Creation and application of fluoropolymer photoconversion films for greenhouses: Concept.

S V Gudkov1,2,3, A V Simakin1, V E Ivanov4, E V Barmina1, I V Baimler1,5, I I Rakov1, L A Katicheva2, V A Vodeneev2 and G A Shafeev1,6

1 Prokhorov General Physics Institute, Russian Academy of Sciences, 38 Vavilova st., Moscow, 119991 Russia
2 The Institute of Biology and Biomedicine, Lobachevsky State University of Nizhni Novgorod, Nizhni Novgorod, 603950 Russia
3 All-Russia Research Institute for Phytopathology, B. Vyazyomy, Moscow Region, 143050 Russia
4 Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Institutskaya St. 3, Pushchino, Moscow Region 142290, Russia
5 Moscow Institute of Physics and Technology, Institutsky lane 9, Dolgoprudny, Moscow region, 141700 Russia
6 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, Moscow, 115409 Russia

E-mail: S_makariy@rambler.ru

Abstract. The purpose of this investigation is to create a scientific basis and technology of the production of fluoropolymer photoconversion films for greenhouses to improve the performance of greenhouses in the area of risk farming. The aim basis of photoconversion technology in greenhouses is reduced to photoconversion of UV radiation into blue-violet, and green and yellow light into red light necessary for plants. In other words, when sunlight passes through fluoropolymer photoconversion films, the intensity of the blue-violet and red regions of the spectrum should increase, and the intensity of the UV, green and yellow regions of the spectrum should drop. The article presents the manufacturing technology of fluoropolymer photoconversion films and examples of its use in greenhouses.

1. Introduction

Visible light is electromagnetic radiation with wavelengths of 380–780 nm and quantum energy of 1.6–3.2 eV, perceived by the human eye. Visible light is very important for life on Earth, for most ecological communities it is the main source of energy [1]. The exception, perhaps, are only the deep-water communities of “black smokers”, unable to use the energy of solar radiation and living at the expense of the energy of chemical compounds released on the fractures of lithospheric plates [2]. In general, visible light can modulate various biological processes [3,4], and applied in the diagnosis and treatment of various diseases [5,6]. With the participation of light, such important processes as, phototaxis, phototropism, photoperiodism, circadian rhythms and vision take place [1]. It is known that in order to obtain energy in the process of photosynthesis, plants use mainly quanta of the red and blue-violet part of the spectrum [7]. Most of the Russian Federation and other northern countries are located in the zone of risk farming, which is determined, among other things, by the insolation regime.
For many crops grown on greenhouse conditions in the zone of risk farming, the average daily intensity of the red and blue-violet part of the spectrum is usually sufficient only on clear summer days. The problem of insufficient illumination in greenhouses is usually solved with the help of artificial light sources [8]. This project involves the creation of scientific basis and technology for the production of polymer photoconversion coating for greenhouses. The coating produces photoconversion of UV light into blue-violet light, and green and yellow light into red light. In the future, the use of such a coating will significantly improve the performance of greenhouses and move on to their year-round use without “extra illumination” during the day in the area of risk agriculture.

Figure 1. The concept of the presented work. The upper graph shows the energy spectrum of the sun on the surface of the Earth. When passing through the control film, it does not significantly change (lower left graph). When passing through fluoropolymer photoconversion films, its contribution to the blue and red components increases (lower right graph). As a result, in high latitude conditions, plants growing under a fluoropolymer photoconversion films have an advantage.

The task of creating photoconversion polymer coatings is long standing. The first coatings contained organic fluorophores, the main problem of such coatings was the rapid bleaching of the fluorophore [9]. Later, rare-earth metals and their compounds, often europium, were used as phosphors. The stability problem was partially solved, but the quantum yield was small [10]. At the present stage, nanoparticles with plasmon or exciton emission are used, cadmium-selenium, zinc-sulfur pairs, etc. are popular [11]. These fluorophores have significant problems with their inclusion in the polymer matrix and the stability of relatively active oxygen forms, which are always formed in vapor-permeable materials. Thus, there is the problem of quantum yield, inclusion in polymers and vapor permeability. In this article we will show how can solve the indicated problems. We use gold nanoparticles doped with fluorophores. Such particles are relatively low toxic and fairly stable.
Nanoparticles with fluorophore are able to effectively convert UV radiation, a part of green and yellow light into blue light, and red light needed by plants. The concept of the work is shown in Figure 1.

2. Methods
Gold nanoparticles were obtained by laser ablation of solid target in a deionized water. Au bulk was located at the bottom of a glass cuvette under a thin layer of working fluid (several millimeters) and irradiated with radiation of Ytterbium fiber laser (90 J/cm² at 1060-1070 nm, pulse width of 90 ns, repetition rate of 20 kHz) (Figure 2). The optical density of the samples was measured using an Ocean Optics USB3000T spectrometer. Morphology of the generated nanoparticles was investigated by Libra 200 FE HR transmission electron microscope (Carl Zeiss). The size of the nanoparticles was determined using an analytical centrifuge DC24000 (CPS Instruments) [12].

The combination of gold nanoparticles and fluorophore was made using laser technology. Laser ablation of nanoparticles and fluorophore in the absence of the solid target was carried out using the radiation of the Nd:YAG laser at a wavelength of 1064 nm, pulse duration of 4 ns and fluence 140 J/cm² [13]. The transfer of nanoparticles to a fluoropolymer Functionalization of fluoropolymer by nanoparticles was carried out using the technology developed earlier [14]. Various routine procedures were used to study the spectral characteristics of fluoropolymer photoconversion films [3]. A CMP-3 pyrorometer (Kipp & Zonen), a UV-BC spectrometer USB3000T (OceanOptics), an IR spectrometer Alf (Bruker), a measuring station of wide range Field Master (Coherent) were used as measuring stations. Practical tests of the developed fluoropolymer photoconversion films were carried out in greenhouses. The main indicator was the biomass of the studied plants.

3. Results
The generated gold nanoparticles are characterized by its size and morphology (Figure 3). As can be noticed absorption spectrum of Au nanoparticles has a maximum at 520 nm (Figure 3A) that corresponds the transverse plasmon resonance of spherical nanoparticles with size 10-20 nm [15]. This data is confirmed TEM imaging and disc centrifuge analysis (Figure 3B-D). As can be seen nanoparticles have a size of less than 30 nm. Remarkably, the portion of nanoparticles with average sizes of 15-20 nm amounts to more than 95% of all the gold weight in colloid while the number of nanoparticles with average sizes of 6-10 nm is less than 5% (Figure 3B). The data obtained by disc centrifuge were correlated with TEM image (Figure 3C). As can be seen all nanoparticles have a spherical shape (Figure 3D).

In this work, we attached fluorophores (Cd/ZnSe and Eu ions) to gold nanoparticles. Composites of gold nanoparticles and Cd/ZnSr showed a higher quantum yield compared with gold nanoparticles doped with Eu ions. With the help of the technology developed by us, nanoparticles were incorporated into the photoconversion fluoropolymer. In this case, nanoparticles are combined into aggregates of the "chain" type. Obviously, nanoparticles cannot be directly incorporated into polymer chains, and the matrix flows around them. This process is shown schematically in figure 4. This aggregation is
accompanied by a change in the plasmon resonance spectrum of metal nanoparticles and synergistic amplification of the optical wave field. It should be noted that the fluoropolymers are practically water vapor impermeable. This judgment supports the recent soak study of sulfonated tetrafluoroethylene-based fluoropolymer-copolymer [16-18].

Figure 3. Characteristics of gold nanoparticles obtained by laser ablation. A – Absorption spectrum of gold nanoparticles in water; B – Nanoparticles size distribution by weight determined by an analytical disc centrifuge; C – Size distribution of nanoparticles from TEM images; D – TEM image of gold nanoparticles. Scale bar, 20 nm.

With the help of artificial light sources simulating sunlight, primary tests of fluoropolymer photoconversion films were carried out. It was shown that when illuminated with model sunlight through a photoconversion polymer films, a noticeable increase in the biomass accumulation of lettuce plants (30%), cabbage (25%) and peas (15%) is observed. We assume that this is due to the more efficient operation of the photosynthetic apparatus. Of course, this assumption needs further verification.

4. Conclusions
The purpose of this study is to create a scientific basis and technology for the manufacture of fluoropolymer photoconversion films for greenhouses. Such films should increase the productivity of greenhouses in the zone of risk farming (high latitudes). The essence of the photoconversion technology in greenhouses is reduced to photoconversion of UV radiation, green and yellow light into blue and red light necessary for plants. Gold nanoparticles are used effectively as a fluorophore
carrier. The technology of incorporating nanoparticles into fluoropolymer films in the form of chains has been used for supersharing enhancement of the optical wave field. The obtained fluoropolymer photoconversion films passed primary agricultural tests and showed their effectiveness. In the future, work is needed on consumer qualities (increase quantum yield, increased service life, cheaper prices, etc.).

**Figure 4.** Polymer molecules align gold nanoparticles into chains in the nanocomposite. Gold nanoparticles are red.

**Acknowledgements**
The work was partially supported by the Grant MD-3811.2018.11 of the President of the Russian Federation for Governmental Support of Young Russian Scientists - Doctors of Sciences and RFBR Projects 19-02-00061_a, 18-52-70012 e-Asia_a. The optical part of the work was carried out with the support of R&D program (AAAA-A18-118021390190-1). The authors are grateful to the Center for Collective Use of the GPI RAS for the equipment provided.

**References**

[1] Gudkov SV, Andreev SN, Barmina EV, Bunkin NF, Kartabaeva BB, Nesvat AP, Stepanov EV, Taranda NI, Khramov RN and Glinushkin AP 2017 *Phys. Wave Phenom.* **25** 207–213.

[2] Weiss MC, Sousa FL, Mrnjavac N, Neukirchen S, Roettger M, Nelson-Sathi S and Martin WF 2016 *Nature Microbiol.* **1** 16116

[3] Chernov AS, Reshetnikov DA, Kovalitskaya YuA, Manokhin AA and Gudkov SV 2018 *J. Photochem. Photobiol. B.* **188** 77-86

[4] Ivanov VE, Usacheva AM, Chernikov AV, Bruskov VI and Gudkov SV 2017 *J. Photochem. Photobiol. B.* **176** 36–43.

[5] Guryev EL, Volodina NO, Shilyagina NY, Gudkov SV, Balalaeva IV, Volovetskiy AB, Lyubeshkin AL, Sen’ AV, Ermilov SA, Zvyagin AV, Alferov ZI and Deyev SM 2018 *PNAS* **115** 9690-9695

[6] Brilkina AA, Peskova NN, Dudenkova VV, Gorokhova AA, Sokolova EA and Balalaeva IV 2018 *J. Photochem. Photobiol. B.* **178** 296–301.

[7] Shindy HA 2017 *Chem. Int.* **3** 97-105

[8] Nelson JA and Bugbee B 2014 *PLoS One* **9** e99010.

[9] Amin F, Yuschenko DA, Montenegro JM and Parak WJ. 2012 *Chemphyschem.* **13** 1030-1035

[10] Garcia-Murillo A, Le Luyer C, Garapon C, Dujardin C, Bernstein E, Pedrini C and Mugnier J 2002 *Opt. Mater.* **19** 161-168

[11] Reda SM 2008 *Acta Materialia* **56** 259-264

[12] Barmina EV, Mel’nik NN, Rakov II, Ivanov VE, Simakin AV, Gudkov SV and Shafeev GA 2018 *IOP Conf. Series: Materials Science and Engineering* **347** 012005

[13] Barmina EV, Gudkov SV, Simakin AV and Shafeev GA 2017 *J. Laser Micro/Nanoeng.* **12**, 5
254-257

[14] Barmina EV, Mel’nik NN, Rakov II and Shafeev GA 2017 Phys. Wave Phenomen. 25 165–169
[15] Creighton JA and Eadon DJ 1991 J. Chem. Soc., Faraday Trans. 87 3881-3891
[16] Bunkin NF, Kozlov VA, Shkirin AV, Ninham BW, Balashov AA and Gudkov SV 2018 J. Chem. Phys. 148 124901
[17] Bunkin NF, Shkirin AV, Kozlov VA, Ninham BW, Uspenskaya EV and Gudkov SV 2018 J. Chem. Phys. 149 164901.
[18] Bunkin NF, Kozlov VA, Aliev IN, Molchanov II, Abdullaev SA, Belosludtsev KN, Astashev ME, Gudkov SV 2015 Phys. Wave Phenomen. 23 255-264.