Activation of Tomato Growth Under Photoconversion Coatings with Nanoluminophor $Sr_{0.76}Ba_{0.20}Yb_{0.02}Er_{0.02}F_{2.04}$.

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Abstract. The effect of coatings containing upconversion luminescent nanoparticles on the cultivation of Solanum lycopersicum has been studied. $Sr_{0.76}Ba_{0.20}Yb_{0.02}Er_{0.02}F_{2.04}$ particles capable of converting infrared radiation into visible light (λem = 660 nm, 545 nm, and 525 nm) were used as the phosphor. It was shown that the cultivation of tomatoes under photoconversion coatings accelerated the adaptation of plants to ultraviolet radiation. A more efficient distribution of the energy of absorbed light between the processes of photosynthesis and thermal dissipation under upconversion coatings was revealed. As a result, plants grown under photoconversion coatings increased the number and total leaf area, stem length, and leaf chlorophyll content.

1 Introduction

Intensification of agriculture is impossible without the introduction of "smart" technologies into the process [1-3]. Photoconversion materials capable of converting the transmitted light through them have found wide application in many industries, from optics to medicine. [4-6]. Moreover, photoconversion materials have great potential for agricultural applications, as they are able to convert little-used or harmful light to plants into photosynthetically active radiation (PAR) [7,8]. Unfortunately, most modern photoconversion coatings (PCC) have critical disadvantages. Organic dyes burn out quickly, losing the quantum efficiency of photoconversion. Relatively stable rare earth fluorophores have low luminescence yield [9-11]. Nanoparticles based on cadmium selenite, zinc sulfide, etc. with plasmon or exciton luminescence [12], generate reactive oxygen species, that damage phosphors.

Luminescence in the PAR region can be led as a result of the so-called photon downconversion upon excitation of phosphors in the UV region or as a result of the so-called upconversion upon excitation in the near-IR region. Downconversion is accompanied by the absorption of high-energy photons and the emission of photons of lower energy.

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During upconversion, low-energy photons are absorbed and high-energy photons are emitted. [13,14]. Currently, most of the luminescent materials used act as downconversion luminophores. In agronomy, upconversion phosphors can be used to convert IR radiation into PAR. Phosphors based on pairs of rare earth cations containing a sensitizer with a wide absorption cross section (for example, Yb^{3+}) and an activator (Er^{3+}, Tm^{3+} or Ho^{3+}) are best suited for this task. [14,15]. To ensure high efficiency of upconversion, the sensitizer and activator must be included in the matrix, for example, strontium or barium fluorides [16,17].

The aim of the work was to study PCP containing upconversion particles $Sr_{0.76}Ba_{0.20}Yb_{0.02}Er_{0.02}F_{2.04}$, on agricultural plants.

2 Materials and methods

Synthesis of upconversion nanoparticles with a nominal composition of $Sr_{0.76}Ba_{0.20}Yb_{0.02}Er_{0.02}F_{2.04}$ was carried out according to the procedure described in the article [18]. The nanoparticles were dissolved in a 7% acetone solution mixed with Ftoroplast-32L fluoropolymer [19] and sprayed on the glass surface. Luminescence spectra of nanoparticles in the visible range were recorded using a fiber optic spectrometer USB2000 (OceanOptics, USA).

Tomato plants (*S. lycopersicum*) were grown at a 16-hour day, at a temperature of 25–26 °C and low light intensity. (400–700 nm, 70 μmol photons m^{-2} s^{-1}).

At the seventh leaf stage, the plants were placed under glass coated with a fluoroplastic polymer with or without photoconversion nanoparticles. Added UVA to the light spectrum (λ = 370 nm, 10 μmol photons m^{-2} s^{-1}). The leaf area was determined using the GreenImage program [19]. The chlorophyll content in the leaves was determined using a chlorophyll meter CL-01 (Hansatech, UK). The number of leaves and stem length were determined manually. Light intensity was measured using a PAR Meter PG200N spectrometer (UPRtek, Taiwan).

Chlorophyll a fluorescence (FChl) was measured on a leaf at room temperature using a fluorimeter DUAL-PAM-100 (Walz, Germany). Before measurement, the plants were kept in the dark at a temperature of 25–26°C for 1 hour. To measure the maximum quantum yield of PS2 photochemistry and the parameters of FChl after light adaptation (10 min, λ = 625 nm, 250 μmol photons m^{-2} s^{-1}), the samples were illuminated with a saturating pulse with a width of 500 ms (λ = 625 nm, 12 000 μmol photons m^{-2} s^{-1}). The FChl parameters were calculated using the software DualPAM [20].

To determine statistically significant differences, one-way analysis of variance (ANOVA) was performed followed by comparison using Tukey's and Student's t-test for independent means. The difference was considered significant if $p \leq 0.05$.

3 Results

Excitation of $Sr_{0.76}Ba_{0.20}Yb_{0.02}Er_{0.02}F_{2.04}$ nanoparticles by IR radiation at a wavelength of 975 nm induced photoluminescence with characteristic Er^{3+}/Yb^{3+} emission bands in the red (about 660 nm) and green (545 nm and 525 nm) regions of the spectrum (data not shown), which corresponds to the luminescence spectra of SrF2 single crystals doped with Er^{3+} and Yb^{3+} [17,21-24].

Table 1 shows the results of morphometric studies of *S. lecopersicum* plants. It is shown that PCC have a significant positive effect on plant growth and leaf surface area. At the same time a moderate, but statistically significant effect on the rate of leaf formation was revealed. The chlorophyll content in plants grown under PCC was also higher.

Table 1. Effect of upconversion luminescent coating on the growth and development of S. lycopersicum. The presented data are the result of averaging from four (for leaf area) to eleven (for other parameters) measurements.

Parameter	**Before experiment**	**25th Day from the Start of the Experiment**	
		Control	PCC
Leaf number, ±σ	7.0 ± 0.3 [a]	11.0 ± 0.9 [b]	13.0 ± 1.3 [c]
Leaf area, cm^2 ± σ	22.9 ±3.8 [a′]	89.7 ± 12.0 [b′]	121 ± 19.8 [c′]
Stem length, cm ±σ	5.8 ± 0.3 [a″]	13.2 ± 0.7 [b″]	19.4 ± 3 [c″]
Chlorophyll content, r. u. ±σ	6.5 ± 0.6 [a‴]	7.0 ± 0.7 [a‴]	8.6 ± 0.5 [b‴]

Letters indicate statistically significant differences ($p \leq 0.05$). ′, ″ and ‴ superscripts above the letters indicate the presence of statistically significant differences between groups of plants for each parameter.

Analysis of light-induced changes in FChl showed that the maximum quantum yield (ΔF/Fm) in the dark-adapted plants leaves before the start of the experiment was 0.82 and practically did not change during the experiment in both plants group (data not shown). The effective photochemical quantum yield of photosystem II (Y(II)) in plants growing under control coatings decreased from 0.3 to 0.1 during the first week after the start of the experiment (Figure 1A), indicating an imbalance between electron transport and utilization of NADPH in plants. Subsequently, Y(II) increased and gradually reached the initial values within three weeks in control plants. In plants growing under experimental coatings, the drop in Y(II) was less. After that, the Y(II) rapidly increased and reached a maximum within a few days. Y(NO) in control plants in the first five days of the experiment increased from 0.4 to 0.5, while in experimental plants Y(NO) practically did not change. The differences observed in the development of Y(NPQ) in the control and experimental groups may be related to different efficiency of adaptive mechanisms to changed lighting conditions. The development of Y(NPQ) in both groups of plants practically did not differ.

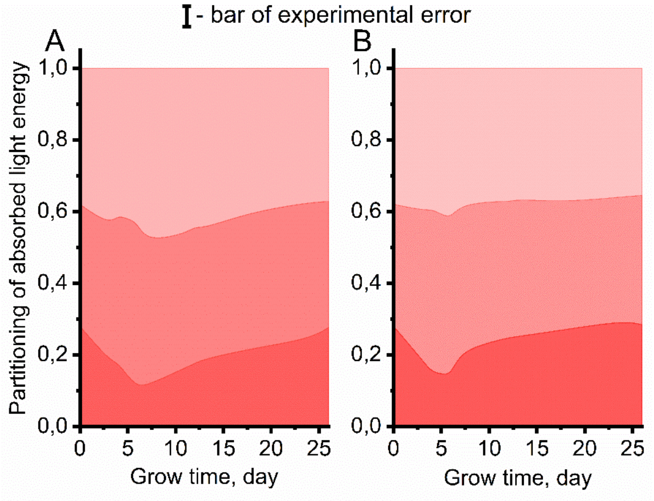

Fig. 1. Dependence of the distribution of absorbed light energy between Y(II) (red), Y(NPQ) (pink) and Y(NO) (light pink) on the growing time of control plants (A) and experimental plants (B). Data are the mean of 11 measurements with standard deviation.

4 Discussion

In this work, we have created a photoconversion material based on nanoparticles with upconversion luminescence for greenhouse glass coating. Despite the lower quantum efficiency compared to downconversion materials [25–27], our nanoparticles are among the most efficient upconversion luminophors [17]. An additional advantage of the presented coatings is the ability to convert UV radiation into PAR [17, 28].

In our work, we have demonstrated that PCCs have a positive effect both on plant growth, which is reflected in an increase in plant height and biomass, and on the efficiency of the conversion of absorbed light energy. It can be assumed that the reasons for this are an increase in intensity in the red region of the PAR, a change in the ratio of the spectral bands of light, absorption of UV radiation by luminophors, etc. It is known that the growth and development of plants determines not only the intensity of illumination, but also its spectrum. Likewise, it is known that, under conditions of low illumination, red light effectively intensifies photosynthesis [29], which could also be the case in our work. Also, the contribution of red light emitted by phosphors can stimulate a change in the content of phytohormones [30]. IR absorption and luminescence in the red region can change the ratio of red and far red light and thus activate the phytochrome system, which, in turn, can intensify photosynthesis, increase stress resistance and accelerate plant growth [31,32]. On the other hand, PCCs reduce the amount of UV, which can adversely affect plants [33]. An increase in the chlorophyll content in plant leaves under PCC by about 2 times (calculated from relative units in mg Chl (g fresh weight)$^{-1}$) [34] may indicate a restructuring of the photosynthetic apparatus. Similar results were obtained earlier using downconversion coatings [35]. It is known that PCCs also affect the number of soil microorganisms, which has a positive effect on plant growth [36].

5 Conclusion

Thus, $Sr_{0.76}Ba_{0.20}Yb_{0.02}Er_{0.02}F_{2.04}$ nanoparticles have been successfully used in growing tomatoes and can be recommended for use in greenhouses under conditions of insufficient natural insolation.

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