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Cover Page Footnote

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Optical Properties of Toluene-soluble Carbon Dots Prepared from Laser-ablated Coconut Fiber

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Abstract

In this study, we used laser ablation to fabricate toluene-soluble carbon nanoparticles from coconut fiber. In response to excitations at various wavelengths, the fabricated carbon nanoparticles exhibit three distinctive emission peaks at wavelengths of 300 nm, 440 nm, and 540 nm. These three emission peaks correspond to the π orbital state, σ orbital state, and surface state, respectively. Photoluminescence excitation measurements indicate a high probability of energy transfer between the surface state and σ orbital state, whereas the π orbital state is likely independent of the other states. The results of time-resolved photoluminescence measurements indicate that electrons are likely to remain longer in higher-energy states. Given that the carbon dots fabricated in this study were made from natural resources, these findings may find application in photonic devices that feature tunable emissions.

Keywords: carbon dot, molecular states, surface states, photoluminescence

Introduction

Over the last decade, carbon-based nanoparticles have attracted a great deal of attention because of their strong optical and electrical properties. Carbon-based nanoparticles can be applied in many optical devices, including solar cells and light-emitting diodes. Carbon-based nanoparticles also have excellent electrical properties that can be used in applications such as photocatalysis, luminescent devices, chemical sensing, biosensors, bioimaging, and drug delivery [1,2]. Several types of carbon-based nanoparticles have been studied, including fullerene, carbon nanotubes, carbon nanowires, graphene dots, and carbon dots [2,3], each of which has unique optical and electrical properties. In some cases, carbon-based nanoparticles are luminescent, and the most common emission color is cyan or bluish green [2]. In several studies, researchers have found that carbon-based nanoparticles of different sizes emit light in the range from blue to red [1,4]. Furthermore, the functional surface of carbon-based nanoparticles significantly affects the color of their emissions. Various fabrication techniques are used to synthesize carbon-based nanoparticles, including bottom-up and top-down processes [1,2], as well as hydrothermal action, metal-graphite intercalation, arc discharge, nanolithography, and laser ablation [1-9].

In this work, we focus on spherical-shaped carbon-based nanoparticles known as carbon dots. Unlike other types of carbon-based nanoparticles, carbon dots have a solid carbon structure. Carbon dots are used mainly in optical devices and those less than 10 nm in size are fluorescent [1-3]. However, the mechanism underlying the fluorescence of carbon dots has yet to be understood since many factors affect their emission properties. One factor in the origin of their fluorescence is the presence of specific functional groups on the surface of carbon-dot nanoparticles. Thus far, no researchers have put forth a valid argument regarding the origin of fluorescence that can be generalized to all types of carbon-dot nanoparticles. Carbon dots are usually synthesized using chemical processes that require high-purity chemical precursors, which must be very pure to guarantee that the fabricated carbon dots will have the desired structural properties. Since carbon is the most abundant element in all natural products, the synthesis of carbon dots from natural resources could be very cost- and resource-efficient. Few researchers have attempted to fabricate carbon dots from natural resources. In this work, we aimed to (1) synthesize carbon dots from coconut fiber using laser ablation rather than ultra-pure chemicals and (2) optically characterize fabricated carbon dots to better understand the mechanism underlying their fluorescence.

Experiment

The carbon used in this work was derived from coconut fiber. Figure 1 shows a schematic of the experimental procedure used to obtain carbon dots. First, dried coconut fiber is dried in an oven to remove all water from the material. Then, the dried coconut fiber is manually ground into a powder using a mortar and pestle. Further grinding is performed by ball milling after another baking step to remove any remaining water content at temperatures up to 1300 °C. The resulting carbon powder is then ready to be ablated with a laser in a toluene solvent.

The laser ablation process used to obtain carbon dots is performed by dissolving carbon powder in toluene solvent at a concentration of 0.02 mg/mL. Then, a pulsed Nd:YAG laser is directed at a glass vial containing the solution of toluene and carbon powder at a repetition rate of 10 Hz, a wavelength of 1064 nm, and an energy level of 60 mJ. This ablation process is continued for 1 hour. Then, using a centrifuge, the resulting carbon dots are separated from the remaining carbon powder and the carbon-dot samples are ready for characterization.

We obtained three types of optical measurements—photoluminescence, photoluminescence excitation, and time-resolved photoluminescence—to study the origin of luminescence and the electron dynamics of the carbon dots. Photoluminescence was the basic luminescence measurement obtained to briefly observe

the luminescence range of carbon dots. Photoluminescence excitation was performed to verify the main absorbance energy, which indicated the origin of the luminescence of the three emission wavelengths, as described in the next section. Finally, we measured the time-resolved photoluminescence to verify the energy levels of the emissions and determine the defect levels.

We recorded the emission spectra using a photoluminescence system, in which a broad light source from a xenon-halogen lamp is filtered and a monochromator obtains the specific excitation wavelength. This filtered light source is directed at the toluene-carbon-dot solution held in a quartz cuvette. Emissions from the carbon dots were collected using two plano-convex lenses focused onto the fiber input of a spectrometer. We tuned the excitation wavelength from 250 nm to 550 nm at 1-nm intervals. We also performed photoluminescence excitation tests to determine how the excitation wavelength influences the specific emission-peak wavelength.

To obtain the excitonic-decay lifetime of the carbon dots, we used a standard streak camera (Hamamatsu) in combination with a femtosecond laser excitation source that could output several excitation wavelengths. Due to the limited range of our femtosecond laser, 250-nm wavelength excitation was not available for this experiment. However, we recorded the time-resolved photoluminescence at excitation wavelengths of 355 nm, 400 nm, and 440 nm.

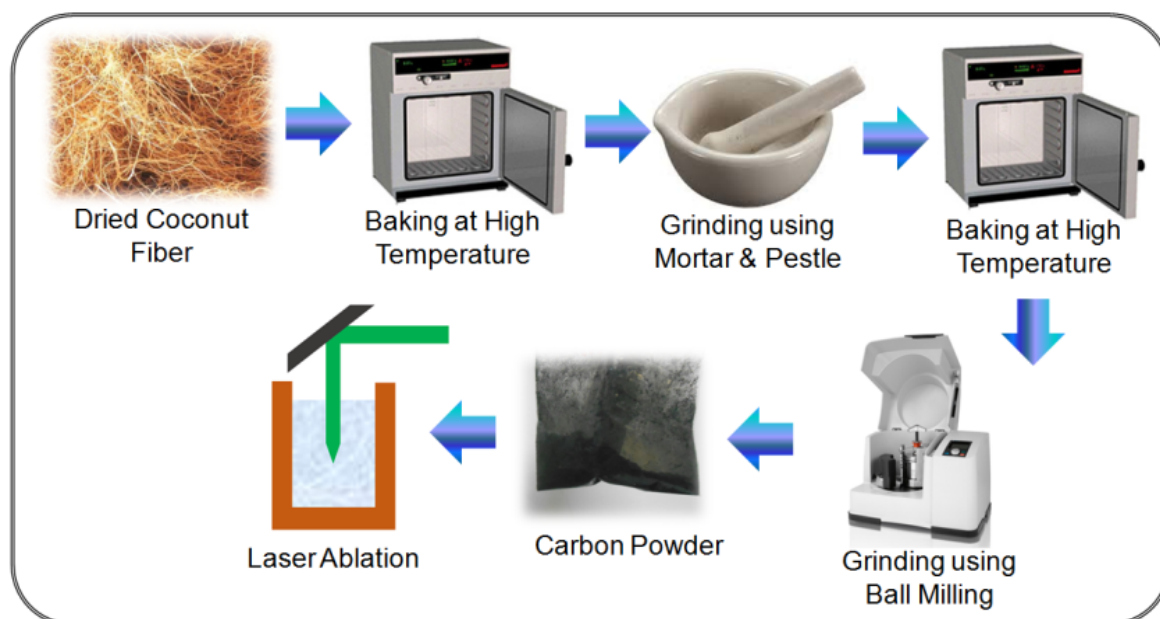


Figure 1. Schematic of Procedure for Synthesizing Carbon Dots from Coconut Fiber

Results and Discussion

After went through sample preparation process, we found the synthesized carbon dots to have good solubility in toluene. No carbon agglomerations or depositions were observed even after several months, which indicate that fabricated carbon dots have excellent solubility in toluene solvent. For comparison, Figure 2 shows photographs of the toluene solution that contain carbon powder (before laser ablation) and that containing carbon dots (after ablation). In this image, the samples are illuminated by a blue laser pointer (wavelength 405 nm) in ambient conditions. We can see that a clear cyan color is emitted from the carbon-dot sample, which indicates that the carbon nanoparticles are very small and can be thought of as carbon dots. The emission of cyan is an early indicator that carbon dots less than 10 nm in size have been synthesized [2, 3]. The estimated sizes of these cyan-emitting carbon dots are 2 nm to 5 nm. The cyan emission from this carbon-dot sample is not very strong, likely because its carbon-dot concentration is quite low.

Next, we investigated the emission spectra of carbon dots excited at different wavelengths, and the results are shown in Figure 3. The excitation wavelengths were 260 nm, 340 nm, 400 nm, and 440 nm. When the carbon-dot solution is excited by 260-nm light, the main emission peak is around 300 nm, and a small peak appears at around 500 nm (green color emission). When the carbon-dot solution is excited by 340-nm light, an emission spectrum around 440 nm is clear. Moreover, the emission peak shifts smoothly when the carbon dot is excited using 440-nm light. A clear emission spectrum also appears under excitation at 540 nm. The emission spectra differ clearly when the carbon dots are excited using 340-nm or 440-nm light. These two spectra are apparently unrelated to one another. One indication of the independence of these two spectra appears when the carbon dots are excited by a 400-nm excitation wavelength. The two spectra are distinctly superimposed (the red curve in Figure 3), and this curve is clearly a superposition of the two individual spectra mentioned earlier. Therefore, we expected three separate emission peaks to be generated by our carbon-dot sample. To confirm these findings, we measured the excitation-wavelength photoluminescence of the carbon-dot sample in response to excitation wavelengths from 250 nm to 550 nm, which varied at 1-nm intervals. Figure 4 shows the results.

These results clearly show the origin of the carbon-dot emissions. We can identify at least three peaks (A, B, C in Figure 4) at which emissions are generated by the carbon dots. The emission peak D in Figure 4 may also have contributed to the emissions, but we believe that peak D is the same as emission peak C and arose in response to excitation by short wavelengths. This finding

indicates that emission peaks A and C are somehow related, which means that energy may be transferred between energy levels that correspond to A and C. Emission peak B is rather narrow, so no energy seems to be transferred between the energy levels corresponding to peaks B and C. We also note the sharp lines occurring at T2 (between energy peaks B and C) and T1 (between energy peaks A and B), which indicate a sudden energy transition between the corresponding energy peaks.

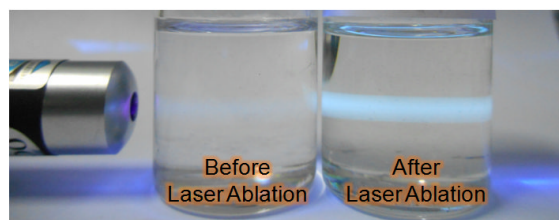


Figure 2. Photograph of Emission Luminescence from Carbon-solution Samples Before and After Laser Ablation

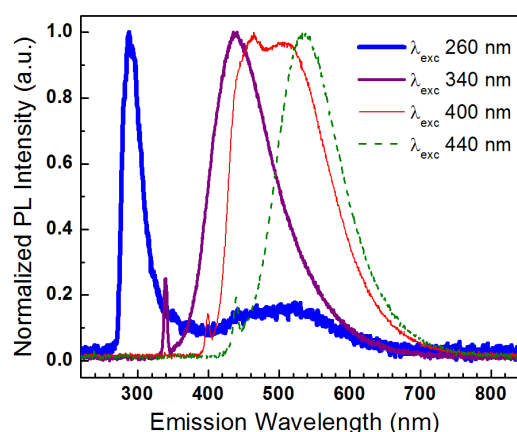


Figure 3. Carbon-dot Emission Spectra when Subjected to Four Different Excitation Wavelengths

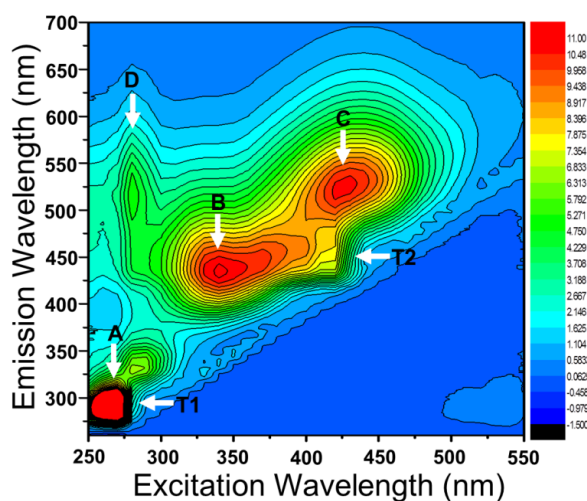


Figure 4. Dependence of Carbon-dot Photoluminescence on Excitation Wavelength. Red Color Indicates Strong Emission Intensity

Next, we confirmed the correlations between emission peaks (A, B, and C) in another photoluminescence excitation experiment, the results of which are shown in Figure 5. When we set the emission wavelength to 300 nm (blue curve in Figure 5), we found the main contributions to that emission to be excitation wavelengths ranging from 260 nm to 275 nm. The main contribution to emission at the 440-nm wavelength is the excitation wavelength at around 340 nm (the purple solid line in Figure 5). The 260-nm excitation wavelength did not contribute to the 440-nm emission, which indicates that the emissions at 440 nm (emission peak B in Figure 4) and 300 nm (emission peak A in Figure 4) are independent. Furthermore, we found the emissions at 540 nm (emission peak C in Figure 4) to be strongly related to the excitations at 260 nm and 440 nm, but this emission wavelength was not affected by excitation at 340 nm. Thus, we conclude that the emissions at 300 nm and 540 nm are strongly related, which means that energy transfer occurs between the levels corresponding to the peaks at 300 nm (emission peak A in Figure 4) and 540 nm (emission peak C in Figure 4). We also determined that the emission peaks at 440 nm and 540 nm were not related.

Based on the results of the photoluminescence and photoluminescence excitation tests, we expect that the energy levels of the carbon dots can be diagrammed as shown in Figure 6. In this energy diagram, we applied a simplification in which the *highest occupied molecular orbital (HOMO)* energy levels are equal to all the lowest unoccupied molecular orbital (LUMO) energy levels [10,11]. We assumed three LUMO energy levels at 2.4 eV, 2.75 eV, and 4.25 eV, which correspond to energy peaks C, B, and A (in Figure 4), respectively. The first energy level is assumed to be the surface-state energy level, and the upper two energy levels to be the molecular states, i.e., the π^* - π and σ^* - σ orbital energy levels. Although the surface-state energy level is close to the π orbital energy level, no energy is transferred between them. We found no evidence for any energy level below the surface-state energy level. The σ orbital energy level was the highest energy detected in this study. Due to the technical limitations of the equipment available for use in this study, we were unable to observe any higher-energy level.

In addition, we observed the exciton-decay lifetimes of the carbon dots at various excitation and emission wavelengths (Figure 7). We calculated the exciton-decay lifetimes of carbon dots excited by 355 nm light ($\lambda_{\text{emission}}$ 380–600 nm) and by 440 nm light ($\lambda_{\text{emission}}$ 450–650 nm) to be 7.294 ns and 4.318 ns, respectively. The instrument response function of these tests was only 0.459 ns, which means that electrons tend to stay longer in the π orbital energy level than in the surface state. The surface state of these carbon dots behaves like a defect state, so the electrons remain in this state for a longer

period of time and tend to quickly recombine with the holes in the HOMO energy level. Additionally, we measured the time-resolved photoluminescence at the emission and excitation wavelengths at the boundary transition between the π orbital state and the surface state (Figure 8). In the photoluminescence spectrum (Figure 8.a), we can divide the emission spectra into

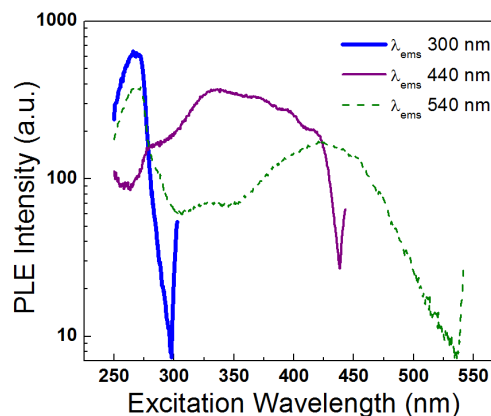


Figure 5. Photoluminescence Excitation Spectra of Carbon Dots at Three Different Emission Wavelengths

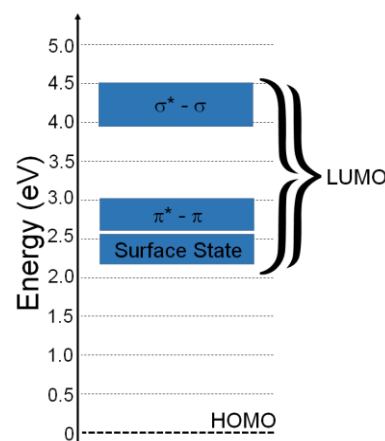


Figure 6. Predicted Energy Diagram of Carbon Dots

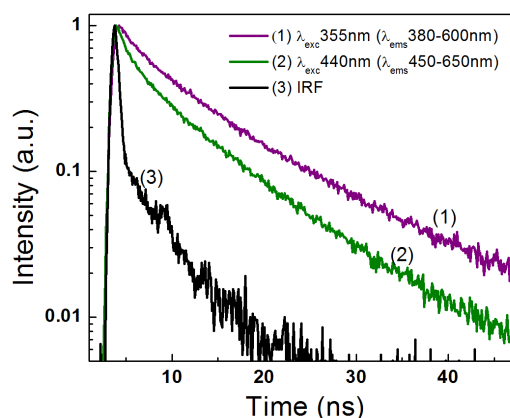


Figure 7. Time-resolved Photoluminescence of Carbon dots

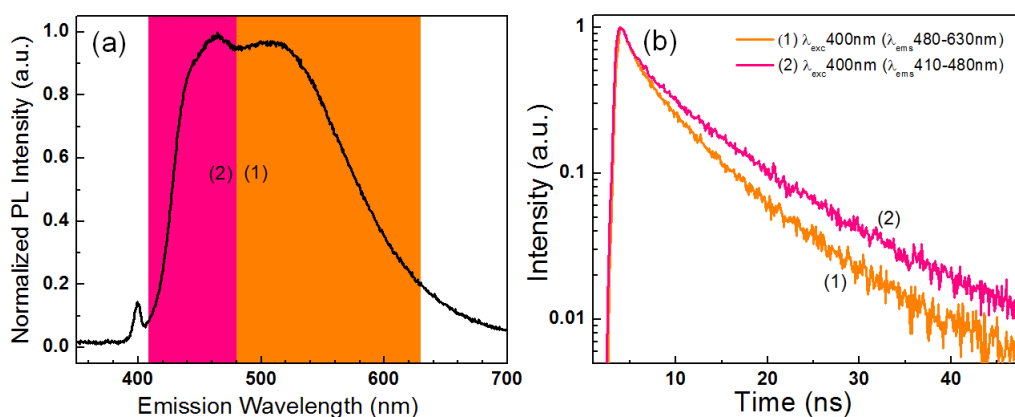


Figure 8. Photoluminescence of Carbon dots at Excitation-wavelength Transition (a) and Time-resolved Photoluminescence (b)

two regions, i.e., (1) emission wavelengths from 480 nm–630 nm and (2) emission wavelengths from 410 nm–480 nm. Figure 8.b shows the corresponding time-resolved photoluminescence curves. We calculated the decay lifetimes for region (1) and region (2) to be 5.654 ns and 6.357 ns, respectively. These results agree with those shown in Figure 7.

The three emission peaks observed for our carbon-dot sample show potential for application in bioimaging and photonic devices. By adjusting the excitation energy, the emission wavelength can be tuned for specific applications. Further tests will be needed to ensure the readiness of this carbon-dot material for application in photonic devices.

Conclusion

In this study, we successfully synthesized toluene-soluble carbon-dot nanoparticles from coconut fiber using laser ablation. When excited by a blue laser, the fabricated carbon dots emit cyan light. Furthermore, when excited by energy at different wavelengths, the carbon-dot material emits three different colors with wavelengths of 300 nm, 440 nm, and 540 nm. These emission colors correspond to the σ orbital state, the π orbital state, and the surface state, respectively. It is very likely that energy is transferred between the σ orbital state and the surface state. We found no correlation between the π orbital state and the surface state. Additionally, we observed that the electron decay time is longer in the higher-energy state than in the lower-energy state. The decay time in the surface state is very brief.

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