Near infrared radiation shielding using CsₓWO₃ nanoparticles for infrared mini light-emitting diodes

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ABSTRACT

Recently, near infrared LEDs have been used in small electronic devices due to the trend of manufacturing compact systems. The intensity of near infrared (NIR) optical device needs to be moderated if the chip emits too much power. In tradition, color pigments are used as additives in the encapsulant of LEDs to reduce the intensity of over irradiated NIR, a strategy which results in unaesthetic appearance. Cesium doped tungsten trioxide (CsₓWO₃) nanoparticles (NPs) have good near infrared absorption ability. Applying very few amount of CsₓWO₃ NPs into the encapsulation materials of NIR optical device can decrease NIR intensity while still maintain high visible light transmittance without losing aesthetic touch of those devices such as LED transmitters. The addition of only 0.0021 wt% CsₓWO₃/PMA dispersion in epoxy encapsulant can drop 15.5% NIR (860 nm) intensity but barely reduce visible light (only 3.2% at 450 nm). The excellent performance of CsₓWO₃ NPs; i.e., good NIR absorption and visible light transmission properties, can be suitable for maintaining the moderate luminescence intensity of small optoelectronic devices like NIR mini- or micro- light-emitting diodes.

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1. Introduction

Windows with infrared shielding function are popular for reducing temperature inside buildings and vehicles [1,2]. Recently, near infrared (NIR) shielding nanoparticles have been introduced into transparent coating for optical devices and they exhibit excellent NIR blocking efficiency [3,4]. Other nanoparticles can also be used in optoelectronic and electronic applications [5–9].

To adjust the NIR intensity of optical devices like mini Light-Emitting-Diode (LED), pigments are often added into encapsulation materials for reducing the intensity of NIR. Unfortunately, pigments not only absorb NIR but also lower the intensity of visible light. Moreover, pigments cause different colors of device appearance and may drop the aesthetic feeling. For a better outcome of an optical device, introducing good NIR shielding materials into encapsulant is a good way to achieve this goal [10]. Good NIR shielding materials need to show great NIR cut off performance and high visible light transmission [11].

It is known that rare-earth hexaborides (LaB₆, PrB₆, NdB₆, etc.) [12,13], transparent conductive oxides (ITO, ATO, AZO) [14–16] and tungsten bronzes (MₓWO₃, M = Na, K, Cs, etc.) [4,17,18] have been used to block NIR base on the localized surface plasma resonances (LSPRs) effect. However, rare-earth hexaborides are expensive and only can impede specific wavelengths of NIR. Their rigid bulk nature takes efforts to grind them into small nanoparticles. Transparent conductive oxides such as ITO, ATO and AZO are well known NIR insulating materials with fair visible light transmission. Nevertheless, their good blocking performance only affect NIR wavelengths over 1600 nm, a regime which is not suitable for mini LED application for outside the wavelength range of 800 nm – 960 nm.

Cesium doped tungsten trioxide (Cs₂WO₃) nanoparticles (NPs) show excellent visible light transparency and broad absorption of 780–2600 nm [17,19]. The best wavelength blocking region of Cs₂WO₃ is from 800 to 1200 nm, which is beneficial for mini LED NIR shielding. Moreover, Cs₂WO₃ NPs have more advantages over organic pigments such as better heat resistance and longer lifetime. To the best of our knowledge, the introduction of Cs₂WO₃ into mini LED epoxy encapsulant as the NIR shielding material has not been studied yet.

In this research, a small amount of 70 wt% Cs₂WO₃ NPs solution in propylene glycol monomethyl ether acetate (PMA) were added into epoxy base resin of mini LED NIR lamps. The transmittances of epoxy containing various concentrations of Cs₂WO₃ were measured. The Cs₂WO₃ epoxy resins show outstanding NIR shielding property and high visible light transmission.
2. Materials and methods

2.1. Cs$_x$WO$_3$ NPs and epoxy

Cs$_x$WO$_3$ NPs in propylene glycol monomethyl ether acetate (PMA) dispersant (70 wt%) were provided by Just Nanotech. In brief, Cs$_x$WO$_3$ NPs were synthesized according to previous report [17] and then followed by bead mill with 30 μm yttria stabilized zirconia beads in PMA for 6 h. The epoxy resin EP511HF was purchased from Boluo Santong Electronics Matialco. The NIR LED used in this study is a high intensity diode, molded in a water clear resin package.

2.2. Preparation of composite

To prepare 0.0014 wt% and 0.0021 wt% Cs$_x$WO$_3$ epoxy composite, 0.0004 g and 0.0006 g of Cs$_x$WO$_3$ in PMA dispersions (70 wt%) were added into 20 g of EP511HF epoxy resin (A:B = 1:1), respec-
tively and stirred for 15 min before degassing in a vacuum chamber (about 100 Pa) until no bubbles generated. Then, 2 g of each prepared mixture was poured into a circular aluminum pan with 3 cm diameter and 2 mm depth and the degassing process were repeated. Those pans were sprayed with mold releasing agent and dried for 20 min in the air before epoxy was poured in. Then those pans were kept in an oven and cured at 135 °C for 6 h. Subsequently, the epoxy cakes were taken out from the aluminum pan and measured the optical transmission. For testing the epoxy composites of LEDs, each mixture was filled in a syringe with a needle but without a piston, and then degassing. After that, the mixture was dispensed on the LED chip (254 μm²) for encapsulation followed by cured at 135 °C for 6 h.

2.3. Characterization

The crystallographic structure of CsxWO3 NPs was characterized by X-ray diffraction (XRD, Ultimate IV, Rigaku, Japan) with a Cu-Kα radiation 1.541 Å. The size and shape of the nanoparticles were observed by a transmission electron microscope (TEM, FEI Talos F200X). Energy dispersive spectrometer (EDS) combined with TEM was used for selected area of nanoparticles element analysis. UV–Vis spectrometer (Perkin Elmer, Lambda 650S) was used to measure UV–Visible spectrum of composite resin. NIR LED intensity was measured by Instrument System ISP-75.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of CsxWO3 NPs. The characteristic peaks of CsxWO3 NPs corresponded to the (0 0 2), (1 1 0), (1 0 2), (2 0 0), (1 1 2), (2 0 2), (2 2 0), (2 0 4), (3 1 2), (4 0 0) and (2 2 4) planes, which are consistent with hexagonal C0.333WO3 (JCPDS card no. 83-1334). The chemical composition analysis based on the EDS signified the elements of Cs and W at a Cs/W atomic ratio of 0.33 (see Fig. 1(b)). Fig. 1(c) shows TEM image and (d) size distribution of C0.33WO3 NPs. The average particle size is about 24.7 nm. Fig. 1(e) is the SAED pattern of C0.33WO3 NPs indicating the crystal planes of (2,0,0) and (1,1,0), a result agrees with XRD measurement. Fig. 1(f) is HR-TEM images of C0.33WO3 NPs, demonstrating the d spacing (about 0.321 nm) of (2,0,0) plane. According to previous reports [20–21], the best performance of the required optical property shown below is at Cs/W = 0.33.

Fig. 2(a–c) displays the appearance of composite cake of Csx-WO3. From Fig. 2(b), there is no obvious color produced by adding 0.0014 wt% CsxWO3 NPs into epoxy as compared with pure epoxy shown in Fig. 2(a). A very slight blueish but not sensible color is shown after 0.0021 wt% CsxWO3 NPs is added (see Fig. 2(c)). Fig. 2(d) and (e) illustrate the color appearance of NIR LED lamps without and with 0.0021 wt% CsxWO3 NPs added into epoxy encapsulant, respectively. Those two LED lamps show similar opacity by the naked eyes. The transmission spectra of those composite cakes are shown in Fig. 2(f). Adding 0.0021 wt% CsxWO3 NPs into epoxy results in dropping 24.6% NIR (at 860 nm) transmission intensity and about 3.2% (at 450 nm) reduction in the visible region. Our purpose is to cut off 15 – 25% NIR (860 nm) transparency to reduce the high intensity of our NIR LED chip. Fig. 2(g) is the NIR LED lamp intensity before and after the addition of 0.0021 wt% CsxWO3 NPs. The NIR intensity was 15.5% reduced at 860 nm after incorporating CsxWO3 NPs. Introducing CsxWO3 NPs in NIR LED encapsulant results in high visible light transparency and moderate shielded NIR intensity, which is suitable for the package application of small NIR LED transmitters.
4. Conclusions

Cs$_x$WO$_3$ NPs were incorporated into epoxy base NIR LED encapsulant to modulate NIR optical property. We found that a very small amount of Cs$_x$WO$_3$ NPs in the encapsulant can perform excellent NIR shielding while still keep high visible light transmission. Our finding provides an effective solution for the requirement of NIR intensity reduction of small NIR optical devices including mini- and micro- LEDs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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