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Roll to Roll fabrication of synthesized Light Conversion Film

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The phase, dimension of synthesized lanthanide-doped nanoparticles dictates the optical properties of these nanoparticles and influence their light conversion properties. A systematic study on the effect of rare earth doping in the formation of $NaYF_4$ upconversion nanoparticles was conducted. The rare earth element doping has a dual function of tuning particle size of hexagonal phase $NaYF_4$ nanoparticles and stabilizing cubic phase $NaYF_4$ nanoparticles as dependent on composition and concentration of the dopant ions of Erbium and Ytterbium. The Lanthanide-based upconversion nanoparticles (UCNPs) are able to convert two or more photons from lower energy levels to a higher energy level. The synthesized solution displayed good transmittance of 80% with significant dip in the transmittance at 980m nm, 1185 nm and 1418 nm. These signature dip of transmittance can be induced by light absorbance for conversion based on the bandgap energy of the $NaYF_4$:Yb,Er. By combining the effects of $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm, we are able to achieve the conversion of 980 nm wavelength light into visible light by tuning the composition of the lanthanide molar ratios. These nanoparticles are then dispersed uniformly in ethanol and fluoroethylene vinyl ether (FEVE) fluoropolymer, and then coated onto a polyethylene terephthalate (PET) film using a roll-to-roll film coater for application onto greenhouse facades. The modular acrylic enclosure shows a reduction of thermal radiation from black body positioned in the enclosure by 1.5^{o}C over 1 hour duration under a strong LEDs lamp. The techniques reduced the solar irradiance, reduces the demand for active cooling technique and save the overall cost and yield for operation.

NOMENCLATURE

UCNP = upconversion nanoparticles
FEVE = fluoroethylene vinyl ether
PET = polyethylene terephthalate
LED = light emitting diode
IR = infrared
SEM = scanning electron microscope

1. Introduction

Upconversion is a process in which lower energy photons are converted into higher energy photons. Parameters such as the synthesis method, size, shape, crystal structure and chemical composition of UCNP will affect their luminescence properties. This inherent property of UCNPs are of particular interest to applications in fields like solar cells, lasers and bioimaging, etc. [1-4] One of the most widely researched and established UCNPs are $NaYF_4$ lanthanide-doped nanoparticles. [5-8] By tuning the molar ratio of the lanthanide ions taking part in the reaction, the emission of the UCNPs can be manipulated to emit different visible wavelengths of light upon excitation by near IR photons. [9,10] Taking advantage of the UCNPs ability to absorb longer wavelength photons and convert it to visible light, incoming heat can be converted to reduce temperature buildup in an enclosed envelope structure.

To achieve this, in this work, the UCNPs are surface modified during synthesis to be soluble in ethanol which then allows the UCNP in ethanol solution to be incorporated into FEVE resin. The UCNP infused FEVE resin is then transferred onto a roll-to-roll film coater to fabricate a thin film of UCNP on the PET roll film. The use of the roll-to-roll film coater is crucial in the scaling up of the production of UCNP films for architecture such as greenhouses, glass façade of buildings which encompass large surface areas. Optimization of the film coating parameters like the thickness of the coating, coating speed, heating temperature and time leads to a continuous production of the UCNP coated PET films. The film which can have an adhesive side can then be adhered to any flat clean surface of windows panels and skylight visible transparent rooftop. Applying this coated film to a modular acrylic enclosure in the lab, the heat reduction efficiency of the UCNPs was studied using a strong LED lamp simulating the effect of the morning Sun, entering the side façade of the enclosure.

2. Experimental Setup

2.1. Synthesis of Light Conversion Nanoparticles

$NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm nanoparticles were synthesized via a hydrothermal reaction according to published methods. [10] The precursor lanthanide oxides were reacted with hydrochloric acid to create lanthanide chlorides to create a trichloride solution, and the other precursors were added. The well mixed solution is then transferred into Teflon cups and sealed within the autoclaves, followed by heating at 200 °C for 2 hours.

2.2 In-Lab enclosure to model the greenhouse and light conversion film

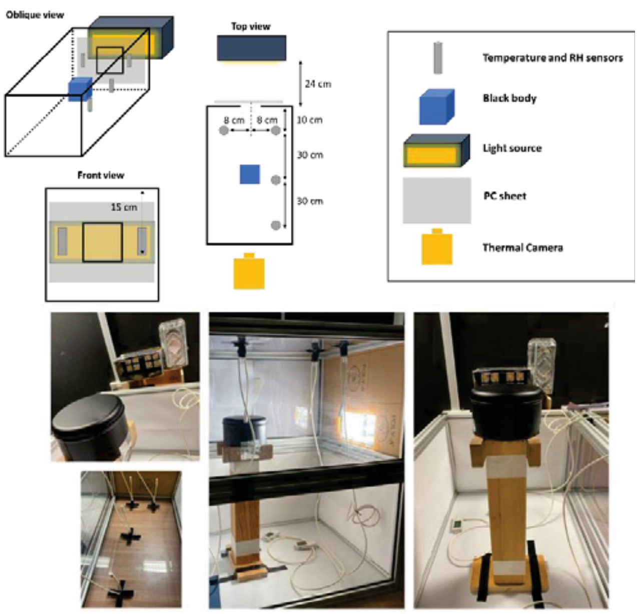

Fig. 1 Schematic and actual photos of a scale-down version of the greenhouse for installed with temperature and RH sensors with a black body in the enclosure and polycarbonate film placed at the open windows and illuminated by strong heated light source

An acrylic enclosure was used to simulate a scaled down version of a large-scale greenhouse. To simulate the Sun, a strong LED lamp with a power of 125W was used, and a small window was cut on one face of the enclosure. Four temperature and relative humidity sensors are placed in the enclosure to monitor the conditions in the "indoor environment". A black metal tin is placed in the center of the enclosure to simulate furniture that will be placed in the indoor environment which absorb heat and further radiate its back to the enclosure. A polycarbonate (PC) sheet is placed at the small window to simulate the transmittance of light and heat through the window panels or glass side facade. The positions of the sensors are chosen to analyze the depth of heat penetration through the PC sheet into the enclosure. A FLUKE IR camera was also used to capture the heat transmittance through the window. The setup is as shown in Fig. 1.

2.3 Roll-to-Roll Film Coater System

The roll-to-roll film coater used doctor blade to apply a controlled thin layer of coated nanoparticles in the matrix media onto PET film. The system allows precise control of the feed rate of the source with a syringe pump controller. The coated film is rolled and collected by the drum powered by a variable speed motor which allows adjustment of collection rate from 1 mm/min to 400 mm/min. The system comes with a UV Lamp and heating stage with adjustable temperature to modulate the heating temperature to ensure the film is completely cured and dry before they are collected by the drum.

3. Results and Discussion

3.1 Characterization of $NaYF_4$ upconversion nanoparticles

The upconversion nanoparticles were synthesized and its crystal structure is studied with SEM imaging. The nanoparticles were observed to be uniform in size and are 90 nm in width.

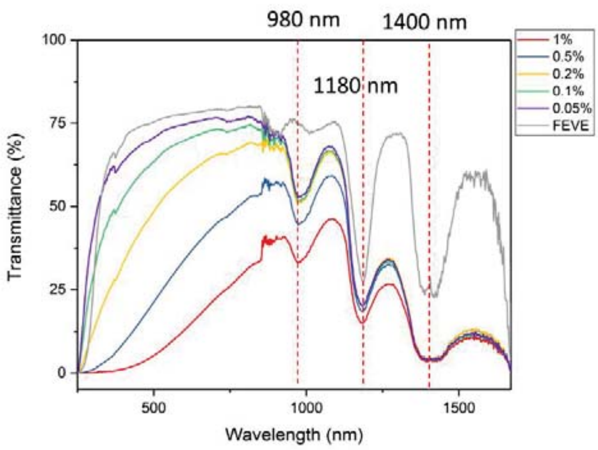

Fig. 2 UV-Vis spectrum of the $NaYF_4$:Yb,Er UCNP dissolved in ethanol at varying concentrations and the FEVE resin

UV-Vis characterization was also done on the $NaYF_4$:Yb,Er nanoparticles, as shown in Fig. 2. Various weight concentrations of $NaYF_4$:Yb,Er in ethanol were measured, all of them showing an obvious dip in transmittance at 980 nm, 1180 nm and 1400 nm. These peaks correspond to the wavelengths at which $NaYF_4$:Yb,Er is known to absorb IR light. The 980 nm peak is not observed in the UV-Vis measurement of the FEVE resin, attributing it directly to the $NaYF_4$:Yb,Er nanoparticles. Higher optical transmittance in the visible regime from 300 to 700 nm, is observed for lower concentrations of the $NaYF_4$:Yb,Er, The FEVE resin shows a high transmittance of close to 80% transmittance in the visible region and this suggested that the dip in transmittance is independent of FEVE matrix and likely it corresponds to the absorbance peak of the nanoparticles.

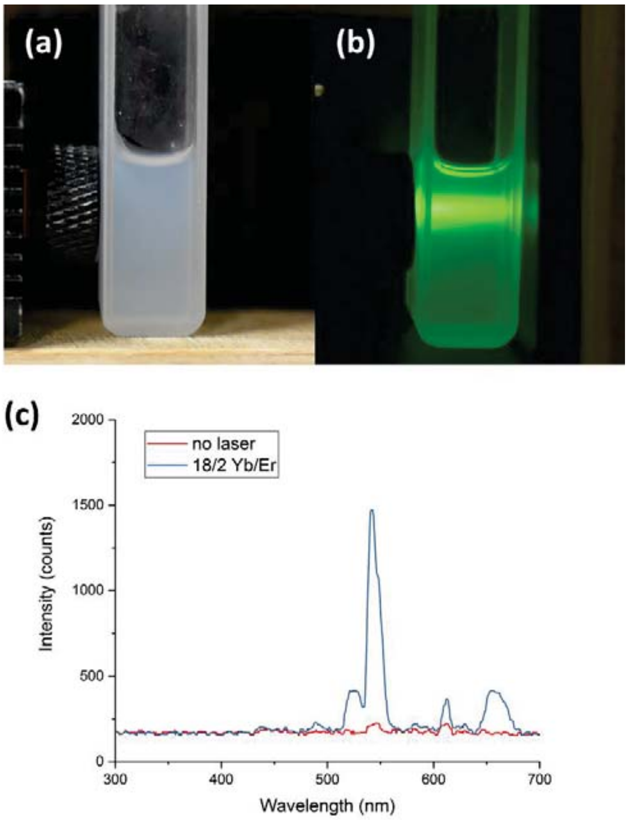

Fig. 3 (a) $NaYF_4$:Yb,Er nanoparticles in ethanol before the 980 nm laser is switched on (b) Green visible light emission observed under 980 nm excitation (c) Fluorescence spectrum of the emitted light under 980 nm excitation

The $NaYF_4$:Yb,Er nanoparticles in ethanol were subjected to excitation from a strong 980 nm laser source (Fig. 3) and a visible green light emission was observed and captured using a Nikon camera. This verifies the upconversion capabilities of the $NaYF_4$:Yb,Er nanoparticles from the NIR region to the visible region. The emission spectrum, as seen in Fig. 3(c), was also obtained using a QEPro spectrometer showing a clear green peak at the 550 nm region which corresponds to the green emission seen in Fig. 3(b).

3.2 Coated nanoparticles film generated by the roll-to-roll coater

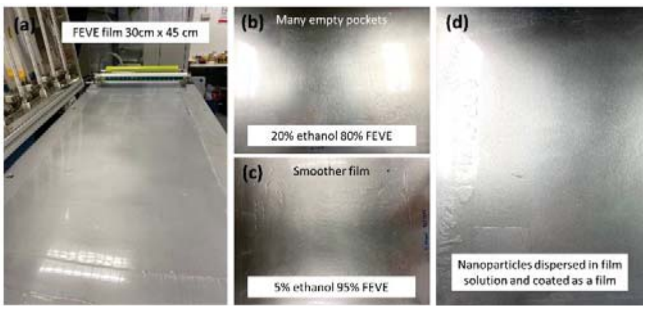

Fig. 4 Films coated using the roll-to-roll film coater (a) FEVE film (b) 20% ethanol mixed into 80% FEVE (c) 5% ethanol mixed into 95% FEVE (d) Nanoparticles infused film

The film coater was able to produce a large and uniform FEVE film as seen in Fig. 4(a). However, the $NaYF_4$:Yb,Er nanoparticles are insoluble in FEVE. Therefore, the concentration of ethanol in FEVE was varied to test the uniformity of the film coating, as the inclusion of ethanol changes the viscosity of the coating solution. At 20:80 ethanol to FEVE ratio, there were large pockets of empty spaces in the film coating, as seen in Fig. 4(b). However, after reducing the ethanol content to 5:95 ethanol to FEVE ratio, a uniform film is produced, as the viscosity of the coating solution is similar to that of the pure FEVE resin. Using this ratio of ethanol to FEVE, $NaYF_4$:Yb,Er nanoparticles were first dissolved in ethanol then incorporated homogeneously into the coating solution and coated using the roll-to-roll film coater, as shown in Fig. 4(d).

3.3 Heat reduction measurements using modular acrylic enclosure

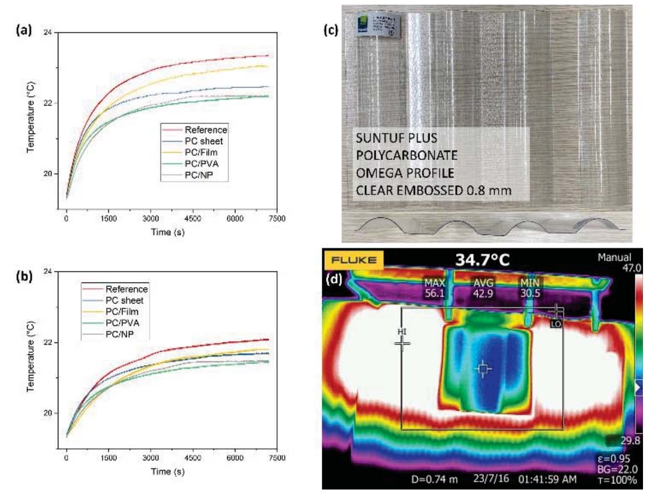

Fig. 5 Temperature measured by sensors in the modular acrylic enclosure simulating a greenhouse at a position (a) close to the LED lamp (b) 30 cm away from the LED lamp (c) actual photo of a PC sheet (d) IR image of the PC sheet after 1h of heating

The reference was taken to be without anything between the light source and the black body, labelled as Reference in Fig. 5. Subsequently, measurements were taken with the PC sheet between the light source and black body, and it is shown as PC in Fig. 5. PC/film represents measurements taken through the PC sheet and a PET film without any coating. PC/PVA represents the measurements taken through a PC sheet and a PET sheet coated with PVA which acts as the film matrix in which the $NaYF_4$:Yb,Er nanoparticles will be incorporated. PC/NP represents the measurements through the PC sheet and PET film coated with the PVA matrix with 1% of $NaYF_4$:Yb,Er nanoparticles in the coating solution. The inclusion of the PC sheet evidently decreases the heat transmittance into the chamber. The temperature measured by the temperature and humidity sensors in the chamber showed that there is a gradual decrease of temperature relative to the distance from the light and heat source, comparing the final temperatures in Fig. 5(a) and (b). There is a decrease of 1 °C with a distance of 30 cm from the heat source, however, the temperature of the chamber reaches a stable value after

30 minutes of heating. Fig. 5(c) shows an actual photo of the PC sheets used in the experiments and Fig. 5(d) is a thermal image of the PC sheet after 1h of heating, showing that there is a significant difference in the temperature of the surface of the PC through the small window and

Table 1 Temperature of chamber after 1 h of heating

	Reference	PC sheet	PC/Film	PC/PVA	PC/NP
Front	23.4	22.5	23	22.2	22.2
30 cm	22.1	21.7	21.8	21.4	21.5

Table 1 shows the temperatures measured by the temperature sensors at the front and at 30 cm away from the light source after 1 hour of heating. While the addition of the film onto the PC sheet introduced an air gap that created a layer of insolation. The inclusion of the $NaYF_4$:Yb,Er nanoparticles further decreased the temperature of the chamber to 1.2 °C below that of the reference. The dimensions of the enclosure and the distance between the light source and temperature sensors can be seen in Fig. 1. This shows that the nanoparticles effectively reduced the heat transmittance to the enclosure through the film coated polycarbonate.

3. Conclusions

In this work, $NaYF_4$:Yb,Er nanoparticles were synthesized via a hydrothermal reaction method and incorporated into a film for coating. Successful synthesis was confirmed via observation of the 90 nm sized hexagonal nanoparticles under SEM analysis and the upconversion excitation peak at 980 nm was verified via UV-Vis characterization. The upconversion of IR light into visible light has also been confirmed via fluorescence spectroscopy and visual observation. The film was then coated and transferred onto a modular acrylic enclosure and the reduction of heat passing through into the chamber was reported.

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