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XPS, UV−Vis, FTIR, and EXAFS Studies to Investigate the Binding Mechanism of N719 Dye onto Oxalic Acid Treated TiO_2 and Its Implication on Photovoltaic Properties

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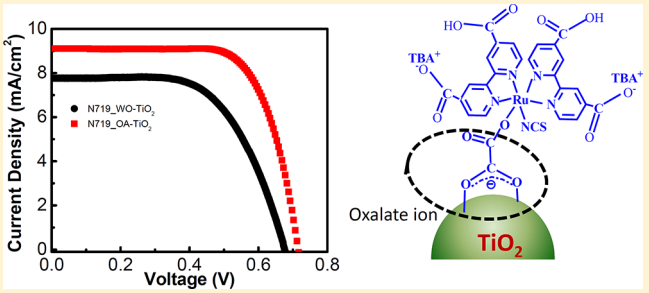
ABSTRACT: The anchoring mechanism of N719 dye molecules on oxalic acid treated TiO_2 (OA-TiO_2) electrodes has been investigated using extended X-ray absorption fine structure (EXAFS) measurements, Fourier transform infrared spectroscopy (FTIR), UV−vis spectroscopy, and X-ray photoelectron spectroscopy (XPS). The FTIR spectroscopy of OA-TiO_2 electrodes revealed that the oxalic acid dissociates at the TiO_2 surface and binds through bidentate chelating and/or bidentate bridging. Analyses of EXAFS, FTIR, UV−vis, and XPS measurements of N719 dye loaded onto OA-TiO_2 revealed that the binding of N719 molecules takes place via interaction between the Ru atom of the dye and O^- of bidentate bridged oxalate ions at the TiO_2 surface. This mechanism is quite different from the binding of N719 onto untreated TiO_2 (WO-TiO_2) surface, where −COOH and SCN groups of the dye directly bind to the TiO_2 surface. The analyses of UV−vis data show that the amount of N719 dye loading onto OA-TiO_2 surface is much higher than that onto the native TiO_2 surface. In addition, the incident photon-to-current conversion efficiency (IPCE) measurements show that the presence of oxalate ions between the dye and TiO_2 surface favors efficient electron transfer and therefore improvement in device efficiency. The dye-sensitized solar cells fabricated using N719 dye sensitized onto OA-TiO_2 showed an efficiency of ∼4.6%, which is significantly higher than that based on a WO-TiO_2 electrode (∼3.2%).



1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are being investigated extensively as potential devices for harnessing solar power owing to ease of fabrication and their relatively low cost compared to conventional silicon solar cells.[1−3] Devices with efficiency exceeding 10% have been fabricated using nanoporous TiO_2 sensitized with Ru(II)-polypyridyl complexes, such as N3, N719.[4] It is well-established that modification of the TiO_2 surface plays a major role in determining the efficiency of the DSSCs. It has also been demonstrated that the short circuit current (J_{SC}) and therefore the efficiency of the DSSC improves by the treatment of the TiO_2 electrode with 0.1 M HCl.[5] In addition, other acids such as HNO_3, H_3PO_4, and H_2SO_4 have also been reported to affect the photovoltaic properties and therefore the device efficiency.[6−8] The improvement in efficiency as a result of surface treatment in the DSSCs has been attributed to the negative movement of the TiO_2 conduction band edge (CBE), enhanced dye absorption, and reduced charge recombination. To understand the improvement in the device performance as a result of surface modifications, it is important to have knowledge about the interfacial properties of the materials involved in the fabrication of DSSCs. In general, at the TiO_2 semiconductor−dye interface, ultrafast electron injection from the excited dye to the conduction band of the TiO_2 takes place, which is responsible for the improvement in the device efficiency. However, several recombination processes also occur at this interface that affect the overall device efficiency. Both injection and recombination dynamics are influenced by the electronic coupling between the dye and TiO_2 and thereby the binding mode of the dye to the TiO_2 surface. Therefore, the efficiency of the DSSCs, in addition to TiO_2 CBE movement, depends upon the interaction of the dye molecules with the TiO_2 surface.

In spite of the fact that the modified TiO_2 surface might lead to a change in the electron injection dynamics owing to a different binding mechanism of N719 dye molecules on the modified surface, this aspect has not been discussed in literature and there is no report yet describing the binding mechanism of the ruthenium complexes onto surface-modified TiO_2. Nevertheless, the absorption orientation and electronic coupling of N719 on TiO_2 has been studied and discussed by several groups using vibrational spectroscopy, X-ray absorption spectroscopy, and computational model studies. Despite the

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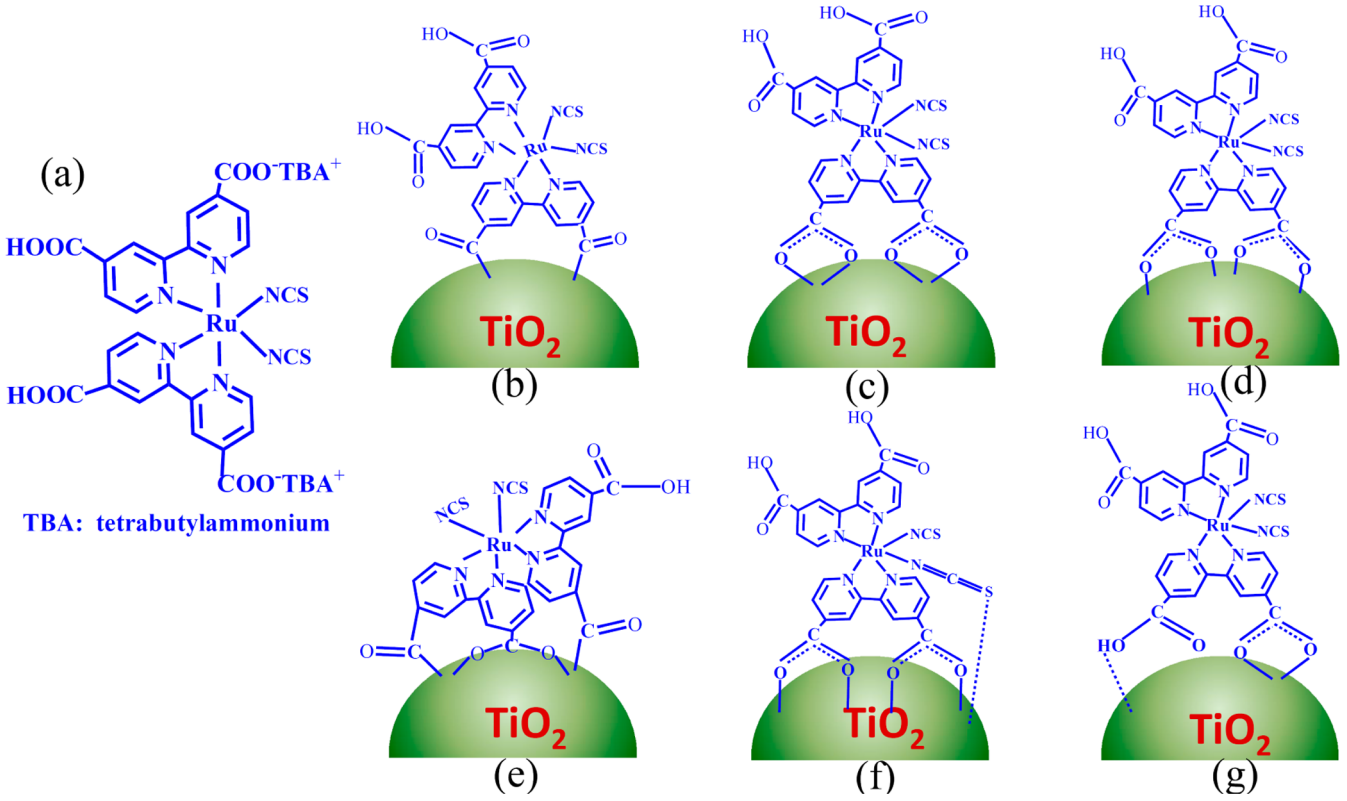

Figure 1. (a) N719 dye structure and Schematic presentations of binding of N719 dye on the TiO_2 surface: (b) ester linkage, (c) bidentate chelating, (d) bidentate bridging, (e) mixed bidentate and monodentate mode, (f) NCS group interacts with the TiO_2 surface, and (g) bidentate chelating and hydrogen bonding.

volume of work, the binding mechanism of N719 dye onto TiO_2 surface is not yet fully understood and remains a subject of debate. The various binding mechanisms proposed in the literature are summarized in Figure 1. The structure of N719 dye is shown in Figure 1a. As shown in Figure 1b, the first type of binding, known as ester type linkage, involves interaction of one or two oxygen atoms of the −COOH group with the Ti atoms of the TiO_2 surface, resulting in unidentate or bidentate co-ordination mode. Falaras et al. suggested this type of linkage based on a 20 cm^{-1} shift in the carbonyl group observed in FTIR spectra.[9] The second type of binding involves the interaction of both oxygen atoms of COOH groups with either one or two Ti atoms, resulting in bidentate chelating or bridging, as depicted in Figure 1c and Figure 1d, respectively. This mechanism was proposed by Finnie et al., who studied the co-ordination of the dyes and of benzoic acid onto the TiO_2 surface.[10] On the basis of their results, they suggested that carboxylate attaches to the TiO_2 surface via bidentate chelating or bridging co-ordination using two carboxylic acid groups per dye molecule. Later, Nazeeruddin et al. investigated different ruthenium complexes to determine the specific carboxylic group (COO^- or −COOH) involved in TiO_2 binding.[11] On the basis of FTIR analysis, they deduced that N719 dye absorbs on the TiO_2 surface in bridging mode via two carboxylic groups trans to the NCS group. Further, supporting data were provided by Leon et al. who carried out UV−vis, FTIR, and Raman measurements to investigate the absorption mechanism of N719 sensitizer on TiO_2.[12] From the Raman measurements, the co-ordination of the N719 dye was proposed to occur through bridging or bidentate linkage. They confirmed their results by attenuated total reflectance FTIR (ATR-FTIR) spectra, which provided a direct fingerprint of the deprotonation state of the carboxylic moieties. A third binding mechanism (Figure 1e) was also proposed on the basis of molecular dynamics simulations and electronic structure calculations. Accordingly, the N719 dye binding to the TiO_2 surface occurs through three carboxylic groups, one of which is attached to two Ti atoms in bidentate form while the other two are bound via monodentate mode.[13] In contrast to these findings, a fourth binding mechanism (Figure 1f), was also proposed in which the N719 dye molecules interact with the TiO_2 surface though the NCS group in addition to the bidentate bridging.[14] Recent studies by Lee et al. elucidated the role of Ti−OH/$TiOH_2$ groups in the binding mode of the dye.[15] On the basis of detailed vibrational spectroscopic studies of N719 dye absorbed on the TiO_2 surface, they proposed that the binding of the dye to TiO_2 occurs through two neighboring carboxylic acid/carboxylate groups via a combination of bidentate bridging and H-bonding involving a donating group from the N719 dye and acceptor from the Ti−OH group (Figure 1g).

Though most studies suggest anchoring of N719 dye on the TiO_2 surface via two carboxylate groups, the role of various kinds of surface treatments of the TiO_2 surface has not been reported to date. In our earlier work, we reported that the efficiency of the DSSC is improved significantly when a photoanode consisting of N3 dye loaded onto a formic acid treated TiO_2 surface or N719 dye loaded onto a carboxylic acid treated TiO_2 surface are utilized.[16,17] The analyses of the device characteristics in both cases revealed that the efficiency improvement occurred because of enhanced dye absorption onto the TiO_2 electrode and reduced recombination. This

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resulted in an increase in both the J_{SC} and V_{OC} and therefore enhanced efficiency.

In this work, we report a detailed investigation of the binding mechanism of N719 dye onto the oxalic acid treated TiO_2 surface using various characterization techniques, i.e., X-ray absorption fine structure (EXAFS) measurements, Fourier transform infrared spectroscopy (FTIR), UV−vis spectroscopy, and X-ray photoelectron spectroscopy (XPS). The results of these studies revealed that the binding of N719 molecules takes place via interaction between the Ru atom of the dye and O^- of bidentate bridged oxalate ions at TiO_2 surface. This is in contrast to the binding of N719 onto untreated TiO_2 surface, in which −COOH and SCN groups of the dye directly bind to TiO_2 surface. The results of incident photon-to-current conversion efficiency (IPCE) measurements show that the presence of oxalate ions between the dye and TiO_2 surface favors efficient electron transfer and therefore improves the device efficiency.

2. EXPERIMENTAL SECTION

2.1. Fabrication of DSSC. The photoelectrode was fabricated using the procedure reported earlier.[17] Briefly, a TiO_2 compact layer was deposited on the fluorine-doped tin oxide (FTO, Solaronix, TCO22-7) by dipping the substrate into $TiCl_4$ followed by an annealing at 450 °C for 30 min. A mesoporous TiO_2 was subsequently deposited from precursor paste (Solaronix, Ti-Nanoxide HT) by doctor blading. The electrodes were sequentially annealed at 75 °C for 10 min, 135 °C for 10 min, 175 °C for 20 min, 425 °C for 10 min, and 450 °C for 10 min. The TiO_2 electrode thus prepared was treated with oxalic acid (0.05 M in ethanol solution) for 1 h, washed in ethanol thoroughly, and finally dried in an N_2 flush. Hereafter untreated TiO_2 and oxalic acid treated TiO_2 are termed WO-TiO_2 and OA-TiO_2 electrodes, respectively. For dye sensitization, both WO-TiO_2 and OA-TiO_2 electrodes were dipped in N719 dye solution (0.3 mg/mL in ethanol) for 24 h. These electrodes are termed N719_WO-TiO_2 and N719_OA-TiO_2, respectively. The DSSC (area ∼0.1 cm^2) was assembled by clipping together a photoelectrode and Pt electrode having a 20 μm spacer. A solution of 0.1 M LiI and 0.05 M I_2 in dry acetonitrile was used as an electrolyte.

2.2. Characterization of the Oxalic Acid Treated Electrode. The current−voltage (J−V) characteristics of the cells were recorded on a potentiostat/galvanostat (PGSTAT 30, Autolab Eco Chemie, Utrecht, The Netherlands) under the irradiation of 100 mW/cm^2 at AM 1.5 G using a solar simulator (Sciencetech, London, Ontario, Canada). Prior to the measurements, the intensity of the solar simulator was calibrated using a reference silicon solar cell. To estimate dye loading, the UV/vis spectroscopy was carried out using a double-beam UV−vis spectrophotometer (Jasco, V 530), and all spectra were baseline corrected for quantitative analysis. The extent of dye loading was estimated by desorbing a dye-sensitized electrode (area ∼1 cm^2) from 0.1 M aqueous KOH (2 mL) solution and then recording the absorbance spectrum. The binding modes of oxalic acid on the TiO_2 surface as well as dye molecules after treating the TiO_2 surface with oxalic acid were deduced from FTIR spectroscopy using a Bruker spectrometer (Vertex 80 V) at a resolution of 4 cm^{-1}. To investigate further the anchoring mode of the N719 dye molecules to the oxalic acid treated TiO_2 surface, XPS was carried out using Mg Kα source (Riber MBE system). The binding energy scale was calibrated to the Au $4f_{7/2}$ line of 83.95 eV. Because the actual binding mode of ruthenium complexes is often hindered due to the overlapping absorptions in the 1400−1600 cm^{-1} range, we confirmed the results by using EXAFS, which is a useful technique for probing the co-ordination changes occurring around the element of interest. EXAFS experiments were carried out at Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany, at the P06 beamline in transmission mode. The energy calibrations were carried out using the characteristics Ru k-edge at 22 127 eV of ruthenium.

3. RESULTS AND DISCUSSION

Figure 2 shows typical photovoltaic characteristics of the DSSCs fabricated using N719_OA-TiO_2 and N719_WO-TiO_2

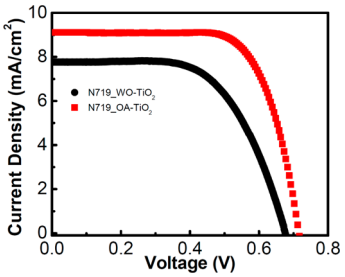

Figure 2. J−V measurements of the DSSCs based on untreated and carboxylic acid treated TiO_2 electrode sensitized with N719 dye, under AM 1.5 G intensity 100 mW/cm^2.

photoanodes under illumination of AM 1.5 G (intensity, 100 mW/cm^2). As shown in the figure, the photovoltaic parameters of the devices fabricated using N719_OA-TiO_2 are superior to those fabricated using N719_WO-TiO_2 electrodes. The overall efficiency of 4.6% (±0.1) is obtained for the device using N719_OA-TiO_2 photoanodes as compared to 3.2% (±0.16) device efficiency using N719_WO-TiO_2 electrodes. The detailed analyses of various photovoltaic parameters of devices are presented in our earlier paper.[17] It has been demonstrated that OA-treatment of TiO_2 leads to the following beneficial effects: (i) improvement in V_{OC} due to the CBE and quasi Fermi level shift as well as reduced recombination and (ii) increase in the amount of dye loading, e.g., the amount of N719 dye loaded onto OA-TiO_2 was 3.2×10^{-5} mol/cm^2, which is significantly higher than that onto TiO_2 electrodes (2.3×10^{-5} mol/cm^2). In this paper, we focus on the investigation of the binding mechanism of N719 dye onto oxalic acid treated TiO_2 electrodes using various techniques discussed below.

3.1. UV−Vis Spectroscopy. The UV−vis spectra of dye loaded on WO-TiO_2 and OA-TiO_2 were recorded taking TiO_2 as reference electrode, and the results are presented in Figure 3a. As shown in the figure, the N719 dye exhibits peaks at 399 and 540 nm, corresponding to metal-to-ligand charge transfer (MLCT) transitions. It may be noted that the higher-energy MLCT has some character of π−π^* (ligand centered) transition. Major inferences drawn from this figure are as follows:

(i) The absorbance of the dye loaded onto OA-TiO_2 is higher than that onto WO-TiO_2 electrodes, which corroborates our earlier results that higher N719 dye loading takes place onto OA-TiO_2 electrodes.
(ii) The low-energy MLCT band reveals a blue shift from 540 to 525 nm for N719 dye loaded onto OA-TiO_2 electrodes. The blue shift may be attributed to an increase in the energy of the LUMO of the ligand,

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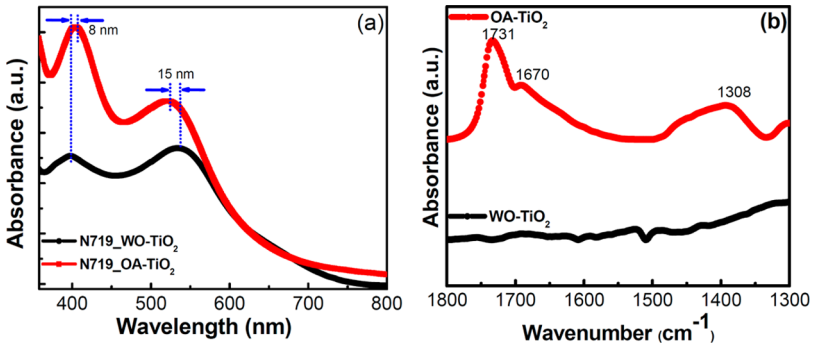

Figure 3. (a) UV−vis spectra of N719 dye-loaded TiO_2 and OA-TiO_2 surfaces and (b) FTIR spectra of WO-TiO_2 and OA-TiO_2 surfaces.

causing $\pi-\pi^*$ transitions to occur at higher energies. Because the shape of the absorbance curve has not changed, we rule out dye aggregation as the cause of this shift. Therefore, this blue shift might arise because of an interaction between N719 dye and the oxalate ions present on the TiO_2 surface.

(iii) There is a slight red shift in the higher-energy MLCT band from 399 to 407 nm for N719_OA-TiO_2. This is expected to have resulted from the increased delocalization of π-electrons in the system for N719_OA-TiO_2 electrodes. This suggests that the anchoring of the N719 dye to OA-TiO_2 is different from the anchoring of the dye on the WO-TiO_2 electrode. To understand the effect of the type of dye anchoring on device efficiency, we examined the anchoring mechanism of the dyes on the OA-TiO_2 electrodes using various spectroscopic techniques as discussed below.

3.2. Fourier Transform Infrared (FTIR) Spectroscopy.

Before analyzing how the dye is anchored onto OA-TiO_2 electrodes, we first investigated the changes that occurred to the TiO_2 surface when subjected to oxalic acid treatment. For this purpose, we recorded the FTIR spectra of OA-TiO_2 as well as that of TiO_2 electrodes, and the results are shown in Figure 3b. The FTIR spectra of oxalic acid absorbed on TiO_2 shows two bands at 1731 and 1697 cm^{-1}, which are due to splitting of two similar carbonyl (C═O) groups.[18] These bands are assigned to either bidentate chelating or bidentate bridging ring structure with one oxygen of each carboxylic group coordinated to the surface sites and two C═O double bonds pointing away from the surface. DFT calculation and ATR-FTIR spectroscopic results by Mendive et al. propose the existence of both types of binding modes at the TiO_2 surface.[19] The increase in loading of N719 dye OA-TiO_2 electrode as discussed earlier may be attributed to the bridging mode of oxalic acid on the TiO_2 surface. Furthermore, we recorded the FTIR spectra for dye loaded onto WO-TiO_2 as well as OA-TiO_2 electrode and normalized the spectra using intensity of the bipyridine (C═C) at 1542 cm^{-1} as an internal standard (Figure 4a,b). The peak assignments are summarized in Table 1.

The IR spectra of the free dye show the presence of carboxylic acid and carboxylate groups as evident by the $\upsilon_{C=O,}$ υ_{C-O}, and $\upsilon_{COO^-,asym}$ and $\upsilon_{COO^-,sym}$ vibrational modes.[10] In the case of dye loaded on WO-TiO_2, the asymmetric and symmetric stretching modes of COO^- are observed at 1615 and 1373 cm^{-1}, respectively.[10] On the other hand, these bands are shifted to slightly higher binding energy (~6 cm^{-1}) in the case of N719 dye loaded onto the OA-TiO_2 surface. This suggests that interaction of N719 dye molecules on the OA-

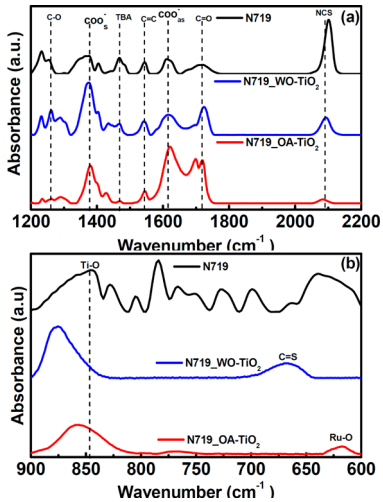

Figure 4. FTIR spectra of free N719 dye as well as N719 dye loaded onto WO-TiO_2 and OA-TiO_2 surfaces in the (a) 1200−2200 cm^{-1} and (b) 600−900 cm^{-1} frequency ranges.

Table 1. Peak Assignments of the FTIR Spectra of the N719 Dye-Sensitized WO-TiO_2 and OA-TiO_2 electrode

mode of vibration	υ (cm^{-1}) N719 dye	υ (cm^{-1}) N719_WO-TiO_2	υ (cm^{-1}) N719_OA-TiO_2
bulk TiO_2	-	554	565
C═S	836	832	absent
Ru−O	absent	absent	864
C−O	1256	1261	1261
Sym (COO^-)	1372	1373	1379
Bpy	1400	1403	1401
TBA	1464	1468	1471
C═C	1542	1542	1542
Asym (COO^-)	1624	1615	1621
C═O (oxalic acid)	absent	absent	1698
C═O (dye)	1710	1723	1719
NCS	2102	2095	2085

TiO_2 surface is different than that on the WO-TiO_2 surface. In addition to these peaks, two bands at 1698 and 1719 cm^{-1} are also observed in the N719 dye loaded onto OA-TiO_2 electrode; these bands arise because of the carbonyl group of oxalic acid as well as that of the dye. The relative intensity of the band at 1719 cm^{-1} with respect to that at 1698 cm^{-1} is decreased, implying the involvement of oxalate ions present at the TiO_2 surface in the binding of N719 dye. Furthermore, the occurrence of TBA peaks in the case of dye loaded onto

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WO-TiO_2 and OA-TiO_2 rules out the possibility of anchoring of the dye through covalent bonding of carboxylate groups. It was suggested by Hirose et al. that in order to dissociate TBA from the N719 molecule, it must react with the Ti−OH/$TiOH_2$ groups.[20,21] The difference ($\Delta\nu$) between $\upsilon_{COO^-,asym}$ and $\upsilon_{COO^-,sym}$ vibrational modes has been related to the type of co-ordination mode of carboxylate group to metal ions by an empirical rule derived by Deacon and Phillips.[22] In particular, the solid state ($\Delta\nu_{salt}$) and the absorbed state ($\Delta\nu_{ads}$) have been used to determine bond coordination in carboxylate and carboxylic acid groups. Accordingly, the nature of binding mode can be inferred from the following criterion: if $\Delta\nu_{ads} > \Delta\nu_{salt}$, the bonding is unidentate, but if $\Delta\nu_{ads} < \Delta\nu_{salt}$, the chelate or bridge mode occurs. Under the condition $\Delta\nu_{ads} \ll \Delta\nu_{salt}$, the chelating is the binding mode. The $\Delta\nu$ value for free dye and the dye absorbed onto WO-TiO_2/OA-TiO_2 is 252 and 242 cm^{-1}, respectively, suggesting bidentate chelating or bridging bonding. It may be noted here that this mode could arise because of bidentate chelating or bridging bonding of COO^- group of oxalate ions present at the TiO_2 surface in the case of dye loaded on OA-TiO_2 electrode.

To further clarify the binding mechanism, we have focused on the region 1200−2200 cm^{-1} (Figure 4a), where peaks corresponding to C═O, COO^-, and NCS appear. The major observations from this region are:

(i) The peak corresponding to C═O is present in the case of free dye as well as N719 dye on WO- and OA-TiO_2 electrodes, suggesting that some of the absorbed dye is not bound to the TiO_2 surface via bidentate chelating or bridging bonding mode and some additional binding modes of N719 dye to the WO- and OA-TiO_2 electrodes may be present.

(ii) The peak corresponding to the NCS group is shifted toward a lower wavenumber (from 2102 to 2095 cm^{-1}) when the dye is absorbed onto the WO-TiO_2 surface. Though such observations were also made by previous studies, the role of NCS in binding of the N719 dye to TiO_2 electrode was not elaborated much. It was suggested by Johansson et al.[14] as well as Lee et al.[15] that N719 dye may also bind to the TiO_2 surface through the NCS group. The striking features of the dye absorbed onto the OA-TiO_2 electrode are (a) a large shift of ∼10 cm^{-1} for the peak corresponding to NCS group toward lower wavenumbers and (b) significant reduction in intensity of this peak.

These observations suggest that an NCS group plays a significant role in the anchoring of N719 dye to the OA-TiO_2 surface. This is also confirmed by the disappearance of the 843 cm^{-1} peak corresponding to C═S groups in the case of N719 dye-sensitized OA-TiO_2 electrode (Figure 4b). The peak at 832 cm^{-1} is assigned to C═S of NCS group of the N719 dye absorbed onto WO-TiO_2 electrode. However, this peak is missing and instead an intense peak is observed at 864 cm^{-1} in the case of N719 dye-sensitized on OA-TiO_2 electrode. This peak cannot be assigned to the C═S stretching mode. The reason is that the intensity of the peak corresponding to NCS in the N719_OA-TiO_2 electrode is much less than that in the N719_WO-TiO_2 electrode; therefore, we should have observed a very weak peak, if any, corresponding to the C═S bond. This peak is assigned to Ru−O, which might have resulted from the interaction of the N719 dye with oxalate ions present at the OA-TiO_2 surface.[23]

Furthermore, the relative amount of bound N719 dye molecules on the TiO_2 surface has been estimated by the relative intensity of the peak at free carboxylic acid (C═O, 1723 cm^{-1}) and carboxylate groups (COO^-, 1373 cm^{-1}).[24,25] Because the carbonyl group peak at 1719 cm^{-1} for the OA-TiO_2 electrode has contributions from the dye as well as oxalic acid, it is difficult to determine quantitatively the amount of N719 dye on the OA-TiO_2 surface. Nevertheless, the decrease in the intensity of this peak may be related to the increased amount of dye loading on the OA-TiO_2 surface as compared with the WO-TiO_2 surface. This corroborates our results of a higher amount of N719 dye loading on the OA-TiO_2 surface as compared with the WO-TiO_2 surface. The presence of more N719 dye molecules on the OA-TiO_2 electrode then resulted in enhanced light harvesting and additional photoinduced electrons in the DSSC as compared with the results of WO-TiO_2 electrodes.[26]

3.3. X-ray Photoelectron Spectroscopy. To further confirm our findings of FTIR spectra, we have recorded XPS spectra of N719 dye loaded on WO-TiO_2 and OA-TiO_2. XPS is a highly surface sensitive technique to distinguish between different chemical states of the same atom. The obtained findings are discussed below.

Ti 2p. As shown in Figure 5, the splitting due to spin−orbit coupling is observed in the case of dye sensitized on the WO-TiO_2 and OA-TiO_2 electrodes. These Ti 2p peaks at 459.3 eV and 465.1 eV can be attributed to Ti^{4+} $2p_{3/2}$ and Ti^{4+} $2p_{1/2}$ states, respectively. This suggests that the surface of TiO_2 electrodes comprises only titanium(IV) dioxide and suboxides, i.e., TiO, Ti_2O_3, etc. are not present.[15] In the case of dye-sensitized on OA-TiO_2, these Ti 2p peaks are shifted to binding energies that are slightly higher than those of WO-TiO_2. The shift to higher binding energies could be due to a change in the surface dipole and/or a change in the Fermi level position in the band gap as a result of oxalic acid treatment of TiO_2 surface. Such changes were also reflected in the UV−vis spectrum, where a blue shift of 15 nm is observed for dye-sensitized OA-TiO_2 electrodes. In addition to the shift in binding energy, a decrease in intensity of Ti 2p peaks is also observed, indicating absorption of oxalate ions on the TiO_2 surface.

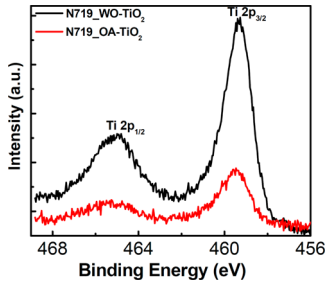

Figure 5. XPS spectra of Ti 2p states for N719 dye-sensitized TiO_2 and OA-TiO_2 electrodes.

C 1s. The C 1s spectra of dye-sensitized WO-TiO_2 and OA-TiO_2 are shown in Figure 6a,b. The spectra reveal four peaks upon deconvolution having full width half-maximum (FWHM) of 1.48 and 1.46 eV for N719_WO-TiO_2 and N719_OA-TiO_2, respectively. It is to be noted here that the Ru $3d_{3/2}$ peak is hidden under the major C 1s peak (285.9 eV).[27] The XPS studies of pyridine and pyridine−carboxylic acid adsorbed on TiO_2 surface showed that the C 1s peak due to the pyridine ring and carboxylic group occurs at 284 and 289 eV,

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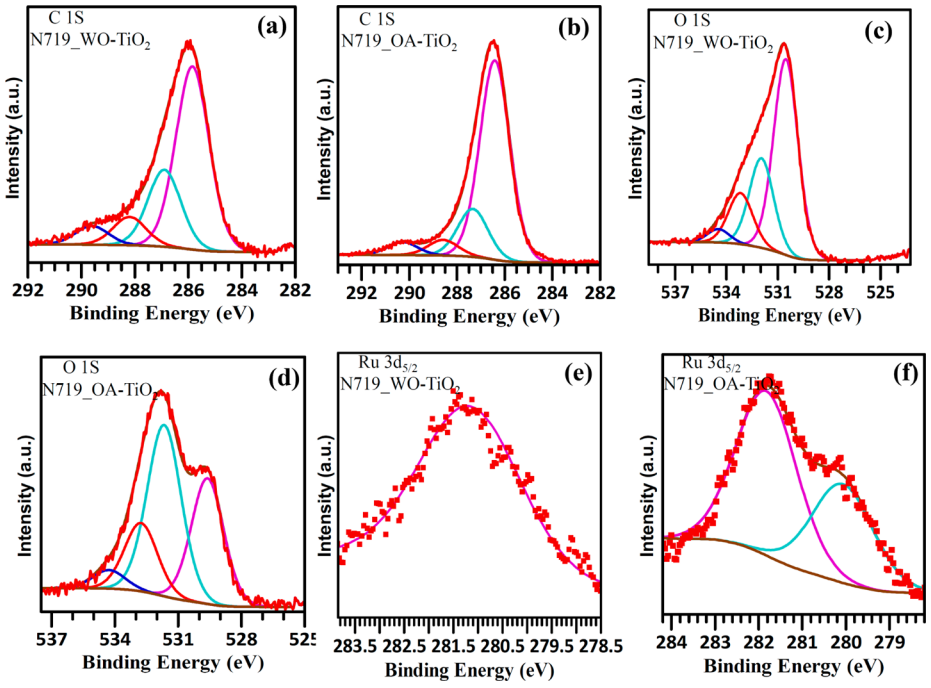

Figure 6. XPS spectra of (a, b) C 1s, (c, d) O 1s, and (e,f) Ru $3d_{5/2}$ states for N719 dye-sensitized WO-TiO_2 and OA- TiO_2 electrodes.

respectively.[28] However, in the case of dye-sensitized TiO_2, the main C 1s peak contains contributions from TBA and NCS groups as well. Therefore, the main C 1s peak at 285.9 eV is contributed by C═C, C−C, C−O, C═N, TBA, and Ru $3d_{3/2}$. The smaller peaks at 288.3 and 289.6 eV are attributed to O−C═O/C═O from COOH/COO^- groups and adsorbed CO_2, respectively.[29] The contributions from the adsorbed organic contaminants in the sample is associated with the peak at 286.9 eV.[30] C 1s XPS spectrum for dye-sensitized OA-TiO_2 electrodes upon deconvolution shows peaks similar to that of WO-TiO_2 electrodes loaded with N719 dye. However, a small shift in peak positions to higher binding energy is observed, indicating that the chemical environment of the C is changed when TiO_2 is treated with oxalic acid.

O 1s. The O 1s spectra can provide information about the bonding interaction and surface geometrical structure of the anchoring group. The O 1s XPS spectra of dye-sensitized WO-TiO_2 and OA-TiO_2 both exhibit asymmetrical broadening toward the higher binding energy side, as shown in Figure 6c,d. The deconvolution of the dye-sensitized TiO_2 shows four well-resolved peaks; FWHM for all the fitted peaks of N719_WO-TiO_2 and N719_OA-TiO_2 are 1.67 and 1.65 eV, respectively. The peaks at 530.5 and 531.9 eV are attributable to O^- and Ti−OH from the TiO_2 surface, respectively. The peak at 531.9 eV also has some contribution from a C═O group of the dye. The peak at 533.2 eV is assigned to COOH groups of the dye as well as Ti−OH_2. In addition, the peak at 534.5 eV can be attributed to the adsorbed organic contaminants. The observed deconvoluted peaks are in accordance with those reported in the literature.[15] When the N719 dye is loaded onto the WO-TiO_2 electrode, the peak corresponding to COOH and C═O groups of the dye are shifted to the lower binding energy side. This suggests that the chemical environment around O is different from that of the dye-loaded WO-TiO_2 electrode. The main feature of the O 1s XPS spectrum of N719 sensitized on OA-TiO_2 is the appearance of a new well-resolved peak at 529.5 eV and the disappearance of the peak corresponding to the O^- at the WO-TiO_2 surface. The new peak at 529.5 eV is assigned to a Ru−O bond.[31,32] The origin of this new peak may be due to the substitution of an NCS group of the dye by O^- of the oxalic acid. In addition, the disappearance of the O^- peak could be due to large electron scattering arising from the presence of oxalate ions and the dye layer on the WO-TiO_2 surface.

Ru $3d_{5/2}$. The splitting due to spin−orbit coupling is observed corresponding to the Ru of the dye, i.e., Ru $3d_{3/2}$ and Ru $3d_{5/2}$. The Ru $3d_{3/2}$ peak overlaps with the C 1s peak, and therefore, it is difficult to extract information by deconvolution of this peak. However, the Ru $3d_{5/2}$ peak reveals a shift of 4.2 eV from the Ru $3d_{3/2}$ peak.[27] Therefore, the Ru $3d_{5/2}$ peak can be utilized to extract further information about the chemical state of Ru. Figure 6e,f shows the XPS spectrum of Ru $3d_{5/2}$ for N719 dye-sensitized onto TiO_2 and OA-TiO_2. In the case of Ru, FWHM for all the fitted peaks of N719_WO-TiO_2 and N719_OA-TiO_2 are 1.63 and 1.64 eV, respectively. As shown in Figure 6e, the peak at 281.3 eV is attributed to Ru $3d_{5/2}$ arising because of the adsorbed N719 dye molecules on the WO-TiO_2 surface.[15] In the case of N719 loaded onto OA-TiO_2, the Ru $3d_{5/2}$ is deconvoluted into two peaks: the peak at 281.9 eV is attributable to the dye molecules absorbed on TiO_2 surface as in the case of the N719_WO-TiO_2 surface, while a well-resolved peak at 280.1 eV is assigned to the Ru−O bond. This Ru−O bond occurs because of a chemical bond between dye molecules and oxalate ions present at the OA-TiO_2 surface. This is in line with our earlier observation of FTIR data in which the signature of the Ru−O bond is observed in dye loaded onto the OA-TiO_2 electrode.

S 2p. The S 2p spectra of N719 dye loaded onto WO-TiO_2 show contributions from the sulfur of NCS groups due to spin−orbit coupling. This is similar to the reports by other researchers of two peaks that are observed and assigned to the contributions arising from the interaction between an NCS ligand and the dye. More strikingly, these peaks are not observed in the case of N719 dye-sensitized onto OA-TiO_2, as shown in Figure 7. This confirms our earlier assumption based

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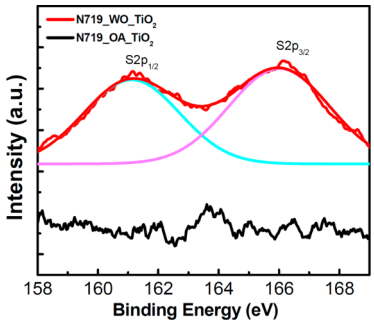

Figure 7. XPS spectra of S 2p states for N719 dye-sensitized WO-TiO_2 and OA-TiO_2 electrode.

on FTIR data and O 1s XPS data that an NCS group of the N719 dye is substituted by the O^- group of oxalate ions present at the OA-TiO_2 surface.

3.4. Extended X-ray Absorption Fine Structure. Because the NCS ligand is the weakest one in the dye molecule, it is likely to be replaced more easily than the other carboxylate or carboxylic acid group ligand upon absorption onto the TiO_2 surface, as was suggested by our FTIR and XPS data. To confirm this, we have focused on the Ru atom and its surroundings and recorded EXAFS spectra in the spectral region extending from 100 eV below to 1000 eV above a core level excitation k-edge of ruthenium. After the atomic background absorption subtraction, the EXAFS (χ) was extracted from the measured data. For a quantitative comparison of the local structural properties, the data was Fourier transformed to R-space to obtain radial distribution function. A set of EXAFS data analysis program available within the IFEFFIT software package has been used for fitting of experimental data using the following equation:

$$\chi = \sum_j \frac{N_j f_j(k) \exp[-2k^2\sigma_j^2] \exp\left[\frac{-2R_j}{\lambda}\right]}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

where $f(k)$ is the amplitude function for jth shell, $\delta(k)$ the phase shift, λ the electron mean free path, and N_j the number of neighboring atoms in the jth shell at a distance R_j from the central atom. For the fitting of the data, bond distance (R), co-ordination number (N), and disorder (Debye–Waller) factor (σ^2) were used as variable parameters. As shown in Figure 1a, N719 dye has a complex structure having two nitrogen atoms bonded to NCS groups and four nitrogen bonded to the bypyridine ligand. Owing to the complex structure, we have fitted only the first two peaks of the EXAFS spectra. In the case of N719_WO-TiO_2, these peaks correspond to the first two co-ordination shells having two and four nitrogen atoms, respectively, (Figure 8a). The parameters derived from fitting results are summarized in Table 2. As shown in the table, the bond lengths for Ru and nitrogen are 2.052 and 2.108 Å, respectively, for nitrogen bonded at NCS group and bypyridine, respectively. These bond lengths values are similar to those reported in the literature for free N719 dye.[33] A slight deviation of the bond lengths could arise because of the chemical bonding of N719 to the WO-TiO_2 surface.

However, for N719_OA-TiO_2, reasonable fitting could not be established under these assumptions, i.e., considering only the first two co-ordination shells of nitrogen atoms. When Ru–O bonding, as revealed from our XPS and FTIR data, was taken into account, the best fit was obtained (Figure 8b). Therefore,

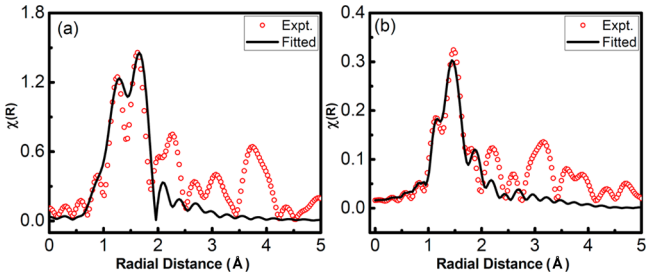

Figure 8. Fourier transforms of the EXAFS function $\kappa^3\chi(\kappa)$ for (a) untreated and (b) carboxylic acid treated dye-sensitized TiO_2 samples.

Table 2. Local Structural Parameters of the N719 Dye-Sensitized WO-TiO_2 and OA-TiO_2 Electrode as Derived from Fitted EXAFS Spectra

photoelectrode (coordination shell)	parameter	N719_WO-TiO_2	N719_OA-TiO_2
Ru–N(1)	N (atoms)	2	1
	R (Å)	2.052 ± 0.03	2.057 ± 0.04
	σ^2(Å^2)	0.005	0.005
Ru–N(2)	N (atoms)	4	4
	R (Å)	2.108 ± 0.02	2.125 ± 0.05
	σ^2 (Å^2)	0.003	0.006
Ru–O(1)	N (atoms)	–	1
	R (Å)	–	1.657 ± 0.06
	σ^2 (Å^2)	–	0.003

in this case, three co-ordination shells were considered during fitting; the first co-ordination shell has one oxygen atom, the second one nitrogen atom, and the third 4 nitrogen atoms. The Ru–N bond length deduced from the fitting curves are 2.057 and 2.125 Å, corresponding to nitrogen at the NCS group and bypyridine, respectively. These values are almost the same as those in the case of N719_WO-TiO_2. In addition, the Ru–O bond length, as estimated from the fitting, is 1.657 Å, which is in agreement with the values reported in the literature.[34]

3.5. Proposed Binding Scheme and Implication of Dye Binding on Photovoltaic Properties. On the basis of all spectroscopic and EXAFS data, we propose the binding of N719 dye on WO-TiO_2 and OA-TiO_2 surfaces. In the proposed model, N719 dye molecules adsorb on the WO-TiO_2 surface via the COOH groups as well as through some interaction via an NCS group, as shown in Figure 1f. However, the anchoring of the N719 dye via carboxylate/carboxylic acid groups is ruled out at the OA-TiO_2 surface. Since NCS is the weakest ligand in the N719 dye, the possibility of binding the N719 dye to the OA-TiO_2 surface through this group is greater than that via the carboxylate/carboxylic acid groups. This was complemented by our FTIR data, where a peak corresponding to NCS diminishes significantly. The same is also confirmed by EXAFS data, where a better fit is observed, corresponding to a Ru–O bond and not a Ru–NCS bond. Therefore, on the basis of these results, it is suggested that the N719 dye binds to the OA-TiO_2 surface through interaction between the Ru atom of the dye and O^- present at the OA-TiO_2 surface due to oxalate ions, as shown schematically in Figure 9.

The role of oxalic acid treatment of TiO_2 surface can be summarized as follows:

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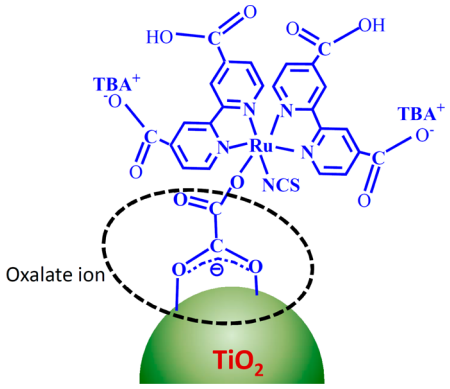

Figure 9. Schematic presentation of binding of N719 dye on oxalic acid treated TiO_2 surface.

(i) The binding of the N719 via carboxylate ions present at the OA-TiO_2 surface may allow more effective transfer of electrons because of increased conjugation as compared to untreated TiO_2 surface.[35]

(ii) Being a strong acid (pK_a 1.23), the oxalic acid chelates to Ti atoms on the TiO_2 surface via strong bridging binding and allows more dye loading onto the OA-TiO_2 electrode as described earlier.

(iii) In addition to providing assistance for more dye loading, the oxalic acid occupied sites also act as a passivation layer. This was confirmed in our earlier observations of impedance spectroscopy measurements, where an increased recombination lifetime is observed for OA-TiO_2-based DSSCs.[36]

4. CONCLUSION

In summary, we have studied the binding behavior of the N719 dye through detailed spectroscopic investigation, namely, FTIR, UV−vis, and XPS spectroscopy and EXAFS measurements. The UV−vis spectra imply a strong interaction between the dye and the oxalic acid, which assists more dye loading onto the OA-TiO_2 surface. The FTIR and XPS spectroscopy revealed that binding of N719 dye onto the OA-TiO_2 surface is different from that onto the WO-TiO_2 electrode. The N719 dye binds to the OA-TiO_2 surface through interaction between the Ru atom of the dye and O^- present at the OA-TiO_2 surface due to oxalate ions. On the other hand, the binding of the dye to untreated TiO_2 surface occurs through carboxylic acid group. The results were confirmed by EXAFS measurements, which also show reasonable fitting for Ru−O bond in the case of N719_OA-TiO_2 electrodes. The different binding mechanism of the N719 dye on the oxalic acid treated TiO_2 electrode resulted in improved photovoltaic characteristics of DSSCs based on N719 dye-sensitized OA-TiO_2 electrodes.

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Notes

The authors declare no competing financial interest.

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