Ligand Mediated, Spatially Confined Carbonization of Biomass Forming High-Performance Colloidal Carbon Dots

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the intricate electron transfer and trapping from carbon core/functional groups to surface bound-ligand multiple emissions. The OLA-CDs can be stably dispersed in various solvents and facilely fabricated into thin-film devices. This work establishes the versatility and tunability of ligand-induced, spatially confined carbonization in forming colloidal CDs for optoelectronic devices from crude biomass.

KEYWORDS: carbon dots, colloidal synthesis, biomass conversion, spatially confined carbonization, ligand-surface electron transfer

INTRODUCTION

Converting renewable biomass into value-adding chemicals and materials is an important pathway to implementing the circular economy and sustainable development. Recent discoveries on various forms of nanocarbon such as graphene and carbon dots have created new opportunities for biomass conversion.¹⁻⁵ Carbon dots (CDs) are environmental-friendly fluorescent nanomaterials composed of largely sp²-hybridized carbon and rich surface functionalities. They exhibit low toxicity, tunable photoluminescence, excellent biocompatibility, and ease of functionalization. Importantly, carbon dots are promising candidates to substitute toxic heavy metal-semiconductor quantum dots.⁶⁻⁹ Various sustainable biomass resources have been used for synthesizing CDs, with applications established in sensing, bioimaging, and optoelectronics.^{2,10,11} Seaweeds, one of the fastest-growing plants on earth with multiple benefits to decarbonization^{12,13} are primarily composed of polysaccharides (e.g., laminarin, alginate, carrageenan, agar), which provide not only highvalue health products but also unique carbon precursors.¹

Deriving CDs from crude biomass such as plant parts, fruits, and seeds involve biomass decomposition and carbonization. Current methods of synthesis include pyrolysis, microwave, hydrothermal, solvothermal, and chemical oxidation.^{1,15} One of the challenging issues in biomass-derived CDs are their size control, uniformity, and reproducibility. The lack of morphological uniformity has also hindered fundamental studies on the photophysics of biomass-derived CDs. Other drawbacks with biomass-derived CDs include low quantum yield (QY), low production yield, and use of harsh chemicals.¹ A salient advantage of CDs is that they can be readily synthesized into either aqueous- or oil-dispersed fluorescent nanoparticles.^{16,17} While water-dispersity is critical for biomedical applications, colloidal stability in solvents is highly desirable for optoelectronic device applications, which calls for ligand-assisted synthesis. Studies on the ligand-assisted colloidal synthesis of CDs associated with surface passivation from bioresources are limited, likely due to ligand compatibility issues.

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OLA is a long-chain (C18) primary amine with an alkene function at the C9-C10 junction, functioning as a solvent and surfactant having a high boiling point of 350 °C.¹⁸ OLA is a widely used solvent and passivation agent for the colloidal synthesis of semiconductor quantum dots. The interactions between OLA and quantum dots in terms of the photoluminescence (PL) are well known as passivation of the trap states without exception.¹⁸ On the other hand, most CDs reported so far possess multiple emission centers, which can be attributed to the carbon core, doped element(s), and surface functional groups.^{19–21} These emission centers are intricately related, for instance, it has been observed that the internal/ core energy level can be modulated by changes of surface functional groups.²² However, the reverse influence, namely, the effect of carbon core on the emission of surface functional groups, has not been reported. The electron transfer between carbon core and surface ligands and the consequential electronic energy level change on both sides remain less understood.

Herein, we report a spatially confined carbonization synthesis of highly uniform CDs from brown seaweed Undaria pinnatifida in OLA. In this colloidal synthesis, OLA can assist the degradation of the biomass and facilitate the formation of the nanoaqueous phase for biomass oligomers to carbonize in nanocompartments, directly forming uniform and highly crystalline CDs. The as-synthesized CDs do not require demanding separation processes such as membrane dialysis or column chromatography to obtain a narrow size distribution. It is found that the OLA ligands not only serve as a passivating agent for improving the quantum efficiency of the CDs but also introduce a carbon core-ligand electronic transition phenomenon, enriching the emission profile. Moreover, this results in OLA-CDs' intricate interactions with organometallic species, exhibiting PL responses to Zn^{2+} and Fe^{3+} in opposite directions. Solid-state CD films for cyclic detection of trace amounts of Zn^{2+} and Fe^{3+} in organic solvents have been demonstrated here. The distinct signatures of radiative electron transfer from the colloidal CDs to surface ligands provide a new tuning mechanism for the optoelectronic properties.

EXPERIMENTAL DETAILS

Chemicals and Materials. 1-Dodecanethiol (98%) (DDT), oleylamine (approximate C18 content 80–90%), octadecene (90%, technical grade), oleic acid (90%, technical grade), 1-octanol (99%, anhydrous), and chloroform (99% anhydrous) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. The dry brown seaweeds (*Undaria Pinnatifida*) were purchased from the market.

Colloidal Carbon Dots Synthesis. The Undaria pinnatifida seaweeds were processed either through wet or dry seaweeds. The fresh seaweeds were washed in Milli-Q water by ultrasonication for several times and then dried at 60 °C in oven overnight, whereupon they were then ground into powder. Subsequently, 0.1 g of dry seaweed powder was washed with Milli-Q water under sonication for 10 min. After settling, the bulk water was tipped out, and ethanol was added, whereupon the mixture was sonicated again for another 10 min. The sample was then dried at 60 °C for 1 h to remove ethanol and water. Subsequently, 2 mL of OLA (or water, ODE, DDT, in respective synthesis) was added, and the mixture was sealed in a Teflon autoclave (25 mL) and kept in an oven at different temperatures (180, 200, and 240 °C) for 12 h. Upon cooling down to room temperature, the contents were removed from the autoclave.

For obtaining the water-dispersed CDs, the CDs synthesized in water were sonicated in 50 mL of distilled water for 60 min to obtain a homogeneous suspension.

For oil-dispersed CDs, for example, the OLA-CDs were dispersed in 5 mL of OLA (ODE-CDs in ODE and DDT-CDs in DDT) under sonication for 60 min. In all cases, the suspension was then filtered using a silica gel column to remove any reaction by-products, and the resulting solution was finally passed through a 0.22 μ m membrane filter to obtain a colloidal suspension of CDs.

Reaction Yield Determination. The OLA-CDs were dispersed in methanol and centrifuged at 5000 rpm (7 cm rotor radius; ~1957g) for 5 min to remove excess ligands. The collected purified samples were used to calculate the reaction yield. For reaction yield determination, a thermogravimetric analyzer (TGA) was employed to differentiate the weight of the carbon cores from that of the ligands. The ratio between the weight of carbon cores and that of the seaweed precursors is regarded as the conversion yield.

Thin Film Fabrication. For the hydrophobic CD film fabrication, 1 mL of OLA-CD solution was dropcast on the surface of a glass substrate, forming a thin film, which was oven dried at 70 °C overnight. For fabricating CD-embedded polymer films, poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate) was dissolved in toluene to obtain a uniform solution, which was mixed with a solution of OLA-CDs dissolved in chloroform, mixed by sonication for 0.5 h. The resultant homogeneous solution was heated at 60 °C in an oven until the solvents were fully evaporated, forming a CD-polymer film.

Characterizations. Powder X-ray diffraction (XRD) patterns were collected from a Bruker D8 advance MKII with Cu K irradiation ($\lambda = 1.54$ Å). High-resolution transmission electron microscopy (HRTEM) was performed on a Hitachi HT 7700 high-resolution transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra X-ray photoelectron spectrometer. The UV–vis absorption and PL spectroscopy was performed on a Horiba Duetta. The PL lifetime measurement was carried out using Horiba DeltaFlex time-correlated single photon counting (TCSPC) system. The Fourier transformation infrared (FTIR) spectroscopy was performed on a Perkin Elmer. The thermal stability of suspensions of CDs was tested from room temperature to 100 °C.

Ecotoxicity Evaluation. The toxicity of OLA-CDs was assessed in the BLT-Screen and the IPAM assays. The BLT-Screen was used to evaluate toxicity to bacteria, which is also indicative of acute toxicity to aquatic organisms.²³ The assay was performed as previously described.²⁴ In brief, bioluminescent Photobacterium leoignathi were exposed to serially diluted concentrations of CDs in a white 96-well plate (Greiner Bio-One, Austria), and luminescence was measured after 30 min of exposure in a Tecan Spark plate reader (Tecan, Switzerland). The IPAM assay is a measure of both inhibition of photosynthesis and toxicity to algae and was performed as previously described.²⁵ In brief, Pseudokirchneriella subcapitata was exposed to serially diluted concentrations of CD in 96-well plates, and photosynthetic yield was measured at 0, 2, and 24 h using image pulse amplitude modulation (IPAM) fluorometry (Walz GmbH, Germany). Reduced photosynthesis at 2 h indicates that the sample specifically inhibits algal photosynthesis, while a reduced photosynthesis at 24 h indicates delayed phytotoxicity and includes both specific and nonspecific effects. The samples were run in two independent assays on separate days, for both the BLT-Screen and the IPAM. The concentration causing 20 and 50% effects were derived from log-logistic concentration effect curves using a least-square nonlinear regression using the Solver add-in in Microsoft Excel version 2018 (Microsoft Corporation, USA).

Sensing. Selective sensing of metal ions was performed through the standard addition method. The PL intensity changes were recorded during the process to identify the ion sensing response. The ionic chlorides were used in ion detection. Limits of detection (LODs) of the ion response were calculated through the slope method of the PL intensity corresponding to the concentration of the ions.²⁶ Different concentrations of analyte solution were separately added to 2 mL of CD solution (abs 0.35), and the change in fluorescence $(I_0 - I)/I$ was calculated. The $(I_0 - I)/I$ was plotted against the analyte concentration, and regression analysis was used to determine the standard error σ of the *y*-intercept.



Figure 1. (a) Schematic of the ligand-controlled, spatially confined synthetic strategies. TEM images of CDs synthesized in (b) the absence of a solvent, (c) water (water-CDs), and (d) 1-octadecene (ODE-CDs), where the insets are the HRTEM images of the corresponding CDs (scale bars are 10 nm). (e) TEM images of CDs synthesized in oleylamine (OLA-CDs) and their HRTEM image (f). (g) Size distribution of OLA-CDs based on panel (f).

Limit of detection was estimated using the equation

$$LOD = 3. \ 3\sigma/S \tag{1}$$

where σ is the standard deviation of the *y*-intercept of the regression line and *S* is the slope of the calibration curve. For sensing tests using water-CDs, 2 mL of aqueous water-CD solution (3 mM, 0.35 absorption) was prepared as a stock solution. The ions were dissolved in Milli-Q water and added to the water-CD solution. For sensing tests with OLA-CDs, the OLA-CDs were dissolved in the chloroform as a stock solution. The ions were dissolved in methanol and added to the OLA-CD solution. For the hydrophobic CD film sensing, the films on the glass substrate were dipped into the ion solutions in Milli-Q water.

RESULTS AND DISCUSSION

Ligand-Mediated Conversion of Crude Seaweeds to Single Crystalline CDs. In this solvothermal synthesis as illustrated in Figure 1a, the crude biomass needs to be broken down into its primary or secondary building blocks with the assistance of the solvent and heat. The solvent and the fragmented biomass should form a nanoemulsion with the former as the continuous matrix phase. Moreover, when the biomass oligomers are carbonized, the solvent matrix needs to provide strong interactions to prevent the aggregation of the resulting nanocarbons. Based on these considerations, we have compared different solvents to find out their effects on the formation of CDs. Water and a few high boiling point ligands commonly used in colloidal synthesis including OLA, 1octadecene (ODE), oleic acid (OA), octanol, and 1dodecanthiol (DDT) were employed as the reaction medium for comparison, as well as the case of no solvent added. The reactions took place in autoclaves at 180 °C for 12 h. The transmission electron microscopy (TEM) images in Figure 1b and Figure S1 (in the Supporting Information) show that in the absence of a solvent, the ground seaweed powder has been converted into large carbonaceous particles of a diameter



Figure 2. (a) HRTEM image of OLA-CDs. (b, c) FFT patterns of the selected areas 1 and 2 highlighted by the red frame in (a). (d) Line profile of highlighted line in (a). XRD pattern of OLA-CDs synthesized at different temperatures (e) and with varied reaction times at 180 °C (f). (g) XRD pattern of water-CDs synthesized at different temperatures. (h) FTIR spectra of water-CDs, OLA-CDs, and ODE-CDs. (i–k) High-resolution XPS of OLA-CDs for C, N, and O elements, respectively.

around 200 nm. This suggests that at 180 $^\circ$ C, 12 h of thermal treatment of seaweeds in the enclosed system is sufficient for carbonizing seaweeds. When MilliQ water is added as the solvent in the synthesis, a clear, fluorescent solution was produced. However, the resultant CDs (water-CDs) do not exhibit a clear presence of discrete nanoparticles, appearing as carbon nanoparticles (within 10 nm in diameter) distributed in a low-density matrix, Figure 1c. Distinctively, when the ground seaweed was placed in OLA, a coordinating solvent, highly uniform and dispersed CDs (OLA-CDs) were formed, as shown in the TEM image, Figure 1e, and the HRTEM image, Figure 1f. The size of the OLA-CDs is determined as 3.6 ± 1.5 nm (Figure 1g). In comparison, when the ground seaweed was placed in ODE, a noncoordinating solvent with a high boiling temperature of 315 °C, nonuniform aggregates (ODE-CDs) ranging from 20 to over 100 nm in size were formed, Figure

1d. The inset HRTEM image shows that each particle is composed of smaller particles of <2 nm. In comparison with ODE-CDs, the uniform size distribution of OLA-CD highlights the effect of ligand in controlling particle morphology.¹⁶

TGA (Figure S2) shows a drastic weight loss from 300–400 °C followed by another weight falling region from 500 to 600 °C, which is due to the combustion of the ligands and the carbon cores, respectively. The reaction yield is determined to be 8% for OLA-CDs based on the ratio of the weight of carbon cores derived from TGA over that of seaweed precursor. This yield is that of carbon, exclusive of the surface ligands.

The HRTEM in Figure 2a demonstrates the highly crystalline structure of OLA-CDs. The fast Fourier transform (FFT) patterns of selected area 1 of Figure 2a show the hexagonal carbon structure with two lattice distances of 0.21 and 0.18 nm, corresponding to the (100) and (102) facets of

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Figure 3. Illustration of the carbonization process of ground seaweed in different solvents: (a) water, (b) octadecene, and (c) oleylamine. The arrows indicate the resistance direction. (d,e) TEM images of a droplet of OLA-CDs dispersed in methanol, showing uniformly sized as-synthesized OLA-CDs maintaining a separation distance among individual particles. (f) Schematic of OLA-CDs dispersed in methanol; owing to the covalently bonded surface ligands, the CDs maintain a separation distance defined by the ligand length.

hexagonal carbon, respectively. The lattice spacing in area 2 is measured to be 0.21 nm, corresponding to the (100) facet of graphitic carbon and in agreement with the FFT pattern (Figure 2c). The line profile in Figure 2d reveals a consistent interlayer spacing of 0.21 nm.

The XRD pattern further confirms the high crystallinity of the OLA-CDs as shown in Figure 2e. The XRD patterns for OLA-CDs synthesized at varied temperatures all show a 21.71° peak, the most intense for the material synthesized at $180 \,^{\circ}$ C, which also presents other two extraordinary sharp diffractions at 20.21 and 20.82°, in agreement with the hexagonal carbon. This single crystal-like XRD pattern demonstrates the high uniformity of the size and face orientation of the OLA-CDs, likely forming mesocrystals.²⁷ This suggests that the optimal temperature for the synthesis of OLA-CDs is 180 °C. The XRD spectra of OLA-CDs synthesized under different durations, Figure 2f, suggests an optimal reaction time of 12 h. In the parallel aqueous-based synthesis, the XRD pattern of water-CDs formed at different temperatures has an apparent peak around $23-24^{\circ}$, which is left-shifted from 24.15° (180 °C) to 22.45° (200 °C) and then to 22.96° (240 °C), with a concomitant increase in *d*-spacing for increasing temperature, Figure 2g. The water-CDs synthesized at 200 °C exhibit the narrowest full width at half maximum (FWHW), thus having a better particle size distribution. In summary, the choice of solvent, temperature, and reaction time are all critical

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Figure 4. (a) Absorption, photoluminescence (PL), and PL excitation (PLE) spectra of water-CDs (PL under 330 nm, PLE@380 nm), ODE-CDs (PL under 330 nm, PLE@380 nm), and OLA-CDs (PL under 410 nm, PLE@470 nm). (b) PL spectra of the water-CDs, ODE-CDs, and OLA-CDs with an excitation increment of 20 nm (water-CDs: from 320 to 520 nm; ODE- and OLA-CDs: from 330 to 530 nm). (c) PLE spectra of OLA-CDs at different emission wavelengths compared to the absorption and PL spectrum. (d) PL decay of the water-CDs, ODE-CDs, and OLA-CDs. (e) Quantum yields of CDs synthesized in different solvents. (f) Fluorescence spectra of the CDs in as prepared solutions.

parameters to generate high quality CDs using the biomass solvothermal treatment.

FTIR spectra reveal the presence of the functional groups and surface ligands for the three types of CDs (Figure 2h). In water-CDs, -OH (3419 cm⁻¹), C=C stretching (1565 cm⁻¹), C-O stretching (1290 cm⁻¹), and -OH bending (1122 cm⁻¹) vibrations are present. ODE-CDs have an apparent C=C bending (993 cm⁻¹) and C=C stretching (1638 cm⁻¹), confirming the presence of an alkene moiety. For OLA-CDs, the weak C-N bending (1080 cm⁻¹) and N-H bending (1665 cm⁻¹) bands confirm the presence of OLA ligand on the surface of the CDs.²⁸

High-resolution XPS provides information on the bonding states of OLA-CDs. The C 1s spectrum in Figure 2i has the peaks assigned to C=C/C-C bonds (284.4 eV), C-N/C-O/C-S bonds (285.5 eV) and C=O bonds (287.84 eV). The existence of C-S and C-N bonds establishes the presence of a trace amount of doping from the innate elements in the seaweed. In the N 1s spectrum (Figure 2j), the two peaks at 399.5 and 401.3 eV can be assigned to the C-N/pyrrolic bond and N-H/graphitic N, respectively.²⁹ The nitrogen peaks establish the presence of two different chemical environments for the element, as -NH2 and C-N moieties, and thus Ndoping arises from OLA. By comparing the XPS spectra with that of water-CDs (Figure S3a), the contrast ratio of N-H is increased, indicating surface modification of OLA. The C-N peak of water-CDs suggests that the self-doping from the nitrogen-containing seaweed. In the O 1s spectrum, Figure 2k, the C=O (531.28 eV) and C-O-O/C-OH (532.9 eV) confirm the presence of abundant functional groups such as

-COOH and -OH groups.^{29,30} We also found the trace amount of S and C-S bonds, which may originate from the protein precursors present in seaweed (Figure S3b).² Both natural seaweeds (*Undaria pinnatifida*) and ligand (OLA) allow nitrogen doping not only in the core but also at the interface and within surface functional groups.

Role of Coordinating Ligands in the Spatially Confined Formation of CDs from Crude Biomass. Based on the results, we observe that the solvent plays a critical role in the morphology control of the CDs derived from crude seaweed. Among all the solvents that have been examined, OLA resulted in CDs with the best uniformity and crystallinity. The distinctive difference between OLA and ODE is the amine terminal on the alkyl chain on OLA.

The formation of the CDs is a ligand-controlled, spatially confined top-down synthesis. The effects of the solvents used can be categorized into three models, namely, water-based, noncoordinating oil, and coordinating oil, as shown in Figure 3a-c. Under the same reaction condition, the fibers of seaweeds decompose, releasing laminarin monomer moieties or small oligomers thereof, which tend to polymerize and dehydrate at high temperature. When the solvent is water, carbonization takes place in a distributed manner as evidenced by the inset in Figure 1c. However, since there is no second phase to effectively separate them apart, these ultrafine carbon nanoparticles are loosely joined together by less carbonized material, Figure 3a.

On the contrary, in an oil-based solvent like ODE or OLA in an enclosed reaction vessel, a repellent layer is formed between the carbonization center in the water phase and the



Figure 5. (a) Absorption, PL excitation @ 470 nm and emission spectra under 410 nm of OLA-CDs. (b) Schematic of OLA-CD structure. (c) Schematic illustration of the band transition mechanism of OLA-CDs.

hydrophobic solvent as illustrated in Figure 3b,c. A distinct feature in biomass carbonization is the formation of water. In a solvothermal synthesis immersed in high boiling point solvents such as ODE and OLA, the formed water is trapped around carbon precursors under the enclosed solvothermal synthesis condition.³¹ Because this repellent layer is dependent on the surface tension of the water phase in the solvent, the emulsion may break up once reaching their size limit, as shown by the morphology for ODE-CDs and OLA-CDs, Figure 1. In the case of a noncoordinating oil-based solvent, such as ODE, spatially confined carbonization occurs. However, since the ODE ligands are not tightly bound to the nanocarbon surface, the CDs tend to agglomerate, forming larger particles, as evidenced in Figure 1d. In the case of OLA, an unsaturated long-chain oil with a polar terminal, OLA molecules can function as a surfactant, likely orienting their amine terminals toward the biomass oligomers, forming a stable reverse emulsion, thereby encapsulating the biomass. Due to the surface tension and the strain of the repellent layer confinement, the resultant CDs possess highly crystalline structure. Moreover, there are abundant carboxyl, hydroxyl, and carbonyl groups on the biomass-derived carbon cores, and therefore the OLA ligands on the surface of the CDs are likely covalently bonded through the amine terminal, effectively separating each dot and preventing aggregation. This is clearly shown in the TEM image in Figure 1f.

To further explore the formation of the covalently bound ligand layer around the CD cores, OLA-CDs were redispersed in methanol and dropcast on a TEM grid for observation, which reveals a "blob" with the OLA-CDs pushed into a circle with a high dispersion density, Figure 3d and Figure S4. The distance between individual CDs is around 1.8 nm, which is consistent with the ligand effect range of OLA, Figure 3e. Given that OLA-CDs have an outer hydrophobic layer, they can be readily dispersed in apolar solvents such as chloroform and toluene, whereas for the less apolar solvent methanol, they aggregate into "blobs" while maintaining their equilibrium distance due to the surface-bound OLA ligands, as illustrated by the schematic in Figure 3f. This phenomenon is consistent with the presence of a repelling layer of oriented OLA ligands attached on the surface of the CDs through their amine termini. Overall, the extraordinary size uniformity and layered single-crystalline structure of OLA-CDs appear to arise from a combination of ligand-controlled, spatially confined carbonization.

Multiple Emission of Colloidal Carbon Dots. The fluorescence of OLA-CDs is unique in comparison with that of ODE-CDs and water-soluble CDs due to its N-doping and dual excited passivation layer. As shown in Figure 4a, the water-CDs and ODE-CDs have a similar emission wavelength excited at 330 nm. This suggests that two types of CDs may share a similar fluorescence center. In comparison, the emission OLA-CDs is complex, presenting multiple emission peaks with multiple emission centers as shown in Figure 4a-c. A larger Stokes shift of more than 60 nm is observed in the first emission peak (470 nm) of OLA-CDs, while for water-CDs, it is 56 nm, and that for ODE is 51 nm.³² Of note is the narrower absorption peaks of OLA-CDs compared to water-CDs and ODE-CDs, which is consistent with the uniform size distribution when using OLA-mediated colloidal synthesis. All three types of CDs show two sets of absorption peaks, clearly indicating the presence of the core band and edge bands



Figure 6. (a) PL spectra of OLA-CDs after adding different concentrations of Zn^{2+} (0–400 ppm) with excitation at 370 and 410 nm, respectively. (b) Linear relationship between $1 - F_0/F$ and the concentration of Zn^{2+} (0–50 ppm) in OLA-CDs under 370 nm excitation. (c) PL spectra of OLA-CDs after adding different concentrations of Fe³⁺ (0–200 ppm) with excitation at 370 and 410 nm. (d) Linear relationship between $F_0/F - 1$ and the concentration of Fe³⁺ (0–100 ppm) in OLA-CDs under 370 nm excitation. (e) Illustration of solution-processed colloidal carbon-dot-based solid-state film sensing. (f) Normalized PL spectra response of OLA-CDs film in different ions at 12 cycles (insets are the photo of the films under excitation comparing enhanced emission with quenched emission in the presence of Zn^{2+} and Fe^{3+} , respectively).

in the carbon dots.¹⁹ We further compared the full emission spectrum from 320 to 540 nm excitation at an increment of 20 nm, Figure 4b. All three CDs showed an excitation-dependent emission. Remarkably, the OLA-CDs presented multiple emission peaks starting from 380 nm excitations. The relative intensity of the emission peaks varies as the longer-wavelength

emissions intensify and as the excitation bathochromically shifts.

To understand the origin of the emission, the excitation spectra were measured at emissions of 479, 590, 621, 640, and 677 nm (Figure 4c). The PLE spectra show two peaks at 370 and 410 nm that are present for all emission wavelengths. The comparison between the excitation@470 nm and the UV-vis

absorption spectra reveals that the excitation peak at 370 nm coincides with the OLA-CD absorption band edge, indicating that this emission is due to the internal electronic band gap, or in other words, the $\pi - \pi^*$ transition. On the other hand, the broad distribution of this excitation peak centered at 370 nm suggests that there are more involved other than $\pi - \pi^*$ transition, which is likely due to defects such as N-doping and oxygenated functional groups. The small peak at 410 nm on the UV-vis matches with the 410 nm peak on PLE spectra, which can be attributed to $n-\pi^*$ transition. From the series of PLE spectra from @590 to @677 nm, this 410 nm emission center makes the dominant contribution. The conjugation of the OLA ligands on the seaweed-derived carbon core gives rise to this unique emission profile of OLA-CDs. As a comparison, Figure S6 in the Supporting Information shows that the pure OLA is weakly emissive with a distinctively different emission profile, in particular, exhibiting no emission beyond 550 nm.

The fluorescence lifetime of OLA-CDs is similar to that of water-CDs, while the average lifetime of ODE-CDs, 0.61 ns, is significantly shorter than that of OLA-CDs, 2.34 ns, likely due to the aggregation of particles, which is in agreement with the TEM results (Figure 4d and Table S1 SI for the lifetime). In addition, we compared the QYs for CDs synthesized in different solvents, as shown in Figure 4e. The OLA-CDs in chloroform have the highest QY of 15%, twice as high as that of water-CDs, 7%. Furthermore, the QY of OLA-CDs can reach 37% when dispersed in OLA solvent. This implies that the high crystallinity and uniform size distribution significantly improve quantum efficiency¹⁶ as well as the solvent. Figure 4f presents the emissions of a crude solution product, which suggests an acceptable emission quality to be used directly without purifications for applications such as sensing. In addition, the seaweed-derived OLA-CDs possess high colloidal stability and consistent emission behavior.

Mechanism of Radiative Surface-Ligand Electron **Transfer.** Based on the experimental evidence, we propose a new surface ligand band electron transfer in the full transition mechanism. As illustrated in Figure 5a-c, OLA-CDs contain three parts: (i) the carbon core, (ii) the carbon-ligand interface, and (iii) the surface ligands. Due to the innate nitrogen in the seaweeds and OLA solvent, the core of the OLA-CDs is likely N-doped, which narrows the band gap by reducing the energy of the lowest unoccupied molecular orbital (LUMO) levels and increasing the energy of the highest occupied molecular orbital (HOMO) level, leading to the redshift PL spectra in comparison to frequently reported CDs in the literature.³² These results are in accordance with the UV-vis absorption and emission spectra (Figure 4a,c), with the emission of OLA-CDs having a significant redshift and larger Stokes shift compared to water-CDs (Figure 4a). Given that the carbon core, doping states, and functional group shell can all contribute to the overall PL of the CDs, the shorter wavelength emission of OLA-CDs is excitation-dependent. In addition, the presence of the OLA surface ligands on OLA-CDs results in one more emissive center, which enriches the emission profile. In detail, as shown in Figure 5a, the OLA-CD structure is reflected by the excitation-dependent PL behavior, which shows the effect of surface states on the band gap of the CDs. As to absorption, there are two bands (325 and 410 nm), which are associated with the core and surface, respectively. For the excitation (Figures 4c and 5a), the emission center is confirmed as the core band (383 nm) and edge band (428 nm), in agreement with the absorption spectrum. For the

emission, the four main peaks at 455, 507, 580, and 637 nm can be assigned to the core band transition (2.7 eV), core band heteroatom transition (2.4 eV), surface band (also termed as edge band) transition (2.1 eV), and surface-ligand band transition (1.9 eV), respectively, as illustrated in Figure 5c. Based on the emission and absorption spectra, the band transition of OLA-CDs can be associated with four pathways, as illustrated in Figure 5c. In the proposed mechanism, the 325 and 428 nm absorption bands are associated with the core and surface ligands accounting for the major excitation-dependent emission peaks at 433 and 472 nm, respectively.³³ The emission induced by n-electron transition that is associated with functional groups and ligand interactions occur at 582, 637, and 677 nm, respectively. Compared with classical watersoluble CDs, the colloidal CDs exhibit ligand-induced multiple emissions. Importantly, we experimentally observed the direct evidence of electron transfer from the carbon core/functional group to surface bound-ligands, which is shown by the distinctive emission peaks at 582, 637, and 677 nm under 410 nm excitation.¹⁹ Comparing with previous works, the colloidal CDs exhibit a highly dispersed and improved crystallinity with multiple emissions induced by electron transfer from the carbon core/functional group to surface bound-ligand.³⁴⁻³⁶ This finding is without precedence, providing a new concept for tuning the emission profile of CDs.

Multiple Sensing Signals due to Intricate Interactions with Ligands and Core. Given the rich surface chemistry, the as-synthesized CDs exhibit intricate emissive responses to their chemical environments. The PL of water-CDs exhibits significant quenching in the presence of Fe³⁺ (16%) and Cu²⁺ (34%) at 100 ppm, Figure S7a. This quenching is dependent on the Fe³⁺ concentration, as displayed in Figure S5b,c, with the LOD of Fe³⁺ ions determined at 70 ppb.

The emission of OLA-CDs also quenches in the presence of Fe^{3+} and Cu^{2+} but increases in the presence of $Zn^{2+}.$ As shown in Figure S7d, the OLA-CD emission is decreased to 0.007% at 400 ppm Fe³⁺ and 5.5% at 400 ppm Cu²⁺, whereas the OLA-CD emission is increased by 288% in response to 400 ppm Zn²⁺ solution, in contrast to water-CDs, which has essentially no response to Zn²⁺. OLA-CDs show higher responsiveness to different ions with a multiple-emission response in the longer wavelength range, as displayed in Figure 6a-d. The LOD of Zn^{2+} was calculated to be 80 ppb, and that for Fe³⁺ was 460 ppb. Furthermore, the PL response ratio is different at different peak positions. While the OLA-CDs are excited at 370 nm, there is only one intensive and broad emission band peaking at 440 nm, with the longer wavelength emissions likely confounded by the broad peak (Figure S8). In the presence of Zn^{2+} , when excited at 410 nm, the 478 nm emission peak of OLA-CDs shows the most pronounced response, compared with emission peaks at 584 and 634 nm (Figure 6a,b and Figure S7f). On the other hand, in the presence of Fe^{3+} solution at concentrations of <100 ppm, when excited at 410 nm, the 634 nm emission peak of OLA-CDs shows the highest contrast response, followed by emissions centered at 587 and 478 nm (Figure 6c,d and Figures S8 and S7g). However, when the Fe^{3+} concentration is >200 ppm, the 478 nm emission has a larger response compared to that at 440 nm.

We also tested the effect of pH change of the medium and found that OLA-CD emission quenched in alkaline solution, while that of water-CDs unchanged, Figure S3e. This confirms the presence of surface functional groups and attached OLA ligands, with alkali affecting the surface ligands resulting in a



Figure 7. Concentration–effect curve of OLA-CDs (open circles) and reference compounds (open triangles) in the different bioassays used here. (a) Acute toxicity to bacteria in the BLT-Screen, compared to that of the reference compound, pentachlorophenol (PCP), with the IC_{20} of 75 mg/L for OLA-CDs identified by the dotted line. (b) Inhibition of photosynthesis after 2 h of exposure in the IPAM assay, compared to that of the reference compound, diuron. (c) Inhibition of photosynthesis after 24 h of exposure in the IPAM assay, compared to that of the reference compound, diuron. Each sample was tested in two independent runs for each bioassay.

reduction of emission intensity. Notably, both OLA-CDs and water-CDs are selectively sensitive to the ionic species of concern in the harsh environment as shown in Figure S7h,i. Therefore, the colloidal CD-based sensor demonstrates remarkable multiple yet specific sensing signals toward Fe³⁺ and Zn²⁺ species in organic solvents.

The FTIR spectra in Figure S9a have pronounced differences, highlighting different interactions between the metal ions and OLA-CDs. The barely changed FTIR spectra of OLA-CDs in the presence of Fe³⁺ suggests that Fe³⁺ quenching of OLA-CDs is likely due to the inner filter effect of $Fe^{3+.37-.1}$ Fluorescence quenching in the presence of Fe³⁺ without noticeable new chemical interactions is also exhibited on water-CDs, Figure S9b. Both confirm the inner filter effect of Fe^{3+} . On the contrary, after the addition of Zn^{2+} in the OLA-CD suspension, the FTIR spectra show that there is a new prominent broad band at 3400 cm⁻¹ and an accentuated band peaked at 1620 cm^{-1} , which can be assigned to alcohol -OHstretch and alkenyl C=C stretch, respectively. A similar new alkenyl C=C stretch is also evident in the OLA-CDs when treated with an alkali solution. This is because Zn²⁺ is introduced by dissolving ZnCl₂ in methanol before addition into the chloroform-dispersed OLA-CDs. Zn²⁺ can coordinate with -OH groups of methanol, forming an organometallic complex.⁴⁰ This Zn²⁺-centered complex appears to bind on OLA-CDs, as evidenced by the FTIR spectrum and the enhanced PL, thereby providing a localized strong alkali environment and performing a reduction effect, which gives rise to the new C=C bonds.⁴¹ The Zn^{2+} centered complex could bind on OLA-CDs through various interactions including electrostatic attraction and hydrogen bonding, functioning as a passivation agent. In addition to the PL intensity increase, the PL lifetime of the OLA-CD in the presence of Zn^{2+} is prolonged by approximately 25% in comparison to that of OLA-CD alone (Table S1 in the Supporting Information). This corroborates the deepened surface trapping states in the presence of Zn²⁺ and its passivation effect.

OLA-CDs were dropcast on a glass substrate, forming a film upon drying, and this film was then tested for ion detection, as shown in Figure 6e. The film is water-resistant; therefore, it can be used for water samples without dissolution and damage. As shown in Figure 6f and Figure S10, the PL of the OLA-CDs film shows distinctive PL intensity increase upon the addition of a solution of Zn^{2+} and quenching on the addition of a solution of Fe³⁺, which is also captured by Video S1.

The thermal stability test shows that the water-CDs fluorescence dropped when heated above 50 $^{\circ}$ C, which is likely due to aggregation. In contrast, OLA-CDs show no change or decay on the fluorescence after being heated even over 100 $^{\circ}$ C (Figure S11). Benefitting from the hydrophobic ligand, the waterproof OLA-CDs film can perform ion detection in a cyclic fashion, with good thermal stability.

In addition, we also made a PVA polymer film incorporating the OLA-CDs, which also showed a stable emission, as shown in Figures S12 and S13. The polymer film is water-resistant and stable under a humid environment. The emission properties of the polymer film are retained after exposure in water, establishing that the CD polymer film is stable and thus promising for real-life applications as emissive materials.

Ecotoxicity Assessment of Colloidal Carbon Dots. A critical issue with CDs is our limited understanding on their ecotoxicity. It is an urgent task to systematically assess the potential impact of CDs on water and soil, whose health can be reflected by a set of abiotic and biotic parameters. In addition to bioassays based on aquatic animals, various in vitro assays using soil and water microbes and algae as well as fish cells have been established as critical indicators for assessing potential ecotoxicity of chemical and biological materials,⁴¹ which can be readily adopted in CDs research and development. In vitro ecotoxicity assay tests showed that OLA-CDs did not affect photosynthesis or algal viability (Figure 7b,c), even at concentrations as high as 910 mg/L. It did, however, produce measurable toxicity to bacteria, albeit at very high concentrations (IC₂₀ = 75 mg/L; IC₅₀ = 200 mg/L; Figure 7a), several orders of magnitude higher than that of the reference compound in this assay, pentachlorophenol (PCP) (IC₂₀ =

0.006 mg/L; $IC_{50} = 0.02$ mg/L; Figure 7a). The results suggest that OLA-CDs have minimal acute toxicity, on par with the water-CDs.

CONCLUSIONS

Crude seaweeds have been converted into highly crystalline CDs using colloidal solvothermal treatment. The choice of solvent not only results in different surface functionalities but also has a strong influence on the morphology of the CDs. Among the solvents studied herein, OLA directly resulted in CDs with a narrow size distribution, 3.6 ± 1.5 nm, without the need for tedious separation procedures to refine the particle size. The emission spectra of OLA-CDs show distinctive peaks with a surface ligand transition band; surface-bound OLA ligands exhibit strong interactions with the carbon core and surface functional group, involving covalent bonding through the amine functional group, resulting in surface band-induced multiple emissions. In addition to demonstrating the high performance of OLA-CDs in their rich emission profile and Zn^{2+} sensing capability, the preliminary *in vitro* ecotoxicity assessment shows that OLA-CDs exhibit minimal acute toxicity to aquatic organisms and algae. More importantly, we establish here the versatility and tunability of ligandinduced, spatial confinement in biomass-derived CDs. By employing different solvents with varying in polarity, boiling temperature, and functional groups, we unraveled the formation mechanism of CDs from biomass and proposed a ligand-mediated, spatially confined synthesis methodology, which is instructive to valorization process designs for converting crude bioresources into high quality functional nanomaterials. Moreover, in the OLA-CDs, we observed a unique broad range (400-700 nm) yet a distinctive emission profile owing to the strong interactions between the carbon core and its surface functional groups with OLA ligands.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00371.

OLA-CD film first dipped into the 500 ppm FeCl3 aqueous solution before dipping into the 500 ppm ZnCl2 aqueous solution (MP4)

HRTEM, TGA, HRXPS of OLA-CDs; Emission spectra of pure OLA; additional Stern–Volmer plot of ions; FTIR of OLA-CDs and after detection of Fe^{3+} , Zn^{2+} ; normalized PL spectra response of OLA-CDs film to Fe^{3+} and Zn^{2+} in sea water; PL lifetime of CDs synthesized in different solvents, lifetime of OLA-CDs under different excitation wavelength, and in the presence of Zn^{2+} ; emission intensity of water-CDs and OLA-CDs after being heated at different temperatures; and photograph and emission profile of the OLA-CD film (PDF)

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Notes

The authors declare no competing financial interest.

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