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Hunting for the elusive shallow traps in TiO2 anatase

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Understanding electron mobility on TiO2 is crucial because of its applications in photocatalysis and solar cells. This work shows that shallow traps believed to be involved in electron migration in TiO2 conduction band are formed upon band gap excitation, i.e., are not pre-existing states. The shallow traps in TiO2 results from large polarons and are not restricted to surface.

TiO2 anatase is among the most promising metal oxides for several applications; indeed it is used in advanced photovoltaic systems (*e.g.* dye–sensitized solar cells and perovskite solar cells),[1] photocatalysis of thermodynamically uphill reactions (*e.g.* fuel production from CO_2)[2] and self-cleaning surfaces.[3] For all these purposes, high mobility of charge carriers (*i.e.* electrons and holes) generated upon photoexcitation has a key role in improving the efficiencies. The mobility of charge carriers is controlled by the trapping processes, which have been investigated extensively in the past using different experimental methods.[4-8] This is valid for electrons promoted via direct band gap excitation or from excited sensitizers in solar devices.

The most common approach to categorize the trapping sites of electrons below the conduction band (CB) is purely based on their energy position in respect to CB and depicted as pre–existing defect states,[5,8-10] suggestively called "shallow" and "deep" traps. The deep traps are consensually associated to oxygen defect sites, namely vacancies,[11] which are more abundant on TiO2 surface due to unsaturated coordination related to crystal termination. The shallow traps on the other hand are a matter of intense discussion and there is not to date an unambiguous structural feature associated with them that is consensual. The shallow traps have been placed in the range of 50-100 meV below the CB in TiO2. [12,13] A better understanding of their origin will by default help understand electrons mobility.

Experimental methods

TiO2 films (~2 μm) were prepared on CaF_2 windows via doctor–blading Solaronix Nanoxide-T paste (15-20 nm anatase particles in a mixture of water, alcohol and organic binders) followed by gradually heating in an oven (Nabertherm Controller P320) to remove the solvent and organic additives. The temperature gradient program had four levels at 180 °C (10 min), 320 °C (10 min), 390 °C (10 min), and 500 °C (60 min).

Transient absorption spectroscopy of the TiO2 films was carried out in a femtosecond transient absorption spectrometer (Helios IR, Ultrafast Systems LLC) at room temperature. A one-box Ti:Sapphire based amplifier with integrated oscillator and pump lasers (800 nm, 40 fs, 3 kHz, Libra LHE, Coherent Inc.) was used to pump two TOPAS Primes coupled with frequency mixers (Light Conversion Ltd) to produce the depolarized UV excitation pulses ranging from 370 to 400 nm and the broad mid–IR probe spectrum. Pulse energies were adjusted to give matching incident photon densities of $6\text{-}7 \cdot 10^{15}$ photons/(cm^2·pulse) at all excitation wavelengths. The pulse energies were therefore 70–90 nJ, except for 400 nm which was 150 nJ (larger spot size).

Results and discussion

To study the origin of the shallow traps below TiO2 CB, we used transient mid-infrared spectroscopy, tuning the pump at different energies around the band gap and probing in the mid–IR (2100–1950 cm^{-1}). The central wavelengths of the excitation pulses ranged from 370 to 400 nm (3.35 – 3.1 eV) and had FWHM values between 7–10 nm. The steady-state absorption spectrum of the TiO2 film was used to draw a Tauc plot (Fig. 1), [14] where the root of absorbed energy $(\alpha h\nu)^{1/2}$ is presented as a function of the energy of the incident light $h\nu$. The absorption coefficient α for a given wavelength was calculated from the thickness d and absorbance A of the film as $\alpha = dA$. The indirect band gap was determined to be 3.3 eV by extrapolating the linear region of the plot to $\alpha = 0$.

It should be mentioned that the rising edge of the band gap (Urbach tail) does not show evidence of trap states. Thus, we opted to use infrared spectroscopy because it provides clear and unmistakable signals related to electrons in conduction or trap

states. Conceptually the measurement could be carried out with UV-Vis absorption, which should display a signal related to the trap states at ca. 100 meV after TiO_2 absorption edge. However the expected signal change is small and could be difficult to observe due to the strong band gap absorption. Furthermore, infrared is less prone to data artefacts, resultant from scattering of the probe. Finally, the use of pump-probe methodology ensures that before any excitation the material is in the ground state.
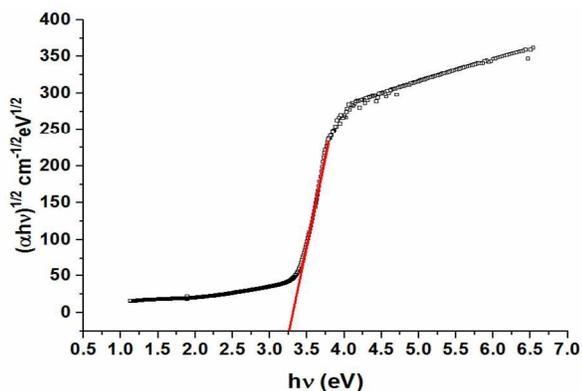

Figure 1. Tauc plot obtained from the steady-state absorption spectrum of the TiO_2 film.

Upon band gap excitation we observed the photoinduced mid−IR absorption originated from the metallic state, which is given by free charge carriers (Fig. 3).[15] The transient shows a Drude behaviour,[16] although in our case considering the narrow range of energies probed, it is difficult to clearly observe such a dependence of the energies versus the intensity. When the pump energy is tuned below the band gap, resonantly with the shallow traps (3.18 eV − 3.10 eV, blue and pink lines in Fig. 2, respectively), we should observe photoinduced absorption signal (Fig. 3) as well. Indeed in this case, upon direct population of a trapping state, the probe energies (about 250 meV) will ionize the localized electron into the unbound continuous states of the CB showing a photoinduced absorption transient signal. The measured spectra showed no statistically
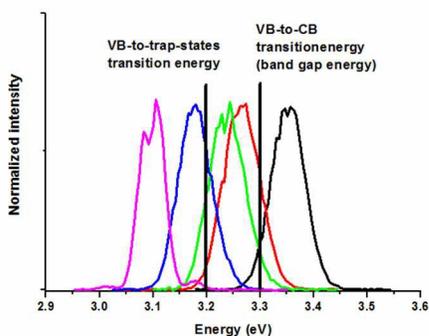

Figure 2. Schematic representation of pump pulse profiles at different excitation wavelengths (energies), which reflect the probability profile for final state of excited electrons upon excitation.
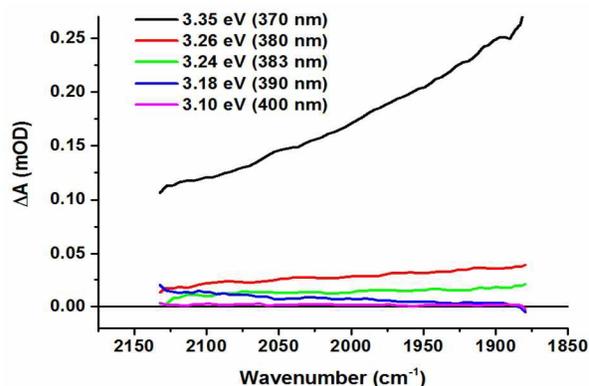
Figure 3. Differential (ΔA) mid−IR absorption spectra of the TiO_2 film on CaF_2 upon photoexcitation at different excitation wavelengths (3.10–3.35 eV) measured 1 ps after pump pulse.

relevant signal when the system was excited resonantly with the shallow traps (minimum detectable signal 10 μOD) indicating that no trap state population could be created by direct excitation from the valence band.

This is further demonstrated in Figure 4 that shows the time evolution of the mid−IR absorption upon photoexcitation at different wavelengths. The decay of the mid-IR signal is similar throughout the measured mid-IR range, but for clarity only the trace at the central wavenumber 2000 cm^{-1} is shown. To serve as a guide to the eye, the time−dependence of the mid−IR absorption spectra was fitted with a double−exponential decay convoluted with a simulated Gaussian response. Since the amplitude of the mid-IR signal from the TiO_2 film significantly decreases when the pump energy is tuned below the band gap it becomes increasingly difficult to fit the traces. To aid the fitting procedure, the time zero at different excitation wavelengths was determined with a reference sample consisting of a similar TiO_2 film on CaF_2 window sensitized with an osmium bipyridine complex, $Os(dcbpy)(CO)_2I_2$.[17] The Os complex absorbs light at all wavelengths used in the present study, and due to electron transfer from the excited state to the TiO_2 conduction band,
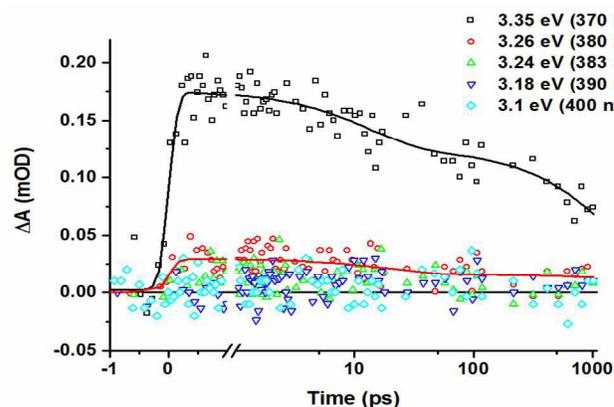
Figure 4. Time−evolution of differential mid−IR absorption at 2000 cm^{-1} of TiO_2 film on CaF_2 upon photoexcitation at different wavelengths. Solid lines relate to exponential decay fitting. The time resolution of the experiment was ~200 fs according to the fits.

gives rise to a photoinduced mid-IR absorption also with sub–band gap excitation. The time zeros in the fits of the time traces obtained from the transient absorption spectra of the TiO_2 film were then restricted to the vicinity of the time zeros of the reference time traces. Nevertheless, the fitting of the time trace was only successful for the two highest excitation pump energies, 3.35 eV and 3.26 eV, suggesting that no detectable mid-IR signal could be obtained with sub-band excitation of the TiO_2 film.

The fact that we could not observe transient signal when we excited at different energies below the band gap of TiO_2 can be explained in two ways:

i) pre-existing structural trapping sites populated with the pump pulse decay within the instrument response time of our setup (around 200 fs) and therefore cannot be probed efficiently;

ii) pre-existing structural trapping sites cannot be populated directly with electrons promoted from the valence band.

The latter interpretation is in agreement with the physics of metal oxides, indeed for a corrected microscopic picture of electron's localization in materials with a strong electron–phonon coupling (*e.g.* TiO_2),[18] cannot be considered the passive population of a trap state which is represented as a pre–existing energy level. The localization of an electron below the conduction band is actually an intrinsic self-trapping process, which is related to a structural distortion of the local environment. The idea that a free electron in a polar lattice can be trapped by "digging its own potential hole" goes back to Landau.[19] Therefore we attribute the origin of the shallow traps involved in electron migration in TiO_2, not to pre–existing defects in the lattice that could be directly populated (inactive in electron mobility, at least on faster time scales), but to polaronic states in which the electrons are self-trapped for the coupling with the surrounding lattice (active states responsible for electron mobility). Polaronic states in TiO_2 anatase have been predicted theoretically in the past [20] and recently measured with a direct method.[21,22] In particular, in case of TiO_2 anatase an intrinsic formation of large polaron has been observed,[21] meaning states in which the electronic density and structural distortion is extended over several sites.

Conclusion

This work confirmed the predictions that anatase TiO_2 trapping sites involved in TiO_2 electron migration, known as shallow traps, are due to large polarons, bridging a well–known phenomenon in condensed matter physics [23] and applied fields, such as photocatalysis and photovoltaics. Other pre-existent structural trap states are inactive in electron mobility at least on the faster time scales. Polaronic trap states (active in electron mobility) are intrinsically related to the material, thus inescapable in the different applications of TiO_2 as semiconducting system. Shallow traps are not restricted to the surface since it relates to metal oxide bulk properties. However, self-trapping is sensitive to material's anisotropy and disorder.[24] Finally, it should be mentioned that large polarons could retain mobility in the lattice through coherent motion

(tunnelling mechanism), as it has been found for specific orientation in TiO_2 anatase.[20]

It should be emphasized that this study only changes the picture on the origin of shallow traps involved in electron migration, not the mechanism responsible for electron mobility in TiO_2. Electron mobility mechanism occurs via trapping and detrapping process between shallow trap and conduction band states, which are thermally accessible. The mechanism is valid for electrons promoted via direct band gap excitation or from excited sensitizers in solar devices.

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Notes and references

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