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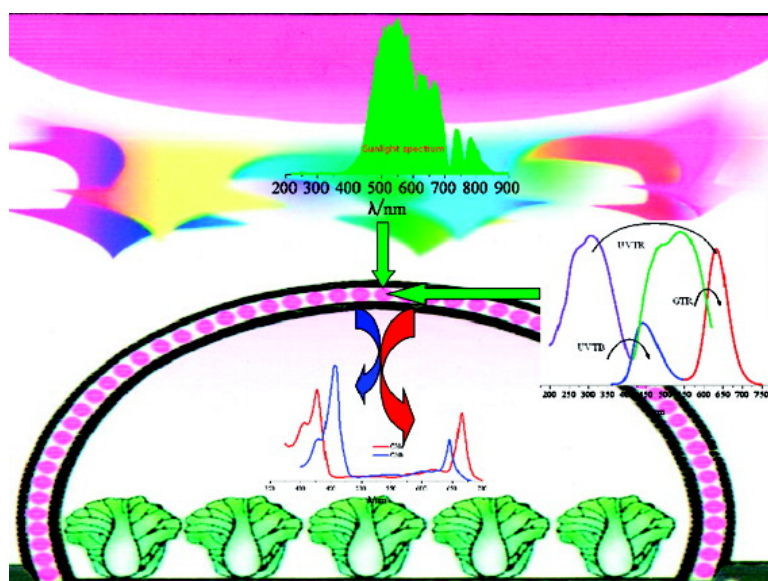
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Enhancing Solar Energy Conversion Efficiency: A Tunable Dual-Excitation Dual-Emission Phosphors and Time-Dependent Density Functional Theory Study

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The concept of dual-excitation dual-emission (DE²) phosphors for the enhancement of solar energy conversion is introduced in this work. Doping alkaline earth cations as an aggregated energy trap within the sulfur host in a controlled manner resulted in the DE² phosphors with tunable fluorescent emission properties. It had been found the Ca_{0.6}Sr_{0.4}S:0.005Cu⁺,0.001Eu²⁺ phosphor is the optimal DE² composition. We demonstrated by field testing results their potentials in enhancing sunlight harvesting to increase production of agricultural plants. Time-dependent density functional theory calculations provide insights about their excitation and emission mechanisms. These DE² phosphors can be applied to a variety of fields, as additives to increase production of agricultural crops, as nanosensor and biolabeling materials for ultrasensitive or green-sensitive detection of biological species such as antibodies, DNA and cells, and other places.

1. Introduction

As the ongoing energy crisis deepens and the global warming threat becomes a reality, to search for greener energy alternatives and to improve the energy consumption efficiency have been becoming a pressing task.¹ Because solar energy is both endlessly abundant and environmentally friendly, countless efforts have been dedicated to look for ways to leverage this cheap energy resource. Among the many facets of the endeavor is to boost the light conversion efficiency in the photosynthetic process of agricultural crops such as rice, wheat, sugar cane, vegetables, etc., to augment their production. Plants, algae, and some bacteria and protists use solar energy to produce sugar and other life-essential compounds.^{2,3} They harvest sunlight primarily through the green pigment chlorophyll antenna complexes with accessory carotenes and xanthophylls with near-perfect transformation efficiency. However, these compounds only absorb blue and red light, leading to other parts of sunlight unused.^{4–6} To improve the sunlight conversion efficiency of the photosynthetic process is to convert unused portions of sunlight to blue and red light. One of the possible devices to realize this conversion is phosphors. Also, since different plants have a slightly different adsorption spectrum, it is desirable if the maximal emission peak of the converters can be fine-tuned.

In the present work, we establish and evaluate an approach to design tunable sunlight converters through dual-excitation and dual-emission (DE²) phosphors to enhance light conversion efficiency. The gist of the current approach is that the DE² phosphors make use of ultraviolet and green light for excitation and subsequently discharge blue and red light as fluorescent emission. In addition, the emission is tunable in both wavelength and intensity, dependent on the cationic composition of the DE² phosphors. Dual emission has been reported in the literature^{7–13} in both rare earth organic complexes and fluorescent dye

systems, but UV and green light was not used for their excitation. Elsewhere, double light conversion in both UV and visible regions was observed,¹⁴ but their emission wavelengths do not match the absorption spectra of chlorophyll complexes. What we report here is the first photoluminescent material that uses the reflection spectra (in UV and green regions) of chlorophyll for excitation and absorption spectra (in blue and red regions) as emission, termed as the DE² approach, standing for dual-excitation dual-emission. We will show that the material consists of two kinds of cations as an independent activator in the system, with one absorbing mainly UV light and emitting blue light and the other absorbing green light and emitting red light. Our success comes from a careful selection of blue-emitting^{15–17} and red-emitting cations^{18–20} whose absorption spectrum falls in the UV and green regions, respectively. In addition, the emission wavelength and intensity of the DE² phosphors can be fine-tuned and selectively controlled by the concentration of the host or activator cations (Cu⁺ and Eu²⁺). Time-dependent density functional theory (TD-DFT) calculations have been performed for CaS:Cu⁺, one of the key ingredients of the DE² phosphors, providing insights in its excitation and emission mechanisms.

2. Experimental Section

Alkaline earth sulfide (AES) phosphors doped with copper or europium cations have been extensively examined in the literature^{18,21} because of their potential applications as excellent fluorescent materials. A DE² phosphor consists of AES coactivated by Cu⁺ and Eu²⁺, denoted as AESCE, whose design formula is Ca_{1-k}M_kS:xCu⁺,yEu²⁺ (M = Mg²⁺, Sr²⁺, Ba²⁺). The numbers, *k*, *x*, and *y* in the nominal composition of AESCE indicate the concentration of different metal cations on the molar basis added before firing. The polycrystalline AESCE was prepared by the solid-state reaction technique at high temperature and in the CO-reduction atmosphere (For details of synthesis, see Supporting Information). In the present work, the CO-reduction atmosphere was introduced by the elemental carbon powder reacting with O₂ in the crucible. The starting materials,

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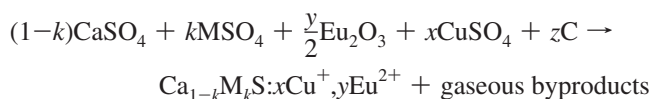
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TABLE 1: Dependence of the Emission Wavelength (λ) and Luminescent Intensity (I) of DE² Phosphor on Alkaline Earth Metal Cation Compositions with the Activator (A = 0.005Cu⁺, 0.001Eu²⁺) Unchanged

samples	blue emission		red emission	
	wavelength (λ_{em})	intensity (I/au)	wavelength (λ_{em})	intensity (I/au)
CaS:A	420.6	35.9	638.6	100.0
Ca _{0.8} Mg _{0.2} S: A	423.8	208.6	641.4	983.3
Ca _{0.6} Mg _{0.4} S:A	421.6	75.1	641.4	834.6
Ca _{0.4} Mg _{0.6} S:A	422.8	24.3	642.8	244.6
Ca _{0.2} Mg _{0.8} S:A	436.0	13.5	641.8	66.7
MgS:A	390.4	140.2	626.2	26.9
Ca _{0.8} Sr _{0.2} S:A	438.8	466.5	632.4	1741.9
Ca _{0.6} Sr _{0.4} S:A	471.2	395.1	624.2	1900.0
Ca _{0.4} Sr _{0.6} S:A	487.2	455.5	616.4	1645.6
Ca _{0.2} Sr _{0.8} S:A	494.0	123.0	614.8	648.9
SrS:A	507.0	326.3	600.0	311.9
Ca _{0.6} Ba _{0.4} S:A	435.4	90.3	638.8	281.9
Ca _{0.2} Ba _{0.8} S:A	423.6	11.6	569.6	31.8

MgSO₄ (AR), CaSO₄ (AR), SrSO₄ (AR), BaSO₄ (AR), CuSO₄ (AR), and Eu₂O₃ (4N) and elemental carbon powder were weighed at the stoichiometric ratio (Table 1) with the NH₄Cl (AR) flux concentration of 2 wt %. They were well mixed by an agate mortar and pestle, and the mixture was fired in a capped fire brick crucible at 1473 K for 2 h. The overall reaction for the formation of alkaline earth sulfide (AES) phosphors by the solid state reaction can be expressed as follows



Our present synthesis method is different from the conventional approaches where alkaline earth carbonate was deoxidized

by elemental sulfur or H₂S and CS₂, generating a large amount of poisonous and environmentally unfriendly gas in the preparation process. Also, replacing quartz tubes by Al₂O₃ fire brick crucible considerably reduces the preparation cost. Although AES is chemically unstable, coated sulfides have shown improved stability with the help of the microencapsulation technology.

The synthesized DE² phosphors were at first characterized by powder X-ray diffraction using a Rigaku D/max 2500 Model diffractometer with a graphite monochromator and Cu K α radiation ($\lambda = 0.1541$ nm) at 40 kV and 250 mA. Photoluminescence spectra and the decay curves were measured by a F-4500 spectrofluorometer. The UV–visible absorption measurements were carried out by U-3310 Ultraviolet–Visible spectrometer (HITACHI) by mixing and compressing 1 mg of DE² phosphors into 100 mg of KBr powder. All measurements were performed at room temperature.

To provide insights about excitation and emission mechanisms, TD-DFT calculations have been performed for the Cu⁺-doped CaS system. A $6 \times 6 \times 6$ super cell was built as the cluster model for the system. The doped copper cation is placed in the middle of the super cell. Experimental evidence has shown that these phosphors take different mechanisms in excitation and emission processes. To account for these differences, we propose different cluster models for both the processes as well. For the excitation model, 27 atoms (1 Cu⁺, 13 Ca²⁺, and 13 S²⁻ neighboring ions) were treated quantum mechanically. For the emission model, 26 atoms (13 Ca and 13 S) were used. In the emission model, the origin is shifted to S²⁻ anion and the sulfur anion in the origin is removed to reflect the nature of phosphor emission. A total of 2170 point charges on the Ca²⁺ and S²⁻ vertices with +2 and −2 charges, respectively, were employed to simulate the electrostatic environment of the phosphor. The Cartesian coordinates of the both excitation and emission models and their point charges are attached as

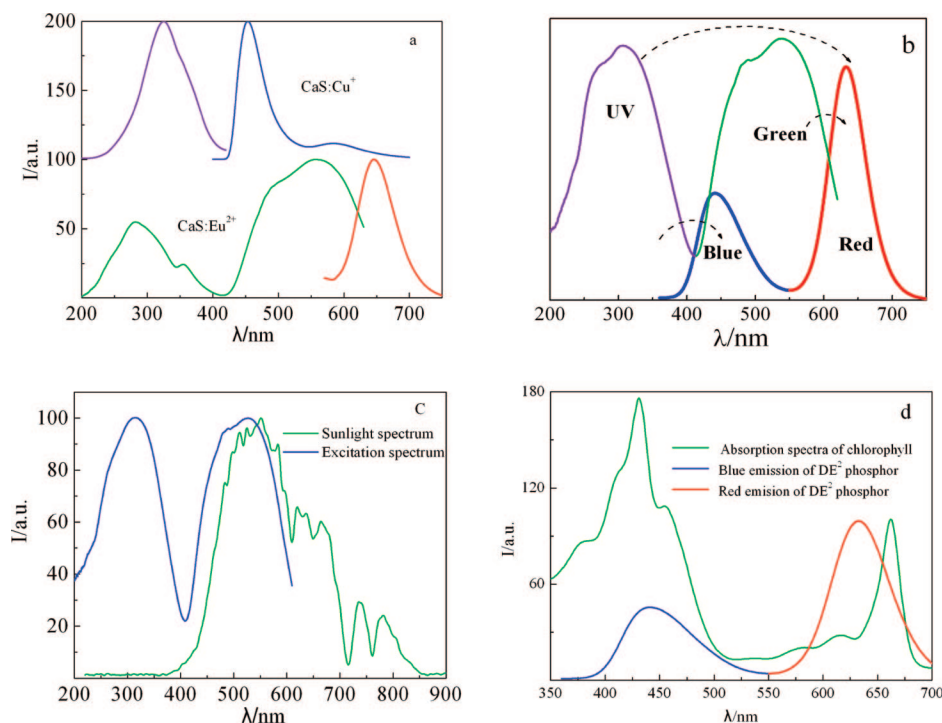


Figure 1. (a) Excitation (violet) and emission (blue) spectra of CaS:Cu⁺ (top panel) and excitation (green)/emission (red) spectra of CaS:Eu²⁺ (bottom panel). (b) Excitation (violet + green) and emission (blue + red) spectra of the DE² phosphor, CaS:Cu⁺,Eu²⁺. (c) Comparison of DE² phosphor's excitation spectra and sunlight spectrum. (d) Comparison of DE² phosphor's emission spectra and absorption spectrum of chlorophyll.

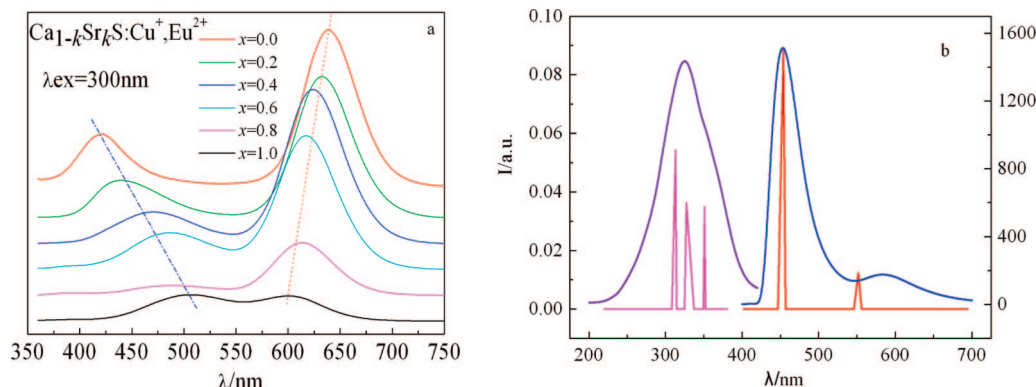


Figure 2. (a) Tunability of the emission spectra of DE² phosphors. (b) Comparison of theoretical (peaks) and experimental (curves) excitation (left) and emission (right) spectra for CaS:Cu⁺. A systematic discrepancy of 25 nm has been applied to the theoretical peak values to account for the differences between experimental and computational conditions.

Supporting Information. These models are not QM/MM in nature; they are cluster models embedded in an electrostatic environment through a large number of positive and negative point charges to simulate the bulk phase of the crystal structure. TD-DFT calculations were performed using the hybrid B3LYP^{22,23} exchange-correlation energy density functional with the Pople basis set of 6-311+G*²⁴ for all atoms that are treated quantum mechanically (27 for the excitation model and 26 for the emission model). TD-DFT calculations are solved only for singlet excited states and all calculations were conducted using Gaussian 03 D02 package²⁵ with tight self-consistent field convergence and ultrafine integration grids.

3. Results and Discussion

When an AES, CaS, is singly doped with Cu⁺, forming the CaS:Cu⁺ phosphor, one broad excitation band at the ultraviolet region and two emission peaks at blue and green areas, respectively, are found, as shown in the top panel of Figure 1a, leading to the phosphor with single excitation and dual emission. On the other hand, when CaS is doped by Eu²⁺ cation only, creating the CaS:Eu²⁺ phosphor, as shown in the bottom panel of Figure 1a, there result in two broad excitation bands at ultraviolet and green regions and only one emission peak at the red region, producing the dual excitation single emission phosphor. These two singly doped phosphors are not satisfactory in effective solar energy conversion because either part of the sunlight is wasted or the wavelength of emission does not match the absorption spectra of green pigment chlorophyll complexes of plants.

When CaS is codoped with both Cu⁺ and Eu²⁺ cations, the phosphor becomes double excitation and double emission, as shown in Figure 1b, where we observe two peaks in excitation (one purple and the other green) and two peaks in emission (one blue and the other red). This DE² phosphor can be excited by visible light between 480–580 nm where sunlight has the strongest intensity (Figure 1c) and the phosphor possesses a strong emission band (Figure 1b) at 450 nm (blue) and 645 nm (red), matching well with the absorption spectrum (green) of chlorophyll complexes (Figure 1d). Recently, Raehm et al.²⁶ reported that Cu⁺ and Eu²⁺ ions can be incorporated into the hybrid materials leading to the reduction of these Cu⁺ and Eu²⁺ ions, but their hybrid materials only showed single emission with bright yellow luminescence. Sunlight in the ultraviolet region on the earth is less intense than other parts of the spectrum; one might thus argue that its role in improving solar energy conversion is limited. We notice the fact, however, that most damaging insects such as cockroaches, aphids, and other

vermins do not like to live in the greenhouse environment where most UV light is blocked or filtered. This is likely because these insects are of phototaxis to the ultraviolet light. This observation suggests that converting ultraviolet light to blue or red light has dual benefits, conversion enhancement and insect control. Therefore, it is our design principle of the DE² phosphors that both ultraviolet and green light are used to be simultaneously converted into blue and red light. Details of synthesis and characterization are included in the Supporting Information.

One remarkable feature of the above DE² phosphors is that its emission wavelength and luminescent intensity can be fine tuned by the concentration of different alkaline earth cations. This prominent feature is practically useful because different plants have slightly different maximal adsorption peaks, so the property provides the freedom in adjusting emissions of the DE² phosphors to accommodate the difference. Figure 2a displays the dependence of the emission wavelength and relative intensity of one series of phosphors on the composition of two host cations, Ca²⁺ and Sr²⁺. Table 1 exhibits of the tenability for other host cations. These data show that Mg²⁺ does not noticeably change the peak wavelength but significantly affect the peak intensity (Table 1), whereas for Sr²⁺, both the peak wavelength and luminescent intensity are drastically altered (Figure 2a). For Ba²⁺, we see that as its concentration increases, both blue and red peaks shift to green markedly with intensities

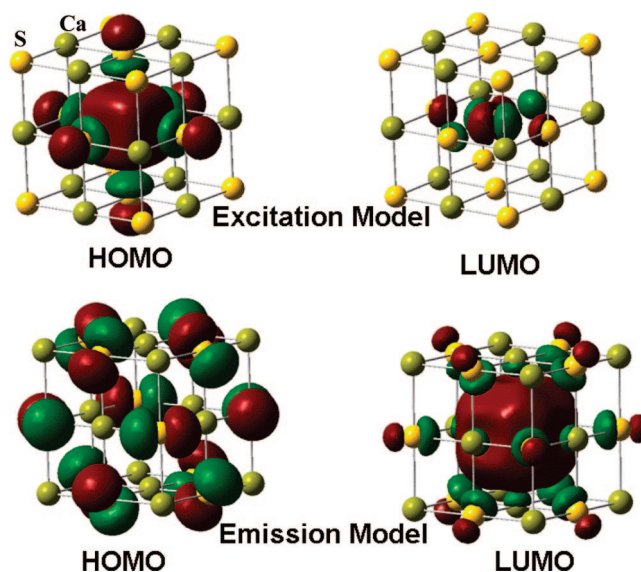


Figure 3. The HOMO and LUMO for the excitation and emission models of the CaS:Cu⁺ phosphor.

TABLE 2: Yield Comparison of Field Tests on Two Agricultural Crops, Cabbage and Pimiento, with DEPF and WPF

crops	test	film kind	test area (m ²)	bearing days	total production (kg)	yield (kg/m ²)	yield increase rate (kg/m ²)
cabbage	1	no film	93.38	71	265.5	2.84	0.0
	2	WPF	93.38	71	300.1	3.21	13.0%
	3	DEPF	93.38	71	328.8	3.52	23.9%
pimiento	1	no film	66.7	156	172	2.58	0.0
	2	WPF	66.7	156	190	2.85	10.4%
	3	DEPF	66.7	156	209	3.13	21.3%

becoming weaker. Only green light emission is seen in pure BaS (Table 1). Overall, the strongest luminescent intensity discovered is $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{S}:\text{Cu}^+,\text{Eu}^{2+}$, which has been employed in field tests to examine its efficiency enhancement in converting solar energy of agricultural crops' photosynthetic processes, whose results will briefly be discussed below.

With regard to the luminescence mechanism, it is commonly believed that the excitation of the $\text{CaS}:\text{Cu}^+$ phosphor takes place in the Cu_{Ca} luminescent center (vertices of cells where Ca^{2+} is replaced by Cu^+)¹⁸ and red emission of $\text{CaS}:\text{Eu}^{2+}$ is from Eu_{Ca} defects.¹⁶ Three excitation bands from UV to green regions in $\text{CaS}:\text{Cu}^+,\text{Eu}^{2+}$ phosphors are observed and can be attributed to the absorption of alkaline earth sulfide base matrix, leading to excitation of $\text{Cu}^{+17,27}$ and $4f^7 \rightarrow 4f^65d^1$ of Eu^{2+} ,^{28,29} respectively. The blue emission band of $\text{CaS}:\text{Cu}^{+18}$ is believed to be originated from the transition of $\text{Cu}_{\text{Ca}} \rightarrow \text{V}_{\text{S}}^{\bullet}$, because the substitution of Ca^{2+} ions with Cu^+ leads to the defect of the cell where one S^{2-} anion is missing. The red emission band is from $\text{Eu}^{2+} 4f^65d \rightarrow {}^8\text{S}_{7/2} (4f^7)$ transition because $\text{Eu}^{2+} 4f^65d$ orbitals are split into two levels (E_g and T_{2g}) in the $\text{CaS } O_h$ crystal field environment, resulting in T_{2g} levels lower than the ${}^6\text{P}_{7/2}$ level of $\text{Eu}^{2+} 4f$ atomic orbital.

To better understand the luminescence mechanism of the DE^2 phosphors, we performed TD-DFT calculations at the B3LYP/6-311+G(d) level of theory to calculate excitation and emission spectra for $\text{CaS}:\text{Cu}^+$, whose mechanism is less unambiguous. The computational results in comparison with experimental data are shown in Figure 2b. The excitation model was built by a $6 \times 6 \times 6$ super-lattice of the CaS crystal, with one Ca^{2+} ion in the origin replaced by one Cu^+ cation that is surrounded by 13 neighboring S^{2-} neutralized by 13 Ca^{2+} ions.³⁰ These 27 ions that are treated quantum mechanically are then immersed in the electrostatic field produced by 2170 points charges at Ca^{2+} and S^{2-} vertices with +2 and -2 charges, respectively, which are used to simulate the electrostatic environment of the bulk environment of the phosphors. The emission model was built similarly except that the origin is shifted to S^{2-} and the sulfur anion in the origin is removed to reflect the nature of phosphor emission mechanism discussed above.¹⁸ As can be seen from Figure 2b, computational results agree reasonably well with the experimental data. TD-DFT results reveal that there exist three peaks in the UV region for the excitation spectra of $\text{CaS}:\text{Cu}^+$ and the blue emission comes from the transition from $\text{V}_{\text{S}}^{\bullet}$ to Cu_{Ca} at 464.5 nm. The detailed analysis of molecular orbital contributions reveals that the excitation transition of $\text{CaS}:\text{Cu}^+$ involves both the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) of the excitation model (Figure 3) as well as the neighboring sulfur atomic orbitals. The emission is originated from the strong interaction between LUMO of the emission model (Figure 3) and sulfur p orbitals near the $\text{V}_{\text{S}}^{\bullet}$ site. In addition, further study (details not shown) discloses that the sensitization of luminescence of Cu^+ to Eu^{2+} is due to the resonant energy transfer from $3d_{z^2}$ orbitals of Cu^+ to $5d (t_{2g})$ orbitals of the Eu^{2+} cation.

Applications of the present DE^2 phosphors with the property of tunable emission wavelength and luminescent intensity can be found in a variety of fields, such as biolabeling, nanosensing, agriculture, etc. As an illustration, they are used as an additive in the manufacture of plastic films as the cover of the greenhouse for plants to harness solar energy utilization. Different alkaline earth sulfide compositions of the DE^2 phosphors could be used for different plants. For example, paddy is more sensitive to blue light, whereas watermelon is more responsive to red light. We used the $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{S}:\text{Cu}^+,\text{Eu}^{2+}$ phosphor for the present tests. Transparent plastic films with DE^2 phosphors as an additive (DEPF) and white plastic films (WPF) were separately manufactured and tested. The two kinds of plastic films were used as the cover of the greenhouse where test agricultural crops were grown. Table 2 shows the comparison of the production yield of two crops, cabbage and pimiento, grown in the greenhouse with the above DEPF and WPF, respectively. It is seen that the yield rate increase by DEPF is 23.9 and 21.3%, respectively, for the two crops, demonstrating that due to the enhanced sunlight conversion efficiency from ultraviolet and green to red and blue light by the DE^2 phosphors, significant gain in production can be achieved for agricultural plants.

4. Conclusions

The concept of DE^2 phosphors with the property of tunable emission wavelength and luminescent intensity for the enhancement of solar energy conversion is introduced in the present work. Doping alkaline earth ions as an aggregated energy trap within the sulfur host in a controlled manner resulted in the DE^2 phosphors with tunable emission properties. It had been discovered that the $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{S}:0.005\text{Cu}^+,0.001\text{Eu}^{2+}$ phosphor has the optimal DE^2 composition. We demonstrated their effectiveness in enhancing sunlight harvesting for different plants. TD-DFT calculations for one of the key ingredients, $\text{CaS}:\text{Cu}^+$, have been performed, providing insights about the excitation and emission mechanisms. Besides applications to increase agricultural production, these DE^2 phosphors can also be utilized in other fields such as nanosensor and biolabeling materials for ultrasensitive or green-sensitive detection of biological species such as antibodies, DNA, and cells.

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Supporting Information Available: Details of DE^2 phosphors synthesis, characterization, crystal lattice parameters, tunable luminescent properties, and Cartesian coordinates of TD-DFT cluster models of excitation and emission for $\text{CaS}:\text{Cu}^+$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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