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Plant Photochemistry under Glass Coated with Upconversion Luminescent Film

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Abstract: It has been shown that the cultivation of plants under glass coated with nano-sized upconversion luminophores led to an increase in plant productivity and the acceleration of plant adaptation to ultraviolet radiation. In the present work, we examined the effect of upconversion nanopowders with the nominal composition $\text{Sr}_{0.955}\text{Yb}_{0.020}\text{Er}_{0.025}\text{F}_{2.045}$ on plant (*Solanum lycopersicum*) photochemistry. The composition, structure and size of nanoparticles were tested using X-ray pattern diffraction, scanning electron microscopy, and dynamic light scattering. Nanoparticles are capable of converting infrared radiation into red and green photons. Glasses coated with upconversion luminophores increase the intensity of photosynthetically active radiation and absorb the ultraviolet and far-red radiation. The chlorophyll *a* fluorescence method showed that plants growing under photoconversion and those growing under common film demonstrate different ability to utilize excitation energy via photosynthesis. It was shown that under ultraviolet and high light conditions, the efficiency of the photochemical reactions, the non-photochemical fluorescence quenching, and the electron transport remained relatively stable in plants growing under photoconversion film in contrast to plants growing under common film. Thus, cultivation of *Solanum lycopersicum* under photoconversion glasses led to the acceleration in plant growth due to greater efficiency of plant photochemistry under stress conditions.

Keywords: photoconversion; upconversion; nanomaterials; greenhouses; plant photochemistry

1. Introduction

Sustainable agriculture has an important role to play in the continuous provision of food to the population. Consequently, for farmers, the problem of increasing the productivity of agricultural crops is always in the forefront of their minds. Everyone knows that for good harvest production, it is necessary to provide the most favorable conditions: lighting, watering, nutrition, and temperature mode. The intensification of agriculture implies a transition to the year-round cultivation of plants, which is effectively realized in modern greenhouses. The design features of greenhouses allow for optimized growth conditions and increased crop yields while reducing costs [1–3]. The protective environment of greenhouse allows the growth of thermophilic plant species ubiquitously, as well as the planting of seeds and harvest of crops several times a year. The most important feature of greenhouses is their maximum transmittance of sunlight to the plants. However, even this property is not always sufficient to achieve the best result, due to sunlight deficit in temperate regions. Currently, artificial lighting is used to solve the problem of the lack of sunlight, but this leads to an increase in energy consumption [4–6]. Photoconversion coatings of greenhouse glass are an example of smart and efficient production technologies, which reduce costs and increase yields. Normally, agricultural photoconversion covers transform the light, which is least absorbed by plants, into photosynthetically active radiation (PAR). It is assumed that the potential economic effect of using photoconversion coatings can be achieved by reducing the cost of electricity, and of the purchase and maintenance of equipment for artificial lighting, as well as increasing the productivity of crops.

Light quantity and quality affect photosynthesis efficiency, plant growth and metabolism [7–9], and farmers should ensure that plants have optimal lighting. PAR is a light with wavelengths 400–700 nm. This waveband at sunny weather can contain approximately 25% of the sunlight photons, which leaves a lot of potential for the application of photoconversion technologies in the greenhouse. In the 19th century, the research of T. W. Engelmann and K. A. Timiryazev demonstrated that red and blue photons are most able to maximize the productivity of plant photosynthesis, and this was later confirmed by McCree [10]. Despite all the advantages of red illumination for photosynthesis, blue, green, yellow, and far-red lights additionally intensify the photosynthesis, optimize plant biochemistry, and improve crop quality [11–18].

A wide range of devices are being developed that are made with luminescent materials (metal complexes, semiconductors, nanoparticles, fluorescent proteins, organic dyes), including some for agriculture [19–22]. The main limitations for the agricultural application of photoconversion devices is the inability to manufacture ideal covers, which have a light transmittance and harvesting performance in given parts of the solar spectrum, high quantum yield and good stability when exposed to rain, high intensity light and extreme temperatures.. Unfortunately, almost all photoconversion coatings produced so far have critical problems. The organic fluorophores incorporated in coatings rapidly photobleach, with a decrease in the quantum yield of photoconversion. The relatively stable rare-earth elements-based fluorophores have a low yield of luminescence [23–27]. The illumination of nanoparticles with plasmon or exciton emissions (cadmium selenide, zinc sulfide, etc.) [28] leads to the generation of reactive oxygen species, which cause damage to phosphors. Moreover, this type of particles is hardly integrated in polymers. An important goal of modern research is the creation of photoconversion coatings, which will include durable phosphors with optimal photoabsorbing and emitting properties [22,29]. Previously, stable photoconversion materials, such as nanoluminophores that are not damaged by reactive oxygen species due to high vapor-proofing, were obtained [30–32]. Moreover, the coverings are characterized by a very high efficiency of photoconversion of ultraviolet radiation into red and blue light. Therefore, photoconversion technologies have great potential to enhance plant growing without additional energy consumption.

Most luminescent materials convert high energy photons into light quanta having lower energy, but a few contrarily phosphoresce with higher energy photons (so-called upconversion luminescence). Upconversion luminophores, suggested in the last cen-

ture [33,34], may be applied in agriculture, but only in the case of converting infrared light into visible light. This requirement is best met by phosphors based on pair of rare-earth cations. Upconversion pair cations should contain a sensitizer with a wide absorption cross-section (for example, Yb^{3+}) and an activator (Er^{3+} , Tm^{3+} , or Ho^{3+}) [33,35–37] incorporated in the matrix to provide a high upconversion yield. Strontium or barium fluoride is preferred as the matrix, as this is proven to provide a high upconversion yield [38–40].

Previously, it has been shown that upconversion coatings with nano-sized upconversion luminophores increase plant productivity and accelerate their adaptation to ultraviolet radiation [41,42]. In this work, we studied the effect of glasses coated with an upconversion luminescent film on the photochemistry of agricultural plants. For this purpose, we prepared $\text{Sr}_{0.955}\text{Yb}_{0.020}\text{Er}_{0.025}\text{F}_{2.045}$ nanoparticles capable of performing upconversion. The present research is aimed at the design of versatile photoconversion coatings for use in greenhouses.

2. Materials and Methods

2.1. Synthesis of Nanoluminophore

In the study, nanopowders with a nominal composition $\text{Sr}_{0.955}\text{Yb}_{0.020}\text{Er}_{0.025}\text{F}_{2.045}$ were used. Nanoparticles have been produced by co-precipitation from nitrate solutions, as described in [43]. The solution containing 0.08 M nitrate was dropwise mixed with 0.16 M ammonium fluoride. Note that NH_4F was taken with 7% excess. The resulting mixture was incubated for two hours with stirring. After incubation, the suspension was allowed to settle and the obtained precipitate was washed with ammonium fluoride until the nitrate ions were completely washed out. The washed sediment was then centrifuged at 10,000 rpm for 5 min. Centrifugation was followed by two-stage drying of the precipitate: first in air at 45 °C, then in a platinum crucible at 600 °C for 1 h. The heating rate was 10 degrees per min.

2.2. Production of Photoconversion Film

To manufacture the photoconversion film (PCF) a solution of nanoparticles in acetone and a liquid component of a fluoroplate polymer were used. Fluoroplast-32L (St. Petersburg Kraski, Russia) was applied to the preparation of the polymer varnish. A 7% solution of nanoluminophore was added to a fluoroplate polymer in a ratio of 1:100 and mixed. Then the resulting mixture was loaded into the spray gun, and the PCF containing luminescent nanoparticles was sprayed on to the glass surface.

2.3. Characterization of Nanoluminophore

X-ray pattern diffraction (XRD) was performed on a BRUKER D8 ADVANCE diffractometer (Billerica, MA, USA). Calculation of the unit cell parameters was performed using POWDER 2.0 software (Moscow State University, Moscow, Russia). Particle shape and size were established from a scanning electron microscopy (SEM) image. For this aim, a Carl Zeiss NVision 40 microscope (Zeiss AG, Oberkochen, Germany) connected with Oxford Instruments XMAX (80 mm²) set-up (Oxford Instruments plc, Abingdon, UK) (using ImageJ software) was used. Hydrodynamic diameter distribution of nanoparticles was determined using Zetasizer Ultra (Malvern Panalytical, Malvern, UK). Registration of particle luminescence was completed using fiber-optic spectrometer USB2000 (OceanOptics, Orlando, FL, USA). The sample was placed inside the integrating sphere Cintra 4040 (GBC Scientific, Braeside, Victoria, Australia) and irradiated by a 50 mW IR light diode ($\lambda = 975$ nm).

2.4. Growth Conditions and Morphometric Measurements

The tomato variety (*Solanum lycopersicum*) “Balcony Miracle” was the one used experimentally in this work. Plants were grown with a 16 h photoperiod at 25–26 °C. Intensities of PAR and overall light (350–800 nm) were ≈ 70 $\mu\text{mol photons s}^{-1} \text{ m}^{-2}$ and about 140 $\mu\text{mol photons s}^{-1} \text{ m}^{-2}$. Plants were grown to the seventh leaf stage. Both experimental and control plants were then covered by glasses with either a common fluoroplastic polymer coating or containing photoconversion nanoparticles. The UVA component ($\lambda = 370$ nm, photon flux density (PFD) ≤ 10 $\mu\text{mol photons s}^{-1} \text{ m}^{-2}$) was added to the illumination

spectrum. PG200N Spectral PAR Meter (UPRtek, Zhunan, Miaoli, Taiwan) was used to estimate light flux density. The relative chlorophyll concentration in leaves was evaluated using portable chlorophyll meter CL-01 (Hansatech, Norfolk, UK). The number of leaves was determined manually. The length of the stem was measured with a graduated ruler to the nearest millimeter. For the definition of the leaf area, the GreenImage software was applied.

2.5. Chlorophyll *a* Fluorescence Kinetics Measurement

The kinetics of chlorophyll fluorescence (ChlF) were measured by a DUAL-PAM-100 fluorometer (Waltz, Eichenring, Effeltrich, Germany). Experiments were performed using non-cut leaves at room temperature. Measurements were preceded by 1 h dark incubation of the plants at 25–26 °C to provide complete relaxation of all photoinduced processes. To measure maximum quantum yield of photosystem II photochemistry (F_v/F_m) and ChlF parameters, the leaves were illuminated with a saturating 500 ms flash ($\lambda = 625$ nm, $12,000 \mu\text{mol photons s}^{-1} \text{m}^{-2}$). Adaptation to actinic illumination ($\lambda = 625$ nm, $250 \mu\text{mol photons s}^{-1} \text{m}^{-2}$) lasted 10 min. ChlF registered at various intensities was studied after 30 min of light adaptation for the leaves. The calculation of the ChlF parameters was performed using DUAL-PAM Software [44] according to the equations:

$$F_v/F_m = (F_m - F_0)/F_m \quad (1)$$

$$Y(\text{II}) = (F_m' - F)/F_m' \quad (2)$$

$$Y(\text{NPQ}) = F/F_m' - F/F_m \quad (3)$$

$$Y(\text{NO}) = F/F_m \quad (4)$$

$$\text{ETR}(\text{II}) = \text{PAR}(\text{II}) \cdot Y(\text{II}) / (F_v/F_m) \quad (5)$$

where F_0 is the initial fluorescence value, F_m is the maximum fluorescence value, F_v is the photoinduced changes of chlorophyll *a* fluorescence yield, $Y(\text{II})$ is the effective quantum yield of PSII, $Y(\text{NPQ})$ is the quantum yield of light-induced non-photochemical quenching, $Y(\text{NO})$ is the quantum yield of non-regulated heat dissipation and fluorescence emission, F is a fluorescence yield measured briefly before application of a saturating pulse, F_m' is light-induced maximum level of chlorophyll fluorescence in light-adapted samples, ETR is the rate of linear electron transport through photosystem II, PAR(II) is the PAR absorbed by PS II (quanta/(PS II·s)).

2.6. Statistics

To determine statistically significant differences between plant groups, one-way analysis of variance (ANOVA) followed by post hoc comparisons by Tukey's test and Student's *t* test for independent means were performed. The normality (Shapiro–Wilk test) requirements were checked. The difference was considered significant if $p \leq 0.05$.

3. Results

To understand which particles we are dealing with, we tested their composition, structure and size. XRD for the 600 °C-treated nanoparticles are shown in Figure 1. The data confirms that the chosen technique of synthesis of nanopowders leads to the formation of fluorite structure particles (JCPDS #06-0262, $a = 5.800 \text{ \AA}$). The monophase and purity of the obtained samples are also confirmed.

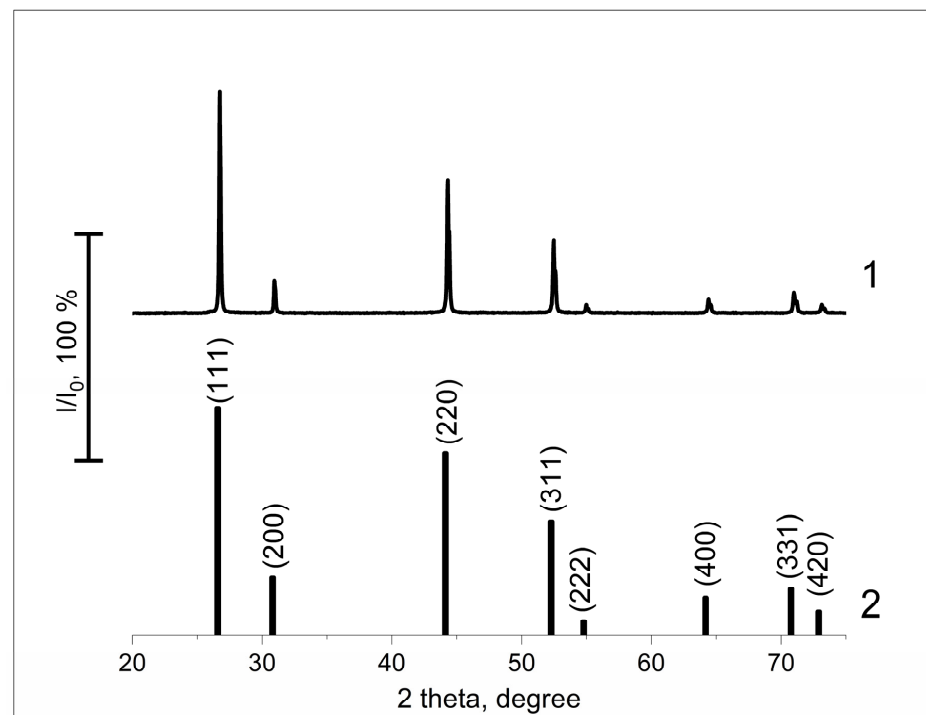


Figure 1. XRD for the $\text{Sr}_{0.955}\text{Yb}_{0.020}\text{Er}_{0.025}\text{F}_{2.045}$ nanoparticles (1) and JCPDS #06-0262 for the strontium fluoride (2).

The scanning electron microscopy image for $\text{Sr}_{0.955}\text{Yb}_{0.020}\text{Er}_{0.025}\text{F}_{2.045}$ samples shown in Figure 2A made it possible to determine the shape and diameter of the particles. Two fractions of spherical particle were identified: primary particles were approximately 75 nm, and agglomerates with a 300 nm diameter. The dynamic light scattering method confirmed the formation of both primary particles and their agglomerates (Figure 2B). The energy-dispersive X-ray analysis clarified the elemental composition of the particles: $\text{Sr}_{0.948}\text{Yb}_{0.024}\text{Er}_{0.028}\text{F}_{2.052}$.

Figure 3A presents the spectra of the semiconductor laser-induced photoluminescence of nanoparticles measured in visible range. Under 976 nm excitation (curve 2), the nanoparticles emit spectra with maximum wavelengths of 660 nm, 545 nm and 525 nm (curve 1). Very weak blue (410 nm) and down-shifted (1520 nm) luminescence are not shown. It must be emphasized that the amplitudes of both the excitation light and the luminescence are given in arbitrary units and should not be used to calculate the luminescence efficiency. Difference spectrum (“light spectrum under photoconversion film” minus “light spectrum under common film”) allowed the visualization of changes in the spectral composition of growth light passed through photoconversion glasses, are shown in Figure 3B. It was shown that the photoconversion glasses we used were capable of increasing PAR intensity and decreasing intensity of UV and far-red. Thus, the luminescent nanoparticles are capable of optimizing the illumination spectrum (increasing PAR intensity and changing the ratio of red and far-red light) and can be used in photoconversion materials for agricultural applications.

Since our study is aimed at optimizing the conditions for growing agricultural plants with a shortage of natural light, we imitated a cloudy day in temperate regions using UV and incandescent lamps. UVA and PAR intensities were $\leq 10 \mu\text{mol photons s}^{-1} \text{m}^{-2}$ and $\approx 70 \mu\text{mol photons s}^{-1} \text{m}^{-2}$. The overall light intensity (350–800 nm) was greater than $140 \mu\text{mol of photons s}^{-1} \text{m}^{-2}$.

The results of morphometric studies are presented in Table 1. It was shown that photoconversion film has a moderate, but statistically significant, effect on the leaf formation. Under control films, the appearance of a new leaf was observed every sixth day, whereas under photoconversion films, new leaves appeared every fourth day. At the same time, the number of leaves in the control samples increased by 55% and by 85% in the experimental conditions.

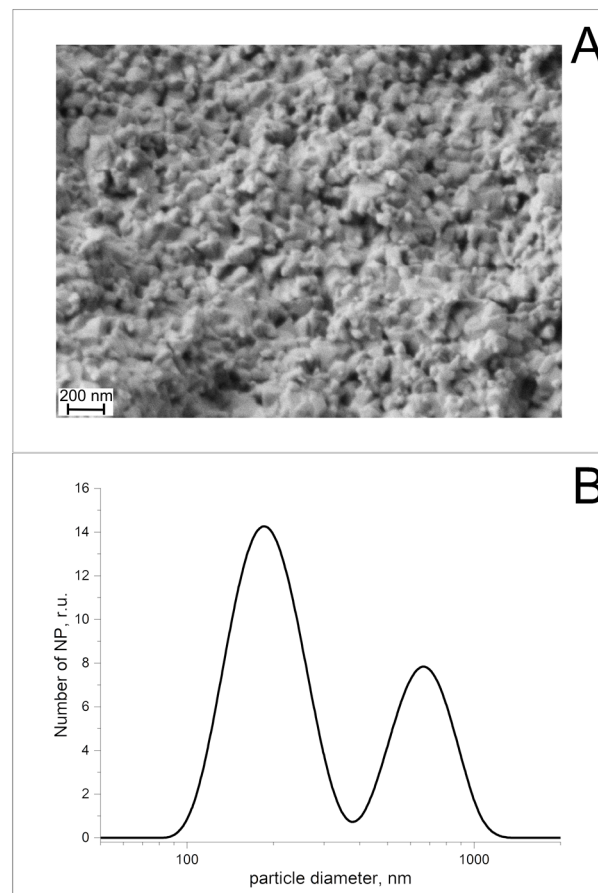


Figure 2. Scanning electron microscopy image for $\text{Sr}_{0.955}\text{Yb}_{0.020}\text{Er}_{0.025}\text{F}_{2.045}$ (A) and particle number as a function of their diameter (B).

In comparison to other parameters, the area of leaves showed the greatest increase. Before the experiment, the average leaf area was 23 cm^2 ; after 25 days, control samples grew by 290% under common film and by 435% under photoconversion film. Thus, the acceleration of leaf growth under photoconversion films was 50%. Note that PCF contributes to acceleration in the length of the stem, while it practically does not affect the length of the internodes. It is interesting to mark that the chlorophyll concentration in the tomatoes leaf remained relatively unchanged under the common film, while PCF increased the amount of chlorophyll in the leaf. Thus, it is shown that plants grow and develop faster under the films containing photoconversion nanoparticles.

To understand the cause of the acceleration in tomato growth under the photoconversion films, we examined the impact of photoconversion films on the plant photochemistry. For this aim, we analyzed the development of changes in the maximum quantum yield of plant photochemistry (which provides information about the general state of the photosynthetic apparatus). This parameter reflects the utilization of excitation energy (Figure 4).

The level of photochemical activity recorded in the plants did not decrease during the experiment, which may indicate similar and stable overall states of the photosynthetic apparatus in both groups of plants (Figure 4A). Illumination of plants led to formation of excited states of pigments of photosynthetic antenna. Part of this energy is used for photosynthesis. The proportion of excited energy routed to photosynthesis is reflected in the level of effective $Y(\text{II})$ (quantum yield of photosystem II photochemistry). Under the unfavorable conditions, the plant can change the proportion of energy directed to photosynthesis and activate mechanisms aimed at the quenching of excitation energy via heat dissipation: so-called processes of regulated and non-regulated heat dissipation. Activity of these processes correlate well with levels of non-photochemical quenching of

fluorescence (NPQ), and non-regulated heat dissipation and fluorescence emission (NO), respectively. The installation of the coating over the plants and the appearance of ultraviolet light in the growth spectrum induce the changes in ChlF parameters. These changes had similar trends in both control and experimental groups. The $Y(II)$ decreases within the first 6–7 days from approximately 0.3 to 0.1 (Figure 4B), which indicates some suppression of photosynthesis in the plants. The reduction of $Y(II)$ is accompanied by an increase in $Y(NPQ)$ (Figure 4C) and $Y(NO)$ (Figure 4D) in both control and experiment plants. The amplitude of $Y(II)$ reduction was equal to the sums of growth of $Y(NPQ)$ and $Y(NO)$. However, the changes described above were reversible: the photochemistry parameters gradually reached initial values. The rate of relaxation of $Y(NO)$ and $Y(II)$ values in plants growing under PCF was relatively fast (initial levels were observed within 3–5 days and did not change later). In control plants, $Y(II)$ and $Y(NO)$ relaxed slowly (achievement of initial levels were observed in only three weeks). Note that the kinetics of $Y(NPQ)$ in both control and experimental plants were practically identical. The above-mentioned data reflect a reversible decrease in efficiency of photosynthesis at the first week of the experiment.

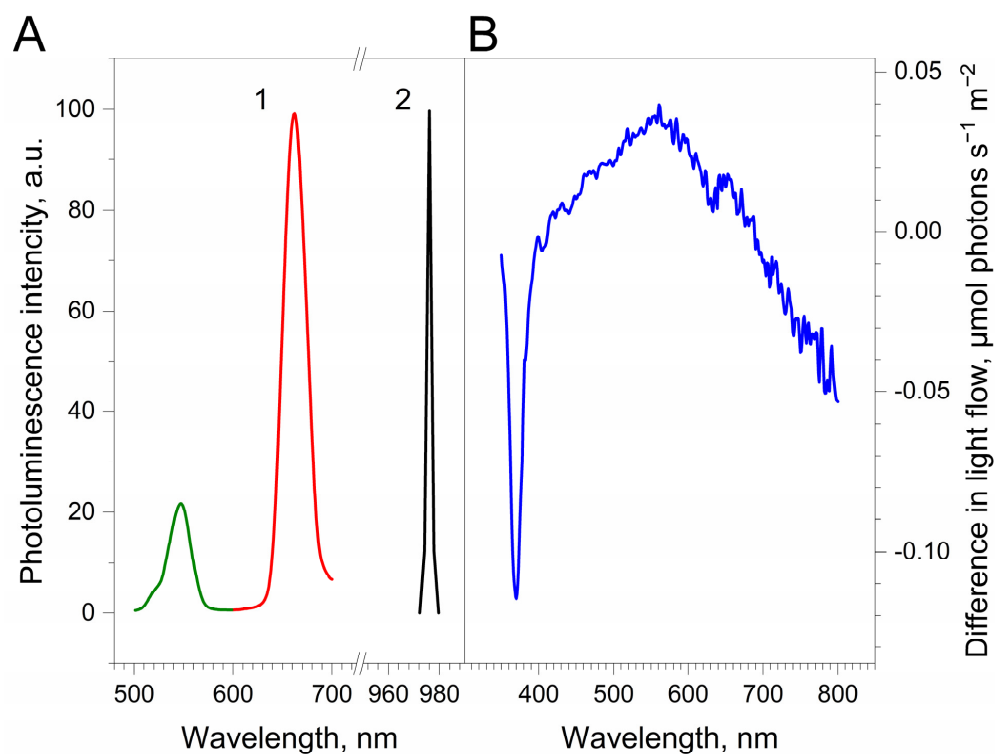


Figure 3. (A) Photoluminescence (1) of the nanoparticles in acetone in PAR range, which was excited by a semiconductor laser (2). (B) Difference spectrum (“light spectrum under photoconversion film” minus “light spectrum under common film”), showing changes in the spectrum of growth light. In figure (A), green and red colors indicate the luminescence in the green and red regions of the spectrum, respectively.

The different capacities of the photosynthetic electron-transport chain, and the activity of enzymes during the dark stage of photosynthesis, show that electron transport and, concurrently the redistribution of excitation energy, changes in plants growing under different conditions, as a result of changes in light intensity. We studied the dependence of $Y(II)$, $Y(NPQ)$ and ETR (the rate of linear electron transport through photosystem II) on light intensity (Figure 5).

Table 1. Effect of an upconversion luminescent film on the growth of tomatoes. Presented data are the result of averaging from four (leaf area) to eleven (all other parameters) measurements.

Parameter	Before Experiment	25th Day from the Start of the Experiment	
		Common Film	Photoconversion Film
Leaf number per plant, \pm SD	7.0 ± 0.3^a	11.0 ± 0.9^b	13.0 ± 1.3^c
Leaf area, $\text{cm}^2 \pm$ SD	$22.9 \pm 3.8^{a'}$	$89.7 \pm 12.0^{b'}$	$123.2 \pm 19.1^{c'}$
Stem length, $\text{cm} \pm$ SD	$5.8 \pm 0.3^{a''}$	$13.2 \pm 0.7^{b''}$	$19.8 \pm 3.2^{c''}$
Chlorophyll content, r.u. \pm SD	$6.5 \pm 0.6^{a'''}$	$7.0 \pm 0.7^{b'''}$	$9.0 \pm 0.1^{a'''}$

Letters indicate statistically significant difference ($p \leq 0.05$). ', '' and ''' superscripts above the letters mean the presence of a statistically significant difference between plant groups for each parameter separately.

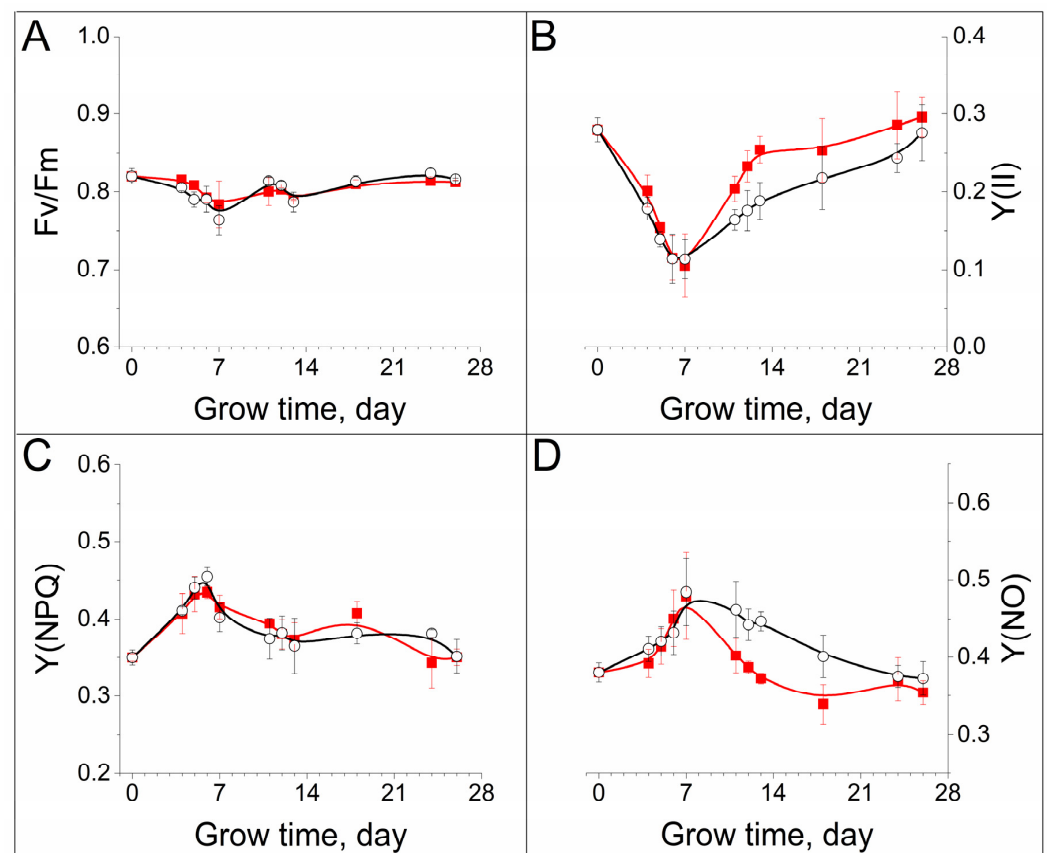


Figure 4. Development of changes in maximum (A) and effective (B) quantum yield of photosystem II photochemistry, quantum yield of light-induced non-photochemical fluorescence quenching (C) and quantum yield of nonregulated heat dissipation and fluorescence emission (D) under common (red, closed squares) and photoconversion (black, opened circles) films. The data are the means of at least three measurements, with the standard deviation of the mean.

The Y(II) and Y(NPQ) in leaves of plants growing under PCF were relatively stable at weak light (up to $100 \mu\text{mol photons s}^{-1} \text{m}^{-2}$) (Figure 5A,B). When Y(II) was relatively high (about 0.72–0.73), the Y(NPQ) value close to zero. Further magnification of light intensity resulted in a simultaneous increase in Y(NPQ) and decrease in Y(NO), which achieved maximum and minimum, respectively, at $1000\text{--}1500 \mu\text{mol photons s}^{-1} \text{m}^{-2}$. In control plants, Y(II) and Y(NPQ) rapidly changed even at low light, however under high light (more than $1000 \mu\text{mol photons s}^{-1} \text{m}^{-2}$) they were equal to levels observed in experiment plants. This may indicate the different ability of plants growing under PCF and common film at utilizing excitation energy via photosynthesis. In addition, an increase in light intensity led to a gradual growth of the ETR (Figure 5C). ETR was higher in plants

growing under PCF under all light intensities, in comparison to plants grown under common film. At 1200 $\mu\text{mol photons s}^{-1} \text{m}^{-2}$, a decrease in ETR was observed, which may be induced by photoinhibition.

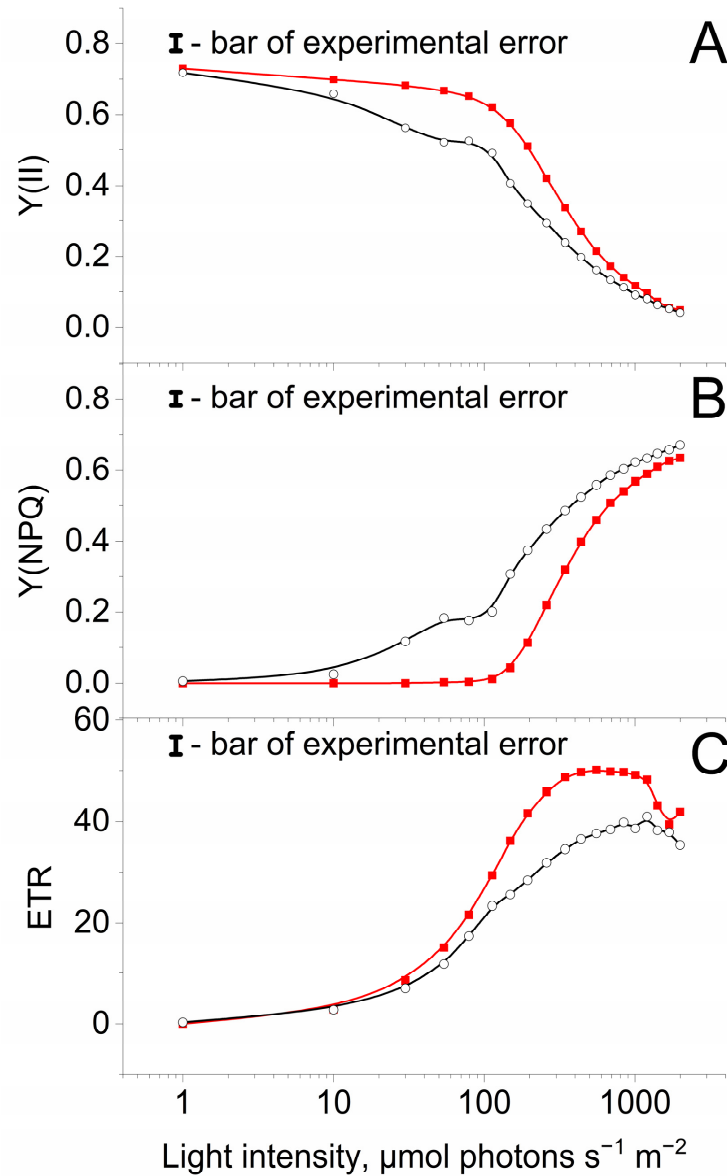


Figure 5. Dependence of $Y(\text{II})$ (A), $Y(\text{NPQ})$ (B) and ETR (C) on light intensity in plants growing under common (red, closed squares) and photoconversion (black, opened circles) films. Measurements were done at room temperature. The data are the means of at least three measurements, with the standard deviation of the mean.

4. Discussion

It is known that the quality and quantity of light affects the growth and development of plants, determining the efficiency of photosynthetic processes, as well as the accumulation of secondary metabolites. Plants are capable of adapting to a wide variety of light conditions; however, improving the quality of lighting always increases the productivity of agricultural plants. Plants are believed to utilize between a third and a half of solar radiation. The remaining photons belong to the ultraviolet, infrared and other light ranges, which are generally unavailable to plants for photosynthesis. This makes the development of photoconversion technologies relevant for the temperate and cold regions of the planet, where usable light is at a premium. Based on the investigations of Engelmann [45],

Timiryazev [46] and McCree [10], we know that additional red light can more efficiently activate photosynthesis in comparison to other light of similar intensity. This principle was applied in this study. For the intensification of plant development, we used a photoconversion coating containing $\text{Sr}_{0.955}\text{Yb}_{0.020}\text{Er}_{0.025}\text{F}_{2.045}$ nanoluminophores. The coating absorbs IR light and emits visible light (at bandwidths of 660 nm, 545 nm and 525 nm; Figure 3A). These luminescence bands are usually observed under the illumination of the phosphors containing the $\text{Er}^{3+}/\text{Yb}^{3+}$ ion pair [39–42,47–50]. Of course, the phosphor we used is much inferior to conventional phosphors in terms of light conversion efficiency (about 6% vs. more than 20%) [30–32,51–61]. However, in comparison with many other upconversion luminophores, this phosphor has a fairly high efficiency of photoconversion. The fact that similar particles can convert ultraviolet radiation into PAR increases their usefulness in greenhouses, as discussed in [39]. The difference spectrum shown in Figure 3B confirmed that photoconversion glasses moderately increase PAR intensity and absorb UVA and far-red. Obviously, this changes the red light:far-red light ratio. The difference spectrum is a broadband radiation with two pronounced peaks at 561 nm and 650 nm, which can be correlated with the erbium luminescence bands. The observed broadband radiation was studied earlier for nanoparticles of various chemical compositions [62–67]. The mechanism of the appearance of such luminescence is the subject of open discussion.

As can be seen in Table 1, plants grow and develop quicker under the PCF in comparison with common film, which is consistent with the previous data [41,42]. The appearance of leaves, and the increase in their area, are accelerated by 50%. PCF accelerates the growth of the stem, without affecting the length of the internodes, which is indicative of accelerated growth rather than avoidance of shadows. Moreover, photoconversion glasses stimulate the accumulation of chlorophyll in the tissues. According to the data published in [68], the obtained values indicate a two-fold increase. A similar improvement in plant growth was previously obtained using a down-shifting red luminophore [32]. As can be seen, luminophore substitution does not significantly reduce the efficiency of photoconversion coatings. It is important to note that only a negligible part of the light absorbed by the coating can be transformed into luminescence in the PAR region. Possible reasons include low absorption of ultraviolet and/ or infrared radiation and high yield of heat dissipation. However, several papers (including the present study) have clearly demonstrated that the application of photoconversion films increases crop yields [30–32,51–53,55–61,69–76]. There are several possible reasons for the activation of plant development under films. Firstly, the functioning of phytochromes, which are very sensitive to the change in the proportion of far-red light: the phytochrome system can regulate plant growth and increase resistance to adverse environmental conditions [55,77,78]. Moreover, a decrease in far-red availability may induce a reduction in chlorophyll content [79] that correlates well with our data (Table 1). Secondly, the positive effects of photoluminescent particles as protectants against UV: UVA radiation can damage the photosynthetic apparatus due to destruction of the pigments and pigment-protein complexes [80,81]. Previously, it was shown that, under insufficient illumination, photoconversion coatings change the content of phytohormones and thus affect plant growth [82]. Importantly, the described coatings luminesced in the red region. Furthermore, photoconversion films can affect soil microflora as well as plants. It was shown that PCF-induced changes in light spectrum stimulated reproduction of native soil microflora, which enhances the effect of transformed light on plant growth [61,83]. Changes in the partitioning of absorbed light energy and the inhibition of plant growth (Figure 3) are most likely induced by the appearance of UVA; although, the addition of UVA can play a positive role in plant development [81].

Later, plants acclimatize to the action of a stress factor, which is reflected in the restoration of the activity of the photosynthetic apparatus. Photoconversion films speed up this process, making it easier for the plant to withstand stress. The different rates of the restoration of the initial activity of the photosynthetic apparatus may be due to the slow establishment of a balance between electron transport and NADPH utilization in control plants, as well as different degrees of damage to the water-oxidizing complex of

photosystem II in control and experimental plants [84]. It is not elucidated that minor alterations in the light spectrum (in light deficiency conditions) (Figure 3B) can increase in the rate of the adaptation processes of plants. Figure 5 demonstrates that after 30 min of adaptation to various actinic light conditions, $Y(II)$ and $Y(NPQ)$ in plants growing under photoconversion film remained relatively stable with increasing AL intensity to comparably high light intensity (in contrast to plants growing under common film). It can be presumed that plants growing under photoconversion films develop resistance to the inhibitory effects of light. It was shown that plants, which adapted to weak illumination, demonstrated the limited ability to acclimate, and experienced photoinhibition after exposition to high light [85].

Thus, it can be suggested that films containing upconversion luminophores can contribute to the acquisition by plants of properties that allow the plant to more effectively adapt to the ultraviolet and high light.

5. Conclusions

The photosynthetic apparatus of plants is very sensitive to the action of such abiotic environmental factors as ambient temperature, humidity, lighting, etc. Light quantity and quality are very important for the growth and development of plants. Even slight changes in the ratio of spectral components can be critical, and this fact opens up great opportunities for the use of photoconversion coatings in agriculture. This study shows that coatings that can convert far-red and ultraviolet light into visible photons can improve the efficiency of solar energy conversion in the photosynthetic apparatus of plants.

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