Excitation-Dependent Photoluminescence from Single-Carbon Dots

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Carbon dots (CDs) are carbon-based fluorescent nanoparticles that can exhibit excitation-dependent photoluminescence (PL) "tunable" throughout the entire visible range, interesting for optoelectronic and imaging applications. The mechanism underlying this tunable emission remains largely debated, most prominently being ascribed to dot-to-dot variations that ultimately lead to excitation-dependent ensemble properties. Here, single-dot spectroscopy is used to elucidate the origin of the excitation-dependent PL of CDs. It is demonstrated that already single CDs exhibit excitation-dependent PL spectra, similar to those of the CD ensemble. The single dots, produced by a facile one-step synthesis from chloroform and diethylamine, exhibit emission spectra with several characteristic peaks differing in emission peak position and spectral width and shape, indicating the presence of distinct emission sites on the CDs. Based on previous work, these emission sites are related to the sp^2 subregions in the carbon core, as well as the functional groups on the surface. These results confirm that it is possible to integrate and engineer different types of electronic transitions at the nanoscale on a single CD, making these CDs even more versatile than organic dyes or inorganic quantum dots and opening up new routes toward light-emission engineering.

Carbon dots (CDs) are a promising class of carbon-based fluorescent nanoparticles that consist of mixed sp^2 and sp^3 hybridizations.[1] Since their discovery in 2004,[2] CDs have drawn much attention due to their facile synthesis,[3] bio-compatibility,[4–7] and resource abundance. Even more interestingly, some synthetic routes yield excitation-dependent photoluminescence (PL) that spans the entire visible spectral region. This multicolor PL allows for flexible "tuning" of the light emission from blue to red via changes in excitation wavelength,[8–11] offering new opportunities for emission color engineering with a single material. Owing to its great application potential, many studies have been devoted to unraveling the mechanism behind the PL of CDs, providing evidence for emission controlled by the CD core size,[9] emission from functional groups on the CD surface,[12] and a combination of both.[10,13,14] The emission tunability has been most prominently ascribed to selective excitation of subsets of CDs within the CD ensemble.[15–17,32] Indeed, multiple studies have shown that it is possible to tune the emission by using different types of CDs that are themselves excitation independent.[18–20] On the other hand, Pan et al.[11] and Fu et al.[21] have suggested that different emission sites within individual CDs are responsible for excitation-dependent emission. Establishing a generic model for the excitation-dependent PL of CDs has proven to be challenging,[22] due to the great variety of chemical and structural compositions resulting from the different synthetic routes[23] and even observed within one and the same CD ensemble. Moreover, the majority of studies focuses on ensemble spectroscopy techniques that provide only limited insight into the microscopic distribution of different emission mechanisms within CD ensembles and within a single CD. Hence, there is an active debate regarding the microscopic origin of the PL, while the possibility of excitation-dependent single CD emission remains largely unexplored.

Here we use single-dot PL spectroscopy to investigate the excitation-dependent emission of single CDs. We show that already individual CDs exhibit excitation-dependent emission spectra with several characteristic emission peaks. These emission spectra slightly vary from dot to dot, but always retain their basic characteristics, indicating the presence of distinct emission sites within the same single CD. Since these CDs are produced via a facile single-step bottom-up synthesis, these results indicate that, surprisingly, a straightforward synthesis route can lead to the integration of multiple emission sites within each single CD. These findings pave the way for color engineering of single CDs, rendering this material

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interesting for single particle tracking in multicolor imaging applications.

We prepared CDs via a mild one-pot process by refluxing of chloroform and diethylamine (DEA), as described in our previous publication by Nie et al.[10] Transmission electron microscopy and Raman spectroscopy data reveal that the resulting CDs are composed of a nanocrystalline core (graphitic sp^2 carbon atoms with sp^3 carbon defects)[10] with an average size of 2.0 ± 0.7 nm, as evaluated by atomic force microscopy (see Figure S1, Supporting Information). Ensemble measurements of our CDs show an excitation-dependent emission spectrum extending across the entire visible spectral region from 400 to 700 nm,[10,11] as shown in **Figure 1**a. In particular, from detailed PL excitation analysis (see Figure S2, Supporting Information), we identify three distinct emission bands, in the blue (490 nm), green (560 nm), and red (660 nm) spectral region. Our previous work[10] showed that these three emission bands are robust features of the synthesized CDs and related their origin to the core, C=O and C=N surface moieties, respectively. However, the microscopic distribution of these emission sites remains unclear.

To obtain insights into the microscopic origin of the three emission bands, we employ single-dot spectroscopy that circumvents ensemble averaging effects and enables investigation of the PL from individual CDs. To do so, we use an inverted microscope equipped with a spectrometer coupled to an EMCCD camera, where either a grating for spectrally resolved measurements is selected, or a mirror to record PL images enabling spatial localization of emissive CDs. We use highly diluted dispersions of CDs in ethanol, which we drop-cast onto quartz substrates, to achieve spatially separated CDs at particle density below 0.1 μm^{-2} to ensure measurements of individual CDs. Indeed, the vast majority of observed bright spots displays two-step blinking behavior (Figure S3, Supporting Information), characteristic for single quantum emitters,[25] as previously reported for single CDs.[24,26] We then use 405, 488, and 638 nm excitation wavelengths and emission band-pass filters around the maxima of the three emission bands to selectively study the blue (490), green (560 nm), and red (660 nm) emission. The filtered images are depicted in Figure 1c–e. Their comparison reveals that many blue and green emitting spots show spatial overlap (arrows). By comparing the location of spots in detail, we find ≈45% overlap between the CDs excited at 405 and 488 nm, suggesting that 45% of the CDs exhibit both blue and green emission. Overlap with red emitting CDs is observed as well: while only a small fraction (≈5%) of them emit in the red, ≈24% of those CDs emitting in red display overlap with the ones emitting in green, and ≈30% with the ones emitting in blue; see Figure 1e. Furthermore, ≈15% of them appear under both blue and green excitation, indicating emission in all three colors.

To record the change in the PL of the spatially localized single CDs of Figure 1c–e, we select individual CDs using a slit to narrow down the field of view (**Figure 2**a) and record single-dot spectra. Several of the selected spectra recorded at the three excitation wavelengths as used before are shown in Figure 2b. In the single-dot spectra, we observe the simultaneous presence of blue and green, and eventually blue and red emission bands. These emission bands differ in their spectral features with red and green spectra being narrower than the blue spectrum, similar to the spectra of the CD ensemble (Figure 1a). Such excitation-dependent PL of single CDs is surprising, as excitation-dependent PL spectra are commonly not observed for molecules or single-quantum dots, indicating the presence of multiple emission sites within one and the same CD. The direct observation of excitation-dependent single-dot PL spectra thus substantiates previous suggestions of excitation-dependent PL from single CDs.[11] In contrast, Ghosh et al.[26] did not observe such shifts in the PL spectra when exciting individual CDs at different excitation wavelengths. However, the 467 and 488 nm wavelength excitation in their experiment might have been too close for efficient excitation of the separate emission centers. Finally, the large degree of overlap observed in Figure 1c–e is clearly different from the observations made by Das et al.,[24] where no overlap was found between green and red emission. In contrast, our
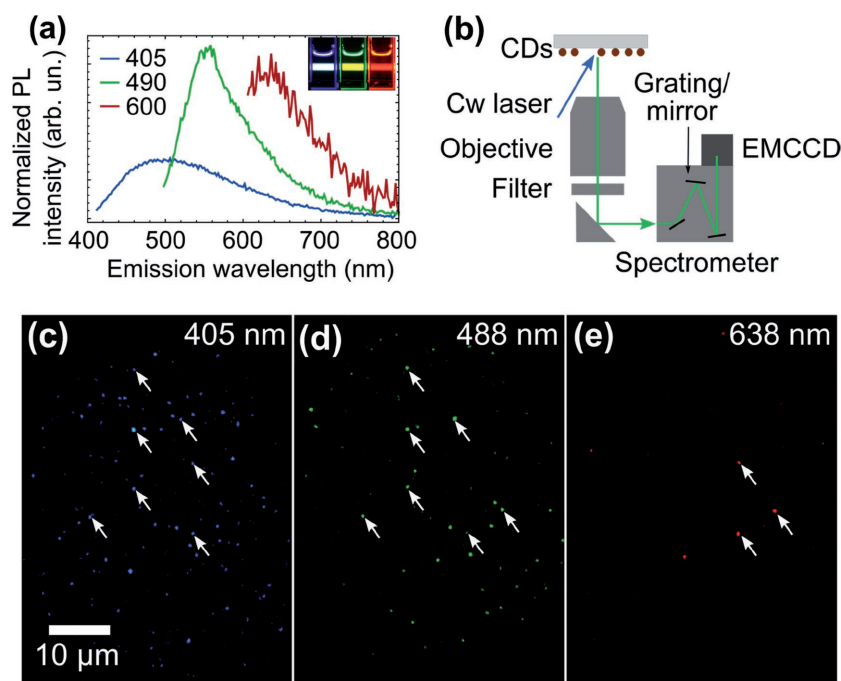

Figure 1. From ensemble to single carbon-dot measurements. a) Ensemble PL spectra of CDs dispersed in ethanol under 405, 490, and 600 nm continuous wave (CW) excitation, normalized to the number of absorbed photons. Inset: Real-color photograph of the sample under 430, 510, and 600 nm pulsed nanosecond laser excitation. b) Schematic of the wide-field single-dot spectroscopy experimental setup. c–e) False-color wide-field PL images of highly dilute drop-casted samples of CDs. The three panels show identical fields of view, taken at c) 405, d) 488, and e) 638 nm wavelength excitation and detecting blue-green (480–520 nm), yellow (580–620 nm), and red (680–720 nm) emission, respectively. Arrows indicate examples of identical CDs luminescing under different excitation wavelengths. The exposure time was kept at 30 s to limit the effect of photodegradation (Figure S3b, Supporting Information).
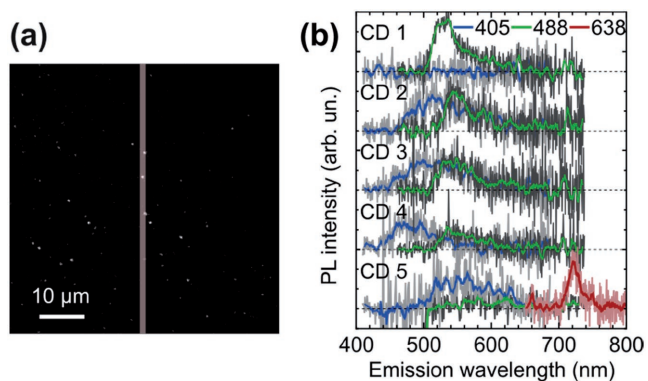
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Figure 2. Single dot spectroscopy. a) Wide-field PL image under 488 nm excitation with the projected position of the slit (projected width ≈1 µm) selecting part of the image for spectrally resolved measurements. b) Resulting single CD PL spectra measured under subsequent excitation at 638 (≈125 W cm^{-2}), 488 nm (≈50 W cm^{-2}), and 405 nm (≈40 W cm^{-2}) CW laser excitation. Smoothed PL spectra are shown in colored lines. These spectra, obtained at different excitation wavelengths, demonstrate the excitation-dependent PL of single CDs.

single-dot spectroscopy results shown in Figure 2b suggest that already the individual CDs exhibit excitation-tunable emission, consistent with the spatial overlap of the blue, green, and red PL in Figure 1c–e.

To obtain further insight into the excitation-dependent PL of the ensemble, we link the single-dot and ensemble properties

and record ≈500 single-dot spectra, superimpose them, and compare the resulting superimposed spectrum to that of the ensemble. Several representative examples taken under 405, 488, and 638 nm wavelength excitations are shown in **Figure 3** (top), while the superposition of all ≈500 spectra compared to the ensemble measurements is shown below. Indeed, the superimposed spectra show good agreement with the ensemble spectra, confirming that the overlapping PL signals of single CDs under different excitation wavelengths shown in Figure 1c–e indeed result from the excitation of different PL spectra. The ensemble emission maxima coincide very closely with the most frequently observed single-dot peaks, while at the same time, there is significant variation in the single-dot spectra. For the green emission band, for example (Figure 3b), the single CD spectra vary between 500 and 750 nm, clearly giving rise to the extended width of the ensemble spectrum, while the individual CD spectra are much narrower (Figure 3d). This is also observed for the red emission band (Figure 3c). Interestingly, many green single-dot spectra display multiple peaks (such as the bottom spectra in Figure 3b) or a peak that is clearly asymmetric toward longer wavelengths, which is typically ascribed to energy replicas due to optical energy losses to local vibrational states.[26,27] The spectral features of these replicas persist irrespective of their spectral position as shown in Figure S4 (Supporting Information), indicating that a common mechanism underlies the green band PL, despite the dot-to-dot variations. In contrast, the blue and red single-dot emission spectra do not show replicas, suggesting a different origin from
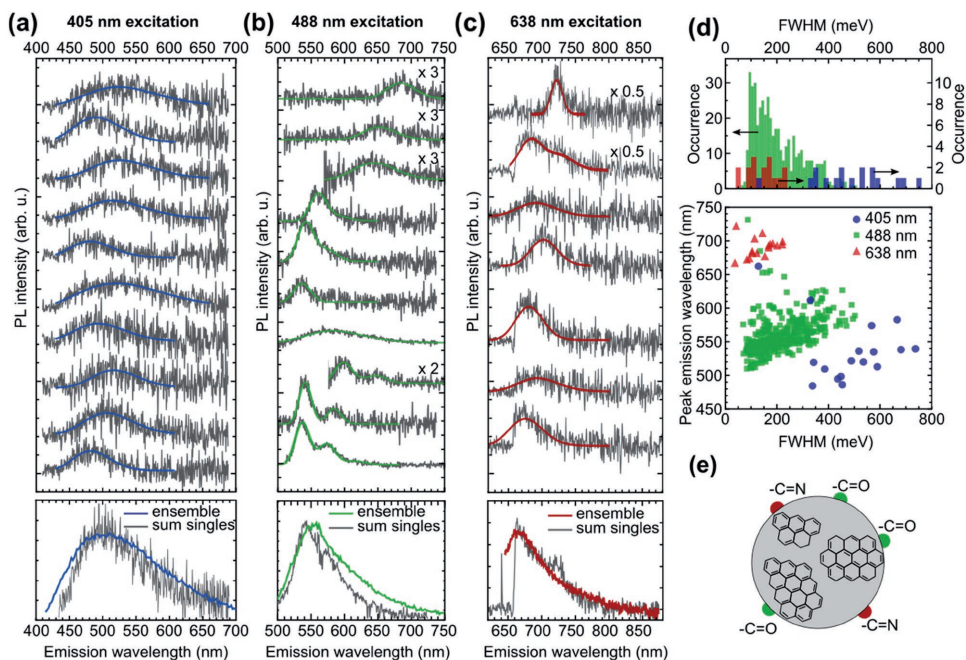

Figure 3. Connecting single-dot and ensemble optical properties. CD spectra under 405 nm [a] ≈40 W cm^{-2}], 488 nm [b] ≈50 W cm^{-2}], and 638 nm [c] ≈125 W cm^{-2}] wavelength excitation, single-dot spectra (top), and superposition of single-dot spectra compared to the ensemble spectrum of a low concentration (0.1 mg mL^{-1}) dispersion of CDs in ethanol (bottom). Solid lines are fits to the data (see the Supporting Information for more information). The superimposed spectra show good agreement with the ensemble spectrum; the small deviation for green excitation in the red (>600 nm) might arise from the low emission intensity of red emitting particles being too weak to be efficiently detected by single-dot spectroscopy, or from the previously reported local environment dependence of the CD PL.[16,32] d) Distribution of the full width at half maximum (FWHM) (top), and its relation to the emission peak wavelength of all recorded single-CD PL spectra (bottom). Colors indicate the different excitation wavelengths (see the legend). e) Schematic of the proposed CD structure giving rise to the three emission bands.

the green emission band. Moreover, for the blue emission band excited at 405 nm (Figure 3a), the single-CD spectra are significantly broader (≈300–700 meV) than those excited at 488 nm (≈100–400 meV) or 638 nm (50–200 meV), respectively, as shown in Figure 3d, again indicating a different origin.

In our previous work by Nie et al.[10] we proposed, based on chemical characterization combined with ensemble spectroscopy, that the blue, green, and red emission sites in these CDs are related to the core and to oxygen and nitrogen containing surface functional groups, respectively. PL was shown to change dramatically after selective reduction of C=O and C=N bonds on the surface,[10] in line with studies available in the literature that show that the PL spectral position and width strongly depend on the type of surface functionalization.[12,14,28,29] The differences in the width, peak position, and structure of the spectra that we observe here for single CDs confirm the different origins of the emission bands on the single CD level and suggest that the excitation-dependent single CD emission arises from the interplay of the core and surface functional groups rather than emission from different sp^2 domains within the CD core.[21] Hence, we arrive at the following mechanism underlying the excitation-dependent single CD emission (see Figure 3e): the green and red emission originates from C=O and C=N containing surface groups, respectively,[10] while the blue emission originates from the core, likely from smaller sp^2 domains[30,31] within the CD core, as our synthesis does not yield graphene-like cores, but rather CDs with mixed sp^2 and sp^3 phase as schematically shown in Figure 3e. Indeed, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements on our dots reveal the presence of O and N containing functional groups (such as −OH, C=O, and C=N).[10] This is in line with the evidence for a common origin of the green emission in carboxyl/carbonyl (O-related) surface functional groups.[12,14,24,26,29]

In conclusion, we have shown that individual CDs prepared by a single one-step chemical synthesis can be excitation-tunable emitters, very much like the ensemble of CDs. Using excitation single-dot spectroscopy (with excitation wavelengths in the red, green, and blue) we identified characteristic single-dot PL spectra with different emission peak positions, spectral widths, and spectral shapes, indicating multiple active and independently excitable emission sites within a single-carbon dot. Superposition revealed that these single-dot spectra are at the origin of the excitation-dependent PL of the ensemble. By quantifying the number of carbon dots that emit multiple colors, we have shown that while not all individual CDs exhibit excitation-tunable emission, it is possible to integrate and engineer different types of electron transitions in nanoscopic dimensions through facile chemical synthesis, making these CDs even more versatile than organic dyes or inorganic quantum dots (QDs). This makes this particular type of CDs interesting for optoelectronic applications as an excitation-tunable broad-band phosphor and for single nanoparticle multicolor imaging.

Experimental Section

Synthesis: CDs were synthesized by refluxing of DEA and chloroform (vol:vol = 1:10) at 62 °C for 60 h as described in our previous work by Nie et al.[10] The products were separated from the solution with a rotary vacuum evaporator and redissolved in ethanol. The CDs were purified by dialysis (weight cutoff: 3500) in water and then in ethanol to remove any molecular byproducts. FTIR and XPS measurements revealed the presence of O and N containing functional groups (such as −OH, C=O, C=N) on the CDs.[10] Oxygen-containing functional groups were presumably introduced from water and oxygen, and nitrogen-containing functional groups were presumably introduced from DEA.

Ensemble Spectroscopy: CDs dispersed in UV-grade ethanol were studied in a quartz cuvette (Hellma Analytics) excited either by pulsed laser excitation provided by an Nd:YAG laser (Solar LS) or by continuous wave (CW) excitation provided by a Xe lamp. PL was detected in a spectrofluorometer (Horiba, Fluorolog3-22) equipped with a double grating monochromator coupled to a photomultiplier tube (Hamamatsu, R36-10). PL spectra were measured at room temperature and were corrected for the spectral sensitivity of the setup.

Single-Dot Spectroscopy: Single-dot PL was detected using an inverted microscope (Zeiss, AxioObserver Z1) coupled to a spectrometer (Princeton Instruments, Acton SP2300) and a charge-coupled device (CCD) (Princeton instruments, Pylon 400B) in a wide-field scheme. For this, a dilute dispersion of CDs in ethanol was drop-casted on a quartz cover slip (Structure Probe Inc.). The cover slips were cleaned by sonication in an alkaline cleaning solution (Hellma Analytics, Hellmanex III) for 60 min, followed by sonication and rinsing with demineralized water (30 min), drying by nitrogen flow and an ozone dry-cleaning procedure (UVP, PR-100) for ≈20 min. CW excitation was provided by laser diodes with 405 nm (ThorLabs, ML320G2-11), 488 nm (Lasos, BLD-488-SMN), and 638 nm (Lasos, RLD-XT) wavelength or by the 488 nm Ar+ laser line (Spectra-Physics, Stabillite 2017). Emitted light was collected using a 100x objective (Zeiss, Epiplan-Neofluar NA 0.75) and was filtered by a long pass filter to remove scattered excitation light. All spectra were measured at room temperature and corrected for the spectral sensitivity of the setup.

For localization of the CD positions, bright domains with significant intensity compared to the background were identified as CDs. The position of the center of this domain was then compared between different images of the same field of view. A tolerance of 1 pixel between center coordinates was allowed to count as overlapping CDs. The different band-pass filters used in the experiments resulted in a slight displacement of the recorded images, which was corrected by quantifying the shift from transmission images taken by white-light illumination on a reference sample.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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