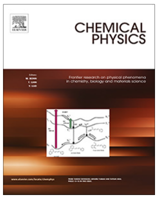
Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys



Electron injection from a carboxylic anchoring dye to TiO_2 nanoparticles in aprotic solvents

Hui Fang [a], Yuhao Wu [a], Danielle L. Kuhn [b], Zachary Zander [b], Brendan G. DeLacy [b], Yi Rao [a,1], Hai-Lung Dai [a,*]

[a] *Department of Chemistry, Temple University, Philadelphia, PA 19122, United States*

[b] *U.S. Army Edgewood Chemical Biological Center, Research & Technology Directorate, Aberdeen Proving Ground, MD 21010, United States*

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Dye sensitized solar cell
Electron injection
TiO_2 nanoparticles
para-Ethyl Red
Aprotic solvent
Reorganization energy
Transient absorption
Ultrafast

ABSTRACT

Injection of photoexcited electrons in the para-Ethyl Red dye to TiO_2 nanoparticles (Anatase, 40 nm diameter) is characterized by transient absorption on ultrafast time scales. This study focuses on understanding the effect of aprotic solvents on the injection rate. Transient absorption at 1900 cm^{-1} is probed following a 400 nm pulse which excites the electronic transition of p-ER adsorbed on TiO_2 through its carboxylic group. Measurements conducted in three different solvents show that electron injection lifetimes are in the 250–300 fs range but display a trend in correlation with solvent polarity: the electron injection lifetime is the shortest (257 fs) in acetonitrile followed by dichloromethane (271 fs) and chloroform (296 fs). This trend can be understood by using the Marcus theory in which the reorganization energy varies correspondingly in the three different solvents. This study shows that for aprotic solvents the one with the highest polarity facilitates the fastest electron injection.

1. Introduction

Understanding interfacial electron injection from molecular adsorbates to semiconductor nanoparticles is a fundamental problem important for improving the efficiency of photocatalytic and photovoltaic processes in systems consisting of semiconductor nanoparticles coated with light absorbing molecules [1–5]. One of the systems of current interests is the dye sensitized solar cell (DSSC) in which a typical device contains TiO_2 particles adsorbed with organic dye molecules [6,7]. So far, the highest efficiency reported for the DSSC is 13% [8]. One of the approaches to improve the efficiency is to understand what the factors are influencing the injection of photo-generated excited carriers in the organic dye molecules into the TiO_2 particles as the basis for better design. Typically a high DSSC efficiency depends on fast carrier injection and slow recombination [5,9–13].

Many factors affect the electron injection dynamic process. These factors include the relative energies of the electronic bands of the molecule and the semiconductor, the coupling between the molecular and semiconductor wavefunctions, and the interfacial environment including the surrounding solvent molecules. There have been studies in recent years on the electron injection rate in systems relevant to DSSC [9,13–19]. Specifically, the solvent effect has been studied though the understanding is still being formed [9,15,16,18].

In principle, the solvent may affect the band edge position of the semiconductor, its electronic coupling with the adsorbate molecules, and the energy of the molecules before and after the injection. The many reports so far have provide abundant information for characterizing the injection process but our knowledge on how the presence of solvent molecules may affect carrier injection dynamics is still evolving. Lian and coworkers reported that the presence of aqueous water or protic solvents like methanol and ethanol lowers the band edge of TiO_2 and increases the electron injection rate from the light absorbing dye to TiO_2 [15]. They have also investigated the pH dependence of electron injection from the perspective of the change of the band edge position [16]. Ellis et al. reported that the nonpolar solvent like hexane has negligible influence on charge transfer dynamics from quantum dots [20]. Durrant et al. found that solvents, either protic or aprotic, do not significantly affect the electron injection rates in $Ru(dcbpy)_2(NCS)_3/TiO_2$ films [21]. In contrast, Lee et al. discovered that the donor number rather than the dielectric constant of the solvent matters

---

[*] Corresponding author.
E-mail address: hldai@temple.edu (H.-L. Dai).

[1] Present Address: Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322, United States.

https://doi.org/10.1016/j.chemphys.2018.02.022
0301-0104/

more to the electron injection rate [22]. Hyun et al. found that the charge transfer rate increases dramatically with solvent dielectric constant which was accounted for by a modified Marcus theory taking into account only the static dielectric effect [23].

In this study, we examine if there is a systematic dependence in the electron injection rate upon the change of solvent among the aprotic solvents. In the aprotic solvents there is a lack of hydrogen bonding for the dye molecules. We have previously found that the adsorption free energy is affected by the polarity of the aprotic solvent, likely due to the change in the solvation energy [24]. In principle the change in solvent molecule polarity may affect the solvent interaction with both the semiconductor and the adsorbate and subsequently the injection rate.

The electron transfer (ET) dynamics at the adsorbate-semiconductor nanoparticle interface in an aprotic solvent in this study was probed by transient absorption spectroscopy which has been widely used for probing electron dynamics [5,11,15,16,20,23,25–30]. Following the laser-pulse excitation of the adsorbate electronic transition, an IR laser pulse probes the absorption through intraband transitions of the electrons in the conduction band of the semiconductor [28]. For the free carrier to absorb a photon, scattering with a phonon is required for momentum conservation, resulting in an absorption coefficient that increases with the photon wavelength. Consequently absorption by free carriers in the conduction band is strong through the mid-IR but becomes negligible in the visible region.

In our study, we chose 400 nm as the pump and 1900 cm^{-1} as the probe to study the excited-electron injection and decay processes in the system of para-Ethyl Red (p-ER) coated TiO_2 nanoparticles. A 400 nm ultrafast pump pulse excited the electrons in p-ER. The 1900 cm^{-1} ultrafast pulse, with varying time delay, probed the absorption of the excited electrons injected into the conduction band of TiO_2. Three different aprotic solvents (acetonitrile, dichloromethane, and chloroform) were chosen to study the solvent effect on the electron injection rate.

2. Experimental

2.1. Transient absorption

A regen-amplified Ti:Saphire laser system (Quantronix) operating at 800 nm and 1 kHz repetition rate [34] was used for the experiments. The 800 nm output from the regenerative amplifier was split into two parts to generate pump and probe pulses. A very small portion was frequency doubled in a BBO crystal to generate pump pulses at 400 nm with the fluence at the sample kept as low as 3 μJ/pulse (using a combination of a halfwave plate and a polarizer) to minimize higher-order annihilation processes. The other part of the output laser pulse was used to pump an IR Optical Parametric Amplifier (Quantronix, Palitra-FS/REV.A) to generate two tunable near-IR pulses in the ranges of 1.2–1.5 μm and 2.4–1.7 μm, separately. These signal and idler pulses were then combined in a $AgGaS_2$ crystal to generate 1900 cm^{-1} pulses through difference frequency generation. The pump and probe pulse focal point sizes were 350 and 160 μm, respectively. The 1900 cm^{-1} radiation was detected by a liquid nitrogen cooled HgCdTe detector (Judson J15D14-M204B-S01M-60-D31316). The pump pulses were chopped by a New Focus Model 3501 Chopper at 500 Hz so that the absorbance change can be measured as the difference between two adjacent probe pulses (one with pump on and the next without). Signals from the probe detector was sent to a lock-in system (Stanford Research, SR830 DSP Lock-in Amplifier). The digitized outputs were processed and recorded by a home-made program based on Labview. The pump-probe cross correlation was represented by a Gaussian with FWHM of 300 ± 10 fs (see Section 3).

2.2. Materials

Titanium oxide powders (Anatase TiO_2, 99.9%, 40 nm diameter) were purchased from US Research Nanomaterials Inc. pare-Ethyl Red (p-ER) was synthesized using the procedure reported before [24]. Chloroform (CF, 99.7%) and dichloromethane (DCM, 99.9%) were purchased from Alfa Aesar Inc. Acetonitrile (AeCN, ≥99.93%) were purchased from Sigma-Aldrich. These solvents were used as received. 0.5 mg/ml TiO_2 particles and 0.37 mM p-ER were prepared as stock solutions which were used for preparing the samples for the transient absorption experiments. For example, the p-ER/TiO_2 in CF solution was mixed with 2 ml TiO_2 stock solution and 2 ml p-ER stock solution.

A 10 mm × 5 mm quartz cuvette (Starna Cells Inc.) was used to host the sample with the short path for light propagation. A 2 mm × 2 mm stirrer (Big Science Inc.) was used to make sure that the colloid solution is uniform during the measurement.

3. Results

Fig. 1 shows traces of transient absorption of the IR pulses measured following the pump pulse excitation of the p-ER/TiO_2 nanoparticles in the CF solution. The green line is from a sample with solvent only without the particles or dye. As there is no chromophores to interact with the excitation pulse, the signal measured here is loss of the laser light through scattering and is treated as the instrument response function. Measurements using solvent-only samples with ten different solvents including CF, AeCN and DCM yielded the instrument response functions which are fitted through a nonlinear least squares procedure with a Gaussian function with 300 ± 10 fs FWHM.

The blue line displays the measurement for only p-ER in CF. This curve is very similar to the instrument response function and indicates that p-ER molecules in the solution (a relatively high 0.18 mM concentration) do not contribute to the transient absorption signal. The black line represents the transient absorption response from a TiO_2 in CF sample. The signal has a rapid rise followed by a decay on a time scale too long for this experiment to resolve. This signal shows that there are excited electrons in the conduction band. Since the 400 nm (3.1 eV) light energy is below the Anatase

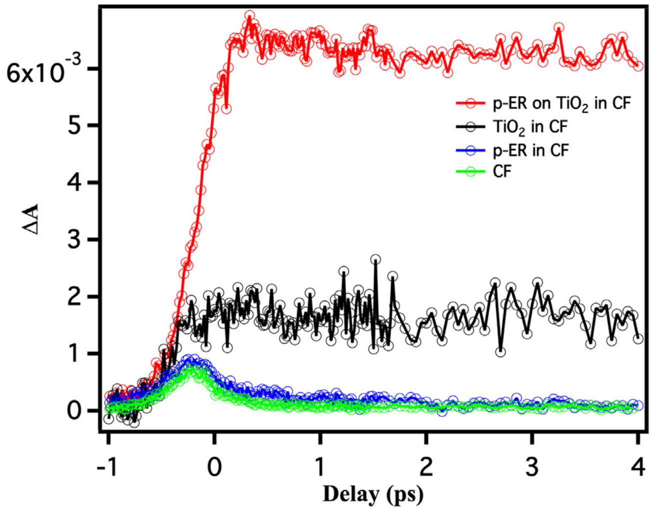


Fig. 1. Transient absorption signal (at 1900 cm^{-1}) following the 400 nm excitation pulse: The green line is obtained with the solvent CF only; the blue line from p-ER in CF; the black line from TiO_2 nanoparticles in CF; and the red curve from p-ER/TiO_2 nanoparticles in CF. t = 0 was set as the first maximum point of the red signal. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Please cite this article in press as: H. Fang et al., Chem. Phys. (2018), https://doi.org/10.1016/j.chemphys.2018.02.022