## Photochemical & Photobiological Sciences

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/pps

Photochem. Photobiol. Sci.

## Dye-injected electron trapping in TiO<sub>2</sub> determined by broadband transient infrared spectroscopy

Peter Friedli<sup>a</sup>, Hans Sigg<sup>a\*</sup> and Jacinto Sá<sup>a,b\*</sup>

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

We report the dynamics of electron injected into TiO<sub>2</sub> due to the excitation of Ru-N719 dye at 532 nm. The synchrotron based broadband transient mid-IR spectroscopy revealed that the injected electrons are quickly confined to a trap state with 10 an averge energy of ca. 240 meV below the conduction band.

The average energy of the trapping states did not change with the increase of the delay time, suggesting a singular electronic identity of the trap states.

- TiO<sub>2</sub> is the most studied photo-catalyst because of its wide 15 band gap (~ 3.0-3.2 eV), high charge mobility and surface reactivity, which enables it to photo-catalyse a plethora of chemical reactions, ranging from water splitting <sup>[1]</sup> to organic synthesis <sup>[2]</sup>. However, its wide band gap also means that in order to promote charge separation UV photons are required. UV
- <sup>20</sup> accounts for only 4% of the solar spectrum. Asahi et al. <sup>[3]</sup> tried to circumvent this difficulty by doping  $TiO_2$  with light elements in order to shift the absorption to the visible range. They reported a significant improvement in the visible light absorption when  $TiO_2$  was doped with nitrogen in substitutional places, making it a
- <sup>25</sup> popular strategy to improve photo-catalytic activity in the visible range. However the strategy very often leads to a drastic decrease in UV photo-catalytic performance, uncompensated by the gains in the visible range <sup>[4]</sup>. Additionally, by narrowing the band gap, one decreases the breath of reactions that can be photo-catalyze.
- <sup>30</sup> An alternative strategy is to use sensitizers able to harvest solar light, and inject electrons into TiO<sub>2</sub>. The most famous strategy is the Grätzel cell <sup>[5]</sup> consisting of a dye sensitizer coated on TiO<sub>2</sub> surface. The success of the Grätzel cell relates to the fast electron injection from dye to TiO<sub>2</sub> (< 10 fs) <sup>[6]</sup>, and slow back
- <sup>35</sup> transfer of electrons to the oxidized dye (up to ms) <sup>[7]</sup>, enabling the transference of the electrons to a counter electrode (increased life time), thus producing electric current.

Electron transport in the  $TiO_2$  is believed to occur via trapping-detrapping events across energetically distributed intra-

- <sup>40</sup> band-gap states (shallow traps) and conduction band states <sup>[8]</sup>. Thus, electron transport depends on the energy of the injected electrons, and the density and energy of the trap states <sup>[6,9]</sup>. According to Tamaki et al. <sup>[10]</sup>, the injected electrons are quickly trapped (< 170 fs). Initially, electron trapping occurs on states</p>
- <sup>45</sup> close to or in intrabands within the conduction bands. After the initial stage, the electrons become confined to deeper trap states,

resulting in a decrease of their mobility, and consequently increase in lifetime, before they start recombining with the oxidized dye. What is not consensual is the nature of the trapping <sup>50</sup> sites, and what is the prefer recombination site.

We used a novel synchrotron-based broadband mid-infrared (mid-IR) spectroscopy setup to determine the average trap state energy, and the ratio between trapped and free carriers in  $TiO_2$  originated from the excitation of the sensitizing dye <sup>55</sup> triisothiocyanato-(2,2':6',6''-terpyridyl-4,4',4''-tricarboxylato)

<sup>55</sup> thisothiocyanato-(2,2 to ,0 -terpyndyl-4,4 ,4 -thearboxylato)
<sup>55</sup> ruthenium(II) tris(tetra-butyl ammonium) (Ru-N719) <sup>[11]</sup> at 532 nm. Advantages of synchrotron-based experiments include large dynamic range and the sensitivity of the system combined with the large spectral bandwidth, which covers the entire mid-IR
<sup>60</sup> range (approx. 625 to 10000 cm<sup>-1</sup>). The sample consisted of monolayer of dye coated onto 3-5 nm particles of TiO<sub>2</sub> anatase. UV-Vis measurements detected a narrow absorption peak between 525 and 535 nm. The experiments were carried out in transmission geometry using samples pressed against Ni-mesh 65 (thickness 25 µm).

The multi-wavelength laser light system uses near-IR laser pulses generated by a Nd:YAG system with 1 kHz repetition rate. A Phase-Lock Loop control system locks the laser system to the Swiss Light Source (SLS) reference frequency of 500 MHz. The 70 delay between the 80 ps pump pulse from the laser system and the relevant synchrotron radiation pulse, the so-called camshaft (4 times the charge of a standard bunch), is electronically tuned by a vector modulator. This allows adding an arbitrary phase delay, and hence a time delay of up to 1 ms. The transmission of the 75 camshaft pulses was measured with a fast Peltier-cooled mercury cadmium telluride detector featuring a bandwidth of 800 MHz. The peak amplitude is digitized with a 14-bit resolution fastsampling card, which records both pumped and unpumped transmission (arriving 1 us in advance) instantaneously. Hence, <sup>80</sup> this detection scheme is not susceptible to instabilities of the synchrotron source (manifested at the 1 to 3 kHz range) and slow drift phenomena, and it allows increasing the signal-to-noise ratio (S/N) of step-scan experiments significantly (typically by a factor of 100) on a time scale relevant to our experiments. The samples 85 were excited with 33 µJ of Nd:YAG pulsed monochromatic green (532nm) light. We used a resolution of 32 cm<sup>-1</sup> to avoid contributions from RuN719 molecular vibrations. Based on pulse  $10E^{14}$ and wavelength, we estimate roughly energy



Photochemical & Photobiological Sciences Accepted Manuscr

photons/pulse. Since we perform the experiments at 1 kHZ, this comes to roughly  $10E^{17}$  photons/s, ~  $10E^{21}$  photons in 2 h (measurement time). It should be mentioned that the signal is not associated with direct excitation of TiO<sub>2</sub> band gap because the

- <sup>5</sup> pump does not have enough energy to overcome it and multiphoton absorption does not occur. To ensure good S/N, the presented spectra correspond to the average of data collected over a period of 24 h (2-3h per average spectrum). The measurement spot was refreshed every 4h to avoid sample degradation.
- <sup>10</sup> However we should mention that we only did this to be in the safe side since preliminary experiments performed over 12h on the same spot show no significant signal change.

Free and trapped electrons yield a broad mid-IR absorption, which increases with the increase of wavelength or peaks at an <sup>15</sup> energy corresponding to the trap energy, respectively <sup>[12]</sup>. Thus, the mid-IR can be used to unequivocally identify electrons in a semiconductor conduction band and/or shallow traps. With this technique we were able to determine average trap state density and energy at different time delays, and able to discuss the <sup>20</sup> preferred location of electrons before getting back transferred to



**Fig. 1.** Time dependence of the mid-IR of TiO<sub>2</sub> coated with Ru-N719 dye irradiated at 532 nm with 100 ps pump pulses with energy of 33 μJ. Experimental resolution 32 cm<sup>-1</sup>. (*Top*) Representation of fitting with 25 combined model for free and trapped carriers. (*Bottom*) Mid-IR signal between 1200 and 3000 cm<sup>-1</sup> at different pump-probe time delays. The solid lines correspond to the best data fit with the combined model.

Figure 1 depicts the transient mid-IR signal for different time <sup>30</sup> delays. The low spectral resolution (32 cm<sup>-1</sup>) was purposively chosen to minimize contributions in the transmission spectra from dye's molecular vibrations. It should be mentioned that the sample was heated up to 150 °C for 1 h to remove traces of moisture and the experiments were carried out under high purity <sup>35</sup> He flow to avoid presence of oxygen (potential electron scavenger). Upon injection into TiO<sub>2</sub> a characteristic broad mid-IR band evolved, which increased monotonically in intensity with the decrease in probe's wavenumber. The broadband absorption signals were fitted according to a combined model (c.f. Eq. 1) <sup>40</sup> composed of intraband optical transition of free carriers in the conduction band (Drude model)<sup>[13]</sup> and in trap states (Lorentz with offset)<sup>[14]</sup>. The possibility to perform the fit over a large spectral range not only increases the fitting accuracy but it is also a requirement to perform the fit in the first place. The current <sup>45</sup> setup has been purposely conceived for time resolved measurements with broad spectral range <sup>[15]</sup>. In Eq. 1:

Eq.1 fit 
$$(\omega) = \frac{A_{FC}}{\omega^2} + \frac{A_{Trap}}{((\omega - \omega_0)^2 + \Gamma^2)}$$

*A* is the amplitude,  $\omega$  is the frequency in cm<sup>-1</sup>,  $\omega_0$  is the frequency <sup>50</sup> offset in cm<sup>-1</sup> (which is zero for the free carrier model), and  $\Gamma$  is a parameter associated with the scattering time in cm<sup>-1</sup>. The scattering time was found to be ca. 6 fs and constant up to 1.5 ns (measuring time). The scattering time was calculated using equation described elsewhere <sup>[14]</sup>. In the fitting, we kept the two <sup>55</sup> amplitudes, and the frequency offset as free parameters. The ratio between models amplitudes, and the average energy of the tap states (offset in eV) are plotted against the time delays in Figure 2. We used high laser pump energy (33 µJ/pulse, pump beam radius 0.5 mm) in order to excite as much as possible dye <sup>60</sup> molecules, and potentially saturate the number of trap states ('trap filling' effect) <sup>[10,16]</sup>. It should be mentioned that fitting with individual models was not reasonable.



Fig. 2. Time evolution ratio between models amplitude, and the average 65 energy of the trap states.

At 0 ps time delay (exact overlap between pump and probe), the ratio between trapped and free electrons is roughly 0.2, suggesting that one in each five electrons injected into TiO<sub>2</sub> are located in a trap state. Surprisingly, the ratio between trapped and free electrons did not deviate significantly from the 0.2 over the measurement time (1.5 ns). Analogously, the average trap state energy was found very similar over the measurement time, with an average value of  $240 \pm 5$  meV. Finally, the signal was a fitted rs with a single exponential decay with  $\tau = 1.9 \pm 0.4$  ns, which relates to electron back transfer to the oxidized dye. The decay was similar to both trap and free carriers (Figure 3), i.e., the electron back transfer to the oxidized dye removes charge from TiO<sub>2</sub> from both trapped and free carriers. Complete 15

recombination occurs on 100s ns scale, which was not covered in this study because it requires the presence f a liquid interface to provide meaningful results.

To determine the preferred location of the injected electrons, s one needs to look at lower fluencies or pump-probe overlaps before 0 ps (e.g. -150 ps). In both cases the ratio between trap and free carriers increases due to a decrease in free electrons contribution. Thus, even at early stages the injected electrons preferred locations is the trap states.



Fig. 3. Time evolution of trapped states signal amplitude.

The experimental results revealed important aspects, namely:

- ✓ Constant ratio between trapped and free carriers
- ✓ Uniform trap state energy (~ 240 meV)
- $\checkmark$  Preferred electron location is the trap states
- ✓ Analogous exponential decay for both trap and free carriers.



20 Fig. 4: Schematic representation of the possible models responsible for the experimental observations.

Concerning the identity of the trap states, mid-IR spectroscopy is unable to elucidate specific geometric structure of 25 the site but it is possible to elucidate its electronic structure. The constant energy of the site suggests singular identity of the trap state distributed throughout the semiconductor, and based on their relatively large concentration the most likely location is TiO<sub>2</sub> surface. In the case of  $TiO_2$  band gap excitation, Tamaki et al.<sup>[10]</sup> 30 mentioned that immediately after photo-excitation electrons are trapped on surface states and in the conduction band, which are in their perspective are energetically equivalent and located close to the conduction band edge, thus enabling electrons to migrate between surface trap and shallow bulk trap that are in 35 equilibrium. Shallow traps electrons relax into deeper states through a hopping process involving energetically distributed trapping sites. However, in Tamaki et al. case photo-generated electrons and holes are located in the material, and their recombination can occur both at the surface and in the bulk, 40 which is not our case since holes are located exclusively at the surface (oxidized dye). Thus, making it logical that the final trap state is located at the surface close to the oxidized dye molecule.

Figure 4 shows two models that can justify the experimental observations. Model A supposes the existence of surface trap 45 states that are energetically equivalent to free carriers in the conduction band. The equivalence ensures that the electrons can hop easily between states, and be in equilibrium (constant ratio between trap and free carriers). In this case, the 240 meV corresponds to the potential energy of the surface trap state. An 50 alternative explanation (model B) is the bending of TiO<sub>2</sub> conduction band due to the positive electrostatic potential created by the oxidized dye. The model supposes that after electron injection, the positively charged dye molecules create an equal number of trap states to the number of injected electrons, which 55 are located close to the oxidized dye molecules (uniform trap state energy). Since the prefer location of the electrons is the surface trap states, the newly created sites are quickly filled and due to the proximity of the oxidized dye, the electrons recombine with the holes leading to the depletion of both free and trap 60 carriers (constant ratio between carriers). None of the models can be discarded but in our opinion model B is more likely to occur since it provides a more convincing argument for singularity of the trap state.

In conclusion, with the help of novel synchrotron based <sup>65</sup> transient broadband mid-IR spectroscopy we were able to determine the ratio between free and trapped electrons, and the average energy of the trap state. In respect to the injected electrons final location, the results suggest they are trapped at the surface near oxidized dye. These trap states originated from the 70 bending of TiO<sub>2</sub> conduction band due to the positive electrostatic potential produced by the oxidized dye. If this model is confirmed to prevail, the use dye-sensitizers solar cells systems with high optical absorption dye molecules and high semiconductor surface coverage is counterproductive because it 75 leads to the formation of unwanted recombination sites. Finally, the proposed experimental technique allows for exclusive and simultaneous determination of trap states energy and density, and electrons lifetime, which can be adapted to study other semiconductor systems, which are important for the understanding and improvement of both photovoltaic and photo-catalysis.

## Acknowledgements

We would like to thank the Paul Scherrer Institute for access to the Infrared beam line.

## Notes and references

"Paul Scherrer Institut, 5232 Villigen PSI, Switzerland,

<sup>10</sup> <sup>b</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland. Email: hans.sigg@psi.ch, jacinto.sa@psi.ch

- a) A. Fujishima, K. Honda, *Nature* 238, **1972**, 37-38; b) T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* 277, **1979**, 637-638; c) T. Kawai, T. Sakata, *Nature* 286, **1980**, 474-476.
- 2 For example: a) D. Stíbal, J. Sá, J. A. van Bokhoven, Catal. Sci. Technol. 3, 2013, 94-98; b) S. D. Senanayake, H. Idriss, Proc. Natl. Acad. Sci. 103, 2006, 1194-1198.
- 3 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293, 2001, 269-.
- 4 S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, C. B. Mullins, *Nano Lett.* 12, 2012, 26-32.
- 5 a) B. O'Regan, M. Grätzel, *Nature* 353, **1991**, 737-740; b) M. Grätzel, *Nature* 414, **2001**, 338-344.
- O. Bräm, A. Cannizzo, M. Chergui, *Phys. Chem. Chem. Phys.* 14, 2012, 7934-7937.
- 7 A. Hagfeldt, M. Grätzel, Chem. Rev. 95, 1995, 49-68.
- 8 a) A. V. Barzykin, M. Tachiya, J. Phys. Chem. B 106, 2002, 4356–4363; b) J. van de Lagemaat, A. J. Frank, J. Phys. Chem. B 105, 2001, 11194-11205.
- 9 a) J. Szarko, A. Neubauer, A. Bartelt, L. Socaciu-Siebert, F. Brikner, K. Schwarzburg, R. Eichberger, *J. Phys. Chem. C* 112, 2008, 10542-10552; b) C. She, N. A. Anderson, J. Guo, F. Liu, W.-H. Goh, D.-T. Chen, D. L. Mohler, Z. -Q. Tian, J. T. Hupp, T. Lian, *J. Phys. Chem. B* 109, 2005, 19345-19355; c) N. A. Anderson, T. Lian, *Annu. Rev. Phys. Chem.* 56, 2005, 491-519.
- 10 Y. Tamaki, A. Furube, M. Murai, K. Hara, R. Katoh, M. Tachiya, *Phys. Chem. Chem. Phys.* 9, 2007, 1453-1460.
- 11 M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, J. Am. Chem. Soc. 123, 2001, 1613-1624.
- 12 a) A. Yamakata, T. Ishibashi, H. Onishi, J. Phys. Chem. B 105, 2001, 7258-7262; b) J. B. Asbury, E. Hao, Y. Wang, H. N. Gosh, T. Lian, J. Phys. Chem. B 105, 2001, 4545-4557; c) S. H. Szczepankiewicz, J. A. Moss, M. R. Hoffmann, J. Phys. Chem. B 106, 2002, 7654-7658; d) R. Nakamura, A. Imanishi, K. Murakoshi, Y. Nakato, J. Am. Chem. Soc. 125, 2003, 7443-7450
- a) G. M. Turner, M. C. Beard, C. A. Schmuttenmaer, J. Phys. Chem. B 106, 2002, 11716; b) E. Hendry, F. Wang, J. Shan, T. F. Heinz, M. Bonn, Phys. Rev. B: Condens. Matter Mater. Phys. 69, 2004, 081101-081103; c) S. R. Nagel, S. E. Schnatterly, Phys. Rev. B: Condens. Matter Mater. Phys. 9, 1974, 1299-1303.
- 14 J. Sá, P. Friedli, R. Geiger, P. Lerch, M. H. Rittmann-Frank, C. J. Milne, J. Szlachetko, F. G. Santomauro, J. A. van Bokhoven, M. Chergui, M. Rossi, H. Sigg, *Analyst* 138, **2013**, 1966-1970.
- 15 L. Carroll, P. Friedli, P. Lerch, J. Schneider, D. Treyer, S. Hunziker, S. Stutz, H. Sigg, *Rev. Sci. Instrum.* 82, **2011**, 063101-063109.
- 16 J. Nelson, A. M. Eppler, I. M. Ballard, J. Photochem. Photobiol. A, 148, 2002, 25.

Page 4 of 4