Covalently Binding the Photosystem I to Carbon Nanotubes

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Abstract. We present a chemical route to covalently couple the photosystem I (PS I) to carbon nanotubes (CNTs). Small linker molecules are used to connect the PS I to the CNTs. Hybrid systems, consisting of CNTs and the PS I, promise new photo-induced transport phenomena due to the outstanding electro-optical properties of the robust cyanobacteria membrane protein PS I.

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INTRODUCTION

Photosynthetic reaction centers are the photochemical active complexes in photosynthetic systems found in plants, algae and photosynthetic bacteria [1]. The photosynthetic reaction centers have evolved approximately 3.5 billion years ago, and they serve as the ultimate source of energy in the biosphere. The process involves an efficient conversion of solar energy to a stable chemical energy. Such is the reaction center photosystem I (PS I) which acts as a nanosize photodiode composed of a protein chlorophyll complex that utilizes light to generate a photopotential of 1.2 V with a quantum efficiency of 1 and an intrinsic energy conversion efficiency of 58% (47% of the total absorbed light) [1-5]. The PS I protein has a cylindrical shape with a diameter of about 15 nm and a height of 9 nm. It is intriguing to incorporate PS I into optoelectronic nanoscale circuits to exploit its outstanding optoelectronic properties [6].

Recently, we have demonstrated the possibility to covalently bind the PS I reaction center directly to gold surfaces [7] as well as indirectly via a small linker molecule to GaAs surfaces [8] and to carbon nanotubes [9]. To this end, amino acids in the extra membrane loops of the PS I facing the cytoplasmic side of the bacterial membrane (oxidizing side) were mutated to cysteines (Cys) [Fig. 1(a)]; enabling the formation of covalent bonds with a metal surface or a chemically functionalized GaAs surface. The Cys located at extra membranal loops of the protein do not have steric hindrance, when placed on a solid surface e.g. of a gold electrode or CNTs as shown here. The mutations D235C/Y634C were selected near the special chlorophyll pair P700 to allow close proximity between the reaction center and the CNTs [7]. Our self-assembly approach facilitates efficient electronic junctions and avoids disturbance in the function of the reaction center. The covalent attachment of the PS I through the Cys further ensures the structural stability of the self-assembled, oriented PS I. As demonstrated recently [7,8] a dry oriented monolayer of PS I assembled on gold electrodes and GaAs surfaces exhibits charge transfer between PS I and the solid state surface.

In Fig. 1(b) the molecular structure of the hybrid system is sketched. In [9] we reported on a four step chemical route utilizing sulfo-SMCC (sulfosuccinimidyl 4-[N-maleimidomethyl] cyclohexane-1-carboxylate) in order to covalently bind amine-reactivated CNTs to the PS I. As a result, the PS I is connected to the CNTs via the linker molecule X\textsubscript{1} [Fig. 1(c) and (b)]. Here, we report on utilizing sulfo-MBS (N-Maleimidobenzoyl-N-hydroxysulfosuccinimide ester), which results in a linker molecule X\textsubscript{2} [Fig. 1(d)] with an aromatic hydrocarbon instead of the cyclohexane in X\textsubscript{1}.

To evaluate the degree of hybridization between the modified CNTs and PS I, a drop of the supernatant solution was placed onto a silicon surface, and incubated for two hours.
The samples were washed briefly with deionized water and dried under nitrogen. Figure 1(e) shows an atomic force micrograph (AFM) of the CNTs-PS I hybrid systems on a surface. The images exhibit a large number of spherical particles [dotted circle in Fig. 1(e)] attached to the surface of the CNTs. The height analysis of the AFM images [e.g. Fig. 1(f) and dotted line in Fig. 1(e)] indicates a height of about 9-20 nm for the spherical particles, in agreement with the actual diameter of the PS I, which suggests that the spherical particles are the PS I proteins. The diameter of the CNTs is in the range between 1 and 6 nm [Fig. 1(g) and dashed line in Fig. 1(e)]. In the particular case, a height of 6 nm suggests that a bundle of CNTs builds the back-bone of the hybrid system, consisting of CNTs and PS I.

**SUMMARY**

In summary the present work demonstrates how to covalently couple carbon nanotubes (CNTs) to the photosynthetic reaction center I (PS I). In particular, we demonstrate that sulfo-MBS can be utilized to bind amine-activated CNTs to the PSI. Hybrid systems, consisting of CNTs and the PS I, promise new photo-induced transport phenomena, since the PS I is a robust cyanobacterial membrane protein with outstanding optical properties.

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