

Ultra-fast electron transfer from adsorbed molecule to TiO₂ substrate studied by the core-hole clock technique

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Introduction

The dye-sensitized solar cell is a promising technology for the efficient conversion of solar energy into electrical energy. The efficiency is critically dependent on a fast electron injection from the sensitizing molecule into the semiconductor substrate. Thus, the interfacial electron transfer processes between adsorbed molecule and semiconductor are yet to be investigated to improve the efficiency. In this study, we studied the electron transfer from the mono-layer pyridine (C₅H₅N) or thiophene (C₄H₄S) molecules to TiO₂(110) semiconductor substrate by the core-hole clock technique.

Experimental

The experiments were performed at BL-13A of the Photon Factory. The valence band X-ray photoelectron spectroscopy (XPS) spectra were measured as a function of photon energy. All the binding energies were calibrated with the peak top position of Ti 2p_{3/2} as 458.6 eV. The resonant photoemission spectra (RPES) were acquired by integrating the intensities of the resonant peaks. The near edge x-ray absorption fine structure (NEXAFS) spectra were measured by the partial electron yield method. The electron-transfer time constant between the adsorbed molecule and the TiO₂ substrate was estimated by comparing the RPES peak intensity with the corresponding NEXAFS one.

Results and Discussion

Figure 1 shows the valence band XPS spectra taken at different photon energies. The resonant peaks were observed at 12.0 and 16.0 eV. The RPES spectra were obtained from the integrated intensity of these peaks. Figure 2 shows the comparison between RPES and NEXAFS spectra. The transfer of the excited electron competes with the decay process to re-occupy the core hole ($\tau = 6$ fs), leading to change in the RPES intensity [1]. The LUMO+1 peak of pyridine observed at 403 eV almost disappears in the RPES spectrum due to significant charge transfer. The transfer time constant from the LUMO+1 was estimated to be shorter than 0.27 fs. On the other hand, the RPES peak of thiophene showed no change, indicating that the electron transfer from thiophene molecule to TiO₂ substrate is slow enough against the decay process of the core excited electron. The slower charge transfer of thiophene suggests the weaker interactions with the TiO₂ surface, compared with those of pyridine, which is consistent with the TPD results.

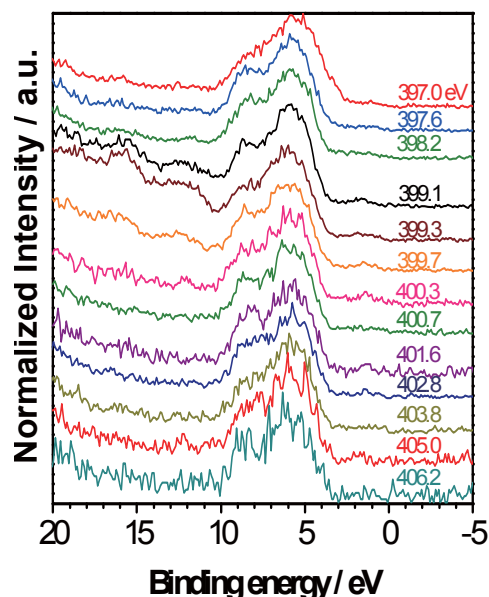


Figure 1. Valence band XPS spectra of the mono-layer pyridine/TiO₂(110) with changing the photon energy.

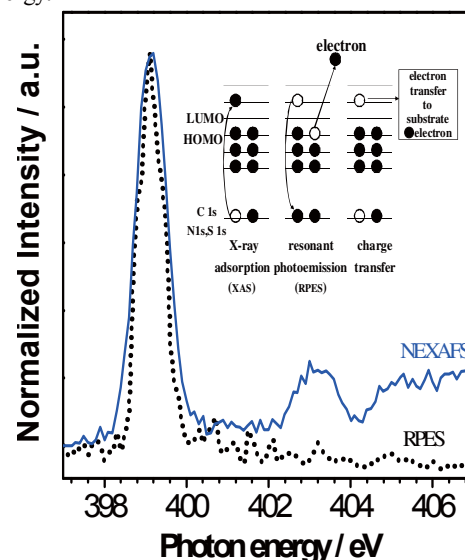


Figure 2. The comparison between RPES and NEXAFS spectra of the mono-layer pyridine/TiO₂(110) substrate. The inset shows schematic overview of the working principle of the core-hole clock spectroscopy.

References

- [1] J. Schnadt et al.: Nature **418**, 620 (2002).

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