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Research on Laser Illumination Based on Phosphor in Metal (PiM) by Utilizing the Boron Nitride-Coated Copper Foams

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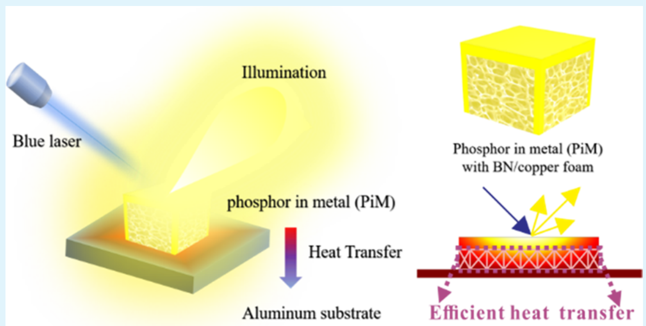
ABSTRACT: Laser-driven illumination has unique advantages in high-power applications. Taking advantage of the valuable experience of light-emitting diodes (LED) development, phosphor in silicone (PiS) is considered to be one of the most potential commercial phosphor converter solutions for laser-driven illumination. However, the thermal quenching of the PiS converter is a bottleneck problem. Herein, a boron nitride (BN)-coated copper foam strategy is introduced for the laser-driven illumination system. The phosphor/silicone is embedded in the designed BN/copper foam to form a phosphor in metal (PiM) converter. Copper foam serves as an internal connected heat transfer channel; the BN coating solves the light absorption problem of the copper foam effectively. Based on this PiM(BN/copper foam) design, the heat dissipation is effectively improved. Under high-power laser excitation (8.13 W), the PiS converter cannot reach thermal equilibrium, and therefore the temperature increases sharply up to 660 °C. In comparison, the thermal performance of an optimized PiM(BN/copper foam) converter is able to maintain excellent stability, where the maximum temperature is only 166.5 °C. The proposed PiM strategy has a maximum temperature that is 493.5 °C lower than that of the reference PiS solution. Due to the superior thermal management, the luminous efficiency of the illumination system is constantly stable at 254 lm/W, though with less phosphor mass; and the related color temperature is about 6000 K all the time. This provides a practical and feasible heat-dissipation solution for high-power laser-driven illumination.



KEYWORDS: *heat dissipation, laser-driven illumination, phosphor in metal (PiM), copper foam, boron nitride, optical stability*

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1. INTRODUCTION

Solid-state lighting (SSL) has shown surprising development speed for general lighting.[1,2] Nowadays, SSL is applied in many fields such as indoor light decoration, outdoor street lamps, car lighting, and so on in our daily life. Light-emitting diodes (LEDs) are an important type of traditional SSL due to their low cost, quick response, low energy consumption, and ecological environmental protection.[3,4] However, LEDs are prone to attenuation of external quantum efficiency (EQE) under high current density, which is known as the “droop effect.”[5,6] Since the droop effect is difficult to eliminate so far, the advantages of LED in high-power lighting are not obvious.

As an emerging alternative, lasers are used for SSL due to their high luminance, narrow bandwidth, directional emission, concentrated light spot, and long lifetime.[7,8] Laser-driven illumination is considered the next-generation high-power lighting potential candidate.[8,9] Differing from LEDs, a laser can maintain high efficiency at an input laser power density of as high as 25 kW/cm^2 and thus allows for an extremely high output luminous flux. The white light of laser-driven illumination is usually obtained by blue laser excitation of yellow phosphor. Taking advantage of the valuable experience of LED development, phosphor in silicone (PiS) is considered to be one of the most potential commercial phosphor converter solutions. However, one of the key challenges for laser-driven illumination is the thermal quenching of the PiS, resulting in a severe light decay problem. Under high-power laser excitation, the PiS suffers instantaneous huge thermal shock and high temperature (>500 °C), resulting in attenuation of phosphor emission and carbonization of the resin.[10,11] The main reason is that the overall thermal conductivity of the phosphor resin is quite low, and therefore the concentrated heat is difficult to conduct to the heat dissipation substrate. As a result, it is difficult to maintain optical stability in a laser-driven illumination system using PiS under high-power laser excitation.

To solve this thermal quenching problem for high-power laser-driven illumination, many research works have been carried out from the following aspects. First, the influence of

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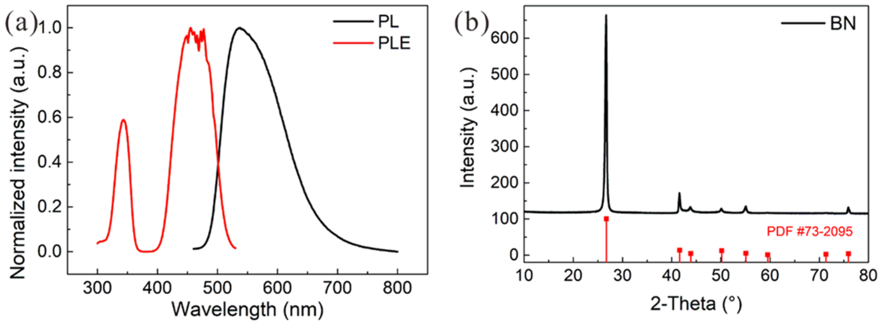

Figure 1. (a) Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of YAG phosphor dispersed in poly(dimethylsiloxane) (PDMS). (b) X-ray diffraction (XRD) of BN nanoparticles.

the excitation method on the thermal stability has been explored. Luo et al.[12] compared the effects of transmissive and reflective laser-driven illuminations and found that the reflective type has advantages in terms of thermal stability. Reflective laser-driven illumination is obtained by laser excitation of a phosphor converter located on a reflective substrate. In addition to mechanical support, the reflective substrate also serves as a heat sink, showing better thermal performance than transmissive laser-driven illumination. Second, to improve the thermal performance of phosphors, new phosphor converters for laser-driven illumination such as single crystals,[13−15] phosphor in ceramics (PiC),[16−18] and phosphor in glass (PiG)[19−21] have been gradually developed. Although single bulk crystal phosphor is a potential all-inorganic converter, the complicated and costly synthesis excludes it from mass production. To obtain PiC or PiG, generally, high-pressure compression and high-temperature sintering processes are inevitable. In addition, the sintering process requires expensive equipment and a long sintering time. A more serious problem is that phosphors usually suffer from quantum efficiency degradation after high-temperature sintering because of strong interfacial reaction with matrix at high temperatures.[22] An effective solution is urgently needed to maintain the intrinsic quantum efficiency of phosphors under a long-time high-power laser thermal accumulation.

Besides the phosphor converter, the design of the heat dissipation component is another research hotspot to improve thermal performance. Kwon et al.[23] fabricated a phosphor−aluminum composite (PAC) fused with low-melting glass for a laser-driven system. Thanks to the PAC, the thermal conductivity of the phosphor converter can be increased to 31.6 W/(m·K). Similarly, Peng et al.[24] introduced a thermoelectric cooler (TEC) in reflective laser-driven illumination. By controlling the input current of TEC, the heat generated from phosphors under high-power laser excitation could be dissipated into the ambient environment. Our team utilized a flattened heat pipe for the high-power laser illumination and confirmed that the heat pipe can lower the phosphor temperature.[25] Adding heat dissipation components to actively dissipate heat is beneficial to reduce the operating temperature. However, even though the dissipation components can spread the heat rapidly, the heat dissipation path from the top surface of the phosphor converter to the heat dissipation substrate is quite long. Because of the lack of effective internal heat transfer channels in the phosphor converter, the concentrated heat could not be quickly and effectively transferred to the bottom heat dissipation substrate.

Herein, a phosphor in metal (PiM) converter based on a boron nitride (BN) coated copper foam strategy is introduced for laser-driven illumination, defined as the PiM(BN/copper foam) converter. Taking advantage of the connected copper skeleton, this special PiM(BN/copper foam) converter owns a superior heat transfer channel inside. This inner channel solves the problem that concentrated heat cannot be effectively transferred to the bottom heat dissipation substrate. Besides, the BN coating makes up for the inherent light absorption defect of copper foams. The effects of different copper foam thicknesses and BN coating mass on the overall laser system are studied, respectively. Then, the PiM converter with the BN/copper foam is optimized and used in laser-driven illumination. Finally, compared with the PiS converter, the light and thermal performance of the PiM(BN/copper foam) converter is analyzed. It is found that the proposed BN-coated copper foam strategy not only maintains the excellent optical performance of laser-driven illumination but also improves the thermal performance effectively.

2. EXPERIMENTAL SECTION

To obtain the required white light for illumination, yttrium aluminum garnet: Ce^{3+} (YAG) phosphor (Shenzhen Looking Long Technology Co., Ltd.) is used in this experiment. The quantum efficiency of YAG is 0.93, determined using an absolute photoluminescence (PL) yield spectrometer (C11347-11, Hamamatsu, Japan). Figure 1a shows the characterization of the photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the YAG phosphor. Both PL and PLE spectra are recorded using a fluorescence spectrophotometer (RF-6000, Shimadzu, Japan). The excitation wavelength of the phosphor is mainly composed of two segments, 310−360 and 400−520 nm. The peak excitation wavelengths are 345 and 455 nm. Therefore, the blue light (450 nm) can effectively excite phosphors. Correspondingly, the emission peak wavelength of the phosphor is 480−720 nm, and the half-peak width is about 110 nm. The wide half-width characteristics of phosphors have an advantage in the color rendering index (R_a) for white light illumination.

Recently, the BN material has attracted widespread attention due to its excellent thermal conductivity.[26,27] The in-plane thermal conductivity of monoisotopic ^{10}B hexagonal boron nitride (h-BN) has been reported to be high as 585 W/(m·K).[28] Figure 1b shows the XRD result of the BN nanoparticles (BN NPs) (Shanghai Xiangtian Nano Materials Co., Ltd.) used in the research. The XRD spectra were measured using an X-ray diffractometer (D8-Advance, Bruker, Karlsruhe, Germany) with a Cu Kα radiation source (λ = 0.15418 nm) over the scanning angle range from 10 to 80°. First, the XRD curve of BN NPs shows sharp characteristic peaks, which proves the high crystallinity and purity of the BN material. Second, the BN NPs correspond to the standard card PDF #73-2095. The main diffraction angles 2θ = 26.7, 41.6, 43.8, 50.1, 55.1, and 75.9° correspond to the

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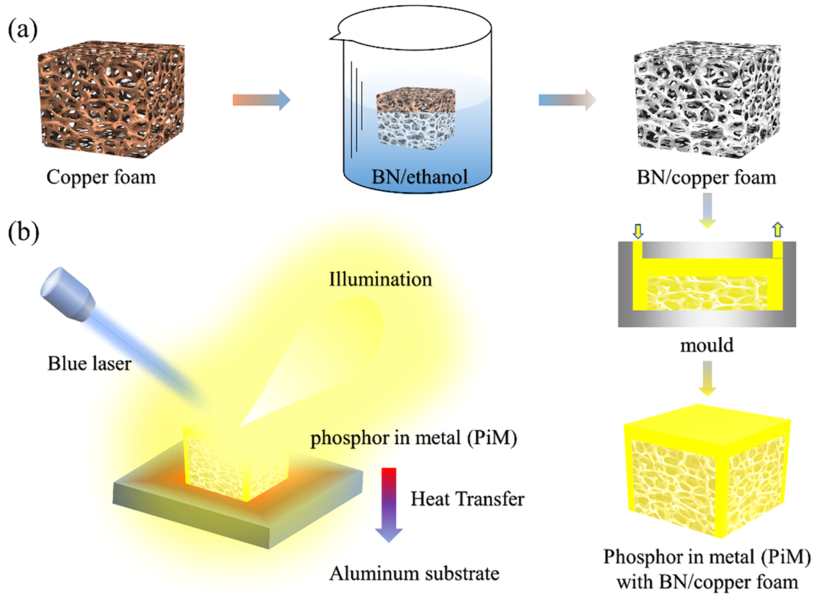

Figure 2. Schematic diagram of (a) preparation process of the phosphor in metal (PiM) converter and (b) reflective laser-driven illumination system using a blue laser to excite phosphors.

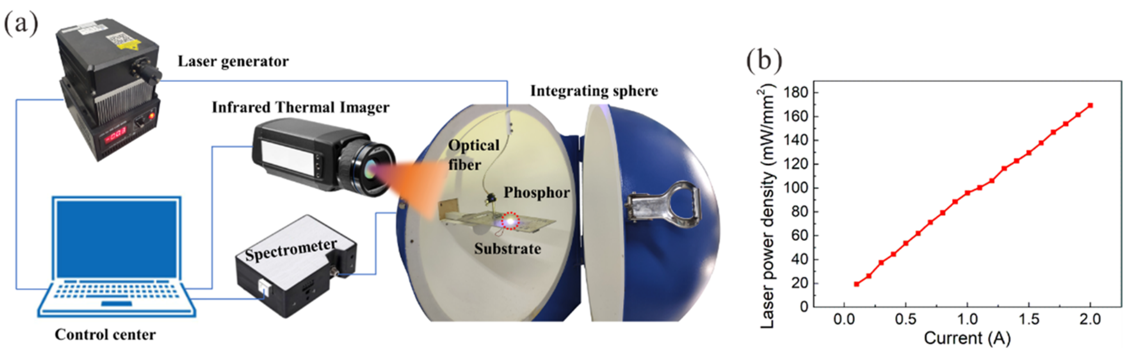

Figure 3. (a) Schematic diagram of the measurement system to obtain the optical and thermal characteristics of laser-driven illumination. (b) Optical power density of the blue laser under different currents.

(002), (100), (101), (102), (004), and (110) crystal planes of BN NPs, respectively. Therefore, the BN NPs belong to h-BN.

The copper foam is a new multifunctional material with a large number of connected copper skeletons distributed in the copper matrix, showing great potential in heat conduction.[29,30] Figure 2a shows the preparation process of a phosphor converter containing a BN/copper foam. First, a copper foam with label of 90 pores per linear inch (90 PPI) is selected and cut into 14.5 × 14.5 mm^2 size, which was purchased from Kunshan Longshengbao Electronic Materials Co., Ltd. Then, BN NPs are dispersed in anhydrous ethanol using an ultrasonic machine at a concentration of 100 mg/mL. The copper foam is soaked in a BN/ethanol solution entirely for 3 min. The volatile ethanol is removed by heating at 100 °C for 5 min. To improve the uniformity of the BN coating and obtain a high BN coating quality, the BN soaking and drying process is repeated several times. As a result, the surface of the copper foam is covered with a layer of white BN coating. Meanwhile, the phosphor/PDMS is prepared by mixing YAG phosphor particles with PDMS (Dow Corning Corporation). The mass concentration of the YAG phosphor powder is 50 wt %. Then, this phosphor/PDMS is vacuumed to remove bubbles for further use. Through a special mold cavity, the BN/copper foam is set on the bottom, and then the cavity is filled with phosphor/PDMS. Utilizing the fluidity of phosphor/PDMS, the pores of the BN/copper foam are gradually filled with phosphor/PDMS. After vacuum curing at 100 °C for 30 min, the required PiM(BN/copper foam) converter is obtained after demolding. In the final prepared PiM(BN/copper foam) converter, phosphor/PDMS is surrounded by the BN/copper foam inside. The size of all samples is 15 × 15 × 2 mm^3. For comparison, a PiS sample with the same size and YAG concentration is also prepared as a reference.

To explore the effect of the designed PiM(BN/copper foam) converter applied in laser-driven illumination, the reflective laser-driven illumination system is adopted, as shown in Figure 2b. Briefly, the blue laser is emitted by the laser generator. The PiM(BN/copper foam) converter is placed on a flat aluminum plate through a thermal conductive grease connection. The laser is incident at a certain angle to excite the phosphor converter. As a result, the white light required for illumination is composed of blue light from the laser and yellow light from the YAG phosphor. Meanwhile, the generated heat is conducted to the aluminum heat sink substrate through the BN/copper foam.

To characterize the optical and thermal performances of the laser-driven illumination, the measurement system is set up, as shown in Figure 3a. The measurement system is mainly composed of a control center, a laser generator (Beijing Laserwave OptoElectronics Technology Co., Ltd), an optical fiber, an integrating sphere, a spectrometer (USB2000+, Ocean Optics, Largo, FL), and an infrared thermal imager (A655SC, FLIR SYSTEMSAB, Switzerland). The typical blue laser is from the laser generator and is adjusted by the control center. The optical characteristics are mainly obtained by collecting the illumination data through the spectrometer; the thermal properties are mainly characterized by infrared thermal imaging.

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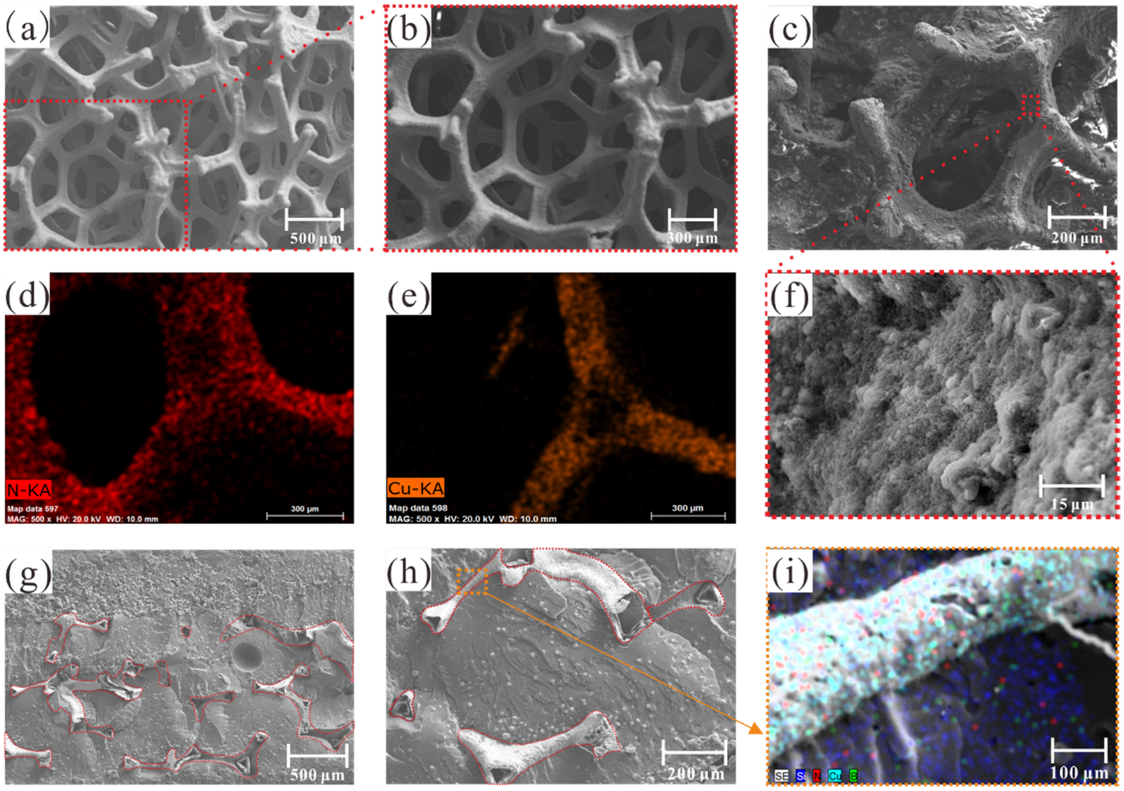

Figure 4. SEM graph of the (a) copper foam and (b) enlarged copper foam, (c) BN/copper foam, and (f) enlarged graph of BN NPs attached to the surface of the copper foam skeleton; mapping of the (d) N element and (e) Cu element on the surface of the BN/copper foam skeleton; (g) SEM graph of the PiM(BN/copper foam) converter and (h) enlarged graph, the red dotted line represents the BN/copper foam skeleton; and (i) mapping of PiM(BN/copper foam) converter.

Figure 3b shows the optical power density of the laser used in this study. The optical power density of the laser has a good linear relationship with the current. In this case, the incident optical power density of the phosphor converter can be adjusted by the laser generator current. The maximum laser power density is 169.4 mW/mm^2 at 2.0 A. In addition, the laser powers are 4.60, 5.09, 6.62, and 8.13 W at 1.0, 1.2, 1.6, and 2.0 A, respectively.

3. RESULTS AND DISCUSSION

Figure 4a,b shows the micromorphology of the copper foam used in this study, which is observed using a scanning electron microscope (SEM-3700N, Hitachi, Japan). The copper foam is composed of a copper framework with high porosity. The size of the copper foam skeleton is about 100−200 μm, and the diameter of the connecting holes is 300−900 μm. The copper foams of different thicknesses (0.5, 1.0, 1.5, 2.0 mm) used in the study have basically similar surface morphologies and slightly different cross-sectional morphologies, as shown in Figure S1. Specifically, a thin copper foam (0.5 mm) is denser, and a thick copper foam (2.0 mm) has more layers of pore density. Further, the corresponding porosity of the copper foam based on weight is calculated. As shown in Figure S2, both weight and porosity increase with the thickness of the copper foam. The porosities of copper foam with 0.5, 1.0, 1.5, 2.0 mm thicknesses are 78.7, 89.1, 92.5, 94.2%, respectively. The interconnected copper skeletons provide superior inner paths for heat conduction, while the large connecting hole reserves enough space for phosphor/PDMS filling. To solve the light absorption problem of copper, BN NPs with high thermal conductivity are introduced. Using the immersion coating method, the copper foam can basically be coated by BN NPs, as shown in Figure S3. After the copper foam is coated with BN NPs, as shown in Figure 4c, the BN/copper foam basically retains the morphology of the copper foam. In contrast, the entire surface of the BN/copper foam is covered with a layer of BN NP "clothing," which leads to a reduction in the diameter of connecting holes. From the enlarged view shown in Figure 4f, BN NPs of the surface of the copper framework are clearly stacked in layers. Moreover, through analyzing the mapping of the N element from BN nanoparticles and the Cu element from the copper foam (Figure 4d,e), it is confirmed that BN nanoparticles are uniformly attached to the surface of the framework. To study the reliability of the BN coating, a vibration test was carried out on the BN/foam copper using a high-speed electric sieving machine (1400 vibrations per minute). As shown in Figure S4, after 42 000 and 84 000 vibrations, the weights of the BN/copper foam are only reduced by 1.6 and 3.2 mg, which is acceptable for application. Finally, after the combination with YAG phosphor, Figure 4g,h proves that the BN/copper foam (red dotted line) is successfully embedded in the phosphor/PDMS as an internal heat conduction channel. More details of the PiM(BN/copper foam) converter are given in Figure S5. The mapping distribution, shown in Figure 4i, also supports that BN NPs are coated on the copper foam, and the BN/copper foam is surrounded by YAG phosphor. In short, a phosphor in metal with the BN-coated copper foam is prepared successfully.

To explore the influence of the copper foam on the optical properties of the laser-driven illumination, a phosphor converter with copper foam of different thicknesses is prepared and compared, defined as the PiM(copper foam) converter.

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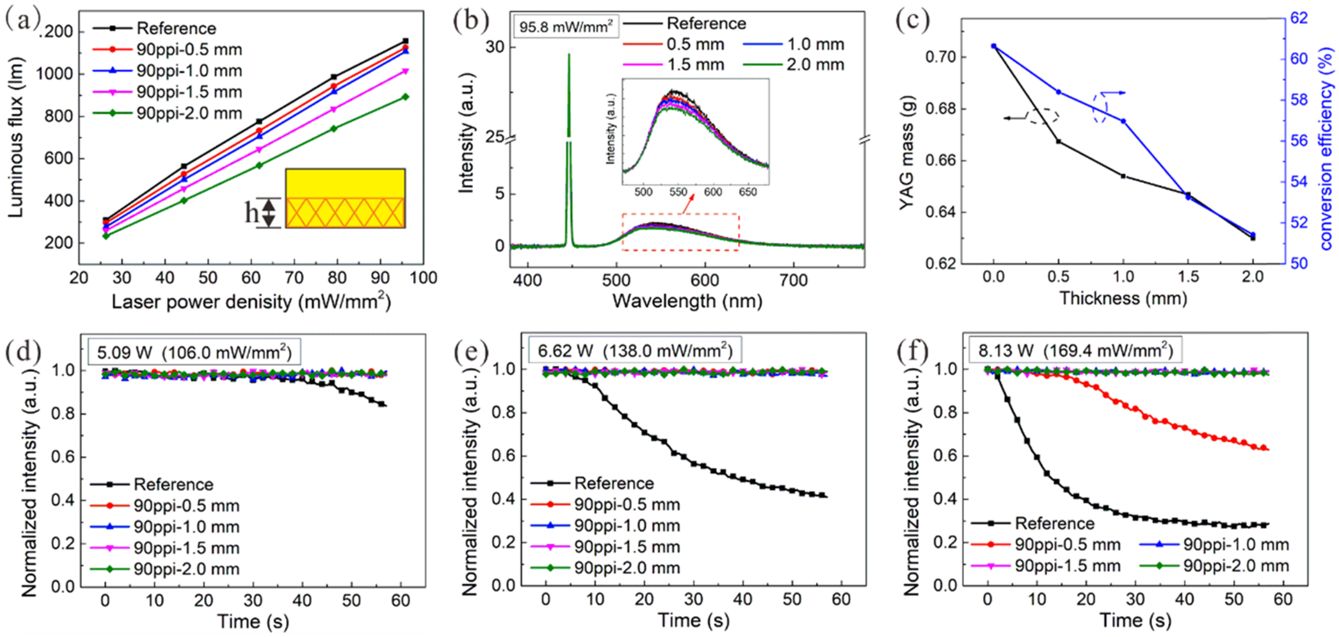

Figure 5. (a) Luminous flux versus laser power density with the copper foam of different thicknesses; (b) electroluminescence (EL) spectra of the samples with copper foam of different thicknesses under 95.8 mW/mm^2 laser power density; (c) YAG mass and corresponding conversion efficiency (CE) versus copper foam thickness; and the normalized emission intensity of the phosphor versus time under high laser powers: (d) 5.09 W, (e) 6.62 W, and (f) 8.13 W.

The reference converter (PiS) only consists of pure phosphor/PDMS and does not contain any copper foam. All samples have a total thickness of 2 mm, and the copper foam is placed at the center of the bottom. As shown in Figure 5a, the luminous flux of all phosphor converters shows a good linear relationship with the increase of the laser power density. This shows that laser-driven illumination has good robust stability, unlike LED lighting that is prone to the droop effect under high current density. When combining the copper foam with different thicknesses, the luminous flux decreases as the thickness of the copper foam increases. Under 95.8 mW/mm^2 (4.60 W laser power) incident laser input, the luminous fluxes of the PiM(copper foam) converter with 0, 0.5, 1.0, 1.5, and 2.0 mm copper foam are 1156.6, 1125.6, 1106.9, 1016.1, and 892.8 lm, respectively. Compared with the reference converter, the light output of the PiM(copper foam) converter with 2.0 mm copper foam is reduced by 22.8%. This indicates that the copper foam is not conducive to the overall light emission. The electroluminescence (EL) spectra, shown in Figure 5b, further illustrates the light emission transformation. The laser emits a sharp blue peak at 445 nm, and the YAG phosphor emits broad yellow light with a 540 nm peak wavelength. As the thickness of the copper foam increases, the blue light gradually increases, while the yellow light gradually decreases.

There are two main reasons for the reduction of light output after applying the copper foam. On the one hand, the copper foam occupies a certain space volume, which leads to a significant decrease in the total amount of phosphors used for excitation. As shown in Figure 5c, the mass of YAG phosphors decreases as the thickness of the copper foam increases. The mass of YAG decreases by 10.56% with 2 mm copper foam than that of the reference converter without copper foam. On the other hand, the copper foam has a relatively strong absorption effect on visible light, which further reduces the light output. The absorption detail will be discussed in subsequence.Further, the conversion efficiency (CE) of YAG samples is calculated by formula 1

$$\mathrm{CE} = \frac{E_y}{E_l - E_b} \times 100\% \tag{1}$$

where E_l, E_b, and E_y represent the incident laser energy, the emitted blue light energy, and the yellow light energy, respectively. The result shows that there is a negative correlation between the CE and the copper foam thickness or YAG mass. The CE decreases from 60.6% (reference converter) to 51.4% with a 2.0 mm copper foam.

Although the introduction of pure copper foam is not conducive to light emission, the stability of optical emission intensity under high-power laser excitation has been significantly improved. This improved stability is supported by experimental results shown in Figure 5d−f. The emission intensities of the reference converter without copper foam (PiS) are reduced by 16.3, 59.1, and 71.4% under 5.09 W (106.0 mW/mm^2), 6.62 W (138.0 mW/mm^2), and 8.13 W (169.4 mW/mm^2) laser powers, respectively, after lighting of 1 min. It is speculated that under high-power excitation, the phosphor suffers extreme heat concentration, which causes the optical attenuation problem. In contrast, except for the 0.5 mm sample under 8.13 W (its luminous intensity is attenuated by 37.3%), the luminous intensity of PiM(copper foam) converters shows excellent stability. These results indicate that the stability of the laser-driven illumination system is significantly enhanced with the introduction of copper foam. Besides, copper foam with higher thickness is conducive to this stability effect. However, considering the negative performance of the copper foam to the light output, it is recommended to choose a balanced thickness of 1.0 mm for further experiments.To solve the severe light absorption characteristics of the copper foam, the BN NPs with high thermal conductivity are coated on the surface of the copper foam

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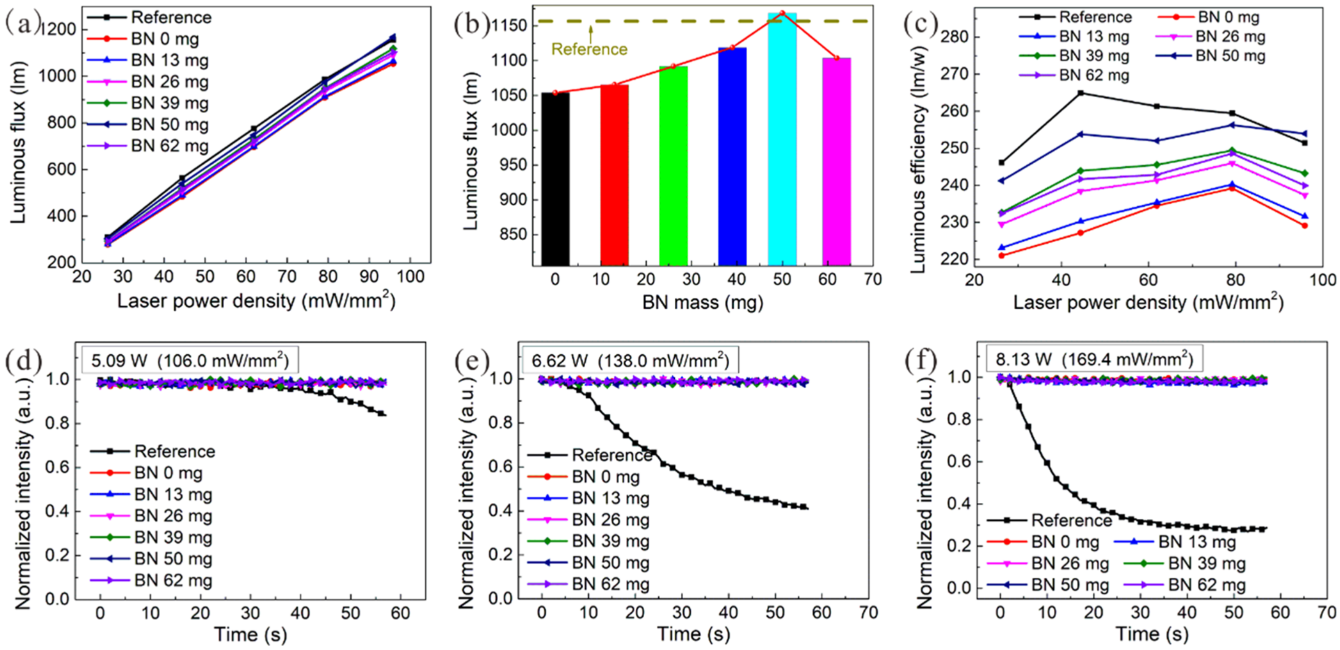

Figure 6. (a) Luminous flux of samples with different BN masses versus laser power density; (b) luminous flux of different samples under 95.8 mW/mm^2 laser power density; (c) luminous efficiency of samples versus laser power density; and the normalized emission intensity of the phosphor versus time under high laser powers: (d) 5.09 W, (e) 6.62 W, and (f) 8.13 W.

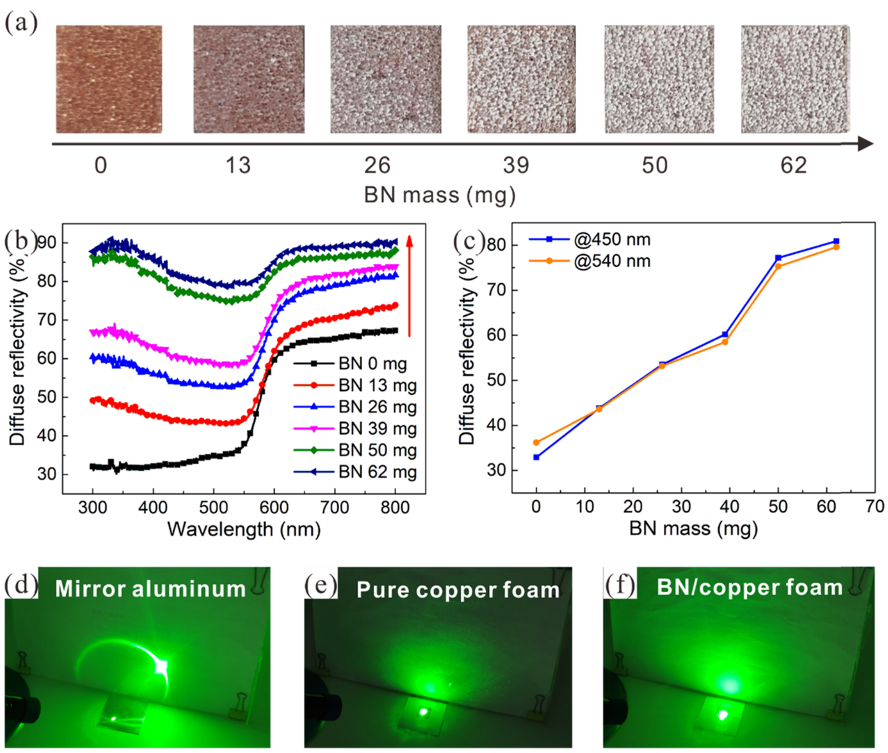

Figure 7. (a) Physical graph of the copper foam with different BN masses; (b) diffuse reflectivity of the BN/copper foam with different BN masses; (c) diffuse reflectivities of the BN/copper foam under typical 450 and 540 nm; and spot pattern of (d) mirror aluminum, (e) pure copper foam, and (f) BN/copper foam under the incidence of green laser pointer.

framework. Different BN adhesion masses are obtained by repeating the BN/ethanol soaking process several times. From Figure 6a, basically, the reference converter (PiS) shows the highest luminous flux, and the PiM(copper foam) without BN NPs shows the lowest emission intensity. After covering the copper foam frame with a BN coating, the luminous flux increases gradually as the weight of the BN NPs increases. The emission intensity is the highest at the BN weight of 50 mg, and then it decreases when the BN weight reaches 62 mg. With excessive BN coating, the pores of the copper foam would be directly connected by BN NPs. Then, it is difficult to be filled by the phosphor/PDMS. Specifically, as shown in Figure 6b, the luminous fluxes of reference PiM(BN/copper foam) with 0, 13, 26, 39, 50, and 62 mg of BN NPs are 1156.6, 1053.7,

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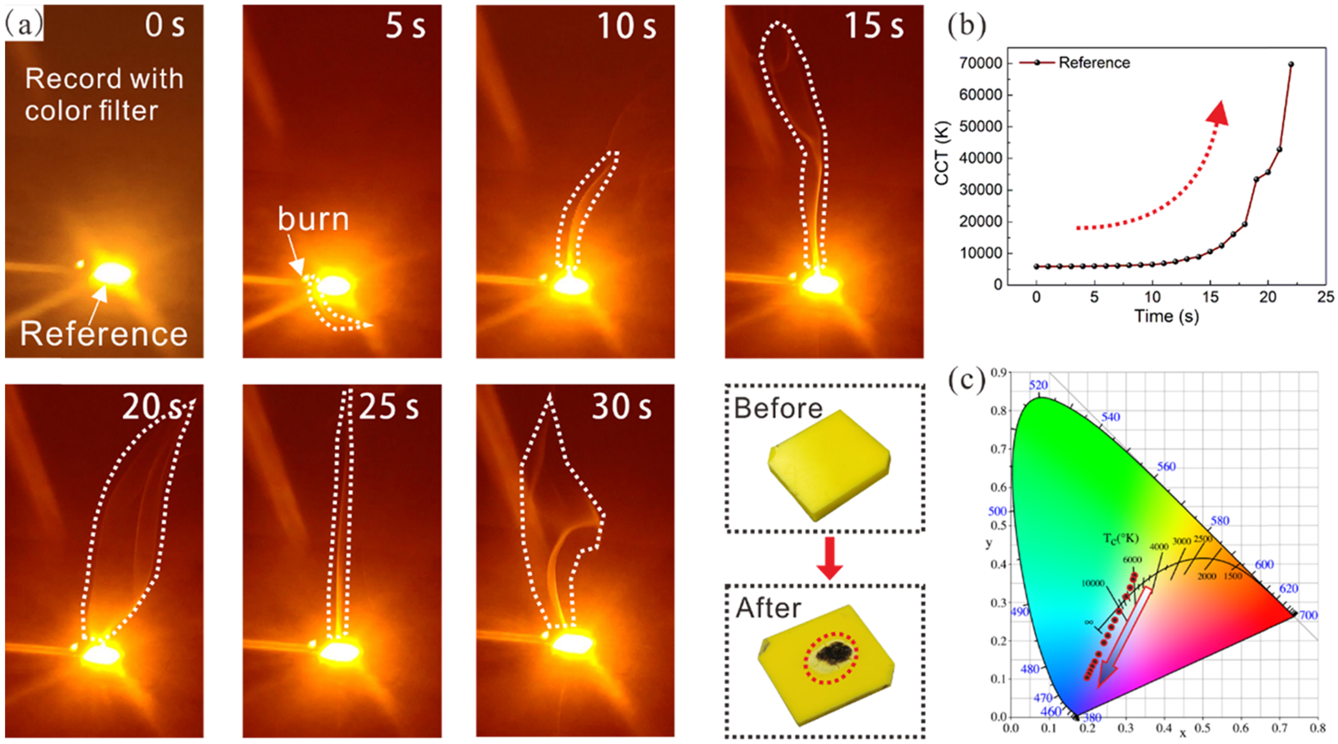

Figure 8. (a) Rapid thermal quenching process of the reference converter under 6.62 W laser excitation, which is recorded with a color filter due to the high brightness, and the white dotted line represents the smoke from burning. (b) Related color temperature (CCT) and (c) the color coordinate transformation for the reference converter during the experiment.

1065.3, 1091.8, 1118.8, 1168.3, and 1103.7 lm under 95.8 mW/mm^2 laser power density, respectively. Therefore, the emission intensity of the PiM(BN/copper foam) converter with 50 mg of BN NPs is improved by 10.8% than that of the PiM(copper foam) sample, and it returns to the original luminescence intensity as the reference converter. This proves that the BN coating has an advantage in improving the light output for laser-driven illumination. Correspondingly, the luminous efficiency (LE) (η) of different samples is calculated according to formula 2, where Φ represents the luminous flux and P_l stands for the incident laser optical power. All of the samples show high luminous efficiency of over 220 lm/W, supporting the great potential advantage of laser-driven illumination in high-power lighting applications. The luminous efficiency (η) of the PiM(BN/copper foam) converter with 50 mg of BN NPs is relatively stable under various laser power densities, while the luminous efficiency of the reference converter has a slight downward trend from 44.4 mW/mm^2 laser power density. This supports that the PiM(BN/copper foam) design is relatively stable for application.

$$\eta = \frac{\phi}{P_l} \times 100\% \tag{2}$$

Further, the effect of the BN coating on the stability of the optical emission intensity of PiM(BN/copper foam) samples is explored in detail. As shown in Figure 6d−f, except for the light decay of the reference PiS sample, all other PiM(BN/copper foam) converters maintain excellent luminous intensity stability at high laser powers of 5.09, 6.62, and 8.13 W. This shows that the introduction of the BN coating maintains the excellent thermal conductivity of the original copper foam. As excessive BN NPs would lead to a decrease in light output, the PiM(BN/copper foam) converter with 50 mg of BN NPs is the optimization experimental result. Besides, compared with the reference converter, similar luminescence intensity is obtained using less YAG phosphors in the optimized PiM(BN/copper foam) converter. Therefore, this BN/copper foam strategy has an advantage in the consumption of rare earth element YAG phosphors.

To explore the internal mechanism of the introduction of BN on light intensity enhancement, copper foam with different BN mass coatings is prepared. From Figure 7a, the BN/copper foam covers the BN NPs and appears white as the BN mass increases. On one hand, it is speculated that the surface reflectivity has increased. To confirm this hypothesis, their diffuse reflectivity is tested and shown in Figure 7b,c. Without BN coating, the copper foam has the lowest diffuse reflectivity, and the diffuse reflectivity of the blue-light band is much lower than that of the yellow-light band. The diffuse reflectivity of the BN/copper foam is improved gradually as the BN mass increases. Specifically, as concluded in Figure 7c, the diffuse reflectivities of the pure copper foam are only 32.9 and 36.2% under typical blue (450 nm) and yellow (540 nm) light, respectively, which supports the light loss of the pure copper foam absorption. With 62 mg of the BN coating, the diffuse reflectivities of the BN/copper foam are increased to 80.9% (@450 nm) and 79.6% (@540 nm). Therefore, the introduction of BN nanoparticles has greatly reduced the light absorption loss of the copper foam by improving the total diffuse reflectivity. On the other hand, the introduction of the BN/copper foam has an excellent scattering effect. As shown in Figure 7d−f, when the green laser pointer hits the mirror aluminum, it shows an obvious reflection halo, while the BN/copper foam sample shows a clear diffusion ring. Moreover, the BN/copper foam with higher diffuse reflectivity exhibits stronger spot brightness than the pure copper foam. This

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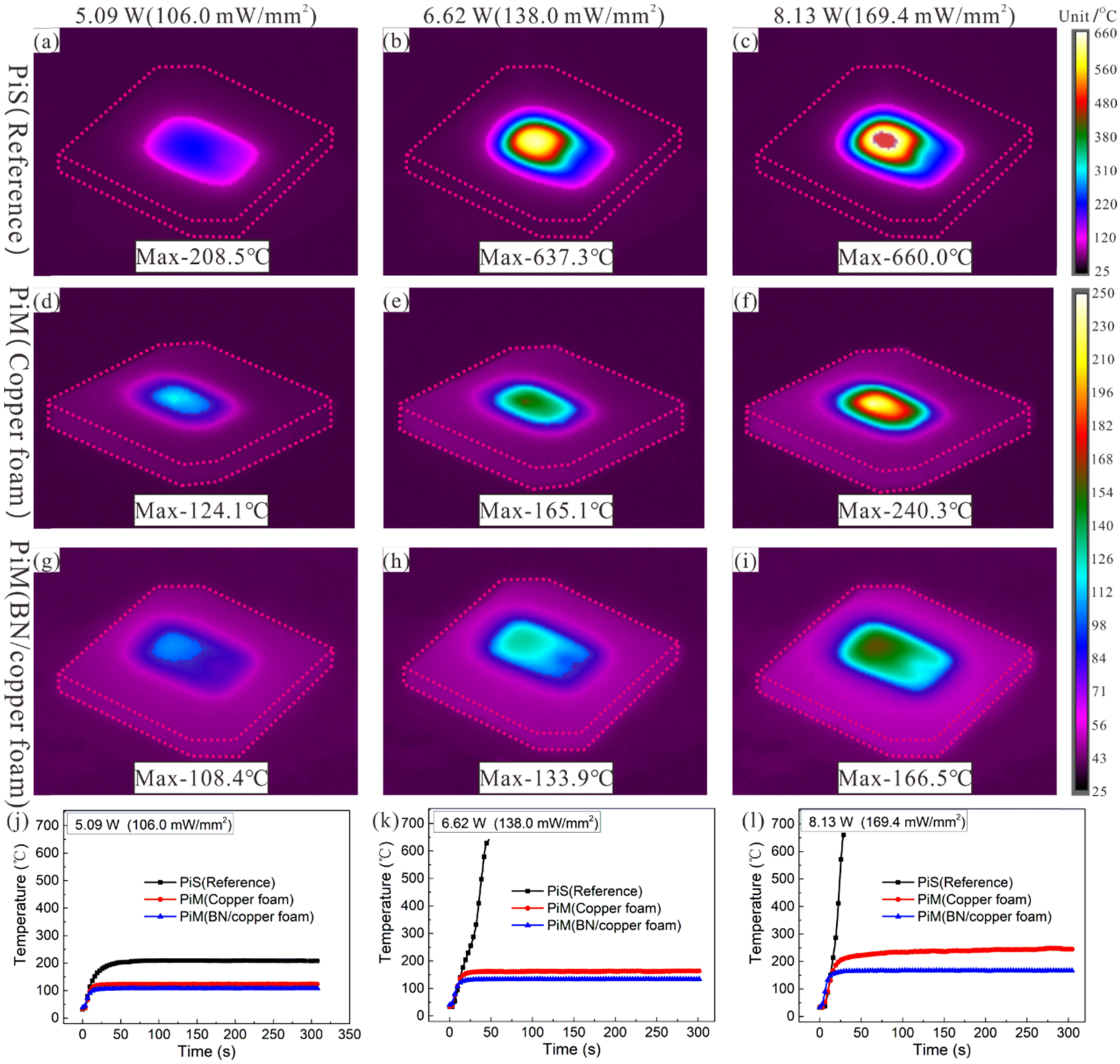

Figure 9. Infrared image of the reference converter under (a) 5.09 W, (b) 6.62 W, and (c) 8.13 W laser excitation; infrared image of the copper foam phosphor converter under (d) 5.09 W, (e) 6.62 W, and (f) 8.13 W laser excitation; infrared image of the BN/copper foam phosphor converter converter under (g) 5.09 W, (h) 6.62 W, and (i) 8.13 W laser excitation; and maximum surface temperature versus time under (j) 5.09 W, (k) 6.62 W, and (l) 8.13 W laser excitation.

scattering effect is also supported by the bidirectional reflectance distribution function (BRDF) test, as shown in Figure S6. With the enhancement of BN mass, the scattering effect of BRDF of the BN/copper foam has been enhanced, and the BRDF scattering distribution tends to be stable with 50 mg of BN. Based on the scattering effect of the BN/copper foam, the blue light of the laser can be dispersed more to excite more yellow phosphors. In short, the BN/copper foam not only improves the overall diffuse reflectance to reduce the original light absorption defects of copper foam but also improves the scattering effect to excite more phosphor, thereby increasing the overall luminous flux of laser-driven illumination. Besides, BN NPs have superior intrinsic thermal conductivity and are believed to contribute to thermal performance.[26]

After the above system optimization, the optimized PiM(BN/copper foam) converter (thickness = 1.0 mm and BN mass = 50 mg) is obtained. For further exploration, the PiS(reference) converter, the PiM(copper foam) converter, and the optimized PiM(BN/copper foam) converter are compared below. It should be noted that the overall size of these three samples is the same (15 × 15 × 2 mm^3). The copper foam used in the PiM(copper foam) or PiM(BN/copper foam) converter is the same (14.5 × 14.5 × 1 mm^3).

Laser-driven illumination has important potential value in high-power lighting applications. First, the PiS converter is applied for high-power illumination. Unfortunately, when the

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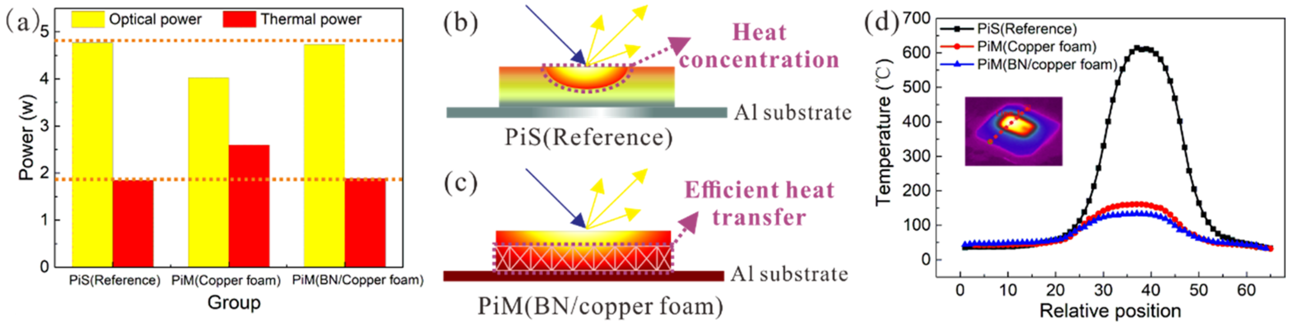

Figure 10. (a) Calculation of optical power and thermal power; schematic diagram of heat conduction of (b) the PiS(reference) sample and (c) the PiM(BN/copper foam) sample used for laser-driven illumination; and (d) temperature profile of different samples under 6.62 W laser power.

PiS sample is excited by large laser optical power (6.62 W, 138.0 mW/mm^2), a serious rapid thermal quenching process occurs. Detail is recorded in Video 1. It should be noted that the color filter was adopted during recording due to the high brightness. As shown in Figure 8a, after only 5 s, the PiS converter begins to burn, and the phenomenon is more obvious in less than 30 s. This is because the heat dissipation problem of the PiS converter is unbearable under high-density laser concentration, and then the rapid thermal quenching occurs. After the experiment, obvious carbonization appears on the surface of the PiS converter. More seriously, this issue is a fatal blow to laser-driven illumination. From Figure 8b, the related color temperature (CCT) increases rapidly, shifting from the original 5845−69 736 K within 25 s; then, the related CCT exceeds the CCT measurement range. This means that the initial white light shifts during the quenching process, and finally, it can not be recognized as white light. This is unacceptable for illumination. Figure 8c shows the corresponding color coordinates. The color coordinate shifts from initial white light (0.326, 0.370) to blue light (0.199, 0.103), which indicates the yellow light decreases seriously. In short, the PiS sample could not maintain high-quality white light due to thermal quenching under high-power laser excitation.

It is speculated that thermal quenching of the PiS sample is caused by excessively high temperatures. Therefore, the thermal performances of the PiS(reference), PiM(copper foam), and PiM(BN/copper foam) converters for laser-driven illumination are tested using an infrared thermal imager. Three incident laser powers are adopted here, 5.09, 6.62 and 8.13 W, corresponding to the laser power densities of 106.0, 138.0, and 169.4 mW/mm^2, respectively. The result is shown in Figure 9. All of the samples show higher temperature as the excited current increases, and the PiS converter shows the maximum temperature increase. From 5.09 to 6.62 W incident laser power, the maximum temperature of the PiS converter increases by 428.8 °C. To be noted, the maximum temperature limit of the infrared thermal imaging camera is 660 °C, so the actual maximum temperature of the PiS converter may be higher than 660 °C at 8.13 W. This proves the PiS converter suffers an extremely high-temperature thermal shock, resulting in the quenching problems. After introducing the designed copper foam, the temperature decreases effectively. The maximum temperature of all of the phosphor converters with copper foam or BN/copper foam is reduced to less than 250 °C. Under the same incident laser power, according to the surface temperature from high to low, the order is as follows: PiS converter > PiM(copper foam) converter > PiM(BN/copper foam) converter.

To analyze the temperature change process in detail, the maximum surface temperature curve versus time is summarized and shown in Figure 9j−l. Under 5.09 W laser power (106.0 mW/mm^2), all three samples can stay at thermal equilibrium at last. After stabilization, the highest temperatures of the PiS, PiM(copper foam), and PiM(BN/copper foam) converters are 208.5, 124.1, and 108.4 °C, respectively. The highest temperature of the BN/copper foam strategy is 100.1 °C lower than that of the reference converter. When increasing the laser power like 6.62 and 8.13 W, the thermal balance of the PiS sample is completely out of control with an explosive heating curve, reaching as high as 660 °C in only 28 s under 8.13 W laser power. In contrast, the highest temperatures of the PiM(copper foam) and PiM(BN/copper foam) converters are 240.3 and 166.5 °C under 8.13 W laser power (169.4 mW/mm^2). Therefore, the proposed BN/copper foam strategy has a maximum temperature that is 493.5 °C lower than that of the PiS converter solution. These experimental results prove that the copper foam improves the thermal conductivity of the phosphor, which effectively improves the thermal performance. Moreover, the PiM(BN/copper foam) converter shows the best thermal performance.

To find out the internal mechanism for the best thermal performance of the PiM(BN/copper foam) converter, first, the optical power (P_o) and thermal power(P_t) are calculated separately according to formula 3, where P_l represents the incident laser power. The result is shown in Figure 10a. The PiM(copper foam) converter owns the lowest optical output and the highest thermal power. Meanwhile, it shows that the reference and PiM(BN/copper foam) converters have similar optical output and thermal power. This is attributed to the BN coating. The introduction of BN NPs leads to an effective increase in light output, which reduces the total amount of heat for the PiM(BN/copper foam) converter. Second, although the reference and PiM(BN/copper foam) converters have similar thermal power, the thermal diffusion performance is completely different. The thermal conductivity is shown in Figure S7. The schematic diagram of heat conduction is shown in Figure 10b. Since the thermal conductivity of the PiS converter is as low as 0.32 W/(m·K), the laser heat is highly concentrated on top. The heat is difficult to transfer to the bottom heat-dissipating aluminum substrate, and therefore the rapid temperature increase leads to thermal quenching.

$$P_l = P_o + P_t \quad (3)$$

In contrast, in the PiM(BN/copper foam) converter, thanks to the copper foam, the thermal conductivity could increase to 1.11 W/(m·K), which is 3.5 times of the PiS converter. In this

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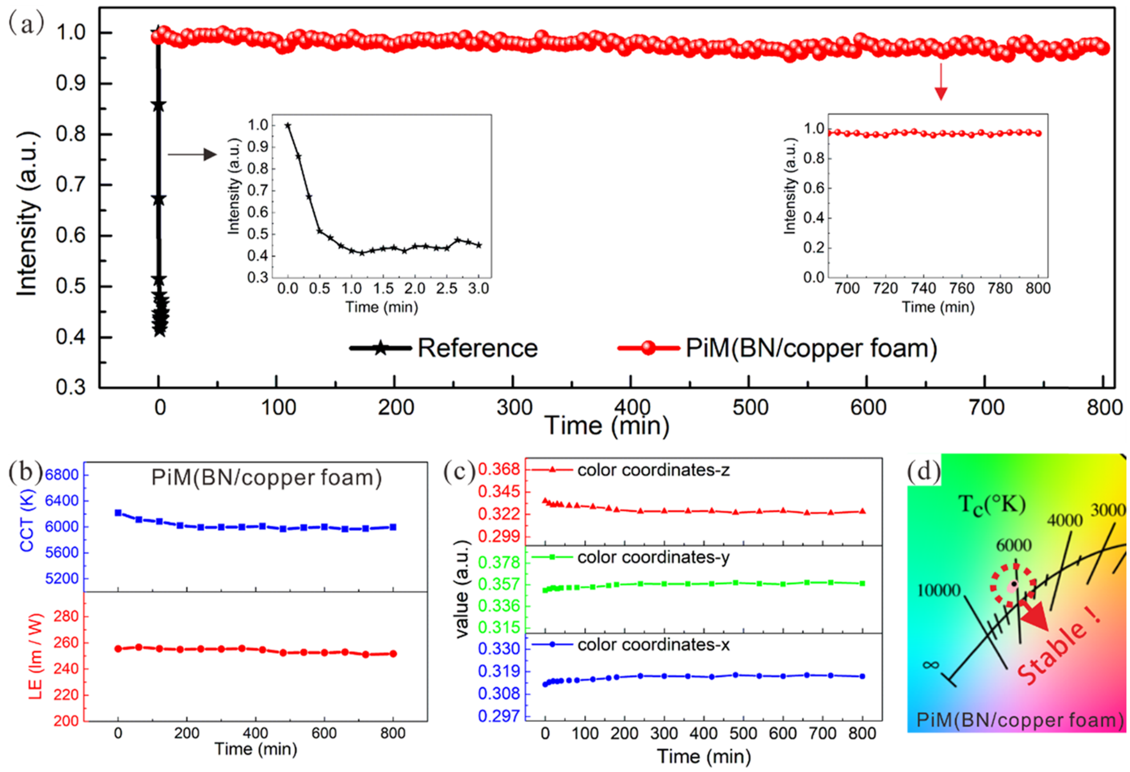

Figure 11. (a) Stability test in a long-time working state under 6.62 W laser power. (b) CCT and luminous efficiency (LE), (c) color coordinates value, and (d) color coordinate spots of the optimized PiM(BN/copper foam) converter versus time.

case, the heat flux can be quickly and efficiently conducted to the heat dissipation aluminum substrate through the internal connected copper foam framework. In other words, the BN/copper foam skeleton acts as a superior inner heat conduction path, which effectively improves the thermal performance of the overall system. The temperature profile, shown in Figure 10c, supports this improved heat dissipation property of the copper foam. Without copper foam, the PiS converter suffers a significant thermal concentration impact. Both the pure copper foam and the BN/copper foam have a more uniform thermal spatial distribution. Therefore, the PiM(BN/copper foam) design not only maintains the initial light output performance in terms of light but also has great advantages in terms of thermal performance.

To verify the actual performance of the designed PiM converter, a long-term lighting test under 6.62 W laser power (138.0 mW/mm^2) is carried out to simulate actual application scenarios. The result is shown in Figure 11. From Figure 11a, the emission intensity of the reference PiS converter shows a sharp downtrend. The emission intensity of the reference converter decreased by 60% in only 3 min, which is unacceptable for practical applications. In contrast, the proposed phosphor converter with optimized BN/copper foam has exhibited superior long-term luminescence stability. After 800 min of continuous lighting, the emission intensity of the PiM(BN/copper foam) converter remains basically unchanged. Correspondingly, as shown in Figure 11b–d, the related color temperature (CCT), the luminous efficiency (LE), and the color coordinates of the BN/copper foam sample also maintain excellent stability under the long-term excitation of the laser for 800 min. The color temperature of white light has been about 6000 K all the time; the luminous efficiency has been maintained at a high efficiency of about 254 lm/W; the *x*, *y*, *z* color coordinates remain basically stable; and the corresponding color coordinates in the 1931CIE standard basically remain on the same spot. In short, thanks to the excellent thermal performance, the proposed laser-driven illumination with the designed PiM(BN/copper foam) converter is believed to be stable in optics, which has excellent potential in laser-driven illumination applications.

4. CONCLUSIONS

To solve the problem of thermal quenching of the phosphor/silicone converter in high-power laser-driven illumination applications, copper foam with BN coating is introduced into the phosphor converter to form a phosphor in metal (PiM) structure. The three-dimensional interconnected copper foam framework is embedded in the PiM converter to form a good inner thermal conductive channel. Meanwhile, because the pure copper foam occupies a certain volume and absorbs light, the luminous intensity of the system is reduced. Further, the BN nanoparticles are introduced to solve this conflict. The BN coating with high diffuse reflectivity and the scattering effect results in the effective recovery of the luminous intensity. After system optimization, the PiM converter containing the BN/copper foam with a thickness of 1.0 mm and 50 mg of BN NPs has the best comprehensive performance. Without the BN/copper foam, the reference converter (PiS) is carbonized in only 28 s under the excitation of an 8.13 W blue laser, suffering severe thermal quenching. Infrared imaging shows that the maximum temperature of the PiS converter surface is as high as 660.0 °C under 8.13 W excitation; and the thermal equilibrium state cannot be obtained. In contrast, the maximum surface temperature of the optimized PiM(BN/copper foam) phosphor converter after equilibrium is only 166.5 °C. The proposed strategy has a maximum temperature that is 493.5 °C

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lower than that of the reference converter solution. In addition, through long-term practical testing, the PiM(BN/copper foam) converter exhibits excellent optical stability, with a luminous efficiency of 254 lm/W and a related color temperature of about 6000 K all the time. This shows that the proposed BN/copper foam strategy has superior practical application value under the high-power laser-driven illumination.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c03746.

Optical morphology, microsurface morphology, and cross-sectional morphology of the copper foam with different thicknesses; weight and corresponding porosity of the copper foam with different thicknesses; optical morphology, microsurface morphology, and mapping distribution of the BN/copper foam and the PiM(BN/copper foam); high-speed vibration reliability test of the BN/copper foam; BRDF performance of the BN/copper foam with different BN masses; and thermal conductivity of three samples, PiS(reference), PiM(Copper foam), and PiM(BN/copper foam) converters (PDF)

Thermal quenching process of the PiS converter under 6.62 W laser irradiation (Video 1) (MP4)

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Notes

The authors declare no competing financial interest.

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