Space-Selective Fabrication of Light-Emitting Carbon Dots in Polymer Films Using Electron-Beam-Induced Chemical Reactions

Yoshio Kamura and Kohei Imura*

Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo 169-8555, Japan

ABSTRACT: Nanocarbon-based materials have excellent properties, including high electrical conductivity as well as charity-dependent optical absorption and luminescence; therefore, the materials are promising in applications for nanoelectric devices, nanophotonics, and so on. Carbon dots (CDs) are one of the carbon materials recently fabricated. Optical properties of CDs have been reported to be similar to those of polycyclic aromatic hydrocarbons (PAHs). For this reason, the CDs are considered to be composed of PAH. Synthesis of CDs has previously been accomplished through hydrothermal synthesis and microwave irradiation. These methods require a long synthesis time, and the processes involve multiple steps. In this study, we developed a fabrication method of CDs in simple and spatially selective ways, by using radical reactions in an organic polymer film with focused electron-beam irradiation. We investigated various organic polymers as reaction materials and found that polystyrene has a higher efficiency for CD formation than other organic polymers investigated. Absorption, photoluminescence, and Raman scattering properties of the electron-beam-irradiated sample were in good agreement with those reported for the CDs. The technique developed in this study is promising for fabricating light-emitting CDs and photonic crystals in a simple and flexible manner.

INTRODUCTION

Nanomaterials, such as quantum dots, metal nanorods, and nanocarbons, have attracted much attention because of their unique electrical, mechanical, and optical properties. Carbon nanomaterials have been extensively studied for their potential uses in structural elements, conductive materials, and light-emitting devices. Synthesis of carbon dots (CDs) was first reported in 2004, and since then, their absorption and luminescence characteristics have been extensively studied. CDs are biocompatible and have low toxicity; thus, they are promising for bioelectronics and bioimaging as well.

Currently, CDs are mostly fabricated by the bottom-up and top-down methods. In the bottom-up method, CDs are chemically prepared by microwave synthesis, combustion reactions, and hydrothermal synthesis using sucrose, glucose, and citric acid as precursors. In the top-down method, CDs are fabricated through electrochemical oxidation and laser ablation using carbon rods as precursors. To fabricate CD-based optical devices such as nanoelectromirroring devices and photonic crystals, positions of the CDs should be controlled with the subwavelength resolution. Spatial control of the nanomaterials can be accomplished by the nanomanipulators. However, it takes a very long time and thus it is not tractable to construct a two-dimensional assembly. Space-selective synthesis of the CDs with the subwavelength resolution enables to fabricate the two-dimensional assembly in a short time with a flexible manner.

In this study, we synthesize CDs using electron beams to induce radical reactions in a polymer and arrange the position of CDs in a space-controlled manner. We examine preparation of CDs using various polymers as starting materials. We found that CDs are produced efficiently from polymers containing phenyl groups. By using this method, we prepared two-dimensional assemblies of the CDs on a glass substrate. From confocal imaging of the assembly, we found that the fabricated sample exhibits very unique optical properties arising from the interactions among nearby CDs. This method open the way to fabricate light-emitting CDs and photonic crystals in a space-resolved manner.

EXPERIMENTAL SECTION

Figure 1 shows a schematic of the fabrication protocol of the CD. First, a polymer film is spin-coated on a glass substrate. The polymer film is then irradiated by a focused electron beam. The electron beam is raster-scanned over the sample to prepare a two-dimensional assembly of the CDs. Organic polymer films used in this study are prepared by polyethylene (PE), polypropylene (PP), and polystyrene (PS). PE (average degree of polymerization, n ∼ 60) and PP (n ∼ 120) were purchased from Sigma-Aldrich, and PS (n ∼ 20) was purchased from National Metrology Institute of Japan.
RESULTS AND DISCUSSION

Figure 2 shows the absorption spectrum of the electron-beam-irradiated PS film. The spectrum was obtained by subtracting the absorption spectrum of the reacted PS film from that of the pristine PS, for elucidating chemically transformed species. The spectrum shows a peak at around 260 nm, and the tail of the absorption band extends toward the long wavelength side over 400 nm. The peak at ~260 nm is ascribable to absorption due to π→π* transitions of the phenyl rings.30 We also found that the peak intensity generally increases with electron-beam irradiation time. The increase in the intensity suggests the formation of new benzene rings resulting from the electron-beam-induced chemical reactions. The absorption at the long wavelength region only emerges after the electron-beam irradiation. Absorption in the longer wavelength side is a typical observation for π-conjugated compounds, and thus the absorption near the visible region may imply the formation of the PAHs.31 Figure 2b shows an absorption spectrum of the CDs prepared by hydrothermal synthesis. Similar to the spectral features in Figure 2a, an absorption peak appears around 260 nm and the tail of the absorption band extends toward the visible spectral region. The spectral profiles in Figure 2a,b indicate the formation of CDs by electron-beam-induced chemical reactions in the polymer film. We should note that the scattering contribution in the transmission of light is negligible since the scattering cross section for the small particle comparable to the CDs is much smaller than the absorption one.32,33 PS exhibits PL near 280 and 330 nm, which originated from monomer and excimer of the phenyl group,30 respectively, and shows negligible PL in the visible-light region. Interestingly, the electron-beam-irradiated PS does show intense PL in the visible region in addition to that in the UV region.34 These facts suggest that the chemical species produced by the electron-beam irradiation show visible PL.

Figure 3a shows the PL spectrum of the sample excited by a UV laser (λ = 375 nm). The spectrum shows a PL peak in the visible-light region (λ~480 nm). The spectral profile observed in Figure 3a is very similar to that of the CDs shown in Figure 3b. Excitation spectra taken by detecting 430 and 480 nm in Figure 3a,b indicate the formation of CDs by electron-beam-induced chemical reactions in the polymer film. We should also note here that the PL spectrum is not dependent on the excitation wavelength in the Supporting Information (Figure S1) are in good agreement with the absorption spectrum in Figure 2a, indicating that the PL is originated from the chemical species excited at the excited wavelength. We should also note here that the PL spectrum is not dependent on the excitation wavelength in the Supporting Information (Figure S2) and hence the radiated photons are not originated from Raman scattering but from the excited state of the sample. PL quantum yield was determined to be ca. 20–30%. The PL intensity increases in proportion to
the dose of the electron beam up to 5 mC/cm², as shown in the Supporting Information (Figure S3). The result indicates that concentration of the PL species formed in the polymer can be controlled by the dose of the electron beam. The dose dependencies of the PL and absorption are nearly identical. This strongly suggests that the absorption and PL in the visible region originate from the same chemical species.

As discussed so far, electron-beam-irradiated PS exhibits optical properties nearly identical with those of the CDs produced by the other methods. To identify the chemical species generated in the reactions, we performed Raman scattering spectroscopy for the sample. Figure 4 shows Raman spectra of the pristine and electron-beam-irradiated PS. Raman spectrum of the pristine PS shows two strong vibrational bands near 1000 and 1600 cm⁻¹. These Raman bands are assigned to the breathing modes in the phenyl groups and the stretching mode of the C=C bond, respectively. Raman spectrum of the irradiated PS, however, does not show these vibrational bands. Instead, two broad Raman bands are observed near 1340 and 1590 cm⁻¹. The band position and their spectral profiles are both typical for the carbon materials and are assigned to the D band and G band, respectively. Note that the Raman spectral properties of the irradiated PS are in very good agreement with those of the CDs reported previously. The fact indicates that the chemical species generated in this study is attributable to the CDs. Size of the carbon dots was characterized to be ~10 nm by TEM images, as shown in Figure 3c,d. High-resolution TEM images show lattice structures (lattice spacing ~0.32 nm), similar to the past studies of the CDs. The fact indicates that the prepared CDs are crystalline carbon.

To examine the precursor polymer dependence of the CD formation, we performed electron-beam irradiation on PE and PP films under nearly identical conditions to those for the PS. The dose of the electron beam was unified to 5 mC/cm². The PS film thickness was 570 ± 20 nm, and the thicknesses of the PE and PP films were 1.57 ± 0.58 and 2.93 ± 1.78 μm, respectively. Figure 5 shows the PL spectra of the reacted samples. In Figure 5, the PL intensity was normalized by the thickness of each polymer. Spectral profiles for these samples are very similar to each other, whereas there are clear differences in the PL intensity. The PL intensity for the PS precursor was more than twice compared to that for the other two. The result may indicate that CD formation is promoted in the presence of the phenyl group in the polymer film.

Next, we consider the formation mechanism of the CDs in this study. Chemical transformation of the organic polymer was initiated by electron-beam irradiation under a pressure of 30 Pa. Kinetic energy of the electrons was about 15 keV. Part of the kinetic energy is transferred to electronic and kinetic excitations of the polymer film. Excited energy is partly used for chemical transformations and is mostly released by radiative and nonradiative processes. Quantum yield of the PL is low in general, and thus most of the energy is released nonradiatively and is converted to thermal energy of the polymer film. For this reason, the temperature of the sample near the irradiated area should increase locally. The temper-
The nucleations of the PAHs produce the CDs.39 For these reasons, we presume that the CD formation by the electron-beam method proceeds through chemical reactions similar to those that occurred during combustion. Namely, the reaction proceeds from small carbon compounds to the CDs, and radical reactions are expected to be predominated.39 For both methods, the reaction proceeds from small carbon compounds to the CDs. Initially, the carbon compounds are transformed into small PAHs. Then, the PAHs are grown in size by the reactions and finally the nucleations of the PAHs produce the CDs.39

CDs have been fabricated by various methods, such as hydrothermal synthesis,26,27 combustion synthesis,24,25 and microwave irradiation.21,22 These methods require several reagents and relatively long reaction time, typically 12 h. The fabrication method described in this study uses only an organic polymer film as a precursor, and the fabrication of CDs can be accomplished in a simple manner within a few seconds. Moreover, concentration of the CDs can be controlled by the dose of the electron beam. The method is compatible with fabrication of a two-dimensional CD assembly in the polymer film, since the fabrication can be performed under SEM. By adjusting the beam-steering condition of the electron beam, we fabricated three types of two-dimensional assemblies of the CDs on the glass substrate. Figure 6 shows PL images of the fabricated sample. PL is excited by 375 nm. Bright parts indicate that the concentration of the CDs is high. Lattice structures with periodic waves and two-dimensional donut patterns were clearly visualized in Figure 6b,c, respectively. Fabrication resolution is mostly limited by scattering of the electrons in the polymer to several hundred nanometers.3 The refractive index of carbon materials is typically 2.5 and is thus larger than that of organic compounds.10 Optical properties of these assemblies can be interpreted similar to those of photonic crystals. Therefore, the fabricated assemblies act as organic photonic crystals with tight light confinement because of the high refractive index contrast. The method developed in this study enables extending to fabrication of nano-optical recording, nano-light-emitting diode, and so on.

CONCLUSIONS

We developed a simple CD fabrication method using electron-beam-induced radical reactions in a polymer thin film. Absorption and PL properties of the fabricated sample showed good agreement with those of samples produced by hydrothermal synthesis reported previously. We also performed Raman spectroscopy to characterize the chemical nature of the sample and found that the sample exhibits the D and G bands attributable to those for the CDs. We used various organic polymers as reaction precursors and found that the CDs are formed irrespective of the polymer type. CD formation is most efficient when the phenyl group is present in the polymer framework. The results indicate that the CD formation proceeds through radical reactions, similar to those for soot-particle formation. The method developed in this study enables spatially selective formation of the CDs with a simple protocol and a shorter time compared with those of previously reported methods. In addition, the method is compatible with fabrication of two- and three-dimensional CD arrays and is therefore promising for applications in nano-light-emitting devices and photonic crystals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00085.

Excitation spectrum of the electron-beam-irradiated PS, PL spectra of the electron-beam-irradiated PS, and the electron dose dependence of the PL (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: Imura@waseda.jp.

ORCID
Kohei Imura: 0000-0002-7180-9339

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported in part by JSPS KAKENHI Grant Numbers JP26107001, JP26107003, JP15K21725, JP16K13939, and JP16H04100 in Scientific Research on Innovative Areas “Photosynergetics” from the Japan Society for the Promotion of Science.

REFERENCES

1. Liu, Y. Y.; Stehlik, J.; Eichler, C.; Gullans, J. M.; Taylor, M. J.; Petta, R. J. Semiconductor Double Quantum Dot Micromaser. Science 2015, 347, 285–287.
(2) Shin, S.-H.; Hwang, B.; Zhao, J. Z.; Jeon, H. S.; Jung, Y. J.; Lee, H. J.; Ju, K. B.; Jeong, H. J. Transparent Displays Utilizing Nanopatterned Quantum Dot Films. *Sci. Rep.* 2018, 8, No. 2463.

(3) Sau, T. K.; Murphy, J. C. Seeded High Yield Synthesis of Short Au Nanorods in Aqueous Solution. *Langmuir* 2004, 20, 6414–6420.

(4) Takahata, R.; Yamazoe, S.; Koyasu, K.; Imura, K.; Tsukuda, T. Gold Ultrathin Nanorods with Controlled Aspect Ratios and Surface Modifications: Formation Mechanism and Localized Surface Plasmon Resonance. *J. Am. Chem. Soc.* 2018, 140, 6640–6647.

(5) De Volder, M. F. L.; Tawfick, H. S.; Baugham, H. R.; Hart, J. A. Carbon Nanotubes: Present and Future Commercial Applications. *Science* 2013, 339, 535–539.

(6) Novoselov, K. S.; Fal’ko, I. V.; Colombo, L.; Gellert, R. P.; Schwab, G. M.; Kim, K. A Roadmap for Graphene. *Nature* 2012, 490, 192–200.

(7) Coleman, J. N.; Khan, U.; Blau, J. W.; Gun’ko, K. Y. Small but Strong: A Review of The Mechanical Properties of Carbon Nanotube–Polymer Composites. *Carbon* 2006, 44, 1624–1652.

(8) Neto, A. H. C.; Guinea, F.; Peres, R. M. N.; Novoselov, S. K.; Geim, K. A. The Electronic Properties of Graphene. *Rev. Mod. Phys.* 2009, 81, 109–162.

(9) Reckmeier, C. J.; Schneider, J.; Susha, S. A.; Rogach, L. A. Luminescent Carbonoid Carbon Dots: Optical Properties and Effects of Doping [Invited]. *Opt. Express* 2016, 24, A312–A340.

(10) Xie, Z.; Yin, Z.; Wu, Y.; Chunyuan, L.; Hao, X.; Du, Q.; Xu, X. White Light-Emitting Diodes Based on Individual Polymerized Carbon Nanodots. *Sci. Rep.* 2017, 7, No. 12146.

(11) Xu, X.; Ray, R.; Gu, Y.; Ploehn, J. H.; Gearheart, L.; Raker, K.; Scrivens, A. W. Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. *J. Am. Chem. Soc.* 2004, 126, 12736–12737.

(12) Zhu, S.; Zhang, J.; Wang, L.; Song, Y.; Zhang, G.; Wang, H.; Yang, B. A General Route to Make Non-Conjugated Linear Polymers Luminescent. *Chem. Commun.* 2012, 48, 10889–10891.

(13) Zhu, S.; Wang, L.; Zhou, N.; Zhao, X.; Song, Y.; Maharjan, S.; Zhang, J.; Lu, L.; Wang, H.; Yang, B. The Crosslink Enhanced Emission (CEE) in Non-Conjugated Polymer Dots: From The Photoluminescence Mechanism To The Cellular Uptake Mechanism and Internalization. *Chem. Commun.* 2014, 50, 13845–13848.

(14) Wang, L.; Zhu, J. S.; Wang, Y. H.; Qu, L. Y.; Zhang, H. J.; Chen, D. Q.; Xu, L. H.; Han, W.; Yang, B.; Sun, B. H. Origin of Green Luminescence in Carbon Nanodots and Graphene Quantum Dots. *ACS Nano* 2014, 8, 2541–2547.

(15) Peng, J.; Gao, W.; Gupta, K. B.; Liu, Z.; Aburto, R. R.; Ge, L.; Song, L.; Alemany, B. L.; Zhan, X.; Gao, G.; Vithayathil, A. A.; Kaippe, A. B.; Marta, A. A.; Hayashi, T.; Zhu, J. J.; Ajayan, M. P. Graphene Quantum Dots Derived from Carbon Fibers. *Nano Lett.* 2012, 12, 844–849.

(16) Léménager, G.; Luca, D. E.; Sun, P. Y.; Pompa, P. P. Super-Resolution Fluorescence Imaging of Biocompatible Carbon Dots. *Nanoscale* 2014, 6, 8617–8623.

(17) Ge, J.; Lan, M.; Zhou, B.; Liu, W.; Guo, L.; Wang, H.; Jia, Q.; Niu, G.; Huang, X.; Zhou, H.; Meng, X.; Wang, P.; Lee, S. C.; Zhang, W.; et al. A Graphene Quantum Dot Photodynamic Therapy Agent with High Singlet Oxygen Generation. *Nat. Commun.* 2014, 5, No. 4596.

(18) Ge, J.; Jia, Q. Y.; Liu, W. M.; Guo, L.; Liu, Q. Y.; Lan, M. H.; Zhang, H. Y.; Meng, X. M.; Wang, P. F. Red-Emissive Carbon Dots for Fluorescent, Photocoagulation, and Thermal Theranostics in Living Mice. *Adv. Mater.* 2015, 27, 4169–4177.

(19) Liu, Y.; Zhi, X.; Hou, W.; Xia, F.; Zhang, J.; Li, L.; Hong, Y.; Yan, H.; Peng, C.; Fuentes, M. J.; Song, J.; Cui, D. Gd3+ Ion-induced Carbon-Dots Self-assembly Aggregates Loaded with a Photocensitizer for Enhanced Fluorescence/MRI Dual Imaging and Antitumortherapy. *Nanoscale* 2018, 10, 19052–19063.

(20) Wang, Q.; Zhang, C.; Shen, G.; Liu, H.; Fu, H.; Cui, D. Fluorescent Carbon Dots as an Efficient siRNA Nanocarrier for its Interference Therapy in Gastric Cancer Cells. *J. Nanobiotechnol.* 2014, 12, 58.