Press Release

Keio University

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Keio University

Laser Direct Writing of Graphene Quantum Dots
—Novel Fabrication Method for Eco-friendly Optoelectronic Devices—

A research group from the Keio University Graduate School of Science and Technology including PhD student Shuichiro Hayashi, Master student Kaneto Tsunemitsu, and Associate Professor Mitsuhiro Terakawa have revealed that fluorescent Graphene Quantum Dots (GQDs)[1] are synthesized by irradiation of laser pulses onto transparent polymers.

Quantum dots are nano-sized particles that exhibit photoluminescence owing to quantum confinement effects,[2] and are suitable for applications such as light-emitting diodes, biomarkers, and anticounterfeiting security tags. Particularly, GQDs have attracted significant attention as an eco-friendly alternative to conventional QDs in the context of sustainable development. In this work, it has been revealed that by irradiating and scanning focused ultrashort laser pulses, GQDs can be simultaneously synthesized and patterned along desired paths, similar to drawing with a pen. Since the presented method is based on multiphoton interactions,[3] GQDs can be patterned, not just two-dimensionally on the surface, but three-dimensionally inside of the transparent polymer substrate. This work expands the possibilities of GQDs for applications in novel flexible optoelectrical devices.

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1. Main Points of Research

- The fluorescent structures composed of graphene quantum dots were patterned via irradiation and scanning of laser pulses onto an elastic polymer.
- Visibly black-colored carbonaceous structures with differing graphene-quantum-dot content can be readily patterned by simply adjusting the laser parameters.
- Since three-dimensional processing is possible, graphene quantum dots can be formed inside the bulk polymer material.

2. Background of Research

Quantum dots (QDs) are nano-sized particles that exhibit photoluminescence owing to quantum confinement effects, and are suitable for applications such as light-emitting diodes, biomarkers, and anticounterfeiting security tags. However, well-known inorganic QDs are typically expensive and highly toxic. Over the past decade, organic carbon-based graphene quantum dots (GQDs), have emerged as a promising eco-friendly alternative to such inorganic QDs. Generally, for the synthesis of GQDs, pre-prepared graphitic derivatives, such as graphite, are fragmented, and although such method allows for the large-volume synthesis of GQDs, multiple time-consuming steps are required. Moreover, the as-synthesized GQDs must be selectively patterned for further applications in optoelectronic devices, and the development of patterning methods, mainly two-dimensional planar methods, have been extensively researched.

The laser-induced graphitization of polymers has been investigated extensively after the mid-2010s and is currently an effective synthesis method for fabricating graphene, generally referred to as laser-induced graphene (LIG). The group has recently indicated that highly crystalline few-layered graphene can be synthesized from a polymer precursor conventionally regarded as difficult

to graphitize, polydimethylsiloxane (PDMS), by using femtosecond laser pulses [Ref.1, 2]. Additionally, the group also achieved the fabrication of LIG from plant-based cellulose nanofibers using femtosecond laser pulses, which exhibited higher electrical conductivity, indicating the possibility of using renewable materials for electronic devices [Ref. 3].

3. Content of Research and Results

In the present work, the group expanded upon the technique for fabricating LIG by using ultrafast laser pulses (Ultrashort Pulsed LIG, UP-LIG), and demonstrated that by irradiating and scanning focused ultrashort laser pulses onto the surface of a transparent polymer, PDMS, fluorescent structures composed of GQDs can be patterned along desired paths, similar to drawing with a pen (Fig. 1). When transmission electron microscopy observations were performed on the visibly black-colored structures that exhibited fluorescence, nanoscale-graphitic crystals were observed, confirming that the structures were composed of GQDs. Since the GQD-content is highly dependent on the laser parameters used for fabrication, the fluorescence intensity of the visibly black-colored structures can be controlled. Thus, by selectively adjusting the GQD-content a black security tag with a concealed QR code, which is imperceptible under normal light, but is revealed under excitation is realized, demonstrating the feasibility of the presented method for the fabrication of anticounterfeiting security tags. Furthermore, since the presented method is based on multiphoton interactions, GQDs can be patterned, not just two-dimensionally on the surface, but three-dimensionally inside of PDMS. It should be noted that this work demonstrated the three-dimensional patterning of GQDs for the first time (Fig. 2).

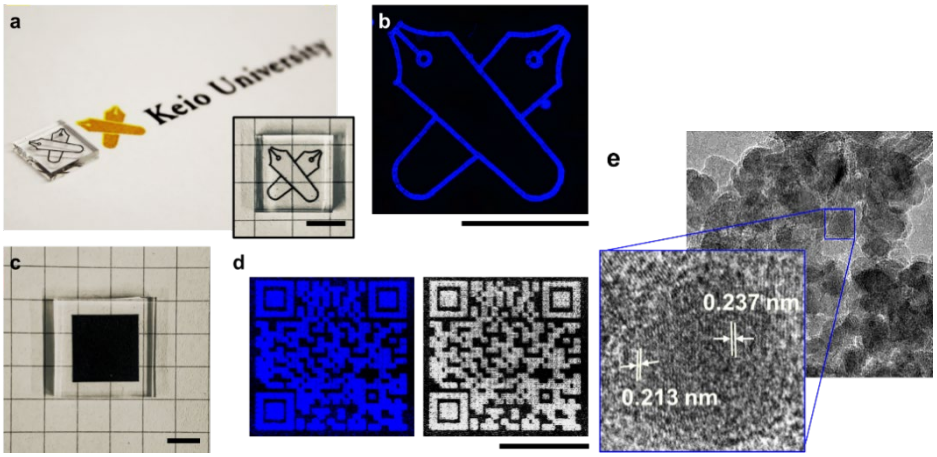

Fig. 1: Laser direct writing of GQDs. a & c: Optical photographs, b & d: Fluorescence microscope images (Excitation wavelength: 360 nm) (Scale bar: 5 mm), e: Electron microscope images of GQDs

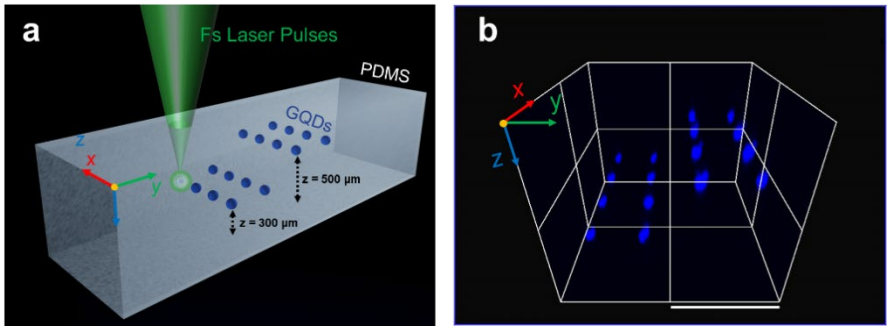

Fig. 2: Generation of GQDs inside a transparent material. a: Illustration of laser irradiation, b: Three-dimensional reconstruction fluorescence image obtained by multiphoton microscopy. (Scale bar: 250 μm)

4. Future Developments

The present work indicates the possibility and versatility of femtosecond laser processing for the simultaneous synthesis and patterning of fluorescent structures composed of GQDs directly on and inside elastic transparent polymers, and opens novel routes for the fabrication of GQDs-based

eco-friendly optoelectrical devices. Furthermore, controlled surface functionalization and diameter control of the GQDs realized by the elucidation of the formation mechanism may allow for the fine-tuning of the emission wavelength, and the direct fabrication of full-spectrum three-dimensional displays inside flexible polymers for novel wearable displays.

References

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Details of Journal Article

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Glossary

[1] Graphene Quantum Dots (GQDs)
GQDs are nano-sized fragments of graphene, which exhibit unique size-dependent optoelectronic properties, particularly photoluminescence, owing to quantum confinement effects.

[2] Quantum confinement effects
When the size of a material become nanoscale, electronic and optical properties change because of the electron behavior, resulting in significantly different properties from those of the bulk material.

[3] Multiphoton interactions
Interactions between multiple photons and the material.

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