APPLICATION NOTE

Enhanced Measurement Throughput of Sensitive External Quantum Efficiency Characterization for Solar Cell and Photodetector Devices

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Introduction

The landscape of photodetector and solar cell technologies has been rapidly expanded with the emergence of numerous novel material paradigms, including organic semiconductors[1], perovskites[2], and two-dimensional materials[3,4]. These technology advances directly impact a broad spectrum of applications from night vision to medical imaging and energy conversion. As materials, device architectures, and manufacturing processes evolve, external quantum efficiency (EQE) is a key metric when comparing devices and competing technologies.

The EQE of a solar cell or a photodetector describes the ratio between the number of charges that are generated and then collected at the electrodes with respect to the number of incident photons that are available for absorption. The EQE is measured as a function of the wavelength of the incident light, and thus it is important to identify whether a solar cell matches the sun spectrum or a photodetector matches the spectrum of a specific light source. An EQE measurement is typically done by detecting the photocurrent with a sensitive multimeter, an SMU, or a picoammeter and requires a dark environment and a sample with a sufficiently low dark current.

Often with photosensitive materials, considerable effort is put into optimizing the power efficiency for which the wavelength range with high EQE values is of particular interest. However, there is also growing interest in measuring the EQE values at the low energy flank of the EQE spectrum in order to study low energy phenomena such as charge-transfer (CT) states as well as traps and defects. These low-energy measurements are referred to as sensitive EQE (sEQE) and follow the same principles as EQE measurements, with the key difference being the concentration on measuring the lowest EQE values as precisely as possible[5].

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This application note discusses the role of sEQE measurements in characterizing and understanding performance issues in organic solar cells (OSCs). OSCs often suffer from potential losses due to the recombination of generated charges; these recombination mechanisms can be better understood by studying a wide energy landscape. OSCs blend donor and acceptor materials, both of which can absorb light and lead to the creation of strongly bound electron-hole pairs (Frenkel excitons). Due to the high exciton binding energy in the constituent materials, the excitons diffuse through the material. When an exciton reaches an interface between the donor and the acceptor material, it can dissociate with one constituent charge transitioning to the neighboring molecule while the remaining constituent stays on the original molecules. Charges that are separated at the donor-acceptor interface are not immediately free but are rather bound at the interface in so-called CT states. In high-efficiency OSCs, these bound charges are selectively transported to their corresponding collection electrode; however, in many lower-efficiency OSCs, the charges are stuck at the interface until they recombine often through a non-radiative channel. These recombination processes must be prevented in order to achieve optimal efficiencies in OSCs. Therefore, it is important to investigate those CT states. Sensitive EQE spectroscopy helps unveil the energy and distribution of CT states and leads to material and processing improvements that diminish internal voltage losses in these devices.

An sEQE measurement is carried out using a current-to-voltage preamplifier in combination with a lock-in amplifier to increase the sensitivity of the setup. The lock-in measurement achieves a better signal-to-noise ratio but requires an alternating signal often achieved by optically chopping the light source. The following section will outline the sEQE characterization setup and discuss novel instrumentation for improving the measurement throughput and accuracy of the system.

Setup

Figure 1 illustrates a typical sEQE measurement platform used in OSC characterization. sEQE setups are equipped with a broad-spectrum light source covering the wavelength range of interest for a given device under test (DUT). Halogen lamps are the standard for measurement in the NIR/VIS range. Here the lamp element acts as a thermal radiator — providing a spectrum close to the blackbody spectrum through the visible wavelength. Halogen lamps lack sufficient intensity at shorter wavelengths in the blue-VIS range. Typically, xenon lamps are added to the setup to cover the blue-VIS range, but their intensity is quite inhomogeneous. Results in this work were generated using only the halogen lamp. Emerging light source alternatives include white light sources shaped from multiple LEDs and laser-based continuum light sources. These light sources offer more consistent spectral content and more control over the light beam; however, the higher intensity illumination provided by these sources could induce additional effects like saturation or self-heating in the DUT.

The intensity of the light source is modulated at a fixed frequency (170 Hz in this work) with a rotating chopper wheel that also generates a square-wave reference signal, which the lock-in amplifier uses to demodulate the signal coming from the DUT. Reflections from the surface of the optical chopper wheel can reach the DUT, and some stray light can also pass the monochromator since no grating is perfect. In either case, this stray light has the same modulation frequency as the reference frequency and will be detected by the lock-in and can be distinguished by their phase relative to the chopper reference. In general, the stray light passing through the monochromator is often in phase with the signal and can be filtered or attenuated with a secondary filter wheel. Light reflected from the chopper wheel is out of phase with the lamp modulation and can be easily identified. It is critical to arrange the DUT and optical components to eliminate all stray light such that the DUT is only illuminated by light that passes through the chopper and the monochromator.

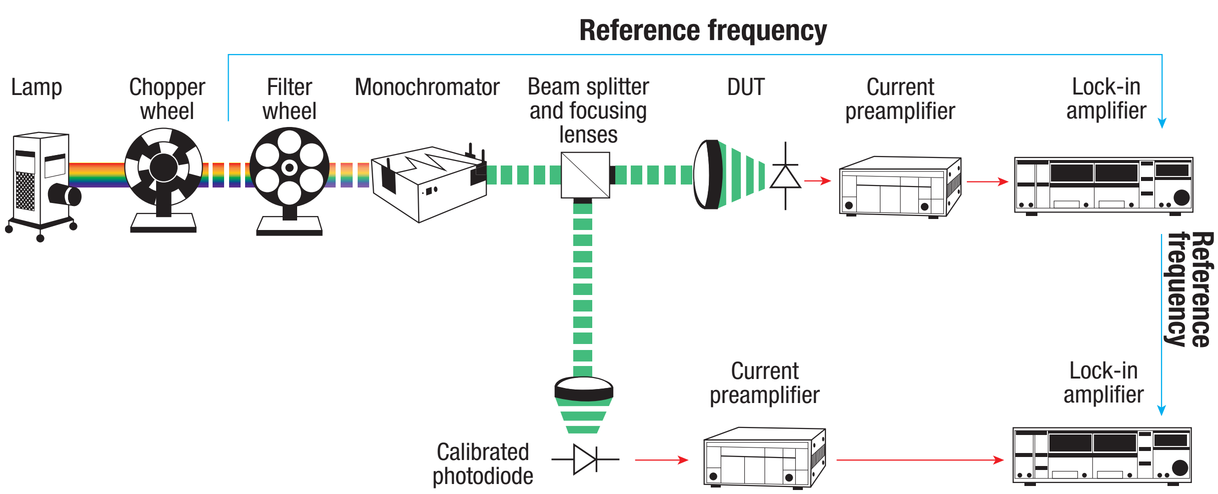

Figure 1 *Conventional instrumentation for a sEQE measurement.*

A grating monochromator strongly reduces the spectral range of the incoming lamp light to an interval of a few nanometers. The spectral width of the monochromatic light can be adjusted by the slit width of the in- and outgoing monochromator port. As the monochromator grating also reflects light at integer harmonics of the selected wavelength, these higher-order modes need to be filtered out as the device could absorb the light from higher harmonics. For that reason, the monochromator typically comes with a built-in filter wheel. Three to four different filters are often needed to cut out the higher harmonics over the entire range of wavelengths.

The sEQE measurement requires a reference measurement of the light intensity to normalize the DUT photocurrent to the number of photons incident on the device. These reference measurements must be regularly acquired to incorporate the effect of lamp degradation and wavelength-dependent influences of the monochromator and the optical filters. The reference signal can be measured by placing a calibrated photodiode with a known response function at the DUT position and acquiring the reference photocurrent measurement before or after the device measurement. This requires only a single lock-in in the setup, but errors such as drift in the lamp intensity are missed with this approach. Alternatively, a small part (~5%) can be branched off before the device to perform a simultaneous reference measurement of the signal intensity. Here the reference square wave from the chopper wheel is propagated to a second lock-in that detects modulated light intensity on the calibrated photodiode. This reference photocurrent can be converted to photon flux and then used to calculate the relative EQE value. Instead of a second lock-in amplifier, an optical power meter with wavelength calibrated diodes (not shown) can be used to measure the reference signal. With a sufficiently long integration time, the power meter time averages the square wave signal generated by the constituent reference diodes.

Finally, the light hits the sample and generates a photocurrent that depends on the reference frequency of the optical chopper. The sample is electrically connected to the lock-in that is used in current mode or in voltage mode if an additional transimpedance amplifier is used. The amplifier might be needed to apply electrical low-pass and high-pass filters and to allow for very sensitive measurements.

With the conventional sEQE instrumentation, external software scans the wavelength of the monochromator and adjusts the filter wheel while monitoring the photocurrent signal and adjusting the gain of the current preamplifier or lock-in amplifier. Because the photocurrent in these devices varies over orders of magnitude, multiple gain adjustments are needed. This monitoring and manual feedback on the gain setting can add substantial time to the spectral sweep. Additionally, because the typical sEQE setup relies on a standalone lock-in amplifier for electrical measurement, any DC I-V characterization of the solar cell devices requires rewiring the instrumentation to the DUT.

For this work, the two lock-in amplifiers, current preamplifier, and SMU for DC characterization found in the conventional sEQE setup were substituted with a single M81 Synchronous Source Measure (M81-SSM) system outfitted with two CM-10 current measure modules (Figure 2). The CM-10 module contains both transimpedance amplification as well as analog filtering for sensitive measurements in a noisy environment.

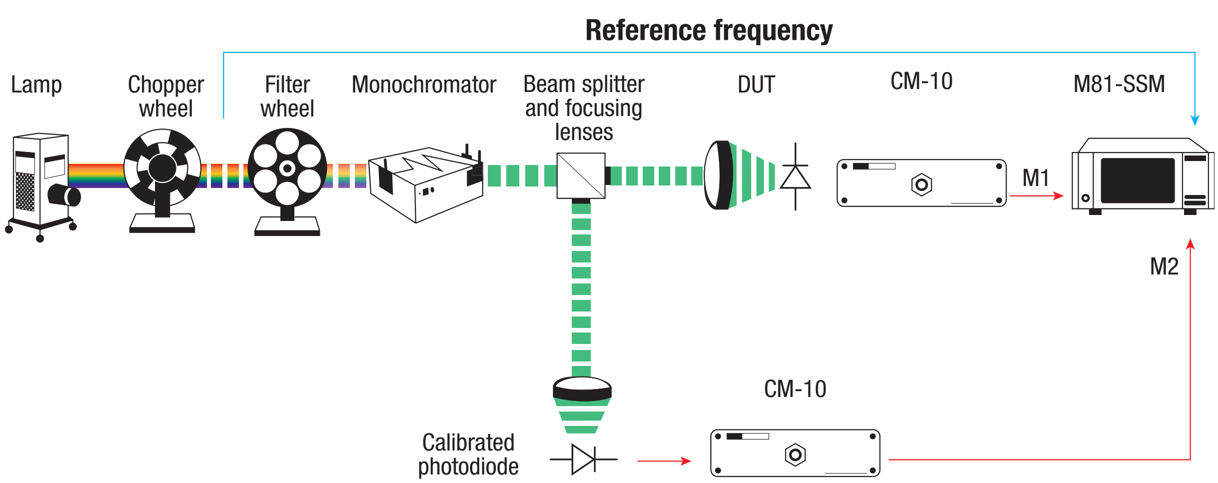

Figure 2
Instrumentation of a sEQE measurement using an M81-SSM with CM-10 module. Here, the M81 can be configured to carry out both DC I-V sweeps as well as lock-in detection of the induced AC photocurrent in the device.

For sEQE measurements, the chopper wheel reference signal is plumbed to the Reference In of the M81 instrument to simultaneously and synchronously demodulate the DUT photocurrent measured by one CM-10 module on Measure channel 1 and the photocurrent signal from the calibrated photodiode on Measure channel 2. Instead of a second CM-10 module, the M81 could demodulate the analog output from a standalone power meter with the photocurrent-to-intensity conversion applied in post-processing. As the internal ADCs of the M81 are synchronously sampled, a single query from the controlling PC can capture the magnitude and phase of both current and optical power signals from the same point in time. Finally, the CM-10 module and M81 instrument can be configured for either lock-in for small signal detection or DC measurements of current versus bias characterization. Details of the DC and AC interoperability and the built-in autoranging of the current measurement are discussed in the Results section of this note.

Using the M81-SSM platform, we demonstrate sEQE characterization of an OSC based on a bulk heterojunction comprising C_{60} acceptor molecules and zinc phthalocyanine (ZnPc) donor molecules. While ZnPc:C_{60} is not the most efficient OSC, this material combination has been heavily studied and can be considered a model system[6]. The device is made by thermal vapor deposition of the constituent organic semiconductors onto a glass substrate mounted in a high-vacuum chamber. Blended layers can easily be achieved by evaporating two materials from two sources at the same time. The rates of each material are monitored via quartz crystal microbalance. Evaporated metal contacts are defined by a shadow mask such that multiple OSC devices can be made on each substrate. The transparent electrode is either made by a thin transparent metal film or by pre-structured ITO (indium-tin-oxide) electrodes. As OSCs are not air-stable, the devices are encapsulated with a glass lid using epoxy resin. The electrodes are deposited such that they can be contacted from outside the glass lid.

The SweepMe! measurement software suite[7] acquires data from the M81 instrument while coordinating the monochromator and filters during a spectral sweep.

Results

Prior to sEQE characterization, an I-V sweep is carried out on the OSC device (Figure 3). As full sEQE measurements can be time-consuming, a simple I-V measurement is often the easiest and quickest way to determine whether the device is operational. Additionally, dark I-V measurements provide insight into the quality of the p-n junction in the device as well as supply feedback on fabrication issues such as high contact resistance. For these measurements, the M81 instrument is configured for DC measurements, and the CM-10 module measures the device current while programmatically sweeping the bias voltage across the DUT.

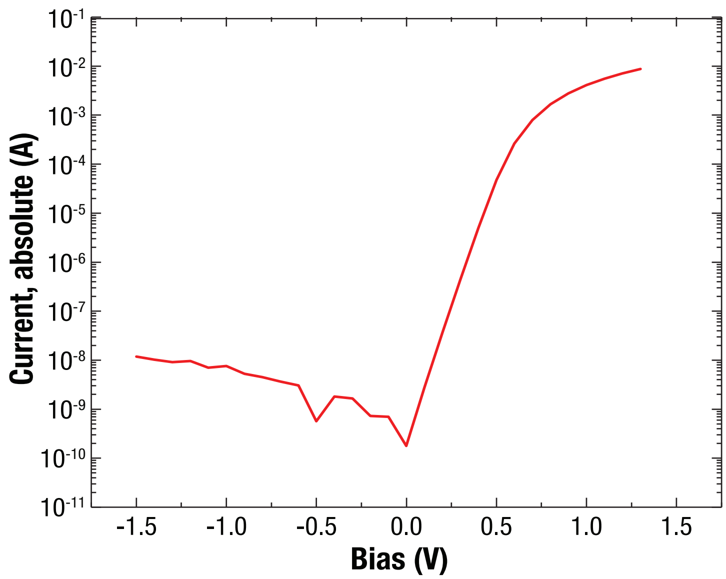

Figure 3 *I-V characterization of an OSC device using the same CM-10 and M81 instrument used for EQE measurements. The configuration change from lock-in to DC mode in the instrument can be made remotely over the computer interface. I-V curves can be used to characterize defect density in working devices as well as used as a screening step to exclude any faulty or sub-optimal devices prior to the EQE measurement.*

After the initial I-V measurement of this OSC device, the sEQE measurement can proceed using the same connection scheme used for the I-V curves with the CM-10 module now configured for lock-in detection. As mentioned earlier, the sEQE measurement consists of the wavelength-dependent photoresponse of the DUT as well as a reference measurement to determine the absolute intensity of light impinging on the DUT. Figure 4 shows the magnitude of the modulated photocurrent of the OSC device as a function of monochromator wavelength. The photocurrent of the device peaks around 675 nm and is determined by the lamp, filter, and monochromator characteristics, electronic structure of the molecular blend, and the recombination processes in the material. In this sample, the photocurrent varies over seven orders of magnitude as the wavelength is swept and requires multiple range changes in the current measure module. These range changes are handled by the autoranging algorithm in the M81 instrument. Autoranging in a DC measurement compares the magnitude of the current relative to the gain setting of the amplifier. When set to lock-in mode, the CM-10 determines ranges based on the frequency of the reference signal as well as the signal level. This is done because as the current range decreases, so does the bandwidth of the current amplifier. To preserve the accuracy of the reading in the OSC data, the CM-10 was configured to autorange to a higher current range if the lock-in reference frequency is greater than 10% of the present range's -3 dB cutoff frequency. With a 170 Hz modulation and the 10% frequency threshold, 1 mA is the lowest range setting for the current amplifier in this measurement. With this configuration, the bidirectional spectral scan, including range changes, as shown in Figure 4, completes in 231 s without any transimpedance amplifier correction. Details of the autoranging scheme, including methods for utilizing lower current ranges, can be found in an accompanying Lake Shore application note.

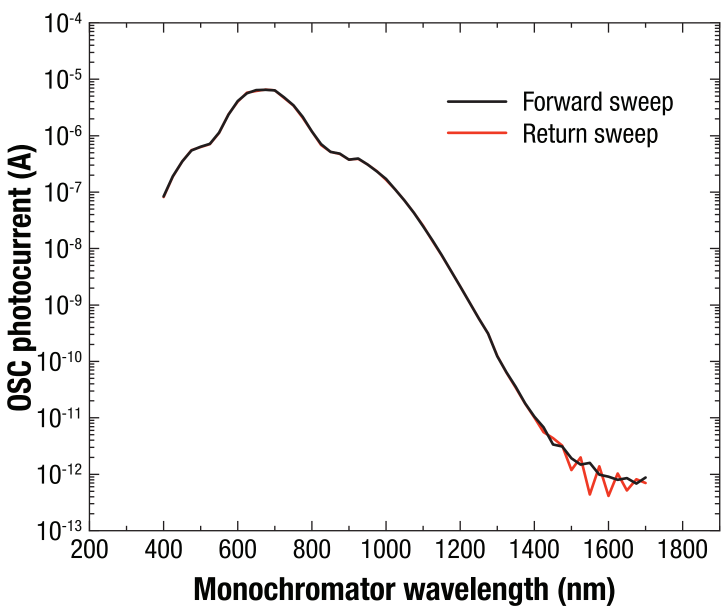

Figure 4 *Raw photocurrent measurement of OSC device. With autoranging in the CM-10 module, the round-trip measurement takes less than 4 min — including filter changes.*

To calculate the EQE, we need to know the light intensity at the sample for each wavelength. To cover the full spectral range of the measurement, calibrated Si and InGaAs photodiodes were used. The response of each diode is interpolated (Figure 5a), the calibration is applied to the measurement data, and the response is stitched together (Figure 5b). By combining the measurement of the Si diode and the InGaAs diode, we get a full-intensity spectrum that includes the lamp as well as all filter and grating changes of the monochromator. The final intensity spectrum is reinterpolated to apply it to arbitrary wavelengths.

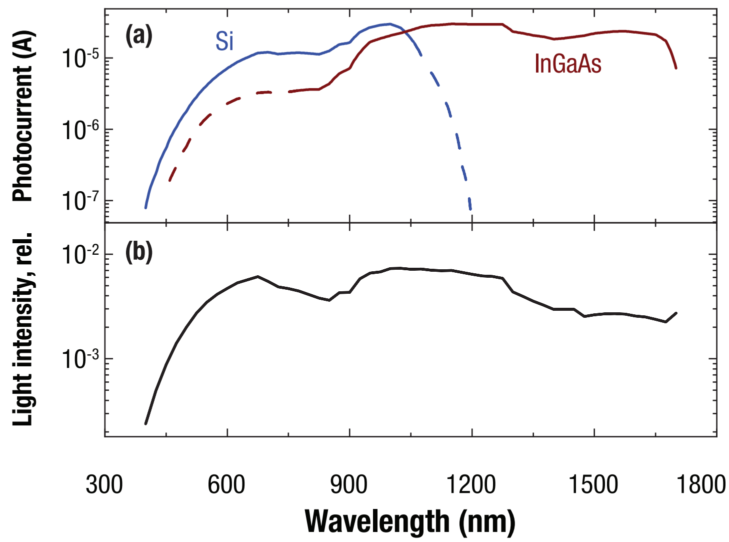

Figure 5 *Reference photodiode measurement used to normalize the DUT photocurrent by the number of incident photons at each wavelength.*

Figure 6 shows the normalized or relative sEQE spectrum of the OSC device. Here the sEQE spectra peaks at exciton energies of the constituent ZnPc and C_{60} material and falls off at lower energies. The sensitive lock-in measurement of EQE reveals, in this low energy tail, the well-known CT state absorption of ZnPc:C_{60} between 1.0 eV and 1.5 eV[8]. This spectrum shows that the sEQE response can easily be measured over six orders of magnitude with the default AC current autoranging scheme of the M81-SSM. With careful implementation of the lower CM-10 current ranges and post-processing, the dynamic range of the sEQE measurement can readily be extended to cover seven to eight orders of magnitude in sEQE.

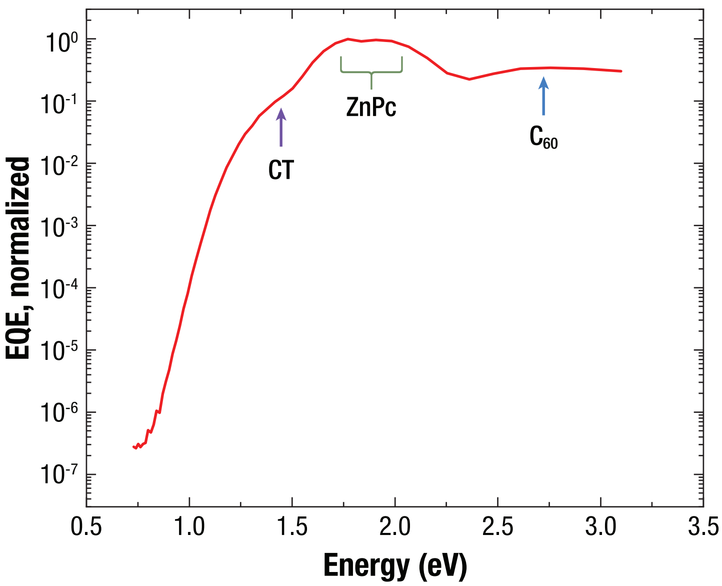

Figure 6 *EQE of a ZnPc:C_{60} OSC device. The plot indicates the exciton peaks of the constituent materials and a broad charge-transfer peak in the low-energy tail of the spectra.*

Conclusions

With the combination of synchronized, multichannel lock-in acquisition and a reliable built-in current autoranging, we demonstrate efficient sEQE spectroscopy. Using a ZnPc:C_{60} OSC device, a wide-bandwidth sEQE spectra covering six orders of magnitude of efficiency was acquired in 4 min; an acquisition time that includes a bidirectional sweep with grating and filter changes. Furthermore, the AC/DC interoperability enables in-situ dark and even illuminated I-V characterization of the same solar cell devices with no need to rewire the instrumentation. The technique and instrumentation efficiencies of the M81-SSM measurement platform are easily extended to other solar cell material systems, such as perovskites, as well as emerging photodetector technologies.

References

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