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Fabrication and remote laser ignition of Al/CuO energetic nanocomposites incorporated with functional dyes for enhanced light absorption

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ABSTRACT

In this study, we investigated the effects of dyes on the laser ignition characteristics of Al nanoparticles (NPs) and CuO NPs-based energetic nanocomposites. Various functional dyes (e.g., N-719, rose bengal (RB), methylene blue (MB)) were employed as a light absorbing medium for Al/CuO energetic nanocomposites. According to UV–vis spectrometer analysis results, N-719, RB, and MB dyes had relatively strong light absorption in the blue, green, and red wavelength ranges, respectively. The results of red, green, and blue (RGB) laser ignition tests for various dye-coated Al/CuO composites demonstrated that the laser ignition threshold power density for the composites gradually decreased with increasing dye concentration. To test the possibility of selective optical ignition, the various dye-coated Al/CuO composites were irradiated using RGB laser beams operating with a fixed and relatively low power density. The results showed that the N-719-, RB-, and MB-coated Al/CuO composites were only successfully ignited under the condition of blue, green, and red laser beam irradiation, respectively. This suggests that energetic nanocomposites coated with special dyes could be employed as potential igniters and heat energy sources, the reactions of which are initiated by selective and remote light-energy irradiation, in various thermal engineering applications.

Introduction

Nanoenergetic materials (nEMs) consist of nanoscale fuel metal and oxidizer particles, and their internal chemical energy is rapidly converted into thermal energy when ignited [1–5]. To initially ignite nEMs, various means such as mechanical friction, electric sparks, hot wires, and flames are often used [6–14]. However, these methods require the ignition source and nEMs to be very close to each other, and the final results are also strongly affected by various environmental factors (e.g., temperature, pressure, and humidity) during the ignition process.

There have been several recent studies on the effective ignition of nEMs employing optical sources such as flash and laser beams; these studies demonstrated that this type of technique can provide many advantages in terms of remote and reliable ignition, and insensitivity to various environmental factors [15–29]. However, the flash ignition of nEMs makes it hard to control the light irradiating area and remote ignition, because flash is not easy to condense; therefore, the flash light source should be located near nEMs for initial ignition. Alternatively, using various laser beams as a condensed light source offers the advantages of controllable power and wavelength. To date, several research groups have used high-power laser beams to demonstrate the various ignition characteristics of nEMs [19–23,30,31]. However, high-power laser sources have inherent problems related to the cost, portability, volume, and complexity. A potential method for easy and versatile ignition is the utilization of relatively low laser power to coat nEMs with optically sensitized materials to ensure that the irradiated light energy can be absorbed and subsequently transformed into sufficient heat energy via a photothermal effect, thus enabling the successful ignition of nEMs.

Abbreviations: NP, nanoparticle; nEM, nanoenergetic material; RB, rose bengal; RGB, red green, and blue; MB, methylene blue; TEM, transmission electron microscopy.

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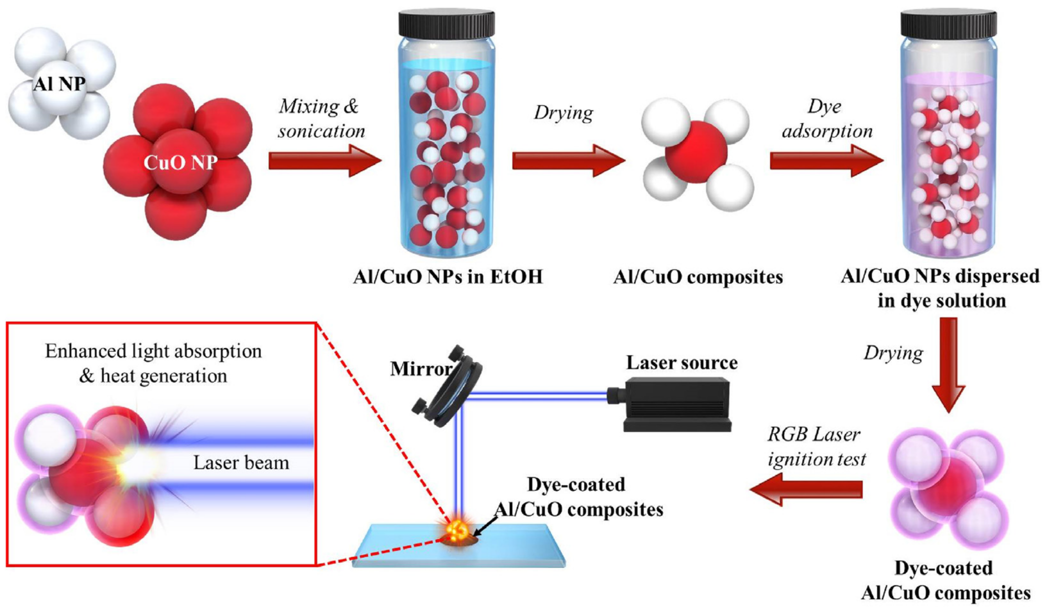

Fig. 1. Schematic diagram of the fabrication method for the dye-coated Al/CuO NP-based nEM composites and the ignitability test using RGB laser beams.

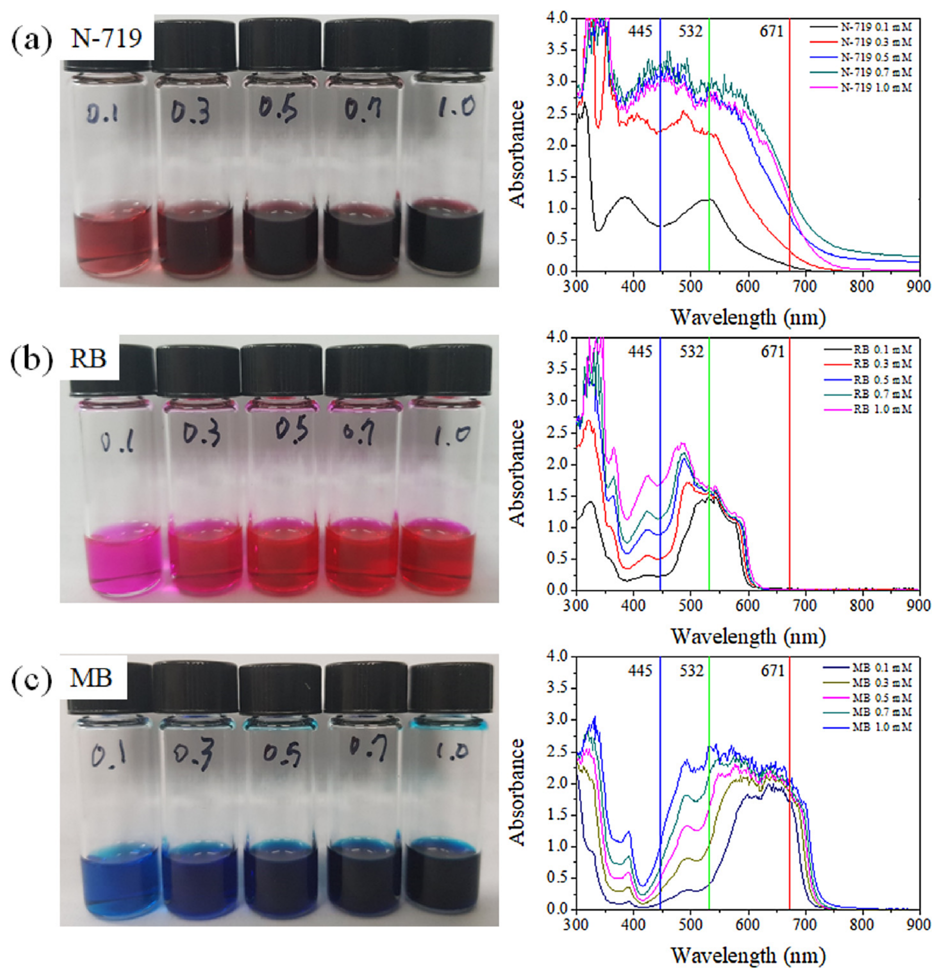

Fig. 2. Images and UV–vis spectra of (a) N-719, (b) rose bengal (RB), and (c) methylene blue (MB) solutions with different molar concentrations.

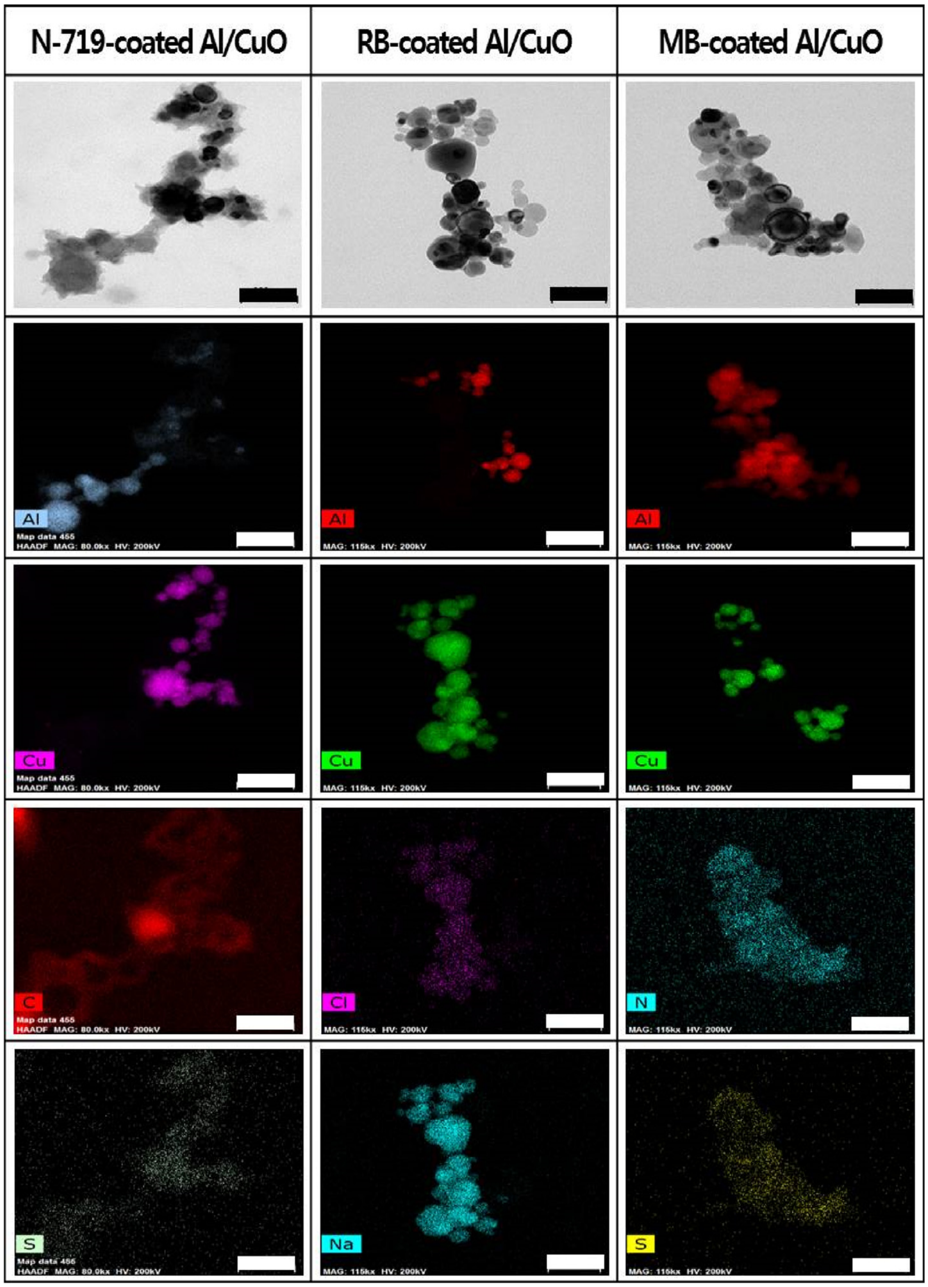

Fig. 3. TEM and elemental mapping images for the Al/CuO composites coated with N-719, RB, and MB dyes (the scale bars commonly correspond to 200 nm).

In this study, we systematically investigated the optical ignition characteristics of nEMs using a relatively low-power laser beam (<20 W cm^{-2}). Specifically, Al nanoparticles (NPs) were used as fuel, and CuO NPs were used as the oxidizer. The Al/CuO-based nEMs were coated with various functional dyes (e.g., N-719, methylene blue, and rose bengal) possessing relatively high light absorption within certain wavelength ranges. Finally, in this study, we demonstrated that relatively low-power laser beams with red, green, and blue visible wavelengths are able to remotely, stably, and selectively ignite the employed organic dye-coated nEMs.

Experimental

Fabrication of dye-coated Al/CuO-based energetic nanocomposites

In this study, Al and CuO NPs were mixed to fabricate nEM composites, as shown in Fig. 1. Commercially available Al (NT base Inc., South Korea) and CuO (NT base Inc., South Korea) NPs with respective average diameters of 78 ± 2.3 and 130 ± 5.3 nm were used without further treatment.

To fabricate the Al/CuO NP-based energetic nanocomposites, Al NPs were mixed with CuO NPs in ethanol (EtOH) solution at a mixing ratio of Al:CuO = 30:70 wt%, which, as we found in our previous study [32–34], corresponds to a fuel-rich condition (i.e., fuel-to-oxidizer ratio = 1.90) with active combustion properties. To achieve the homogeneous dispersion of Al and CuO NPs in the EtOH solution, the mixture was sonicated for 30 min under a power and frequency of 200 W and 40 kHz, respectively. The Al/CuO composite powders were obtained after drying the Al/CuO NP-dispersed solution for 10 min in a convection oven heated at 80 °C. N-719 [di-tetrabutylammonium cis-bis (isothiocyanato) bis (2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II), $C_{58}H_{86}N_8O_8RuS_2$, Sigma Aldrich, USA], RB (rose bengal, $C_{20}H_2C_{14}I_4Na_2O_5$, Sigma Aldrich, USA), and MB (methylene blue, $C_{16}H_{18}ClN_3S$, Sigma Aldrich, USA) dye powders were dissolved in EtOH to prepare the dye solutions. The fabricated Al/CuO composite powders were then dispersed in the dye solution at a mixing ratio of 10 mg of composite powder and 1 mL of dye solution, and immersed for 24 h. The dye-coated Al/CuO NP-dispersed solution was then dried in a convection oven heated at 80 °C until the EtOH solution completely evaporated; finally, the dye-coated Al/CuO composite powders were obtained. These powders were characterized by transmission electron microscopy (TEM; FEI, Model Talos F200X) at ~200 kV. A UV–vis spectrophotometer (Cary 5000, Agilent), with a wavelength range of 300–900 nm and scan rate of 600 nm min^{-1}, was used to examine the light-absorption properties of the dye solution.

Characterization of laser ignition for dye-coated Al/CuO energetic nanocomposites

The fabricated dye-coated Al/CuO energetic nanocomposites were irradiated with RGB laser beams to examine the effects of light wavelength on their ignition properties (Fig. 1). We performed a series of laser ignition tests using diode-pumped solid-state red (wavelength: 671 nm, power range: ~1000 mW, beam diameter: 2 mm, model: RL671T8-1000, Shanghai Laser & Optic Century, China), green (wavelength: 532 nm, power range: ~1286 mW, beam diameter: 2.5 mm, model: SDL-532-1000T, Shanghai Dream Lasers Technology), and blue (wavelength: 445 nm, power range: ~1000 mW, beam size: 4 mm × 1 mm, model: BLM445TA-1000, Shanghai Laser & Optic Century, China) lasers. In order to measure the size of laser beam spot irradiated on the dye-sensitized Al/CuO composites, we employed photosensitized papers. They were placed on top of composite sample, which was kept the distance of ~60 cm from the RGB laser source in this study. The size of laser beam spot was confirmed to be ~2 mm for red laser beam, ~2.5 mm for green laser beam, and ~4 mm × ~1 mm for blue laser beam (Fig. S1 in Supporting information). The power of the laser beam was measured using a laser power meter (model: TUNER, Gentec Electro-Optics, Canada). When a laser beam irradiated the dye-coated nEM composites, which were piled on a dish in a hood, the entire ignition process was monitored using a video recorder in order to determine the ignitability of the composites.

Results and discussion

UV–vis spectroscopy analysis was performed, as shown in Fig. 2, to examine the light absorbance of the N-719, RB, and MB dye solutions employed in this study. The light-absorption characteristics of the dye solution are strongly dependent on the type of dye used, and the magnitude of light absorption is observed to increase as the molar concentration of the dye is increased. The light absorbance seems to be saturated at molar concentrations greater than 0.5 mM, in which the N-719, RB, and MB dye solutions exhibit the relatively high light absorbance in the blue (~445 nm), green (~532 nm), and red (~671 nm) wavelength regions, respectively. Additionally, it is interesting to note that the light absorbance of N-

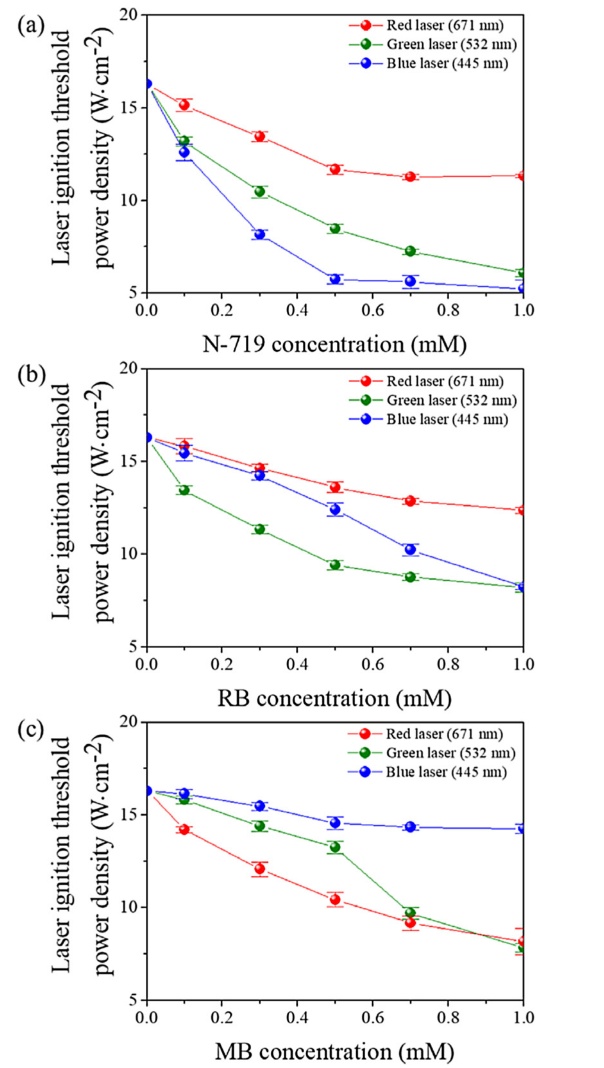

Fig. 4. Laser ignition threshold power density for the (a) N-719-, (b) RB-, and (c) MB-coated Al/CuO NP composites irradiated using RGB laser beams.

719, RB, and MB is significantly increased with increasing the molar concentration greater than 0.5 mM at green (~532 nm), blue (~445 nm) and green (~532 nm) wavelength regions, respectively. This suggests that effectively using the N-719, RB, and MB dyes as a light-absorbing medium can result in different reactions in response to the incoming RGB light sources.

To verify that the dyes were uniformly coated on the Al/CuO composites, TEM and elemental mapping analyses were performed as shown in Fig. 3. The TEM images show that the Al/CuO composites have spherical primary particles with average Al and CuO NP diameters of ~78 ± 2.3 and ~130 ± 5.3 nm, respectively. The elemental mapping results show that the Al/CuO composites are homogeneously mixed, and that the core elements of the N-719 (i.e., carbon/sulfur), RB (i.e., chlorine/sodium), and MB (i.e., nitrogen/sulfur) dyes are uniformly coated on the surface of the Al/CuO composites.

To examine the effects of the dyes on the optical ignition of the Al/CuO composites, we used RGB laser beams to perform a series of laser ignition tests. The laser beam was irradiated on the dye-

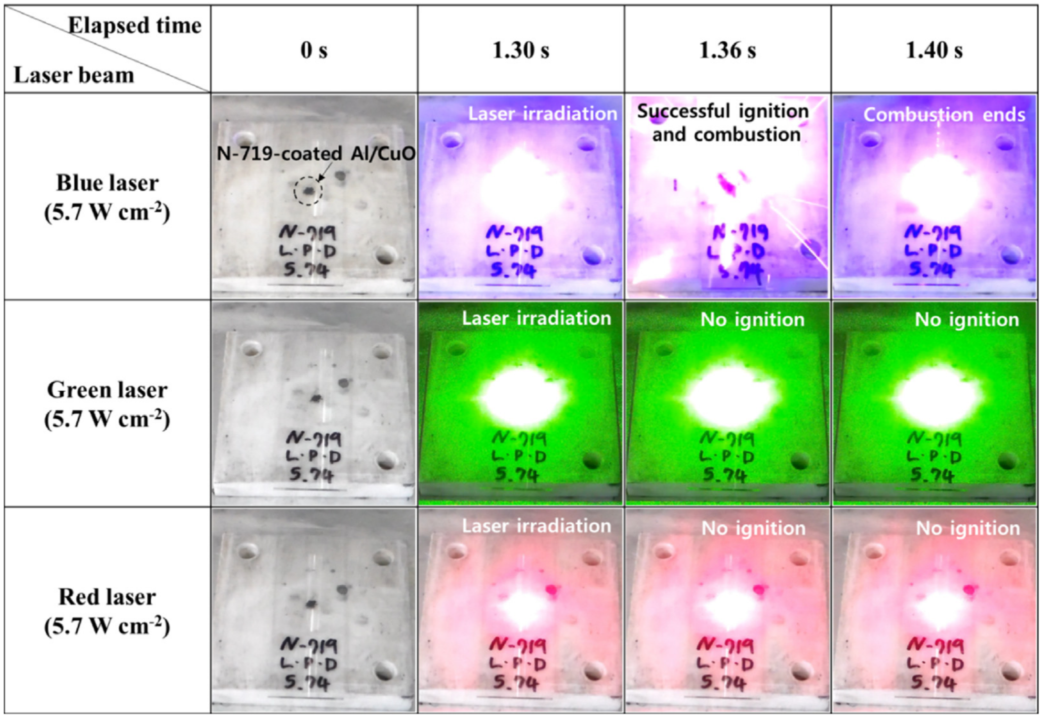

Fig. 5. Snapshots of the N-719-coated Al/CuO composites during laser irradiation with RGB laser beams, and under the condition of a fixed laser power density of 5.7 W cm^{-2}.

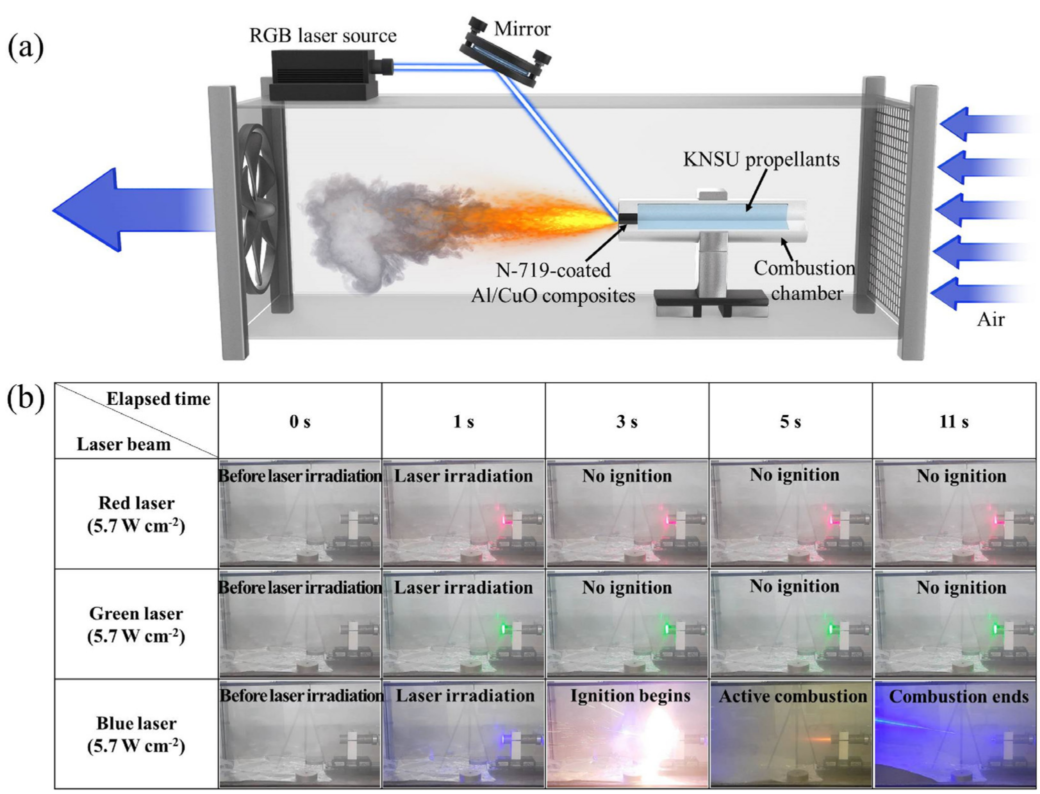

Fig. 6. (a) Schematic of the wind-tunnel RGB laser ignition test setup, and (b) corresponding test progression snapshots of the N-719-coated Al/CuO energetic nanocomposite-based optical igniters and KNSU-based solid propellants filled in a combustion chamber.

coated Al/CuO composites with increasing by the beam power of 5 mW for 3 s at each increment, and then the laser ignition threshold power density was finally determined by calculating the ratio of the laser beam power to beam spot size when the dye-coated Al/CuO composites were ignited. The laser ignition tests were repeated 10 times for each sample, and then the average value was taken as the laser ignition threshold power density. As the molar concentration of each coating dye for the Al/CuO composites was increased, the resulting laser ignition threshold power density decreased as a result of a thicker dye coating layer forming on the Al/CuO composites allowing more light energy to be absorbed. In particular, the laser ignition threshold power density for the N-719-, RB-, and MB-coated Al/CuO composites considerably decreased under the condition of blue, green, and red laser beams, respectively, as shown in Fig. 4a–c. This suggests that each dye had a tendency to strongly absorb light energy within a specific wavelength range (Fig. 2), and that the light energy absorbed by dyes was rapidly converted into thermal energy via a photothermal effect, which resulted in ignition of the Al/CuO composites.

To test the ignitability of dye-coated Al/CuO composites using a laser beam with a specific wavelength range, we prepared Al/CuO composites that were coated using an N-719 dye of molar concentration 0.5 mM. The mixing ratio of the composites was N-719:Al:CuO = 5.67:28.3:66.03 in wt%. The absolute density of each component was 0.32 g cm^{-3} for N-719 dye, 2.7 g cm^{-3} for Al, and 6.31 g cm^{-3} for CuO. Therefore, the resulting theoretical density (TD) was calculated to be ~2.589 g/cm^3. First, when the RGB laser beams with a fixed laser power density of ~5.7 W cm^{-2} irradiated the N-719-coated Al/CuO composites, the blue laser beam resulted in the successful ignition and subsequent combustion of the composites, whereas the green and red laser beams could not ignite the composites, as shown in Fig. 5. Secondly, when the RGB lasers with a fixed laser power density of ~9.4 W cm^{-2} irradiated the RB-coated Al/CuO composites, only the green laser beam resulted in successful ignition (Fig. S2a in Supporting information). Thirdly, when the RGB lasers with a fixed laser power density of ~10.4 W cm^{-2} irradiated the MB-coated Al/CuO composites, only the red laser beam successfully ignited the composites (Fig. S2b in Supporting information). These results suggest that the Al/CuO composites can be selectively ignited by a laser beam with relatively low power and a specific wavelength range.

To demonstrate the selective laser ignitability for solid propellants, we used dye-coated Al/CuO energetic nanocomposites as an optical igniter. Specifically, a series of laser ignition and combustion tests for solid propellants were performed in a wind tunnel, as shown in Fig. 6a. The potassium nitrate/sucrose (KNSU)-based solid propellants were allowed to fill a combustion chamber that had both ends completely sealed with clay, and then one of the ends was drilled to form a gas exhausting nozzle. Then, the N-719-coated Al/CuO composites were introduced into the gas exhausting nozzle as an optical igniter without pressurization. When RGB laser beams with a fixed laser power density of 5.7 W cm^{-2} irradiated the N-719-coated Al/CuO composites, only the blue laser beam was found to successfully ignite the N-719-coated Al/CuO composites, and then the KNSU combustion-generated flame and gases were intensively exhausted at the end of combustion chamber after approximately 10 s, as shown in Fig. 6**b.** However, the red and green laser beams did not successfully ignite the solid propellants, even though the N-719-coated Al/CuO composites were exposed to the red and green laser beams for longer than 10 s. This confirms that the dye-coated Al/CuO composites can be used as specially designed optical igniters purposed to promote reaction upon irradiation with a laser beam that has relatively low power density and wavelength range restrictions.

Conclusions

In this study, we examined the effects of using dyes as a light energy-absorbing medium on the optical ignition properties of Al/CuO-based nEMs. Various dye-coated Al/CuO composites were fabricated via simple immersion of the composites in a dye solution and subsequent solvent evaporation. The results of experiments showed that the light absorbance of the dye-coated Al/CuO energetic nanocomposites increased with increasing dye molar concentration, which consequently significantly decreased the required laser ignition threshold power density for the composites. In addition, the N-719-, RB-, and MB-coated Al/CuO energetic nanocomposites were reliably ignited by the blue, green, and red laser beams, respectively, with relatively low laser power density. These results were subsequently applied to realize the selective laser ignition of dye-coated Al/CuO composites through the use of RGB laser beams. Furthermore, we successfully demonstrated that the N-719-coated Al/CuO composites could only be initially ignited by a blue laser beam, i.e., not by a green or red laser beam, when the laser power density is fixed at ~5.7 W cm^{-2}, and that the flame generated via the initial blue laser-induced ignition rapidly propagated to activate the KNSU-based solid propellants in the combustion chamber. These findings suggest that the specially designed dye-coated Al/CuO composites could be employed as potential optical igniters and heat energy sources in various thermal engineering applications.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jiec.2019.09.040.

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