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White light induced photo-thermal switching in a graphene-flake-mixed ZnO nanoparticle random laser

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Abstract

We experimentally demonstrate lasing mode switching within a graphene-flake-mixed ZnO nanoparticle film, in which the lasing suppression is observed when white light is illuminated on the film. The similar changes are also observed by changing the temperature of the same sample (about 30 °C increase form room temperature), while no lasing suppression is observed in a ZnO nanoparticle film without graphene flakes. In addition, we also observe that a thin glass substrate coated by a graphene-flake-mixed ZnO nanoparticle film shows a bend toward the film-coated side with increasing the white light intensity, due to the negative thermal expansion of graphene flakes. From these results, we consider that, beside the temperature dependent ZnO emission property, the photo-thermal response of graphene flakes is the dominant key for our observed lasing mode changes, in which the local structural change in a graphene-flake-mixed ZnO nanoparticle film would be induced by the white light absorption of graphene flakes. This study suggests the possibility to provide a method to remotely and non-invasively control and tune the lasing modes by external white light illumination.

1. Introduction

Graphene has been one of the attractive materials because of its superior electronic and photonic properties, thermal/chemical stability, and mechanical properties, which has been utilized for various applications including sensors, artificial muscles, and nano/micro electromechanical devices [1–6]. Especially, its high photo-thermal conversion property enables graphene to be employed in novel devices with new types of driven force, such as optically driven actuators, which originated from elastic expansion and contraction of graphene induced by light absorption [1, 2].

On the other hand, we have been interested in random structures and their modal control for the practical applications such as light emitting devices, sensors, and light extracting/harvesting. For this purpose, several approaches for the control of random lasing modes had been proposed such as use of resonant scatterers [7–11], limiting excitation area [12, 13], temperature control [14–16], tuning density of scatterers [17]. Among these approaches, it had been reported that changes in lasing modes were observed in random lasers fabricated on a soft substrate due to the structural changes induced by mechanically stretching the substrate [18–20], which has a merit of *in situ* tuning of lasing modes by adjusting the amount of bending or stretching the substrate. However, for maintaining the reproducibility and achieving the precise tuning, it is indispensable to use driving mechanism equipped with the structure, such as actuators. To realize a remote, non-invasive, and low-cost method, we have paid attention to the characteristic of graphene flakes (large negative thermal expansion and high absorption rate) [22, 23], by which random lasing modes could be modified by the structural change based on the elastic expansion and contraction of graphene flakes induced by light absorption.

In this study, we experimentally demonstrated the modulation of random lasing modes in a ZnO nanoparticle film mixed with graphene flakes, in which the changes in lasing intensities, thresholds, and spatial

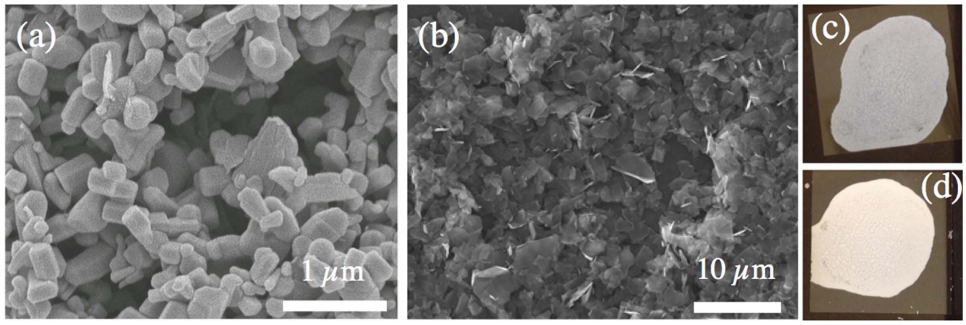

Figure 1. SEM images of (a) ZnO nanoparticles and (b) graphene flakes. (c), (d) Images of ZnO nanoparticle films with and without graphene flakes on a glass substrate.

distributions of ZnO random lasers were observed by the irradiation of white light. Similar changes could also be observed by heating the sample from RT to 50 °C, while no clear change was observed in ZnO nanoparticle films without graphene flakes. From the results, we concluded that the photo-thermal response of graphene flakes were the predominant key for the observed mode change, beside the temperature dependent ZnO emission property [24, 25]. Our findings suggest the possibility to provide a method to remotely and non-invasively control random lasing modes by adjusting the intensity and spatial distribution of external light illumination.

2. Experiment

In the experiments, commercially available ZnO nanoparticles (diameter ~400 nm, Wako Pure Chemical Industries) (figure 1(a)) were used as scatterers and gain materials. The size of ZnO nanoparticles was slightly large and almost same as emission wavelength. There is the possibility that multiple light scattering would also occur inside a particle, which would also induce random lasing [26]. However, we note that any lasing behavior could not be observed from single ZnO particles. These ZnO nanoparticles and graphene flakes (diameter ~600 nm, Graphene Platform Corporation) (figure 1(b)) were mixed and dispersed in water (the weight ratio of ZnO nanoparticles and graphene flakes was 1 : 1). A drop of the solution was casted on a thick cover glass (thickness ~0.5 mm) for avoiding the substrate deformation and dried at room temperature. As references, we similarly prepared ZnO nanoparticle films without graphene flakes. Figures 1(c) and (d) show the images of prepared samples with and without graphene flakes.

The sample was set on a piezo-stage of a confocal microscope (Eclipse Ti-U, Nikon) and pulses from a Q-switched pulsed laser (wavelength 355 nm, repetition rate 1 kHz, pulse duration 300 ps, teem photonics) were irradiated by an objective lens (60×, NA = 0.85, spot size ~60 μm) as an excitation light (figure 2). Emission from the sample passing through a pinhole (~1 μm on a sample surface) was guided to a spectroscope equipped with a cooled CCD camera and a photomultiplier tube (PMT). For the measurements of emission intensity distributions, signals from PMT that detected photons with the wavelength band from 375 to 395 nm passing through the spectrometer were recorded with two-dimensionally scanning the piezo-stage. To observe the changes in lasing modes, a microscope illumination light (100 W halogen lamp) was used and irradiated on whole sample area (spot size: a few cm). Then, lasing spectra and intensity distributions were measured with and without the white light illumination to confirm the photo-thermal response.

3. Result and discussion

Figures 3(a)–(c) represent the random lasing spectra with (red lines) and without (black lines) the white light illumination measured at different positions. From the spectra, we observed multi-mode sharp peaks, when the excitation intensity was well above the threshold, which behavior was similar to conventional random lasers. However, when the white light was additionally irradiated on the samples with keeping the excitation intensity constant, the lasing peak intensity drastically decreased and the lasing peak wavelengths were slightly red-shifted (2 ~ 3 nm). Figure 4 shows the random lasing spectra and their excitation intensity dependence of the integrated emission intensities with and without the white light illumination at the same position (red and black lines and symbols, respectively). From the results, we found that the lasing threshold was increased from about 50 to 100 MW cm^{-2} by the white light illumination, although these thresholds were higher than those in a ZnO nanoparticle film without graphene flakes (blue triangles) due to the strong absorption of graphene flakes. By repeatedly turning on and off the white light, we confirmed the reproducibility. In contrast, in a ZnO

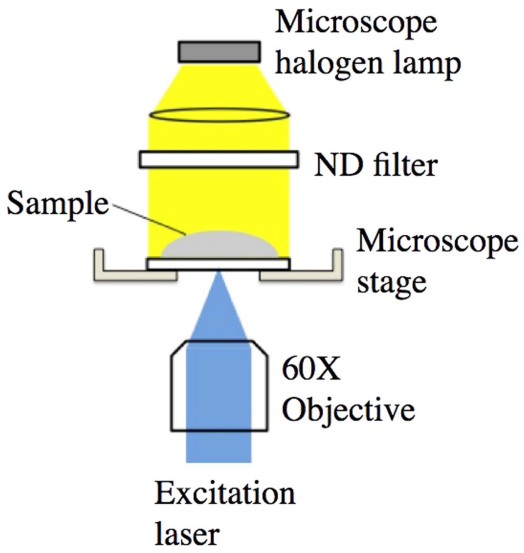

Figure 2. Schematic of optical setup for the measurements of photo-thermal switching.

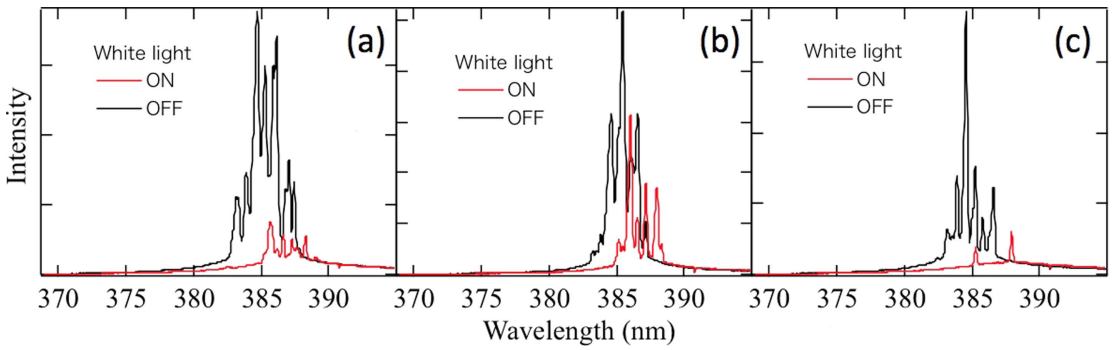

Figure 3. Lasing emission spectra of a graphene-flake-mixed ZnO nanoparticle films with (red line) and without (black line) white light illumination at different positions.

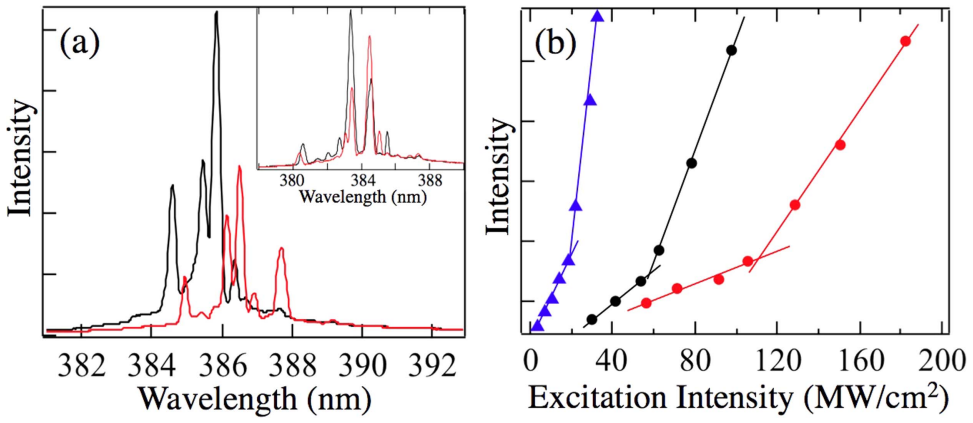

Figure 4. (a) Emission spectra and (b) excitation intensity dependence of integrated emission intensities in a graphene-flake-mixed ZnO nanoparticle film. In each figure, black and red lines and circles indicate the results without and with white light illumination. Blue triangles indicate the data of ZnO nanoparticle film. Inset in (a) indicates the lasing spectra from a ZnO nanoparticle film with and without the white light illumination. Lines in (b) are a guide for the eyes.

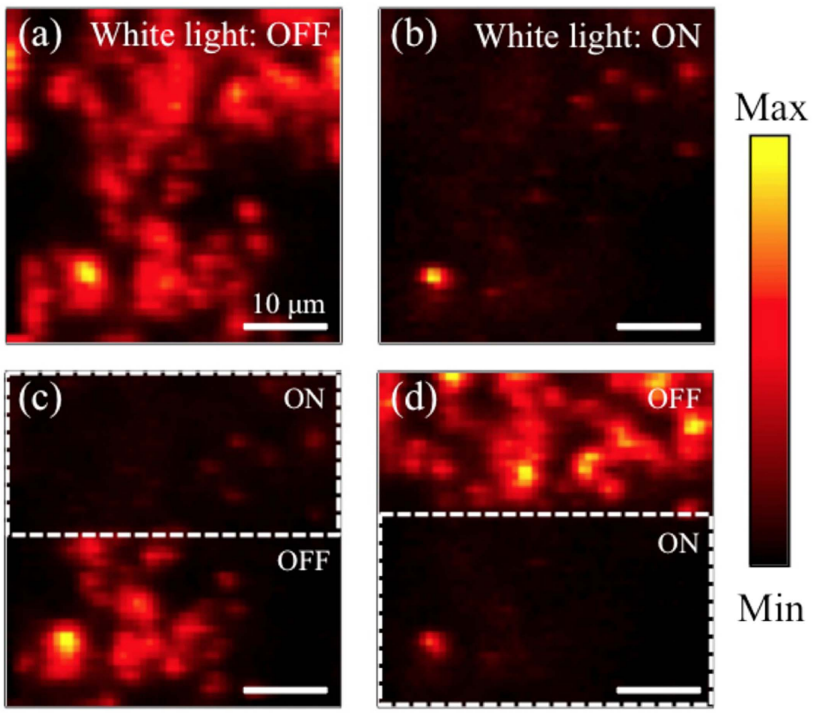

Figure 5. Emission intensity distributions at the same area in a graphene-flake-mixed ZnO nanoparticle film (a) without and (b) with white light illumination. Dotted lines in (c), (d) indicate the partial illumination area of the white light.

nanoparticle film without graphene flakes, no clear change in the threshold was observed by the white light illumination, although the lasing spectra show slight changes in relative peak intensities, but the dominant lasing peak wavelengths were almost unchanged, which would be due to the chaotic fluctuations of conventional random lasers (inset in figure 4(a)) [25].

Figures 5(a) and (b) show the lasing intensity distributions with and without the white light illumination in a graphene-flake-mixed ZnO nanoparticle film at the same area. Bright area indicates higher lasing intensity. By irradiating the white light to the entire sample, we found that the lasing intensity suppressed (figures 5(a) and (b)), similar to the results in figure 4. In addition, figure 5(c) (figure 5(d)) shows the intensity distribution at the same position of the sample when the white light irradiates only the upper (lower) half of the area. We observed that emission intensity only in the region of the white light illumination decreased, resulting in random lasing suppression. These results indicate the possibility that spatial lasing distribution could also be modified by selecting the light irradiating area.

One of the possible origins of these lasing mode changes could be attributed to the saturable absorption effect of graphene that has been used as key optical materials for mode-locked lasers [4, 5]. The ultrafast saturable absorption in graphene was experimentally and theoretically investigated in the femtosecond time regime [21]. However, the observed transition time of random lasing modes was from several to over ten seconds (see supplementary material 1 is available online at stacks.iop.org/JPCO/2/035022/mmedia) and the white light intensity per unit wavelength would be too weak to induce saturable absorption effect. Thus we conjectured that the observed phenomena would not be due to the saturable absorption of graphene flakes.

Considering the slow transition time of lasing mode changes, another possible mechanism of these behaviors is photo-thermal response (negative thermal expansion and high absorption rate) of graphene flakes [22] and temperature dependent ZnO emission property [23, 24], which were caused by the sample temperature change with the white light illumination. To verify this possible mechanism, we performed similar lasing spectral measurements when the sample was heated from room temperature (RT) to 50 °C by using a thermal plate, instead of the white light illumination (figure 6(a)). The excitation intensity was set at about 1.2 times higher than the threshold. The blue and black lines in figure 6 shows the emission spectra at RT with and without the white light illumination, respectively. With the white light illumination, random lasing modes were suppressed and only broad emission at slight longer wavelength region (2 $\sim$ 3 nm shift) was observed, which behaviors were similar to the results in figures 3 and 4. On the other hand, when the sample was heated up to 50 °C without the white light illumination, we observed similar changes with the white light illumination (red line in figure 6(a)), which meant that about 30 °C temperature increase in the sample from RT was induced by the white light absorption. We note that slight difference in emission intensities of red and blue lines at the

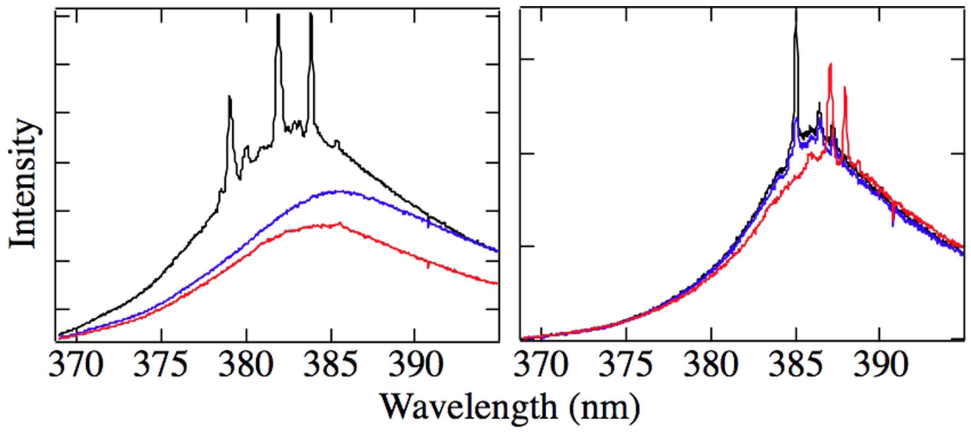

Figure 6. Emission spectra from (a) a graphene-flake-mixed ZnO nanoparticle film and (b) ZnO nanoparticle film. Black lines: without white light at RT, Blue lines: with white light at RT, Red lines: without white light at 50 °C.

longer wavelength region was the influence of the superposition of the weak tail of the white light spectrum. Furthermore, to clarify the thermal effect of ZnO, we also measured emission spectra from a ZnO nanoparticle film without graphene flakes, when the sample was also heated from RT to 50 °C by using a thermal plate (figure 6(b)). If the observed lasing mode changes could be attributed to the temperature dependent ZnO emission property [23, 24], similar changes that observed in a graphene-flake-mixed ZnO nanoparticle film (e.g., lasing suppression) should also be observed in the ZnO nanoparticle film. However, when the sample was heated, only slight wavelength shift and no lasing suppression were observed. Nakamura *et al* investigated the temperature dependence of random lasing properties in a ZnO nanoparticle film and suggested only slight red-sift (∼2 nm) and about 10% increase in threshold was reported against about 30°C temperature increase around RT [23]. In addition, Yang *et al* reported that the threshold of ZnO nanoneedles became twice, when the temperature was increased from RT to about 100 °C [24]. On the other hand, in our experiments, about 30 °C temperature increase with the white light illumination induced that the emission peaks showed similar slight red-shifted (2 ∼ 3 nm), but thresholds became almost twice (see figure 4), which could not be explained only by the temperature dependent ZnO emission property. Thus, we thought that not only the temperature dependent ZnO emission property, but the photo-thermal mechanical response (expansion and contraction) of graphene flakes would be the key for the lasing mode changes. In other words, when graphene flakes absorbed the white light and the sample temperature changed, besides the change in the ZnO emission property (wavelength shift), the expansion and contraction of graphene flakes [22] in the sample film would change the configuration of a ZnO nanoparticles film (e.g., change in the packing density [17]), resulting in the random lasing mode change.

To visualize this photo-thermal expansion and contraction of graphene flakes, we prepared a graphene-flake-mixed ZnO nanoparticle film (film size: diameter ∼1 cm, thickness: several hundred μm) on a thin glass substrate (thickness ∼0.1 mm) and tried to observe the deformation of the thin substrate when the white light was irradiated to the entire sample (figure 7). To discuss the white light intensity dependence, we defined the white light intensity by integrating the spectral intensity without a sample, and the intensity was adjusted by inserting ND filters in order to exclude the influence of the spectral shape change. In addition, to monitor the deformation, we used a weak blue light inserting a color filter as the cases without the white light illumination. From the measurements, we found that the thin glass substrate covered by a graphene-flake-mixed ZnO nanoparticle film showed a bend toward the film-coated side with the white light illumination (figures 7(a) and (b)) (also see supplementary material 2) and these behaviors could be repeatedly observed. Figure 7(c) represents the white light intensity dependence of the displacement of the glass substrate, which was linearly changed against the irradiated white light intensity. Because Yoon *et al* reported that graphene sheets contracted as the temperature increased from RT due to the negative thermal expansion coefficient of graphene [22], the contraction of a graphene-flakes-mixed ZnO nanoparticle film would also be induced and showed the bending behavior toward the film-coated side that increased linearly with increasing the white light intensity. However, this behavior was not observed in a ZnO nanoparticle film, even when the sample was heated by the thermal plate or irradiated by the white light. From these results, we concluded that the possible mechanism of the observed random lasing mode change could be attributed to not only the temperature dependent ZnO emission property, but also the structural change in a random structure induced by the contraction and expansion of graphene flakes with and without the white light illumination.

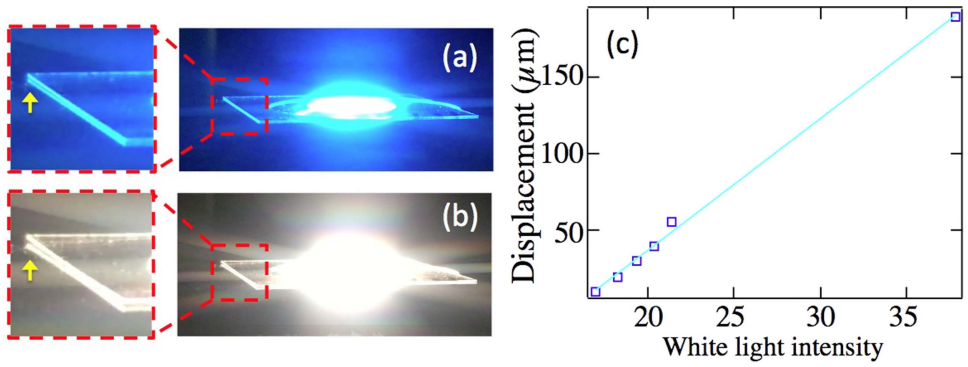

Figure 7. Images of the bending of a thin glass substrate with a graphene-flake-mixed ZnO nanoparticle film by turning (a) off and (b) on the white light (see supplementary material 2). We used a weak blue light as an off state of the white light to monitor the sample deformation in (a). (c) White light intensity dependence of the bending of a thin glass substrate with a graphene-flake-mixed ZnO nanoparticle film.

4. Conclusion

In summary, we demonstrated the modulation of random lasing modes in a graphene-flake-mixed ZnO nanoparticle film by the white light illumination. From the temperature dependent measurements, we concluded that, beside the temperature dependent ZnO emission property, the predominant origins of the lasing mode changes would be attributed to the photo-thermal response of the graphene flakes (negative thermal expansion coefficient), which would induce the structural change in a graphene-flake-mixed ZnO nanoparticle film with the white light illumination. These findings would suggest the possibility to provide a novel method to remotely and non-invasively control and tune the random lasing modes by adjusting the conditions of the white light illumination, even though further investigation is necessary to realize precise switching and tuning.

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