

Ultrafast studies of electron injection in Ru dye sensitized SnO₂ nanocrystalline thin film

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ABSTRACT. By using two-color femtosecond transient absorption spectroscopy, we have measured the electron injection rate for bis(tetrabutylammonium) cis di(thiocyanato) bis (2,2'-bipyridine-4,4' carboxylic acid)Ruthenium (II) dye (called N719) into SnO₂ nanocrystalline thin films. The electron injection rate has been measured by monitoring the formation of the dye oxidized state and the arrival of electrons in the conduction band. Dynamics of electron injection are multiexponential (0.2, 4 and 130 ps) and are therefore slower than the N719-ZnO or N719-TiO₂ systems. The photocurrent action spectrum of N719-SnO₂ shows a quantum efficiency of 0.65 at 530 nm proving that efficient charge separation can take place despite of the relatively slow electron injection rate.

1. INTRODUCTION

Electron transfer processes are the most basic reactions in chemistry and control the existence of life on Earth through the photosynthetic conversion of solar energy to chemical energy. However, knowledge of interfacial electron transfer processes is very poor compared to the similar problem in homogeneous medium [1]. Surface electron transfer reactions are the heart of important applications as photography or solar energy conversion. In the early nineties a new type of solar cells based on dye-semiconductor system has been developed that reaches efficiencies comparable to conventional solar cells [2]. In these dye-sensitized solar cells, interfacial electron transfer processes are governing the efficiency of light to electricity conversion. Up to know, the optimum energy conversion has been obtained with a Ru dye (so called N3 or N719 depending of protonation degree) bis(tetrabutylammonium) cis di(thiocyanato) bis (2,2'-bipyridine-4-carboxylate, 4' carboxylic acid)Ruthenium (II) [3, 4]. In recent years, electron transfer dynamics between anchored dyes and semiconductors have been studied by transient optical studies. Most of these ultrafast interfacial electron transfer studies are focused on TiO₂. Thus, the rate of electron injection for N3 dye adsorbed onto TiO₂ was reported to be multiexponential and mainly in the femtosecond regime [5-8]. In this paper, we have measured the rate of electron injection for the sensitizer (N719) into SnO₂ conduction band by femtosecond transient absorption spectroscopy and determined the quantum efficiency of photon to current conversion. To the best of our knowledge, this is the first reported study of electron injection dynamics for N719 dye adsorbed onto SnO₂.

2. EXPERIMENTAL

2.1. Samples preparation. 0.75 g of polyethylene-glycol (MW 20,000) was dissolved in 10 g of colloidal SnO₂ solution (Nyacol SN15CG, PQ corporation). 2 ml ethanol was added to promote gelling and finally 2 ml of water was added to obtain a paste with good spreading properties. The paste was spread on microscope or conducting glasses using adhesive tape as spacer. Resulting films were fired for 30 minutes at 450 °C in air. The average particle size after firing was 8 nm. Then, the films were immersed still hot (80 C) in an ethanolic dye solution for 15 hours. The samples are thoroughly washed with ethanol and stored in the dark. Film thicknesses were determined by profilometry and were typically 3-4 μm.

2.2. Femtosecond spectroscopy. The Femtosecond Laser system consists of a 1 kHz regenerative amplifier (Quantronix) pumped by a Q-switched frequency doubled Nd:YLF laser (Quantronix) and seeded by a mode-locked Titanium:Sapphire oscillator (Mira, Coherent Radiation), the later pumped by a CW argon-ion laser (Coherent Radiation). The amplified pulses have after compression a temporal width of about 120 fs and an energy of 800 μJ at 800 nm. The red light from the compressor is split by a beam splitter (80/20) into a pump and a probe beam. The 535 nm pump beam is generated by frequency mixing the idler and the signal outputs of the Optical Parametric Generator (OPG) (TOPAS, Light Conversion Ltd.). The pump light passes through a chopper and is then focused in the sample. White light continuum, generated in a fixed quartz plate is used for probing after passing through a delay line. The probe beam is then focused and overlapped with the pump beam in the sample. After the sample, the probe beam is focused onto the entrance of a monochromator and detected by a photomultiplier. The output signal is produced by a lock-in amplifier

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locked to chopper frequency. All measurements were performed at room temperature. The dye sensitized SnO₂ films were covered with 3-methoxy propionitrile containing 0.5 M LiI and 50 mM I₂ and a thin glass cover slide to prevent dye degradation. The electrolyte has no effect on the electron injection rate.

2.3. IPCE measurements. A fully automated set-up was used to record the spectral response of the photocurrent and to calculate the incident photon-to-current conversion efficiency (IPCE). A platinized conducting glass counter electrode was placed directly on top of the dye-sensitized SnO₂ photoanode and the electrolyte, 0.5 M LiI, 0.05 M I₂ and 0.5 M 4-*tert*butyl pyridine in 3-methoxypropionitrile, was introduced between the electrodes. Illumination took place through the photoanode, and the illuminated area was 0.32 cm².

3. RESULTS AND DISCUSSION

The size and the shape of SnO₂ particles in the nanocrystalline thin film were determined using transmission electron microscopy. Figure 1 shows that the particles are nearly spherical and have an average size of 8 nm. The absorption band edge of the SnO₂ films is around 350 nm which implies that quantum confinement effects can be ruled out.

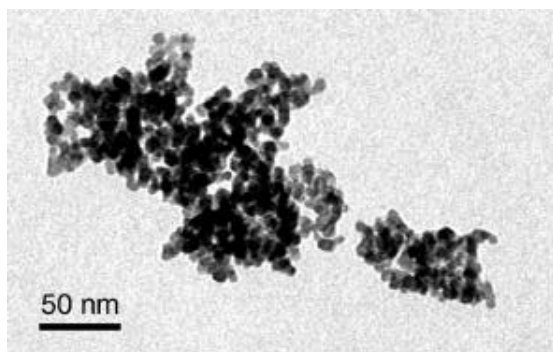


Figure 1. Transmission Electronic Microscop pictures of SnO₂ particles in the thin films. The average particle size was 8 nm.

Figure 2 shows the electronic absorption spectra of naked SnO₂ films, Ru dye (N719) in ethanol and adsorbed onto SnO₂. N719 dye in ethanolic solution exhibits two bands in the visible region at 400 and 531 nm which correspond to the MLCT transition. The absorption maximum for N719 adsorbed onto SnO₂ is 10 nm blue shifted from 530 to 520 nm compared to the dye in ethanolic solution. For TiO₂, no shift or a slight red shift is observed and is accounted for a delocalization of π^* electrons of the bipyridine ring with the conduction band. The blue shift observed for N719-SnO₂ can arise from (i) formation of aggregates on the

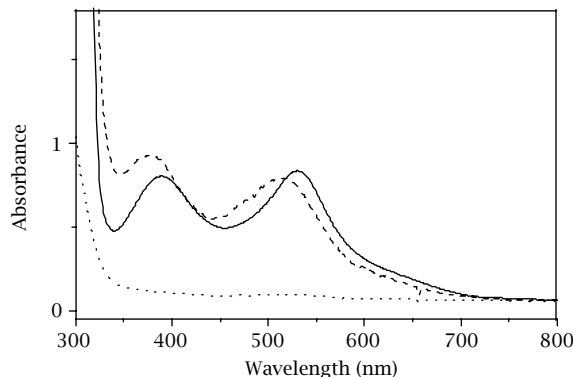


Figure 2. Electronic absorption spectra of naked SnO₂ film (dotted line), N719 dye in solution (solid line) and N719 dye anchored onto SnO₂ film (dashed line).

surface (ii) formation of the fully deprotonated form of Ru dye (iii) a weak electronic coupling between the dye molecule and the semiconductor surface. A similar blue shift has been observed for perylene dyes adsorbed onto SnO₂ nanocrystalline films [9].

Figure 3 shows ultrafast transient absorption profile of N719-SnO₂ system on three different time scales (A) 0–15 ps, (B) 0–200 ps and (C) 0–600 ps. These transient absorption data were obtained with a pump and probe wavelength at 535 and 770 nm respectively. The signal increases up to 300 ps for this probe wavelength. The rise is multiexponential and well fitted with three components with lifetimes of < 0.2, 4 and 130 ps.

Transient absorption in this spectral region has contributions of SnO₂ conduction band electrons and of dye oxidized state. Optical excitation of the attached dye molecule results in electron injection into semiconductor conduction band. N719 excited state could also absorb in this region, but the signal detected is thought to be mostly due to the oxidized dye since the rise time is not instrument response limited (200 fs) but much slower. The oxidised state of N719 is known to absorb in the red to near-IR region [5, 10, 11].

It is surprising to observe a slower electron injection rate for N719-SnO₂ compared to N719-TiO₂ system since the driving force ΔG is expected to be larger for the dye-sensitized film studied here. Indeed, the conduction band edge of TiO₂ lies 0.5 eV higher in energy compared to that of SnO₂. The driving force, also called free energy, is the energetic difference between the acceptor and the donor states and plays a key role for the electron transfer rate. The Marcus theory expresses the electron transfer rate constant in function of the driving force ΔG , the reorganization energy λ and the electronic coupling $|V|$ [12]. In this theory, the nuclear factor k_n brings the two reactants in electronic resonance to overcome the nuclear activation barrier, $k_n = \exp -[(\Delta G - \lambda)^2 / 4\lambda kT]$. This theory implies a weak electronic coupling and a nonadiabatic

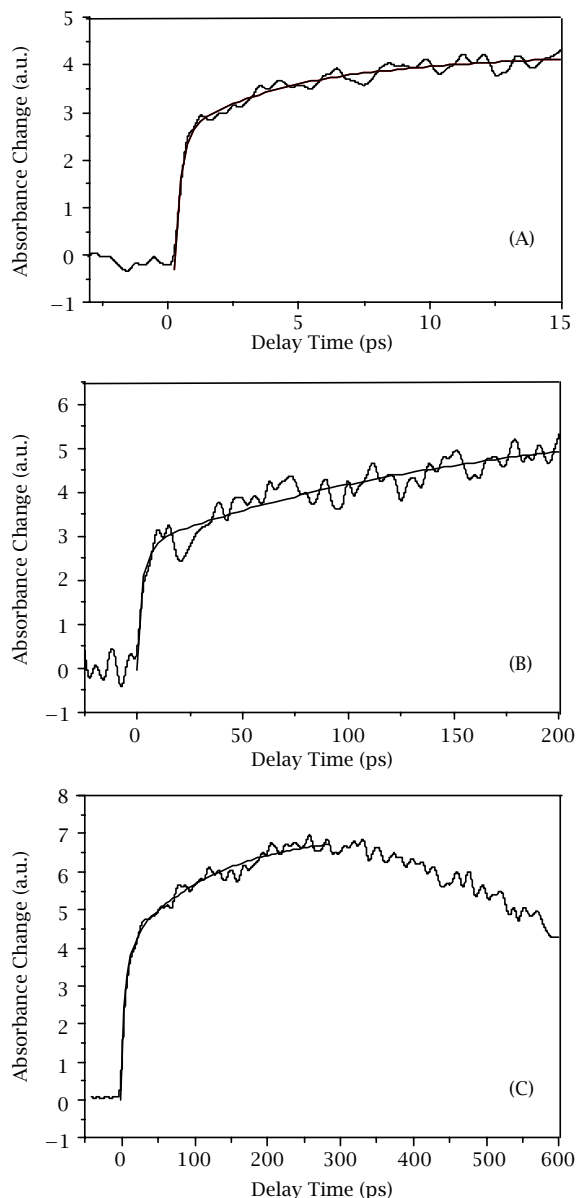


Figure 3. Ultrafast transient absorption kinetics obtained after excitation at 535 nm and a detection at 770 nm for the N719-SnO₂ system. (A) The 0–15 ps, (B) 0–200 ps and (C) 0–600 ps are fit with a triple exponential rise with 0.2, 4 and 130 ps time constants.

electron transfer reaction. But for chemisorbed dye molecules, the interaction with the surface is so strong (formation of an inner-sphere complex) that the system falls in the strong electronic coupling limit and the reaction is thought to be adiabatic. Therefore, the electron injection process can not be formulated in terms of classical Marcus theory. For interfacial electron transfer processes, no clear formulation is available for the estimation of electron transfer rate between a attached dye molecule and a semiconductor conduction

band. The dye discrete molecular state is coupled to a quasi-continuum of empty electronic states of the semiconductor conduction band. We can start with the Fermi Golden rule which expresses the rate constant with electronic coupling $|V|$ and the density of acceptor states $N_c \cdot k_{et} = 4\pi^2/h|V|^2N_c$. In this formula, the nuclear factor which is expressed with λ and ΔG in the Marcus theory is replaced by the density of acceptor states N_c . Unfortunately, it is not possible to compare directly N_c between SnO₂ and TiO₂. But when the N_c is high enough k_{et} becomes independent to the density of acceptor states [13]. This suggests that the most important parameter controlling the electron transfer will then be the electronic coupling, the degree of electronic wave function overlap between the donor and the acceptor states. This factor is linked to the spatial configuration of the two reactants forming the system. The multiexponential kinetics behavior is thought to be due to the inhomogeneity of semiconductor surface. Dye molecules may exhibit different molecular geometry on the surface giving rise to different values of electronic coupling. Different interfacial spatial arrangements can be found with the different crystal faces of the SnO₂ nanocrystallite. It appears in this case that the binding mode of the dye molecules on the surface has a stronger effect on the electron injection process than the energetics of the system. Electron transfer from an excited electronic state of a dye molecule attached on the surface of a semiconductor is a pure electronic process. The energetic position of the acceptor state does not seem to play a significant role for the dynamics of electron injection.

In order to evaluate the photoelectrochemical response of the SnO₂ electrode sensitized with N719 dye, we have measured the IPCE (incident photon to current efficiency). The IPCE is directly linked to the light harvesting efficiency of dyed electrode (LHE), the quantum yield of charge injection into semiconductor conduction band (ϕ_{inj}) and the efficiency of electron collection at the external circuit (η): $IPCE = (LHE)(\phi_{inj})(\eta)$. The action spectra representing IPCE versus excitation wavelength for N719-SnO₂ is shown in Figure 4. A IPCE value of 35% is measured at 540 nm. The APCE (absorbed photon to current efficiency) or quantum efficiency is calculated from light harvesting efficiency. After correction for light absorption by the conductive glass and from the light harvesting efficiency, a quantum yield 0.65 is obtained. The electron injection process is in competition with other relaxation processes of the dye excited state. The charge injection efficiency can be expressed as follows (ϕ_{inj}) = $k_{et}/(k_{et} + k_{rel})$ with k_{rel} the other relaxation pathways. Since the excited state lifetime of N719 dye is quite long lived (50 ns), (ϕ_{inj}) is still close to 1 even with the slower injection rate observed here compared to TiO₂.

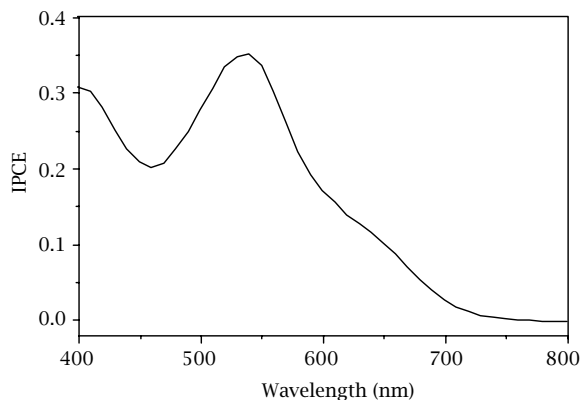


Figure 4. Photocurrent action spectrum of the N719-SnO₂ system.

4. CONCLUSION

For the first time, dynamics of electron injection for N719 dye anchored onto SnO₂ has been investigated by ultrafast transient absorption spectroscopy. The kinetics are found to be multiexponential and slower compared to dye sensitized systems based on ZnO [14] or TiO₂. In the view of theoretical predictions, we can expect at least an electron transfer rate as fast as for TiO₂ or ZnO. But surprisingly, an important part of this process occurs on the picosecond time scale. Our results suggest that k_{et} is not proportional to the driving force but is likely more sensitive to the binding mode with the semiconductor surfaces. The extension of these ultrafast studies with others semiconductors provides some insight in the search of the parameters governing the electron injection processes from optically excited dye into semiconductors. In the future, we hope to systematically compare the electron injection rate as function of the interfacial binding state of the dye molecules.

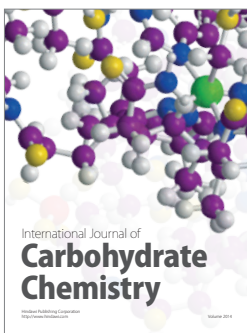
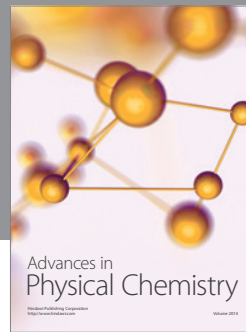
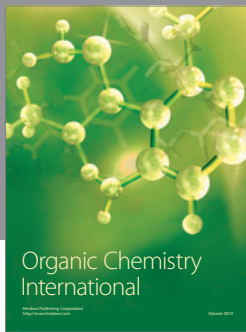
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