

## Time-resolved Fluorescence Spectroscopy and Microscopy in Materials Science

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### Introduction

Studying luminescence lifetime data is a very powerful analytical tool for spectroscopists and microscopists alike, as it provides insights into the excited state dynamics of molecules, complexes, nanoparticles, or semiconductors. The fluorescence or phosphorescence lifetime is an intrinsic characteristic of luminescent species. It indicates how long the species under consideration will remain in an electronically excited state before returning to the ground state. Each emitting species has a characteristic luminescence lifetime that can be influenced by its environment.

A series of spectroscopy and microscopy methods based on luminescence lifetime have been developed and allow obtaining information that would be otherwise not accessible through steady-state experiments. For example, fluorescence lifetime imaging (FLIM) is a very well established imaging method in life science where the lifetime information

is combined with spatial localization in the sample, allowing investigating biochemical or physical processes.<sup>[1]</sup> This combination of data can help detecting changes in the local environment such as pH, temperature, or ion concentration, identify molecular interactions or conformation changes via Förster Resonance Energy Transfer (FRET).

Time-resolved methods such as FLIM or Fluorescence (Lifetime) Correlation Spectroscopy (F(L)CS) are commonly used in biological studies, but these methods can also be important in materials science for the characterization of key parameters like charge carrier dynamics and mobility in semiconductors.

### Time-correlated Single Photon Counting

Time-resolved data acquisition is commonly performed through time-correlated single photon counting (TCSPC); a versatile technique which provides an excellent time resolution and can cover

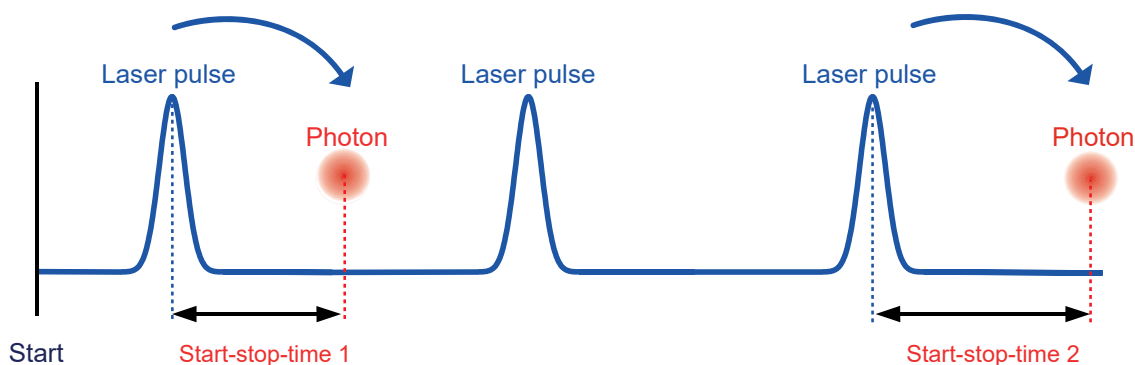


Figure 1: Recording photon arrival times in a time-resolved fluorescence measurement with TCSPC.

lifetime ranges from typically ps to ms. TCSPC requires periodic excitation e.g., from a pulsed laser along with single photon sensitive detectors (such as Photomultiplier Tubes (PMTs), Micro Channel Plates (MCPs), Single Photon Avalanche Diodes (SPADs), or Hybrid PMTs) as well as corresponding counting electronics and optical elements.

An in-depth discussion of the working principles of TCSPC can be found in a corresponding TechNote from PicoQuant.<sup>[2]</sup> In a very simplified way, TCSPC works as follows: molecules in a sample are repeatedly excited with light pulses from an excitation source and the arrival times of emitted single photons are recorded by the detector with high temporal accuracy. The time difference between excitation laser pulse and arrival of the emitted photons by the sample is determined by electronics acting like a highly precise stopwatch, as shown in Fig. 1.

This measurement step is repeated over multiple cycles to account for the statistical nature of the emissive species. All recorded arrival times are then sorted into a histogram (see Fig. 2), from which the lifetime information can be extracted through mathematical methods.

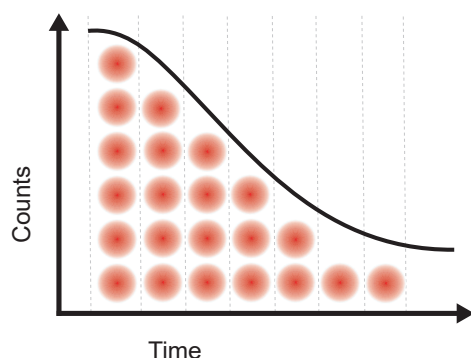


Figure 2: Histogram of start-stop times obtained from a TCSPC measurement. The discrete time bins (channels) are indicated by dashed lines.

### The FluoTime 300 for Materials Science

The aim of this Application Note is to highlight the usefulness of time-resolved spectroscopy and microscopy for characterization of key parameters in materials science through several application examples. In many of these examples, the FluoTime 300 “Easy Tau” from PicoQuant was used for data acquisition and analysis.<sup>[3]</sup>

The FluoTime 300 “EasyTau” is a modular, high performance photoluminescence spectrometer for steady-state and time-resolved measurements with full automation. It can record steady state spectra and luminescence decays by means of Time-Correlated Single Photon Counting (TCSPC) or Multichannel Scaling (MCS) techniques. Therefore, studying luminescence decays whose lifetimes range from a few picoseconds to several seconds is possible. Multiple detector options and a broad range of easily exchangeable light sources (including pulsed and con-

tinuous wave mode lasers, LEDs, and Xenon lamps) are available, which provide access to a broad spectral range from UV up to IR.

The spectrometer can be equipped with double monochromators in both excitation and emission pathways. Due to their very high stray light rejection (signal-to-noise ratio of 29.000:1 (RMS) using standard water Raman test), the FluoTime 300 can be used to also study samples with very strong scattering contributions with extreme sensitivity and temporal resolution. The operation of the emission double monochromator can be switched from additive to subtractive mode via the spectrometer’s graphical user interface. Additive mode is ideally suited for applications requiring high spectral resolutions and can reach values as high as 0.15 nm. Temporal resolution can be significantly increased in subtractive mode, which allows studying very short luminescence lifetimes. In combination with appropriate excitation sources, TCSPC electronics and detectors, an Instrument Response Function (IRF) of less than 60 ps can be achieved.

With this modular instrument design and wide range of accessories, including sample mounting units, the FluoTime 300 can be adapted to your specific sample and measurement needs in a simple and cost effective way. Liquid, solid or powder samples can be accommodated and measurements can be temperature controlled via Peltier cooler, external thermostat or even a cryostat.

All instrument operations are controlled from the intuitive and easy-to-use “EasyTau” system software. Specifically designed application wizards guide the user through the necessary optimization steps for performing typical measurement tasks. A customized measurement mode with full instrument control is available for those who are familiar with the techniques. More sophisticated application tasks, like, for example, alternating between time-resolved decays and steady-state spectra at different temperatures overnight or automation of routine processes can be easily performed through scripted data acquisition using the integrated scripting language.

All time-resolved data can be analyzed with the FluoFit software, which features global decay analysis and iterative re-convolution (up to fourth order) with non-linear error minimization through an easy-to-use graphical user interface. This feature set makes the FluoTime 300 the ideal analysis platform for studying many types of photoluminescent samples in materials science not only for experts but also for novice users.

## Application Examples

### Determining Charge Carrier Dynamics in Semiconductors

Charge carrier dynamics in semiconductors are determined by the architecture and function of the re-

spective device and directly reflect the nature and quality of wafer materials. This makes precise and efficient measurement techniques of the free charge carrier lifetime essential for characterizing these systems. For particular classes of semiconductors, the characteristic charge carrier lifetime is highly dependent on the nature and dimensions of the materials and interfaces involved.

Furthermore, surface effects, passivation, as well as the presence of dopants, impurities and defect sites can introduce significant variations in this parameter. Since the photoluminescence of semiconductors is a direct monitor of the charge carrier dynamics, the general methodology of time-resolved photoluminescence (TRPL) via TCSPC and the attendant technology are highly suited for the analysis of these phenomena. As a result, the mechanism that determines the charge carrier dynamics within a particular system can be characterized directly down to the sub-nanosecond time scale.

A critical parameter in understanding the photo-physics of semiconductor solar cells is the diffusion length of the photo-excited electrons and holes in the material. Time-resolved photoluminescence quenching experiments are a valuable tool for determining diffusion lengths. In an example reported by S. D. Stranks et al., data were obtained from mixed halide and triiodide organometal perovskite layers in presence of either an electron (Fig. 3, blue) or hole (red) quenching layer, or a PMMA coating (black).<sup>[4]</sup> The decay curves were recorded at 780 nm, corresponding to the peak emission of both materials. The decay curves can be fitted to a diffusion model, allowing to derive diffusion lengths. Here, the diffusion length of the electrons and holes in the mixed halide perovskite was 1  $\mu\text{m}$  while the triiodide material featured a much shorter length of 100 nm, correlating well with performance of these materials as solar cells.

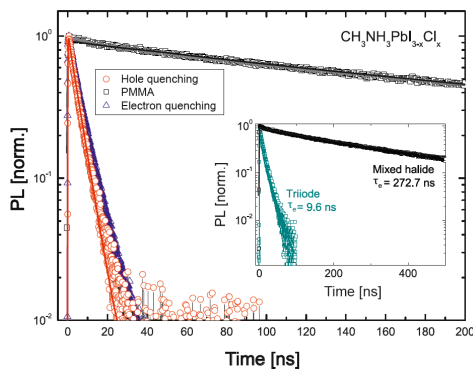


Figure 3: Measured photoluminescence decay curves from mixed halide (inset, black) and triiodide (inset, turquoise) perovskite layers, as well as of the mixed halide material in presence of electron (blue) or hole (red) quenching layer, or PMMA coating (black). The measured decay can be fitted to diffusion models, allowing determining the electron-hole diffusion.

## Spatially Resolved Measurements of Lifetimes in CdTe Solar Cells

The general methodology of TRPL can be expanded by performing imaging of charge carrier dynamics, which allows linking lifetime information with spatial location. This can be exploited to determine the effect and influence of carrier diffusion on the total lifetime measured in conjunction with intensity dependent photoluminescence measurements.

Using this method requires either a time-resolved microscope or coupling a time-resolved fluorescence spectrometer with a scanning microscope. A simple way to realize such a set-up is to use the FluoTime 300 fiber coupling sample mounting unit to interface the spectrometer with a microscope e.g., MicroTime 100 (see Fig. 4). The full range of optical elements from the FluoTime 300 can be used along with the analytical tools of the EasyTau and FluoFit software packages to investigate light originating from the microscope focal volume.

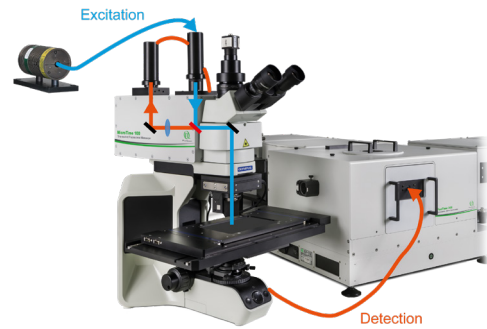


Figure 4: Coupling the FluoTime 300 time-resolved spectrometer with the MicroTime 100 scanning microscope. This combination allows scanning and recording data from any sample mounted on the microscope stage.

TRPL imaging is an exceptionally powerful tool for semiconductor analysis with respect to material and architectural substructures, spatial inhomogeneities and process dependent morphology. Using TRPL imaging, charge carrier diffusion processes and the effect of localized inhomogeneities and defect sites can be identified. With this multi-dimensional approach, a versatile and powerful methodology for the analysis of semiconductor materials can be achieved.

In order to acquire such a TRPL image, the photons have to be attributed to each different pixel, which is done by storing the absolute arrival times of the photons in addition to their relative arrival time with respect to the laser pulse. Line and frame marker signals from the scanner of a confocal microscope are additionally recorded in order to attribute the photon time stream to the corresponding pixels.

As an application example of TRPL imaging, we refer to the study of CdTe polycrystalline wafers by Buschmann *et al.*, where the wafer surface was

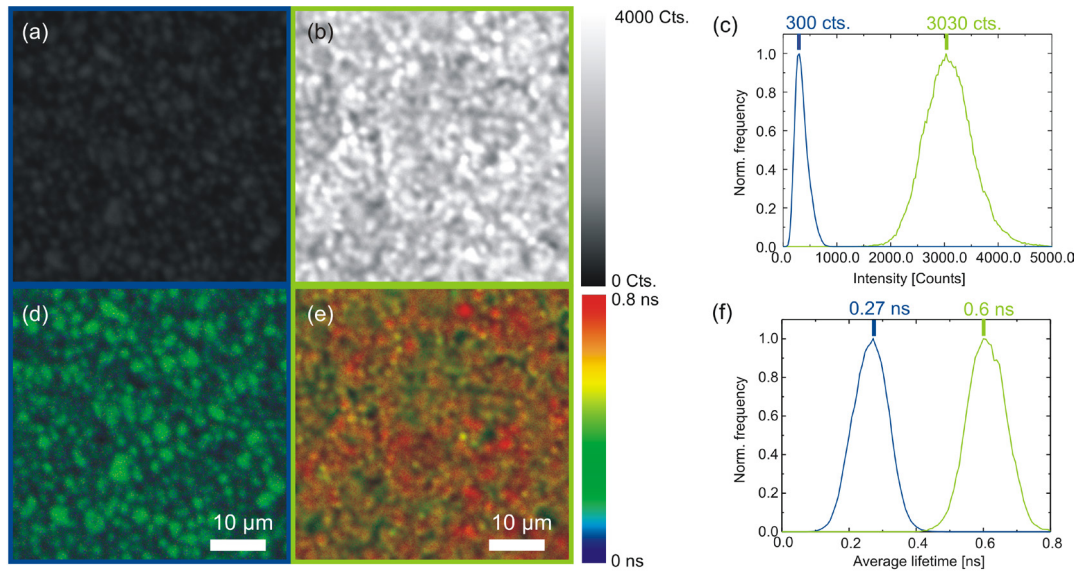


Figure 5: TRPL imaging of CdTe wafers. Left: Intensity and lifetime images of a CdTe wafer before (a, d) and after thermal activation (b, e). Right: Statistical distribution of intensities (c) and lifetimes (e, f) before (blue) and after (green) thermal activation.

scanned with a MicroTime 100 confocal microscope equipped with a fiber coupled detector using a 819 to 865 nm bandpass filter. before and after thermal activation with a chloride compound.<sup>[5]</sup> The respective intensity images (Fig. 5, a and b) as well as the lifetime images (Fig. 5, d and e) show a significant increase in intensity and photoluminescence lifetime after activation. The statistical distribution of the intensities (c) and lifetimes (f) over the full image are given before (blue) and after (green) activation. With only the 3 ms/pixel measurement time, a distinctive change in the average lifetime can be determined as well as significant variations of the lifetime over different regions of the CdTe structure.

### Studying Fluorescence Upconversion in Nanoparticles

Fluorescence upconversion materials absorb light in the near infrared (NIR) and emit photons in the visible range. The main research interest in these materials lies in their prospective application for *in vivo* optical imaging, as they allow excitation in the NIR where light absorption and scattering from biological tissues are minimal.

Another possible application of upconversion nanoparticles is dye sensitized solar cells. A standard solar cell does not absorb in the near infrared spectral range, as the energy of the NIR light is too low for injecting electrons into the conducting band of the solar cells semiconducting material. Using upconversion nanoparticles is one way to overcome this issue and increase light conversion efficiency. In this case, the NIR light is absorbed by the nanoparticles and converted into visible light, which has enough energy to promote electrons from the valence to the

conducting band of the cells material.

Fully characterizing the photophysical properties of such materials requires recording steady-state emission and excitation spectra as well as performing time-resolved measurements. Fig. 6 shows emission spectrum as well as corresponding lifetime decay of NaFY<sub>4</sub> nanocrystals doped with Ytterbium and Erbium.<sup>[6]</sup> In both cases, the nanocrystals were excited at 980 nm with the LDH-D-C-980 diode laser. Data was acquired with a FluoTime 300 and analyzed with the included FluoFit software package.

As a so-called dual mode laser, the LDH-D-C-980 can be operated in either pulsed or continuous wave (cw) mode. The upconverted emission spectrum was recorded while operating the laser in cw mode while pulse burst mode was used to obtain the lifetime decay curve. In the latter mode, a series of picosecond long laser pulses (about 8500 individual shots, each with a 100 ps pulse width) are sent into the sample before stopping excitation long enough to capture the comparably slow decay of the material. Full integration of the laser driver control in the system software of the FluoTime 300 makes setting up such measurements very easy as changing and configuring operation modes is done via an intuitive graphical user interface.

The emission spectra show quite nicely that the absorbed 980 nm light is upconverted and emitted in the green spectral range (520 to 560 nm). The green emission stems from Er<sup>3+</sup> centers that were sensitized by Yb<sup>3+</sup> ions, which absorbed light at 980 nm. Analysis of the time-resolved data reveals a monoexponential decay component with a lifetime of 113 μs along with a shorter rising component.

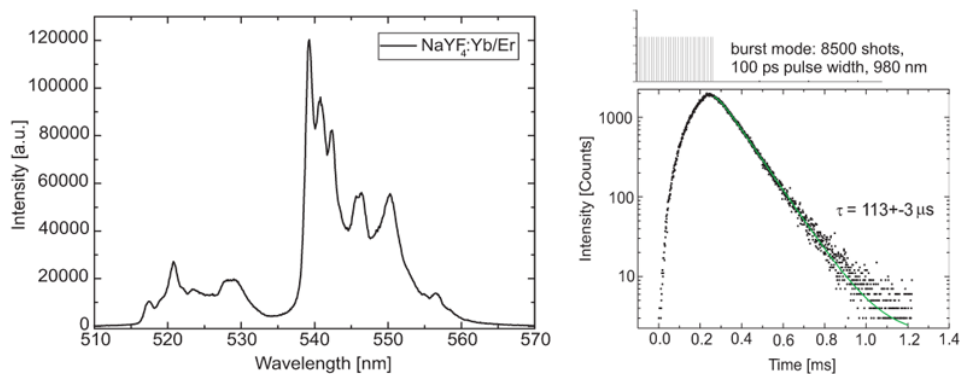


Figure 6: Upconversion nanoparticles based on  $\text{NaYF}_4:\text{Yb/Er}$  suspended in cyclohexane. Left: Steady-state emission spectrum upon continuous-wave (cw) excitation at 980 nm. Right: Lifetime decay (black dots) with fitted curve (green line) upon excitation at 980 nm using a picosecond pulsed diode laser operating in burst mode.

## Conclusion

Using time-resolved spectroscopy or microscopy methods provides additional information in addition to steady-state measurements and helps in understanding the excited state dynamics in a wide variety of materials. Even more information can be obtained by coupling a spectrometer with an optical raster scanning microscope. This imaging approach allows correlating the observed dynamic processes with specific spatial locations in the sample, which, in turn, provides insight into the structure-properties interrelations of the luminescent species.

A time-resolved spectrometer with modular design such as the FluoTime 300 is highly desirable not only for spectroscopists but also for material scientists as it can be easily adapted to meet most sample and experimental requirements. Performing a full characterization of the luminescence properties of a sample in a single set-up also allows to save time and costs. The automation possibilities and easy-to-use software interface of the FluoTime 300 enables you to spend time on the important tasks: analyzing, optimizing, and designing more materials with fascinating properties!



## References and Further Reading

- [1] S. Trautmann, V. Buschmann, S. Orthaus, F. Koberling, U. Ortmann, R. Erdmann, Application Note on Fluorescence Lifetime Imaging (FLIM) in Confocal Microscopy Applications, PicoQuant (2012)
- [2] M. Wahl, Technical Note on Time-Correlated Single Photon Counting, PicoQuant (2014)
- [3] <https://www.picoquant.com/products/category/fluorescence-spectrometers/fluotime-300-high-performance-fluorescence-lifetime-spectrometer>
- [4] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, Science, 2013, vol. 342, 341-344
- [5] C. Kraft, H. Hempel, V. Buschmann, T. Siebert, C. Heisler, W. Wesch, C. Ronning, J. App. Phys., 2013, vol. 113, 124510
- [6] J. M. Taylor, C. Litwinski, T. Nyokong, E. M. Antunes, J. Nanopart. Res., 2015, vol. 17, 85



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