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Use of near-infrared radiation for oxygenic photosynthesis via photon up-conversion

Taras Antal [a,1], Emilia Harju [b], Laura Pihlgren [b,c], Mika Lastusaari [b,d], Taina Tyystjärvi [a], Jorma Hölsä [b,d], Esa Tyystjärvi [a,*]

[a] Molecular Plant Biology, Department of Biochemistry and Food Chemistry, University of Turku, FI-20014 Turku, Finland
[b] Department of Chemistry, University of Turku, FI-20014 Turku, Finland
[c] Graduate School of Materials Research (GSMR), Turku, Finland
[d] Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland

ARTICLE INFO

Article history:
Received 28 November 2011
Received in revised form
16 January 2012
Accepted 21 January 2012
Available online 20 February 2012

Keywords:
Photon up-conversion
Biohydrogen
Photosynthesis
Near infrared radiation
NIR

ABSTRACT

Radiation between 400 and 700 nm, used for oxygenic photosynthesis by cyanobacteria, algae and plants, represents only 44% of total solar energy while the range above 700 nm comprises 52%. An ability to use near infrared (NIR, 700–1200 nm) radiation would greatly improve the efficiency of photosynthesis, but NIR photons have too low energy to excite the photosystems of oxygenic photosynthesis. Here we show that a mechanism called photon up-conversion can turn NIR radiation into an energy source for photosynthesis. In the future, it may be possible to up-convert the NIR part of the solar energy flux to visible light for use in photo-induced biohydrogen production by oxygenic photosynthesis.

1. Introduction

The rate of hydrogen production with photosynthetic systems (for reviews, see [1–4]) is critically dependent on the light use efficiency of the photosynthetic electron transfer chain [3,5–7]. In photosynthesis of plants, algae and cyanobacteria, photosystems II and I convert light to chemical energy. The photosystems can only use photons whose energy exceeds a threshold value of approximately 1.8 eV (700 nm). Longer wavelengths are not even absorbed by chlorophylls and other photosynthetic antenna pigments (Fig. 1). However, radiation between 400 and 700 nm represents only 44% of total solar energy while the range above 700 nm comprises 52%, and therefore the light use efficiency of photosynthetic systems would be greatly improved if photosynthesis could also use near-infrared (NIR) radiation. A possible method for making the energy content of NIR photons available for photosynthesis is to convert NIR radiation to visible light with the photon up-conversion mechanism [8].

Photon up-conversion occurs when successive absorption of NIR photons populates long-lived, metastable excited states decaying radiatively. The highest up-conversion efficiencies

Abbreviations: DCIP, 2,6-dichloroindophenol; NIR, near infrared; PFD, photon flux density.

* *Corresponding author*. Tel.: +358 2 3335771; fax: +358 2 3338075.
E-mail address: esatyy@utu.fi (E. Tyystjärvi).
[1] Present address: Department of Biophysics, Faculty of Biology, Moscow State University, Vorobyovi gori, bldg 1/12, 119992 Moscow, Russia.

0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2012.01.087

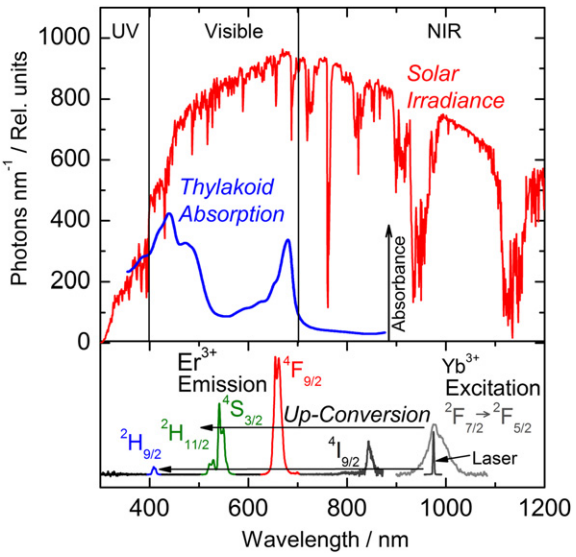

Fig. 1 – The upper panel describes the AM1.5 reference solar spectral irradiance according to ASTM G173-03 (37° global tilt) [22], recalculated to show a photon number spectrum together with a typical absorption spectrum of a plant thylakoid preparation. The lower panel shows the photon up-conversion and generation of green, red and blue light as well as NIR radiation by the Yb^{3+} and Er^{3+} doped $NaYF_4$ phosphor lanthanide phosphors with NIR excitation at 975 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are obtained when two different trivalent lanthanide/rare earth (Ln^{3+}/R^{3+}) ions are doped into a solid state host [8] with strict stoichiometry, well-defined crystal structure and low lattice vibration energies. Emission of the R^{3+} ions is efficient because the intraconfigurational 4f–4f transitions occur between energy levels that are well-shielded by the outer orbitals, ensuring that the interactions of the 4f wave-functions with the host lattice are weak and lead to sharp line emission [8]. Up-converting materials (phosphors) have been applied for the detection of infrared emission, security printing and 3D display technologies. Luminescent nano-particles of R^{3+} doped materials have also been suggested for the detection of antigens [9,10], and up-converting phosphors like $NaYF_4$:Yb^{3+},Er^{3+} [11] or ZrO_2:Yb^{3+},Er^{3+} [12] show great potential in immunoassays [13].

Yb^{3+},Er^{3+} co-doped inorganic materials (Fig. 1) have proven to be the most efficient systems for two-photon up-conversion of NIR radiation to visible light, with up-conversion efficiencies up to 4% [8,13]. NIR radiation at *ca.* 1000 nm is absorbed by Yb^{3+} and transferred non-radiatively to Er^{3+} which has several long-lived intermediate excited states. After accumulation of two NIR photons by successive non-radiative transitions, Er^{3+} emits mainly in green and red [14] though weak blue and significant NIR emission also occur (Fig. 1). Yb^{3+},Er^{3+} doped $NaYF_4$ materials provide high luminescence intensity in red and green, whereas Y_2O_3 based phosphors yield predominantly red light [13]. The color depends on host properties (e.g. lattice vibrations) and on Er^{3+} concentration, green emission dominating with low Er^{3+} concentrations. The red to green emission ratio also depends on the power of the NIR excitation because high laser power heats the sample, which leads to modification of cross-relaxation processes.

In this work we tested the possibility to use selected, commercially available photon up-conversion materials to drive photosynthesis with up-conversion luminescence obtained by illuminating these materials with NIR radiation.

2. Materials and methods

2.1. *Luminescence excitation and recording of the emission spectra*

Emission spectra were measured at room temperature with an Ocean Optics PC2000-CCD optical fiber spectrometer using the OOIIrrad software (Ocean Optics, Dunedin, FL, USA) (Fig. 2). A fiber-coupled NIR-laser diode (L9418-04, Hamamatsu Photonics KK, Tokyo, Japan) with peak emission wavelength at 975 nm and radiation power of 670 mW, controlled with a laser driver (LDTC2/2, Wavelength Electronics Inc., Bozeman, MT, USA), was used as a source of NIR radiation. The optical setup consisted of tubular excitation and emission chambers (Thorlabs, Inc., Newton, NJ, USA) in right-angle configuration. In the excitation chamber, an 850 nm long-pass filter (RG850, Edmund Optics Ltd, York, UK) was used to ensure pure NIR-excitation. An 850 nm short-pass filter (46386, Edmund Optics) was used to block scattered excitation light.

The infrared to visible up-converting phosphors $NaYF_4$:Yb^{3+},Er^{3+} (PTIR550/F) and Y_2O_3:Yb^{3+},Er^{3+} (PTIR660/F) were acquired from Phosphor Technology Ltd. (Stevenage, UK). The phosphors were packed inside a water proof transparent capillary tube (diameter 2 mm). A tube with a given phosphor was fixed vertically to the cuvette wall.

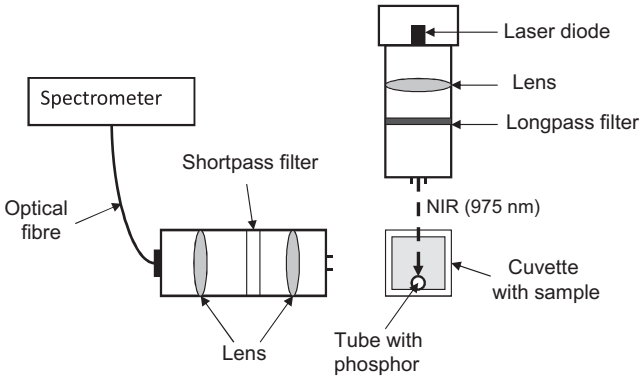

Fig. 2 – Top view of the setup for both measurements of the spectra and the treatments of the thylakoids. The phosphors were packed inside transparent capillary tubes (diameter 2 mm). A tube with a given phosphor was fixed vertically to the inner wall of the cuvette and illuminated with a NIR laser diode. Excitation was through an 850 nm long-pass filter and emission was measured through an 850 nm short-pass filter.