | C | O | N | Si |
| Brown coal | 78.60 | 20.58 | 0.75 | 0.07 |
| Ethanol extracted CDs | 83.39 | 12.21 | - | 4.40 |
| EDA refluxed N-CDs | 62.74 | 15.19 | 15.56 | 6.51 |

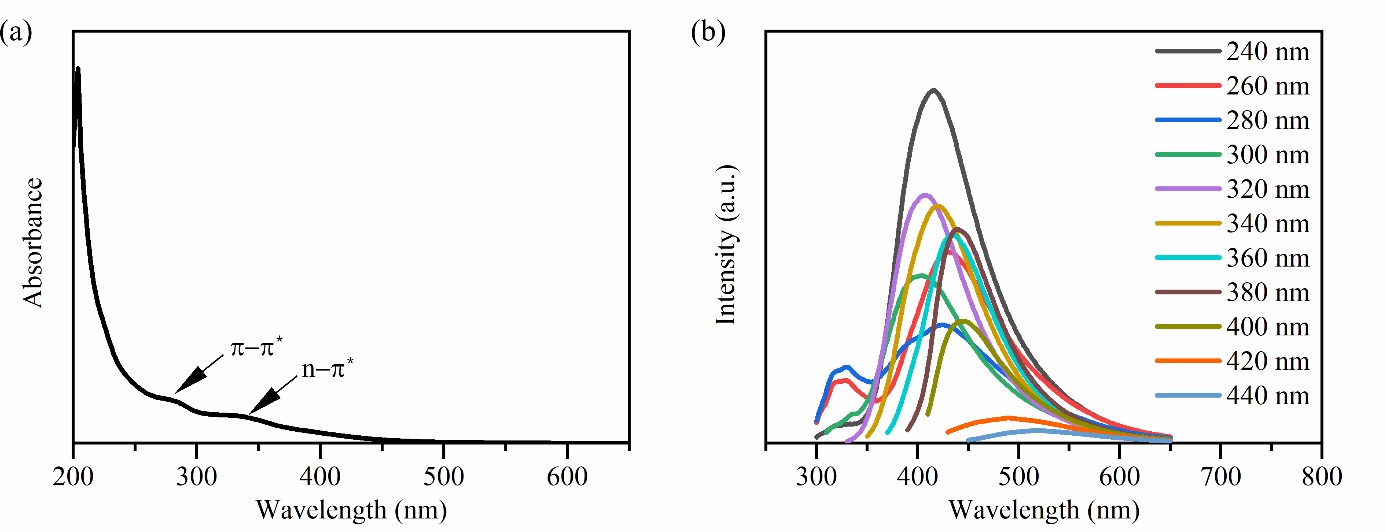
To confirm the amination of EDA-refluxed substances or N-CDs, XPS spectra were conducted, as shown in Figure

10. The wide and narrow scan analyses of the EDA-refluxed samples provided valuable insights. As shown in Table 3, the XPS analysis indicates the presence of C (62.74 at%), O (15.19 at%), N (15.56 at%), and Si (6.51 at%). The relatively high concentration of Si can be attributed to contamination from the glass containers utilized during sample preparation. Notably, the concentration ratio of N in the EDA-refluxed samples exhibits a significant increase compared to that in the raw brown coal and ethanol-extracted samples (Table 3). These findings affirm the successful amination of CDs in brown coal through refluxing with EDA.

The C 1s XPS spectra consist of four components at 284.6, 285.6, 286.2, and 287.5 eV, corresponding to C-sp2, C-N, C-O, and C=O, respectively [38] (Figure 10(b)). Furthermore, the N 1s XPS spectra exhibit three components at 398.4, 399.2, and 400.9 eV, assigned to pyridinic-N, pyrrolic-N, and graphitic-N, respectively [39] (Figure 10(c)). The O 1s XPS spectra reveal three components at 531.6 and 532.2 eV, attributed to C=O and C-O/ SiO2, respectively [34, 38] (Figure 10(d)).



**FIGURE 11.** FT-IR spectrum of EDA-refluxed sample.



**FIGURE 12.** (a) UV-vis spectrum of EDA-refluxed solution containing N-CDs. (b) PL spectra of EDA-refluxed solution containing N-CDs, taken with different excitation wavelengths.

Furthermore, FT-IR spectra were employed to analyse the composition of the EDA-refluxed sample. Figure 11 shows the obtained FT-IR spectrum, which indicates distinct peaks at 1106, 1333, 1647, 2854, 2922, and 3235 cm-1, corresponding to C-O-C, C-N, C=C/ C=O, CH2, CH3, and O-H, respectively [40, 41]. These findings align with the results obtained from XPS analysis. Combining the information from XPS and FT-IR analyses, it can be concluded that the amination of CDs in brown coal occurs successfully through refluxing with EDA.

The UV−vis absorption spectrum of the EDA-refluxed solution containing N-CDs is shown in Figure 12(a). The observed spectrum shares similarities with those of previously reported fluorescent CDs [42, 43]. A prominent absorption peak is observed at 280 nm, which corresponds to the π−π transition of the aromatic carbon structure. Additionally, a shoulder peak is observed around 335 nm, indicating the presence of functional groups with lone pair electrons, including amino-based chromophores. It should be noted that derivatives of the aforementioned structure, connected to various chemical groups such as hydroxyl and amine, can contribute to alterations in the absorption features.

Figure 12(b) shows the PL spectra of the EDA-refluxed solution containing N-CDs at various excitation wavelengths ranging from 240 to 440 nm. The PL spectra exhibit maximum intensity at an excitation wavelength of 240 nm, with a corresponding FWHM of 93 nm and a peak emission wavelength of 416 nm. Notably, the FWHM and peak emission wavelength of the PL spectrum are narrower and shorter, respectively, compared to the ethanol- extracted samples. This indicates that the EDA-refluxed solution with N-CDs exhibits more monochromatic fluorescence with a shorter wavelength compared to the ethanol-extracted solution containing CDs derived from brown coal. Furthermore, the QY value was measured to be 3.8%, even with the excitation wavelength of 360 nm, which is higher than the 2.4% obtained for the ethanol-extracted solution. The QY value might become higher when

measured with 240 nm excitation wavelength which led to the maximum PL intensity. The enhanced fluorescent properties of CDs through amination have been previously reported in various cases [44, 45], and a similar effect is expected to occur for CDs derived from brown coal.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **TABLE 4. Comparison of preparation methods and PL properties of coal-based CDs.** | | | | | | | |
| Coal Type | | Solvent | Method | Condition/ Time | PL wavelength (nm) | QY (%) | Ref |
| 2013 Anthracite Sulfuric acid and Stir 100℃, 24 hours 530 (λex 345) - 46 | | | | | | | |
|  |  | Nitric acid |  |  |  |  |  |
|  | Bituminous coal |  |  |  | 480 (λex 345) | - |  |
|  | Coke |  |  |  | 415 (λex 345) | - |  |
| 2014 | Anthracite | Nitric acid | Oxidation | 140℃, 12 hours | 450 (λex 389) | 8.8 | 47 |
| 2016 | Lignite | EDA | Reflux | 100℃, 12 hours | 468 (λex 360) | 4.5 | 25 |
|  |  |  | Microwave | 600 W, 5 min | 435 (λex 360) | 5.1 |  |
|  |  |  | Laser | 1064 nm, 60 min | 403 (λex 340) | 6.0 |  |

Sonication

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 2017 Lignite Nitric acid Ultra 100℃, 1 hour  2018 Coal tar pitch Hydrogen Reflux 100℃, 2 hours | | | | | 447 (λex 320)  445 (λex 325) | -  2.37 | 48  49 |
|  |  | peroxide |  |  |  |  | |
| 2023 | Brown coal | Ethanol | Extraction | 10 min | 448 (λex 360) | 2.4 This  study | |
|  |  | EDA | Reflux | 100℃, 2 hours | 434 (λex 360) | 3.8 | |

Finally, the preparation methods and optical properties of CDs from various types of coal are compared in Table 4 [25, 46-49]. The optical performance of fluorescent substances or CDs from brown coal shown in this study is comparable to those from high-grade coals such as anthracite, bituminous, and coke, which require chemical reactions at temperatures above 100℃ or for a long time. The improvement of the optical performance was also confirmed by amination. Further development of fluorescent materials from brown coal and its applications are in progress.

# CONCLUSION

We have successfully demonstrated the production of blue light-emitting solutions or CDs from Australian brown coal using both ethanol extraction and EDA refluxing methods. This discovery opens new possibilities for utilizing brown coal as a source of blue-emitting materials, with potential applications in areas such as LED technology. Currently, brown coal is primarily used for power generation through combustion, leading to significant environmental impact [50]. Therefore, there is an urgent need for cleaner and more sustainable utilization of coal resources. Our findings offer a promising avenue towards achieving this goal and can contribute to the development of a resource- efficient, environmentally friendly, and economically viable coal industry.

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