Light energy conversion by photosynthetic reaction center linked specically to carbon nanotubes

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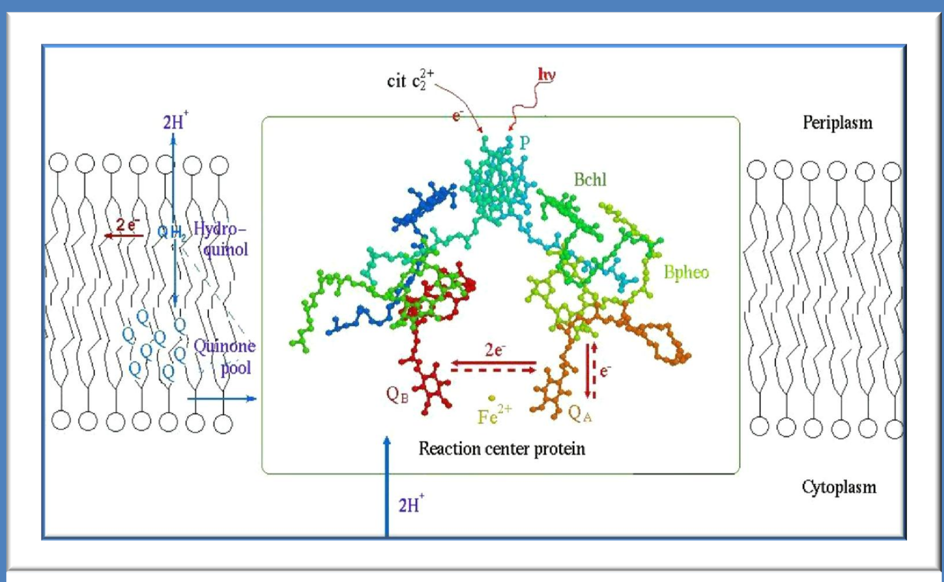
Introduction

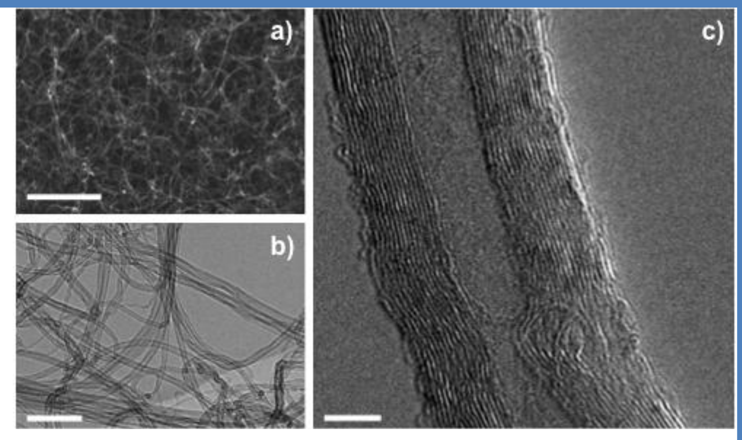


RC in the photosynthetic membrane. P: primary electron donor, bacteripchlorophyll dimer; Bchl: bacteripchlorophyll monomer; Bpheo: bacteriopheophytine; Q_A: primary quinone; Q_B: secondary quinone; QH: reduced quinone in the membrane pool.

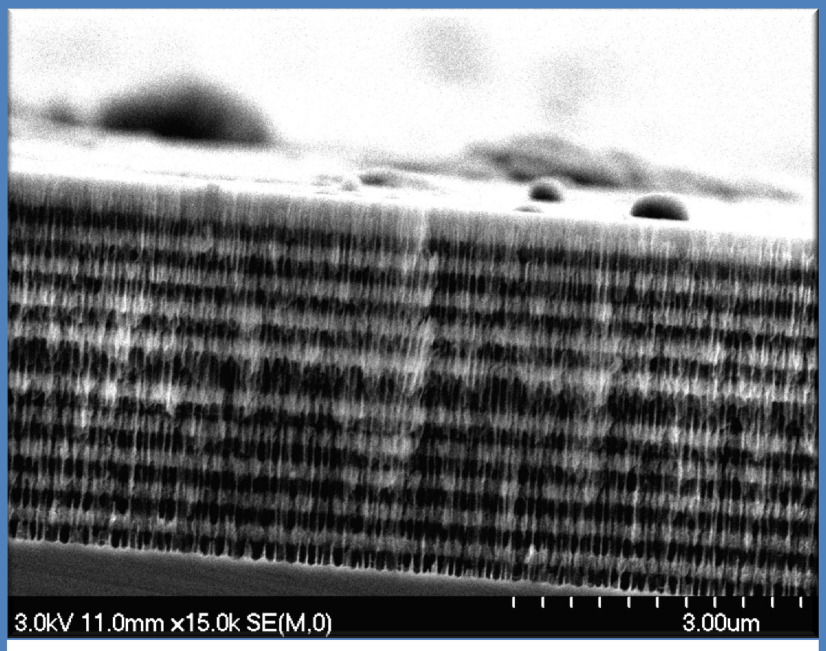
<u>Photosynthetic reaction center (RC)</u> is a pigment-protein complex in the photosynthetic membrane of living cells. The primary steps of the photoelectric energy conversion takes place in this protein during photosynthesis. The yield of harnessing the light energy is nearly 100%.

The RC of purple bacteria is well known and our group can easily purify and separate it from the photosynthetic membrane. This enables the excellent photoactivity of the RC to be harnessed and the fabrication of photoactive nanocomposites.

<u>Carbon Nanotubes (CNT)</u> have an extremely strong, roubust structure. Several applications have been realised because of its unique electric conductivity. It has already been proved that binding the RC to a CNT with a physical bond creates an electric contact between the two materials. Singlewalled (SWNT) and multiwalled (MWNT) nanotubes can be also used to support the photosynthetic peptide complexes.



SEM (a), TEM (b) and HRTEM (c) of Multi Walled Carbon Nanotubes produced by Chemical Vapor Deposition. Scale bars in a), b), c) are respectively 1μm, 100nm and 5nm.



SEM image of the PSi layer structure.

<u>Porous Silicon (PSi)</u> has already been used as a carrier matrix in environmental and medical applications because of its availability and large sensing area. Immobilizing different biological molecules like enzymes, antibodies and photoactive biomolecules, into this porous and laminated system makes it possible to harness the advantages of the carrier and the immobilized material as well.

Aims

- **Binding the RC to the surface of the amine-functionalised SWNT, MWNT and PSi using the glutaraldehyde (GTA) method.**
- **Keeping the photoactivity of the complexes.**
- **Comparing the two different matrixes.**

Experimental method

<u>Sample preparation</u>

<u>Reaction Centres</u> were prepared by LDAO (*N,N*-dimethyldodecylamine-*N*-oxide, Fluka) solubilization and purified by ammonium sulfate precipitation, followed by DEAE Sephacel anion-exchange chromatography.

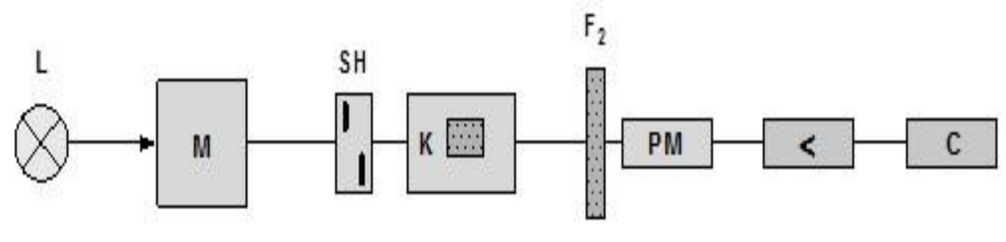
<u>Carrier Matrices</u> were functionalised with amine groups. Chemically oxidized single-walled (SWNTs) and multiwalled carbon nanotubes (MWNTs) were modified using melamine to attach -NH2 to the surface.

3-aminopropyltriethoxysilan (APTES) was used to modify the Psi surface.

<u>Bionanocomposites</u> were prepared by binding the RC to the amine-functionalised matrices using **GTA**, which has the potential to serve as amine-targeted **homobifunctional crosslinker**.

<u>Measurements</u>

The structure of the active surface of the SWNT, MWNT and PSi was also investigated by Atomic Force Mycroscopy (**AFM**), Scanning Electron Microscopy (**SEM**) expanded by Energy Disperse X-ray (**EDX**) analysis.



The arrangement of the single-beam kinetic spectrophotometer

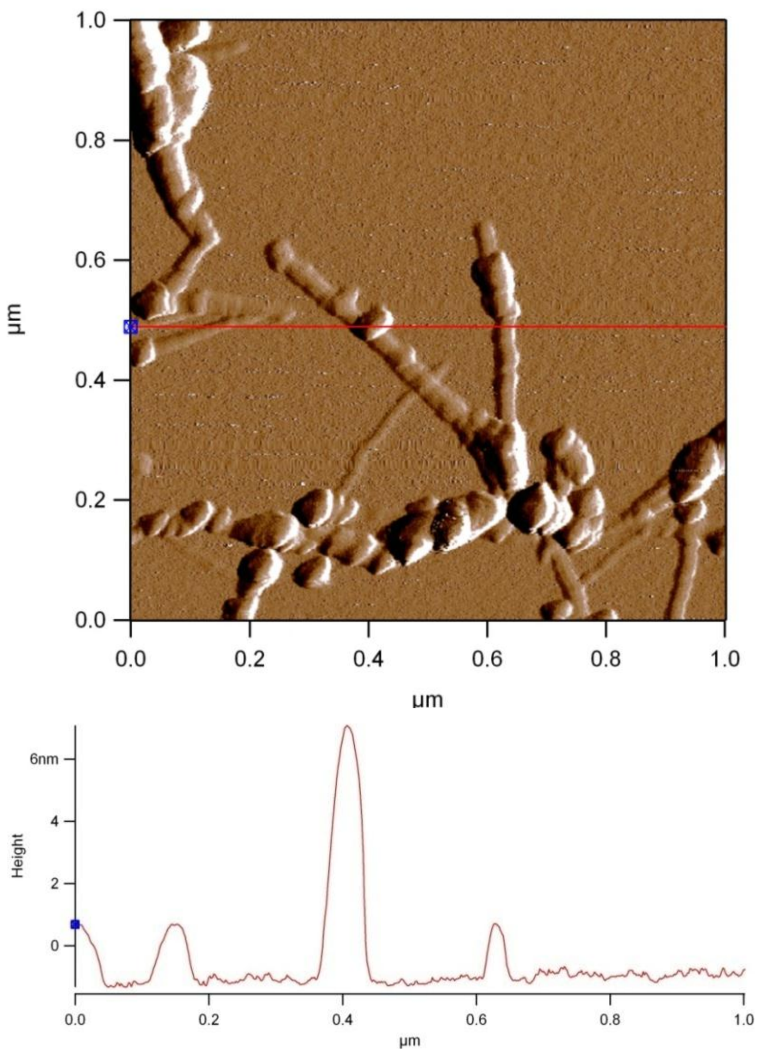
Flash-induced absorption changes were measured by an in-house single-beam kinetic spectrophotometer.

Results

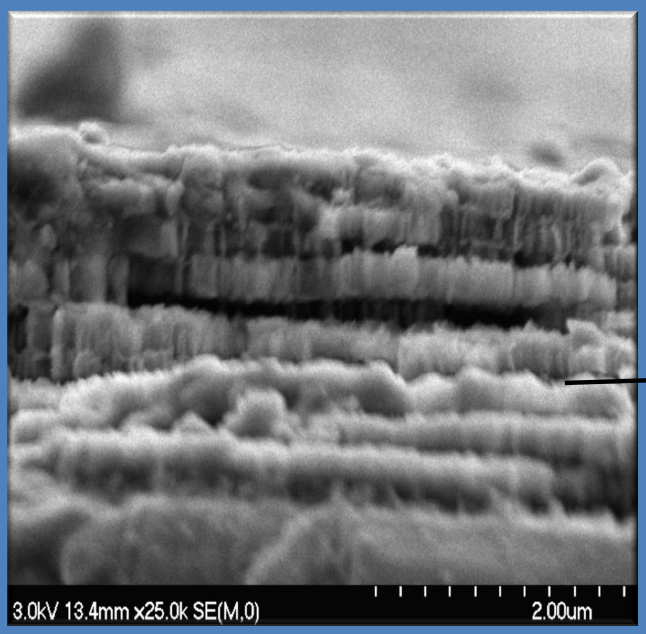
AFM images show that it was possible to bind the RC to the amine-functionalised SWNT and MWNT using the GTA crosslinker molecule.

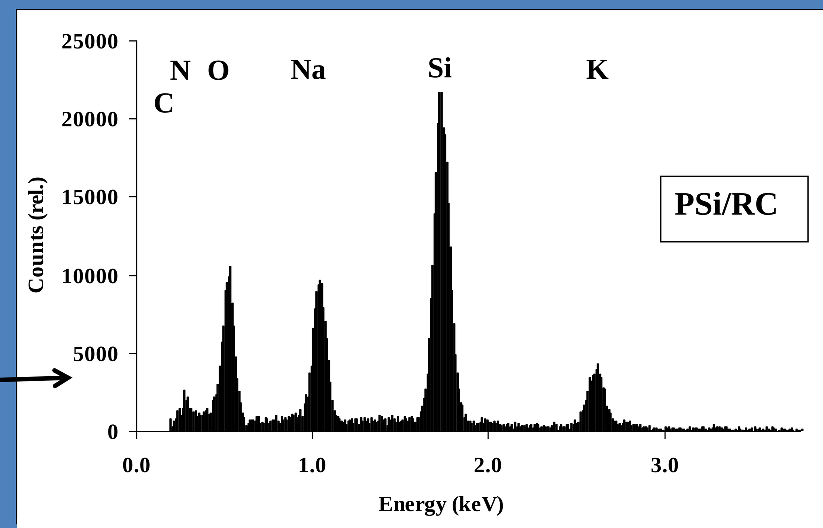
The height of the RC is ~9nm from the surface and according to the height profile, a monolayer RC coating was formed. This binding was chemically attached as the samples were washed with buffer-detergent solutions.

SEM image taken after the silane-GTA-RC treatment is less clear than the untreated one due to the RC binding. EDX analysis was performed on the cross section of the PSi photonic structure. The treated samples display significant amounts of C, N, and O due to the presence of the protein



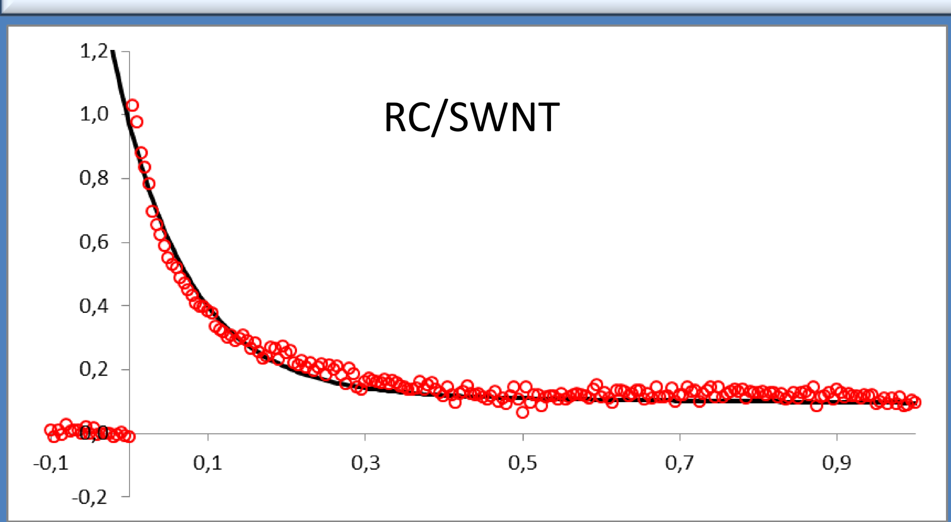
AFM image of SWNT/RC complexe after GTA activation.





SEM image of PSi/RC complexe after GTA activation extended by EDX analysis.

Time resolved, flash-induced absorption change measurements showed that the RC performs a single turnover after light excitation for any carrier matrix without an externally added electron donor. Pairs of positive (P^+) and negative (Q_A^- or Q_B^-) charges are also formed within the protein. The RC can be excited again only if reset by charge recombination.



The decay of the absorption change of RCs bound to SWNT after single saturating light excitation measured at 430 nm.

	RC/SWNT	RC/MWNT	RC/PSi
A_{fast} (%)	90	88	51
τ_{fast} (ms)	90	90	13,5
A_{slow} (%)	10	12	49
τ_{slow} (ms)	3100	2250	240

The results of decomposition of exponential decay curves. A_{fast} and A_{slow}: contributions (%) t_{fast} and t_{slow}: lifetimes of the fast and slow components.

The concentration of the oxidized primary donor, P^+, of the RC bound to PSi, MWNT and SWNT obtained from the 430 nm absorption change in the dark relaxation phase after a single saturating light excitation can give information about the proportion and life time of the quinon molecules.

Using CNTs, the ratio of the slow and fast component is about 1 to 9 with SWNT and MWNT as well.

The life time and proportion of the fast and slow components was different in the case of PSi and CNT. The life time of the slow component was longer on matrices than in detergent. It means that the electron does not get back immediately to the P^+ and there is an electric relation between the two materials. The lifetime was ten times longer on nanotubes than on PSi.

Conclusions

- **The RC was successfully immobilised to the SWNT, MWNT and PSi surface by the GTA method and the peptide complex preserved its activity.**
- **The type of the carrier matrix affects the life time and proportion of the fast and slow component in the RC during the light-excitation.**
- **Conductivity measurements will be done in the future.**

Acknowledgement

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