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学位論文題目	Studies on Dye Cation Reduction and Charge Recombination Kinetics in Dye-Sensitized TiO ₂ Solar Cells (色素増感太陽電池における色素カチオンの還元速度と酸化チタン電極中の再結合寿命に関する研究)
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論文内容の要旨

In this thesis, the effects of molecular structure on the dye cation reduction kinetics and the electron recombination kinetics from TiO₂ electrodes were investigated in dye-sensitized solar cells (DSSCs).

In Chapter 1, the purpose of this dissertation concerning electron transfers in dye-sensitized solar cells was described, following a short history of DSSCs and their status in the research.

In Chapter 2, I outlined the fabrication procedures and explained the characterization methods of DSSCs. I showed that the dye cations absorbed near-infrared light and reduction rate of dye cation related to half time of transient absorption decay in the near-infrared region.

In Chapters 3 and 4, the structure effect of donor- π -conjugated linker-acceptor (D- π -A) type organic dyes on the reduction kinetics of the dye cation was investigated. The dye cation was reduced by I⁻ in the electrolyte (regeneration) or by an injected electron into the TiO₂ electrode (recombination). Marcus theory was employed to explain the differences between the reduction kinetics of the dye cation and various structure dyes. In chapter 3, I examined donor structure effects of D- π -A type organic dyes on the reduction kinetics. I found that a dye with large surface area of accessible HOMO can obtain high regeneration efficiency in DSSCs. The effect of the accessible HOMO area on the regeneration rate was larger than the effect of the around 200 meV energy difference between the HOMO of dye and the redox potential. In Chapter 4, the effects of the alkyl

chains on the dyes were examined, revealing that the introduction of the alkyl chain to the π -conjugated linker of the dye decelerates both the regeneration and recombination rates. The alkyl chains decreased the electronic coupling between the HOMO of the dye and I⁻. Therefore, the regeneration rate was decelerated. I showed that the recombination rate was accelerated by hole hopping between adsorbed dyes. The introduction of alkyl chains prevented the hole hopping between dyes. Thus, the recombination rate was decelerated.

In Chapters 5 and 6, the electron lifetime in the semiconductor electrode was investigated. In Chapter 5, to measure the electron lifetime using a method of the stepped light-induced transient measurements of photocurrent and voltage, the effects of the required uniformity of the electron density in the semiconductor electrode on the electron transfer kinetics in DSSCs were investigated. To measure the electron lifetime without the injection from dyes, a novel method was developed. This method introduces the external circuit for the electron injection into the semiconductor electrode. In chapter 6, I clarified that the electron lifetime was improved by the suppression of the dispersion force by interaction of the dye molecules in DSSCs using organic dyes. The dispersion force is formed by induced dipole moment. The dipole moment attracts I₃⁻ in the electrolyte close to TiO₂ surface, and then the concentration of I₃⁻ near TiO₂ surface becomes higher. Therefore, the electron lifetime is decreased. I showed the interaction between dyes canceled the induced dipole moment.

In Chapter 7, this dissertation was concluded. From the experimental results, I express views concerning the improvement of the power conversion efficiency of DSSCs.