

Ultrafast Stepwise Electron Injection from Photoexcited Ru-Complex into Nanocrystalline ZnO Film via Intermediates at the Surface

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Ultrafast electron injection processes from photoexcited Ru-complex, *cis*-bis-(4,4'-dicarboxy-2,2'-bipyridine)-dithiocyanato ruthenium(II), [Ru(dcbpy)₂(NCS)₂] (N3), into nanocrystalline ZnO film have been investigated by observing the femtosecond transient absorption in the visible and near-IR range (600–2000 nm). After photoexcitation of the metal-to-ligand charge-transfer band of the adsorbed N3 dye, a very broad transient absorption band ranging from 600 to 1500 nm having a maximum at around 1200 nm rose in less than 100 fs. Subsequently, the absorption band in the near-IR showed a multiexponential decay with time constants of ~5 ps, ~150 ps, and >1 ns, leading to the generation of conductive electrons which absorb at around 2000 nm. Therefore, this initial broad band is considered to be due to the intermediates during the electron transfer from excited N3 to the conduction band of ZnO. The origin of the broad absorption band around 1200 nm is discussed in terms of a charge-transfer complex between the excited N3 dye and surface states of ZnO.

Introduction

Ultrafast electron transfer from photoexcited dyes into metal oxide semiconductor crystals is of great significance in surface photochemistry and photophysics as well as in applied fields such as the development of dye-sensitized photovoltaic cells^{1–5} and photocatalytic materials.⁶ It is one of the primary processes in dye-sensitized solar cells (so-called Grätzel cell⁷). In the last several years, the electron injection process from photoexcited Ru-complexes such as N3 dye into TiO₂ nanocrystalline semiconductor films has been investigated extensively by means of ultrafast spectroscopic techniques. It has been found that electron injection takes place on a time scale of 100 fs or shorter,^{8–11} although slower picosecond electron injection can be observed additionally as a minor component. After photoexcitation of the N3 dye adsorbed on TiO₂, the transient absorption bands of its ground state (as bleach), excited states (N3*), and oxidized state (N3⁺) are observed, which are overlapped with each other in the visible wavelength range (400–900 nm). In addition, in the mid-IR range (3–7 μm) a broad absorption band due to free electrons in the conduction band is observed.¹⁰ Ultrafast generation of N3⁺ and the free electrons in TiO₂ is basically considered as due to the existence of a large number of electron acceptor states energetically matched with the electron donor states, that is, LUMO of N3. The continuous energy levels in the conduction band of TiO₂ work as acceptor states. These states are delocalized and give rise to electron transfer to delocalized states. On the other hand, the surface of the nanoparticles is not well defined. There should be many defects that give localized states and can work as acceptor levels.¹² The surface states will cause electron transfer to localized states. Since electron acceptor states have such a

variety and since it is difficult to characterize the nature of injected electrons in a metal oxide by optical absorption, it is still not well understood how the electron from N3* is received by TiO₂.

ZnO is a metal oxide having energy levels of the conduction and valence bands similar to those of TiO₂ and is actually used as one of the alternatives to TiO₂ in many research studies for developing photovoltaic solar cells.^{13,14} The dynamics of photoinduced electron injection into ZnO has been investigated by two groups. Asbury et al. reported in 1999 that the transient absorption in the mid-IR range (5 μm) due to electrons injected from N3* into ZnO showed a slow rise up to 1 ns, and discussed a multiexponential electron injection process.¹⁵ Bauer et al. reported in 2001 by probing the absorption of oxidized N719 at 770 nm that the electron injection occurred in subpicosecond.¹⁶ The structure of N719 dye is very similar to that of N3 dye except that the counterions (protons) are replaced by TBA (tetrabutylammonium). This difference in the time scale by 3 orders of magnitude implies that the electron injection process from N3* into ZnO is not simple and may involve some intermediate state between electron ejection from N3* and generation of conductive electrons in ZnO.

We have focused our attention on the near-IR range. In this range, the absorption of photogenerated electrons in metal oxides can be observed, while those of N3 dye in the ground and oxidized states are not. This reduces the difficulty of analysis that arises from spectral overlaps. It has been reported that N3* can be detected in the near-IR range.^{11,17} The transient absorption spectrum of N3* up to 1600 nm was examined in this paper for a solution sample. In addition, absorption bands due to intermolecular interactions such as charge transfer and charge resonance, if any, are also expected to appear in this spectral region.¹⁸ In this paper, we report the first observation of a strong absorption band around 1200 nm originating from the intermediates during the electron transfer from N3* into ZnO. This band appeared in less than 100 fs, and then decayed in the pico-

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and subnanosecond range with the simultaneous rise-up of an absorption band due to conductive free electrons at around 2 μm . A discussion will be made on the electron injection dynamics along with the origin of the observed absorption band around 1200 nm in terms of a charge-transfer complex of the excited N3 dye and surface states of ZnO. Comparison with the well-known N3-to-TiO₂ electron injection is also made.

Experimental Section

Samples. The samples measured are ZnO nanocrystalline films adsorbed with *cis*-bis-(4,4'-dicarboxy-2,2'-bipyridine)-dithiocyanato ruthenium(II), [Ru(dcbpy)₂(NCS)₂] (generally called N3). We abbreviate this sample as N3/ZnO. The film was prepared on a glass substrate by a similar procedure reported elsewhere,¹⁹ and its thickness was about 5 μm . The dye was loaded by just immersing the bare ZnO film into an N3 dye solution, and the loading amount was adjusted by the immersing time. Absorption spectra of N3/ZnO could be understood as a superposition of absorptions of N3 (metal-to-ligand charge-transfer transition) and ZnO (band gap transition), although the peak of the MLCT transition was shifted to 505 nm compared with that of a methanol solution sample, viz., 535 nm. This indicates that N3 in the ground state does not form a CT complex with ZnO surface states. The LUMO of N3 is known to be located about 0.35 eV above the bottom of the conduction band of ZnO.

Femtosecond Transient Absorption Spectroscopy. The light source for pump-probe transient absorption measurements is a regenerative/multipath double-stage amplifier system of a Ti:sapphire laser (800 nm wavelength, 50 fs fwhm pulse width, 1.4 mJ/pulse intensity, 1 kHz repetition, Super Spitfire, Spectra Physics) combined with two optical parametric amplifiers (OPA-800, Spectra Physics). For a pump pulse the OPA output at 540 nm wavelength with intensity of several microjoules per pulse was used, and for a probe pulse the OPA output or white-light continuum generated by focusing the fundamental beam into a sapphire plate was used. The probe beam was focused at the center of the pump beam on the sample and then detected by a Si, InGaAs, or MCT photodetector after passing through a monochromator (Spectra Pro 150, Acton Research). A part of the probe beam was split and detected by another set of a monochromator and a photodetector. The two output signals of the photodetectors were analyzed with three boxcar integrators and an analogue processor (SR 245, Stanford Research) to get absorbance change, typically 10^{-3} O.D. It should be noted that two-photon band-gap excitation by the 540 nm pump laser was neglected, since a bare ZnO film did not show any transient absorption under the present excitation condition. All measurements were performed at 295 K. The nanosecond transient absorption spectroscopic system was described in detail elsewhere.²⁰

Results and Discussion

To analyze the dynamics of the electron injection process in N3/ZnO, the spectra of N3* and N3⁺ are necessary. It is already known for N3 adsorbed on nano-crystalline ZrO₂ and TiO₂ films that N3* gives a transient absorption band at around 700 nm and N3⁺ at around 800 nm.^{8,11} However, the spectrum of N3* in the near-IR region (1000–3000 nm) has not been reported. Thus we measured the transient absorption spectrum of N3 up to 1600 nm in deuterized methanol solution using the nanosecond laser system, where the delay time was set to be just after excitation of a 10 ns pulse duration. The spectrum obtained is

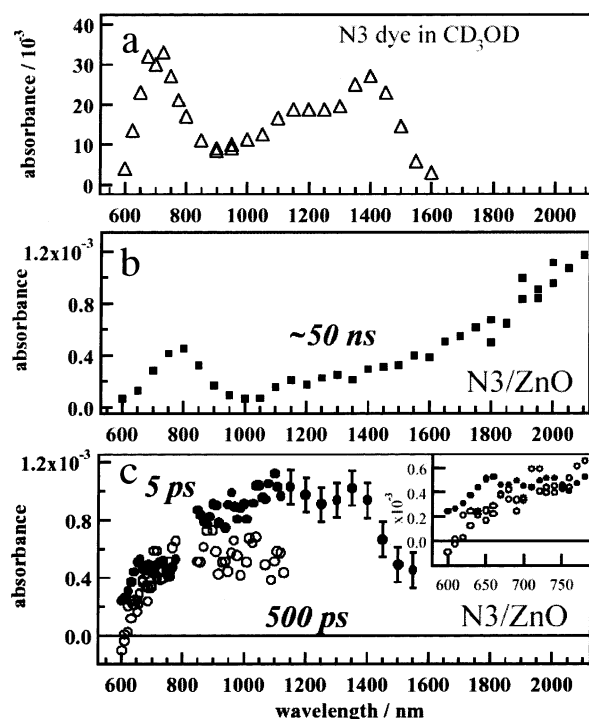


Figure 1. (a) Transient absorption spectrum of N3 dye in deuterized methanol solution at ~ 10 ns delay time. (b) Transient absorption spectrum of N3/ZnO (nanocrystalline ZnO film adsorbed with N3 dye) at 50 ns delay time after excitation. (c) Transient absorption spectra of N3/ZnO at 5 (closed circle) and 500 (open circle) ps delay times after excitation. The inserted figure is for a clearer view of the visible region.

shown in Figure 1a. The concentration of N3 was 4×10^{-4} M and the optical path length was 1 mm. No significant steady-state absorption due, for instance, to vibrational overtones was found up to 1800 nm for the solvent. In addition to the reported absorption peak at 700 nm, another absorption peak was observed at 1400 nm in the near-IR region. The intensities of the peaks at 700 and 1400 nm are comparable. The transient absorption spectrum for N3/ZnO at 50 ns after excitation was also measured using the nanosecond laser system, and is shown in Figure 1b. The observed peak at 800 nm clearly indicates the existence of N3⁺. In the longer wavelength region, another band is observed. The absorption band having the increasing intensity with wavelength can be assigned to the transition of free electrons in the conduction band including shallowly trapped electrons to higher states in the same band.^{20,21}

The transient absorption spectra at delay times of 5 and 500 ps for N3/ZnO measured with the femtosecond system are shown in Figure 1c. Signals around 800 nm could not be measured, because it is the fundamental wavelength of the laser. The probe light used was white-light continuum from 600 to 1150 nm and the OPA output from 1150 to 1550 nm. It is seen that the absorption band at 5 ps is considerably broad and seems to have a maximum at around 1200 nm (between 1000 and 1400 nm), which corresponds to the transition energy of roughly 1 eV (~ 8000 cm^{-1}). This absorption band is completely different from that of N3*, N3⁺, or free electrons shown in Figure 1a,b. Even a superposition of these bands apparently cannot reproduce this near-IR broad band, since at 1000 nm, where the near-IR band has a large intensity, the absorbance intensities of N3*, N3⁺, and free electrons are relatively weak. Also, our result is very different from the case of N3/TiO₂. In the wavelength region from 900 to 1100 nm, only a very peak absorption due to N3* (triplet state of N3) has been reported by Benkő et al.,

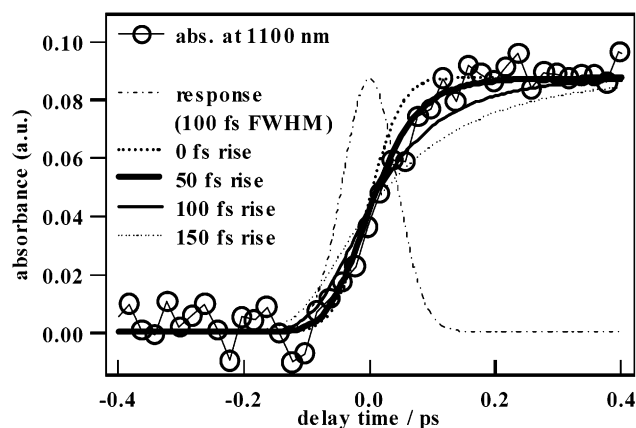


Figure 2. Transient absorption temporal profiles of N3/ZnO at 1100 nm, along with calculated curves obtained by convoluting the response function (dashed line, 100 fs fwhm Gaussian) with exponential rise functions having rise times of 0, 50, 100, and 150 fs.

and its decay with a time constant of 50 ps was ascribed to a minor component of electron injection from N3* to TiO₂.¹¹

The buildup of the broad absorption was examined by measuring the time profile at the wavelength of 1100 nm in the delay time range just around zero picoseconds. At this wavelength the contribution by N3*, N3⁺, or free electrons would be small. Figure 2 shows the transient absorption profile at 1100 nm and the calculated rise curves obtained by convoluting the typical response function of the apparatus (100 fs fwhm Gaussian) with several exponential rise functions having 0, 50, 100, and 150 fs rise times. It is seen that the absorption rise time is within 100 fs. Since the excitation in this experiment corresponds to the MLCT transition of N3 dye, N3* in the singlet state should be generated initially. The intersystem crossing is known to be very fast. In the case of a similar Ru-complex, [Ru(bpy)₃]²⁺, the intersystem crossing time constant is reported as 40 ± 15 fs.²² There was no evidence for the observation of N3*, even in the triplet state, with our apparatus when probing at 700 or near 1400 nm around a delay time of zero picoseconds, where these wavelengths are characteristic maxima of the triplet N3*. This suggests that the lifetime of N3* on ZnO is extremely short, and it is shorter than or comparable to the intersystem crossing time. At present, we cannot resolve the dynamics within 100 fs. However, an important fact is that the species giving the broad absorption band in the near-IR is produced after rapid relaxation of the MLCT excited state of N3 dye, and not by direct photoexcitation, because we excited the MLCT band of N3.

In the following, the picosecond dynamics of N3/ZnO is discussed. Figure 3, parts a–d, show the temporal profiles of the transient absorption of N3/ZnO probed at 650, 750, 1360, and 1960 nm, respectively, which are presented in two time ranges up to 3 and up to 500 ps for a clearer view. In the visible region, a slow decay is seen at 650 nm, while the absorbance is almost constant at 750 nm. The observed absorbance rise at 750 nm is as fast as the instrument response (~150 fs for the white-light continuum probe in the visible region). The difference between these two decay profiles can be seen also as the spectral change from 5 to 500 ps shown in the inserted graph in Figure 1c. Figure 3c shows the temporal profile probed at 1360 nm, which is a signal wavelength of the OPA. The decay could not be analyzed with a single-exponential function, so that we used a biexponential function with a constant component added. Two decay constants of 6.7 ± 2.5 ps and 150 ± 20 ps were obtained with relative amplitudes of 17 and 43%,

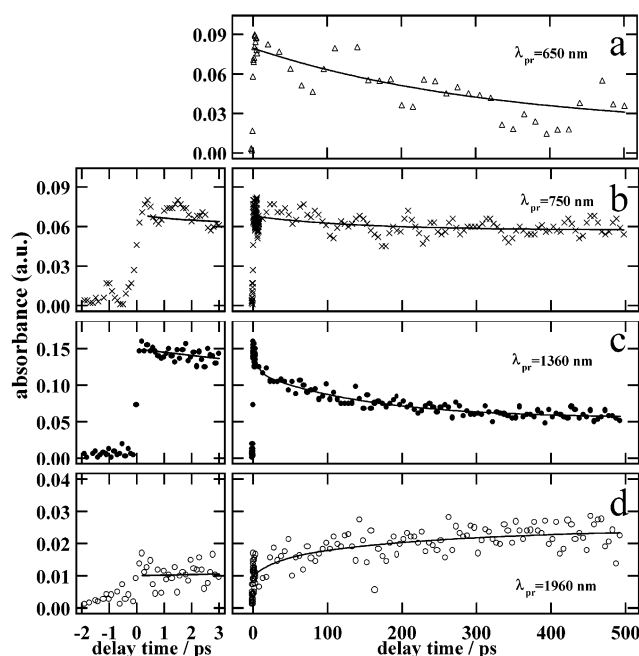
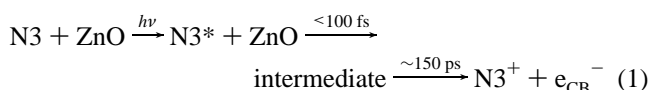


Figure 3. Transient absorption temporal profiles of N3/ZnO at 650 (a), 750 (b), 1360 (c), and 1960 nm (d).

respectively. When the probe wavelength was shifted to longer than 1700 nm, a slow absorption rise was observed as shown in Figure 3d. Here the probe light was set at 1960 nm, viz., an idler wavelength of the OPA. From the result of our nanosecond experiment mentioned above, the absorption at 1960 nm is ascribed to the tail of the absorption band of free electrons, namely conductive electrons. The rise seems to correspond to the decay at 1360 nm. The solid line in Figure 3d is a biexponential function with a constant component added, where the two rise constants of 6.7 and 150 ps were fixed and relative amplitudes obtained are 5 and 47%, respectively. This rise curve is similar to the observation by Asbury et al. using a 5 μm mid-IR probe.¹⁰

According to the picosecond dynamics, the near-IR band around 1200 nm is considered as an intermediate state in the course of electron transfer from N3* to the conduction band of ZnO. Considering that the intermediate has an absorption band with a maximum and is generated very rapidly after photoexcitation of N3 absorbed on the ZnO surface, and that it decays slowly to generate conductive electrons in the ZnO bulk, its origin is likely to be localized states at the surface of ZnO. In other words, the electron injection process in N3/ZnO proceeds stepwise via the intermediate states at the surface as



where e_{CB}[−] indicates a conducting electron in ZnO.

Before going into a detailed discussion on the observed dynamics in N3/ZnO, a comparison should be made with a previous report on the electron injection process in N719 dye on ZnO. In ref 16, the transient absorption at 770 nm, which appeared in a subpicosecond after excitation, was assigned to a superposition of absorptions of oxidized N719 and injected electrons, although the evidence for the injected electron was not clear. The electron injection time was concluded to be less than 300 fs. Our result of a transient absorption profile at 750 nm is similar to that at 770 nm for N719/ZnO. However, attention should be paid to the assignment of transient species

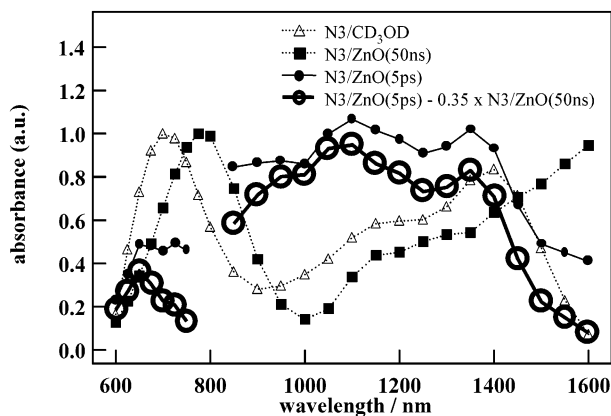


Figure 4. Transient absorption spectra in Figure 1 displayed again for analysis after normalization. N3/CD₃OD: N3 dye in deuterized methanol solution, corresponding to the absorption of N3*. N3/ZnO-(50ns): N3/ZnO at ~50 ns. The absorptions at around 800 nm and at longer wavelengths correspond to N3⁺ and e_{CB}⁻, respectively. N3/ZnO-(5ps): N3/ZnO at 5 ps. By subtracting the suitably factored (0.35) N3/ZnO(50ns) spectrum from the N3/ZnO(5ps) spectrum, the spectrum of the intermediate shown by large open circles was obtained. See text for details.

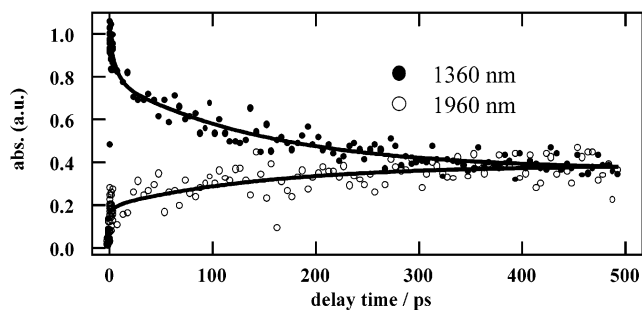


Figure 5. Time profiles of N3/ZnO at 1360 and 1960 nm in Figure 3 normalized at 500 ps.

observed in this wavelength region, because the very broad absorption band in the near-IR region seems to extend to the visible region.

Detailed analysis of the transient spectrum at 5 ps of N3/ZnO will be necessary in order to assign the intermediate. The spectra already presented in Figure 1 are displayed again after normalization in Figure 4. Small closed circles indicate the absorption spectrum of N3/ZnO at 5 ps delay time, abbreviated to N3/ZnO(5 ps). Open triangles indicate the spectrum of N3 in methanol at a delay time of ~10 ns. This corresponds to the spectrum of N3*. Closed squares indicate the spectrum of N3/ZnO at ~50 ns, abbreviated to N3/ZnO(50 ns). The absorption at around 800 nm corresponds to N3⁺, and that at the longer wavelength to e_{CB}⁻. Since almost a half of e_{CB}⁻ seems to be generated already at a few picoseconds delay time (see Figure 3d), the spectrum of N3/ZnO at 5 ps should include the contribution of N3⁺ and e_{CB}⁻ to some extent. It will be meaningful to eliminate this contribution in order to obtain the spectrum of the intermediate itself. We assume that each spectral shape of N3⁺, e_{CB}⁻, and the intermediate does not change with time. At 1360 nm, both the intermediate and e_{CB}⁻ are observed. If we assume that the intermediates complete relaxing into e_{CB}⁻ by 500 ps, about 20% of the observed absorption intensity at 5 ps is due to e_{CB}⁻. This is indicated in Figure 5, where the time profiles at 1360 and 1960 nm are normalized at 500 ps. By subtracting the suitably factored N3/ZnO(50 ns) spectrum from the N3/ZnO(5 ps) spectrum, we obtained the spectrum of the intermediate as shown by large open circles in Figure 4. The

spectrum obtained is clearly recognized to be a very broad absorption band in the near-IR region and, in addition, has a shoulder at around 650 nm in the visible region.

At present, we do not know exactly the nature of the intermediate on the surface. One of the possibilities of such states is simply a pair of N3⁺ and a trapped electron at some kind of surface states, for instance, defects derived from vacancies, interstitials, or steps, etc. Actually a ZnO crystal tends to have excess Zn and vacancies of O, and therefore interstitial Zn atoms provide donor states below the conduction band. Even if the surface does not have defects, a clean Zn–O polar surface can provide localized surface states. For example, the conduction band on the (0001)-surface is reported to give a 2D metallic surface state.²³ The ejected electron from N3* may be trapped by such surface states. The LUMO of N3 is located about 0.35 eV above the bottom of the conduction band of ZnO. It is very difficult to characterize the surface states of ZnO that are lying near the LUMO energy level to accept the electron, especially for nano-crystalline films. After electron transfer from N3* to the surface states occurs isoenergetically, ultrafast relaxation (<100 fs) of the electrons to lower states should be likely to occur in the continuous conduction band. Therefore we may be observing trapped electrons after the relaxation down to energy levels around the conduction band bottom. The slow multiexponential decay and the large spectral bandwidth may reflect inhomogeneity of the trap states. If this is the case, we should observe the N3⁺ component as well in the spectrum of the intermediate in Figure 4. However, any peak around 800 nm cannot be found. It seems that we should rather think of more complex electronic states for the intermediate.

As another and more likely possibility for the origin of the intermediate, we propose that the excited state of N3 and the surface state of ZnO form some kind of exciplex. The former behaves as an electron donor (D*) and the latter as an acceptor (A). The D*A (neutral pair) and D⁺A⁻ (ion pair) states are electronically mixed to form the exciplex states. If the D⁺A⁻ state is lower in energy than the D*A state, the lower and higher exciplex states have ionic and neutral characters, respectively. In this case, the observed species is an ionic exciplex, and the absorption band observed in the near-IR is considered as a CT band corresponding to an ionic-to-neutral transition that transfers an electron back to N3 dye. If the D*A state is lower in energy than the D⁺A⁻ state, the observed species is a neutral exciplex. Generally, on the basis of the spectral shape one can judge whether the observed exciplex is neutral or ionic. An ionic exciplex shows spectral features of D⁺ and A⁻ in addition to the CT band, while a neutral one shows that of D* in addition to the CT band. Since the shoulder at 650 nm is relatively close to the peak of N3* at 700 nm, the whole spectrum can be understood as a superposition of the band of N3* and a CT band around 1000 nm.

It is also possible to regard the spectrum of the intermediate as an ionic exciplex, if we understood it as a superposition of a broadened N3⁺ band and a wide CT band spread up to 1600 nm. The shoulder at 650 nm might be an artifact coming from the subtraction procedure of the intrinsic N3⁺ band from the broadened N3⁺ band. At present, it is difficult to assign whether the exciplex is ionic or neutral. However, the neutral exciplex seems to be more likely because the spectral assignment seems more reasonable. To examine if the exciplex is ionic or neutral, we are planning experiments to change surface environments by, for example, adding polar and nonpolar solvents. In both cases of ionic and neutral exciplexes, we can consider the ultrafast (<100 fs) rise of the near-IR band as due to partial

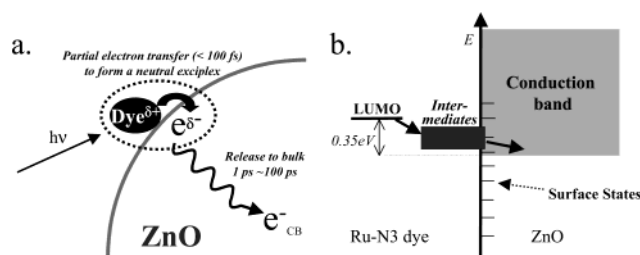


Figure 6. Scheme to represent the electron injection process in a ZnO nanocrystalline film adsorbed with Ru-N3 dye. (a) Electron transfer (partially) occurs from photoexcited N3 to the surface state of ZnO to form the intermediate state, which subsequently relaxes to generate the conductive electrons. Here a possible mechanism of neutral exciplex formation is presented. (b) The corresponding energy diagram. The LUMO of N3 is located 0.35 eV higher than the bottom of the conduction band. Since the energy level of the intermediate is unclear, it is expressed with a thick line. See text for details.

electron transfer from N3* to ZnO surface states to generate a $D^{+a}A^{-a}$ state ($0 < a < 1$). Due to the exciplex formation within 100 fs and the resulting energy stabilization to bound the electron, the subsequent electron injection into the bulk conduction band is considered to be retarded. This would be a reason for the slow generation of free electrons in the conduction band of ZnO. Multiexponential decay of the near-IR band is considered to reflect the inhomogeneous magnitude of the charge-transfer interaction. This can be examined by more detailed experiments on wavelength dependence of the decay or spectral measurements at several delay times. These experiments as well as those on the solvent effect are now in progress. Here, eq 1 is rewritten as eq 2 by taking into account the exciplex formation and its dissociation:

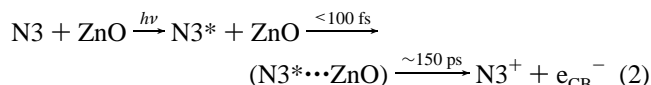


Figure 6a illustrates the electron injection process described above with neutral exciplex as a possible intermediate, and Figure 6b shows the corresponding energy level diagram.

It should be mentioned that in N3/ZnO the N3 dye molecules undergo aggregation by forming a complex with Zn^{2+} ions when the concentration of N3 is relatively high on the ZnO surface.²⁴ We have already examined this effect in detail by nanosecond laser spectroscopy, and the results will be published elsewhere soon.²⁵ We have also measured the transient absorption spectra in the visible and near-IR range below 1100 nm as a function of dye concentration by femtosecond spectroscopy. It was found that the dynamics of the near-IR band did not depend on the amount of N3 loading. On the other hand, the absorption due to the excited state of the aggregates or inactive dyes was observed at visible wavelengths for the high loading sample.

We now compare our results on N3/ZnO with well-known results of N3/TiO₂. Ultrafast (<100 fs) electron transfer from photoexcited Ru-complexes or aromatic dye molecules anchored on the TiO₂ surface into the TiO₂ conduction band is a general phenomenon, if the excited molecule has an enough redox potential and closely contacts on the surface. Very recently there appeared a report of 6 fs electron transfer from photoexcited alizarin to TiO₂.²⁶ One of the reasons for such ultrafast electron transfer is considered to be a large number of electron acceptor states originating from the conduction band. Ellingson et al. observed a fast rise (~50 fs) of strong mid-IR absorption at around 5 μm .¹⁷ In the case of N3/TiO₂ it is concluded that conductive electrons are generated immediately after excitation.

Since the density of states of the ZnO conduction band is lower by a factor of about 190 than that of TiO₂,¹⁰ slower electron transfer to the conduction band is expected. Our results show that in the case of electron transfer into ZnO, the localized surface states play an important role in accepting electrons to form an intermediate state in the course of electron transfer from the adsorbate to the bulk conduction band.

In conclusion, we have shown that electron transfer from excited molecules to a semiconductor can occur stepwise via the intermediate on the surface. The origin of the surface intermediate is at present considered as an exciplex due to the interaction between the photoexcited dye and some kind of surface states. So far, attention has been paid to the absorptions of dye molecules or conduction band electrons by probing absorptions at visible or mid-IR wavelengths, respectively. We have shown that probing absorptions in the near-IR range is very powerful in investigating the electron transfer mechanism, especially how metal oxide nanoparticles accept electrons from photoexcited dye molecules on the surface.

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