Self-Assembly of Light-Harvesting Complex on Electrodes for Construction of An Artificial Photosynthetic Antenna System

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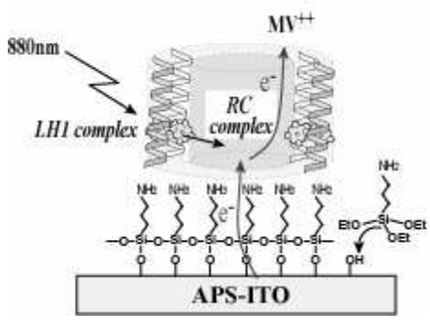
The light reactions occur in closely coupled pigment systems of the light-harvesting (LH) -α and -β polypeptides and reaction center (RC) complexes in photosynthetic bacteria; light energy is absorbed by excitonically coupled antenna pigments bound to the LH polypeptides, and the excitation energy is efficiently transported to RC. [1)] Thus, the construction of the LH 1 complex with the excitonically coupled pigments will be useful for studying the structure and the energy transfer via individual pigments.

We now report molecular assemblies of bacteriochlorophylls (BChl *a* & Zn-BChl *a*) using LH polypeptides separately isolated from photosynthetic bacteria on electrodes. The LH polypeptides organized Zn-BChl *a* complex on electrodes as well as BChl *a* complex, where polar amino acids at N- or C-terminal of the LH polypeptides performed a crucial role on the complex-formation. The stability of the complexes depended upon the structure of lipid bilayers. The proof of the complex-forming on electrodes was noted by monitoring the Qy absorption band-shift of BChl *a* or Zn-BChl *a*, where the Qy band was red-shifted. The Zn-BChl *a* complex in lipid bilayers was more stable than BChl *a* complex. UV-vis., CD and AFM data of these pigment complexes assembled with the LH polypeptides in lipid bilayers were analogous to those of the LH1-type complex of these photosynthetic bacterias.

Further, successful immobilizations of reconstituted light-harvesting 1 (LH1) complexes onto amino terminated ITO electrode (APS-ITO) as well as the LH1-RC 'core' complex were studied (Scheme 1). Our recent work extends this approach to using the combination of the LH-α and -β polypeptides and bacteriochlorophylls as the native LH and RC complexes. [2)] These complexes were immobilized onto the electrode. The assembly of the complexes on the electrode was confirmed by Near-IR absorption spectroscopy. These data showed that the LH 1-type complex consisting of the LH -α and -β polypeptides with BChl *a* or Zn-BChl *a* was stably assembled on the electrode at room temperature as well as on a GC and an ITO modified with lipid bilayers. These absorption spectra were useful to demonstrate the photocurrent response induced by illumination at 880 nm, showing electron transfer between bacteriochlorophylls and these electrodes (Figure 1). Interestingly, the photoelectric current on these electrodes depended on the structures of the LH complexes and the wavelength of the light, and the structure of lipid bilayers. The action spectra revealed a maximum at the wavelength corresponding to the absorption band of the complexes.



Scheme 1. The schematic view of an amino terminated ITO electrode (APS-ITO) modified with LH1-RC core complexes.

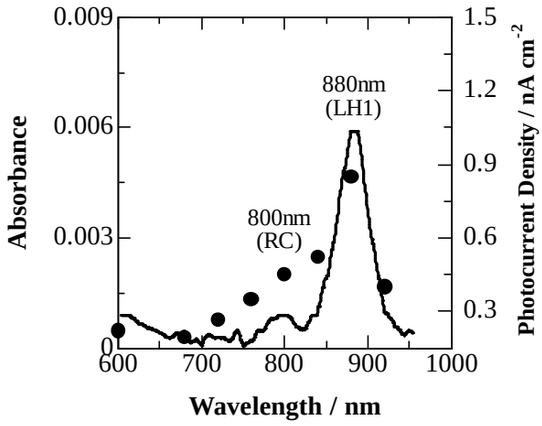


Figure 1. NIR absorption spectrum (solid line) and Photocurrent density (dots) of the LH1-RC core complexes assembled onto an APS-ITO electrode.

References:

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