



## Energy transfer from natural photosynthetic complexes to single-wall carbon nanotubes



Kamil Wiwatowski<sup>a</sup>, Anna Dużyńska<sup>b</sup>, Michał Świniarski<sup>b</sup>, Marcin Szalkowski<sup>a</sup>, Mariusz Zdrojek<sup>b</sup>, Jarosław Judek<sup>b</sup>, Sebastian Mackowski<sup>a,c,\*</sup>, Izabela Kaminska<sup>a</sup>

<sup>a</sup> Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

<sup>b</sup> Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

<sup>c</sup> Wrocław Research Center EIT+, Stablowicka 147, Wrocław, Poland

### ARTICLE INFO

#### Article history:

Received 5 May 2015

Received in revised form

3 August 2015

Accepted 28 September 2015

Available online 21 October 2015

#### Keywords:

Energy transfer

Fluorescence

Time-resolved spectroscopy

Carbon nanotubes

Photosynthetic complex

### ABSTRACT

Combination of fluorescence imaging and spectroscopy results indicates that single-walled carbon nanotubes are extremely efficient quenchers of fluorescence emission associated with chlorophylls embedded in a natural photosynthetic complex, peridinin-chlorophyll-protein. When deposited on a network of the carbon nanotubes forming a thin film, the emission of the photosynthetic complexes diminishes almost completely. This strong reduction of fluorescence intensity is accompanied with dramatic shortening of the fluorescence lifetime. Concluding, such thin films of carbon nanotubes can be extremely efficient energy acceptors in structures involving biologically functional complexes.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

Carbon nanomaterials have been since decades considered to be promising structures in constructing devices for sensing, photovoltaics, optoelectronics. In most cases the underlying physico-chemical properties are related to large surface to volume ratio, ability to functionalize the surface with various active groups, strong potential of being an acceptor of both, charge and energy. Among the most illustrative examples are electron transfer in assemblies of fullerenes and organic dyes [1], energy transfer between semiconductor quantum dots and carbon nanotubes [2], acceptor properties of graphene and reduced graphene oxide visualized using fluorescence microscopy [3,4], sensing of biologically relevant molecules with graphene oxide and its derivatives [5,6], and many others.

In the context of artificial photosynthesis, several attempts were made to assemble a structure, where naturally evolved photosynthetic complexes were attached to carbon nanotubes [7,8]. It required proper functionalization of the nanotubes in order to facilitate efficient coupling between the two nanostructures. Moreover,

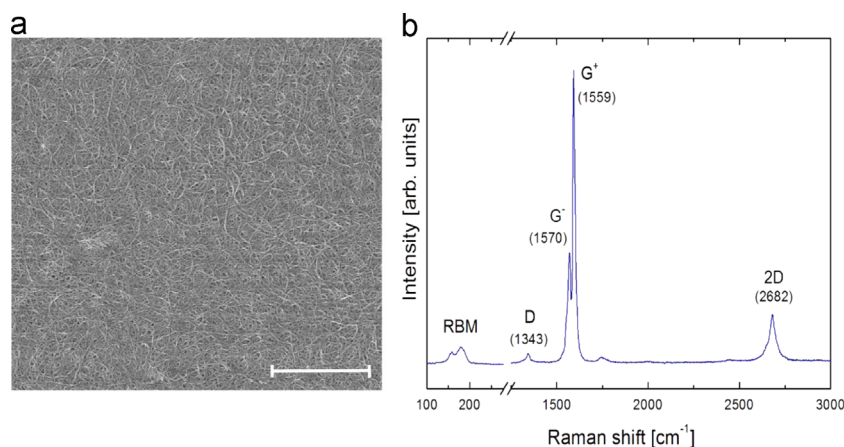
restraints are imposed on the conditions for sample preparation as photosynthetic complexes are proteins that require proper buffer conditions for preserving their function, whether it concerns energy harvesting, energy transfer, or electron transfer. On the other hand, while demonstrated on a single nanotube level, extension of the concept of constructing functional hybrid nanostructures composed of carbon nanotubes and photosynthetic complexes is limited by technology of surface deposition of carbon nanotubes with controlled chirality and their resulting electrical properties.

In this work we explore the possibilities to construct a hybrid assembly of semiconducting single-wall carbon nanotubes (SWCNTs) coupled with light-harvesting photosynthetic proteins responsible – in natural environment – for sunlight absorption and energy transfer. Fluorescence microscopy imaging and spectroscopy indicate that the energy transfer from the photosynthetic complexes to carbon nanotubes is extremely efficient, pointing towards high potential of such nanostructures for designing functional hybrid devices.

Carbon nanotube thin films were produced using the water solution of separated semiconducting SWCNTs from NanoIntegris (Iso-Nanotubes-S, 99% purity) with the tube diameters from 1.2 nm to 1.7 nm and the length in the range of 0.1–4 μm. Initially, nanotubes were stabilized by a combination of ionic surfactants, while the concentration of the SWCNTs in the solution was 0.01 mg/ml. However, to prepare small CNT thin films we removed

\* Corresponding author at: Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland  
Tel.: +48 56 6113217.

E-mail address: [mackowski@fizyka.umk.pl](mailto:mackowski@fizyka.umk.pl) (S. Mackowski).



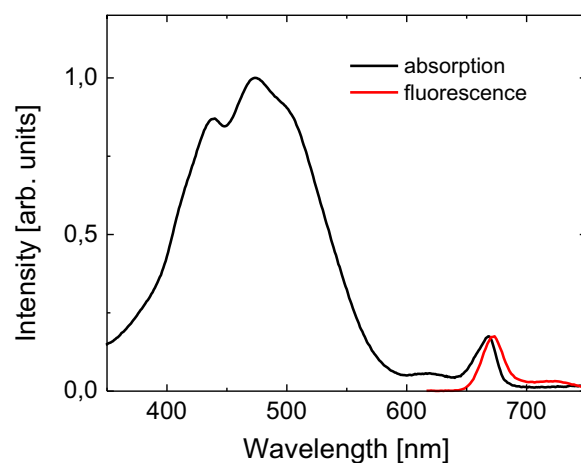
**Fig. 1.** (a) SEM image of a SWCNT thin film on glass; the scale bar represents 2  $\mu\text{m}$ , and (b) Raman spectra of semiconducting SWCNT thin film showing typical Raman modes.

surfactants from the solution of the nanotubes. One part of the CNT solution was added to 2 parts of acetone. After 2 h nanotubes were precipitated from the solution. In the next step, tubes were collected and centrifuged for 10 min at 10,000 rpm to separate them from the acetone. During centrifugation, the nanotubes were re-bundled and collected to the bottom of the centrifuge flask. Acetone was removed and replaced by the water, and solution was mixed vigorously. After this process water was replaced by the methanol and centrifuged, again. The entire procedure was repeated several times to remove residual surfactants. At the end small and clean CNT bundles were kept in the methanol and next the mixture was dropped on a glass substrate (at temperature 50 °C). After methanol evaporation small SWCNT films were placed on the substrate. To increase the adhesion between the thin films and the substrate the samples were immersed in water by 30 min and then gently rinsed by methanol and dried by the nitrogen stream. Fig. 1a shows typical SEM image of the produced thin film and Raman spectroscopy confirms the presence of clean single-walled carbon nanotubes (see. Fig. 1b). From the SEM image we can confirm that a thin film of SWCNTs is formed, although the network is not self-organized, and the nanotubes are randomly oriented onto the surface. The thickness of the film depends on the exact location and is in the range of 10–100 nm.

To probe interactions between photosynthetic complexes and SWCNTs we chose peridinin-chlorophyll-protein (PCP) light-harvesting complex from *Amphidinium carterae*. This complex has simple structure, is soluble in water, absorbs light in a broad spectral range and is characterized with relatively high quantum yield of fluorescence emission. Native PCP has a trimeric form with each monomeric protein subunit consisting of eight peridinins and two chlorophyll *a* molecules [9]. In this work, for simplicity, we used reconstituted PCP complexes (monomers) obtained as described previously [10]. Absorption spectrum of PCP shows three main bands (Fig. 2, black line): from 350 nm to 550 nm, due to carotenoids–peridinins, as well as at 440 nm and 670 nm, ascribed to Soret band and  $Q_y$  band of chlorophyll *a* molecules, respectively. The emission of PCP complexes (Fig. 2, red line), associated with fluorescence of chlorophylls, occurs at 673 nm [11].

For characterization of the SWCNT thin films we used scanning electron microscopy (SEM, Raith eLINE Plus) and Raman spectroscopy. Raman spectra were collected by the Renishaw spectrometer using a 514 nm Ar laser excitation line and a laser power of 41  $\mu\text{W}$ .

Absorption spectrum of PCP was measured using Varian Cary 50 UV–vis spectrophotometer. Fluorescence intensity maps (90  $\mu\text{m}$   $\times$  90  $\mu\text{m}$  in size) were acquired with Nikon Eclipse Ti inverted wide-field microscope equipped with Andor iXon Du-888 EMCCD camera. The samples



**Fig. 2.** Absorption (black) and fluorescence (red) spectrum of the PCP solution. Excitation wavelength of 485 nm was used. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were excited at 480 nm using a light-emitting diode illuminator through a microscope objective (Plan Apo, 100 $\times$ , NA 1.4). Fluorescence was extracted with a combination of a dichroic mirror T505LP (Chroma) and a narrow bandpass filter (Thorlabs FB670-10). Acquisition time and electron multiplying gain of 0.5 s and 300, respectively were used. Prior to fluorescence measurements, we collected light transmission images to locate areas where single-walled carbon nanotubes were present. Time- and spectrally-resolved fluorescence measurements were performed using a home-built confocal fluorescence microscope described in detail elsewhere [12]. The sample was excited at 485 nm with a pulsed laser characterized with a repetition rate 20 MHz and excitation power of 20  $\mu\text{W}$ . The excitation beam was focused on the surface of the sample by LMPlan 50x microscope objective with numerical aperture of 0.5 (Olympus). Fluorescence was filtered by longpass filter (HQ665LP Chroma) and then detected by Amici prism coupled with Andor iDus DV 420A-BV CCD camera. Fluorescence transients were collected by time-correlated single photon counting module SPC-150 (Becker & Hickl) with fast avalanche photodiode (idQuantique id100-20) as a detector.

Fluorescence intensity maps were obtained for two different concentrations of PCP complexes diluted in 0.02% polyvinyl alcohol (PVA from Sigma-Aldrich): 2  $\mu\text{g}/\text{ml}$  and 0.2  $\mu\text{g}/\text{ml}$ . 30  $\mu\text{l}$  of each solution was spin-coated at 20 rps on a glass slide (reference) and SWCNT thin films. For fluorescence spectra and fluorescence transients measurements we used the solution of PCP complexes diluted in water with a concentration of 2  $\mu\text{g}/\text{ml}$ . 1  $\mu\text{l}$  of the

Download English Version:

<https://daneshyari.com/en/article/5398470>

Download Persian Version:

<https://daneshyari.com/article/5398470>

[Daneshyari.com](https://daneshyari.com)