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Spectroscopic Investigations on Degradative Processes of c*is*-Bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) Ruthenium(II) Anchored on Anatase TiO_2 Surface

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Fate pathway of cis-*Ru(dcbpy)$_2$(NCS)$_2$; dcbpy = 2,2′-bipyridyl-4,4′-dicarboxylic acid, attached to the anatase titanium dioxide surface was investigated from time-course of UV-vis absorption spectra as well as FT-IR spectra under photo-irradiation (AM1.5) or under dark at different temperatures (−18°C, 25°C, and 100°C). Series transformation reactions of two NCS ligands to CN, one by one, were evident from those spectral changes and characteristic FT-IR vibrational frequencies.*

Keywords deterioration of dye-sensitized solar cells; transformation of coordinated ligands; nano-crystalline titanium dioxide films

Introduction

Fate pathway of sensitizing dye molecules is becoming common concern towards a robust dye-sensitized solar cell (DSSC). DSSC of *cis*-Ru(dcbpy)$_2$(NCS)$_2$ or N3; dcbpy = 2,2′-bipyridyl-4,4′-dicarboxylic acid, has recorded as high as 11% of conversion efficiency under AM1.5 condition [1, 2]. Due to such high capability and ready availability, N3 has acquired an important role in device evaluation studies of DSSC. On the other, many are known to induce performance deterioration through decomposition of dye, electrode erosion, leakage of interior electrolyte solution and so on. This paper introduces our recent spectroscopic studies on photo- and thermally induced degradation of N3 dye attached to anatase titanium(IV) oxide, TiO_2. N3 degrades to dicyano complex in two-step manner accompanied with recognizable changes in UV-vis absorption spectra as well as IR absorption spectra.

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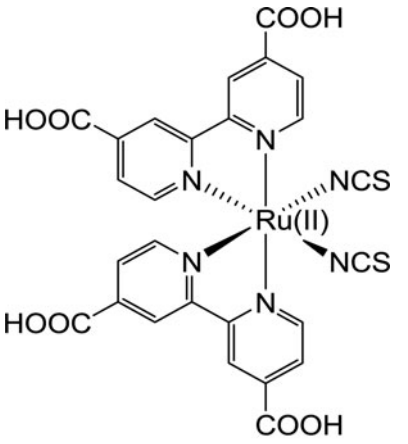

N3

Experimental

N3 was synthesized according to literature [3]. A mixture of a colloidal nano-TiO_2 (10 wt%) [4] and PEG10000 (5 wt%) was spin-casted on a square glass, first annealed at 200°C for 10 min and then fired at 350°C for 20 min to form a transparent anatase film with sub-μm thickness (TiO_2/glass). For dyeing, TiO_2/glass was immersed in a solution of N3 (5 mg in 10 mL of methanol) overnight. Excess dye was thoroughly rinsed off with methanol (1 mL × 5 times) and the plate was air-dried before degradation experiments. For photo-degradation was the sample irradiated under a solar simulator (SAN-EI Electric XES-40S1) with 1000 W/m^2 light power at ambient temperature. Thermal degradation was carried out at three different temperatures, −18°C in a refrigerator, 25°C in a thermo-stated chamber (BAS TB-1), and 100°C in a convection oven. UV-VIS spectra were recorded by Agilent HP8453 diode array spectrophotometer. FT-IR spectra were measured by JASCO FT/IR-4100 or Perkin-Elmer Spectrum One system.

Results and Discussions

Status of N3 Adsorbed on TiO_2

UV-vis absorption of dyed TiO_2 films (N3-TiO_2/glass) were investigated (Figure 1). Compare to the methanol solution, metal to ligand charge transfer (MLCT) absorption bands on TiO_2 are shifted to red (λ_{max} = 382 nm, 520 nm in methanol → λ_{max} = 391 nm, 522 nm on TiO_2) and broaden. Ammount of N3 on TiO_2 was separately determined as 8.5 × 10^{-9} mol/cm^{-2}. Suppose 500 nm of penetration thickness and 50 m^2/g of BET specific surface area, molecular occupation area is roughly calculated to be ca. 1.9 nm^2/molecule, suggesting a scarce chance of bimolecular interaction between surface adsorbed molecules. Red-shifting and broadening indicate destabilization of the ground-state dipole due to lack of solvation and variety of molecular orientation versus agglomerate TiO_2. Figure 2 shows FT-IR spectrum of N3-TiO_2/glass. The peak at 2102 cm^{-1} is attributed to CN stretching of NCS ligand [5]. CO stretching of carboxylate -COO^- and that of carboxylic acid -COOH are found at 1602 cm^{-1} and 1728 cm^{-1}, respectively. The former broaden peak has been

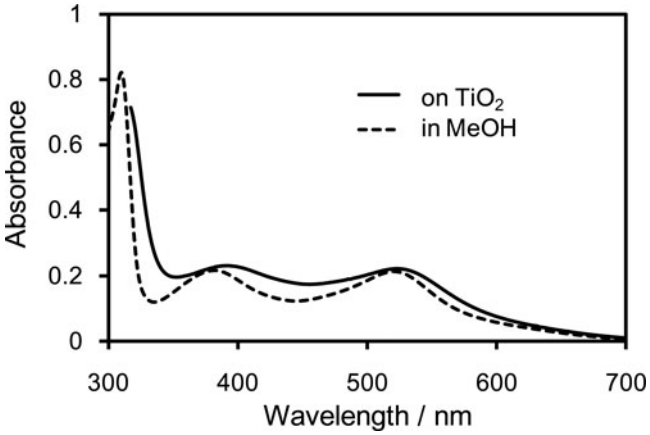

Figure 1. . UV-vis spectra of N3-TiO_2/glass and a solution of N3 in methanol.

assigned for anti-symmetric -COO^- vibration (ν_{as}), while the symmetric -COO^- vibration (ν_s) exhibits at 1369 cm^{-1} [6]. Coordination mode of -COO^- to TiO_2 can be estimated from the subtraction $\Delta = \nu_{as}$ - ν_s, and the present value $\Delta = 233$ cm^{-1} indicates bridged or bidentate type coordination. Nearby the CN stretching of N-coordinated NCS, a peak is present at 2014 cm^{-1}. In the case of a KBr pellet sample without TiO_2, a similar side peak was located at 1987 cm^{-1}, identifiable as S-linkage isomer [7]. The amount of S-linkage isomer in our N3 sample should be less than 4% calculated from IR peak area. The side peak becomes more evident when N3 is attached to TiO_2. According to the previous photoelectron spectroscopic study, about 60% of N3 molecules interact with TiO_2 surface through the terminal sulfur atom of NCS [8]. From recent SERS analysis, this interaction results red-shifting of ν(CN) in N719 case. [9]. Observed peak position 2014 cm^{-1} is somewhat higher than that of reported value for S-linkage isomer, 1992 cm^{-1} or that of the KBr sample. We thus tentatively presume that NCS interacting with TiO_2 contributes to this absorption.

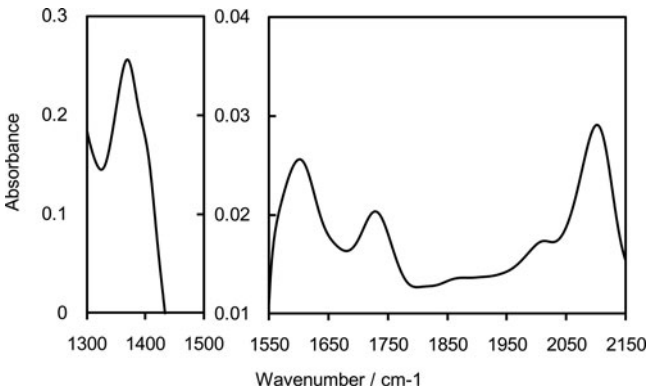

Figure 2. FT-IR spectrum of N3-TiO_2/glass. Region between 1530 cm^{-1} and 1430 cm^{-1} is affected by interference fringe from glass substrate.

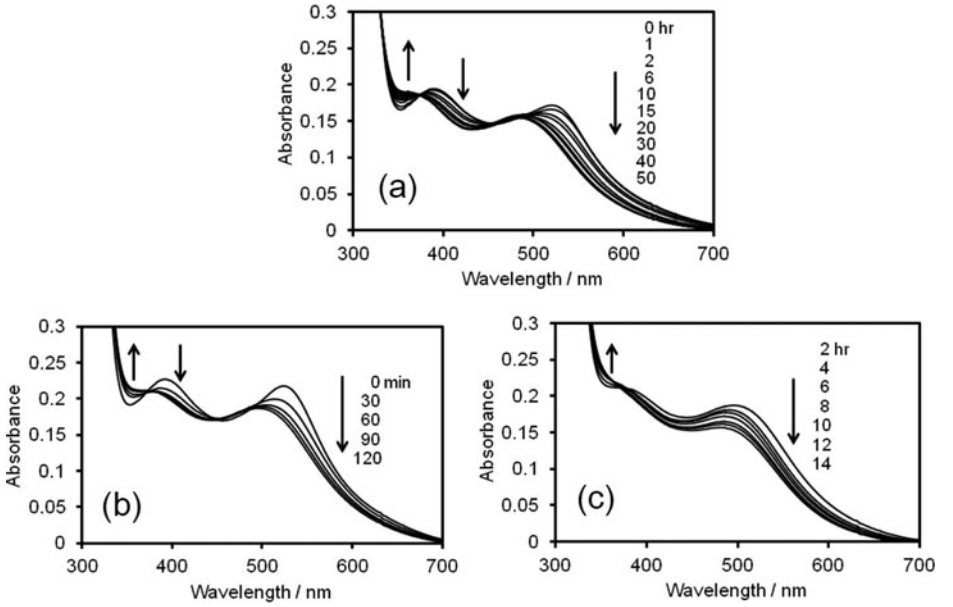

Figure 3. Temperature effect of degradation behaviors in UV-vis absorption spectra of N3-TiO_2/glass. (a) 0∼50 h at 25°C, (b) 0∼120 min at 100°C, (c) 2∼14 h at 100°C

Thermal and Photo-induced Degradation of N3 on TiO_2 Surface

UV-vis absorption spectra of N3-TiO_2/glass were collected for the samples stored at −18°C, 25°C and 100°C under dark, atmospheric condition. At 25°C, MLCT absorptions shifted gradually to blue accompanied with an isosbestic point at 372 nm. Peaks at 391 nm and 522 nm moved to 360 nm and 484 nm after 50 hrs as shown in Figure 3(a). At −18°C, no apparent spectral change was observed up to 16 days. At 100°C, the blue shift of MLCT was accomplished within 2 hrs, then followed by steadily bleaching (Figure 3(b) and (c)). Initial stage may involve small contribution of additional side-reactions, since the isosbestic point was not clearly seen as 25°C. Thus the thermal degradation of N3 on TiO_2 proceeds in two-step manner through a stable intermediate structure resembling MLCT of N3.

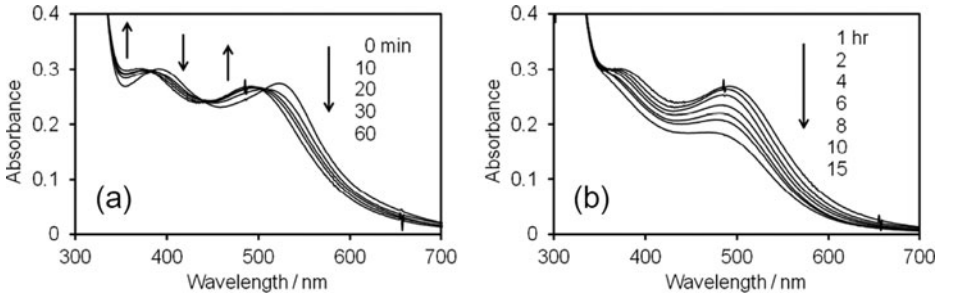

Figure 4. Photo-degradation behaviors in UV-vis absorption spectra of N3-TiO_2/glass. (a) 0∼60 min, (b) 1∼15 h.

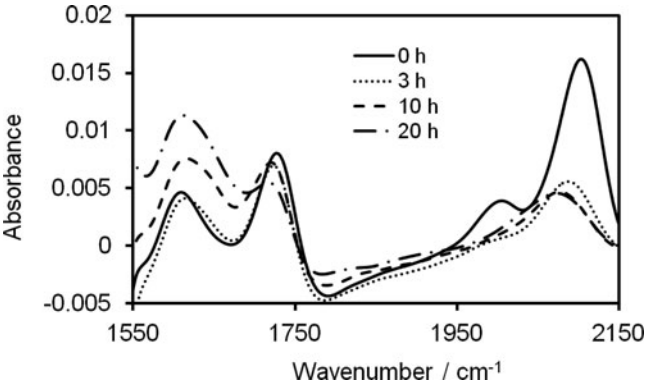

Figure 5. Change of FT-IR spectra of N3-TiO_2/glass under photo-irradiation.

Photo-irradiation also resulted 2-step spectral changes similar to the thermal degradation at 100°C. MLCT absorptions shifted to blue for the initial 60 minutes, but then followed by a long attenuation process of the MLCT absorption. (Figure 4). In FT-IR measurements was found that the absorption of NCS at 2102 cm^{-1} decreased very quickly to one third of the original within 3hrs, then gradually shifted the energy down to 2073 cm^{-1} (Figure 5) in good agreement with ν(CN) of $Ru(bpy)_2(CN)_2$, 2082 cm^{-1} [10]. Broad absorption around 2014 cm^{-1} was banished after 10hrs, which is presumably accounted as a NCS ligand interacting with TiO_2 through S-atom. From above results, we conclude that (1) the first stage of degradation is transformation to monocyano complex $Ru(dcbpy)_2(NCS)(CN)$ which has blue-shifted MLCT absorptions compare to N3, (2) further irradiation or high temperature gives rise to the dicyano complex $Ru(dcbpy)_2(CN)_2$ and banishment of interaction between NCS and TiO_2. Accordantly, photo- and electrochemical transformation of metal coordinated NCS to CN have been reported for solution systems [11, 12]. Isomerization to the S-linkage complex has been eliminated by the fact that it is formed above 135°C [7], and no increments in the corresponding IR was observed actually.

Concluding Remarks

Photo-excitation of N3 on TiO_2 surface resulted bleaching of the MLCT absorption through series transformation of two NCS ligands to CN. In atmosphere, formation of oxidized Ru(III) form of N3 is highly favorable under photo-irradiation, which we propose as a possible precursor for subsequent ligand transformation reactions. We also propose that keys to suppress the degradation pathway would be to sustain the most stable oxidation state through fast redox cycles and/or to stabilize the molecular structure by introducing appropriate interactions through intra-molecular ways or inter-molecular ways. Advanced molecular engineering and reaction design are strongly requested for developing robust solar cell systems.

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