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Development of the multi-scale simulator for the dye-sensitized TiO_2 nanoporous electrode based on quantum chemical calculation

Kei Ogiya[1], Chen Lv[1], Riadh Sahnoun[1], Michihisa Koyama[1], Hideyuki Tsuboi[1], Nozomu Hatakeyama[1], Akira Endou[1], Hiromitsu Takaba[1], Momoji Kubo[1], Carlos A. Del Carpio [1], and Akira Miyamoto[1,2]

[1]Depertment of Applied Chemistry, Graduate School of Engineering, Tohoku University,
6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[2]New Industry Creation Hatchery Center, Tohoku University,
6-6-10 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
Phone: +81-22-795-7233 FAX: +81-22-795-7235 E-mail: miyamoto@aki.che.tohoku.ac.jp

1. Introduction

Recently, TiO_2 is widely applied in oxide semiconductor photocatalyst and photovoltaic materials. Dye-sensitized solar cells (DSC), which use TiO_2 photoelectrode [1], are a promising future solar cell because the low-cost production and high performance are potentially expected. However, their conversion efficiency is not as high as Si-based solar cells, therefore the various researches for improving the efficiency toward the practical use are active. The factors affecting the conversion efficiency are, for example, the physical properties of the sensitizer and the microstructure of an electrode. Therefore, the simulation considering the different scales can help in best designing the efficient electrode system.

Ferber et al. developed a simplified complete electrical model of the DSC [2]. However, the parameters used for modeling the DSC were based on empirical data, therefore it cannot be used for designing new electrode system. In this study, we decided the property of the material using our quantum chemical molecular dynamics program "Colors". Using these values as input data, we heve developed the multi-scale simulator of the dye-sensitized TiO_2 nanoporous electrode based on the property on electronic and atomistic levels.

2. Methods

For estimating the values of the physical properties, we used our tight-binding quantum chemical molecular dynamics program "Colors" [3]. This program has an advantage in computation time compared to the first-principles approach, therefore we can calculate large-scale complex system. In this study, we implemented a function for calculating the oscillator strength to "Colors" and estimated the light absorption characteristics of the dye. First, we calculated the electronic structure at the ground state of the dye. Based on the wave function obtained from the ground state calculation, the transition moment M from i molecular orbital (MO) to j MO was calculated according to eq. (1).

$$M_{(i\to j)} = \sqrt{2}\left(\sum_{A}\sum_{r} c_r^i c_r^j \bar{r}_{rr} + \sum_{A}\sum_{r,s} c_r^i c_s^j \bar{r}_{rs} + \sum_{A,B}\sum_{r,s} c_r^i c_s^j \bar{r}_{rs} \right) \quad (1)$$

Here, c is the coefficient of the molecular orbital and $\bar{r}$ is the coordinate of the atom. The first, second and third term on the right-hand side refers to the transition between the same orbital of the same atom, the different orbital of the same atom and the different orbital of the different atoms. Then, the oscillator strength f of the dye was estimated according to eq. (2).

$$f = \frac{8\pi^2 m \nu}{3h}\left|M\right|^2 \quad (2)$$

Here, m is the electron mass, v is the wave number and h is the Plank's constant.

In addition, we estimated the carrier mobility of TiO_2 anatase by the following method. By using "Colors" program, we calculated the electronic structure of TiO_2 anatase (101) surface. According to the probability density distribution obtained from "Colors" calculation, we calculated the electrical conductivity σ using the Monte Carlo simulation [4]. Then, the carrier mobility of electron μ_e and hole μ_p was estimated by calculating back according to eq. (3).

$$\sigma = e\left(n\mu_e + p\mu_p\right) = \sigma_e + \sigma_p \quad (3)$$

We input the calculated values of the oscillator strength of the dye and the electron mobility of TiO_2 obtained from quantum chemical calculation to the multi-scale simulator for the dye-sensitized TiO_2 nanoporous electrode characteristic. In this simulator, the calculation model was divided to 10 cells along the z-axis. We assumed that the carrier can move by diffusion and the electrical potential difference. By solving differential equations (eq. (4)) at each cell j, we simulated photocurrent characteristics of the electrode system.

$$V_j \frac{dNe_j}{dt} = D\frac{dNe}{dz} - \mu_e N_e E \quad (4)$$

Here, V_j is the volume of the cell j, Ne is the density of the excited electrons, D is the diffusion coefficient and E is the electric field.

3. Results and discussion

The calculation model of the dye sensitizer was cis - di (thiocyanato) - bis(2,2' - bipyridyl - 4,4' – dicarboxylic acid)- Ru(II) complex (N3 dye), which is the typical sensitizer developed by Grätzel et al.[2]. We calculated the oscil-

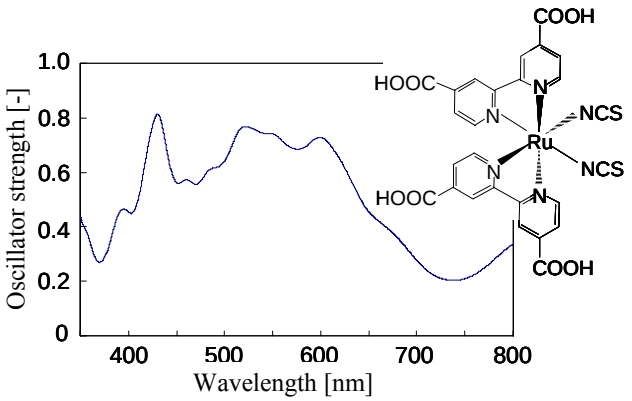

Fig. 1 N3 dye and the estimated UV-visible spectrum

lator strength of the dye using "Colors" program. By plotting the obtained value according to Lorentz function, we estimated the UV-visible spectrum of N3 dye. Fig. 1 shows the calculation model and UV-visible spectrum estimated by our calculation. This spectrum agreed with the experimental value qualitatively [5].

Next, we estimated the carrier mobility of TiO_2 anatase (101) surface. The calculation model was constituted of 48 atoms shown in Fig. 2. The lengths of a-, b-, and c-axis were 10.21, 7.55, and 15.84 Å, respectively. The calculated results and experimental data [5] of the carrier mobility are shown in Table I. From this table, we found that the electron mobility was larger than the hole, which was corresponded with experimental tendency.

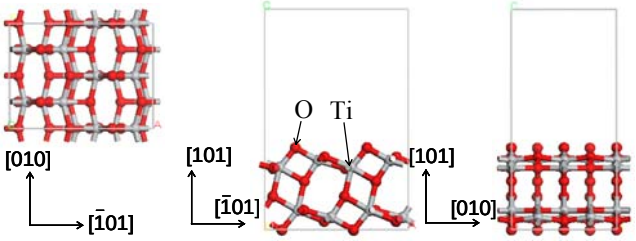

Fig. 2 Calculation model of TiO_2 anatase (101) surface

Table I Calculated carrier mobility and experimental data [6]

	Calculated mobility [cm^2/Vs]	Experimental data [cm^2/Vs]
Electron	10.6	15.0
Hole	1.52	$\sim 10^{-3}$

Finally, we carried out the macro scale simulation for estimating the electrode characteristic of the dye-sensitzed TiO_2 nanoporous electrode. The oscillator strength and the electron mobility of TiO_2 anatase obtained from the quantum chemical calculations as discussed above were used as input values. Fig. 3 shows the calculation model constructed by the three dimensional porous structure simulator. The size of the calculation model is 1.0 × 1.0 × 2.0 μm. The average diameter of the particles is 20 nm and the porosity is 0.3. In this study, we only considered TiO_2 particles in the cell for simplicity. In addition, we assumed that the dye is adsorbed to TiO_2 surface evenly, and the injection coefficient of the excited electron from the dye to the conduction band of TiO_2 is 1.0. Fig.4 shows the distribution of the excited electron density and analysis result at cell 5. In this way, we could analyze the property of the electrode in detail.

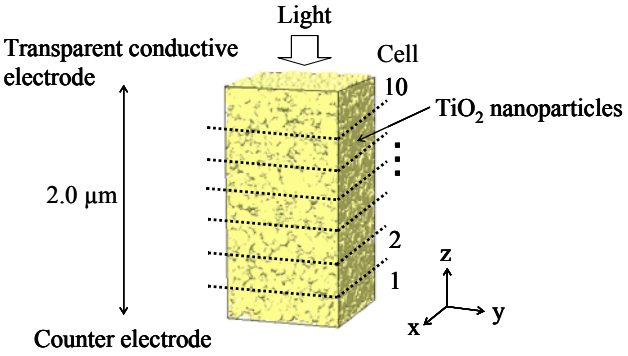

Fig. 3 Three dimensional TiO_2 porous structure

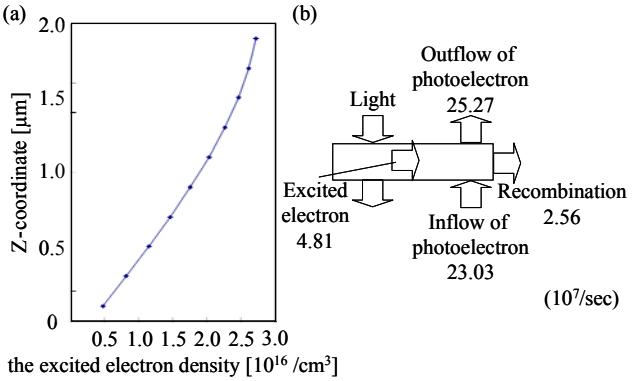

Fig. 4 (a) The excited electron density, and (b) analysis result at cell 5

4. Conclusions

In this study, by using our original tight-binding quantum chemical molecular dynamics program "Colors", we estimated the property of the material. In addition, using the values obtained from quantum chemical calculation as input data, we carried out the simulation of the dye-sensitized TiO_2 nanoporous electrode characteristic. Finally, we succeeded to develop the multi-scale simulator of the dye-sensitized TiO_2 nanoporous electrode based on quantum chemical calculation. By using this multi-scale simulator, we will be able to probe the best electrode system efficiently.

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