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Photocarrier dynamics in anatase TiO₂: Evidence of thermally activated collisions between carriers

Adrien Girault,^{1,2,3} Mathieu Gallart,¹ Marc Ziegler,¹ Olivier Crégut,¹ Matteo Balestrieri,³ Iryna Gozhyk,³ Hervé Montigaud,³ Davide Sciacca,² Lorenzo Mancini,² and Pierre Gilliot^{1, a)}

¹IPCMS UMR7504 CNRS - université de Strasbourg

23, rue du Læss B.P. 43 - F-67034 Strasbourg CEDEX 2 - France

²Saint-Gobain Research Paris

39, quai Lucien Lefranc - F-93303 Aubervilliers CEDEX - France

³Laboratoire "Surface du Verre et Interfaces" UMR125 Saint-Gobain - CNRS

39, quai Lucien Lefranc - F-93303 Aubervilliers CEDEX - France

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The photoluminescence emission spectrum at low temperature of the TiO₂ anatase shows a broad band around 2.3 eV that has been largely attributed to self-trapped excitons (STE). In this work, time-resolved experiments conducted at low temperature on a thin layer and a single crystal give new insights into the carrier dynamics inside TiO₂. The decay of the photoluminescence with time can be described by a single power law from the *ps* up to *ms* time range. The decay rate increases with increasing temperatures.

We propose to interpret these observations by a collision mechanism between self trapped exciton that diffuse via hopping processes. These excitons, which are stabilized by the indirect bandgap of anatase TiO₂, can be ionized at higher temperatures and leads thus to an acceleration of the observed dynamics

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I. INTRODUCTION

Titanium dioxide TiO₂ is a semiconductor known for its photocatalytic activity and its ability to transport carriers¹. It is known as non-toxic, resilient and abundant and is thus widely used in photo-conversion applications¹. TiO₂ can be found in two main crystalline forms, rutile and anatase, that are stable at ambient temperature. Both phases have been widely studied for photovoltaics, especially after the creation of the first dye-sensitized solar cell by Graëtzel in 1991². For photocatalytic application, the most interesting phase is anatase due to its higher photo-conversion efficiency as compared to rutile³. This phase is organized in TiO₆ octahedra¹ and presents an optical gap of 3.31 eV.⁴ The photocatalytic properties come from the photo-generation, within the material, of charge carriers, electrons (e) and holes (h), that will diffuse towards the surface where they become available for redox reactions. Therefore, most photocatalytic applications of TiO₂ use nanoparticles for which the surface to volume ratio is important. Another possibility is to use thin layers (~ 10 -20 nm) deposited on the surface of another material. This configuration avoids the creation of TiO₂ nanoparticles.

The photocatalytic properties are intimately related to the optoelectronic behavior of TiO₂. Several studies were conducted in the 1980's^{5,6} to get a better comprehension of the excitonic states in various TiO₂ polymorphs including rutile and SrTiO₃. The optoelectronic properties of SrTiO₃ are very close to those of anatase TiO₂. A first extensive study on the photoluminescence of anatase has

been made by Tang et al.^{7,8}. The experiments showed an absorption in the near-UV and a broad photoluminescence in the visible spectral range (very large stokes shift) at low temperature that is usually explained by the formation of self-trapped excitons (STE). The analysis of the Urbach tail gave more hints about the presence of STE. Hosaka et al.⁹ also studied the photoluminescence of TiO₂ and its dependence on the polarization of the excitation light proving that the luminescence is not due to defects but is intrinsic of the material. Finally, the dependence with temperature of the luminescence has been studied by Bieber et al.¹⁰ and Gallart et al.¹¹. The decrease of the photoluminescence intensity with temperature has been interpreted using a 4-energy level model that explains the hopping of the carriers to surface states and the quenching of the luminescence. The carriers in TiO₂ can then be considered as polarons that interact weakly with each other but are strongly bound to the lattice. This model has been successfully used by Begin et al.¹² to link this 4-level model to the photoactivity of various commercial powder of anatase.

Time resolved experiments have also been reported^{13,14}. An extremely long dynamics was evidenced and confirmed in other papers^{15,16}. The fit of the data was made either by a double exponential¹⁷ or by a combination of an exponential and an empirical power function^{13,14}. The decay of the photoluminescence in anatase as then been explained by two different STE formation paths.

In spite of this abundant literature, the exact nature of carriers in anatase TiO₂ is still unclear, the respective roles of free carriers, free excitons, polarons, and STE states remain ambiguous, and many interpretations are offered in recent reviews^{1,4,18-20}. In this regard, the

^{a)}Electronic mail: pierre.gilliot@ipcms.unistra.fr

present work is based on a comprehensive experimental study of the photoluminescence time decay and aims at bringing a new and clarified understanding of the experimental data.

II. SAMPLES AND EXPERIMENTAL SETUPS

A. Anatase samples

We used two types of anatase samples. The first one is a commercial single crystal presenting a surface with 110 orientation (SPL, The Netherlands), labeled as "A110" in the following. The second one is a thin (80 nm) layer that has been deposited on commercial glass via magnetron sputtering using an understoichiometric TiO_2 target. The deposition has been made in the presence of oxygen. A thermal activation is needed for crystallization to occur. It is made at 650°C during 10 min in an industrial oven. This sample will be labeled "Magnetron".

B. Temperature dependent photoluminescence measurements

Photoluminescence (PL) experiments have been conducted at different temperatures using a "Cryo Industries" cryostat where the sample was fixed to a cold finger by a silver paste. The explored temperature range goes down to 10K. The excitation source was a LASOS single frequency diode-pumped solid state laser emitting in the UV at 320 nm. The PL emission was spectrally resolved by a SPEX 270M spectrometer and recorded by a liquid nitrogen cooled CCD camera.

A white-light lamp coupled to a monochromator allowed us tuning the excitation wavelength and recording PL excitation spectra (300 to 400 nm).

C. Time resolved photoluminescence measurements: Streak camera

Time-resolved photoluminescence experiments were carried from room temperature down to 10K using an "Oxford Instruments" cryostat. As before, the sample was fixed to the cold finger. The excitation source comes from a 1030 nm pulsed Ytterbium laser (Tangerine laser from Amplitude). Mixing the second harmonic with a continuum generates 320 nm pulses with a duration of 270 fs. The repetition rate is adjustable between 1 and 100 kHz. The detection setup consists of a spectrometer paired with a Hamamatsu streak camera (C10627) synchronized with the excitation pulse. The acquisition were made in photon counting mode.

III. RESULTS

A. Photoluminescence excitation

Let us start by describing the excitation photoluminescence spectra of the two samples. The maximum of emission occurs at an excitation of 3.4 eV (365nm) for the single crystal (Fig. 1) as expected from the literature^{10,11,21}. The maximum of the thin layers is deeper in the UV (Fig. 2) at 3.9 eV (320 nm). This bandgap increase can be explained by confinement effects.

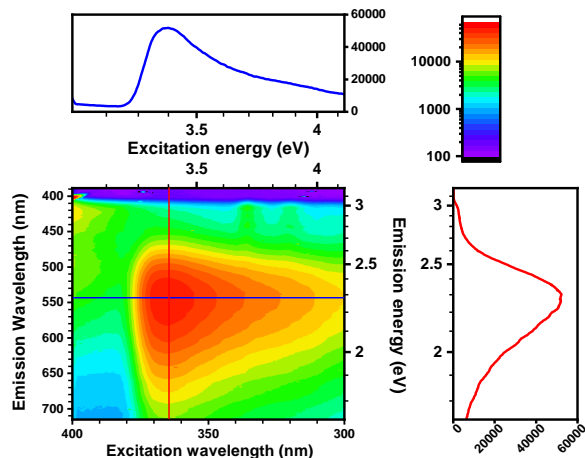


FIG. 1: Low temperature ($T = 10$ K) PLE map of the A110 sample. The top and right graphs are respectively an excitation spectrum (fixed emission at 2.28 eV) and a PL spectrum (fixed excitation at 3.4 eV)

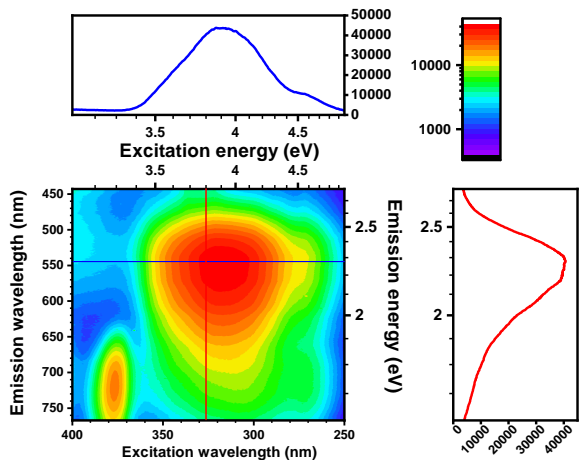


FIG. 2: Low temperature ($T = 10$ K) PLE map of the Magnetron Anatase sample. The top and right graphs are respectively an excitation spectrum (fixed emission at 2.28 eV) and a PL spectrum (fixed excitation at 3.8 eV)

The emission band is nearly the same for both samples. It is characterized by a very broad emission band with a maximum of 2.4 eV. This emission band is asymmetric: a

fit by at least two Gaussian peaks is needed to get a good agreement with the experimental data. The PLE spectra show a large difference of nearly 1.1 to 1.5 eV between the excitation and the emission energies (large Stokes shift), a fact that is usually related to the formation of STE.

B. Temperature dependent photoluminescence

Measurements of the PL intensity as a function of temperature were performed on the thin layers (Magnetron) and the single crystal (A110). The photoluminescence of the samples decreases significantly with temperature as seen in Figure 3. This is described in Ref.¹¹ by a 4-level model that includes thermally activated dark states. The spatial separation of carriers would thus be thermally activated and these carriers could then be transferred to distant sites at the surface where they will be involved in redox reactions: This explains the photocatalytic activity of such samples. This will be discussed in the following.

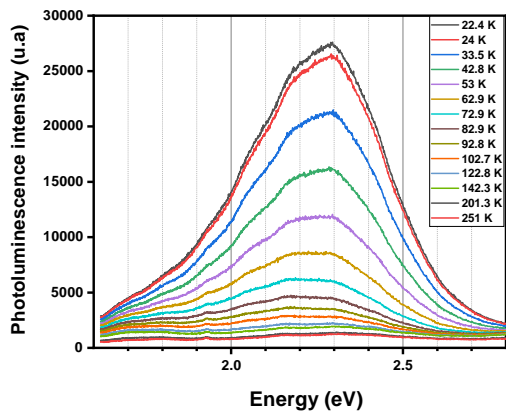


FIG. 3: Temperature decrease of the PL intensity emitted by the Magnetron sample between 22K and 251K

C. Time resolved photoluminescence

Time resolved photoluminescence (TR-PL) measurements were performed on the single crystal and magnetron sample at 10K. As shown in Fig. 4 and 5, the obtained data can be plotted on a 2D map. The abscissa is the wavelength of the detected light. The ordinate is the time scale. Various time resolutions can be attained with the Streak camera. Here, in 4 (a) and 4 (b), the time resolution is respectively 42 ps (240 pixels in 10 ns) and 4.2 ns (240 pixels in 1 μ s).

The two samples are showing a long-lived broad emission between 450 to 580 nm. This emission is comparable to what has been previously observed in the literature¹⁴⁻¹⁶ and in our static experiment as well. It is

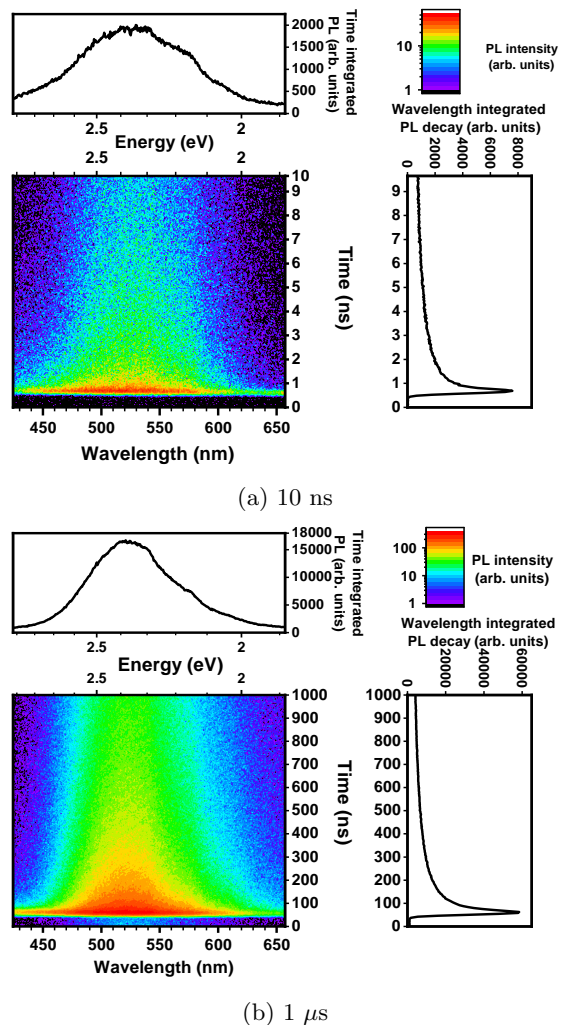


FIG. 4: TR-PL measured on the A110 single crystal at 10K for two different time ranges of the streak-camera.

characterized by a long lifetime: photoluminescence can still be observed several microsecond after the arrival of the laser pulse.

The decay of the photoluminescence with time can be analyzed by integrating the pulse intensity over the whole emission band and at different time ranges of the Streak camera. The PL intensities have been further renormalized with regard to its respective time range: considering for example that 1 pixel in the 10 ns time range merge the same number of photons as 10 pixels in the 1 ns time range. The PL intensity plotted on the y-axis is thus, in arbitrary unit, the value per time unit. Furthermore, as the log-log-scale representation must not suffer any axis shift, we determine precisely the time origin by fitting the TR-PL rise by a Gaussian function and taking the position of its maximum as zero time. This procedure allows us to superimpose all the data measured on different time ranges, as shown on Fig. 6 and 7.

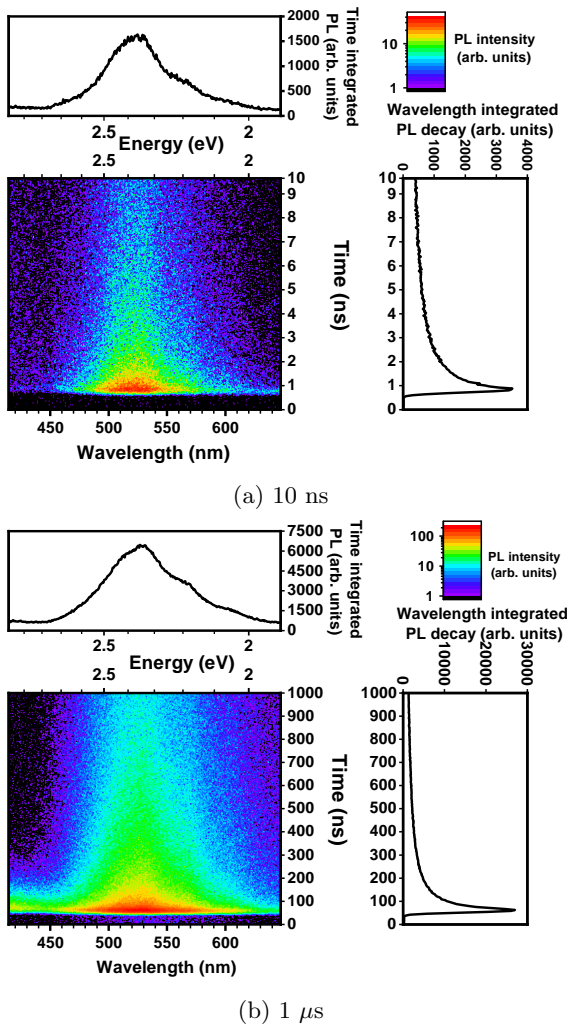


FIG. 5: TR-PL measured on the Magnetron sample at 10K for two different time ranges of the streak-camera.

1. Low temperature experiments

The decays at a temperature of 10 K are shown on Fig. 6 for both samples. The different data acquired for each range of the Streak-camera adjust nicely into a curve that covers nearly 4 orders of magnitude on the signal intensity and 6 orders on the time delay. With the log-log scale that is used, the curve becomes nearly linear for times longer than 1 ns, with a slope around -0.8 for Magnetron sample and -0.6 for the A110 one, showing that the emission dynamics can be described by a single power law with only three parameters (see below). The curvature at shorter time delays fits also well with such a power law with no need of adding an exponential decay (see below the discussion) as shown on Fig. 7.

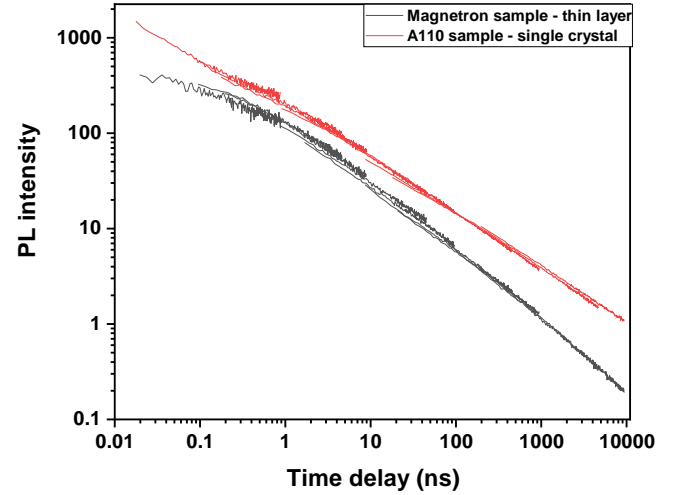


FIG. 6: PL decay of the two A110 and magnetron samples at 10K. The respective slope at long time ($t > 10$ ns) are -0.75 for the thin layer and -0.57 for the single crystal. The experimental curves are the compilation of the data for different streak camera measurement ranges. Fits by a power law are superimposed on the experimental data (see text).

2. Variation of the TR-PL curves with temperature

Fig. 7 shows the evolution of the TR-PL intensity at various temperatures for the Magnetron sample. As expected from the static temperature dependence photoluminescence, the increase of temperature drives a decrease in the photoluminescence intensity. The comparison between the integrated time resolved curves and the static ones on Fig. 8 shows a correlation between the two sets of data. It is reasonable to think that both observations in static and time resolved experiments are the consequence of the same temperature dependent mechanism.

IV. DISCUSSION

The usual emission spectrum feature of the TiO_2 anatase is observed in the thin layer and in the bulk samples as shown on Fig. 2. No notable difference can be seen between the PL emission data of the two samples and the changes in the PLE spectra can be attributed to confinement effect, as a decrease of the domain size can give rise to a blue shift of the transitions. The visible broad emission band with a large Stokes shift has been attributed in the literature to different recombination mechanisms including oxygen vacancies or surface states^{7,13,14,22}. However, the most commonly cited mechanism is the formation of a self-trapped exciton^{8,9,22}. The creation of the STE comes from two different effects that are cumula-

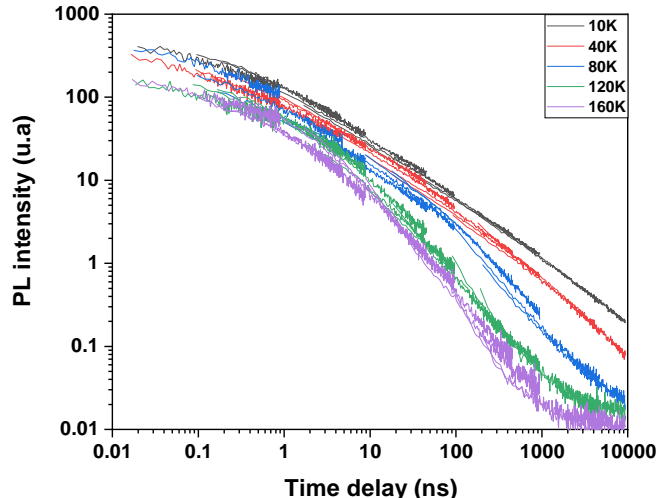


FIG. 7: Dependence on the temperature sample of the time resolved photoluminescence measured on the Magnetron sample. Fits by a power law are superimposed on the experimental data (see text).

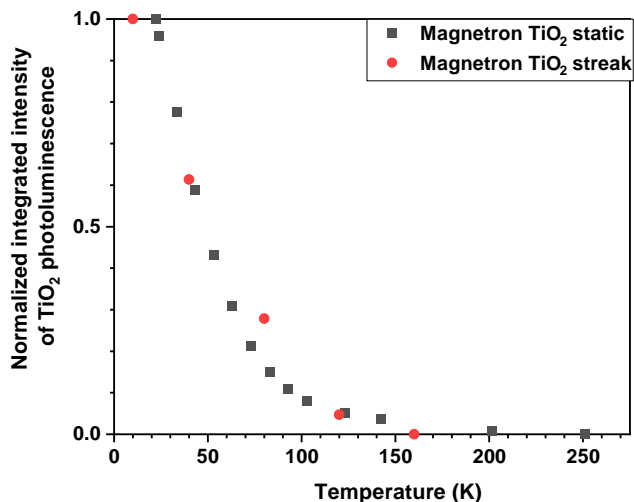


FIG. 8: Comparison of the photoluminescence intensity under CW excitation and of the time-integration of emission signal for pulsed excitation as a function of the sample temperature. Both data sets are normalized to their maximum values, around 20K.

tive. First, a strong electron-phonon interaction tends to create polarons. Second, the Coulomb interaction between carriers leads to their binding into an exciton. As explain in Ref.¹¹, the STE in bulk TiO₂ anatase is intrinsic and is made of two different type of carriers. One is a polaron that is strongly bound and localized in the

lattice. The other is a carrier weakly bound to the first one. This configuration explains the large emission band: such kind of pair of carriers allows the creation of a wide range of configuration that gives rise to the distribution of the emission. Since the two carriers are bound into an exciton and spatially close one to the other, the width of the distribution is similar for the single crystal and the thin film because it is related to local order. Moreover, the detrapping of a weakly bound carrier will explain the quenching of the PL with the temperature, as discussed below.

The main result of our TR-PL measurements is the power-law variation of the photoluminescence with time that we will now discuss in the framework of this description.

A. Power law and collision processes

The main feature that is observed from our data is the decay of the emitted intensities, measured on different samples, that presents a power law dependence with time as evidenced by a straight line at large time delays in a log-log representation. This is a typical feature of a collision process, whose basic equation for the population $n(t)$ describes the interaction between q particles with a nonlinear term:

$$\frac{dn(t)}{dt} = -C n^q(t) \quad (1)$$

that gives, for an initial population $n(0)$

$$n(t) = \frac{n(0)}{(1 + (q-1) C n^{q-1}(0) t)^{\frac{1}{q-1}}} \quad (2)$$

When $t \gg 1 / (C n^{q-1}(0))$

$$n(t) \simeq \left(\frac{1}{(q-1) C t} \right)^{\frac{1}{q-1}} \quad (3)$$

The usual case deals with collisions between 2 particles, ($q = 2$) and:

$$n(t) = \frac{n(0)}{1 + C n(0) t} \quad (4)$$

This standard equation of a collision process implies that the recombination probability is simply the product of the probabilities of having the q particles at the same location, as it would be the case for the superposition of delocalized particle wavefunctions. However, we will see later that taking into consideration particle diffusion introduces an exponent to time.

Such a behavior was already described for TiO₂ by Watanabe et al.^{13,14,23}. They wrote a empirical power law with a general formula¹⁴:

$$n(t) = \frac{n(0)}{\left(1 + \frac{t}{\tau_p}\right)^m} \quad (5)$$

When plotted in a log-log scale, such a graph shows two features: a plateau at low t values, that ends at a value $t \simeq \tau_p$ giving the turning point of the curve, followed by a linear decay at larger times with a slope given by m . But, comparing with (4), we see that τ_p depends actually on the initial excitation: $\tau_p = 1/(C n(0))$. Consequently, there is no characteristic time as it depends strongly on the excitation conditions: Watanabe et al.¹³ used ns pulses and thus the excitation intensity was high, around $100\mu J/cm^2$ at maximum and down to $0.4\mu J/cm^2$ with a large number of photo-injected electron-hole pairs per pulse (up to $n \simeq 2 \times 10^{12} photons/cm^2$). We use here fs pulses, with an energy per pulse of $0.1\mu J/cm^2$ a total number of photons that is significantly lower ($n \simeq 10^{11} photons/cm^2$): the initial photocarrier density is thus lower and the exponential term used by Watanabe et al. to fit the earliest part of the decay is no more visible.

The nonlinear nature of the process makes also difficult the analysis of the emission at very short times. Watanabe et al. proposed an initial exponential decay, with a weight that increases with the excitation intensity. We have seen in our experiments that the instrumental function of the detection apparatus can give rise to such signal as an artefact in the initial dynamics for a power law process. Indeed, since the power law describes a process that slows down with time, the major part of the photons are emitted at short terms giving a contribution that reproduces the instantaneous response of the detection apparatus.

Our data actually show that the power scale behavior is valid even at the smallest time-scale, down to the time resolution of our setup, without a need of involving another process. We can follow that power-law from ps up to μs , over nearly 5 orders of magnitude on both the time scale and the intensity scale during the decay. Taking furthermore the measurements of Watanabe et al.^{13,14,23} who observed a power law up to $10ms$, we know that this observation is valid up to this time range.

B. Colliding particles

There are two general cases that give rise such a decay within photoexcited semiconductors.

The first possibility is to attribute the dynamics we observe to a relaxation process that involves interactions between excitons. It is well known to be a dominant process of the exciton population decay in organic compounds or carbon nanotube. Their dynamics is given by

$$\frac{dN_X(t)}{dt} = -\frac{N_X(t)}{\tau_X} - A N_X^2(t) \quad (6)$$

where N_X is the exciton population. While the dynamics is mainly driven by the second term describing their collisions and proportional to the square of N_X , the recombination and the emitted intensity $I(t)$ is given by the

first term that is proportional to the population. That gives:

$$I(t) \propto N_X(t) = \frac{N_X(0) e^{-t/\tau_X}}{1 + A N_X(0) \tau_X (1 - e^{-t/\tau_X})} \quad (7)$$

When $t \ll \tau_X$, in particular when $A N_X(t) \gg 1/\tau_X$, the decay is only driven by the collision term and one gets:

$$I(t) \propto N_X(t) \simeq \frac{N_X(0)}{1 + A N_X(0) t} \quad (8)$$

Instead of carriers that are bound into excitons, it is possible to consider a second possibility where the dynamics is governed by collisions between separated electrons (e) and holes (h). They would recombine following a bimolecular process: the collision as well as the recombination terms are proportional to the probability to find e and h at the same position. Contrarily to the previous case, the bimolecular term is responsible for the radiative emission and the emitted intensity will now be proportional to the square of the carrier population. Denoting $n(t)$ and $p(t)$ their respective populations, we get:

$$\left. \frac{dn(t)}{dt} \right|_{rad} = \left. \frac{dp(t)}{dt} \right|_{rad} = -B n(t) p(t) \quad (9)$$

In the case of an optical excitation, the densities of e and h are equal: $n(t) = p(t)$. The previous equations reduce to (1) and $n(t)$ and $p(t)$ are given by (4). We would obtain thus a decay of the light emission that is given by the bimolecular term that is quadratic as the other collision terms that follow from Coulomb interactions between the carriers. From (4), we would get:

$$\begin{aligned} I(t) &= -\frac{dn(t)}{dt} \\ &= C n(t) p(t) \\ &\propto C \left(\frac{n(0)}{1 + B n(0) t} \right)^2 \end{aligned} \quad (10)$$

The decays we observe (Fig. 6) at all temperatures are always nicely fitted by power-law decays at any times. For the Magnetron sample, the fitted exponents in the power law range between -0.75 at 10K and -1.4 at 160K. At low temperature, the absolute value of the exponent is lower than 1 and the process could be interpreted as the recombination of excitons as in Eq. (8) (where the exponent is -1) provided that we consider processes that slow down exciton annihilation (see section C). The high temperature value of -1.4 that we observe gives a decay that is too fast for a process related to collision between excitons. Consequently this value is only compatible with a process that involves collisions between single carriers: electrons and holes, or, more precisely, the polarons they form with their surrounding phonon cloud.

C. Finite wave packet

The $1/t$ dynamics given at large times by Eq. (8) is faster to the one we observe (Fig. 6) that displays a power dependence down to $1/t^{0.75}$. Indeed, the collision process that we discussed, with a quadratic term $A N_X^2(t)$ in Eq. (6), considers excitons that are fully delocalized, with wave functions that cover the entire crystal, like plane waves in an infinite volume or, more realistically, carrier wave functions in nanocrystals. But the effect of various collision processes, with phonons or impurities, has to be considered. The wave function becomes then a wave-packet which is spatially finite, with a zero-limit where they can be described as point-like particles that have to move to the same location in order to collide. Such a process belongs to the family of diffusion-controlled reactions and can be seen as a diffusion limited annihilation process.²⁴⁻²⁸ For a 1D random diffusion process, the mean distance between two excitons increases as $D\sqrt{t}$ where D is the diffusion constant. The collision process becomes, for point like particles $-A N_X^2(t)/D\sqrt{t}$ with C combining the collision efficiency A and the diffusion constant D of the particles. Between those two limiting cases (fully delocalized and point-like excitons) the size of the exciton wave packet is finite and, with $C = A/D$ we get

$$-C \frac{N_X^2(t)}{t^\beta} \quad (11)$$

with $0 \leq \beta \leq 1/2$. In a 3D space, the diffusion process can be further slowed, as the probability for two particles to reach the same point within a finite time can decrease to zero: the value of the β coefficient can thus become larger than $1/2$.

The general equation we obtain for colliding excitons with finite wave packets is thus :

$$\frac{dN_X(t)}{dt} = -\frac{N_X(t)}{\tau_X} - C \frac{N_X^2(t)}{t^\beta} \quad (12)$$

The integration of which results, for $t \ll \tau_X$ in:

$$I(t) \propto N_X(t) \simeq \frac{N_X(0)}{1 + \frac{1}{1-\beta} C N_X(0) t^{1-\beta}} \quad (13)$$

That gives a power-law for the intensity that goes between t^{-1} and $t^{-\varepsilon}$ with ε close to zero. Our experimental data for Magnetron sample when the temperature is 10K, where $I(t) \simeq t^{-0.8}$ would give a value $\beta \simeq 0.2$.

The same dependency can be found for the case of uncorrelated electrons and holes, that can collide and that will recombine through a bimolecular process. The general equation we obtain for equal densities of electrons and holes is thus :

$$\frac{dn(t)}{dt} = -C \frac{n^2(t)}{t^\beta} \quad (14)$$

that gives

$$n(t) = \frac{n(0)}{1 + \frac{1}{1-\beta} C n(0) t^{1-\beta}} \quad (15)$$

When t is large enough, the emitted intensity is given by:

$$I(t) \propto \frac{n^2(t)}{t^\beta} \simeq \left(\frac{1-\beta}{C}\right)^2 \frac{1}{t^{2-\beta}} \quad (16)$$

That gives a power-law for the intensity that goes between t^{-2} and t^{-1} . Even if the nature of the collision process changes also when it deals with free carriers instead of excitons, considering only the bimolecular recombination as in Equ. (14) fits already the faster decays. Our experimental data for Magnetron sample when the temperature is 160K $I(t) \simeq t^{-1.34}$ would give a value $\beta \simeq 0.66$.

D. Self-trapped excitons and polarons

The spectral position and shape of the photoluminescence suggests the usual attribution of this emission to self-trapped excitons (STE)²⁹. Moreover, a process involving their collisions has been stated in previous publications to explain why the decay follows a power-law. The identification of the colliding particles to be STE is nevertheless questionable: STE are strongly localized particles that can hardly move and collide.

However, it is known that STE can diffuse in the host crystal through a hopping process^{29,30}. The decay that we observe at low temperature can therefore be explained by collisions between STE: when they reach the same site, one of the interacting STE is annihilated, giving its energy to its partner. The latter is sent to high energy levels, at twice the STE energy of 2.5eV, from which it can relax down to the STE state within a few picoseconds.

To support this hypothesis, we can consider that, even if STE can recombine, their radiative lifetime is nevertheless quite long and they are very stable. We can take into account that anatase is an indirect gap material. Values calculated by Zhu et al³¹ give for example for anatase a direct gap of 4.11 eV at the Γ - point of the Brillouin zone. But there is an indirect gap of 3.57 eV between the minimum of the conduction band (CB) at the Γ - point and the maximum of the valence band (VB) at a Δ - point. After their photo-excitation, electrons (e) and holes (h) are thus quickly separated in the reciprocal space: such e-h pairs hardly recombine radiatively and are thus very stable. They will afterwards merge into STE. This results from strong coupling between the carriers and the lattice that leads to the formation of polarons. Electron and hole are, on the other side, described by wave packets in the k-space that will spread and overlap, as soon as the lattice-carrier interaction will localize them. This allows them to overcome the separation in reciprocal space of the two carriers located at different

k-points. STE show a finite recombination probability, as the separation between the two carriers within excitons is strongly reduced into a volume given by the Bohr radius.

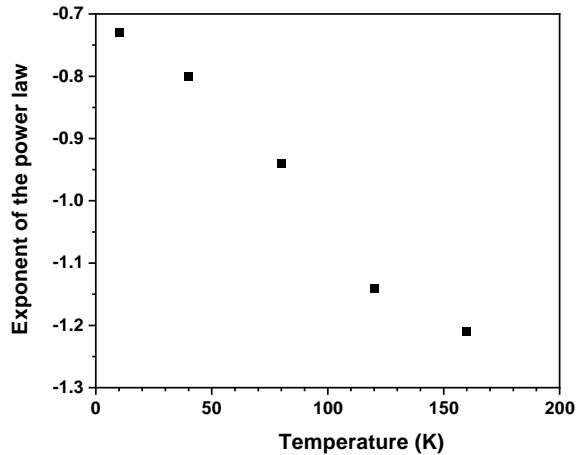


FIG. 9: Exponent of the power law used to fit the experimental data as a function of the sample temperature.

E. Increasing temperature

When increasing the sample temperature, the experimental data remain nicely fitted by the power law indicating that the decay is still driven by diffusion-limited collision mechanisms, without any other involved processes. Nevertheless higher temperatures change the overall process speed that becomes faster, as shown in Fig. 9 by the exponent we deduce from the fits. Higher absolute values for the negative exponent show that the carriers undergo collisions with higher rates.

Moreover we observe that the emission intensity decreases with the temperature, as shown on Fig.8. The signal is time integrated: the total intensity diminishes, following the same law as for static experiments where we used a CW excitation. We have previously proposed¹¹ that the decrease with temperature of the emitted intensity can be described by a thermally activated process. We expect that STE are thermally ionized when temperature is increased and are transformed into separated polarons. We can reasonably estimate that the electron polaron is the lighter particle and can move freely, while the hole polaron shows a higher mass and moves through a hopping process.

The ionization of the STE into separate electron and hole polarons leads to two changes. First, the interactions that are responsible for the fast dynamics will more and more occur now between polarons, instead between STE. Those collisions can expel the carriers from the band extrema and transfer them to trapping states at the crystal

surface, where they can be used in redox reactions. Second, their radiative recombination becomes a bimolecular process described by equations (14) and (16), where the carriers have to reach the same point before being annihilated into a photon.

V. CONCLUSION

Our analysis of the time resolved photoluminescence we measured on anatase TiO₂ samples, shows that the decay dynamics can be fit by a power law at any temperature. In regard of this information, we unveiled the existence of a collision mechanism that drives the recombination in this material. At low temperature, the photo-carriers form self trapped excitons. Their wavefunction is spatially finite and they diffuse by hopping process inside the crystal. The decrease of the population is driven by interactions between STE. As the STE are made of two different carriers: a light electron polaron and a heavier hole polaron, the increase of the temperature can induce the ionization of the STE. The light electron polaron will thus be able to freely move inside the crystal while the hole will still diffuse through a hopping process. The collision process between carrier substitutes to the radiative decay of the carriers, their transport to chemically active sites.

- ¹X. Chen and S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications," *Chem. Rev.* **107**, 2891–2959 (2007).
- ²M. Graätzel, "Photoelectrochemical cells," *Nature* **414**, 338–344 (2001).
- ³M. Xu, Y. Gao, M. E. Martinez, M. Kunst, M. Muhler, Y. Wang, H. Idriss, and C. Wöll, "Photocatalytic activity of bulk TiO₂ anatase and rutile single crystals using infrared absorption spectroscopy," *Phys. Rev. Lett.* **106**, 138302 (2011).
- ⁴K. Bourikas, C. Kordulis, and A. Lycourghiotis, "Titanium dioxide (anatase and rutile): surface chemistry, liquid-solid interface chemistry, and scientific synthesis of supported catalysts," *Chem. Rev.* **114**, 9754–9823 (2014).
- ⁵L. G. J. De Haart, A. J. de Vries, and G. Blasse, "On the photoluminescence of semiconducting titanates applied in photoelectrochemical cells," *J. Solid State Chem.* **59**, 291–300 (1985).
- ⁶R. Leonelli and J. L. Brebner, "Time-resolved spectroscopy of the visible emission band in strontium titanate," *Phys. Rev. B* **33**, 12 (1986).
- ⁷H. Tang, H. Berger, P. E. Schmid, and F. Levy, "Photoluminescence in TiO₂ anatase single crystals," *Solid State Commun.* **87**, 847–850 (1993).
- ⁸H. Tang, F. Levy, H. Berger, and P. E. Schmid, "Urbach tail of anatase TiO₂," *Phys. Rev. B* **52**, 11 (1995).
- ⁹N. Hosaka, T. Sekiya, and S. Kurita, "Excitonic state in anatase TiO₂ single crystal," *J. Lumin.* **72–74**, 874–875 (1997).
- ¹⁰H. Bieber, P. Gilliot, M. Gallart, N. Keller, V. Keller, S. Bégin-Colin, C. Pighini, and N. Millot, "Temperature dependent photoluminescence of photocatalytically active titania powder," *Catal. Today* **122**, 101–108 (2007).
- ¹¹M. Gallart, T. Cottineau, B. Hönerlage, V. Keller, N. Keller, and P. Gilliot, "Temperature dependent photoluminescence of anatase and rutile TiO₂ single crystals: Polaron and self trapped exciton formation," *J. Appl. Phys.* **124**, 133104 (2018).
- ¹²S. Bégin-Colin, A. Gadalla, G. Le Caër, O. Humbert, F. Thomas, O. Barres, F. Villieras, L. F. Toma, G. Bertrand, O. Zahraa, M. Gallart, B. Hönerlage, and P. Gilliot, "On the origin of the

- decay of the photocatalytic activity of TiO₂ powders ground at high energy,” *J. Phys. Chem. C* **113**, 16589–16602 (2009).
- ¹³M. Watanabe, S. Sasaki, and T. Hayashi, “Time-resolved study of photoluminescence in anatase TiO₂,” *J. Lum* **87-89**, 1234–1236 (2000).
- ¹⁴M. Watanabe and R. Hayashi, “Time-resolved study of self-trapped exciton luminescence in anatase TiO₂ under two-photon excitation,” *J. Lum* **112**, 88–91 (2005).
- ¹⁵N. Harada, M. Goto, K. Iijima, H. Sakama, N. Ichikawa, H. Kunugita, and K. Ema, “Time-resolved luminescence of TiO₂ powders with different crystal structures,” *Jpn. J. Appl. Phys.* **46**, 4170–4171 (2007).
- ¹⁶T. Hashimoto, K. Takahashi, H. Kunugita, H. Sakama, and K. Ema, “Dynamics of photo-excited carriers in anatase TiO₂ thin film investigated by pump-probe method,” *J. Phys.: Conf. Ser.* **193**, 012051 (2009).
- ¹⁷K. Wakabayashi, Y. Yamaguchi, T. Sekiya, and S. Kurita, “Time-resolved luminescence spectra in colorless anatase TiO₂ single crystal,” *J. Lumin.* **112**, 50–53 (2005).
- ¹⁸J. Zhang, X. Chen, Y. Shen, Y. Li, Y. Hu, and J. Chu, “Synthesis, surface morphology and photoluminescence properties of anatase iron-doped titanium dioxide nano-crystalline films,” *Phys. Chem. Chem. Phys.* **13**, 13096–13105 (2011).
- ¹⁹S. M. Gupta and M. Trpathi, “A review of TiO₂ nanoparticles,” *Chin. Sci. Bull.* **56**, 1639–1657 (2011).
- ²⁰J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, and D. W. Bahnemann, “Understanding TiO₂ photocatalysis: Mechanisms and materials,” *Chem. Rev.* **114**, 9919–9986 (2014).
- ²¹D. K. Pallotti, L. Passoni, P. Maddalena, F. Di Fonzo, and S. Lettieri, “Photoluminescence mechanisms in anatase and rutile TiO₂,” *J. Phys. Chem. C* **121**, 9011–9021 (2017).
- ²²K. Iijima, M. Goto, S. Enomoto, H. Kunugita, K. Ema, M. Tsukamoto, N. Ichikawa, and H. Sakama, “Influence of oxygen vacancies on optical properties of anatase TiO₂ thin films,” *J. Lumin.* **128**, 911–913 (2007).
- ²³M. Watanabe, T. Hayashi, H. Yagasaki, and S. Sasaki, “Luminescence process in anatase TiO₂ studied by time-resolved spectroscopy,” *Int. J. Mod. Phys. B* **28-29-30**, 3997–4000 (2001).
- ²⁴S. H. Northrup and J. T. Hynes, “On the description of reactions in solution,” *Chem. Phys Lett.* **454**, 244–247 (1978).
- ²⁵Z. Zhu, J. Crochet, M. S. Arnold, M. C. Hersam, H. Ulbricht, D. Resasco, and T. Hertel, “Pump-Probe spectroscopy of exciton dynamics in (6,5) carbon nanotubes,” *The Journal of Physical Chemistry C* **111**, 3831–3835 (2007).
- ²⁶A. Srivastava, H. Htoon, V. I. Klimov, and J. Kono, “Direct observation of dark excitons in individual carbon nanotubes: Inhomogeneity in the exchange splitting,” *Physical Review Letters* **101**, 087402 (2008).
- ²⁷Y. Murakami and J. Kono, “Nonlinear photoluminescence excitation spectroscopy of carbon nanotubes: Exploring the upper density limit of One-Dimensional excitons,” *Physical Review Letters* **102**, 037401 (2009).
- ²⁸J. Allam, M. T. Sajjad, R. Sutton, K. Litvinenko, Z. Wang, S. Siddique, Q.-H. Yang, W. H. Loh, and T. Brown, “Measurement of a reaction-diffusion crossover in exciton-exciton recombination inside carbon nanotubes using femtosecond optical absorption,” *Phys. Rev. Lett.* **111**, 197401 (2013).
- ²⁹K. S. Song and R. Williams, *Self-Trapped Excitons*, 2nd ed. (Springer Verlag, 1993).
- ³⁰K. Tanimura and N. Itoh, “The hopping motion of the self-trapped exciton in nacl,” *J. Phys. Chem. Solids* **42**, 901–910 (1981).
- ³¹T. Zhu and S.-P. Gao, “The stability, electronic structure and optical property of TiO₂ polymorphs,” *J. Phys. Chem. C* **118**, 11385–11396 (2014).