

## 論文内容の要旨

As a new-type of photovoltaic devices, dye-sensitized solar cells (DSSCs) have been the subject of intensive research activities over the last quarter century. In DSSC devices, dyes play a key role in the conversion of solar energy into electricity. Compared with other dyes investigated so far, ruthenium poly(pyridine) complexes have been well-studied and found to be most effective. The robust immobilization of dye molecules onto a nanocrystalline semiconductor surface is critical to ensure effective electron injection and device durability. Generally, hydrophilic groups, such as -COOH, -PO<sub>3</sub>OH, -SH, and -OH, are indispensable in the rational design of dyes for DSSCs. Up to now, dyes without these functional groups cannot be candidates for dye research. This drawback has limited the development of DSSCs. Therefore, the author made his endeavor to develop a novel separated electrolysis method to graft a new ruthenium poly(vinylsubstituted pyridine) complex onto a TiO<sub>2</sub> electrode surface and explored the capability of the incident photon-to-electricity conversion of the resulting TiO<sub>2</sub> electrode in DSSCs. The author confirmed that the deposition of the ruthenium complex onto a TiO<sub>2</sub> electrode was strongly influenced by working potential, immobilization time and various solvents used as the electrolysis solvent, washing solvent, and immobilization solvent.

Unfortunately, the DSSC fabricated with the resulting TiO<sub>2</sub> electrode just presented inferior incident photo-to-electricity conversion efficiency (at 440 nm, 1.2%). To improve the capacity of incident photo-to-electricity conversion of the resulting DSSC, sodium 4-vinylbenzenesulfonate was introduced into the immobilization system to form a composite film. The incident power conversion capacity of the composite film was sharply enhanced to 31.7% at 438 nm.

On the other hand, a photocathode which collects external circuit electrons and assists the regeneration of I<sup>-</sup> from I<sup>3-</sup> is also an essential component of DSSCs. Commonly, Pt film, which is optimal in electro-conductivity, catalytic activity of I<sup>3-</sup> reduction, is coated onto a fluorine-doped tin oxide glass (FTO) to construct a photocathode. However, Pt is too expensive to apply in a large scale in DSSCs. Recently, poly(3-alkylthiophene)s, which are excellent in electro-conductivity, catalytic activity of I<sup>3-</sup> reduction, and cost-effectiveness, have been employed to replace Pt to assemble a photocathode of DSSCs. For the large scale application of poly(3-alkylthiophene)s in DSSCs, it is essential that the polymerization of 3-alkylthiophenes proceeds with a simple route and in high yield. To date, the FeCl<sub>3</sub> oxidative method is the most popular in the synthesis of poly(3-alkylthiophene)s. To the best of the author's knowledge, details on their synthesis is, however, still unavailable. Then, the author devoted his effort to investigate the polymerization of 3-alkylthiophene. By monitoring the progress of the polymerization of 3-hexylthiophene with FeCl<sub>3</sub> in CHCl<sub>3</sub>, the author successfully constructed the reaction profile and estimated the activation energy of this polymerization reaction. The effect of solvent on the polymerization of 3-hexylthiophene with FeCl<sub>3</sub> was also studied. Other than chlorinated methanes, aromatic solvents, especially benzene and toluene, are applicable for the polymerization reaction. Different from the chlorination of the resulting polymer obtained the FeCl<sub>3</sub> oxidative method in CHCl<sub>3</sub>, the incorporation of the solvent molecule(s) into the polymer was observed when the aromatic solvents were used. The author also found that the polymerization reaction proceeded by using TEMPO/FeCl<sub>3</sub> combination as the oxidant and discuss its reaction mechanism. Moreover, The polymerization activity of brominated 3-hexylthiophene with iron(III) halide was firstly established,

even though the activity was rather low.