HORIBA Scientific

Measurement of carrier lifetime in perovskite for solar cell applications

TRFA-17

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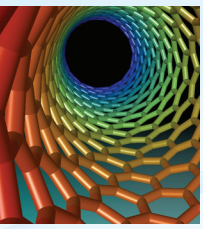
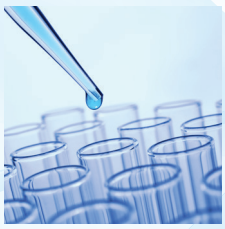
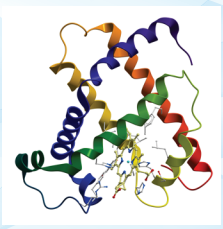
RAMAN
SPECTROSCOPIC ELLIPSOMETRY
SPR IMAGING


HORIBA's TCSPC instruments enable the monitoring of efficiencies of perovskite materials for photovoltaic applications

Hybrid perovskite photovoltaics (PV) show promise because of their good efficiencies, which can be around 20%. Along with their PV characteristics, perovskite materials exhibit a high degree of radiative recombination. The apparent carrier lifetimes can be several hundreds of nanoseconds; and the longer-lived the photoluminescence decay, the greater the efficiency of the material. Thus, the use of time-resolved luminescence with HORIBA TCSPC instrumentation provides a suitable means by which to monitor the efficiencies of this type of material for photovoltaic applications, as well as to uncover the presence of doping anomalies and trapping by deviation from single exponential decay kinetics.

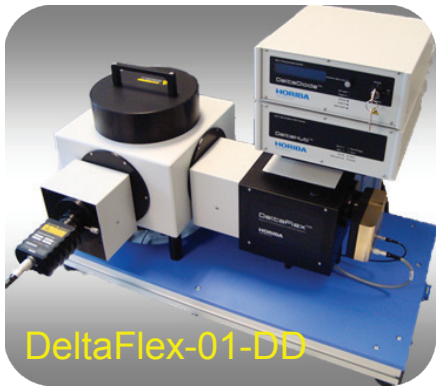
Perovskite photovoltaic materials

The general perovskite structural motif can be denoted ABX3, where X is an anion (usually oxygen), A is a large metal cation and B a smaller metal cation. This structure provides some interesting properties, and in materials science has lead to investigation of applications in microelectronics and telecommunication; principally because of their conductivity / resistance properties. One major application area is that of inexpensive high efficiency photovoltaics. The perovskite commonly used in this application is based on methylammonium lead triiodide ($CH_3NH_3PbI_3$). The efficiency relates to the large diffusion length that photoinduced electrons and holes have. This enables better current extraction, and also makes them suitable for use in a thin film form allowing more flexibility in device design. The perovskite material can be used in different cell architectures, either as sensitizer (i.e. as light absorber) or thin film (charge transport role).

The fact that the charge carrier recombination can be radiative, which is critical in achieving the efficiency limit, also means that time-resolved photoluminescence is a good technique with which to assess these systems. Generally the longer-lived the decay, the better the performance of the material, as the carriers would have diffused further before radiatively recombining. The kinetics of the photoluminescence decay can also provide information. The recombination can consist of trap-assisted, monomolecular (i.e. first order) and bimolecular (second order) processes and consequently modelling of the decay kinetic has made use of single, bi- and stretched exponential functions. Distribution of lifetimes has been related to charge trapping or the nature of doping. It is clear that photoluminescence can be employed to give important information concerning the optimization and characterization of perovskite photovoltaic materials.

Experimental

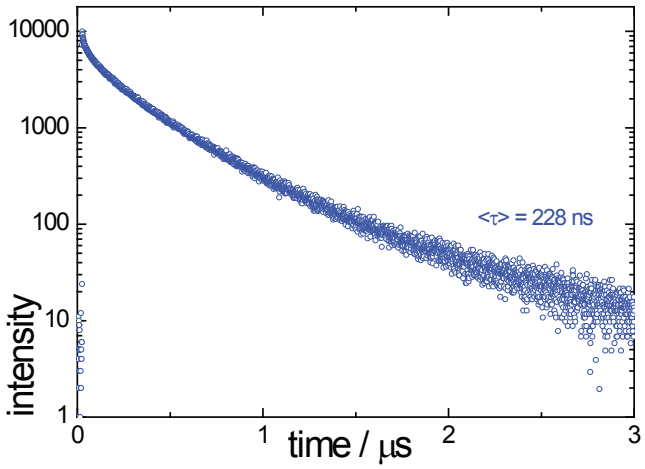
In this work, the time-resolved emission from a perovskite photovoltaic material is measured using a DeltaFlex lifetime system, with DeltaDiode excitation (see below). The sample was placed on a front surface holder for the measurements. This kind of equipment can measure a wide range of lifetimes (tens of picoseconds to seconds) and is well suited to cope with the large dynamic range of lifetimes that these samples can exhibit.



The DeltaDiode (DD-485L) laser was used, and the acquisition time range chosen from the drop-down menu was 3.2 µs. On this time range the influence of the instrumental response function (IRF or "prompt") is negligible, so reconvolution of the IRF is not required and the data can be simply tail fitted.

Results

The measured decay is shown plotted below and from a multiexponential (4 component) analysis, an average decay time of 228 ns was recovered.



To further explore the decay, a distribution model based on a gamma function (the NED - non extensive decay - distribution model) was employed and is represented by the form

$$I(t) = A + \sum B_k \left[1 - (1-q)\frac{t}{\tau_k}\right]^{\frac{1}{1-q_k}}$$

where k=1 up to a maximum of 5, τ_k is the mean value of the lifetime distribution and q is a parameter of heterogeneity defined by

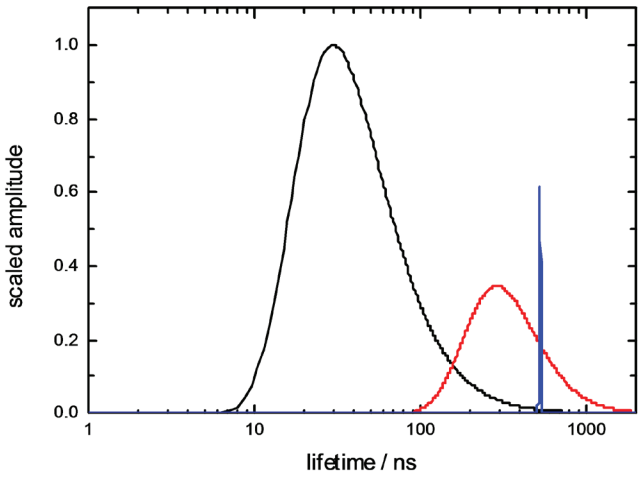
$$q = 1 + \frac{2}{N} = 1 + \frac{\left\langle \left\langle \gamma - \langle \gamma \rangle \right\rangle^2 \right\rangle}{\langle \gamma \rangle^2}$$

This gives the fluctuation according to the mean value of the decay rate, the γ function and plotted graphically, indicates the width of the distribution

$$g(\Delta\tau; q, \tau_k) = \frac{1}{\Gamma\left(\frac{1}{q-1}\right)} \frac{\tau_k}{q-1} \left(\frac{1}{q-1}\frac{\tau_k}{\tau}\right)^{\frac{q-2}{q-1}} \exp\left[-\frac{1}{q-1}\frac{\tau_k}{\tau}\right]$$

Using this form of analysis, when the q value is close to 1, the decay is exponential in nature, whilst values closer to 1.3 are indicative of a wide distribution. This fitting model is available in HORIBA's EzTime (and DAS6) analysis software.

The outcome of this form of analysis is shown below. It is clear that there is one well-defined component (exponential in nature) with a decay time of ~530 ns.



The other two shorter-lived decays are more distributed. In this case, 3 distribution components were sufficient to provide a good fit compared to the alternative of 4 discrete components needed from the multiexponential decay analysis. This is indicative of one process of carrier recombination that is quite efficient, however occurring in the presence of two other impeding processes. It is clear from this approach that time-resolved photoluminescence can be used effectively to study these systems.

Conclusion

The DeltaFlex equipped with a DeltaDiode source can be used to measure perovskite type photovoltaic materials and the EzTime software, in addition to multiexponential fitting of the data, also allows distribution models (in this case NED) to be used. However, a stretched exponential model and others are also available to help explore the underlying processes present.

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