Nanostructured Light-Harvesting and Photocurrent Generation Systems

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Self-assembled monolayers (SAMs) of photoactive chromophores on the flat gold surface have merited special attention as artificial photosynthetic materials and photonic molecular devices. In particular, donor-acceptor linked molecules or donor-acceptor mixed components have been employed in such systems to mimic photosynthetic electron transfer (ET) and energy transfer (EN) on the gold electrode. However, strong EN quenching of the excited states of chromophores by the gold surface has precluded achievement of a high quantum yield for charge separation (CS) on the surface as attained in photosynthesis. In order to surmount such an EN quenching problem, transparent semiconductor electrodes [i.e., indium-tin oxide (ITO)] and metal nanoclusters seem to be the most promising candidates as platforms which may suppress the quenching of the excited states of adsorbed dyes on the surfaces. In this talk we present preparation, photophysical, and photoelectrochemical properties of porphyrin SAMs on ITO electrodes and metal nanoclusters.

A systematic series of ITO electrodes modified chemically with SAMs of porphyrins and porphyrin-fullerene dyads have been designed to provide valuable insight into the development of artificial photosynthetic devices. At first the ITO and gold electrodes modified chemically with SAMs of porphyrins with a spacer of the same number of atoms have been prepared to compare the effects of EN quenching of the porphyrin excited singlet states by the two electrodes. Less EN quenching was observed on the ITO electrode as compared to the EN quenching on the corresponding gold electrode, leading to remarkable enhancement of the photocurrent generation (ca. 280 times) in the porphyrin SAMs on the ITO electrode in the presence of the triethanolamine (TEA) used as a sacrificer. The porphyrin (**H_2P**) was then linked with C_{60} which can act as an electron acceptor to construct the **H_2P-C_{60}** SAMs on the ITO surface in the presence of hexyl viologen (HV^{2+}) used as an electron carrier in a three electrode system, denoted as ITO/**H_2P-C_{60}**/HV^{2+}/Pt cell. The quantum yield of the photocurrent generation of ITO/**H_2P-C_{60}**/HV^{2+}/Pt cell (6.4 %) is 30 times larger than that of the corresponding cell without C_{60}: ITO/**H_2P-ref**/HV^{2+}/Pt cell (0.21 %). These results clearly show that self-assembly of porphyrin-fullerene linked molecules on ITO is a highly promising approach for the realization of molecular-level photovoltaic devices in which efficient multistep electron transfer occurs on the electrodes as attained in photosynthesis.

Porphyrin monolayer-modified gold clusters (three-dimensional system) have been prepared successfully and the electrochemical and photophysical properties have been compared to those of the corresponding two-dimensional system of SAMs of the porphyrin as well as the porphyrin reference in solutions. In particular, the time-resolved single-photon counting fluorescence studies have demonstrated that the undesirable quenching of the porphyrin excited singlet state via energy transfer from the porphyrin to the gold surface of the three-dimensional system is much suppressed, as compared to the quenching of the porphyrin SAMs on the two-dimensional flat gold surface. The effects of alkyl chain length on the structures and photophysical properties of porphyrin-alkanethiols as SAMs on gold nanoclusters will also be reported.

References

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