Charge carrier dynamics in photovoltaic materials
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6 Depolarization fields in colloidal TiO$_2$ films

6.1 Introduction

Titanium dioxide (TiO$_2$) is a wide bandgap semiconductor commonly used in photovoltaics [85, 190] where it can be sensitized by optically active molecular dyes [31, 34] or semiconductor quantum dots [191, 192], see section 1.3. TiO$_2$ also finds applications in photocatalysis [193, 194], for instance for photosplitting of water [195]. Porous films with large surface area made from TiO$_2$ nanoparticles are often employed for these purposes, and the electronic transport properties of such films are therefore of great importance. Despite their technological importance, the electron transport mechanisms in films composed of connected particles have remained poorly understood. For example, the room temperature dc mobility in porous TiO$_2$ ($\sim 7 \cdot 10^{-6}$cm$^2$/Vs) [196] is many orders of magnitude smaller than the mobility of the bulk material ($\sim 1$ cm$^2$/Vs) [197].

In order to investigate the interplay between the local conductive properties of the bulk TiO$_2$ material and the morphology of particle films, we employ time-resolved Terahertz (THz) spectroscopy, chapter 2. We investigate two colloidal TiO$_2$ films composed of submicron-sized (150 – 250 nm), and nanometer-sized (15 – 20 nm) particles respectively. Measuring the THz photoconductivity with two significantly different particle sizes allows us to draw conclusions about the relation between the effective response of the particle film and the local photoconductivity of the particles.

In bulk TiO$_2$ the photoconductivity follows the predictions of the common Drude model for free charges undergoing momentum randomizing scattering [197]. To describe the strongly non-Drude response observed in nanoparticle films, preferential carrier backscattering at grain boundaries has frequently been included via the Drude-Smith (DS) model [74, 81, 83], section 2.4.2. In TiO$_2$, however, the relatively small room temperature charge carrier mean free path ($\sim$1 nm) [82] suggests that only a small fraction of the total carrier scattering
events will occur from surfaces, even for films of nanoparticles [84]. This calls for an alternative explanation for the significantly different conductivities observed in bulk and porous TiO$_2$: the effect of depolarization fields introduced in section 2.4.4. It has been shown [82] that the applied THz probe field is screened because of the contrast in electric permittivity between the oxide particles and the surrounding medium, and by the photoinduced free carriers inducing dipoles in the highly polarizable TiO$_2$ particles. This leads to a non-trivial relationship between the measured macroscopic conductivity and the local conductivity of charge carriers in the particles, as the level of field screening depends on both probe frequency and photoinduced conductivity through the change in permittivity, as well as the film morphology. Note that the influence of local fields is a purely electromagnetic effect which acts in addition to potential preferential backscattering of charge carriers, if present [85]. The applicability of the two alternative models is under debate: Both carrier backscattering and depolarization fields have previously been employed to explain results from various films of TiO$_2$ nanoparticles [81, 82, 84].

Here we demonstrate experimentally, using different samples, that the characteristic photoconductive response is caused by depolarization fields rather than scattering at particle boundaries. We compare our data with a model based on the effective medium theory. The comparison between numerical modeling and measured spectra confirms that depolarization fields are the cause of the observed response, and allows us to conclude that the TiO$_2$ films studied have rather complex percolation pathways, responsible for long range charge transport within the films.

6.2 Samples

Two different films made from different commercial pastes of TiO$_2$ particles were investigated. One was prepared from the Solaronix Ti-Nanoxide T paste which contains particles with diameter 15 – 20 nm (referred to as nanoparticles), the other from Dyesol TiO$_2$ paste WER2-O with particle sizes in the range 150 – 250 nm (referred to as microparticles). The pastes were doctorbladed onto a sandblasted fused silica substrate, dried for 30 min at 115$^\circ$C, and finally sintered for 1 hr at 500$^\circ$C. SEM images of the films are shown in Figure 6.1. Both films consist of the anatase crystal form as confirmed by Raman spectroscopy. Anatase TiO$_2$ has a bandgap of $\sim$3.3 eV [193], meaning that charge carriers can be directly excited by 4.66 eV pulses.
6.3 Results and Discussion

6.3.1 Photoinduced conductivity

Figure 6.2 shows the THz frequency resolved complex photoconductivity normalized to incident excitation photon flux for the microparticle film (a) and the nanoparticle film (b), measured 4 ps after photoexcitation. In agreement with previous works [81, 82, 84], we find that the effective photoconductive response of nanoporous TiO$_2$ films qualitatively differs from the response of bulk in that the photoconductivity exhibits a real component which increases with increasing frequency, and a negative imaginary component. The nature of these features, and thus how to relate the effective photoresponse to the local response of the particles, is still a subject of debate [42, 85].

At this point we can, without further analysis, exclude backscattering at the particle boundaries as the main cause of the shape of the conductivity spectra: The spectra of photoconductivities $\Delta\sigma_{\text{eff}}(\omega)$ are almost identical for films of nanoparticles and films of microparticles, whereas boundary effects would lead to considerably different conductivity spectra in particles with different sizes [84]. This finding is also consistent with the fact that the carrier mean free path of $\sim 1$ nm inferred from bulk measurements [197] is much smaller than the particle radii for both films as mentioned above. Further, a distinct change in the frequency dependence of the conductivity as the photon flux is increased is evident from Figure 6.2. This is particularly noticeable in the imaginary compo-
Figure 6.2. Frequency dependent effective photoconductivity normalized by the photon density recorded at a pump-probe delay of 4 ps in the microparticle film (a) and the nanoparticle film (b) at a number of photon fluxes. Filled symbols show the real part, and open symbols show the imaginary part.

The component of the conductivity, which is positive at high frequencies for low excitation powers, but negative over the entire probe spectrum for the highest excitation powers. Note that the employed excitation powers are not high enough to induce significant carrier-carrier scattering [100]. At this point it is also important to note that most linear models that describe the effects of backscattering on the microscopic conductivity, such as the Drude-Smith (section 2.4.2), exhibit conductivities that simply scale with carrier density, in which case $\Delta \sigma(\omega)/N$ should be independent of $N$. This is in contrast to our findings. These considerations provide evidence that the observed intensity dependence is caused by depolarization fields, which are carrier density dependent [82].

Figure 6.3 (a) shows the magnitude of the pump induced THz absorption $\Delta T/T$ versus pump-probe delay for a number of fluences measured on the nanoparticle sample. Figure 6.3 (b) shows the same pump-probe data normalized to the peak amplitude just after excitation. Here it is clear that the dynamics are independent of excitation density. A similar behavior was observed for the microparticles. Given the diffusion coefficient of $D = 0.025 \text{ cm}^2/\text{s}$ [82] for bulk (rutile) TiO$_2$, we can estimate the carrier diffusion length using $d = \sqrt{\pi D \tau}$ [70] to be $\sim 50 \text{ nm}$ within a time of $\tau = 300 \text{ ps}$. Our measurements suggest that particle boundaries play a small role in the decay of the THz conductivity.

Below we employ the effective medium formalism to account for the effects of depolarization fields. We show that by comparing the effective photoinduced
Figure 6.3. (a) Magnitude of pump induced THz absorption ($\Delta T/T$ recorded on the THz peak) vs. pump-probe delay for nanoparticles at various excitation densities. (b) shows the same data normalized to the peak amplitude.

permittivity changes ($\Delta \epsilon_{\text{eff}}$) measured in our THz experiments to predictions from a numerical model, one can gain insight into the microscopic morphology of the films.

6.3.2 Effective medium and photoinduced permittivity

Since we deal with particles much smaller than the probing wavelength, we account for the depolarization fields via the effective medium formalism, section 2.4.4. Here the permittivity change in the composite film consisting of oxide particles and the surrounding medium is described by a single effective permittivity $\epsilon_{\text{eff}}$ which is experimentally accessible. $\epsilon_{\text{eff}}$ is related to the local permittivity $\epsilon_{\text{loc}}$ of the TiO$_2$ particles through the nature of the morphology of the film, for instance percolated versus non-percolated. However, a scaling of the entire structure to larger or smaller dimensions will not affect the relationship between $\epsilon_{\text{eff}}$ and $\epsilon_{\text{loc}}$ as long as the particles are much smaller than the probing wavelength. $\epsilon_{\text{eff}}$ can be calculated from $\epsilon_{\text{loc}}$ analytically only in very specific cases: for example, the Maxwell-Garnett model describes sparse spherical particles separated in a non-conducting matrix [198]. However, numerical calculations are generally required to characterize more complex morphologies.

In many situations, we are asking the inverse question: can we gain information on the morphology from the measured response? This question can be addressed when it is possible to measure the effective permittivity $\epsilon_{\text{eff}}$ as a function of the local particle permittivity $\epsilon_{\text{loc}}$, since the morphology uniquely defines the mapping $\epsilon_{\text{loc}} \rightarrow \epsilon_{\text{eff}}$ in the effective medium theory.
Here we take advantage of the possibility to control the local photoconductivity \( \Delta \sigma_{\text{loc}} \) by varying the excitation photon density.

A total local permittivity \( \epsilon_{\text{loc}} = \epsilon_{\text{loc},0} + \Delta \epsilon_{\text{loc}} \) (where \( \epsilon_{\text{loc},0} \) is the permittivity of the unexcited material and \( \Delta \epsilon_{\text{loc}} = i\Delta \sigma_{\text{loc}}/\omega \epsilon_0 \) is the permittivity induced by the photoexcitation) leads to an effective permittivity \( \epsilon_{\text{eff}} = \epsilon_{\text{eff},0} + \Delta \epsilon_{\text{eff}} \), where \( \epsilon_{\text{eff},0} \) is the permittivity of the unexcited film and \( \Delta \epsilon_{\text{eff}} = i\Delta \sigma_{\text{eff}}/\omega \epsilon_0 \) is the photoinduced effective permittivity which is experimentally accessible. For bulk TiO\(_2\) at room temperature, the local photoconductivity follows the Drude model (eq. (2.14)) with a very short scattering time [197], which can be very well approximated by a real frequency-independent value \( \Delta \sigma_{\text{loc}} \approx Ne\mu \), where the electron mobility \( \mu \approx e\tau/m^* \) is assumed to be constant. Accordingly, the photoinduced local permittivity

\[
\Delta \epsilon_{\text{loc}} = iNe\mu/\omega \epsilon_0
\]  

is purely imaginary, and is controlled solely by the ratio \( N/\omega \). Therefore, if we simultaneously increase the excitation photon density and the frequency, keeping \( N/\omega \) constant, \( \Delta \epsilon_{\text{loc}} \) should remain the same. Consequently, since \( \epsilon_{\text{loc}} \) and \( \epsilon_{\text{eff}} \) are related only through the morphology of the film, the same photoinduced effective permittivity, \( \Delta \epsilon_{\text{eff}} \) should be observed. In order to verify this prediction we plot in Figure 6.4 the measured THz photoresponse data from Figure 6.2 expressed as \( \Delta \epsilon_{\text{eff}} \), versus the ratio \( N/\nu \) where \( \nu = \omega/2\pi \). Indeed, we see that the imaginary parts measured for various excitation densities overlap with each other to form a single curve (similar \( \Delta \epsilon_{\text{eff}} \) values are obtained for similar values of \( N/\nu \)). This lends further support to the conclusion that the response is primarily and predominantly determined by depolarization fields (other processes such as carrier-carrier scattering should not depend solely on the ratio \( N/\omega \)). The agreement between the data traces of the real part of \( \Delta \epsilon_{\text{eff}} \) appears to be worse. While the absolute errors in the real and imaginary parts are comparable, they seem more pronounced for the real part in the log-log plot, since the real part is considerably smaller than the imaginary part. Moreover, in the Drude response we neglected the imaginary part of \( \Delta \sigma_{\text{loc}} \) which gives the real part of \( \Delta \epsilon_{\text{loc}} \): its inclusion is expected to affect the real part of \( \Delta \epsilon_{\text{eff}} \) more than the imaginary part.

The black lines in Figure 6.4 (a) and (b) show the result of a numerical model simulating the relation \( \Delta \epsilon_{\text{eff}}(\text{Im}\Delta \epsilon_{\text{loc}}) \) for the 2-dimensional model system shown in Figure 6.4 (c) (neglecting the real part of \( \Delta \epsilon_{\text{loc}} \) following the discussion above). Simulations were performed by Hynek Němec and Ivan Rychetský, and are described in more detail in [199]. A system of particles and voids
6.3 Depolarization fields in colloidal TiO$_2$ films

![Graph showing depolarization fields in colloidal TiO$_2$ films](image)

**Figure 6.4.** Effective photoinduced permittivity $\Delta\varepsilon_{\text{eff}}$ for microparticles (a) and nanoparticles (b) calculated from the conductivity data shown in Figure 6.2, as a function of inverse probe frequency times excitation density. Lines in (a) and (b) show the calculated effective response of the structure in (c) plotted versus the imaginary part of the local photoinduced permittivity $\Delta\varepsilon_{\text{loc}}$. Simulations performed by Hynek Němec and Ivan Rychetský [199].

With a single complex percolation path was found to describe the observed behavior well (Figure 6.4 (c)). This structure gives an idea about how the particles in the colloidal oxide film are connected, but should not be interpreted as an exact reconstruction of the actual film. What we can conclude based on the data is that the particles are largely separated by voids, but percolation pathways exist through the film. Qualitatively similar results to the simulations shown in Figure 6.4 are also expected in 3-dimensional structures. The important factor determining the response is the presence or absence of a percolation path in the direction of the applied electric field [199]. 3-dimensional calculations would, however, require a lot more computer power.
The morphology of the film in Figure 6.4 allows for long-range transport, which is necessary for applications that rely on high surface to volume ratios combined with efficient electron harvesting, such as dye-sensitized solar cells [31, 34]. The carrier mobility $\mu$ in (6.1) was estimated so as to get the best agreement between the simulated dependence and the measured data. We found a value of 20 cm$^2$V$^{-1}$s$^{-1}$, comparable to the value $\sim 1$ cm$^2$V$^{-1}$s$^{-1}$ found in a bulk rutile TiO$_2$ sample [197]. It should be noted that the mobility $\mu$ deduced from the numerical model is only an approximate value as it is extracted from a simplified model. The model reproduces the trend of the photoinduced permittivity data shown in Figure 6.4 (a) and (b), and allows us to draw conclusions about the percolation of the film, but does not describe the film morphology in detail. As will be shown in the next section, adsorption of atmospheric water in the oxide film has an influence on the magnitude of the effective permittivity, which was not included in the analysis above.

### 6.3.3 The effect of atmospheric water

The observation that depolarization fields dominate the effective photoresponse of TiO$_2$ particle films has interesting implications. One particular feature of depolarization effects is that they are very sensitive to the polarizability of the environment surrounding the photoconducting particles. Figure 6.5 (a) shows the change in effective photoinduced permittivity measured on the nanoparticle TiO$_2$ film upon changing the environment from ambient air to vacuum. A decrease in $\Delta \varepsilon_{\text{eff}}$ is observed, particularly in the real component, of a factor of $\sim 2$. We ascribe this decrease to a reduction of the field screening as the environment surrounding the particles is changed. In ambient air at room temperature, water molecules efficiently adsorb to TiO$_2$ surfaces [193], and can be (partially) removed when going to vacuum. Since water has a larger permittivity than air ($\varepsilon_{\text{H}_2\text{O}} \approx 4$ at 1 THz [200], $\varepsilon_{\text{air}} = 1$), water will cause the permittivity contrast between the particles and their surroundings to be smaller. The presence of water thus leads to smaller depolarization effects and a larger effective photoinduced permittivity.

In order to compare this effect with the predictions of the numerical model presented above, the effective photoinduced permittivity of the model system shown in Figure 6.4 (c) was calculated while varying the permittivity of the surrounding matrix ($\varepsilon_m$). In order to simulate the effect of increased percolation, connecting regions were also introduced between adjacent particles (see Figure 6.5 (c)) of permittivity $\varepsilon_j$. In Figure 6.5 (b) the blue curves represent the situation where the voids between the particles are completely...
Figure 6.5. (a) Effective photoinduced permittivity measured with excitation photon flux of $6.0 \times 10^{17} \text{ m}^{-2}$ on the nanoparticle TiO$_2$ film in ambient air and in vacuum, plotted versus inverse probe frequency times excitation density. The bottom axis shows the corresponding change in imaginary microscopic permittivity calculated from (6.1) assuming $\mu = 20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. (b) Real (solid lines) and imaginary (dashed lines) effective photoinduced permittivity as function of the imaginary part of the microscopic permittivity calculated for varying degrees of water percolation. (c) Model system used for permittivity calculations, same structure as that shown in Fig 6.4 (c) with permittivity of surrounding medium $\epsilon_m$ and permittivity of connecting regions $\epsilon_j$. Simulations performed by Hynek Němec and Ivan Rychetský [199].

filled with water, the green curves correspond to roughly 33% water filling ($\epsilon_m = 33\% \epsilon_{H_2O} + 67\% \epsilon_{vac} = 2$) distributed evenly in the pores, the red curves correspond to a small amount ($\sim 15\%$) of water concentrated at the connecting regions, and the black curves correspond to total absence of water. From the data in Fig 6.5 (b) we conclude that if water is randomly distributed in the isolating matrix, an unrealistically large water content is needed to increase the effective permittivity significantly. However, the more physically relevant picture of small amounts of water concentrated at the pores between close parti-
cles can also qualitatively explain the magnitude of the experimentally observed shift in permittivity shown in Figure 6.5 (a). Note that the real and imaginary permittivities measured in vacuum, shown in figure 6.5 (a), do not cross, in accordance with the simulations. In [199] it is shown that the observed behavior where the real and imaginary parts of $\Delta \epsilon_{\text{eff}}$ approach each other, but do not cross, is a signature response of a film of separated particles with few percolation paths such as the suggested structure in Figure 6.4 (c). A film of well percolated particles or a film of completely separated particles are expected to show very different behaviors. The simulated magnitude of $\Delta \epsilon_{\text{eff}}$ is larger than the measured data by about a factor $\sim 2$. This discrepancy can be expected as this is a simulation of one model system with a particular morphology, and as stated above, the goal is not to find the exact morphology that reproduces the magnitudes. Similarly, even though the simulations presented above in Figure 6.4 were carried out without accounting for the effect of water in ambient air, the conclusions remain the same.

These observations lend further support to the conclusion that the observed non Drude-like photoconductivity in colloidal films is related to the contrast in permittivity of particles and the surrounding environment, which controls the strength of the depolarization fields. Moreover, the sensitivity of the effective THz photoresponse to the permittivity of the environment offers possible applications in fields such as gas sensing.

6.4 Conclusions

We have shown that the characteristic THz photoconductivity of anatase TiO$_2$ nanoparticle films can be explained by depolarization fields caused by the contrast in permittivity between the conducting particles and the surrounding medium without the need of correction for preferential carrier backscattering at particle surfaces. Numerical calculations of the effective conductivity of a model structure provides insight into the degree of percolation of the nanoparticle films, confirming the presence of charge carrier pathways responsible for the materials long range conductive properties. Finally, the microscopic electron mobility in anatase TiO$_2$ nanoparticles was estimated to be 20 cm$^2$V$^{-1}$s$^{-1}$, in agreement with bulk measurements.