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Infrared Spectroscopic Study of α-Cyano-4-hydroxycinnamic Acid on Nanocrystalline TiO_2 Surfaces: Anchoring of Metal-Free Organic Dyes at Photoanodes in Dye-Sensitized Solar Cells

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Adsorption structures of the self-assembled thin films of α-cyano-4-hydroxycinnamic acid (CHCA) anchoring on TiO_2 surfaces have been studied by using temperature-dependent diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy. From the presence of the strong ν(COO^-) band at ~1390 cm^{-1} along with the disappearance of the OH bands in the carboxylic acid group in the DRIFT spectra at room temperature, CHCA appeared to adsorb onto TiO_2 surfaces as a carboxylate form. The absence of the out-of-plane benzene ring modes of CHCA in the DRIFT spectra suggests a rather vertical orientation of CHCA on TiO_2. Above ~220 °C, CHCA seemed to start to thermally degrade on TiO_2 surfaces referring from the disappearance of most vibrational modes in the DRIFT spectra, whereas the ν(C≡N) bands were found to remain relatively conspicuous as the temperature increased even up to ~460 °C.

Key Words: Cyanoacrylic acid, Metal-free organic dye, Self-assembly, TiO_2, Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

Introduction

Dye-sensitized solar cells (DSSCs) have been extensively investigated due to their potential application in a low-cost solar-to-electricity conversion system as an alternative to inorganic silicon semiconductors.[1] Designing and synthesizing suitable dyes for a dye-covered TiO_2 photoanode thin film attracted considerable attention to the discipline of material sciences, since the performance of DSSCs generally depends on the relative energy levels of the sensitizers.[2]

Although Ruthenium (II) polypyridyl complexes[3,4] have been widely utilized as photosensitizers, metal-free organic dyes were being applied in DSSCs because of their considerably low cost-effective preparation in recent years.[5] There have been a few reports on the metal-free organic dyes whose solar-to-electric power conversion efficiencies are comparable to those of Ruthenium(II) complexes.[5] In most cases of organic dyes, aryl amines as donor groups and cyanoacrylic acid as the acceptor have been commonly used in metal-free DSSC systems. Since the cyanoacrylic acid group can anchor the dyes to the surface and direct the electronic transfer between the donor and the conduction band of the semiconductor,[5] it should be significant to study how this anchoring group binds on TiO_2 surfaces.

Thin films have received much attention due to their potential applications in electronic devices, colorimetric sensors, and surface-sensitive probes.[6] Although various techniques have been applied to study semiconductor/adsorbate interfaces, vibrational spectroscopy is one of the most useful tools to provide structural information about adsorption phenomena on the surfaces.[7] In addition temperature-dependent interfacial vibrational spectroscopic tools can provide information on the energetics or phase transition of adsorbates on surfaces.[8-10]

Despite several spectroscopic reports on Ruthenim (II) complexes,[11-14] there has not been either investigation on the spectroscopic study or the thermal degradation and the resulting change in molecular architecture in detail for a cyanoacrylic acid film fabricated on the TiO_2 surfaces to the best of our knowledge. In this present work, temperature-dependent diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy was applied to understand the nature of adsorption and structural change of α-cyano-4-hydroxycinnamic acid (CHCA) on the TiO_2 surfaces. This work should help to elucidate the stability of the different anchoring of metal-free organic dyes in DSSCs on the TiO_2 surfaces.

Experimental Section

CHCA (99%) was purchased from Sigma Aldrich and used without further purification. For the self-assembly of CHCA on TiO_2 powders (Degussa P-25), approximately 0.050 g of TiO_2 powder was placed in a clean vial. A stock solution of CHCA with a 3 ~ 5 mL of 10 mM ethanolic solution was immersed into TiO_2 powders for overnight. The sample was centrifuged at 1200 rpm (Hanil micro 17TR) and dried for 4 ~ 5 hr at room temperature. After the solution phase was decanted, the remaining solid particles were washed with a large quantity of ethanol and left to dry in ambient conditions.

A portion of the CHCA-assembled powdered sample was transferred onto a DiffuseIR heated chamber (Pike Technologies) equipped with a temperature controller to control temperatures up to 460 °C. The infrared spectra were obtained using a FT-IR spectrometer with a maximum resolution of 0.09 cm^{-1} (Thermo Nicolet 6700). A total of 64 or 128 scans were measured in the range of 800 - 4000 cm^{-1} with a nominal resolution of 4 cm^{-1}. The infrared measurements are described in the previous report.[15] At each temperature, the sample was heated for approximately three minutes. The spectra were measured by heating up the temperature by ~40 °C. Thermogravimetric analysis was carried out in N_2 atomosphere by heating solid samples at a rate of 10 °C/min up to 800 °C using a SCINCO TGA

N-1500 analyzer.

Results and Discussion

Figure 1 shows the diagram of fundamental operating principle in a dye-sensitized solar cell which consists of a dye sensitizer-covered TiO_2 photoanode thin film.[5] Nowadays metal-free organic dyes with the cyanoacrylic acid group as the acceptor and linker on TiO_2 surfaces have been applied in DSSCs. To investigate how the cyanoacrylic acid functional groups can anchor the dye to the TiO_2 surfaces, we performed an infrared spectroscopic study.

Infrared spectra of CHCA. Figure 2(a) shows an external reflection absorption spectrum of CHCA in its solid state at room temperature. Their peak positions are listed in Table 1, along with the appropriate vibrational assignments. Our assignment is mainly based on previous literatures.[16] The vibrational bands at 1671 cm^{-1} can be ascribed to the C = O stretching bands. The band at ~3300 cm^{-1} could be ascribed to the OH band. The weak band of the CH band at ~3040 cm^{-1} may be ascribed to the benzene ring C-H stretching modes. The inset shows a magnified view of the 3000 - 3100 cm^{-1} wavenumber region for a better illustration. The vibrational features appeared in the wavenumber region between 2500 and 3000 cm^{-1} are assumed to be due to the CHCA dimer *via* the intermolecular hydrogen bonding as in the case of benzoic acid.[17-19]

Infrared spectra of CHCA on TiO_2 powder surfaces. On TiO_2 surfaces, quite a few strong vibrational bands such as those at 1598 and 1577 cm^{-1} could be ascribed to the in-plane benzene ring modes. It is noteworthy that the ν(CH) bands are observed at ~3070 cm^{-1}, albeit weakly, in the DRIFT spectra. In the surface-enhanced Raman (SERS) spectra, it has been previously documented that the presence of the ν(CH) band indicates a vertical orientation of the aromatic adsorbates.[20,21] These observation might indicate a perpendicular orientation of CHCA on TiO_2 surfaces. Although the ν(CH) band of CHCA in itself was found to be weak in its spectrum as shown in the inset of Fig. 2, it reproducibly appeared in the 3040 - 3070 cm^{-1} wavenumber region. Along with the presence of the ν(CH) band, the adsorption geometry was mainly inferred from the vibrational analysis of the relative intensities or enhancements of the in-plane and out-of-plane modes in the aromatic ring on TiO_2 surfaces. Due to the absence of many modes representing the molecular symmetry, we could not apply the surface selection rules[21] for the present study. From the selection rule,[21] it was reported that the out-of-plane modes should be weakened for the perpendicular orientation of adsobates on surfaces. The absence of the out-of-plane benzene ring modes of CHCA in the DRIFT spectra also supports a rather vertical orientation of CHCA on TiO_2. In the DRIFT spectrum at room temperature as shown in Figure 2(b), due to the antisymmetric and symmetric ν(COO^-) modes, the two bands were found at 1514 and 1393 cm^{-1}, respectively. Along with the absence of the OH bands in the carboxylic acid group, these results clearly indicate that CHCA should adsorb on TiO_2 powder surfaces in its carboxylate form. But it is also possible that a monodentate binding structure of CHCA on TiO_2 powder surfaces. In this case, the OH band may appear when the surface condition or temperature may be changed. It is intriguing that a broad peak that can be ascribed to the OH stretching band was observed at ~3356 cm^{-1}, albeit weakly. The weakness of the OH band supports the presumption that CHCA should bind to TiO_2 powder surfaces as a bidentate carboxylate form. It is likely that multiple binding scheme may be possible when CHCA adsorb on TiO_2, since powder surfaces have a mixture of multiple crystalline facets of anatase and rutile phases. To further investigate the binding scheme and adsorption energetics of CHCA TiO_2 surfaces, we performed a temperature-dependent DRIFT spectroscopic study.

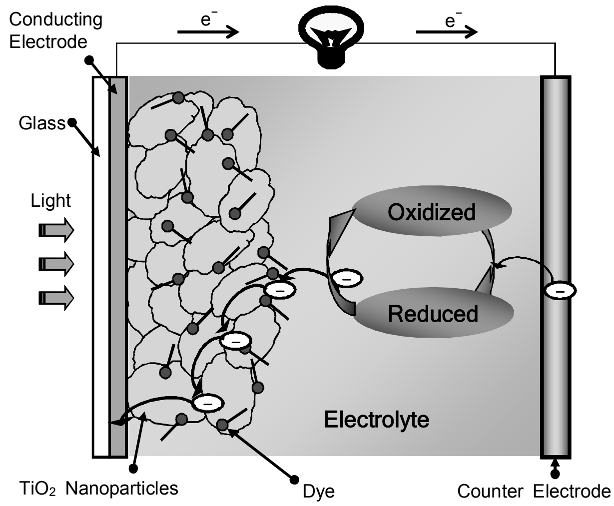

Figure 1. Diagram of fundamental processes in a dye-sensitized solar cell.

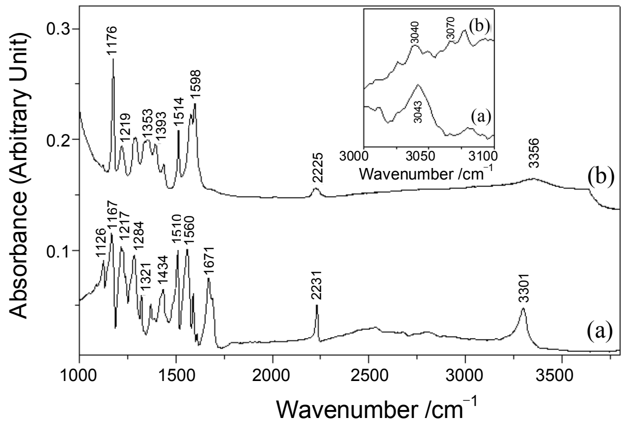

Figure 2. Infrared spectra of CHCA (a) in its solid state and (b) after the assembly on TiO_2 powder surfaces.

Temperature-dependent infrared spectra of CHCA on TiO_2 powder surfaces. Figure 3 shows the temperature-dependent infrared spectra of CHCA on TiO_2 powder surfaces, in the temperature range between 20 and 460 °C. It was found that all the vibrational bands almost disappeared above ~420 °C. At the temperatures between 220 and 420 °C, most ring modes of CHCA were found to become weak considerably. It is interesting that the CN stretching band did remain quite strongly even at higher temperatures, whereas the other modes disappeared substantially. It may be possible that the thermal decomposition of

Table 1. Spectral Data and Vibrational Assignment of CHCA[a]

CHCA		Assignment[b]
ATR (solid)	DRIFT on TiO_2	
3301	3356	OH stretching
3043w	3040w	ring C-H stretching (i.p.)
2231	2225	$C \equiv N$ stretching
1671		C = O stretching
1610	1615sh	ring CC stretching (i.p.)
1590	1598	ring CC stretching (i.p.)
1560	1577	ring CC stretching (i.p.)
	1514	$\nu_{as}(COO^-)$
1510	1514	ring CC stretching (i.p.)
1496		bending (OH)
1434	1438	ring CC stretching (i.p.)
	1393	$\nu_s(COO^-)$
1369	1353	ring CC stretching (i.p.) or CH wagging in C = C
1321		C-OH stretching in acid
1284	1289	ring CC stretching (i.p.)
1217	1219	ring CC stretching (i.p.)
1167	1176	ring CC stretching (i.p.)
1126		O-H bending in acid

[a]Unit in cm^{-1}. Abbreviation: w; weak, sh; shoulder, ν_s; symmetric stretching band, ν_{as}; asymmetric stretching band, i.p.: in plane mode. [b]Based on ref. 16.

CHCA may lead to the CN group directly binding to the surfaces, resulting in strong spectral intensities. Figure 4 shows a magnified view of the CN stretching region. As the temperature increased the CN stretching region became much larger broadened above 140 °C. The band positions were shifted from 2225 to 2231 cm^{-1} close to the neutral state. Although not shown here, the Ruthenium 505 dye (*cis*-dicyano-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) containing the two cyano groups showed quite different spectral behaviors depending on the temperature. At ~220 °C, the bands at 1350 and 1390 cm^{-1} which could be ascribed to the symmetric $\nu(COO^-)$ modes became quite weakened in the DRIFT spectrum. Also, the ν(OH) mode at ~3600 cm^{-1} remained conspicuous. It is interesting that the OH bands became quite stronger at higher temperature above ~300 °C. Referring from the different spectral position of the OH band at ~3300 cm^{-1} for CHCA, it is likely that these OH bands came from the OH group remaining near to the TiO_2 surfaces. As temperature increased, it is also possible that the monodentate structure should become also favorable on TiO_2 surfaces, resulting in strong intensities of the OH bands, although a bidentate structure is preferable at room temperature. Figure 5 illustrates thermogravimetric analysis of CHCA. Above ~220 °C, CHCA seemed to start to thermally degrade on TiO_2 surfaces as shown in Fig. 5(a) as consistent with the DRIFT spectra. As shown in Fig. 5(b) CHCA did not exhibit much weight loss, which may be in line with the observation that $\nu(C \equiv N)$ bands were found to remain relatively conspicuous as the temperature increased even up to ~460 °C in the DRIFT spectra. It seems that the decomposition behaviors of CHCA appear to be dissimilar from those of Ruthenium dyes which showed significant loss above 300 °C from the previous report.[22]

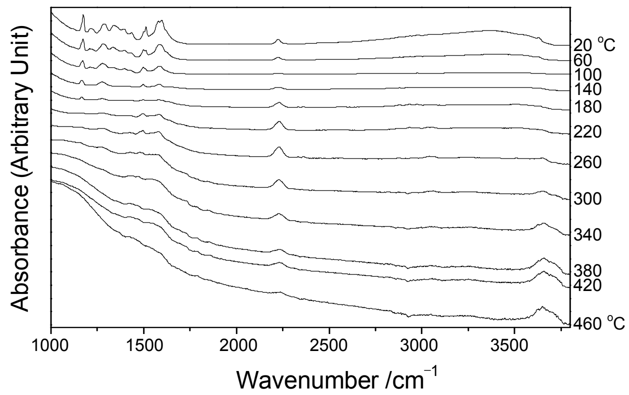

Figure 3. Infrared spectra of CHCA on TiO_2 powder surfaces, taken at increasing temperatures at 20 - 460 °C.

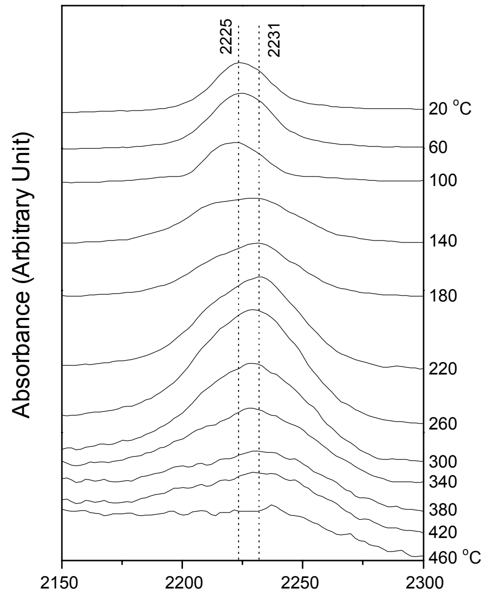

Figure 4. A magnified view of the CN stretching region in the infrared spectra of CHCA on TiO_2 powder surfaces at different temperatures.

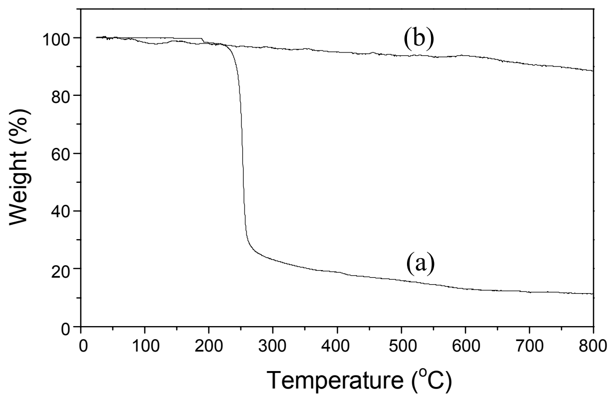

Figure 5. Thermogravimetric analysis of (a) CHCA and (b) CHCA on TiO_2.

Conclusions

The adsorption of the self-assembled thin films of CHCA anchoring on TiO_2 surfaces has been examined using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. At room temperature, CHCA appeared to adsorb on TiO_2 surfaces *via* its carboxylate group from the strong appearance of the carboxylate stretching band in the infrared spectra. The surface geometry of CHCA was assumed to be a rather perpendicular orientation on TiO_2 surfaces due to the presence of the strong inplane ring modes in the DRIFT spectra. The decomposition behaviors of CHCA appeared to be different from those of Ruthenium dyes from our DRIFT and thermogravimetric analysis.

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