A Systematic Study of Laser-Engineered Fluorescence in Carbon Black

Kae Lin Wong, Sharon Xiaodai Lim,* Zheng Zhang, Junyong Wang, Xiao Wu, Qing-Hua Xu, and Chorng-Haur Sow*

The feasibility of laser-engineered fluorescence emission from carbon black (CB) with three laser sources of different wavelengths—660 nm (red), 532 nm (green), and 405 nm (blue)—is demonstrated. From which the 660 nm focused laser beam produces the most intense fluorescence. Detailed systematic studies on how the laser-engineered fluorescence emission from CB depends on laser power, laser patterning speed, and environmental control during the laser modification process are carried out. From the systematic studies, the CB samples in ambient undergo most noticeable modifications with a laser power of \( \approx 7 \) mW and patterning speed of \( \approx 12 \) \( \mu \)ms\(^{-1}\). The fluorescence emission is attributed to the creation of complex defects states into the oxidized form of the pristine system by the formation of 1) C60 fullerene and fullerites; 2) ZnO; 3) \( \text{Zn}_2\text{SiO}_4 \), and more complex hybrid such as 4) carbon-induced mid-gap states in \( \text{Zn}_2\text{SiO}_4 \), and 5) Ca-induced defects in ZnO. Such incorporations resulted in the formation of intermediate states in the large bandgap materials. As a result, distinct multicolored fluorescence is emitted by these laser-quenched material systems. Accordingly, multicolored fluorescence designs can be created with elaborative control of focused laser treatment in an ambient and helium environment.

1. Introduction

Carbon black (CB), an economical black powder form material, can be obtained through various processes, for example, acetylene black, channel black, furnace black, gas black, lampblack, etc. It is mainly mass-produced by the incomplete or partial combustion of the hydrocarbons such as petroleum oil and natural gas under controlled conditions.\(^{[1–3]}\) The primary particle of CB is named as nodule by Hess and Ford\(^{[4]}\) or aggregates by Janzen and Kraus\(^{[5]}\) with a size around 10–300 nm. They are categorized into four types: spheroidal, ellipsoidal, linear, and branches.\(^{[1,3,4]}\) Unlike the ABA stacking of pure graphite, these aggregates tend to form the turbostratic structure with parallel layers but are rotatable at the c-axis.\(^{[1]}\) As a result, CB tends to be between amorphous material and graphite.

Over the years, CB has been most commonly used as pigments and in rubber manufacturing industries.\(^{[1,1,4]}\) As a result of its interesting surface area, particle sizes and structures, surface chemistry, and binder chemistries,\(^{[3,3,5]}\) CB has been widely investigated for its applicability in nanotechnologies. It was reported that the decomposition of gaseous or liquids carbon-containing fuels contains high content of carbon (\( \approx 90\% \)), organic impurities (metal), and inorganic impurities (sulfur, alkaline metal).\(^{[1,4]}\) This led to the implementation of CB, as carbon-based fullerene derivatives in some perovskite cell to improve efficiency, as stabilizers for n-type organic semiconductors commonly used in solar cells and as carbon-based sorbents for hydrogen storage.\(^{[5]}\)
Previously, Lim et al.\textsuperscript{[6]} had reported that the CB exhibits bright fluorescence emission after focused green (532 nm) laser modification in the ambient. The laser-modified CB emits 1) blue, yellow, and red luminescence under ultraviolet light (UV, 300–390 nm) excitation, 2) yellow fluorescence under blue light (B, 450–500 nm) excitation, 3) red fluorescence under green light (G, 500–560 nm), and yellow light (530–580 nm) excitation, respectively. The emission of pale yellow, yellow, and red fluorescence under UV, B, G, and Y light excitations were detected from the laser-treated CB in helium. Hence, the laser-modified CB can serve as a photodetector and fluorescent watermark.\textsuperscript{[6]} The fluorescent CB is reported to be arising from the 1) formation of the carbon infusion into zinc oxide during the laser patterning in ambient, 2) presence of sulfur impurities in CB powder, and 3) light scattering from periodically arranged carbon atoms.\textsuperscript{[6]}

We have followed up on our earlier study of laser-modified fluorescent CB with more detailed and extended studies in this work. While our previous work\textsuperscript{[6]} provided some insights into the mechanism behind the observed phenomenon and showcased some possible applications, we believe some questions are left unanswered, such as is this phenomenon laser dependent? If yes, why is it so? If not, can we use a more economical laser source to make it more enticing for such upcycling process to be upscaled and cost effective? In conducting a more detailed study of this amazing system, we hope to establish better control over the end product and develop ways to make this upcycling process more economical and favorable for business uptake and future applications. We have explored the feasibility of this engineering process with three different laser sources with three different emitted laser wavelengths of 660 nm (red), 532 nm (green), and 405 nm (blue). We find that the red-focused laser beam produces the most significant effect. Hence, a focused laser beam with a wavelength of 660 nm is selected for this work. Such laser source is also relatively more economical and more readily available in the industry. We carry out detailed systematic studies on how the observed phenomenon depends on laser power, laser patterning speed, and environmental control during the laser modification process. An optimized set of engineering parameters is achieved. We find that the surface allotrope of the CB sample undergoes noticeable modifications under a condition of higher laser power and lower patterning speed. Our studies propose the following mechanism for the observed fluorescence from the laser-modified CB in addition to what was previously proposed by Lim et al.\textsuperscript{[6]} Namely, we attribute the fluorescence emission to the formation of 1) C60 fullerenes and fullerites; 2) Zno; 3) Zn2SiO4, and the induction of complex defects states into the hybrid system such as 4) carbon-induced mid-gap states in Zn2SiO4, and 5) Ca-induced defects in ZnO. Such incorporations resulted in gap states in the large bandgap materials. As a result, these lasers’ quenched material systems have distinct multicolored fluorescence. Accordingly, multicolored designs can be created with elaborative control of focused laser treatment in an ambient and helium environment.

2. Results and Discussion

2.1. Laser-Assisted Modification of CB

Figure 1 provides an overview of the technique and observed phenomenon. A schematic of the scanning focused laser beam setup is shown in Figure 1a. Pristine CB sample is placed on the sample stage under a 660 nm focused red laser beam for laser treatment. A custom-made system with an optical microscope utilizing a 50× optical lens is used in this work. As a result, a laser beam spot of ≈1 μm is focused on the CB sample. The sample stage is connected to the computer system to raster a 30 μm × 30 μm box on the CB sample. The laser beam remains fixed, while the sample is controllably translated in rastering mode to the laser beam.

The outcome is a laser-initiated, site-selective, photothermal reaction in the CB. Figure 1b depicts the setup where the CB sample can be placed inside a customized transparent vacuum chamber (Figure 1c) to control the environment (e.g., vacuum or helium) in which this process takes place. Figure 1d shows a bright-field image of a micro-box created on the CB sample in ambient conditions. Remarkably, fluorescence microscope images of the same micro-box under different excitation condition exhibit bright fluorescence color, as shown in Figure 1e–g. The scanning-focused laser beam is a facile technique that can transform CB from a fluorescence-inactive material into a hybrid that emits bright, multicolored fluorescence light. The presence of multiple color emissions suggests that the fluorescence spectrum is broad, and different excitation light-activated different species are found in the laser-treated sample. Upon illumination of the focused laser beam, black CB absorbs the laser energy effectively, giving rise to the sample’s rapid thermal heating. The intense heat facilitates the rapid chemical reaction of the carbon atoms, oxygen atoms, and other elements found in the CB, forming different chemical compounds. In addition, since we have a scanning laser beam, the laser beam (spot size of ≈1 μm) does not stay on the same spot for a long time (since the patterning speed is ≈12 μm s\textsuperscript{-1}). As a result, locally, the sample undergoes rapid thermal heating that can go as high as (≈2400 K) and followed by rapid cooling to room temperature of ≈295 K. The process gives rise to a quenched system where many defects are quenched into the sample. And these defects contribute to the defect states in the bandgap of the oxides formed and transform the CB into highly fluorescence species. Figure 1h shows SEM images of the laser-treated CB. A higher magnification SEM image (Figure 1i) shows the formation of small nanoparticles, and some take on a semi-circular/molten state. The SEM image thus provides strong evidence of the above-mentioned bond breaking/formation process and the premature termination of laser interaction with the sample, which leave the newly created material in a semi-formed (quenched) state.

2.2. Comparing the Performance of Different Laser Wavelength

Our first systematic study probes the effect of different laser wavelengths on the observed fluorescence emission. In our
previous work, only a 532 nm laser was used in the study. Herein, we repeated the experiment using three different laser sources with laser wavelengths of 660, 532, and 405 nm. And using the same laser power of 7 mW for each of these laser sources, we managed to reproduce a similar engineering achievement of converting the CB into fluorescence active species. The fluorescence spectra emitted by these lasers modified CB under UV excitation is shown in Figure 2a. The corresponding FM images of the micro-box under UV excitation are shown in Figure 2b. It is clear from Figure 2a that all three spectra exhibit a similarly peak position around 515 nm. The peak position is consistent with the green fluorescence emitted from these lasers modified samples.

Similarly, the broad peaks suggest that multiple fluorescence species are formed due to laser beam modification. These fluorescence species are attributed to the defective species created in

![Figure 1](image1.png)

**Figure 1.** a) Schematic diagram of the scanning focused laser system. b,c) Schematic of the sample treated by the focused laser system in (b) ambient and (c) controlled vacuum/helium environment. d) Bright-field image of the micro-box created on the CB sample under ambient environment and e–g) multicolor fluorescence images of the micro-box obtained under UV, B, and G excitations. h,i) SEM images of the laser-patterned CB sample.

![Figure 2](image2.png)

**Figure 2.** a) Fluorescence spectra of the laser-modified CB under UV excitation using three different laser sources. The laser source wavelengths are 660, 532, and 405 nm, and the laser power used to achieve the modification is \( \approx 7 \text{ mW} \) in each case. b) FM images of the micro-box created under UV excitation.
these samples. It is also evident from Figure 2a that laser modification using the red laser (660 nm) gives rise to fluorescence emission with the highest intensity. On the other hand, the blue laser is less effective than its counterpart with a longer wavelength. Such a difference can be attributed to the difference in the absorption coefficient of the CB for different wavelengths. More effective absorption of the red light can give rise to an even higher elevated temperature to achieve rapid thermal heating and subsequent quenching. As a result, the intensity of the emitted fluorescence becomes even more prominent. Given the observation that red laser produces the most prominent effect by way of fluorescence intensity, we decide to concentrate our systematic studies of this laser-induced fluorescence in CB using the red laser source from here on. Another more practical reason for such a choice is that solid-state red laser is relatively more economical and more readily available in the industry.

2.3. Laser Power Dependence Study—An Ambient Condition

The laser power dependence study is the first systematic study on this focused laser beam-induced fluorescence emission from the CB. In this study, a laser beam with a measured power of 3, 5, 7, 10, and 13 mW is focused onto a CB sample to create an array of micro-boxes. The focused laser patterning speed is fixed to be 12 μm s⁻¹, and the CB sample is under ambient conditions. Figure 3a show bright-field (BF) and fluorescence images of the micro-boxes under different excitation (UV, Blue, Green, and Yellow). The micro-box created using a focused laser beam with 7 mW shows the highest fluorescence intensity. As such, 7 mW is the optimum focused laser power for the laser patterning on CB. A lower focused laser power does not change the allotrope structure, and a higher focused laser power overly burns out the new structure produced. 13 mW treated CB shows the least fluorescence due to the uneven distribution of impurities in the CB powder.

As shown in Figure 3b, the photoluminescence (PL) spectra of the patterned region under UV light excitation (laser excitation wavelength for the PL measurement is 325 nm) shows broad spectra again attributable to the multiple defect species quenched into the CB materials. The same figure also shows that pristine CB does not exhibit any prominent fluorescence emission before the laser modification. Figure 3b also shows a small peak at ≈390 nm, which is attributed to the near bandgap emission of ZnO due to the recombination of free excitons through an exciton–exciton collision process.[7] Hence, providing evidence for the formation of ZnO nanoparticles. Figure 3c shows the intensity of the fluorescence peak (≈595 nm) versus the laser power consistent with the observation that 7 mW gives the best yield.

It is also interesting to compare Figure 3c with 2 where the peak of the PL spectra and the fluorescence spectra under UV excitation captured by the fluorescence microscope are slightly different. The difference in peaks is attributable to the difference in the excitation light source. The excitation light is a monochromatic He-Cd laser emitting a single wavelength at 325 nm in the PL spectra. In comparison, the UV excitation light source in a fluorescence microscope corresponds to a band with a wavelength range of 330–390 nm. From this study, 5, 7, and 13 mW focused laser power is then selected for detailed studies on the effect of a controlled environment in the laser-induced

![Figure 3](https://www.advancedsciencenews.com/)

Figure 3. a) Focused laser power-dependent study of CB interaction with controlled laser patterning process in ambient. b) PL UV emission spectra collected from as-received CB and CB treated with 5, 7, and 13 mW focused laser in ambient. c) Fluorescence intensity versus focused laser power at ≈595 nm under the focused laser treatment in ambient.
fluorescence emission. The Raman shifts collected using 532 nm Raman spectroscopy (Figure S1, Supporting Information) of the focused laser-engineered micro-boxes shows an extremely high fluorescence background and cover the presence of both defects (D) and graphitic (G) peaks.

2.4. Laser Speed Dependence Study—An Ambient Condition

The second set of systematic studies probes different laser patterning speeds on fluorescence emission. The patterning speed of the focused laser beam varies from 6 to 200 μm s\(^{-1}\) while maintaining the laser power at 7 mW. Similar 30 μm × 30 μm Micro-Boxes are patterned at constant 7 mW focused laser power, while the sample is kept under the ambient condition. The results of the systematic study are presented in Figure 4. Micro-Box patterned using the focused laser at a patterning speed of 12 μm s\(^{-1}\) exhibits the highest PL intensity. On the other hand, Micro-Box patterned via a laser patterning speed of 200 μm s\(^{-1}\) emit the lowest PL intensity. It is assumed that when the focused laser patterning speed is too fast, the duration for the focused laser treatment is short. Thus, the heat that reaches the patterning region is lesser and creating a shallower cut with lesser changes being applied to the structure of CB powder. On the other hand, when the focused laser treatment duration is longer with a slower focused laser patterning speed, the focused laser can penetrate the CB sample deeper, leading to a more complete chemical infusion among the impurities.

Interestingly, at 50 μm s\(^{-1}\), the fluorescence detected shows a blue shift by \(\approx 30\) nm than those detected from patterning at 12 and 200 μm s\(^{-1}\). The shift can be attributed to the difference in the population of different defective species created. Three focused laser patterning speeds resulting in the highest, moderate, and lowest PL emission are further selected for comparison in different environments.

To gain insight into the chemical nature of the fluorescence species formed in the CB in ambient conditions after laser treatment, we use EDX to probe the active species in a micro-box created by focused red laser power of 7 mW at focused laser patterning speed of 12 μm s\(^{-1}\). The laser-patterned micro-box emits blue fluorescence (Figure 5b) under UV excitation, yellow fluorescence (Figure 5c) under B light excitation and red fluorescence (Figure 5d–e) under G and Y light excitation. The corresponding SEM image of the micro-box is shown in Figure 5f. EDX map obtained shows carbon (C) atoms to be distributed evenly outside the patterned micro-box (Figure 5g). In contrast, oxygen (O), silicon (Si), and zinc (Zn) atoms are being detected to be rich at the patterned micro-box (Figure 5h, i, k). Calcium (Ca) atoms are seen to be accumulated in patches inside and outside the patterned micro-box (Figure 5j). The loss of carbon element in the patterned laser region suggests that the laser introduced enough energy to break the carbon bonds, resulting in the following possible effect: 1) releasing the carbon atoms into the ambient; 2) forming composites with other elements such as Zn, Si, and Ca; 3) creating amorphous carbon, and 4) forming

![Figure 4](http://www.advancedscien...)

**Figure 4.** a) Focused laser patterning speed-dependent study of CB interaction with controlled laser patterning process in ambient. b) PL UV emission spectra collected from as-received CB and CB treated with 12, 50, and 200 μm s\(^{-1}\) focused laser in ambient. c) Fluorescence intensity versus focused laser patterning speed at \(\approx 595\) nm under the focused laser treatment in ambient.
oxidized form of the new composites. The outcome results in a relatively small amount of carbon present within the laser-patterned region, existing as defects, oxidized or an amorphous state, compared to the surrounding carbon source present in the pristine sample. The outcome created a contrast in the elemental map where insufficient carbon elements are detected in the laser-treated region. The elemental spectrum is plotted and shown in Figure 5l. The presence of sulfur and its influence on the fluorescence effect detected was previously discussed in detail by Lim et al.[6] Herein, we will focus our attention on the influence of other elements detected on the observed fluorescence. The fluorescence originates from the photothermal reaction that leads to the changing of chemical processes among the impurities in the CB powder when there is excess oxygen flowing through during the focused laser treatment. The fitting of multiple peaks for the PL spectrum in Figure S1a, Supporting Information, highlights the \( \approx 390 \) nm peak attributed to the formation of ZnO atoms, as shown in the EDX results.

2.5. Focused Laser Patterning Environment Dependent

In the next phase of the systematic study, we repeat the laser modification experiment with the CB sample housed in a different controlled environment. Figure 1c shows that we can still achieve laser modification in a controlled environment by housing the CB sample in a transparent chamber where the laser beam can shine through. The different environments studied include 1) under ambient conditions, 2) under a helium environment, and 3) under a “vacuum” environment that is created by removing the air in the sample chamber via a mechanical pump. In our previous work, no study in a vacuum environment was conducted.[6] The measured pressure in the sample chamber is 0.05 torr. Hence, it should be regarded as an environment with reduced oxygen concentration. With focused laser treatment of 7 mW focused red laser power and 12 \( \mu \text{m s}^{-1} \) focused laser patterning speed, micro-boxes are created in the CB sample under different environments before further characterization. Figure 6 shows the result obtained from these experiments. Figure 6a shows that the PL spectra of the pristine CB sample and the CB sample modified in the helium environment are almost identical. On the other hand, the PL spectra of the CB sample modified in a vacuum environment show significantly lesser PL intensity compared with the CB modified under ambient conditions. These spectra provide clear evidence that oxygen plays a critical role in transforming the CB into fluorescently active species. The FM images in Figure 6b–d show the destruction caused by the focused laser beam without creating active fluorescence species within the micro-box patterned. On the other hand, it is also noted that the CB sample surrounding the micro-box emit pale-yellow fluorescence.

2.5.1. Laser Patterning Environment-Dependent—Vacuum

Figure 7 shows the results of a more detailed characterization of the CB sample modified by laser beam in a vacuum environment, a value-add to this phenomenon that was not mentioned in our previous work.[6] With focused laser treatment of 7 mW focused red laser power and 12 \( \mu \text{m s}^{-1} \) focused laser patterning speed in vacuum (down to 0.05 Torr), the region outside the focused laser engineering region was detected to exhibit fluorescence in pale yellow (Figure 7b), bright yellow (Figure 7c), and red (Figure 7d,e) under UV, B, G, and Y light excitation. Randomly distributed specks of blue, yellow, and red

![Figure 5. a–e) FM images of region patterned using 7 mW laser at 12 \( \mu \text{m s}^{-1} \) in ambient under a) BF and b) UV, c) B, d) G, and e) Y light excitation. f) Corresponding SEM image. g–k) Elemental map of g) C, h) O, i) Si, j) Ca, and k) Zn. l) EDX spectrum of the studied region.](image-url)
fluorescence (Figure 7b–e) were found at the edge of the focused laser-patterned square under UV, B, G, and Y light excitation. The specks could be due to small traces of oxygen molecules in the chamber that cause incomplete pure laser destruction. As shown in the elemental map depicted in Figure 7g–k, C, O, Si, Ca, and Zn atoms are absent inside the focused laser-patterned region but distributed evenly outside the patterning square.

Interestingly, the zinc (Zn) atoms are only detected approximately \( \approx 30 \mu m \) away from the edge of the focused laser-patterned region (highlighted by the white arrow in Figure 7k). This region corresponds to the darkened area surrounding the laser pattern region highlighted by the dotted white line in Figure 7b–e. The darkened region is likely to result from the focused laser beam’s Gaussian profile. The region beyond the focal point is also affected by the intense heat of the focused laser beam. The absence of all impurities at the focused laser-patterned region agrees with the observed nonfluorescent focused laser-patterned square, indicating oxygen plays an important role in producing PL during the focused laser treatment. The PL peak for the focused laser treatment in a vacuum is being fitted into four peaks that are \( \approx 591 \text{ nm (2.10 eV)}, \approx 756 \text{ nm (1.64 eV)}, \approx 917 \text{ nm (1.35 eV)}, \) and \( \approx 980 \text{ nm (1.27 eV)}, \) as shown in Figure 7n. Compared to the PL spectrum obtained from the sample treated in ambient condition, a missing \( \approx 390 \text{ nm peak (attributed to the presence of ZnO)} \), highlighted by the purple box in Figure 7m,n suggests that the presence of oxygen flow in ambient during focused laser treatment is important for forming metal oxides.

2.5.2. Laser Patterning Environment-Dependent—Helium

With focused laser treatment of red laser with 7 mW power and laser patterning speed of 12 \( \mu m \text{s}^{-1} \) applied in helium (\( \approx 12 \text{Torr} \)) environment, the laser-patterned patterns are studied and compared. Like the results of the focused laser-engineered square in a vacuum, a lighter shade of rainbow was observed to be emitted around the patterned region under BF light excitation (Figure 8a). Meanwhile, pale yellow, yellow, and red PL were detected at the rainbow graduate under UV, B, G, and Y light excitation, respectively (Figure 8b–e). Unlike the patterned square in a vacuum, no dots of blue fluorescence are observed from the patterned square in helium under UV light excitation. The corresponding SEM image is shown in Figure 8f. From the elemental map, a lesser proportion of carbon (C), oxygen (O), silicon (Si), calcium (Ca), and zinc (Zn) atoms are detected within the focused laser patterned region. At the same time, a majority of these elements are distributed more evenly outside the engineered square (Figure 8g–k). Intriguingly, the C atoms were observed to accumulate at the edge of the patterned square (Figure 8g). Similar to that observed when patterned in a vacuum environment, more Zn atoms were detected to be spreading from \( \approx 20 \mu m \) outside the patterned square (white arrow in Figure 8k). The PL peak for the focused laser treatment in helium is being fitted into four peaks which are \( \approx 423 \text{ nm (2.93 eV)}, \approx 595 \text{ nm (2.09 eV)}, \approx 765 \text{ nm (1.62 eV)}, \) and \( \approx 894 \text{ nm (1.39 eV)}, \) While the PL peak at \( \approx 390 \text{ nm peak (ascribed to the presence of ZnO)} \), highlighted by the purple box in Figure 8m,n is absent for this sample treated in a helium environment, a small peak at \( \approx 423 \text{ nm}, \) which can be attributed to the transition from zinc interstitial (Zn) in the ZnO nanoparticle to the valence band suggests that ZnO is still present in this sample.

By tuning the focused laser power from 3 to 19 mW and setting the focused laser patterning speed at 12 \( \mu m \text{s}^{-1} \), it was detected that the gradient of rainbow color becomes bigger and more visible when the focused laser power is increased under BF light excitation (Figure 9a). Likewise, the PL of the color gradient region outside the focused laser-pattern square becomes brighter, with a bigger black region observed outside the patterned square. From Figure 9b,c, PL spectrum from sample pattern using 5 mW laser power shows strongest PL intensity. The phenomenon can be attributed to the incomplete chemical transformation of the surface allotrope of the CB powder due to...

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**Figure 6.** a) PL spectra of the pristine CB and CB samples after laser modification with the sample in ambient, vacuum, and helium environments. b–d) FM images of the micro-box under UV light excitation.
insufficient heating from the low laser power. The outcome matches the EDX earlier results, which indicates the minimal presence of the impurities within the laser pattern region. From the collected Raman spectra (Figure 9d), it is found that there are four peaks that are the D ($\approx 1332 \text{ cm}^{-1}$), G ($\approx 1597 \text{ cm}^{-1}$), 2D ($\approx 2647 \text{ cm}^{-1}$), and D + G ($\approx 2915 \text{ cm}^{-1}$) peaks. The $I_D/I_G$ ratio calculated and shown in Figure 9e highlight that higher focused laser power could change the surface allotrope of the CB sample as more defects are induced into the system at higher annealing temperature contributed by an increase in the laser power.

2.5.3. Laser Patterning Environment-Dependent—Raman and Lifetime PL Analyses

Laser-induced defects in carbon systems can readily be detected using Raman spectroscopy. A 633 nm laser is used to obtain the Raman spectrum from as-received samples and samples treated under ambient, vacuum, and helium (Figure 10a–h). Raman spectra from these samples are separated into two regions of interest. Namely, 130–450 cm$^{-1}$ (Figure 10a–d) and 1250–1650 cm$^{-1}$ (Figure 10e–h).

At lower wavenumbers, samples treated under ambient and helium exhibit multiple Raman peaks (Figure 10a,c). However, none was detected from samples treated in vacuum and as-received (Figure 10b,d). The multiple peaks from sample treated in ambient condition correspond to sulfur ($148 \text{ cm}^{-1}$), radial breathing mode of carbon element ($199, 243, \text{ and } 298 \text{ cm}^{-1}$), $[9]$ E$_{2g}$(TO) mode of ZnO ($408 \text{ cm}^{-1}$).[10] Compared to samples treated in a helium environment, samples treated in ambient show stronger intensity with narrow FWHM at 13.7 cm$^{-1}$ for the peak at 148 cm$^{-1}$. The result agrees with sulfur’s role in contributing to the fluorescence detected from the ambient treated sample, as suggested by Lim et al.[6] Some shifts in the multiple peaks from samples treated under helium...
environment compared to that under ambient condition are also detected and likely to be attributed to variations in bond formations given the vast number of defects present in both systems.

At higher wavenumbers (Figure 10e–h), typical carbon-related defective and graphitic bonds situated at \(\approx 1300\) and \(\approx 1580\) cm\(^{-1}\) are identified from all four different types of samples.\(^{[11]}\) While the wavenumber of the graphitic band remains consistent among the samples, defect-related band shows a significant shift of \(24–25\) cm\(^{-1}\) toward the lower wavenumber from samples treated in vacuum and helium (Figure 10f–g), while the sample treated in ambient shows an opposite shift toward a higher wavenumber (Figure 10e), compared to as-received sample (Figure 10h). Recent work by Schuepfer et al.\(^{[12]}\) suggests that a reduction in the crystallite size contributes to such shift toward lower wavenumbers due to phonon confinement where a mixture of phonons with different frequencies are restricted within a confined state.\(^{[13]}\) It was also reported that as the crystallinity of the carbon structure reduces beyond a certain limit, the wavenumber exhibits an opposite shift toward a higher wavenumber. Considering that the Raman spectra (Figure 10e–h) exhibit a similar trend, it is likely that laser-initiated bond-breaking, which occurs more readily in ambient conditions, constitutes the formation of smaller defect rich carbon-doped nanoparticles. At the same time, it is also important to take note that the position of the defect-related Raman peak is also dependent on strain experienced by the crystal structures.\(^{[14]}\) This phenomenon could also be introduced into our system due to defects.

Of these samples, the sample treated in ambient shows the highest \(I_D/I_G\) ratio of 1.81, followed by 1.16 from the sample treated in helium and 0.77 from the sample treated in a vacuum. With the most intense fluorescence detected from samples treated in ambient, the above results further support the

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**Figure 8.** a–e) FM images of region patterned using 7 mW laser at 12 μm/s in helium under a) BF, b) UV, c) B, d) G, and e) Y excitation. f) Corresponding SEM image. g–k) Elemental map of g) C, h) O, i) Si, j) Ca, and k) Zn. l) EDX spectrum of the studied region. m,n) Multipeak fit of PL spectrum from focused laser-patterned CB in m) ambient and n) helium.
hypothesis mentioned above that laser-induced defects contributed to the formation of these fluorescence species. It is also worth noting that two new peaks situated at 1290 and 1484 cm$^{-1}$ are unique to the sample treated in ambient condition and are attributed to the presence of more C-H bending within the laser-treated region. While XPS results presented in Figure 11 highlight the presence of C–C/C–H bond from the C1s scan of all samples, the lack of significant C–H bending in the other samples could be why these two peaks are not present in the Raman spectra of the other samples.

Lifetime PL spectra of the sample treated in ambient, vacuum, and helium environment are obtained under a 350 nm monochromatic excitation laser source. Combined plots of lifetime PL from the three samples (Figure 10i) depict that the sample treated in ambient has the longest lifetime, followed by the sample treated in helium and, lastly, the sample treated in a vacuum. The biexponential decay curve fit is applied to the three graphs and is presented separately in Figure 10j–l. The fast decay constant is associated with a nonradiative, defect-related re-combinatory process in such a decay process. In contrast, the slower decay constant is attributed to the radiative lifetime of the free excitons. Fitted results show that the average lifetime of the sample treated in ambient has longer nonradiative decay than samples treated in helium and ambient conditions. The outcome is indicative of the presence of more defects, which could have served as mid-gap states where electrons can de-excite without experiencing any re-combinatory effect before undergoing recombination upon de-excitation to the ground state. The result agrees with the findings from the Raman spectroscopy that more defects are present in samples treated in ambient and helium compared to those treated in vacuum.

2.5.4. Laser Patterning Environment-Dependent—XPS Analysis

X-Ray photoemission spectroscopy (XPS) obtained from as-received and laser-treated CB samples, using similar laser power and pattern speed, in ambient, vacuum, and helium conditions is shown in Figure 11. With both axes range for each elemental scan kept constant across all samples, it can be observed that among the four samples tested, the sample treated in ambient contains the highest proportion of ZnO while samples treated in helium uniquely host Ca$^{2+}$ and have a high content of SiO$_2$ with lesser ZnO present.

Compared to the as-received sample, C1s scan of the sample treated in ambient and vacuum condition exhibits a shift toward lower binding energy for C=O/O─C─O and C─O bonds. The shift is likely to be contributed by the presence of less electronegative Zn (1.65) and Si (1.9) in the presence of C atoms that has higher electron negativity of 2.6. For all four samples, no shift is detected for the peak associated with C─C/C─H bonds. In comparison, these peaks shifted toward higher binding energy for the sample treated in helium condition.

The shift, in this case, could be due to the presence of more oxidation processes taking place, as depicted by the stronger O-Zn/O-Si signal detected for O1s scans, even though Ca$^{2+}$, which has a lower electronegativity than carbon, is present in the system. The effect from the oxidation process is likely to be more significant than that contributed by a change in the chemical environment from the newly identified Ca$^{2+}$, which is of low concentration. The XPS results thus underscored the influence that C, ZnO, SiO$_2$, and Ca have on the observed fluorescence from the laser-treated samples.
2.5.5. Laser Patterning Environment-Dependent—TEM Analysis

Transmission electron microscopy (TEM) images obtained from the fluorescent part of the focused laser-treated CB samples (using similar laser power) in ambient, vacuum, and helium are shown in Figure 12a–g, h,i, and j,k, respectively. The TEM image (Figure 12b) shows the formation of nanoparticles with a size $\approx 8$ nm from the laser-treated CB sample in ambient. Figure 12c shows SAED obtained from the region is presented in Figure 12a. The observation of diffraction spots in a ring formation suggested that the laser-treated CB has a polycrystalline structure and is further supported by multiple regions with different lattice spacings, as depicted in Figure 12d–g. HRTEM (high-resolution TEM) images obtained shows crystal with the lattice of 4.358 Å corresponding to orthorhombic (110) silicon dioxide (SiO$_2$) crystal plane (JCPDS #50-1423). The lattices spacing 3.022, 2.464, and 2.463 Å correspond to orthorhombic (300) and (141) zinc silicate (Zn$_2$SiO$_4$) crystal plane (JCPDS #40-0007, #24-1469). The other lattices 2.778, 2.830, and 2.153 Å agree with hexagonal (006) fullerene (C$_{60}$) crystal plane (JCPDS #47-0787) and monoclinic (313) and orthorhombic (130) crystal planes of fullerite (C$_{60}$, JCPDS #49-1719, #49-1718). Lastly, lattices spacing of 2.690 Å agrees with zinc oxide’s hexagonal (002) crystal plane (ZnO, JCPDS #36-145).

Interestingly, while most areas investigated reveals no clear lattice from CB samples treated in vacuum (Figure 12h), a small region with some relatively clear lattice is detected (Figure 12i), and the 3.269 Å lattice spacing matches to the orthorhombic (109) zinc silicate (Zn$_2$SiO$_4$) crystal plane (JCPDS #14-0653). Very disrupted lattices formations are observed from samples treated in a helium environment (Figure 12j–k). Attempts are made to identify these short lattices with a spacing of 4.231 and 4.338 Å. These agree with the monoclinic (102) and (−102) crystal plane of fullerite (C$_{60}$, JCPDS #49-1719).

A possible explanation for the drastic difference in crystal lattice formation for samples treated in ambient versus those in vacuum and helium environment could be as follows: in a vacuum, heat dissipation is likely to be limited to radiative process, the more heat is likely absorbed by the CB sample, causing greater destruction to the crystallinity of the material, thus transforming it into amorphous states with minimal crystallite formations. In the case of laser treatment in a helium environment, which dissipates heat more readily than air, heat absorbed by the sample might be insufficient to complete any
transformation, resulting in the disintegrated formed of carbon structure observed (Figure 12j–k). Furthermore, the results from HRTEM analysis are in agreement with the results from XPS scans—the binding energy of Zn2p3 (≈1022 eV) and Si2p (≈103 eV) suggested that the chemical nature of Zn and Si is likely to be Zn2+ and Si4+, thus making it possible for the formation of Zn2SiO4 molecules to take place as the system undergoes bond breaking and re-formation during the laser patterning and quenching process.

2.6. Mechanism

Upon the irradiation of the focused laser beam, the CB sample absorbs the light energy and turns this rapidly into heat energy. The earlier claim is supported by work from Lim et al., who reported that laser-treated CNTs could emit blackbody radiation of ≈2400 K. With oxygen and other elements such as Zn, Ca, and Si in the sample, rapid oxidation follows and results in oxide formation. Moreover, with a plentiful supply of carbon, the carbon atoms can be readily incorporated into the oxide species, creating a rich variety of defective species into the oxide compound. And when the laser beam moves away, these defects do not have time to reach a more stabilized state as the rapid cooling results in quenched states in the sample. These defects, quenched states provide the platform for fluorescence emission. Proposed mechanisms for the observed fluorescence from the laser-treated CB samples are listed later. These reference the PL spectra presented in Figure 7m,n and 8n.

Upon irradiation, PL peak at 390 nm (3.18 eV) from the sample treated in ambient is attributed to recombination of exciton peaks from the presence of ZnO. While PL peak at 423 nm (2.93 eV) from sample treated in helium condition is associated to transition from zinc interstitial (Zni) to the valence band. Though not identified in HRTEM, the presence of ZnO from samples treated in helium environment is readily found through XPS Zn2p and O1s scans. PL peaks identified from samples treated in ambient, vacuum, and helium environment exhibit emissions within the range of 601–781 nm (2.06–1.59 eV). These emissions are attributed to the formation of C60 fullerene and fullerites, which has a substantial presence in all three types of the sample as mentioned in the earlier TEM and XPS results.

The calculated fundamental bandgap of Zn2SiO4 molecules takes the values of 2.22, 2.83, and 2.78 eV, while that of the second gap has values of 2.45, 1.44, and 2.11 eV, depending on the polymorphs formed. Some of these values are in good agreement with the energy gap predicted from the PL spectra.
shown in Figure 7m,n and 8n. In particular, PL peaks obtained from the three types of samples treated separately in ambient, vacuum, and helium, which are located at 555 nm (2.23 eV), 591 nm (2.10 eV), 595 nm (2.09 eV), 8.91 nm (1.39 eV), 8.96 nm (1.38 eV), and 917 nm (1.35 eV). Given that the HRTEM identified more lattices due to the formation of orthorhombic zinc silicate, the quenched system’s complexity means that the formation of other polymorphs is also possible. Furthermore, although we cannot identify any Zn$_2$SiO$_4$-related lattices through HRTEM analysis of CB samples treated in helium, which is a drawback from the small sample size of the HRTEM analysis, XPS scans that show the presence of Zn$^{2+}$ and Si$^{4+}$ highlight the possibility of the formation of these molecules from the laser treatment process.

It is important to note that while we can identify the majority of the contributors leading to the observed PL, the complex nature of such a quenched material system requires more vigorous computational analysis to sieve out some of the more complex outcomes of other contributing factors such as carbon doping of the molecules during the quenching phase of the formation process. At the present phase, it is suggested that such a carbon-doping effect effortlessly contributed to the formations of mid-gap states, resulting in a slight shift in the experimental values from the theoretical calculation listed earlier. An illustration of the energy levels with carbon-doped mid-gap states is shown in Figure 12l.

Similarly, HRTEM did not pick up any Ca-related lattice formation due to the small sample size. However, XPS scans, which collected signals from a much larger area, identified Ca$^{2+}$ from samples treated in a helium environment. Though in a modest amount, these Ca atoms can contribute as defects in ZnO, producing the fluorescence emission of $\approx$1.63 eV due to the presence of different complex defects such as exciton levels (E*), oxygen vacancies which have varying ionization levels (V$_{O}^{*}$ and V$_{O}^{*\ast}$), zinc vacancies (V$_{Zn}$), and oxygen interstitials (I$_O$) could effectively contribute to additional de-excitation pathways at the patterned laser region. In this case, the donor–acceptor transition band of V$_{O}^{\ast}$–V$_{Zn}$ is likely responsible for the emission.$^{[25]}$

In short, the observed fluorescence from laser-treated CB in three different controlled environments is attributed to the formation of the following elements: 1) C60 fullerene and fullerites; 2) ZnO; 3) Zn$_2$SiO$_4$; 4) carbon-induced mid-gap states in Zn$_2$SiO$_4$; and 5) Ca-induced defects in ZnO.

Figure 12. HRTEM images of the focused laser-patterned CB in a–g) ambient with inset showing b) TEM c) diffraction image of the region presented in (a). HRTEM of sample patterned using the laser in h,j) vacuum and j,k) helium. l) Proposed mechanism: possible effect of carbon-doped mid-gap states.
Taking advantage of the insight gained into the fluorescence properties of the laser-modified CB and the engineering control we can employ during the process, we demonstrate that we can create a multicolor micro-display using a combination of laser micropatterning and environmental control. As an illustration, we use the scanning focused laser beam to create the “GCB” micropattern onto the sample. Figure 13 show the bright field, dark field, and fluorescence microscope images of the micropattern created. First, we create the background by laser treatment on the designed word in a helium environment. Then, the same laser treatment is carried out in ambient to create the designed words with different light emissions.

3. Conclusion

In conclusion, the focused laser power and duration of focused laser treatment with CB powder can result in the diverse intensity of PL spectrum due to different depths of focused laser penetration, suggesting the different formation of the allotrope structures. 7 and 10 mW are observed to be the most optimum focused laser power to produce an intense PL spectrum for the focused laser treatment with CB powder in the ambient environment. However, higher focused laser power is preferred for more obvious results for the patterning under vacuum and helium. The luminescent mechanism is proposed to originate from the formation of 1) C60 fullerene and fullerites; 2) ZnO; 3) Zn2SiO4, and more complex hybrid such as 4) carbon-induced mid-gap states in Zn2SiO4, and 5) Ca-induced defects in ZnO. With precise control over the site selectivity of the laser patterning process, coupled with a mixture of different environments, a multicolor micro-display made out of the economical CB is achieved.

4. Experimental Section

**Preparation of Compact CB Powder on Si Substrate:** Powdered graphitized CB (Hi-Green SH665) was purchased from [Hi-Green]. Silicon wafer (1 cm × 1 cm) was cut with a diamond cutter. Then, a 5 mm × 5 mm size double-sided vacuum tape was placed on the silicon wafer. Powdered graphitized CB was layered on the tape. After that, a piece of the clean glass slide was used to press down the CB powder until a compact slab of CB was formed on the Si substrate before the glass slide was removed. Lastly, a blower was used to remove any excess CB powder.[6]

**Lifetime PL Spectra:** These were obtained using an integrated system of microscopy and fs pulsed laser. The excitation source was a mode-locked Ti: sapphire laser (Chameleon Ultra II, Coherent) with a repetition rate of 80 MHz, pulse duration of 100 fs. The output of 700 nm was employed to generate the double frequency 350 nm, then used as excitation wavelength. In an inverted microscope (Nikon Eclipse Ti), the laser beam was focused on samples by a 10× objective lens (NA = 0.3) with a focus radius of 5–1 μm. The emission signals from the samples were collected by the same objective lens and passed via a bundled optical fiber to a monochromator (Acton, Spectra Pro 2300i) coupled with a CCD (Princeton Instruments, Pixis 100B). Time-resolved PL measurements were detected using Time-Correlated Single Photon Counting (TCSPC) system (HydraHarp 400) integrated with the same monochromator (Acton, Spectra Pro 2300i).

**XPS:** X-Ray photoelectron spectroscopy (XPS) analysis uses Thermo Fisher Scientific Theta Probe XPS with monochromatic Al Ka X-Ray (1486.7 eV). Charge correction for binding energy was based on C1s from adventitious carbon at 285.0 eV.

**Further Characterization:** Fluorescence microscope (FM, Olympus BX51 Microscope) with filter cubes U-MWU2 (330–390 nm) for ultraviolet (UV) excitation, U-MWB2 (450–500 nm) for blue (B) excitation, U-MWG2 (500–560 nm) for green excitation, and U-MWIY2 (530–580 nm) for yellow (Y) excitation. The microscope can be utilized in imaging mode or spectroscopic mode to capture the emitted fluorescence spectra. Surface imaging using scanning electron microscope (SEM, JEOL JSM6700-F), energy dispersive spectroscopy (EDX, Oxford Instruments X-Max® 150 EDX detector), transmission electron microscope (TEM, JEOL JEM 2010F), Raman spectroscopy (Raman, Renishaw inVia...
Qontor) with 633 nm and 532 nm excitation, and PL spectroscopy (PL, Renishaw inVia Qontor) with 325 nm excitation.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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