

Labeling co-sensitizer dye for XPS quantification in coadsorption dye-sensitized solar cells

Mitsunori Honda^{1,*}, Masatoshi Yanagida¹, Liyuan Han and Kenjiro Miyano²
¹National Institute for Materials Science, Tsukuba 305-0047, Japan

1 Introduction

Research is being directed at improving the efficiency of dye-sensitized solar cells (DSCs). This has been achieved by combining a nanoporous TiO₂ electrode (hereafter TiO₂ surface) and a Ru complex dye. The efficiency of DSCs can also be improved by increasing the photon conversion efficiency through “co-sensitization”. However, it is difficult to quantify the amount of dye adsorbed during coadsorption.

In this study, we have developed a Cl-terminated D131 dye as a labeling co-sensitizer and used X-ray photoelectron spectroscopy (XPS) to quantify the amount of dye in a coadsorption system containing a Ru complex dye on a TiO₂ surface. The change in the amount of adsorption in the coadsorption system was determined by the intensity ratio of the Cl 1s to the Ti 2p XPS peak, and the chemical states of Cl-terminated D131 and TiO₂ were elucidated.

2 Experiment

All experiments were carried out at the BL-27A station. To determine the changes in the surface chemical states of Cl-terminated D131, XPS measurements of D131, Cl-terminated D131, and a 1:1 mixture of N719 and Cl-terminated D131 were carried out. Cl-terminated D131 was synthesized by Chemiecrea Inc. The photon energy for measuring the Ti 2p, S 1s, and Cl 1s XPS spectra was 3000 eV. The binding energies were calibrated by using the C 1s peak of D131 at 284.4 eV. NEXAFS measurements were conducted using the total electron yield method.

3 Results and Discussion

The Cl-terminated D131 + N719 coadsorption system was quantified by XPS. Figure 1 shows the XPS spectra on the TiO₂ covered by pure Cl-substituted D131 and a mixture of Cl-terminated D131 and N719. Figure 1 shows the (a) and (b) Cl 1s and (c) and (d) Ti 2p XPS spectra excited with $h\nu = 3000$ eV for the Cl-terminated D131 and Cl-terminated D131 + N719 coadsorption systems. The Cl 1s XPS spectra for Cl-terminated D131 shows one main peak at 2823.5 eV. In the Cl-terminated D131 system, the Cl 1s peak energy was also 2823.5 eV. Figure 1 (c) and (d) shows the Ti 2p XPS spectra recorded with TiO₂ substrates carrying Cl-terminated D131 and Cl-terminated D131 + N719 and Cl-terminated D131. In (c), the spin-orbit ($2p_{3/2}$ and $2p_{1/2}$) split peaks located at 457.9 eV and 463.6 eV, respectively, correspond to Ti (IV) in a tetragonal structure. On close inspection, however, a small overall shift of the doublet from (d) to (c) is discernible. The upward shift of the doublet binding energies by about 1.5 eV has been reported when a Ti-S linkage is formed on TiO₂[1] and our group was already

reported in our previous paper [2]. Although the observed chemical shift in (c) of about 0.8 eV is certainly less significant, this is a clear indication of the strong S-substrate interaction, which is effective only when N719 is adsorbed on TiO₂ surface. Large Cl 1s and Ti 2p peaks were observed, indicating that the TiO₂ surface was covered with a thin film of Cl-terminated D131 or D131. To determine the saturated thickness of the Cl-terminated D131 and Cl-terminated D131 + N719, we estimated the thickness using the peak intensities of the Ti 2p (substrate) and Cl 1s (adsorbate) XPS peaks. As the result of the estimation from XPS analysis, corresponding to thicknesses of 62 and 27 nm for the Cl-terminated D131 and Cl-terminated D131 + N719 systems, respectively.

These result indicated that the peak intensity ratio of the Cl 1s to Ti 2p peaks for Cl-terminated D131 + N719 was only 44% that of Cl-terminated D131. Thus, in the coadsorption system, the Cl atom on the Cl-terminated dye functioned as a labeling compound for quantitative XPS analysis. The technique implemented here, using Cl-terminated dyes, could also be used to quantify other coadsorption systems in DSCs.

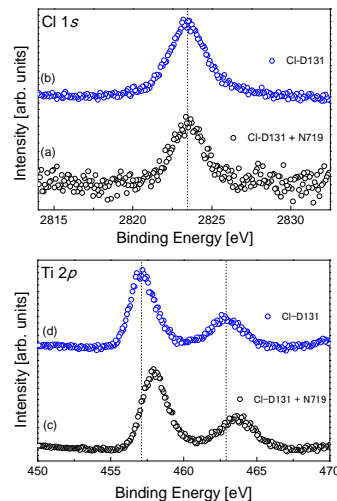


Fig. 1: Cl 1s XPS spectra for (a) Cl-terminated D131 + N719 and (b) Cl-terminated D131, and Ti 2p XPS spectra for (c) Cl-terminated D131 + N719 and (d) Cl-terminated D131, at $h\nu = 3000$ eV.

References

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* honda.mitsunori@jaea.go.jp