

Supplementary Information

Recomposition and storage of sunlight with intelligent phosphors for enhanced photosynthesis

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Experimental section

Materials and Measurements

CaS, SrS, Eu₂O₃, and Dy₂O₃ were purchased from Strem Chemicals (USA). MgCO₃·Mg(OH)₂·5H₂O, SrCO₃, activated charcoal powder, HBO₃, Tetraethyl orthosilicate (TEOS), (3-Aminopropyl)triethoxysilane (APTES), ammonia, 2',7'-Dichlorodihydrofluorescein diacetate (DCFH-DA), and other chemicals were purchased from Sigma-Aldrich. All chemicals were applied without further purification.

SEM imaging was performed with JEOL-JSM-7600F microscope (JEOL Ltd., Japan). The energy dispersive X-ray spectroscopy (EDS) mapping were measured with the detector in the JEOL-JSM-7600F microscope. X-ray diffraction (XRD) studies were conducted using a Rigaku SmartLab X-ray diffractometer (Rigaku Co., Japan). The fluorescence images were collected on a ZEISS LSM 800 confocal laser scanning microscope (Carl Zeiss Microscopy GmbH, Germany). The solid state luminescent spectra were measured on Quantaaurus-QY Absolute PL quantum yield spectrometer (C11347-11) (Hamamatsu Corporation, USA). Afterglow emission was studied with a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technology, USA). Afterglow intensity of the scaffold was measured with a Newport 843-R Hand-Held Laser Power Meter (Newport, USA). Elements analysis was recorded on an Agilent 7700 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Agilent Technology, USA).

Synthesis of the phosphors Sr_{0.2}Ca_{0.8}S: Eu²⁺

The phosphor was synthesized by a solid-state reaction method.^[1] Briefly, stoichiometric ratio of the starting materials CaS, SrS and trace amount of Eu₂O₃ were fully mixed and ground, to which NH₄Br (1.5 wt.%) and elemental sulphur (1.5 wt%) were added as flux agent. Then the white powder was put into a crucible and covered with activated charcoal powder. After that, the solid-state reaction was performed with a muffle furnace over 1000 °C for 5 h.

Synthesis of long persistent phosphor material Sr_{0.2}Ca_{0.8}S: Eu²⁺@Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺

The synthesized Sr_{0.2}Ca_{0.8}S: Eu²⁺ was first silicified with TEOS/APTES as the silica source. Generally, in an ethanol solution with 10 mg/mL of Sr_{0.2}Ca_{0.8}S: Eu²⁺, APTES (200 μL), TEOS (500 μL) and ammonia (700 μL) were added. After stirring at room temperature for 2 hours, the silica-encapsulated phosphor was separated by centrifugation. The encapsulation was repeated

until to achieved silica layer of the $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{S: Eu}^{2+}@ \text{SiO}_2$ with the stoichiometric ratio. The dried powder was then fully mixed with $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, SrCO_3 , in stoichiometric ratio, and trace amount of Eu_2O_3 , Dy_2O_3 and HBO_3 before the solid-state reaction.^[2] The mixture was then calcined over 1100 °C for 2 h under reductive atmosphere. Thereafter, the powder is washed several times and dried for further use.

Fabrication of the phosphors doped porous three-dimensional (3D) scaffold (PP3DS)

The porous 3D scaffold was fabricated by using a polystyrene (PS) sponge as the template and agarose hydrogel as the matrix. The PS sponge template was first built by thermal treatment of commercially available PS beads (~ 0.5 mm) at 135 °C with a Buchner funnel as mould. The 2% agarose aqueous solution was heated until boiling, and then added with the phosphors. After cooling to about 40 °C with stirring, the suspension was poured to the PS sponge under filtration. Then, the hydrogel filled sponge was further cooled at 4 °C for 1h. Subsequently, the PS template was thoroughly removed by etching with tetrahydrofuran for two days. After removal of the template, the finally obtained **PP3DS** was washed with pure water and stored at 4 °C for further use.

Afterglow intensity measurement

Afterglow intensity of the scaffold was measured with a Newport 843-R Hand-Held Laser Power Meter (Newport, USA). The meter can detect light in the wavelength range from 190 nm to more than 10 μm , which measures the intensity of afterglow in all wavelength ranges. For the afterglow intensity measurement, the scaffold was first irradiated under sunlight for 30 minutes, then it was immediately put on the detector of the Meter and transferred to a dark box, and finally the energy density was collected at different time interval.

Microalgae culture

The microalgae and culture medium were commercially obtained. The combined microalgae contents the species of *Scenedesmus quadricauda*, *Chlorella pyrenoidosa*, *Spirulina platensis*, and *Chlorella vulgaris*. For indoor culture, a metal-halide lamp (150 W) was used as the light source to mimic the sunlight. The beaker (25 mL) was acted as the reactor, and a fan was used to keep the temperature around 28 °C. The distance between the lamp and the culture reactor was fixed at the light density of 35 mW/cm^2 during the cultivation. The initial microalgae optical density at 680 nm (OD680) was kept at 0.15 with a volume of 18 mL. During cultivation, the

reactors were shaken once every two hours. Typically, a four-day cultivation with a total 9h of daily light irradiation was performed. After cultivation, the microalgae were concentrated by centrifugation and redispersed to measure the density. In the growth with the **PP3DS** scaffold, the microalgae were harvested by flushing with pure water. Except for the concentration dependent experiments, the concentration of phosphors in **PP3DS** was kept at 60 mg/mL. The data from each culture condition was averaged from three parallel reactors. Different filters were used for the UV, green or UV-filtered light cultivation.

The investigation of the direct contribution of the afterglow effect to the photosynthesis was performed by monitoring the growth of microalgae under dark conditions. In order to facilitate the measurement, a thin-layer bioreactor with the inner thickness less than 500 μm was used. This thin-layer bioreactor was built with two cover slips (22×50 mm, thickness 0.13-0.16 mm, Marienfeld Superior). Before cultivation, one **PP3DS** was illuminated by the metal-halide lamp for 30 minutes. During the cultivation in dark condition, the microalgae ($\text{OD}_{680} = 0.15$) filled thin-layer bioreactor is sandwiched in the middle of the **PP3DS** to harvest the afterglow emission. This photosynthesis system was kept under dark condition for 12 h, during this period, the **PP3DS** placed in dark condition was exchanged with a newly illuminated one every 30 minutes. Finally, the optical density of the microalgae culture medium was measured. As comparison, the growth in dark condition without irradiated **PP3DS** was also performed.

For outdoor culture, the reactors were covered with quartz slides and settled at an open roof. Extra water was added every evening to keep the volume of the culture medium constant; meanwhile the samples were collected for monitoring the optical density at 680 nm.

ROS detection

The generation of ROS was estimated by ROS sensing probe 2',7'-Dichlorodihydrofluorescein diacetate (DCFH-DA).^[3] DCFH-DA is a non-fluorescent, cell-permeable dye which is hydrolyzed intracellularly by intracellular esterases. The resulting 2',7'-dichlorodihydrofluorescein (DCFH) is a polar, but non-fluorescent form that will be retained in the cell. Oxidation of DCFH by the action of intracellular ROS converts the molecule into its highly fluorescent form 2',7'-dichlorofluorescein (DCF). In the ROS test, 2 mL of culture sample was centrifuged at 5000 rpm for 3 min and the supernatant was discarded. The microalgal pellet was then resuspended with pH 7.2 PBS buffer and the number was counted with a hemocytometer. DCFH-DA (10 μM final concentration) was added to the microalgae suspension and incubated on a shaker at room

temperature in the dark for 1 h. After the incubation, the samples were subjected to fluorescence microscopy. And the samples were washed with pH 7.2 PBS buffer three times before fluorescence spectrophotometric analysis.

Reference

1. a) Q. Xia, M. Batentschuk, A. Osvet, A. Winnacker, J. Schneider, *Radiat. Meas.* **2010**, 45, 350-352; b) H.-J. Sung, Y.-S. Cho, Y.-D. Huh, Y. R. Do, *Bull. Korean Chem. Soc.* **2007**, 28, 1280-1284.
2. a) Y. Lin, Z. Tang, Z. Zhang, X. Wang, J. Zhang, *J. Mater. Sci. Lett.* **2001**, 20, 1505-1506; b) Q. Fei, C. Chang, D. Mao, *J. Alloys Compd.* **2005**, 390, 133-137.
3. R. P. Rastogi, S. P. Singh, D.-P. Häder, R. P. Sinha, *Biochem. Biophys. Res. Commun.* **2010**, 397, 603-607.

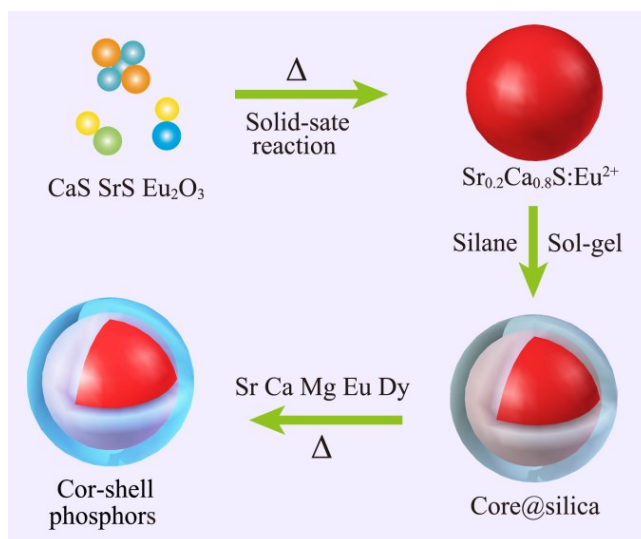


Fig. S1 Synthesis of the core-shell phosphor material.

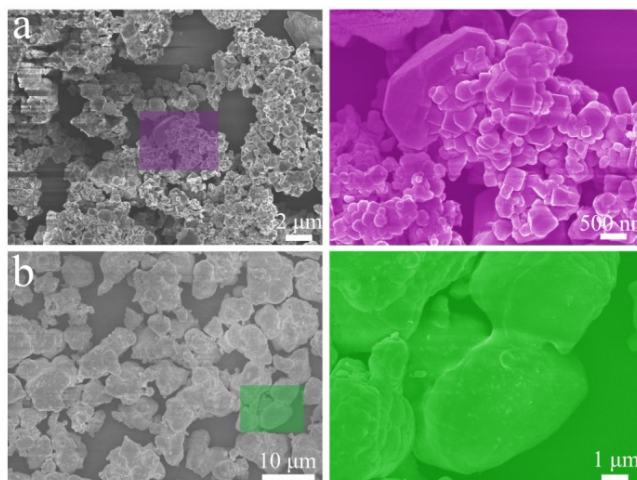


Fig. S2 SEM images of the phosphors a) $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{S}:\text{Eu}^{2+}$ and b) $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{S}:\text{Eu}^{2+}@\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$.

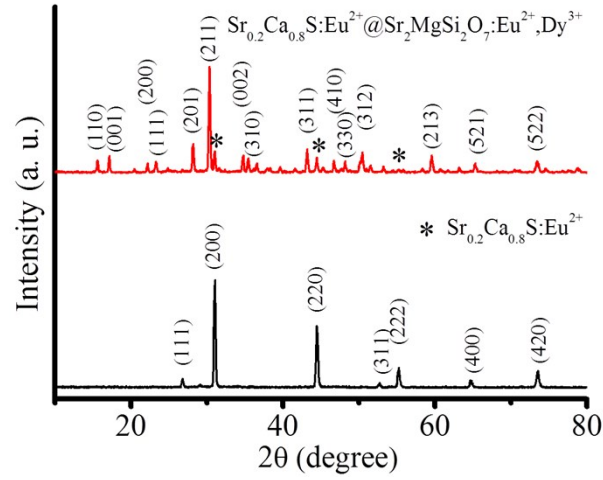


Fig. S3 XRD patterns of the phosphors.

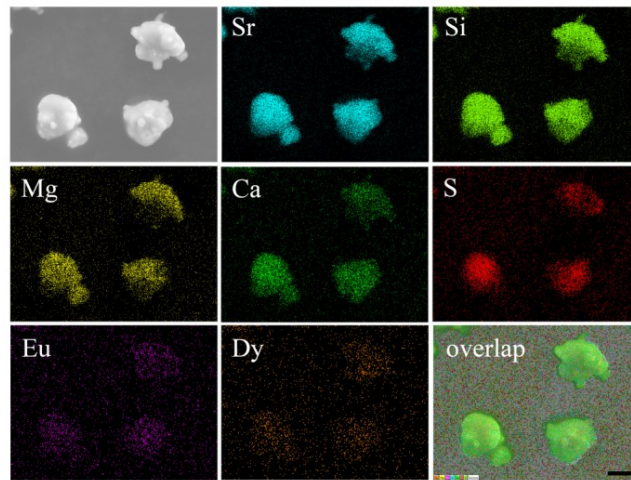


Fig. S4 The SEM and element mapping of $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{S}:\text{Eu}^{2+}@\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$. Scale bar = 5 μm .

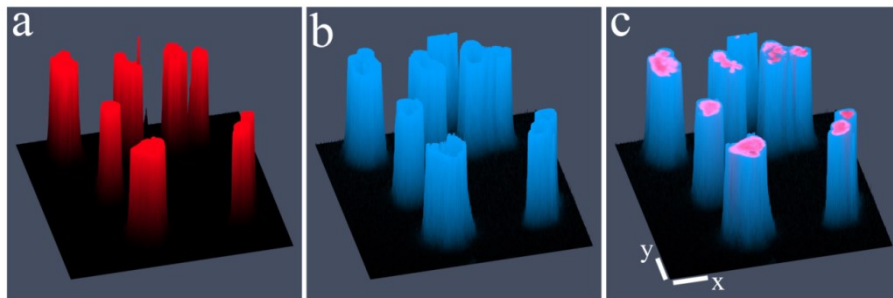


Fig. S5 Confocal microscopic images (2.5D stacked) of the phosphors: (a) Red channel (E_x : 560 nm, E_m : 600-700 nm), (b) Blue channel (E_x : 405 nm, E_m : 430-500 nm), (c) the merged. Scal bar = 10 μm .

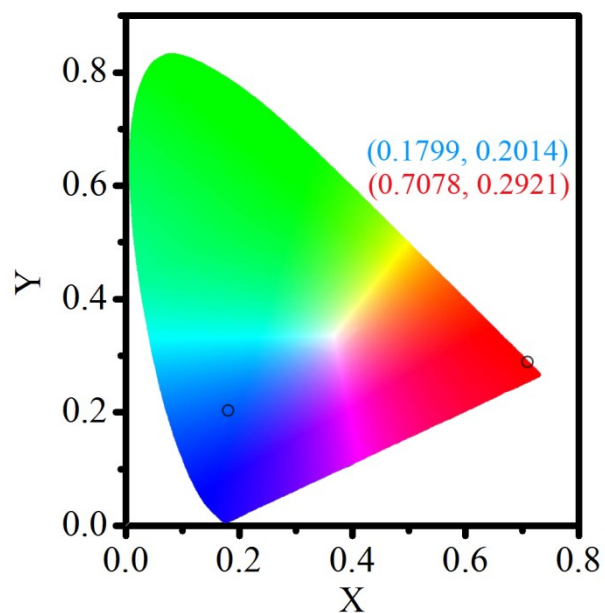


Fig. S6 The CIE 1931 color coordinate for the core-shell phosphors.

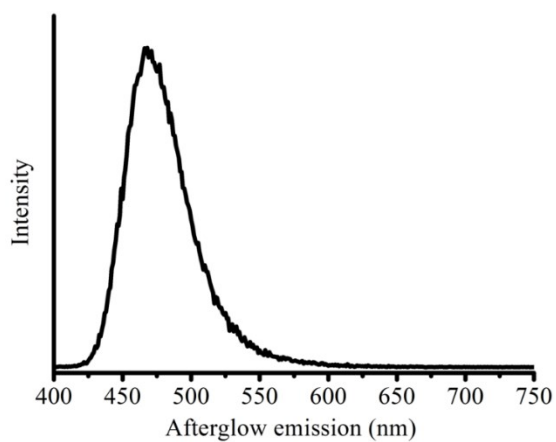


Fig. S7 Afterglow emission spectrum of the phosphors.

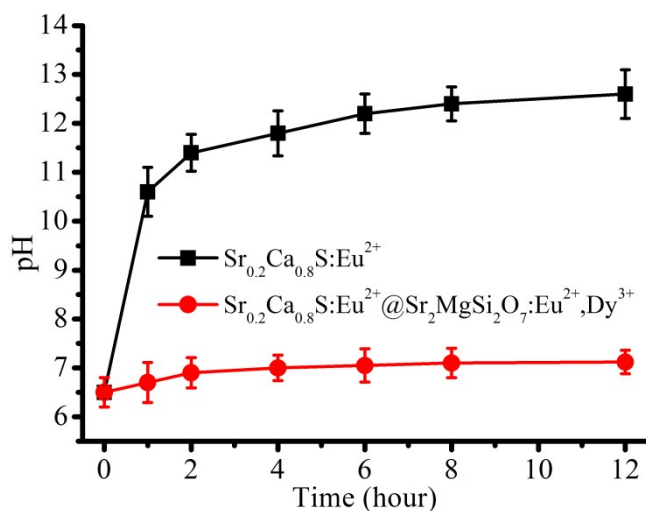


Fig. S8 Changes of pH values indicate the water-resistance of the phosphors.

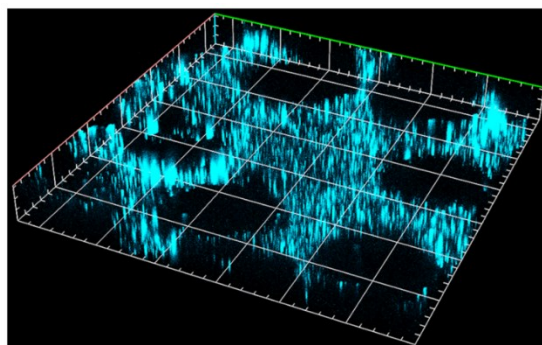


Fig. S9 The three-dimensional reconstruction micrograph of PP3DS imaged by a confocal laser microscopy (408 nm excitation).

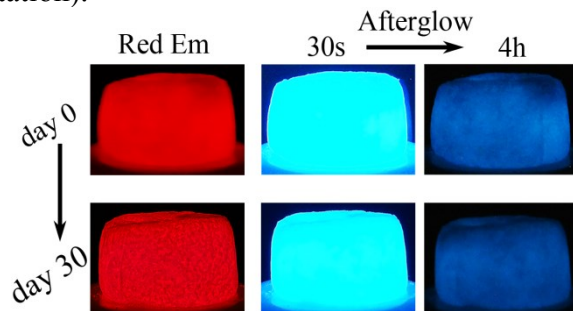


Fig. S10 The red emission (530 nm excitation) and afterglow images of as-prepared PP3DS and that after 30 days placement.

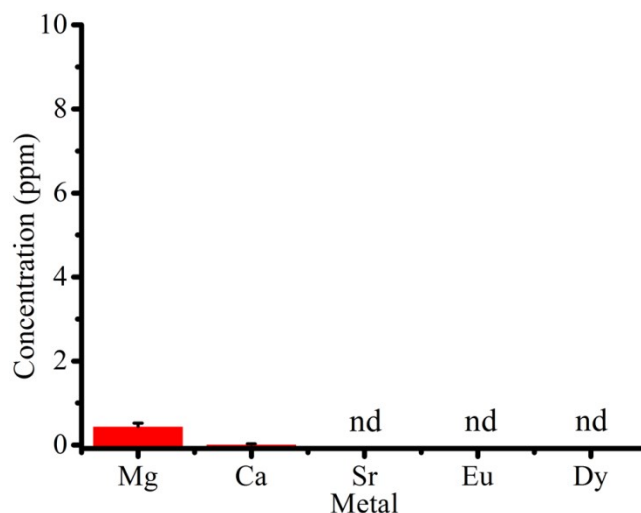


Fig. S11 Metal elements content in water after immersion with PP3DS for one month. nd - not detected.

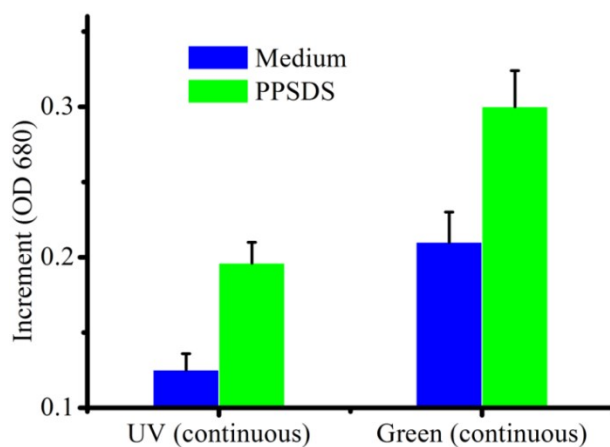


Fig. S12 Growth of *Chlorella vulgaris* in medium with and without **PP3DS** under different light conditions. UV and Green light were generated by using band pass filters, and the cultivation was exposed to continuous light irradiation for 9 h and then was placed in dark for 15 h every day. After cultivation under four days, the microalgae were harvested and the density was quantified by monitoring the absorbance at 680 nm.

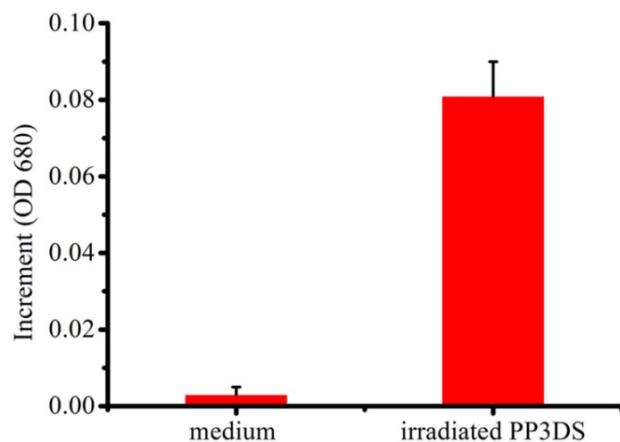


Fig. S13 Growth of *Chlorella vulgaris* in medium with and without the irradiated PP3DS under dark condition.

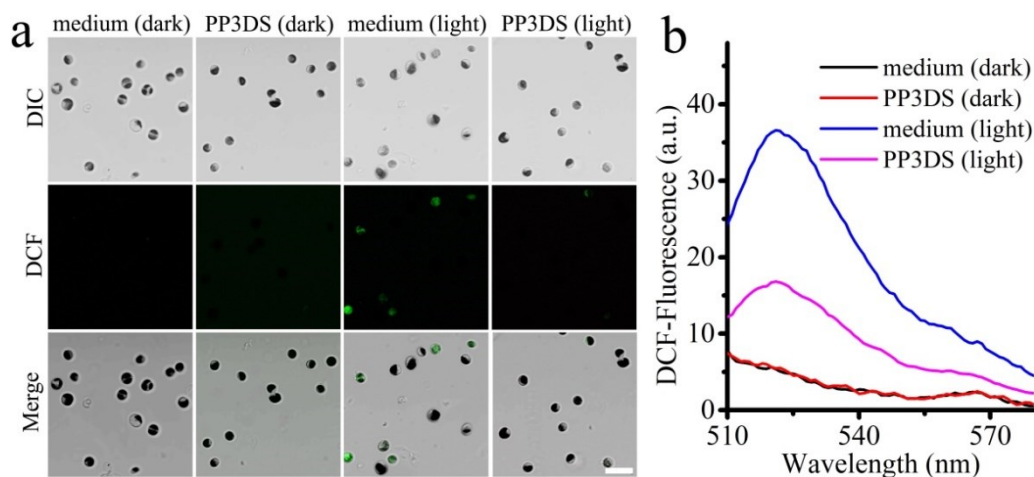


Fig. S14 a) Confocal images indicating the ROS generation in *Chlorella vulgaris*. Scale bar = 10 μm . b) The DCF fluorescence of the *Chlorella vulgaris* ($\text{ex} = 488 \text{ nm}$). Cell concentration: 2.5×10^7 cells/ml.

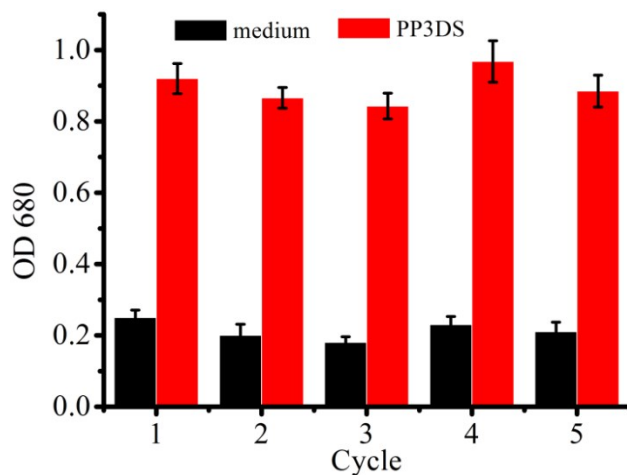


Fig. S15 Reusable performance of PP3DS for a 6-day cultivation of *Chlorella vulgaris* under outdoor solar radiation.