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Long persistent greenhouse film

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Thin films for greenhouse application were prepared by doping with long persistent blue and red nanophosphors. Ultra violet and green light in the Sun spectrum were converted into blue and red light by using the nanophosphors. A more efficient blue and red light absorption by the chlorophyll in the plants can let the plants to grow faster. The blue and red light stored in the long persistent nanophosphors can also extend the growth time for the plants in the greenhouse which will increase productivity.

Introduction

Photosynthesis process is the most important part for crop growth. During photosynthesis, sugar was synthesized by using carbon dioxide and water under the assistance of solar light, chlorophyll and carotene etc. A general formula for the overall reaction is give by

$$6CO_2 + 6\ H_2O - \mathit{light} - C_6H_{12}O_6 + 6\ O_2$$

One of the key elements in photosynthesis process, chlorophyll, is a complex molecule. Several modifications of chlorophyll occur among plants and other photosynthetic organisms. All photosynthetic organisms have chlorophyll a. There are some accessory pigments absorb the energy that chlorophyll a does not take. Accessory pigments include chlorophyll b (c, d, and e) and carotenoids (such as beta-carotene) etc. Chlorophyll a absorbs solar light energy from the violet to blue and from reddish orange to red wavelengths but very little from the intermediate (green-yellow-orange) wavelengths. These elements in the crop contribute to the energy conversion from photon energies to chemical energies. Because of the absorption spectral properties, leaves are looked green (1).

Photosynthesis is more productive under blue and red light illustration. More crop growth was observed by using blue and red color lighting system such as using blue and red LEDs. The research results are in very good agreement with the absorption spectra of chlorophyll a, b and carotenoids. But, if the energy efficiency is taking into account, the LED system would cost a lot of electrical energy which may not commercially applicable.

For economical reasons, crop growth on earth will not use LED system. Solar energy is still the major resources for crop growth. The solar light contains a large amount of light that can not be used by crops. Therefore, it becomes essential to convert UV and green to orange wavelength light into red or blue light for efficient plant growth (2,3).

In this work, some efforts were made to prepare light efficient greenhouse film by using long persistent phosphors.

Experimental

Phosphors can be used to down convert the UV light to blue light, and green to orange light to red light. There are a number of blue and red phosphors as listed in Table 1 and 2. Among these phosphors, long persistent phosphors are better to use because the stored light can extend the photosynthesis. During the day time not all the solar light can be absorbed by the crops so that some solar light storage in the long persistent phosphors will increase the light efficiency (4-9).

Table 1. Some good blue down conversion phosphors

Phosphors	**Absorption (nm)**	**Emission (nm)**
$Ca_xSr_{1-x}S:Bi^{3+}$	310, 408	447
$ZnS:Ag^+$	>320	452
$BaAl_2O_4:Ce^{3+}$	200 – 400	450
$CaAl_4O_7:Ce^{3+}$	200 – 400	440
$Sr_{10}(PO_4)_6Cl_2:Eu^{2+}$	200 – 400	447
$Ba_3MgSi_2O_8:Eu^{2+}$	200 – 400	443
$CaAl_2O_4:Eu^{2+}$	200 – 400	450
$BaMg_2Al_{16}O_{27}:Eu^{2+}$	200 – 400	450

From Table 1 $CaAl_2O_4:Eu^{2+}$, Dy^{3+} is selected as the blue phosphor to down convert UV light. The 450 nm emission of Eu^{2+} is just at the blue absorption peak of the crops. From Table 2, $CaS:Eu^{2+}$, Tm^{3+} is selected as the red phosphor to down convert UV and green to orange light to red light. The 650 nm emission is at the red absorption peak of the crops. It can be further shifted to 670 nm by incorporation of Cl^-. Because the persistence of these phosphors is long the photosynthesis hence can last all night (10,11).

Table 2. Some good red down conversion phosphors

Phosphors	Absorption (nm)	Emission (nm)
$CaS:Eu^{2+}$	200– 400, 500 – 610	650
$SrS:Eu^{2+}$	230 – 350, 400 – 580	610
$MgSiO_3:Mn^{2+}$	410 –500, some UV	660
$LiAlO_2:Fe^{3+}$	200 – 400	735
$Y_2O_3:Eu^{3+}$	200 – 400	616
$CaTiO_3:Pr^{3+}$	200 – 400	610

For greenhouse film doped with long persistent phosphors, one of the major issues is transparency. Large grain size phosphors will create internal scattering due to refraction and reflection of the solar light. This will make the light conversion effort worthless. To overcome this problem, nanophosphors are prepared. Nanophosphors have a size less than the light wavelength so that internal scattering is reduced.

Polyethylene film is used as for greenhouse film in this work. Nanophosphors are prepared with sol gel and precipitation. Greenhouse film doped with nanophosphors is spin coated onto glass, transmission spectrum of film is measured. UV and green to orange light is successfully converted to blue and red light.

Results and Discussion

Nanophosphors $CaAl_2O_4:Eu^{2+},Nd^{3+}$ (blue) and $CaS:Eu^{2+},Tm^{3+}$ (red) were prepared by using the salted sol-gel method and the precipitation method (12,13). The size of the nanophosphors are about 50 nm to 200 nm as shown in Fig. 1a,b.

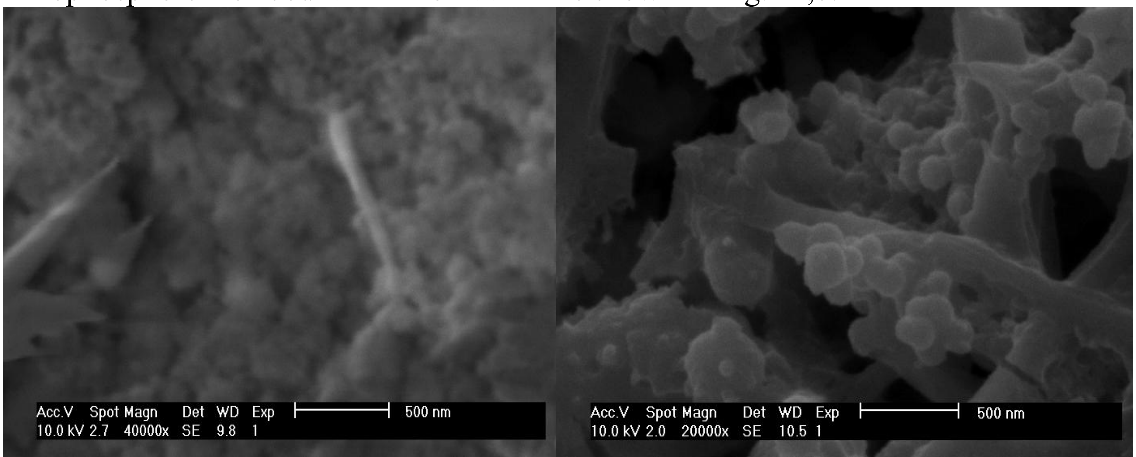

Fig. 1 Nanophosphors (a) left: $CaAl_2O_4:Eu^{2+},Nd^{3+}$ prepared by using the salted sol-gel method, (b) right: $CaS:Eu^{2+},Tm^{3+}$ prepared by using precipitation method.

Emission spectra of the samples excited by using a full range Xe lamp are measured and are shown in Fig. 2a,b for the two nanophosphor converters. The emission peaks are found to be at 450 nm and 650 nm for $CaAl_2O_4:Eu^{2+},Nd^{3+}$ (blue) and $CaS:Eu^{2+},Tm^{3+}$ (red) nanophosphors respectively. $CaS:Eu^{2+},Tm^{3+},Cl^-$ is hard to be made because $CaCl_2$ is dissolvable.

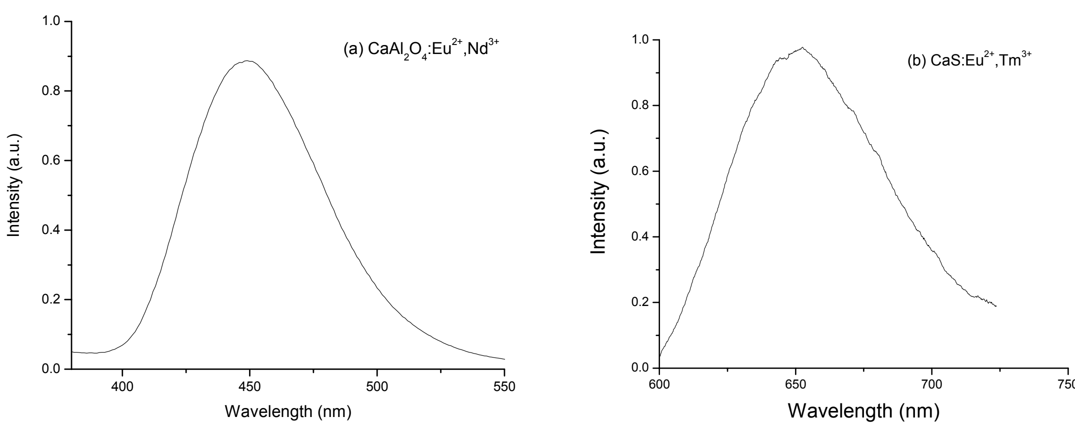

Fig. 2 Emission spectra under Xe lamp excitation (a) $CaAl_2O_4:Eu^{2+},Nd^{3+}$ (b) $CaS:Eu^{2+},Tm^{3+}$.

Greenhouse thin film was prepared with polyethylene (PE). Low density solid PE are used and dissolved in xylene at about125 ^oC. (About 0.5g LDPE in 30 mL xylene). The PE solution is distilled to evaporate the xylene slowly. A nearly saturated solution is made. A glass slide was dipped coated into the top layer, which contained PE but in small enough amounts as not to turn crystalline when dried. A thin PE film without doping phosphors is made for comparison. A mixture of blue and red nanophosphor with a 3:10

ratio was made and was dispersed with iso-propanol. They were added to PE solution to make PE with converters.

A Xe lamp is used as a light source (sun light) to measure transmission spectrum for the samples. The transmission spectra of the samples were normalized to the Xe lamp profile and are shown in Fig. 3a,b. The PE film has an average transmission in the visible range for about 80% normalized to Xe lamp profile. After nanophosphors were mixed, the PE film is translucent and glow purple color under Xe lamp. The transmission spectrum (actually it is a transmission + emission spectrum) of the phosphor mixed thin film has only an average of 55% transmission. Contribution of blue and red phosphor can be seen in the spectrum.

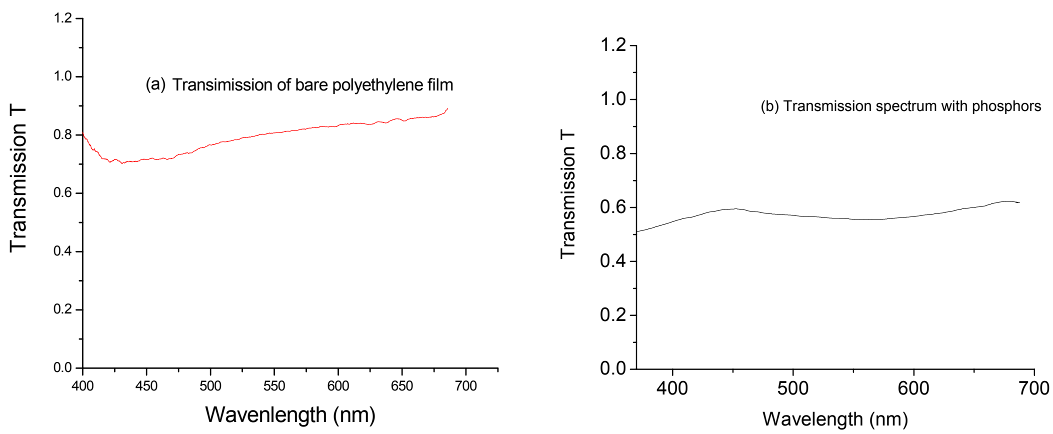

Fig. 3: Transmission spectra a) bare PE film b) with blue and red phosphors

The phosphor doped thin film persists after Xe lamp is off which will give extra glowing time for plants to grow. The low transparency is still a problem to improve. It is mainly due to dispersion of nanophosphors. To add more nanophosphors will reduce the overall transmittance but it will increase the production of blue and red light.

Conclusion

Nanophosphors were prepared by using salted sol-gel method and precipitation method. PE thin film with nanophosphors was prepared and shown an enhanced blue and red light content in the transmission spectrum. Transparency of the thin film is low due to dispersion of nanophosphors (aggregation of nanoparticles).

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