



## Article

# Photoconversion Covers Based on CdSe/CdS-ZnS Quantum Dots Improve Photosynthetic Performance and Vegetative Growth of Tomato Plants (*Solanum lycopersicum*)

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## Abstract

The effect of light spectrum conversion using photoconversion covers (PCCs) containing CdSe/CdS-ZnS quantum dots (PCC-QDs) on the growth and photosynthesis of tomato plants was studied. Luminophore-free covers and covers containing rhodamine B as a luminophore (PCC-RB) were used as reference covers. The obtained covers had a luminescence maximum in the red region (618 nm for PCC-QDs and 615 nm for PCC-RBs). It was shown that both types of PCC promoted plant growth, with PCC-QDs increasing leaf number by 28% and chlorophyll content by 6%, while PCC-RB enhanced stem length (17%) and leaf number (23%), with no effect on chlorophyll content after a reduction in the thermal dissipation of absorbed light energy and intensifying electron transfer in the photosynthetic electron transport chain, which was accompanied by a 40–50% increase in the hydrogen peroxide content in plant tissues and a 2–3-fold increase in ascorbate peroxidase activity. Light-induced activation of transpiration in PCC plants was found to occur within 1–2 min, while control plants exhibited greater stomatal inertia with a 4–5 min delay in response to light. It is assumed that changes in the light spectrum induced by PCCs led to the optimization of electron transport in chloroplasts, triggering H<sub>2</sub>O<sub>2</sub>-mediated activation of gas exchange in leaves.



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## 1. Introduction

Despite a steady slowdown in global population growth, increasing crop yields remains a priority [1]. Climate change, along with high anthropogenic pressure, is reducing the amount of land suitable for agriculture. Currently, land degradation has affected about 40% of the land surface to varying degrees [2,3]. One solution is the agricultural development of new territories, including those with cold climates and insufficient natural

light. Greenhouses are typically used for growing plants in such regions, where producers use modern technologies to increase yields [4]. One such technology is the use of photoconversion covers (PCCs), which, by converting the light spectrum, stimulate plant growth by modulating physiological and photochemical processes [5]. PCCs can not only stimulate plant growth [6–12] but also increase their resistance to adverse abiotic and biotic factors [13].

Photoconversion covers used in protected horticulture can be classified according to the type of luminophore as materials based on organic compounds, rare-earth elements, inorganic nanoparticles, carbon-based structures, and semiconductor nanomaterials [5,14,15]. These materials absorb radiation in spectral regions that are used less efficiently by plants and re-emit it at wavelengths more favorable for photosynthesis and photomorphogenesis. Tomato is one of the most widely cultivated and commercially important crops in protected horticulture. Consequently, photoconversion covers incorporating nearly all major classes of luminophores have been evaluated during tomato cultivation. Covers containing organic and rare-earth-based luminophores have been associated with increases in leaf area, leaf number, chlorophyll content, vegetative growth, and productivity, as well as with faster adaptation of the photosynthetic apparatus to ultraviolet radiation and high-light conditions [11,13,16,17]. Carbon-based and hybrid photoconversion covers have also been tested on tomato, where spectral conversion affected photosynthetic activity, biomass accumulation, and crop productivity [10]. Semiconductor nanomaterial-based covers converting ultraviolet and violet radiation into red light have been evaluated on tomato, pepper, and eggplant. These covers stimulated vegetative growth in the studied solanaceous crops and were also associated with increases in leaf area and fruit yield in tomato [18].

Currently, covers containing organic dyes, such as rhodamine (sold under various trade names), are very popular in the budget segment of the PCC market [5,14,19,20]. This dye very efficiently converts light into red-orange photons, but its significant drawbacks include a small Stokes shift and a short lifetime under light, which can be increased by introducing the dye into the matrix or adding stabilizers [21–23]. Typically, such covers are used for no more than one season but provide a significant increase in yield. Another class of PCCs are covers using expensive but durable rare-earth ions, such as europium complexes [5,14,15].

Quantum dots (QDs) are promising materials that can be used in the production of photoconversion covers for greenhouses. QDs have proven to be effective dopants in composite materials used in electronics, biology, and medicine [24–28]. The unique property of QDs, namely that their luminescence spectrum depends on their particle size [29–31], can be very useful in creating photoconversion covers for greenhouses. The luminescence spectrum of such covers can be smoothly tuned by adding quantum dots of varying sizes. From an agricultural perspective, quantum dots emitting photons in the red region of the spectrum, which are effectively absorbed by plants, are of great interest. QDs made of CdSe satisfy this requirement. Depending on their size, the luminescence of such particles varies from the blue to the red region [28,32–35]. However, such QDs have a high probability of non-radiative charge recombination due to Auger recombination, low photostability, and the presence of surface defects [36]. One of the most effective ways to improve the luminescent properties of QDs is to combine several types of semiconductors, as well as doping with various metals, since this regulates and stabilizes their luminescent properties and increases their lifetime [37–40]. For the CdSe core, the most preferred materials for stabilizing the optical properties are CdS or ZnS shells [41–44]. However, these shells have drawbacks. In the case of CdSe/CdS, a lattice mismatch between the used materials is observed, which leads to a decrease in the quality of the resulting QDs. A ZnS shell solves

this problem, but interfacial strain is formed at the layer boundaries, which reduces the photostability of the QDs. Previously, composite CdSe/CdS-ZnS core-shell-shell QDs were successfully synthesized [28,32], in which the ZnS shell grown on the surface of CdSe/CdS quantum dots ensures efficient confinement of electrons and holes inside the quantum dots, as well as high photostability, and the middle shell (CdS) allows suppressing the strain caused by a lattice mismatch between the CdSe core and the ZnS shell. It was shown that the ZnS shell increases the thermal stability of the luminescence of the CdSe/CdS core of quantum dots with changing temperature [32]. Moreover, the CdS and ZnS shells can additionally affect the luminescence spectrum of CdSe QDs [35,45–48]. At the same time, the use of Cd-containing quantum dots in agricultural technologies requires consideration of potential environmental and food-safety aspects [49,50]. Important steps toward their safe use include immobilization of the QDs within chemically resistant polymer matrices, prevention of their direct contact with plants and the growing substrate, and assessment of long-term coating stability, possible Cd or nanoparticle release, and accumulation in plant tissues.

Despite considerable progress in the development of photoconversion materials, currently available covers still involve a compromise between spectral characteristics, luminescence efficiency, and operational stability. Rhodamine-based covers are available as relatively inexpensive commercial materials, but their service life is limited by photodegradation, whereas more durable rare-earth-based systems are considerably more expensive [5,14,15]. Quantum dots represent a promising alternative because their luminescence spectrum can be precisely adjusted by controlling particle size and shell thickness, while multishell structures and immobilization within a fluoropolymer matrix can improve their photochemical stability [28,32,35,46,51–53]. Thus, the development of a stable quantum-dot-based photoconversion cover with red emission favorable for plant light utilization represents an important step toward improving existing photoconversion technologies.

In the present study, we examined the effect of light spectrum conversion using photoconversion covers containing CdSe/CdS-ZnS quantum dots (PCC-QDs) on the growth and development of tomato plants. The QDs were synthesized with dimensions selected to provide red luminescence and were immobilized within a PCTFE-co-PVDF matrix to improve their stability under operating conditions. The objective of the study was to evaluate the functional performance of the developed PCC-QD using tomato plants as a biological test system. Covers without luminophores were used as the control, whereas covers containing Rhodamine B as an organic dye (PCC-RB), representing an established photoconversion technology, were used solely as reference covers. We hypothesized that the developed PCC-QD would provide spectral conversion favorable for plant light utilization and induce positive photosynthetic and vegetative responses relative to the luminophore-free control.

## 2. Materials and Methods

### 2.1. Preparation of Photoconversion Covers Containing Nanoparticles and Quantum Dots

To fabricate PCC-QDs, hybrid CdSe/CdS-ZnS quantum dots (QDs) (CdSe core, CdS and ZnS shells) synthesized by the method described in [28] were used. CdSe cores with an average diameter of approximately 3.0 nm were prepared by a colloidal method in a mixed aqueous-organic medium according to the general procedure described in Ref. [28]. CdS was subsequently deposited by the sequential growth of shell layers around the CdSe cores. The outer ZnS shell was deposited onto the pre-synthesized CdSe/CdS particles in a water-ethanol medium at 50 °C by adding zinc acetate and thioacetamide in the presence of excess oleic acid, which was used as a surface-stabilizing agent. The nominal thicknesses of the CdSe/CdS/ZnS particles were approximately 10 nm, respectively. To stabilize the

obtained particles, PTVP (Poly (thiol-vinyl pyrrolidone)) was added, which increased the size of the obtained QDs to 23 nm.

A 0.5 mL volume of a colloidal solution containing 15% (*w/v*) QDs in acryloyl morpholine was mixed with 10 mL of acetone. The resulting mixture was sonicated for 10 min using an ultrasonic bath (ODA Service, Moscow, Russia) and then added to 40 mL of PCTFE-co-PVDF varnish (LG-32 LN, Plast Polymer-Prom, Saint Petersburg, Russia), dissolved in a mixture of acetone, butyl acetate, cyclohexanone, and toluene at a mass ratio of 25:40:10:25. The mixture was homogenized via ultrasonic treatment for 20 min and spray-coated onto pre-cleaned, degreased glass substrates with an area of  $0.6 \text{ m} \times 1 \text{ m}$ .

To fabricate PCC-RBs, 1.5 g of a polystyrene–rhodamine mixture (10:1) was dissolved in 20 mL of acetone by stirring on a magnetic stirrer for 30 min. Then, the mixture was introduced into 40 mL of the PCTFE-co-PVDF varnish and homogenized by ultrasound for 20 min. The resulting solution was spray-coated onto pre-cleaned, degreased glass substrates with an area of  $0.6 \text{ m} \times 1 \text{ m}$ .

## 2.2. Study of the Properties of Nanoparticles and Covers

Dynamic light scattering measurements were carried out at 25 °C using a Zetasizer ULTRA RED LABEL (Malvern Panalytical Ltd., Malvern, UK) to determine the hydrodynamic diameter of the QDs in an aqueous dispersion. Samples (1.5 mL) were held in DTS0012 polystyrene cuvettes with a 10 mm optical path length, and backscatter detection (174.7 degrees) was applied. Data were collected as a set of 8 individual measurements for each experimental trial.

The fluorescence properties of the photoconversion covers were characterized by three-dimensional fluorescence spectroscopy at room temperature using a Jasco FP-8300 instrument (JASCO International Co., Ltd., Tokyo, Japan).

The differential spectra (the spectrum of the photoconversion cover with PCC-QDs or PCC-RBs minus the spectrum of the blank PCTFE-co-PVDF cover) of the photoconversion covers were measured using a PG200N Spectral PAR Meter (UPRtek, Zhunan, Miaoli, Taiwan).

## 2.3. Plant Growing Conditions

Tomato plants (*Solanum lycopersicum* ‘Balkonnoe Chudo’) were grown from seeds in a 3:1 (*v/v*) mixture of commercial soil for tomato (Terra forte, Saint-Petersburg, Russia) and vermiculite in 0.3 L pots, with one plant per pot. The cultivation experiment was conducted once and included three separate cover units for each treatment: a luminophore-free control cover, PCC-QD, and PCC-RB. Each cover unit had an area of  $0.6 \text{ m} \times 1 \text{ m}$  and was positioned above two trays containing eight individually potted plants each. Thus, each cover replicate contained 16 plants, giving a total of 48 plants per treatment. Plants were cultivated in growth chambers under a 16 h photoperiod at 25 °C (day) and 17 °C (night) and relative humidity 40%. A PG200N spectrometer confirmed light intensities of  $120 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$  (PAR, 400–700 nm) and  $10 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$  (UV, 365 nm) at a distance 57 cm from light source to pot. Watering was performed every five days, rotating between deionized water and a nutrient solution containing (per liter): 0.05 g  $\text{NH}_4\text{NO}_3$ , 0.17 g  $\text{KNO}_3$ , 1.06 g  $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ , 0.38 g  $\text{K}_2\text{SO}_4$ , 0.135 g  $\text{KH}_2\text{PO}_4$ , and 0.49 g  $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ . Plants were rotate every day inside the growth chamber.

## 2.4. Determination of Morphological and Chlorophyll Content Properties of Tomato Plants

The measurements were at 45 days of plants after seeding. Leaf number and stem length were determined through manual counting and measurement with a ruler (1 mm accuracy), respectively. Chlorophyll content was measured using a CL-01 chlorophyll meter

(Hansatech Instruments Ltd., King's Lynn, Norfolk, UK) according to the method described previously [13].

### 2.5. Determination of Photosynthetic Activity

Gas exchange parameters were recorded with a Walz GFS-3000 system (Heinz Walz GmbH, Effeltrich, Germany) using GFS-win v. 3.79 software, with calculations performed automatically according to the standard manufacturer equations [54]. The system determined the assimilation rate of CO<sub>2</sub>, transpiration rate, stomatal conductance to water vapor and CO<sub>2</sub>, and intercellular CO<sub>2</sub> concentration, leaf water use efficiency parameters (WUE<sub>leaf</sub> and WUE<sub>i</sub>), with chamber settings maintained at 25 °C and 40% humidity, a leaf area of 2 cm × 2 cm, a laminar airflow (400 µmol/s) containing 400 ppm CO<sub>2</sub>, and actinic light of 625 nm at an intensity of 138 µmol photons m<sup>-2</sup> s<sup>-1</sup>. For details on the calculation formulas, see [54].

A DUAL-PAM-100 fluorometer (Heinz Walz GmbH, Effeltrich, Germany) was employed to record chlorophyll fluorescence induction kinetics in tomato leaves. The measuring chamber replicated growth chamber conditions during the light phase, maintaining 25 °C, 40% humidity, and a laminar CO<sub>2</sub> airflow (400 µmol/s) of 400 ppm under 138 µmol photons m<sup>-2</sup> s<sup>-1</sup> of actinic light. Dark adaptation of the plants for one hour preceded all measurements, ensuring full relaxation of photoinduced processes. After an actinic light switching on saturating flashes of 300 ms duration (625 nm, 33,500 µmol photons m<sup>-2</sup> s<sup>-1</sup>) were triggered. The quantum yields of photosystem II photochemistry (Y (II)), non-photochemical quenching (Y (NPQ)), and non-regulated energy dissipation (Y (NO)) were automatically calculated using PamWin-3 software according to the manufacturer's manual [55].

### 2.6. Measurement of Antioxidant Enzyme Activities and Hydrogen Peroxide Concentration

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) content, catalase (CAT) activity, and ascorbate peroxidase (APX) activity were determined spectrophotometrically in fresh tomato leaf tissue using a Cintra 4040 spectrophotometer (GBC Scientific Equipment, Braeside, Victoria, Australia) according to the protocols described by Borisova et al. [56] based on the methods of Bellincampi et al. [57], Aebi [58] and Nakano and Asada [59].

For H<sub>2</sub>O<sub>2</sub> determination, 0.3–0.5 g of fresh leaf tissue was homogenized in 2 mL of distilled water, and the final extract volume was adjusted to 3–4 mL. The homogenate was centrifuged at 12,000 × g for 15 min, and the resulting supernatant was used for analysis. The xylenol orange reagent was prepared by dissolving 9.5 mg of ammonium iron (II) sulfate (Mohr's salt) and 7.6 mg of xylenol orange in distilled water, adding 260 µL of H<sub>2</sub>SO<sub>4</sub> and 1.82 g of sorbitol, and adjusting the final volume to 50 mL. One milliliter of the supernatant was mixed with 1 mL of the xylenol orange reagent and incubated for 1 h at room temperature. The mixture was then centrifuged at 10,000 × g for 5 min, and absorbance was measured at 560 nm against a blank containing the xylenol orange reagent and distilled water at a 1:1 ratio. H<sub>2</sub>O<sub>2</sub> content was calculated using a calibration curve prepared with H<sub>2</sub>O<sub>2</sub> concentrations of 5–300 ng mL<sup>-1</sup> and expressed as µmol H<sub>2</sub>O<sub>2</sub> g<sup>-1</sup> fresh weight.

For APX extraction, 0.5 g of fresh leaf tissue was homogenized on ice in 1.5–2.0 mL of 50 mM potassium phosphate buffer (pH 7.0), and the total buffer volume was adjusted to 5 mL. The homogenate was centrifuged at 15,000 × g for 20 min at 4 °C. The supernatant was maintained on ice and used within 2 h. APX activity was measured at 30 °C in a 3 mL reaction mixture containing 1.5 mL of 50 mM potassium phosphate buffer (pH 7.0), 0.5 mL of 2.5 mM ascorbate, 0.5 mL of 1 mM H<sub>2</sub>O<sub>2</sub>, 0.1 mL of 0.5 mM Na-EDTA, and 0.4 mL of enzyme extract. The reaction was initiated by adding the enzyme extract, and the decrease

in absorbance at 290 nm was recorded every 10 s for 2–3 min. A corresponding reagent blank was measured in parallel. APX activity was calculated from the linear portion of the absorbance curve using an ascorbate extinction coefficient of  $2.8 \text{ mM}^{-1} \text{ cm}^{-1}$  and expressed as  $\mu\text{mol ascorbate oxidized min}^{-1} \text{ mg}^{-1} \text{ protein}$ .

For CAT extraction, 0.5 g of fresh leaf tissue was homogenized on ice in 1.5–2.0 mL of 0.1 M potassium phosphate buffer (pH 6.8–7.0), and the total buffer volume was adjusted to 5 mL. The homogenate was centrifuged at  $15,000 \times g$  for 20 min at  $4^\circ\text{C}$ , and the supernatant was maintained on ice and used within 2 h. The CAT reaction medium was prepared by adding 30  $\mu\text{L}$  of 33%  $\text{H}_2\text{O}_2$  to 50 mL of 0.1 M potassium phosphate buffer (pH 6.8–7.0). The assay was performed at  $30^\circ\text{C}$  in a 3 mL quartz cuvette containing 2.8 mL of the reaction medium and 0.2 mL of enzyme extract. The decrease in absorbance at 240 nm was recorded every 10 s for 2–3 min. In the blank, the enzyme extract was replaced with an equal volume of extraction buffer. CAT activity was calculated from the linear portion of the absorbance curve using an  $\text{H}_2\text{O}_2$  extinction coefficient of  $0.036 \text{ mM}^{-1} \text{ cm}^{-1}$  and expressed as  $\mu\text{mol H}_2\text{O}_2 \text{ decomposed min}^{-1} \text{ mg}^{-1} \text{ protein}$ .

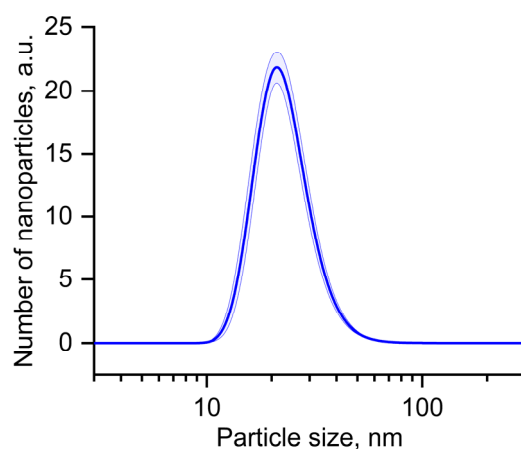
Soluble protein content was determined using the Bradford method. The enzyme extracts were diluted 20–30 fold, and 1 mL of the diluted extract was mixed with 3 mL of Coomassie Brilliant Blue reagent. Absorbance was measured at 595 nm between 5 min and 1 h after reagent addition. Bovine serum albumin solutions ranging from 5 to  $80 \mu\text{g mL}^{-1}$  were used to construct the calibration curve. CAT and APX activities were normalized to the soluble protein content. Enzyme activity measurements were performed in triplicate for each biological sample.

### 2.7. Statistical Analysis

To determine statistically significant differences between the plant groups, a one-way analysis of variance (ANOVA) was performed, followed by a post hoc comparison using Tukey's honestly significant difference (HSD) test. Differences were considered statistically significant at  $p \leq 0.05$ .

## 3. Results and Discussion

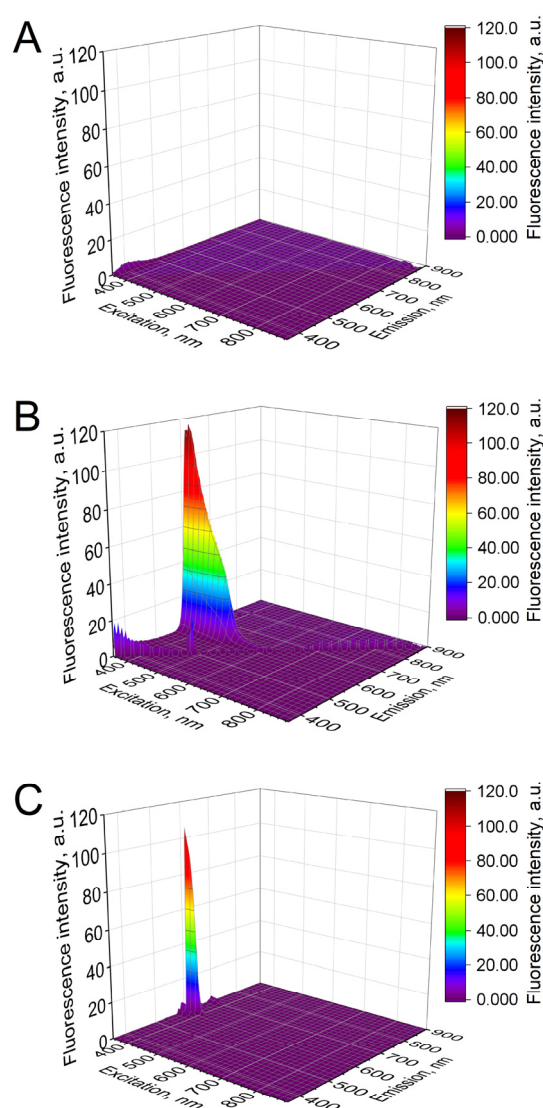
Using the dynamic light scattering method, the particle size of CdSe/CdS-ZnS quantum dots used to create PCC-QDs was studied. It was shown that the median hydrodynamic diameter of the QDs is 23.2 nm, that roughly corresponds to that intended during synthesis (Figure 1).



**Figure 1.** Size distribution of CdSe/CdS-ZnS particles. Measurements were performed in suspensions of particles in water at room temperature at a particle concentration of 1.2%. Shaded areas above and below the curves represent the standard error of the mean.

The size of the obtained particles determines the optical properties of both the QDs themselves and the covers based on them. Previously, in our work [28] it was shown that an increase in the size of CdSe/CdS-ZnS QDs from 11.7 nm to 15.6 nm shifts the luminescence maximum from the green (506 nm) to the orange (574 nm) region. Therefore, it is natural that the QDs obtained in this study exhibited red luminescence. The long-wavelength (red) shift in the luminescence peak is caused by an increase in the CdS shell thickness and is due to the effect of partial delocalization of the electron wave function from the core to the shell zone, which leads to an effective narrowing of the band gap of the resulting heterostructure [45–47].

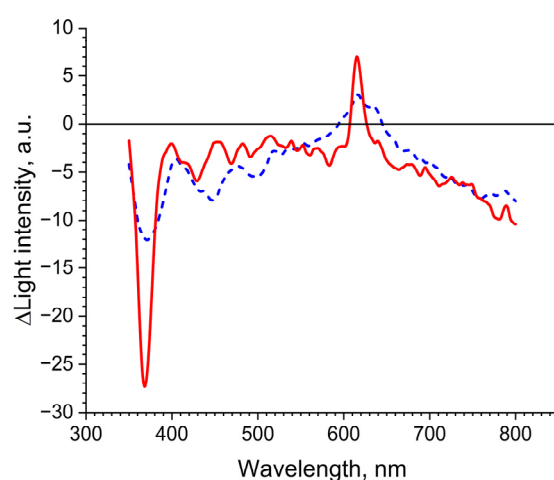
Figure 2 shows the three-dimensional luminescence spectra of photoconversion covers obtained using QDs and R<sub>BS</sub>. Glass coated with a film formed from PCTFE-co-PVDF in the absence of any luminophores exhibits virtually no intrinsic fluorescence, indicating that PCTFE-co-PVDF can be used as a matrix for creating a PCC (Figure 2A).



**Figure 2.** Three-dimensional fluorescence maps of the covers without luminophores (A), PCC-QDs (B), and PCC-RBs (C).

When QDs were added to the matrix (at a weight fraction of 1.2% relative to the dry polymer residue) and the resulting mixture was applied to glass, PCC-QDs were formed, with an excitation maximum at 361 nm and an emission maximum at 618 nm. When PCC-RBs were formed with RB dye (at a weight fraction of 1.2% relative to the dry polymer

residue), the excitation maximum was recorded at 351 nm and the emission maximum at 615 nm. It should be noted that the excitation band of the PCC-QDs was significantly broader (from 355 nm to 440 nm at half-maximum) than that of the PCC-RBs (up to 380 nm at half-maximum), while the emission bandwidths of both PCC types were comparable. Consequently, the advantage of PCC-QDs is their broad absorption band, which allows a larger proportion of solar energy to be converted into red photons than in the case of PCC-RBs, while the advantage of PCC-RBs is their higher luminescence yield and the absence of absorption in the blue region. The differential grow light spectrum shows that both covers have a pronounced absorption band in the ultraviolet region ( $\lambda_{\text{max}} = 370$  nm for PCC-QD and  $\lambda_{\text{max}} = 368$  nm for PCC-RB) and a luminescence band at 615 nm. The luminescence bands shown in Figure 3 correspond in position and width to those shown in Figure 2, which indicates that the selected matrix material does not significantly affect the luminescent properties of the particles integrated into it.



**Figure 3.** Differential illumination spectra in the growth chamber (the spectrum under PCC minus the spectrum under the cover without luminophores) for PCC-QDs (red solid curve) and PCC-RBs (blue dashed curve).

It is widely known that the lifetime of photosensitizers, such as the QDs and RBs used in this work, is determined by their ability to interact with molecular oxygen and water vapor and the products of this interaction (singlet oxygen, superoxide anion radical, hydroxyl radical, etc.). However, the introduction of luminophores into a fluoropolymer matrix significantly protects them from photodestruction. On the one hand, the matrix acts as a hermetic barrier, blocking the diffusion of water vapor and oxygen to the luminophores [60,61]. Even in the presence of trace amounts of oxygen in the matrix, the aprotic hydrophobic nature of the fluoropolymer makes some of these reactions energetically unfavorable. For example, under hydrophobic conditions, a significant decrease in the redox potential of the  $\text{O}_2/\text{O}_2^-$  pair occurs from  $-120$  mV to between  $-550$  and  $-600$  mV [62–64], which makes the appearance and existence of the superoxide anion radical virtually impossible. Another advantage of the fluoropolymer matrix is its inherent resistance to solar ultraviolet radiation, allowing it to maintain optical transparency for a long time [65]. The synthesized QDs, in addition to protection from the fluoropolymer matrix, have their own protection from photodamage, as they have a “giant” CdS–ZnS shell, which prevents the interaction of the core with molecular oxygen and water vapor [46,66]. In contrast, Rhodamine B in the covers lacks such intrinsic protection. The CdSe/CdS–ZnS QDs used in the present study were immobilized within a hydrophobic PCTFE-co-PVDF matrix and were not applied directly to the plants, soil, or nutrient solution. Preliminary stability tests

performed with the present PCC-QD, including tests conducted under the tomato cultivation conditions used in this study, showed that the coating remained photochemically and chemically stable throughout the experimental period. Similar operational stability has previously been demonstrated for photoconversion coatings based on the same type of fluoropolymer matrix [51–53]. Thus, both the preliminary tests of the present PCC-QD and earlier results obtained for analogous fluoropolymer-based coatings support the short-term operational stability of the developed material under the tested cultivation conditions.

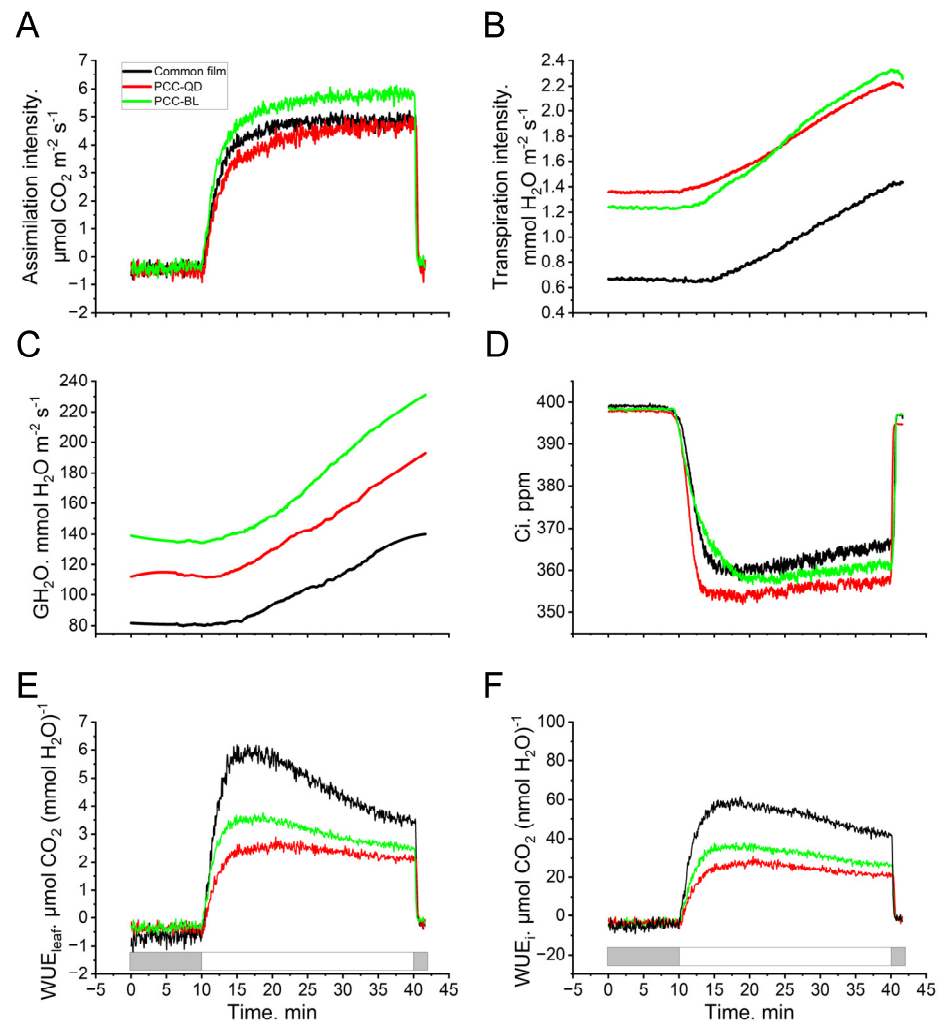
Thus, the optical properties of both types of PCCs meet the requirements for such covers used in greenhouse plant cultivation.

The obtained PCCs were used for tomato cultivation. The kinetic curves of CO<sub>2</sub> assimilation after the onset of illumination exhibited three phases: a fast phase, characterized by a rapid increase in CO<sub>2</sub> consumption during the first few minutes; a slow phase, consisting of a gradual increase in the assimilation rate over the next seven minutes; and a steady-state phase, where the maximum intensity of CO<sub>2</sub> assimilation was reached (Figure 4A). In the fast phase (1–2 min), the reserve of ribulose-1,5-bisphosphate or other intermediate products of the Calvin cycle available in the dark was consumed; in the subsequent slow phase (about 4–5 min), photoactivation of Rubisco by Rubisco activase occurred [67–69].

Plants grown under PCC-RB were shown to have the highest (approximately 20%) CO<sub>2</sub> assimilation rate during the stationary phase compared to other plants. The amplitude of the rapid growth phase of CO<sub>2</sub> assimilation varied across all plant groups; it was 15% higher in PCC-RB plants but 23% lower in PCC-QD plants than in the control, indicating different reserves of Calvin cycle intermediates in the dark. The slow growth phase of CO<sub>2</sub> assimilation in control plants was the shortest, which, on the one hand, may indicate an increased rate of Rubisco activation, but on the other hand, may indicate a limited capacity for such activation. Measurements of the transpiration rate showed that in the dark, the transpiration rate of control plants was approximately two times lower than that of experimental plants (Figure 4B). The onset of illumination activated transpiration in all plant groups, but control plants still exhibited a reduced transpiration rate. It should be noted that transpiration activation did not occur immediately after the onset of illumination but was somewhat delayed. For control plants, the delay was approximately 4–5 min, while for PCC-RB and PCC-QD plants, it was approximately 1–2 min. Similar patterns were revealed in the kinetic curves for changes in stomatal conductance to water (GH<sub>2</sub>O) (Figure 4C) and CO<sub>2</sub> (GCO<sub>2</sub>) as the kinetic curves closely mirrored those for GH<sub>2</sub>O). GH<sub>2</sub>O and GCO<sub>2</sub> in control plants were significantly lower than in experimental plants, and their activation occurred simultaneously with the transpiration activation. The intercellular CO<sub>2</sub> concentration (Ci) in the leaves of all plant groups in the dark was approximately the same, amounting to about 400 ppm (Figure 4D). Turning on the light decreased Ci to 360 ppm in control plants, to 357 ppm in PCC-RB plants, and to 354 ppm in PCC-QD plants, indicating carbon dioxide fixation by plants during photosynthesis. After reaching the minimum values, the decrease in Ci was replaced by an increase under illumination, indicating, on the one hand, that the maximum intensity of CO<sub>2</sub> fixation in the leaves was reached, and on the other hand, a photoinduced increase in GCO<sub>2</sub> [70–73]. Moreover, the rate of increase in Ci under illumination was higher in control plants than in experimental plants, suggesting that CO<sub>2</sub> delivery to the fixation sites in control plants exceeded their assimilation capacity to a greater extent than in experimental plants. Furthermore, the water use efficiency of control plants significantly exceeded that measured in experimental plants (Figure 4E,F).

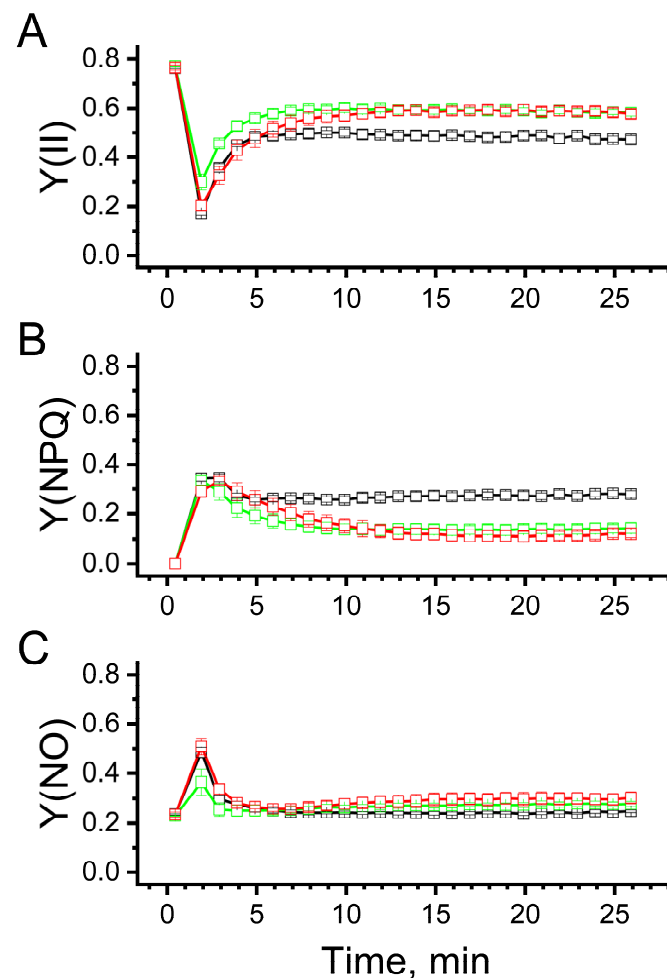
Plants are known to utilize the energy of absorbed light in various ways, redistributing it depending on the action of environmental factors. By measuring the kinetics of chlorophyll *a* fluorescence (ChlF) induction, it is possible to estimate the pathways (and their proportions) of energy utilization. One of these pathways is the use of absorbed light

energy in carbon dioxide fixation, which correlates well with the ChlF parameter known as the effective quantum yield of photochemistry in photosystem II. Another pathway is the dissipation of excitation energy into heat as a result of regulatory and non-regulatory mechanisms. Regulatory thermal dissipation correlates with the yield of non-photochemical quenching of ChlF ( $Y(NPQ)$ ), while non-regulatory dissipation correlates with the quantum yield of unregulated excitation energy loss ( $Y(NO)$ ).



**Figure 4.** Light-induced changes in the  $\text{CO}_2$  assimilation rate (A), transpiration rate (B), stomatal conductance to  $\text{H}_2\text{O}$  (C), intercellular  $\text{CO}_2$  concentration (D), and water use efficiency calculated from the transpiration rate ( $\text{WUE}_{\text{leaf}}$ ) (E) and stomatal conductance ( $\text{WUE}_i$ ) (F) in *S. lycopersicum* leaves on day 45 of growth under different covers: control (without luminophore)—black curve, PCC-QD—red curve, and PCC-RB—green curve. In the panel, the measurement times in the dark and in the light ( $\lambda = 625 \text{ nm}$ ,  $138 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ ) are shown in gray and white, respectively. Data are presented as the means of three independent replicates ( $n = 3$ ). Each level replicate was calculated by averaging measurements obtained from 3 plants grown under the same cover.

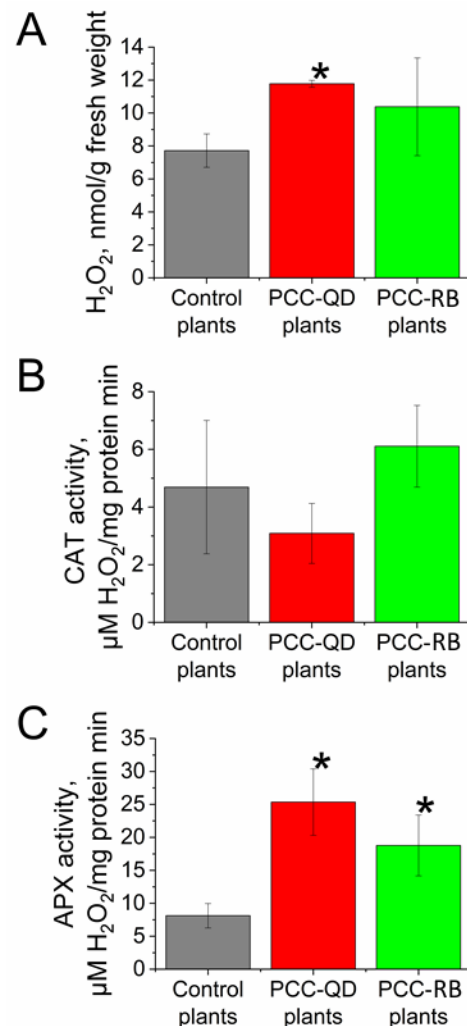
The  $Y(II)$  value in experimental plants adapted to light for 25 min was 0.6, while in control plants it was 0.47 (Figure 5A). This indicates that the proportion of absorbed light energy directed to the Calvin cycle is greater in the experimental plants. It should be noted that the maximum quantum yield of photosystem II photochemistry was virtually identical across all plant groups (the initial dark-adapted point on the curves in Figure 5A). However, the rate at which steady-state  $Y(II)$  values were reached in the experimental plants was lower than in the control plants.



**Figure 5.** Light-induced changes in chlorophyll a fluorescence parameters in the leaves of *S. lycopersicum* plants grown under different covers: control (without luminophore)—black curve, PCC-QD—red curve, and PCC-RB—green curve. Effective quantum yield of photosystem II photochemistry ( $Y(II)$ ) (A), quantum yield of non-photochemical quenching of ChlF ( $Y(NPQ)$ ) (B), quantum yield of non-regulated excitation energy loss ( $Y(NO)$ ) (C). Before measurements, the plants were dark-adapted for 1 h at 25 °C. The intensity of the 500 ms saturating light flashes was  $33,500 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ . The actinic light ( $\lambda = 625 \text{ nm}$ ,  $138 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ ) was applied 2 min after the start of the measurement. Data are presented as the means of three independent replicates ( $n = 3$ ). Each level replicate was calculated by averaging measurements obtained from 3 plants grown under the same cover.

The value of non-photochemical ChlF quenching in the first minutes after the onset of illumination, measured in experimental and control plants, was similar, indicating a roughly equal activation of the defense mechanisms responsible for ChlF quenching (Figure 5B).  $Y(NPQ)$  reached its maximum value most rapidly in PCC-RB plants. Subsequently, a decline in this parameter was observed in all plants. However, after 25 min of light adaptation, the decrease in  $Y(NPQ)$  in the leaves of experimental plants was more pronounced than in the control. This may indicate the need to maintain a higher non-photochemical quenching level in the leaves of plants growing under a luminophore-free covers, likely due to less efficient electron transport within the photosynthetic electron transport chain.  $Y(NO)$  rapidly decreased in plants of all groups after a brief initial increase upon illumination and was maintained at a low level. Nevertheless, in control plants, this parameter was 25% lower than in plants growing under PCCs. Thus, plants growing under both types of PCCs direct a larger proportion of the absorbed energy to  $\text{CO}_2$  fixation, while control plants dissipate excitation energy to a greater extent into heat.

Further studies were aimed at elucidating the redox status of plants. It was shown that the hydrogen peroxide content in the leaf tissues of plants growing under PCCs was 40–50% higher than that of control plants (statistically significant differences from control plants were observed only in PCC-QD plants) (Figure 6A). These data correlate with the  $Y(NO)$  value, which may reflect the degree of reduction in the chloroplast electron transport chain and, consequently, the potential for electron transfer to molecular oxygen, leading to the formation of the superoxide anion radical and hydrogen peroxide [74–76].



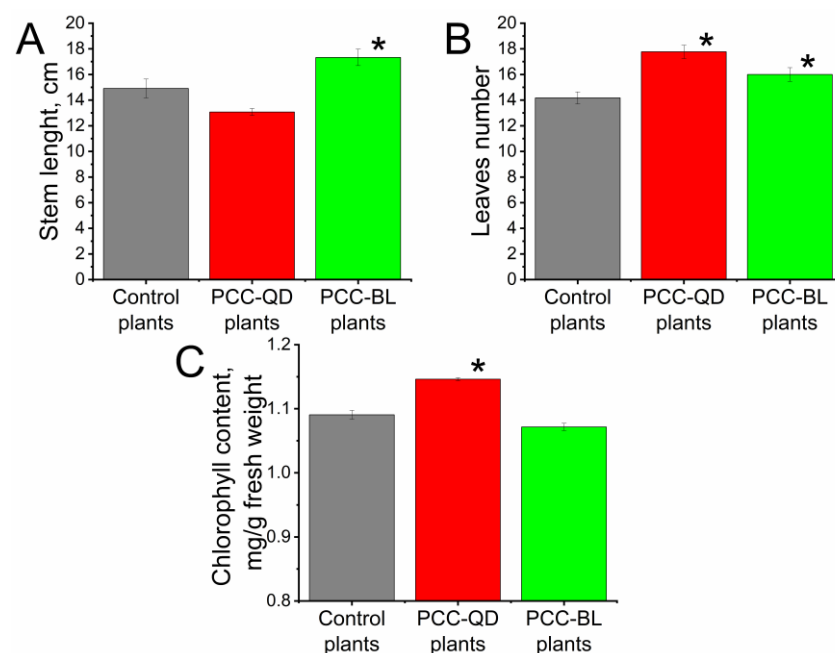
**Figure 6.**  $H_2O_2$  content (A), catalase activity (B), and ascorbate peroxidase activity (C) in the leaves of tomato plants grown under different covers: without luminophore (gray columns), PCC-QD (red columns), and PCC-RB (green columns). The asterisk (\*) indicates statistically significant differences in comparison with the control group ( $p \leq 0.05$ ). Data are presented as the means of three independent replicates ( $n = 3$ ). Each level replicate was calculated by averaging measurements obtained from 5 plants grown under the same cover.

However, it is known that electron transfer to molecular oxygen and the formation of hydrogen peroxide occur not only in the photosynthetic electron transport chain but also in mitochondria and peroxisomes. To determine the cause of the increased hydrogen peroxide content in the experimental plants, we analyzed catalase and ascorbate peroxidase activity in the tissues of the studied plants. It was found that catalase activity in the tissues of all plant groups did not differ statistically significantly (Figure 6B), indicating that the production of hydrogen peroxide in peroxisomes did not differ among the plant groups. Conversely, ascorbate peroxidase activity was increased in the experimental plants

(Figure 6C), indicating that the photosynthetic electron transport chain was the main source of additional hydrogen peroxide in plants growing under PCCs. These data may be further evidence that the absorption of light energy and electron transport in the electron transport chain of chloroplasts of experimental plants occurred more actively than in plants growing under covers that do not contain a luminophore.

Thus, the data presented in Figures 3–6 indicate a higher intensity of photosynthetic processes in plants growing under PCCs, which is reflected in increased rates of CO<sub>2</sub> assimilation and transpiration, higher stomatal conductance, as well as more efficient use of absorbed light energy and electron flow within the chloroplast electron transport chain.

The above-mentioned characteristics of the plants grown under photoconversion covers were also reflected in their vegetative growth parameters (Figure 7). Specifically, both groups of experimental plants were shown to have a greater number of leaves, with PCC-RB plants exhibiting increased stem length and PCC-QD plants showing higher chlorophyll content.



**Figure 7.** Stem height (A), leaf number (B), and leaf chlorophyll content (C) of *S. lycopersicum* plants on day 45 of cultivation under different covers: without luminophore (gray columns), PCC-QD (red columns), and PCC-RB (green columns). The asterisk (\*) indicates statistically significant differences in comparison with the control group ( $p \leq 0.05$ ). Data are presented as the means of three independent replicates ( $n = 3$ ). Each level replicate was calculated by averaging measurements obtained from 15 to 20 plants grown under the same cover.

A comprehensive analysis of gas exchange parameters, chlorophyll fluorescence, and antioxidant enzyme activity reveals fundamentally different regulatory strategies in the studied plant groups. Control plants exhibited reduced transpiration rates, both in the dark and under illuminated conditions. Even a modest increase in red light intensity is known to enhance plant transpiration by promoting stomatal opening and accelerating photosynthesis, provided that the overall spectrum already contains the minimum required amount of blue light. Research demonstrates that background red light (which supplies cells with energy through photosynthesis) is necessary for a complete stomatal response to blue light. Their combination causes maximum stomatal aperture and, consequently, peak transpiration [77–80]. Stable limitation of stomatal conductance provides the control plants with higher calculated values of water use efficiency, reflecting a more water-saving

operating model. This strategy is associated with the high inertia of the stomatal apparatus: after the onset of illumination, activation of transpiration in the control occurred only with a pronounced delay of 4–5 min [81–83]. At the photochemical level, this was accompanied by reduced Y (II) and increased Y (NPQ) levels, which indicated the need to maintain high thermal energy dissipation due to a less efficient outflow of electrons from the photosynthetic ETC [84,85]. In contrast, plants from the experimental groups showed a significant acceleration of growth processes, accompanied by a qualitative restructuring of the light stages of photosynthesis and stomatal dynamics. Increased transpiration intensity in the experimental plants was recorded both in the light and in the dark. This may indicate a change in the anatomical and morphological characteristics of the stomatal apparatus (e.g., an increase in the size or density of stomata) or a shift in their basal tone, leading to an increase in residual stomatal conductance in the dark [86,87]. A decrease in the need to maintain high thermal dissipation led to a decrease in the Y (NPQ) value and a concomitant increase in Y (II). Since the rate of CO<sub>2</sub> assimilation differed little from that observed in the control, it is likely that this intense electron flow was partially redirected to alternative acceptor pathways (e.g., pseudocyclic electron transport), leading to an increase in hydrogen peroxide content. The localization of this process within the photosynthetic apparatus is confirmed by the biochemical profile: a selective increase in ascorbate peroxidase (APX) activity was recorded in the experimental plants, while catalase (CAT) activity remained unchanged. Since APX is a key enzyme in the antioxidant defense of chloroplasts (where CAT is absent), its selective activation indicates that hydrogen peroxide generation and utilization occurred directly in the plastids [76,88–90]. The fact that this was combined with accelerated plant growth indicates a regulatory (signaling) rather than a toxic function for this hydrogen peroxide pool. Chloroplast H<sub>2</sub>O<sub>2</sub> acted as a trigger for retrograde signaling, inducing a priming (preactivation) effect on the stomatal apparatus [91–93]. This reduced the initiation time of light-induced transpiration in the experimental groups to just 1–2 min and maintained a consistently higher stomatal conductance. Rapid stomatal opening in the light, coupled with increased nocturnal conductance, allowed the experimental plants to very quickly optimize gas exchange upon illumination, to provide the metabolic demand for accelerated growth. The physiological price for such accelerated metabolism was an increase in uncontrolled energy losses, manifested as a slight increase in Y (NO) and a drop in the integrated water-use efficiency due to a constant increase in transpiration.

#### 4. Conclusions

The present study demonstrates that photoconversion covers based on CdSe/CdS–ZnS quantum dots and Rhodamine B can modify the light environment and affect the physiological state of tomato plants under controlled growth chamber conditions. Plants grown under photoconversion covers showed changes in gas exchange parameters, increased efficiency of photochemical energy use in photosystem II, reduced non-photochemical energy dissipation, and activation of H<sub>2</sub>O<sub>2</sub>-associated redox responses. The increase in leaf H<sub>2</sub>O<sub>2</sub> content, together with enhanced APX activity and unchanged CAT activity, suggests that the observed response may be associated with chloroplast-related redox signaling rather than with general oxidative stress. The obtained results indicate that PCCs can improve the photosynthetic performance and selected vegetative growth traits of tomato plants. This study did not evaluate final tomato yield or cadmium content in plant tissues. These aspects represent important directions for future research focused on the agronomic efficiency and biosafety of such nanocomposites.

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data curation, D.A.Z. and G.A.O.; writing—original draft preparation, D.V.Y., S.V.G. and V.A.K.; writing—review and editing, D.V.Y. and V.A.K.; visualization, S.A.S., M.O.P. and D.A.Z.; supervision, D.V.Y., V.A.K. and S.V.G.; project administration, D.V.Y. and V.A.K.; funding acquisition, S.V.G. and V.A.K. All authors have read and agreed to the published version of the manuscript.

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## Abbreviations

The following abbreviations are used in this manuscript:

|                     |                                                                         |
|---------------------|-------------------------------------------------------------------------|
| PCC                 | Photoconversion covers                                                  |
| PCC-QD              | Photoconversion covers containing CdSe/CdS-ZnS quantum dots             |
| PCC-RB              | Photoconversion covers containing rhodamine B                           |
| QD                  | Quantum dot                                                             |
| PCTFE-co-PVDF       | Fluoroplast-32L                                                         |
| PAR                 | Photosynthetic active radiation                                         |
| WUE <sub>leaf</sub> | Water use efficiency calculated on the basis of transpiration intensity |
| WUE <sub>i</sub>    | Water use efficiency calculated on the basis of stomatal conductance    |
| Y(II)               | Quantum yields of photosystem II photochemistry                         |
| Y(NO)               | Quantum yields of non-regulated energy dissipation                      |
| Y(NPQ)              | Quantum yields of non-photochemical fluorescence quenching              |
| CAT                 | Catalase                                                                |
| APX                 | Ascorbate peroxidase                                                    |
| GH <sub>2</sub> O   | Stomatal conductance to H <sub>2</sub> O                                |
| GCO <sub>2</sub>    | Stomatal conductance to CO <sub>2</sub>                                 |
| C <sub>i</sub>      | Intercellular CO <sub>2</sub> concentration                             |
| ChlF                | Chlorophyll <i>a</i> fluorescence                                       |
| ETC                 | Electron transport chain                                                |
| PAM                 | Pulse-amplitude modulation                                              |

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