Electron Dynamics in Anatase TiO_2 Nanoparticles by Ultrafast Broadband Deep-Ultraviolet Spectroscopy

Edoardo Baldini[1,*], *Tania* Palmieri[1], *Enrico* Pomarico[1], *Gerald* Auböck[1] and *Majed* Chergui[1]

[1]Laboratory of Ultrafast Spectroscopy, ISIC and Lausanne Centre for Ultrafast Science (LACUS), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Abstract. The optical bandgap of anatase TiO_2 nanoparticles is dominated by bulk absorption bands in the deep-ultraviolet due to strongly bound excitons. These spectral features can be utilized as a sensitive probe of carrier and lattice dynamics inside the TiO_2 nanoparticles. Here, we implement ultrafast broadband spectroscopy tuned to the exciton resonances in order to track the electron cooling in the conduction band of bare anatase nanoparticles and monitor the electron injection dynamics from an external dye in the case of sensitized anatase nanoparticles.

Anatase TiO_2 is a relevant material for several technologies, such as photocatalysis, photovoltaics, transparent conductive substrates and sensors. Crucial for device optimization is the elucidation of the charge carrier dynamics in this indirect bandgap oxide. In anatase TiO_2, once a non-equilibrium distribution of uncorrelated electron-hole pairs is created, the electrons thermalize to the bottom of the conduction band (CB) at the Γ point of the Brillouin zone and the holes to the top of the valence band close to X (Fig. 1(a)). Thereafter, the electron-hole pairs undergo a number of recombination pathways, which include trapping at impurity states, radiative mechanisms (extremely weak in indirect bandgap materials) and Auger processes. So far, most time-resolved studies have focused on the electron-hole recombination and on surface effects; in contrast, the relationship between the carrier dynamics and the electronic structure of the material has remained unexplored, leaving the details of the intraband carrier cooling still elusive. The carrier cooling is governed by their interaction with phonons, and is predicted by theory to occur within tens of femtoseconds [1]. The issue of intraband carrier cooling in the CB of anatase TiO_2 is central to the working principles of photocatalytic and photovoltaic devices. In photocatalysis, the relevant energy states are the lower ones, thus fast thermalization is desirable. In dye-sensitized solar cells, the large driving force of hot electrons is often used for efficient injection, especially when the coupling between the sensitizer to the TiO_2 substrate is weak.

A powerful method to address this question is to track the renormalization of some spectroscopic feature, at high temporal resolution, that directly reflects the electron cooling

---

* Corresponding author: ebaldini@mit.edu

dynamics. Recently, using advanced steady-state and time-resolved techniques (in particular two-dimensional deep-UV spectroscopy), as well as state-of-the-art computational calculations, we revealed the existence of strongly bound excitons in anatase TiO_2 with an intermediate character between the Wannier-Mott and the Frenkel regimes [2]. These excitons are very robust against external perturbations, persisting up to room temperature and emerging in the defect-rich samples (e.g. nanoparticles or mesoporous films) used for applications. A deep-UV pump/deep-UV continuum probe can be used to track the exciton bleaching dynamics, which is closely related to the carrier dynamics. Indeed, as the single-particle states contributing to the first exciton lie along the Γ-Z direction of the Brillouin zone [2], the phase-space filling contribution to the exciton bleach arises exclusively from an electron population close to the bottom of the CB.
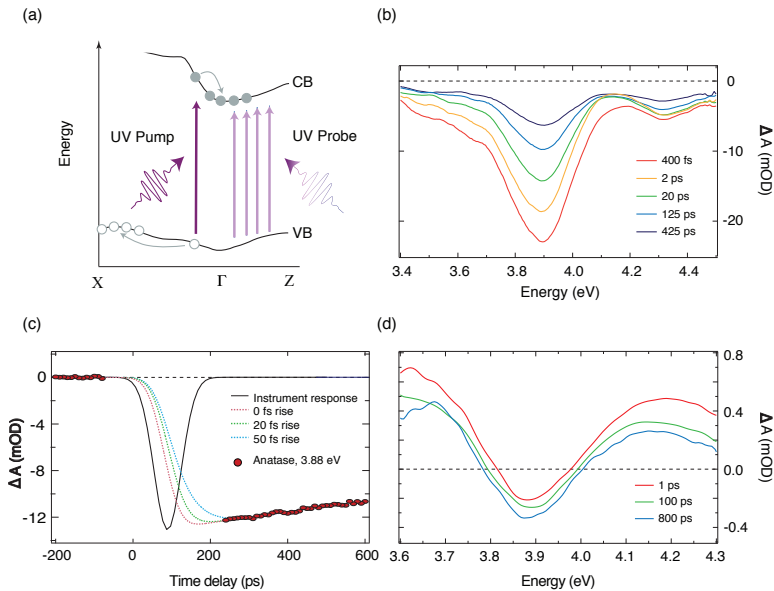

Fig. 1. (a) Schematic representation of the deep-UV based detection of the ultrafast carrier dynamics in anatase TiO_2 nanoparticles. The pump photon at 4.05 eV (purple arrow) excites electron-hole pairs through direct transitions. The broadband UV pulse (violet arrows) probes the exciton feature at 3.88 eV. The direct transitions contributing to this collective state lie along the Γ-Z region of the Brillouin zone. (b) Deep-UV pump/deep-UV probe experiment on a colloidal solution of bare anatase TiO_2 nanoparticles, excited at 4.05 eV with a fluence of 176 μJ/cm^2. The ΔA spectra are shown as a function of probe photon energy at representative delay times between pump and probe. (c) Evaluation of the rise-time of the ΔA signal by interpolating the response of anatase TiO_2 using a rising function (convoluted with a Gaussian instrument response function of 80 fs) at three different times. (d) Visible pump/deep-UV probe experiment on a colloidal solution of N719 dye-sensitized anatase TiO_2 nanoparticles, excited at 2.25 eV with a fluence of 168 μJ/cm^2.

Above-gap excitation at 4.05 eV of a colloidal solution of nanoparticles creates uncorrelated electron-hole pairs, and results in the transient absorption (ΔA) spectra of Fig. 1(b). The long-lived feature at 3.88 eV corresponds to the a-axis exciton band, while the

weaker shoulder at 4.35 eV is due to the c-axis exciton [2]. The band position at 3.88 eV does not change with time, but its linewidth undergoes an initial broadening followed by a subsequent narrowing. These results imply that phase-space filling is the main mechanism behind exciton bleaching, and that only a small contribution from long-range Coulomb screening modifies the excitonic linewidth over time [2]. As a consequence, this observation allows us to use the exciton bleaching dynamics as a probe of the intraband electron cooling to the CB minimum in anatase TiO_2. In this respect, we focus on the rise-time of ΔA at 3.88 eV. To provide an upper limit to the rise time of the bleach signal, in Fig. 1(c) the TiO_2 signal (red dots) is compared to three computed time traces convoluted with the Gaussian instrument response function of 80 fs. They consist of different rise times and an exponential recovery time of 200 fs. It can be seen that the 20 fs rise time interpolates nicely between the t < 0 points and the t > 200 fs ones, and that in any case the upper limit cannot exceed 50 fs. Thus, the rise of the exciton bleach is < 50 fs, which is the timescale for the intraband electron cooling. The most effective coupling mechanism is represented by the electron-longitudinal optical phonon scattering described by the Fröhlich interaction. This result is in excellent agreement with the strong electron-phonon coupling predicted by theory for TiO_2 [1], and demonstrates the power of ultrafast broadband deep-UV spectroscopy as a novel technique for tracking the carrier dynamics in wide-gap insulators. Not obvious in these figures is the occurrence of coherent acoustic phonons, which have been recently analysed [3].

Finally, by unravelling the origin of the bound exciton bleaching in nanoparticles [4], we can now use their spectral signatures as substrate-sensitive probes of charge injection in photovoltaics based on sensitized transition metal oxides. In this respect, we recently demonstrated the effectiveness of our approach by probing the interfacial electron transfer in dye-sensitized anatase TiO_2 nanoparticles via the bleaching of the excitonic features upon visible pumping of an external dye (N719) adsorbed to the nanoparticles (Fig. 1(d)) [5]. This methodology has been extended to materials, such as ZnO, and to other sensitizers.

The above results lead us to conclude that, in anatase TiO_2, fast relaxation processes impose serious limitations to the practical use of the full photon energy in photovoltaic applications, while they favour the prompt electron availability in low-energy states in photocatalysis. This scenario is radically different from the physics of semiconductor quantum dots, in which the spacing between the discrete electronic levels is large enough to prevent fast phonon-mediated carrier cooling processes. In anatase TiO_2, alternative excitation schemes, such as resonant excitation of the strongly bound exciton species, may be preferable in which the energy can be temporarily harvested.

References

1. V. P. Zhukov, E. V. Chulkov, J. Phys. Cond. Matt., **22**, 43 (2010)
2. E. Baldini, L. Chiodo, A. Dominguez, M. Palummo, S. Moser, M. Yazdi-Rizi, G. Auböck, B. P. P. Mallett, H. Berger, A. Magrez, C. Bernhard, M. Grioni, A. Rubio, M. Chergui, Nat. Comm. **8**, 13 (2017)
3. E. Baldini, T. Palmieri, A. Dominguez, P. Ruello, A. Rubio, M. Chergui, Nano Lett. DOI: 10.1021/acs.nanolett.8b01837 (2018)
4. E. Baldini, T. Palmieri, E. Pomarico, G. Auböck, M. Chergui, ACS Photonics **5**, 1241-1249 (2018)
5. E. Baldini, T. Palmieri, T. Rossi, M. Oppermann, E. Pomarico, G. Auböck, M. Chergui, J. Am. Chem. Soc., **139**, 11584-11589 (2017)