# Multifunctional Graphene Sheets Embedded in Silicone Encapsulant for Superior Performance of Light-Emitting Diodes

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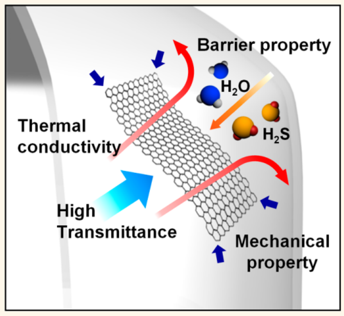
**ABSTRACT** Graphene nanosheets with uniform shape are successfully incorporated into a silicone encapsulant of a light-emitting diode (LED) using a solvent-exchange approach which is a facile and straightforward method. The graphene nanosheets embedded in the silicone encapsulant have a multifunctional role which improves the performance of light-emitting diodes. The presence of graphene gives rise to effective heat dissipation, improvement of protection ability from external stimuli, such as moisture and hazardous gas, and enhancement of mechanical properties such as elastic modulus and fracture toughness. Consequently, the LEDs composed of a graphene-embedded silicone encapsulant exhibit long-term stability without loss of luminous efficiency by addition of relatively small amounts of graphene. This novel strategy offers a feasible candidate for their practical or industrial applications.




**KEYWORDS:** light-emitting diode · encapsulant · graphene · silicone resin · long-term stability

Light-emitting diodes (LEDs) are widely used because of their high-speed responses, low-power consumption, long lives, small sizes, and light weights. Packaging technology has provided high intensities, improved efficiencies, and higher outputs.[1,2] Various approaches have been explored to enhance LED efficiency, such as for backlighting, electrodes, and lenses.[3−7] Although much attention has been paid to various parts of the LED device structure, relatively little research has been reported on the encapsulant.

An encapsulant is a capping material that protects the individual diodes. The encapsulant must have a high refractive index, excellent transparency, high thermal conductivity, good thermal stability, good chemical resistance, and be an excellent barrier to moisture and gases.[8,9] High refractive index as well as transparency is required for enhancement of illumination performance by increasing the light extraction efficiency.[10] In addition, effective heat dissipation is important to improve the luminous output because the junction temperature of devices is high during operation.[11] Thermal stress originated from residual heat remaining inside the device can cause serious failures such as discoloration of encapsulant and reduction of light efficiency.[12] Furthermore, to prevent device deterioration and corrosion, the ability to protect against hazardous gas and moisture is essential.[13] Many materials have been evaluated as encapsulants, such as epoxies, polyurethanes, and silicones. For instance, Bae's group synthesized UV-curable epoxy−siloxane hybrid materials with high thermal resistance for use as an LED encapsulant.[9] The LEDs comprising the UV-curable epoxy hybrid showed high performance maintenance during thermal aging. Moreover, Hsu *et al.* demonstrated that the optical and dynamic mechanical properties of LEDs under thermal aging conditions are improved by introducing phenylmethylsiloxane-modified epoxy to the encapsulant.[14] Although various studies have been done, they are substantially focused on the thermal stability and refractive index of the encapsulant.[15−17] Therefore, it is still challenging to design an encapsulant having high efficiency and long-term stability; these properties are requirements for high-performance LEDs.

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Graphene is a one-atom-thick carbon layer. It has received great attention because of its high transmittance, outstanding thermal and electrical conductivities, excellent mechanical strength with flexibility, and superior thermal and photochemical stabilities.[18−25] High transmittance and inertness toward external stimuli such as heat and chemicals are especially important considerations for an encapsulant application. The mechanical properties of conventional encapsulants can be improved by using graphene as a reinforcing filler.

Herein, we report a facile and reliable method for fabricating a graphene-containing encapsulant that improves the long-term stability of an LED. To the best of our knowledge, this is the first attempt to use graphene as a reinforcement in LED encapsulants. Highly stable dispersions of graphene in silicone resin were prepared *via* a solvent-exchange approach. Graphene-containing silicone resin was applied to the LED as an encapsulant, and the performance of these LEDs was analyzed using the moisture sensitivity level (MSL) and anti-sulfur tests.

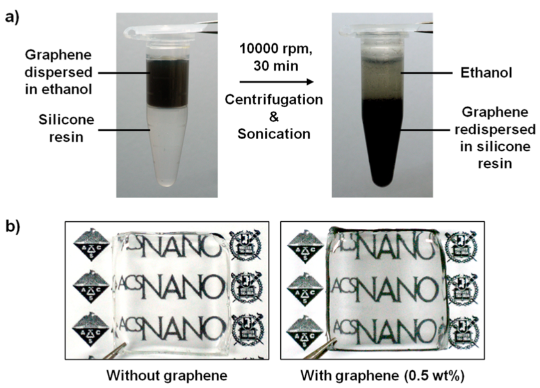


**Figure 1.** (a) Photographs of graphene dispersion at each step of the solvent-exchange method. The dispersion of graphene in ethanol (left image) is centrifuged and sonicated with silicone resin to redisperse graphene layers in silicone resin (right image). (b) Photographs of pristine silicone resin (left image) and graphene-embedded silicone resin (right image). Graphene sheets were highly dispersed in silicone resin without any aggregation.

## RESULTS AND DISCUSSION

**Fabrication of Graphene Sheets Embedded Silicone Encapsulant.** Graphene sheets were successfully introduced into a silicone resin using a solvent-exchange process.[26] Graphene layers obtained after solvent evaporation are difficult to redisperse because of the strong $\pi-\pi$ interactions between the graphene layers.[27,28] However, a highly stable graphene dispersion in a silicone resin can be readily prepared by the solvent-exchange method (Figure 1a). Figure 1b shows that the graphene sheets were readily redispersed without any aggregation at relatively high concentration (>0.5 wt %). This technique ensures that the unique properties of graphene are retained in the silicone resin.

The structure of an LED device is schematically illustrated in Figure 2a. A white LED package is made using a blue LED chip, an encapsulant consisting of a silicone resin and a phosphor, solder used for die bonding, bonding wire for electric connections, and a lead frame and body. A graphene-embedded silicone encapsulant must have the following functions: (1) dissipate heat effectively, (2) protect the LED chip from external environments such as moisture and hazardous gases, (3) improve the mechanical properties, and (4) have high transparency (Figure 2b).

**Multifunctional Graphene Embedded in Encapsulant.** The fundamental role of an encapsulant is to ensure long-term durability by protecting the LED and allowing light emission. High transmittance of the encapsulant is one of most important properties because it has a direct effect on the package efficiency and the reliability of the final product. Silicone resins with various graphene contents are highly transparent in the visible wavelength region (Figure 3a). High transmittance values (>98%) can be achieved over 400−800 nm for

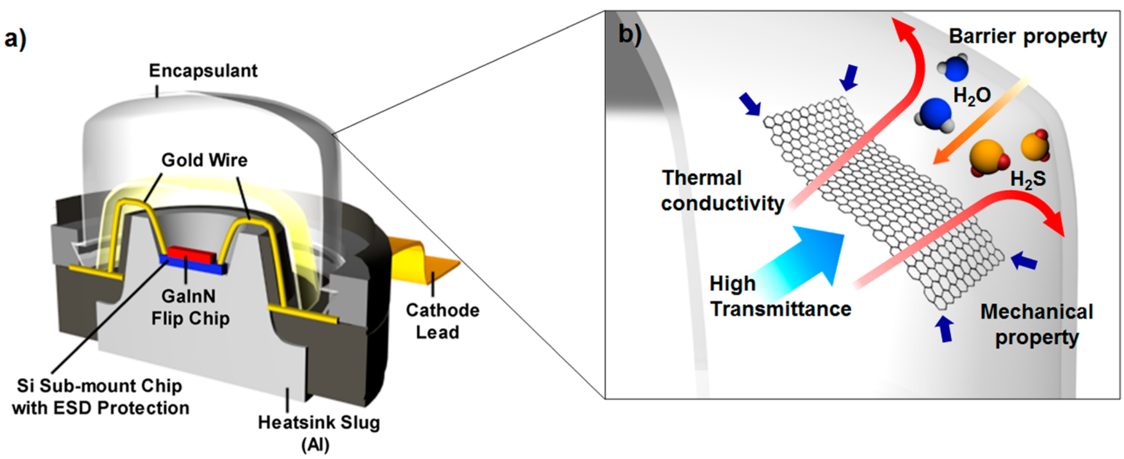


**Figure 2.** (a) Schematic illustrating the white LED device structure. The encapsulant is a protective silicone layer designed to provide improved light performance, extended product life, and environmental protection. (b) Schematic summary of the function of graphene nanosheets in the silicone encapsulant.

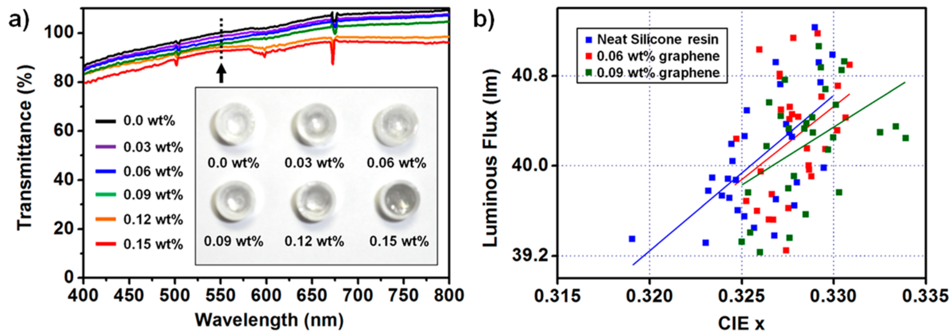


**Figure 3.** (a) UV transmittance of silicone resin with various contents of graphene. Silicone resins containing various contents of graphene are highly transparent in the visible wavelength region. In the visible region of 400−800 nm, high transmittance values of >92% can be achieved with composition of 0.15 wt % graphene at 5 mm thickness. (b) Luminous flux of white LED with neat silicone encapsulant and graphene-embedded silicone encapsulant.

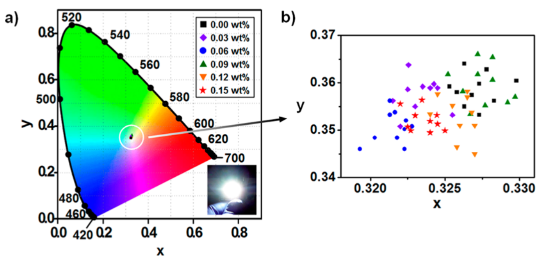


**Figure 4.** (a) CIE 1931 color space chromaticity diagram. CIE coordinates for white LED with an encapsulant composed of neat silicone resin and silicone resin containing various concentrations of graphene. Inset shows a photograph of the LED while generating white light. All devices emit similar wavelength range of white light. (b) Enlarged CIE coordinate.

5 mm thick compositions containing 0.03 wt % graphene. Highly transparent encapsulants can improve light output and lumen maintenance. The luminous flux value of a graphene-filled silicone resin encapsulant was similar to that of an unfilled silicone resin encapsulant (Figure 3b). This was attributed to the high transparency of graphene. Because graphene is very thin (0.34 nm for a single layer), it can be used in an encapsulant with little degradation in the optical properties of the neat silicone resin.[29] The Commission Internationale de L'Eclairage (CIE) 1931 chromaticity coordinates were measured for LEDs having graphene-embedded encapsulants (Figure 4); the values are listed in Supporting Information Table S1. The color coordinates of the LED devices having graphene-embedded encapsulants were similar to those of white LED devices having a neat silicone encapsulant.

To enhance the luminous output, a method must be designed for effective heat dissipation that operates at high junction temperatures over a long time. Residual heat that remains inside the device can cause deterioration in light emission, shorter working lifetime, and high-power consumption. For these reasons, it is crucial to solve the heat dissipation issue to improve the reliability. The conventional silicone resin encapsulant had a low thermal conductivity (1.42 × 100 W cm$^{-1}$ K$^{-1}$), which was insufficient to adequately

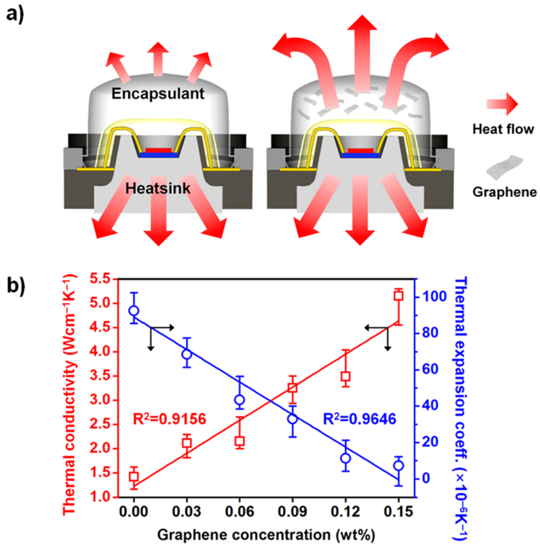


**Figure 5.** (a) Schematic illustrating heat radiation mainly occurring through the heatsink of the encapsulant composed of neat silicone resin (left side) and encapsulant containing graphene (right side). The conventional encapsulant composed of silicone resin has low thermal conductivity, which causes insufficient heat dissipation. On the other hand, the graphene-embedded encapsulant represents remarkable thermal conductivity. (b) Thermal conductivity and thermal expansion coefficient of silicone resin with various concentrations of graphene.

dissipate heat. The graphene-embedded silicone resins, however, had remarkable thermal conductivities (Figure 5a). The thermal conductivity of the encapsulant increased with graphene content because the thermal conductivity of graphene is high (*ca.* 4.84 × 103 W cm$^{-1}$ K$^{-1}$).[30,31] The thermal conductivity of 0.15 wt % graphene-embedded silicone resin was *ca.* 5.15 × 100 W cm$^{-1}$ K$^{-1}$, which is 263% higher than that for the neat silicone resin (Figure 5b).

In addition to high thermal conductivity, dimensional stability upon exposure to high temperatures is also important because LEDs operate at high junction temperatures. A low thermal expansion coefficient provides dimensional stability. Graphene has a negative thermal expansion coefficient (−8.0 × 10$^{-6}$ K$^{-1}$) between 0 and 700 K.[32] The measured thermal expansion

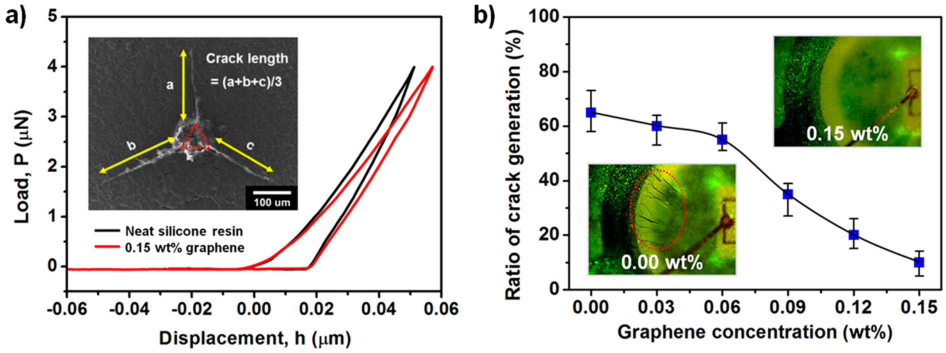


**Figure 6. (a) Load−displacement curve of nanoindentation. The inset image represents the SEM image of indentation on 0.15 wt % graphene-containing silicone resin using the Berkovich indenter with a force of 4.9 N showing a residual indent impression. (b) Ratio of crack generation of encapsulant depending on graphene concentration. The number of cracks was measured in conditions provided by the moisture sensitivity level test (100 °C/24 h, and 60 °C/90% RH/168 h, and reflow three times). The inset images are photographs of the LED with neat silicone encapsulant and 0.15 wt % graphene-embedded silicone encapsulant. The red dotted ellipse indicates cracks generated during the MSL test.**

coefficient of neat silicone resin was $92.5 \times 10^{-6}$ $K^{-1}$, which decreased to $7.1 \times 10^{-6}$ $K^{-1}$ with the addition of 0.15 wt % graphene. This reduction in the thermal expansion coefficient is attributed to the high dispersibility and rigidity of graphene in the silicone resin, resulting in improved dimensional stability.

The mechanical properties of the neat silicone resin and with various concentrations of graphene were investigated to better understand the role of graphene as a reinforcing material. Nanoindentation is commonly used to study mechanical properties on a nanoscale because it provides precise measurements of small-volume deformations.[33−36] The elastic modulus of the graphene-embedded silicone resin increased with increasing graphene concentration because of the high intrinsic modulus of the graphene.[37] The elastic modulus of the silicone resin reinforced with 0.15 wt % graphene was *ca.* 160% higher than that for the neat silicone resin (Table S3). The detailed analytical method for estimating the elastic modulus is described in the Supporting Information. Fracture toughness was measured with a scratch indenter and the variation in fracture toughness with graphene concentration followed the same trend as the Young's modulus (Figure 6a). The fracture toughness of the 0.15 wt % graphene-embedded silicone resin was *ca.* 307% higher than that of the neat silicone resin. The improvements in fracture toughness and modulus are attributed to the uniform distribution of graphene and good interfacial adhesion between the graphene and the silicone resin.

A moisture sensitivity level (MSL) test was conducted to identify the resistance to moisture-induced stress of an LED device having a graphene-embedded encapsulant. The number of cracks was measured under the MSL level 2 condition (100 °C for 24 h, 60 °C/90% RH for 168 h, and reflow three times). As shown in Figure 6b, the rate of crack generation decreased as the graphene content increased. This was ascribed to the excellent mechanical properties and high moisture protection offered by the graphene. These data indicate that the graphene acted as a reinforcing material as well as a barrier to gas penetration.

The ability to protect a device from the external environment is crucial for long-term operation and high luminous efficiency. Encapsulants having poor gas barrier properties can lead to electrode corrosion and device deterioration. The power conversion efficiency of a white LED (including the encapsulant) as a function of graphene concentration was studied using the anti-sulfur test. With this test, hydrogen sulfide gas ($H_2S$) is injected at a concentration of 1000 ppm for 4 h. The test proceeded at 25 °C and 90% relative humidity (RH). Power conversion efficiency increased from 0.085 to 0.12 after the gas barrier test (Figure 7a). This phenomenon is attributed to the size difference between a hydrogen sulfide molecule and a single graphene pore. Because a $H_2S$ gas molecule is larger (at 3.1 Å) than a graphene pore (2.8 Å), it is difficult for $H_2S$ gas to pass through the graphene (Figure 7b).[38] Accordingly, the barrier property was significantly improved with increasing graphene content.

The moisture barrier behavior was determined by measuring the weight increase of a 5 mm thick specimen after soaking in water at 85 °C for 2 h. As the graphene content in the silicone resin increased, the moisture absorption decreased (Figure S1). The water uptake value for the 0.15 wt % graphene-embedded silicone resin was 0.24%, which was considerably lower than that measured for the neat silicone resin (0.27%). This is again explained by the size difference between a water molecule and a single graphene pore; a water molecule is *ca.* 2.8 Å, which is similar to the size of a single graphene pore. Water molecules cannot easily penetrate through the graphene, thereby improving the barrier toward moisture penetration.

Luminous flux was measured over 1000 h to confirm the long-term stability of the LED with the new encapsulants (Figure 8). There was no significant difference in behavior up to 500 h between the encapsulant containing 0.09 wt % graphene and that

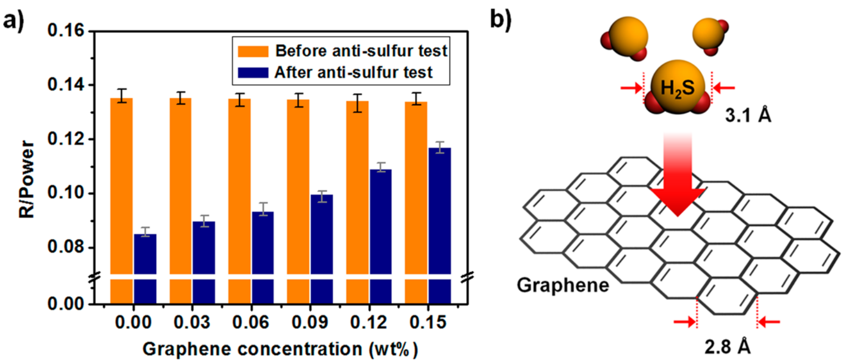


Figure 7. (a) Power conversion efficiency (*R*/power) of white light-emitting diode with graphene-embedded silicone encapsulant after anti-sulfur test (test conditions: 1000 ppm $H_2S$, 25 °C, 90% RH, 4 h). (b) Schematic illustrating the reason why the graphene-embedded encapsulants exhibit superb sulfur gas barrier property. The size of hydrogen sulfide gas is *ca.* 3.1 Å, which is bigger than the size of a single graphene pore (2.8 Å).

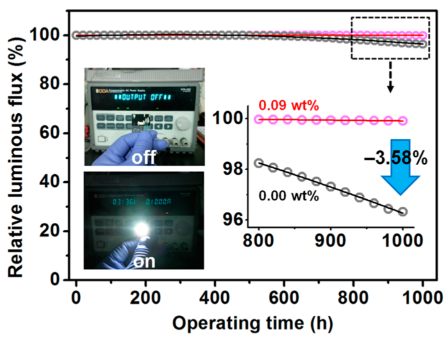


Figure 8. Changes of relative luminous flux for neat silicone encapsulant and 0.09 wt % graphene-embedded silicone encapsulant depending upon operating time. (The initial value of luminous flux is considered to be 100%, and the changes of luminous flux depending on operating time is plotted.) The part shown in the rectangule is enlarged on the inset on the right side. Inset on the left side shows photographs of the LED while the light is turned on or off.

comprising neat silicone resin. However, the relative luminous flux of the LED with the neat silicone encapsulant gradually decreased after 500 h. At 1000 h, the difference in the relative luminous flux between the two devices was *ca.* 3.58%. Introducing graphene into the encapsulant improved the long-term stability of the LED device.

## CONCLUSION

In conclusion, graphene was successfully incorporated into a silicone resin using a solvent-exchange method, and the graphene-embedded silicone was then used to encapsulate an LED. The presence of graphene increased the thermal conductivity by 263% and decreased the thermal expansion coefficient by 92%, without diminishing the optical properties. The barrier properties against hydrogen sulfide gas and moisture were significantly improved. The elastic modulus and fracture toughness of the encapsulant increased by 160 and 307%, respectively. Consequently, addition of relatively small amounts of graphene improved the long-term stability of the LEDs without loss of luminous efficiency.

## MATERIALS AND METHODS

**Materials.** Carbon nanofibers (CNFs) used to prepare graphenes were purchased from Suntel Co. Silicone resin, OE-6630, was obtained from Dow Corning and used as received. Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) was provided by Nichia Co. and used without further purification.

**Preparation of Graphene.** Nanometer-sized graphenes were prepared through transversal cutting of carbon nanofibers. The detailed synthesis procedure for the graphenes is described in our previous paper.[39] The oxidation and reduction processes of graphitized CNFs were carried out according to Hummer's method.

**Synthesis of Graphene-Embedded Silicone Encapsulant.** Stable graphene dispersion in silicone resin can be formed using a solvent-exchange method which is an effective and simple approach. Prepared graphene nanosheets were exfoliated in ethanol by using sonication. The exfoliated graphene in ethanol was mixed with pristine viscous silicone resin. The weight ratios of silicone resin and graphene were 0.03/0.97, 0.06/0.94, 0.09/0.91, 0.12/0.88, and 0.15/0.85. The mixture was then centrifuged and heated to remove ethanol completely. To evenly disperse graphenes in silicone resin, a magnetic stirrer was used at ambient temperature (25 °C) for 1 h and then mixed with YAG phosphor. The YAG:$Y_3Al_5O_{12}$ was obtained from Nichia Co., and the content of YAG phosphor was 5 wt %. After the hardener was added to the mixture, curing proceeded for 3 h at 150 °C. The match ratio of base resin to hardener was 4:1.

**Packaging Process.** The packaging process of white LED was described as follows. At first, a lead frame was cleaned and baked before using it. Using an electrically conductive epoxy, a blue LED chip was put in the middle of a reflector cup of the lead frame, followed by curing at 150 °C for 25 min. The LED die was electrically connected to the lead frame by wire bonding. Then, the reflector cup of the lead frame was filled with graphene-embedded silicone encapsulant to form a flat-top surface. After the curing process by heating, an optical lens was placed on the top surface of the encapsulant.

**Measurement.** Optical properties, including CIE coordinates, current−voltage, luminous flux, and efficiency of devices, were measured with a Spectrascan PR670 spectrophotometer in the forward direction and with Keithley 2400. Optical characteristics were evaluated according to CIE 127. Measurement of LEDs, which was published in 1997 by the Commission Internationale de L'Eclairage (CIE) to set guidelines for measuring the luminous intensity of LEDs, especially part 6; measurement of luminous flux and part 7; and spectral measurement were used to analyze performances of optical properties.

More detailed experiment procedure and characterization are presented in the Supporting Information.

*Conflict of Interest:* The authors declare no competing financial interest.

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*Supporting Information Available:* (1) TEM images of graphene-embedded silicone resin prepared through the solvent-exchange process and direct-mixing method; (2) photographs and optical microscope images of graphene-embedded silicone resin fabricated by the solvent-exchange process and direct-mixing method; (3) UV transmittance of graphene-embedded silicone resin prepared *via* the solvent-exchange process and direct-mixing method; (4) optical properties of white light-emitting diode composed of silicone encapsulant with various graphene contents; (5) properties of silicone resins with various graphene content; (6) moisture absorption value of silicone resin with various graphene content; (7) optical microscope images of light-emitting diode composed of neat silicone encapsulant and 0.15 wt % graphene-embedded silicone encapsulant after moisture sensitivity level (MSL) test; (8) investigation of mechanical properties by nanoindentation; (9) measurement of fracture toughness by indentation; (10) SEM image of indentation impression on neat silicone resin and silicone resin containing 0.15 wt % graphene; (11) mechanical properties of silicone resin with various contents of graphene. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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