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Investigation of the influence of coadsorbent dye upon the interfacial structure of dye-sensitized solar cells

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The interface between $Ru(tcterpy)(NCS)_3TBA_2$ [black dye (BD); tcterpy = 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine, NCS = thiocyanato, TBA = tetrabutylammonium cation] and nanocrystalline TiO_2, as found in dye-sensitized solar cells, is investigated by soft-X-ray synchrotron radiation and compared with the adsorption structure of cis-$Ru(Hdcbpy)_2(NCS)_2TBA_2$ (N719; dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) on TiO_2 to elucidate the relationship between the adsorption mode of BD and the photocurrent with and without coadsorbed indoline dye D131. The depth profile is characterized with X-ray photoelectron spectroscopy and S K-edge X-ray absorption fine structure using synchrotron radiation. Both datasets indicate that one of the isothiocyanate groups of BD interacts with TiO_2 via its S atom when the dye is adsorbed from a single-component solution. In contrast, the interaction is slightly suppressed when D131 is coadsorbed, indicated by the fact that the presence of D131 changes the adsorption mode of BD. Based upon these results, the number of BD dye molecules interacting with the substrate is shown to decrease by 10% when D131 is coadsorbed, and the dissociation is shown to be related to the short-circuit photocurrent in the 600–800 nm region. The design of a procedure to promote the preferential adsorption of D131 therefore leads to an improvement of the short-circuit current and conversion efficiency. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4900640]

I. INTRODUCTION

Research related to dye-sensitized solar cells (DSCs) has attracted much attention because of the lower cost of DSCs compared to ordinary solar cells and because of the sheer number of these scientific reports in recent years.[1,2] It is essential to understand the interfacial engineering and adsorption mode of dyes on nanocrystalline TiO_2 electrodes[3,4] and the effect of the adsorption mode upon the mechanism of current generation in the cell. Yella *et al.*[5] reported that their DSCs achieved an energy conversion efficiency greater than 12%, and we have recently achieved high photoconversion efficiencies in DSCs using a coadsorbed system to expand the light absorption spectrum and to reduce the recombination of electrons in the TiO_2.[6] However, the interaction between a dye molecule and the TiO_2 surface is still not well understood, and analogous interactions are even more complicated when multiple dye species are involved, as is the case in a coadsorbed system. To understand the interactions within DSCs in greater detail, our group recently studied model systems that consisted of a Ru complex dye and a dye mixture. Those studies have demonstrated that the efficiency of DSCs can be increased compared with DSCs fabricated using conventional methods for adsorbing dye mixtures.[7] In our pre-

vious work using X-rays,[8] we investigated the interface between cis-$Ru(Hdcbpy)_2(NCS)_2TBA_2$ (N719; dcbpy = 4,4′-dicarboxy-2,2′-bipyridine, NCS = thiocyanato, TBA = tetrabutylammonium cation) and a nanocrystalline TiO_2 surface, as is found in DSCs, to determine whether the adsorption mode of the first dye would be modified by the influence of the coadsorbed secondary dye.

The adsorption structures of dyes have been determined using methods such as scanning tunneling microscopy, X-ray photoelectron spectroscopy (XPS), and computational techniques.[9–16] However, it is unclear whether the behavior of dye molecules on a single crystal surface is faithfully reproduced by molecules on nanocrystalline TiO_2, which is the material used for photovoltaic cell electrodes. Direct observations are very difficult because of the complex structure of nanocrystalline TiO_2, so a high-resolution method with high specificity is required for observing the microscopic structure of the surface morphology of these porous materials. X-ray spectroscopy is one of the most powerful tools for characterizing these complicated structures, and we have recently reported the adsorption mode of N719 and D131 coadsorption systems on a nanocrystalline TiO_2 surface.[8] One result of that study was the observation of a specific structural change between N719 and the TiO_2 surface, wherein the local structure of the S atom in the isothiocyanate (NCS) group (ligand) was seen to influence the photocurrent action spectrum. In addition to reiterating this earlier work on N719, in this paper we also compare the
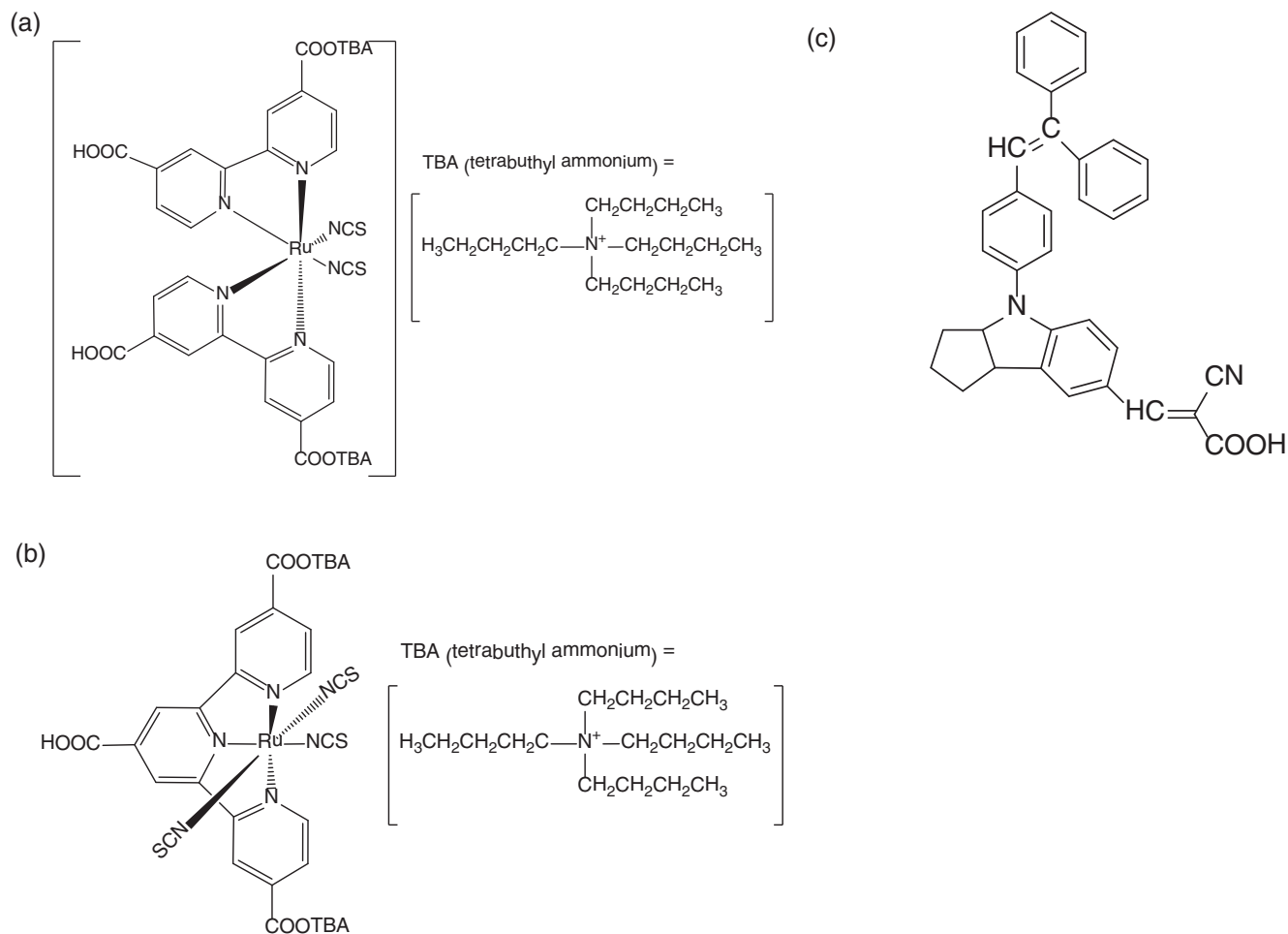
FIG. 1. Molecular structures of the (a) N719 dye, (b) BD, and (c) D131 dye.

effect of D131 as a co-sensitizer upon the adsorption structures of the Ru complexes, Ru(tcterpy)(NCS)$_3$TBA$_2$ (tcterpy = 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine) for BD and N719[17] on TiO$_2$, as shown in Fig. 1.

We examine in detail the effect of the adsorption structure upon the surface of nanocrystalline TiO$_2$ by using XPS and by determining the near-edge X-ray absorption fine structure (NEXAFS). The major difference between BD and N719 is the number of NCS groups, and it is thought that the adsorption structure is more complicated in BD, which has three NCS groups, than the adsorption structure in N719, which has two NCS groups. Because the samples for X-ray measurements and device fabrication are prepared in parallel and under identical conditions, we are able to directly relate the microscopic structure to the macroscopic cell performance. Information in our previous report indicated that the dye was anchored to TiO$_2$ via carboxylate groups, but the adsorption structure and the number of anchors are still under discussion.[18–20] To obtain more information about the adsorption mode of the dyes onto nanocrystalline TiO$_2$, we make the following new kinds of measurements: We selectively observe one of the coadsorbed dyes by focusing on the S atom in the NCS functional group of the BD, which is useful because the D131[21] molecule does not contain S atoms (Fig. 1). To assist in construction, core-level spectroscopy

(such as spectroscopy of the 1s shell, which has the simplest spectral characteristics) and high-intensity synchrotron radiation soft-X-ray spectroscopy are effective. We characterize the depth profile with NEXAFS and XPS measurements and compare the differences of the binding modes of BD and D131 onto the TiO$_2$ surface for a single-dye and a coadsorption system. In this study, we also investigate the effects of different adsorption modes, we improve the performance of the solar cells, and we elucidate the relationship between the NCS adsorption state and the photocurrent in the nanocrystalline TiO$_2$ electrodes used in actual DSCs.

II. METHODS

All experiments were carried out at the BL-27A station of the KEK laboratory Photon Factory (KEK-PF), Japan. The measurements of the S K-edge effect were made using NEXAFS, and those of the S 1s orbital characteristics were made using XPS, where both sets of measurements were conducted using soft X-rays at the KEK-PF BL-27A station. The NEXAFS measurements were carried out using the total electron yield. For XPS measurements, the main analyzing chamber consisted of a hemispherical electron energy analyzer at a photon energy of 3000 eV. The X-ray spectra were recorded with a HAC5000 spectrometer (VSW Atomtech Ltd.,

Oxfordshire, UK),[22,23] and all XPS spectra were normalized with the carbon C 1s main peak at 284.5 eV as a reference. The TiO$_2$ film (18NR, JGC Catalysts and Chemicals Ltd., Japan) was sintered at 500 °C, cooled to 100 °C, and then immersed into 0.1 M of ethanol solution for 24 h. Four types of dye solutions were prepared, comprising BD alone, N719 alone, BD + D131, and N719 + D131, where the molar ratio of BD or N719 to D131 was 1:1. The IPCE (incident monochromatic photon-to-current conversion efficiency) spectra were measured with monochromatic incident light (CED99-W, Bunko Keiki Co., Japan) containing 1×10^{16} photons cm^{-2} in the direct current mode and with a xenon arc lamp (SX150C, Bunko Keiki Co.).[24]

III. RESULTS AND DISCUSSION

Figure 1 shows the molecular structures of N719, BD, and D131. The N719 and BD are well known as Ru complex dyes used in DSCs, but their steric structures are greatly different. First, N719 and BD have four and three carboxyl groups, respectively. These Ru complexes are believed to be adsorbed on TiO$_2$ through the carboxyl groups, but the adsorption mode of these complexes and how they are anchored on the nanocrystalline TiO$_2$ is still under debate. Second, N719 has two NCS groups and BD has three groups, and we focus our XPS and NEXAFS measurements on the S atoms contained in these NCS groups. In a previous investigation, we reported that the adsorption structure of N719 has two NCS groups,[8] and showed that the NCS group in N719 interacts with TiO$_2$ through the S atom. The adsorption mode of BD must be also determined by X-ray analysis of the S atom in NCS group, and be compared with N719 on TiO$_2$. The DSCs based on BD as a sensitizer need a coadsorber because the BD easily aggregates on TiO$_2$ surface, and the lack of light adsorption around 400 nm in BD needs to be compensated by the coadsorber. The D131 molecule has been used as a coadsorber in DSCs based on BD and does not contain any S atoms, which allows the interface structure of BD on TiO$_2$ to be determined using a direct X-ray analysis of the BD on TiO$_2$ coadsorbed with and without D131.

Figure 2 shows the S 1s XPS spectra for a single dye (N719 and BD) and a mixture of dyes (N719 + D131 and BD + D131) adsorbed onto the surface of nanocrystalline TiO$_2$. In the XPS measurements, the mean free path of photoelectrons for S 1s (2.4 keV) is short (4–6 nm)[25] and, as just described, XPS is a powerful tool for elucidating the adsorption modes of N719 dye onto nanocrystalline TiO$_2$.[8] We observe one peak at 2481.6 eV for N719 alone (Fig. 2(a), peak A) and at 2472.8 eV for the coadsorbed N719 + D131 (Fig. 2(b), peak B). Peak A corresponds to the S–TiO$_2$ bond formation, and peak B arises from the S atom in the NCS functional groups. For BD alone, however, one main peak is observed at 2472.8 eV, and for BD coadsorbed with D131, a small peak is visible at 2481.6 eV (Figs. 2(c) and 2(d), respectively).

Johansson *et al.*[15] have previously reported that S–TiO$_2$ interactions cause an energy shift of about 1 eV in the S 2p XPS spectra of dyes containing the NCS groups of N719 on TiO$_2$,[26,27] and the presence of a slight S–substrate interaction
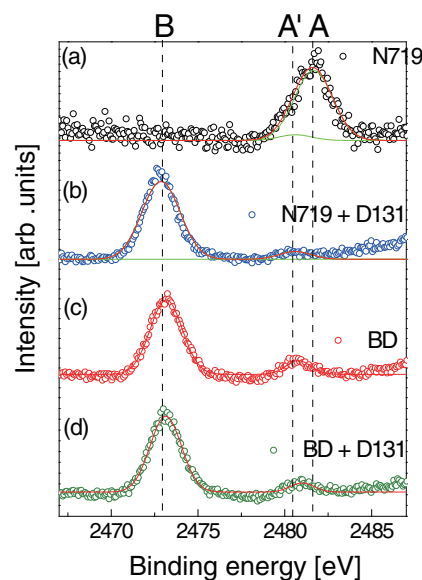

FIG. 2. S 1s XPS spectra for (a) N719 alone, (b) the N719 + D131 (1:1) coadsorption system, (c) BD alone, and (d) the BD + D131 (1:1) coadsorption system on a nanocrystalline TiO$_2$ surface measured at $h\nu = 3000$ eV. The S atom belongs to the NCS group in N719 and BD, whereas D131 does not contain an S atom.

has been previously suggested for an N719/nanostructured TiO$_2$ system and a BD/nanostructured TiO$_2$ system.[15,26] We also consider the adsorption mode of BD to the TiO$_2$ surface, and have already shown that the NCS group is important to the adsorption at the interface. Even though it is reasonable to expect that the effect of chemical modification is stronger upon the 1s spectra than the 2p spectra,[28] our results, together with the absence of a lower energy peak in Fig. 2(a), indicate a much stronger S–TiO$_2$ interaction than previously thought. Kley *et al.*[29] have reported that the N3 dye molecules [cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)] have two NCS groups adsorbed in numerous different states, and the state accordingly determines which S atom in the NCS interacts with the TiO$_2$ anatase (101).[29]

We therefore assume that the S atom in NCS is not involved in strong interactions when N719 is coadsorbed with D131, but that the binding of the S atoms in N719 to the TiO$_2$ is strong in the single-component system. The coadsorbed D131 molecule appears to inhibit the S-mediated interaction between N719 and TiO$_2$.[8] The XPS analysis of the BD adsorption shows that the S atom in NCS is not involved in strong interactions either before or after BD is coadsorbed with D131, and that the S atoms in BD are bound to TiO$_2$.

For peaks A and A′, we deconvolute the peaks in the range 2478−2485 eV by Gaussian peak-fitting. Although in some spectra we cannot completely separate the A′ peaks from the A peaks, we are still able to find evidence of the A′ peak by the presence of a shoulder on the side of the A peaks at lower binding energy. In the cases of N719 alone and the N719 + D131 mixture, the A′ peak overlaps the S–TiO$_2$ interaction at 2480 eV. In contrast, in the cases of BD alone and the BD + D131 mixture, the A′ peak binding energy can be attributed to the sulfur atom in S–TiO$_2$. It is also thought

that some adsorption mode of the S–TiO$_2$ interaction will exist in this system. The weak peak at 2480.6 eV (peak A′) in the XPS spectrum suggests that, in the adsorption structure of BD, one of the NCS groups interacts with nanocrystalline TiO$_2$. The BD molecule has three NCS groups, but when one NCS group interacts with TiO$_2$ the steric structure may prevent the remaining two NCS groups from coordinating to the surface. Usually, because it is the X-ray cross-section of isolated molecules that is being measured, the peak intensity of the S atom in the interacting NCS groups should be smaller in the case of BD adsorption to TiO$_2$. As a result, in the S $1s$ XPS measurements, the peak intensity of the S atom that does not interact with the substrate becomes larger, whereas the peak intensity of the S atom that does interact becomes smaller. To find the ratio of the S atoms between the interacting NCS groups, we estimate the intensity ratio of the B to A′ peaks and find a peak intensity ratio of approximately 5:1. The S–substrate interaction is also confirmed by the Ti $2p$ XPS spectra of the TiO$_2$ substrate, as is shown in the following paragraph.

Figure 3 shows the Ti $2p$ XPS spectra of TiO$_2$ substrates with BD alone (Fig. 3(a)) and the BD + D131 coadsorption system (Fig. 3(b)). In Fig. 3(a), the spin-orbit ($2p_{3/2}$ and $2p_{1/2}$) split peaks located at 459.3 and 465.1 eV, respectively, can be identified with the tetragonal coordination of Ti(IV), although no shift of the doublet is apparent between Figs. 3(a) and 3(b). A chemical shift of the doublet to higher binding energies of about 1.5 eV has been reported when a Ti–S bond is formed on TiO$_2$.[30] For N719 alone, a substantial chemical shift is apparent between Figs. 3(c) and 3(d). For BD adsorption, however, the chemical shift is negligible between the Ti $2p$ peaks for BD alone and for the BD + D131 coadsorption system. These results indicate that the S atoms in BD do not interact with TiO$_2$ over the surface to a depth of about 5 nm, which is in contrast to the N719 adsorption.[13,27] These two scenarios can be reconciled with the molecular arrangement proposed in the top-right panel of Fig. 4. The arrangement demonstrates that simultaneous interaction via the carboxylate and NCS groups is structurally allowed, which substantially affects the photovoltaic performance.
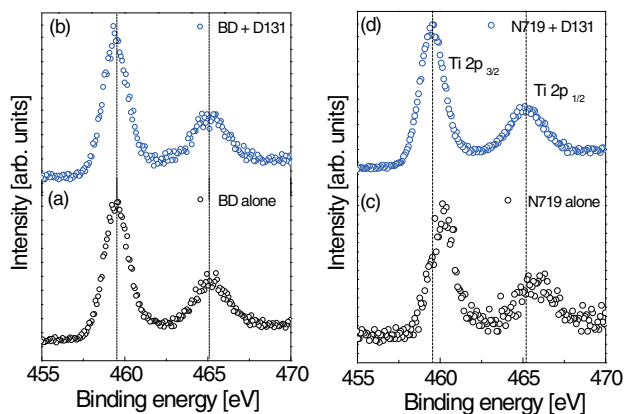
To investigate the microstructure of the DSCs, we perform more detailed NEXAFS measurements around the S atoms. Figure 4(a) shows the NEXAFS spectrum of the TiO$_2$ substrate covered with N719 under a normal incidence angle of 90°, the NEXAFS spectrum of the N719 + D131 coadsorption system, and the difference spectrum; and Fig. 4(b) shows the analogous spectrum for BD, the spectrum for the BD + D131 coadsorption system, and the difference spectrum. In this energy region, the C=S moiety has two peaks in the S K-edge at 2474 eV (peak A) and 2478 eV (peak B), corresponding to the $\pi*$ (S=C) and $\sigma*$ (S–C) bonds, respectively.[31] Peak C at 2483 eV can be attributed to the oxidized sulfur atoms,[32] which probably arises from the S–TiO$_2$ interaction. When the S atom in the NCS group interacts strongly with the substrate, the C=S bond valence is so heavily altered that peaks A and B disappear (Fig. 4). The contributions to peaks A and B and the contributions to peak C by the NCS groups are thus mutually exclusive.[8]

The spectra in Fig. 4, excepting the difference spectra, are normalized to the high-energy region around 2510 eV where the chemical state of the S atom should not affect the signal intensity. The fact that the difference spectra show a peak at C and dips at A and B indicates that contributions to peaks A and B and the contributions to peak C by the NCS groups are mutually exclusive.

For N719, the separation into two adsorption modes is incomplete. Even for the spectrum of N719 alone, there is a large contribution from peaks A and B, in contrast to Fig. 2(a), in which all S atoms interact with the substrate. This is because of the difference in the probe depth of the XPS and NEXAFS techniques.[8] The adsorption modes of BD are more complicated because it contains three NCS groups.

Determination of the orientation of molecules adsorbed onto a well-defined surface can be obtained from angle-dependent polarized NEXAFS.[33] However, because the nanocrystalline TiO$_2$ plate used in this study exhibits morphological features about 20 nm in size,[34] it is not easy to extract the orientation information directly. We therefore estimate the proportion of NCS groups in BD that interact with nanocrystalline TiO$_2$ based on the information from the N719 dye.

We next discuss the XPS and NEXAFS results. The electron mean free path for the XPS measurements is short, so the N719 molecules that contribute to the XPS photocurrent are only those near the surface of the outermost nanoparticles because the particles are larger than the mean free path. Therefore, on these surfaces nearly all of the S atoms interact with TiO$_2$ in the case of N719 alone, and none interact with the dye mixtures. In the NEXAFS measurements, however, the total electron yield measurements make it possible to estimate a depth of about 70 nm,[35] and because the photon penetration depth of the 3 keV incident X-rays is large, they penetrate the entire depth of the DSCs independent of the normal incidence angle. Therefore, all molecules within a depth of 70 nm, or possibly more because of the pore structure, contribute to the signal.

In Fig. 4, the difference spectra of the BD and N719 plots are similar in the appearance of the peaks and dips though they are noisy, which is especially true of the difference

FIG. 3. Ti $2p$ XPS spectra for (a) BD alone, (b) the BD + D131 (1:1) coadsorption system, (c) N719 alone, and (d) the N719 + D131 (1:1) coadsorption system on a nanocrystalline TiO$_2$ surface measured at $h\nu = 3000$ eV. The S atom belongs to the NCS group in N719 and BD, whereas D131 does not contain an S atom.
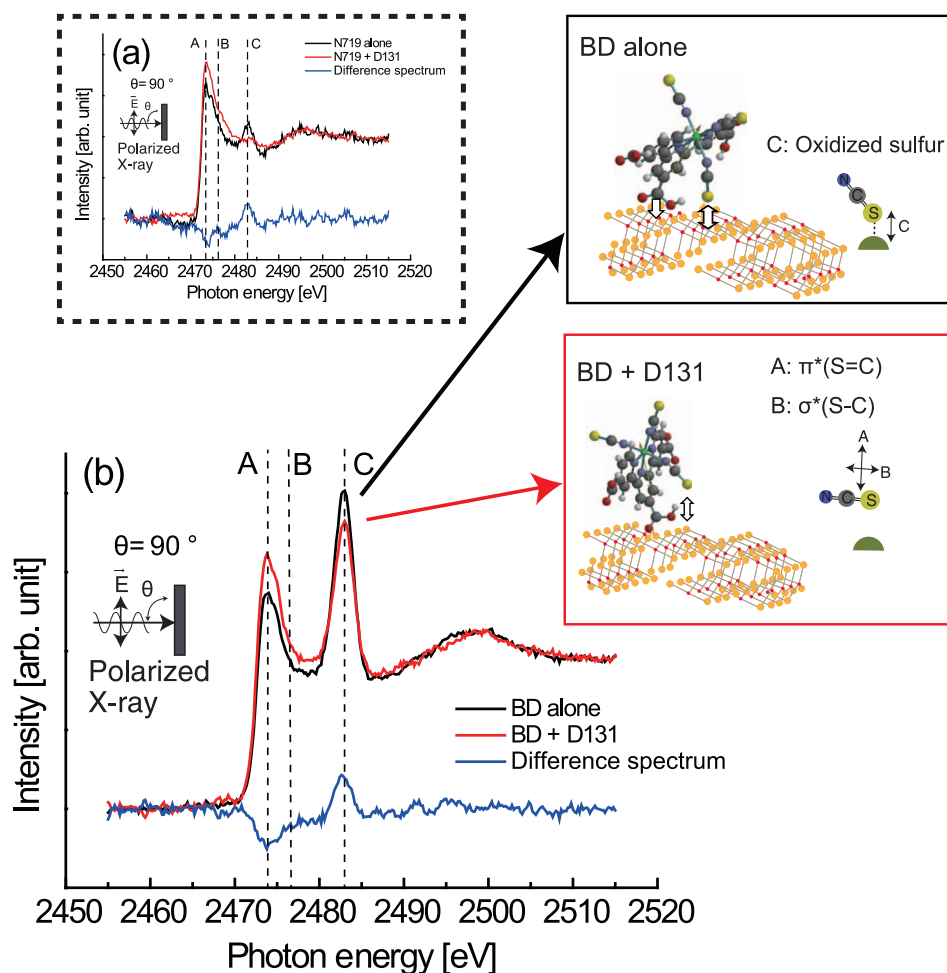
FIG. 4. S *K*-edge NEXAFS spectra for (a) N719, the N719 + D131 coadsorption system, and the difference spectrum on TiO$_2$ at an incidence angle of 90°, and (b) analogous spectra for BD and the BD + D131 coadsorption system. The inset shows the definition of the incidence angle. Peaks A, B, and C are identified as originating from π*(S=C) and σ*(S–C) bonds and oxidized sulfur, respectively. The right panel shows possible molecular arrangements with (top black line) and without (bottom red line) strong S–substrate interactions. The orientations of the respective transition dipole moments for peaks A–C are also shown.

spectrum in Fig. 4(a). Assuming that the joint density of states is conserved within the energy region including the dip and peak, the ratio of the areas of peaks A and B to the area under peak C in the case of the difference spectrum (normalization and background subtraction by the step-function-like background at the edge is moderately subtracted) is the ratio of BD molecules with no S–substrate interaction to BD molecules with a strong interaction, and averaged over a depth of 70 nm.

Based on this rough estimation, about 10% of the BD molecules strongly interact with the TiO$_2$ via their S atoms. A steep gradation of the probability of a strong interaction between molecules is apparent, with very high probabilities at the surface and dropping to very low probabilities in the inner area. The implication is that the adsorption mode is not uniform across the cross-section of the nanocrystalline TiO$_2$, and it is probable that the diffusion adsorption of dye in porous TiO$_2$ influences the adsorption mode. An investigation of how the diffusion of dye molecules is influenced by its solvent, porosity, pore size, and particle size has been reported.[36] For instance, it is likely that the initial concentration of the dye solution decreases considerably as the solution penetrates into the pores. This operation is therefore an effective way to con-

trol the interfacial structure because the adsorption and dissolution eventually reach equilibrium. Based on this finding, we test different fabrication protocols to identify the one that produces the most efficient interfacial surface. We evaluate a method that involves adsorbing BD first and then immersing the cell into a mixture (device 3, which is described below) to compare the dynamics of dye adsorption and relate it to cell performance.

It has previously been shown that photoexcitation causes the NCS group to accept an electron from iodide anions.[37,38] The S–substrate interaction is therefore detrimental to charge transfer and should be increased to reduce charge transfer. We therefore fabricate a large number of DSCs designed to enhance the suppressing effect of D131.

Table I provides a summary of the cell performance results. Three types of cells are tested, including device 1, with BD alone; device 2, with a 1:1 mixture of BD and D131; and device 3, prepared by a custom method. The procedure of this custom method is to first immerse the sample in a solution containing BD alone for 3 h, and then immerse the sample in the D131 solution for 4 h. Next, we immerse the sample in the 1:1 mixture solution for 14 h. We compare the photovoltaic cell performance of the DSCs with BD and with a mixture of

TABLE I. Photovoltaic performance of DSCs sensitized with BD alone or with BD and a coadsorbent. Several cells with an Eff within 0.05% are fabricated for each system. The term V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, FF is the fill factor, and Eff is the solar energy conversion efficiency.

Device	Coadsorbent	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	Eff (%)
1	BD alone	0.69	12.61	0.75	6.32
		0.70	11.95	0.75	6.22
2	BD + D131 (1:1)	0.70	13.40	0.75	6.96
		0.69	13.07	0.74	6.73
3	BD → D131 → BD + D131	0.69	14.48	0.75	7.49
		0.69	13.76	0.75	7.09

BD and D131 fabricated under the same conditions. The photovoltaic characteristics of the BD + D131 cell are different from those with just BD (Fig. 5), and this difference is consistent with the light absorbance of the D131 dye, which is itself influenced by the different adsorption procedures used in devices 2 (BD + D131) and 3 (custom method). To investigate the differences in these D131 processes, the IPCE spectra of devices 2 and 3 are compared with the IPCE spectrum of BD alone (Fig. 5). The different structure of device 3 is seen to affect the IPCE spectrum of this coadsorption system, and the altering of the adsorption process is seen to improve the IPCE spectrum compared with that of the BD cell. This improvement is seen mainly around the 550–650 nm range, which is consistent with the effect of the NCS group in this region in device 3. Because the IPCE spectra of devices 1 and 2 are similar in the 600–950 nm region where device 1 (BD alone) shows a photoresponse, the effect of the adsorption procedure on the adsorption of BD is seen to be negligible, and D131 is adsorbed only on the unoccupied surface of nanocrystalline TiO$_2$. These results suggest that device 2 does not induce aggregation or interaction with BD in the coadsorbed system. We intend to examine the recombination process in detail in the future, but the effect on the recombination process is difficult to assess because a dramatic improvement in the open-circuit voltage, V_{oc}, is not observed. We assume that the increase in the electronic diffusion coefficient in TiO$_2$ is not caused by coadsorption of D131.
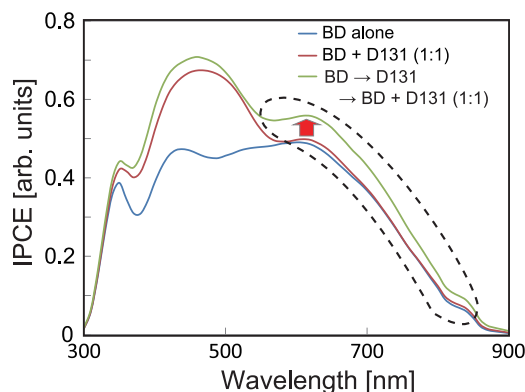

FIG. 5. IPCE spectra of DSCs with coadsorbed D131 and those without a coadsorbent (see Table I).

As previously noted, when the intensity of peak C (Fig. 4) decreases in the coadsorption system, the intensity of peak A increases. It is estimated that about 10% of the S atoms in BD interact with TiO$_2$, which is consistent with the increase in the photocurrent in the IPCE spectra.

Thus, when D131 dye is added to BD, about 10% of the S–TiO$_2$ interactions participate in the reverse photocurrent conversion, though the recombination of electrons in the TiO$_2$ is unclear. Even for BD alone, we consider the recombination process to be delayed and assume that it is not altered by D131 coadsorption. We therefore suggest in this report that coadsorption is effective in promoting electron transfer.

The XPS results should be interpreted with caution. In the device, the dye molecules are not isolated, but are instead influenced by the solvent and various anions. Therefore, the clear distinction between the two types of adsorption reported in our previous paper[8] may be moderated in this study. However, a part of the interaction of S atoms freed by the D131 treatment (∼10%) is similar to the increase in the short-circuit current density, J_{sc}, of devices 1 and 2 relative to device 3 (∼8%).

Many attempts have been made to optimize the relative positions of the anchoring moiety and highest occupied molecular orbital in the dye molecules.[37] Our results suggest that a similar procedure could also be used for mixtures of dyes. Part of the carboxyl group of the coadsorbed dye adsorbed onto TiO$_2$ transforms to other functional groups (alkyl-carboxyl group, silane coupling agent, etc.) because many more of the bound S atoms are released. As a result, optimization of coadsorbent dyes improves the efficiency of DSCs.

IV. CONCLUSIONS

X-ray photoelectron spectroscopy and XAFS measurements are used to investigate the interfacial adsorption structure between TiO$_2$ and the Ru dyes BD and D131. For the BD + D131 coadsorption system, bonds form between the NCS groups and the surface, and the dye-sensitized coadsorption system exhibits specific interactions with part of the NCS group. For BD alone, bonds form between the dye NCS groups and the surface in about 10% of molecules, while in the dye-sensitized BD + D131 coadsorption system, about 10% of the BD molecules release from the surface via one or two NCS groups. Our results show that there is a large and direct effect of the interaction between the substrate and the dye molecule upon the electronic structure of the dye, and the result is an improvement of the J_{sc}. This discovery is important for understanding the relationship between the composition and performance of DSCs. In this study, we elucidate the relationship between the NCS adsorption state and the photocurrent in nanocrystalline TiO$_2$ electrodes, which are the electrodes used in actual DSCs. In future work, we intend to optimize the interfacial structures of the coadsorbed dyes to achieve a higher J_{sc}.

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