

Performance Characterization of Dye-Sensitized Photovoltaics under **Indoor Lighting**

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Supporting Information

ABSTRACT: Indoor utilization of emerging photovoltaics is promising; however, efficiency characterization under room lighting is challenging. We report the first round-robin interlaboratory study of performance measurement for dye-sensitized photovoltaics (cells and mini-modules) and one silicon solar cell under a fluorescent dim light. Among 15 research groups, the relative deviation in power conversion efficiency (PCE) of the samples reaches an unprecedented 152%. On the basis of the comprehensive results, the gap between photometry and radiometry measurements and the response of devices to the dim illumination are identified as critical obstacles to the correct PCE. Therefore, we use an illuminometer as a prime standard with a spectroradiometer to quantify the intensity of indoor lighting and adopt the reverse-biased current-voltage (I-V) characteristics as an indicator to qualify the I-V sampling time for dye-sensitized photovoltaics. The recommendations can brighten the prospects of emerging photovoltaics for indoor applications.



ndoor application has become the important research and development of emerging photovoltaic (PV) devices, such as dye-sensitized, 1-6 perovskite, 7-10 and organic thin-film 11-15

Received: March 2, 2017 Accepted: April 7, 2017 Published: April 7, 2017

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solar cells. The main reason is that the spectral response of the new-generation photovoltaics falls predominantly in the visible region, which promises an efficient conversion of the roomlight photons into electricity. Moreover, the colorfulness, flexibility, and low manufacturing cost of the PV devices are attractive features for powering wireless sensors and consumer electronics under various modern room lighting sources, for example, fluorescent lamps and light-emitting diodes (LEDs). Nevertheless, for indoor utilization, the PV performance characterization under standard testing conditions (STCs; AM 1.5 global, 1 kW m⁻², 25 °C), which were established for rating all of the terrestrial photovoltaics, is insufficient and may also be misleading. This dilemma is due to not only the spectral mismatch but also the differences in the light intensity and the degree of diffusion between the indoor lighting and the AM 1.5 global sunlight. Typically indoor lighting has much lower intensity (100-1000 times lower) than the AM 1.5 global standard and diffuses easily (depends on the bulb designs and environment). Therefore, it is very challenging to evaluate correctly the incidence intensity and the performance of PVs under indoor dim-light conditions.

Furthermore, even under the STCs, the efficiency characterization of the new generation photovoltaics is more difficult than that for the conventional PV technologies based on crystalline silicon. This scenario is ascribed to their diverse materials, architectures, and unique responses. Hence several guidelines and protocols for improving the reliability of the results under the STCs have been proposed. 16-26 Despite this, a broad spread (or even errors) of the efficiency reports is still inevitable, 27 due to the multitudinous divergence in measuring instruments and staff trainings. To obtain the "true" PV parameters under room lighting is more difficult than under the STCs, and the researchers generally have limited experience. We can expect the efficiency data will be more dispersed compared with those measured under the STCs. Therefore, to identify the key elements and blind spots for correctly evaluating the performance of new-generation photovoltaics under weak room lighting is very important for research and commercial applications. In this study we carry out the first round-robin interlaboratory study among 15 research groups on the performance characterization of the dye-sensitized solar cells (DSCs) and mini-modules under room lighting. The DSCs devoted to the practical indoor utilization have attracted great attention recently because of their efficient harvesting capacity for the diffuse light and good performance under lowintensity illumination. 4,28 However, the performance characterization of DSCs under indoor lighting is complicated because of the nonlinear spectral response and the thorny hysteresis in the current-voltage (I-V) curves. 17,20,21

Three DSC cells and two mini-modules as well as one crystalline silicon solar cell having a KG-3 filter were used as samples. The photographs of the DSC samples with detailed dimensions are displayed in Figure 1. The indoor light designated for this round-robin activity was the T5 fluorescent light (Philips TL5 Essential 14W/865) with a color temperature of 6500 K and an illuminance of 600 lx. The temperature of devices under test was kept at 25 \pm 1 $^{\circ}$ C. From the discrepant results between 15 laboratories, the critical issues of the performance characterization under the indoor lighting can be diagnosed distinctly and the recommendations of the measurements are provided. This "top-down" strategy is the most efficacious avenue to improve the accuracy of DSC

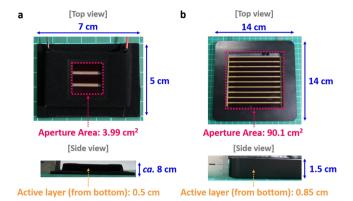


Figure 1. Photographs and dimensions of dye-sensitized photovoltaic (a) cell and (b) mini-module.

performance measurement, which is urgently needed for research, indoor applications, and international standardization. The relative deviation in efficiency of the six samples between 15 groups is presented in Figure 2. The corresponding

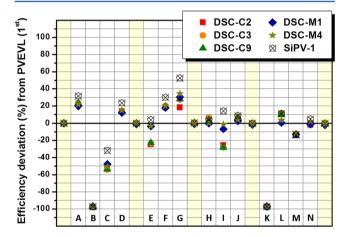


Figure 2. Relative deviation in efficiency of the six samples between the 15 groups. The data embedded in yellow columns were measured by the PVEVL.

current density-voltage (I-V) curves were displayed in Figure S1. In this round-robin proficiency test, the PVEVL ((Photovoltaic Efficiency Verification Laboratory) of the Research Center for New Generation Photovoltaics (RCNPV), National Central University (NCU), Taiwan) had repeated the efficiency measurements five times to trace the performance evolution of the samples. The detailed PV parameters are listed in Table S1, and the efficiency data (relative) are embedded in the yellow columns of Figure 2. From the initial and final (1 month later) data obtained by the PVEVL, the excellent stability in efficiency (<2% degradation) of the five DSC samples was confirmed. On the basis of the data from PVEVL, the maximum discrepancy in the efficiency among the 15 laboratories is 152% (from -99% of Lab-B to +53% of Lab-G). Such an unprecedented deviation is significantly higher than the previous round-robin intercomparison results obtained under the STCs. 29-32 In other words, the performance characterization of the DSCs under the dim light is more arduous than that carried out under the STCs. Moreover the importance of correct PV efficiency evaluation should be equal to the development of new materials and device fabrication techniques because the efficiency "quantum jump" can easily result from any incorrect measurement. To

explore the main reasons for the dispersive data, the incident irradiance $(P_{\rm in})$, the maximum output power $(P_{\rm max})$ of the sample, and the area of the specimen (A) should be scrutinized according to eq 1 to evaluate the power conversion efficiency (η) . The $P_{\rm max}$ is determined by multiplying short-circuit current $(I_{\rm sc})$, open-circuit voltage $(V_{\rm oc})$, and fill factor (FF) extracted from the I-V curve of sample.

$$\eta(\%) = \frac{P_{\text{max}}}{P_{\text{in}} \times A} \times 100(\%) = \frac{I_{\text{sc}} \times V_{\text{oc}} \times \text{FF}}{P_{\text{in}} \times A} \times 100(\%)$$
(1)

In this study the difference in the area of samples can be ignored because the 14 collaborators used the same values measured by the PVEVL. Hence the intercomparison can be concentrated only on the $P_{\rm in}$ and I-V curves. For $P_{\rm in}$, the conversion of light intensity from the photometric unit (lx) to the radiometric scale (W m⁻²) is essential for rating the efficiency of PV samples under the indoor lighting. All laboratories integrated the spectral irradiance from 380 to 780 nm according to the wavelength terminals defined in the CIE photopic curve $(V(\lambda))$. The relative deviation in $P_{\rm in}$ for the 14 collaborators toward the datum of PVEVL (196.45 μ W cm⁻²) is displayed in Figure 3. Despite the fact that T5

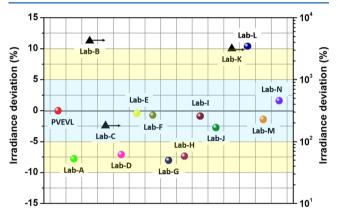


Figure 3. Relative deviation in incident power of the T5 fluorescent tubes among 15 laboratories.

fluorescent tube and illuminance of 600 lx were assigned specifically in this test, only seven groups have the discrepancy within $\pm 5\%$. Surprisingly, Lab-B, Lab-C, and Lab-K have a deviation of over 2 orders of magnitude. From the output spectra of the T5 fluorescent tubes normalized at 545 nm (Figure S2), we found that the performance of spectroradiometers (wavelength accuracy, resolution, signal-to-noise ratio, linear dynamic range, calibration validity, etc.) and the batch-to-batch variation in the fluorescent tubes play important roles in spreading $P_{\rm in}$ values. However, the enormous divergence in $P_{\rm in}$ values for Lab-B, Lab-C, and Lab-K cannot be explained by only these reasons, which will be discussed further in the following paragraph.

The derivations in the PV parameters, $P_{\rm max}$, $I_{\rm sc}$, $V_{\rm oc}$, and FF, among the 15 groups are illustrated in Figure 4. The B-spline curves of the DSC samples based on the data from the PVEVL were given to mitigate the influence of sample instability on data interpretation. Figure 4a shows that the maximum deviation (116%) in $P_{\rm max}$ (from -29% (Lab-B) to +87% (Lab-C)) is slightly lower than the divergence (152%) in efficiency. Interestingly, the dispersion in $P_{\rm max}$ between 15 laboratories is distinct from that in efficiency, in particular, the

data from Lab-B, Lab-C, Lab-K, and Lab-L. These results imply that there are other key factors seriously affecting the efficiency characterization besides the measurement of P_{in} . For Lab-B, Lab-C, and Lab-K, the deviations in I_{sc} averaged from six samples (Figure 4b) are -7.9, +51.5, and -7.5%, respectively. These values are extremely lower than the serious deviations in Pin (Figure 3) for those laboratories. Therefore, the conversion of the light intensity units (from photometric to radiometric) is diagnosed as a vital problem apart from the dynamic range and calibration of the spectroradiometers at those three groups. On the contrary, it was found (from several laboratories) that the $I_{\rm sc}$ discrepancy conflicts with the difference in $P_{\rm in}$. This phenomenon is quite abnormal because the samples (DSC-C2, DSC-M1, and SiPV-1) all show good linearity of I_{sc} versus light intensity at the illuminance ranges from ca. 510 to 710 lx (Figure S3). The scattering patterns of I_{sc} deviation for the six samples versus P_{in} deviation (Figure S4) reveal that the degree of the data dispersion is not identical for each sample but correlates well with the type of specimen. These results indicate that the difference in the position of the active layers encapsulated inside the samples (see Figure 1) should be the reason for the nonequivalent I_{sc} . In other words, the alignment among light source, samples, and light detectors as well as the nonuniformity of irradiance should carefully considered for correctly characterizing the PV performance under diffused indoor light.

The maximum deviation in V_{oc} (Figure 4c) is surprisingly high (up to 37%, from -23% of Lab-B to +14% of Lab-C). Only six collaborators have the $V_{\rm oc}$ variation within $\pm 2\%$ for all of the samples. It is noted that Lab-E, Lab-I, and Lab-K have the $V_{\rm oc}$ drifting more seriously than $I_{\rm sc}$. According to the Shockley equation, 34 the shift in $V_{\rm oc}$ comes from the variation of sample temperature and the incident light intensity. The $V_{
m oc}$ versus temperature and illuminance data (we measured and displayed in Figure S5) show that V_{oc} of the three samples (DSC-C2, DSC-M1, and SiPV-1) is linearly dependent on the temperature and illuminance. The corresponding voltagetemperature coefficient (β) and voltage—illuminance coefficient (δ) fitted from Figure S5a,b are summarized in Table S2. Compared with SiPV-1, DSC cells and mini-modules all show smaller β and δ values, which demonstrates the advantages of DSCs for the indoor applications. It is convinced that the remarkable deviation in V_{oc} for SiPV-1 (Figure 4c) was caused by incorrect control of the sample temperature and the intensity of illumination. However, the spread in V_{oc} (DSC-C2 > SiPV-1 > DSC-M1) is not parallel to that in β and δ (SiPV-1 > DSC-C2 \approx DSC-M1). For DSC-C2 sample, the deviation in $V_{\rm oc}$ of the five groups (Lab-B, Lab-C, Lab-E, Lab-I, and Lab-K) ranges from -14.3 to -22.8%. If $V_{\rm oc}$ is affected only by the sample temperature (β = -0.42% $^{\circ}{\rm C}^{1-}$) and the illuminance (δ = $0.01\% \text{ lx}^{-1}$), then the temperature of DSC-C2 at the five laboratories estimated from the deviation in $V_{\rm oc}$ is about 61–79 °C. Such high sample temperature was unlikely reached under illumination of 600 lx. Hence there must be another factor (which will be discussed in detail in the later paragraphs) that affects the deviation of $V_{\rm oc}$ for the DSC cells more seriously than the temperature of sample and the light intensity.

The comparative FF values among the 15 research groups shown in Figure 4d reveal that FF is more uniform than $V_{\rm oc}$. This is attributed to the fact that the variation in FF induced by the changes of sample temperature and the light intensity is less influential than that in open-circuit voltage (Figure S5c,d). Among the three types of samples, DSC cells show the highest

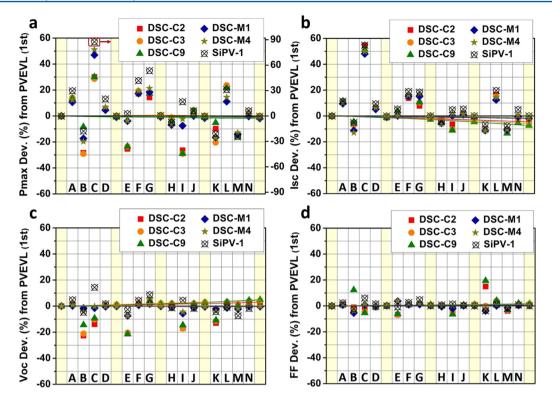


Figure 4. Comparative (a) P_{max} (b) I_{sc} (c) V_{oc} and (d) FF of samples.

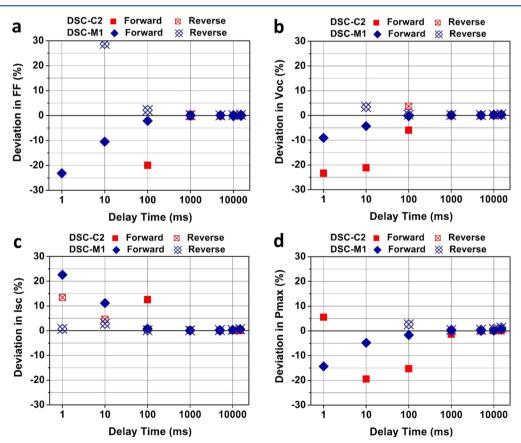


Figure 5. Comparative (a) FF, (b) V_{oo} (c) I_{so} and (d) P_{max} of DSC-C2 and DSC-M1 under various I-V sampling delay time and directions.

degree of dispersion in FF (from -7.1% of Lab-E to +18.2% of Lab-K) despite the fact that their FF is less sensitive to the temperature (coefficient κ_1 of -0.15% °C⁻¹) and illuminance

 $(\kappa_2 \text{ of } \sim 0\% \text{ lx}^{-1})$. It was well known that DSCs often show the noticeable hysteresis in their I-V curves. 17,20,21,32 This phenomenon is ascribed to the nonequilibrium conditions of

cells induced by the applied bias voltage, incident photon, and temperature.²⁰ Under the STCs, in general, several hundred milliseconds of *I*–*V* sampling delay time is sufficient to alleviate the hysteresis for the DSCs based on volatile liquid electrolytes. However, the hysteresis of DSCs under dim light was never clearly addressed. The hysteresis in the *I–V* curves for DSC-C2 and DSC-M1 was investigated under the T5 fluorescent light (600 lx) with various sampling delay times (from 1 ms to 15 s) and different sweeping directions (the forward way is from I_{sc} to $V_{\rm oc}$ and the reverse mode is from $V_{\rm oc}$ to $I_{\rm sc}$), as provided in Figures S6 and S7, respectively. The comparative PV parameters are summarized in Figure 5. The delay time longer than 1 s (~5.5 mV s⁻¹ of the scan rate) is recommended to relieve the hysteresis based on the comparative FF values (Figure 5a). The longer sweeping time required for the dim light condition compared with STCs indicates that the hysteresis is affected by the sweeping rate more influentially under dim light conditions. It can be deduced that the charge gradient (the major driving force for electron diffusion) in the mesoscopic TiO2 film produced by the indoor dim light is limited. The corresponding electron diffusion coefficient (D in cm² s⁻¹)³⁵⁻³⁷ should be too small to respond quickly to the bias voltage switched rapidly. Furthermore, DSC-C2 shows the current hysteresis more seriously than DSC-M1, which implies that the hysteresis may also be induced by the inefficient charge collection, as the former sample does not include any patterned

Under the STCs, the major impact of the I-V sampling delay time for DSCs with volatile electrolytes is revealed on FF values. However, it is noted from Figure 5b that $V_{\rm oc}$ can also be critically affected under room lighting. The drift in $V_{\rm oc}$ for DSC-C2 is up to -23.4% when the delay time is 1 ms in the forward direction. Thus the short sampling time can be identified as the main reason for the negative deviation in $V_{\rm oc}$ (Figure 4c) of the five groups (Lab-B, Lab-C, Lab-E, Lab-I, and Lab-K). Data in Figure 5c show that $I_{\rm sc}$ will be easily overestimated at the short delay time no matter when the sweeping direction is forward or reverse. These consolidated results, as presented in the deviation of $P_{\rm max}$ (Figure 5d), conclude that the sampling time for the PV characterization of the DSCs under dim light condition is more decisive than that under the STCs.

The efficiency evaluation of the PV samples can be divided roughly into three parts of measurements: the incident light intensity, I-V curves, and the area of samples. On the basis of the comparative PV data discussed above, accurately measuring the intensity of indoor lighting is not straightforward work. The illuminance ($E_{\rm v}$ in lx) and total irradiance ($E_{\rm e}$ in W m⁻²) can be evaluated, respectively, with eqs 2 and 3

$$E_{\nu} = K_{\rm m} \int_{\lambda_1}^{\lambda_2} E_{\rm e,\lambda}(\lambda) V(\lambda) \, d\lambda \tag{2}$$

$$E_{\rm e} = \int_{\lambda_3}^{\lambda_4} E_{\rm e,\lambda}(\lambda) \, \mathrm{d}\lambda \tag{3}$$

where $K_{\rm m}$ is the maximum spectral luminous efficiency of photopic vision (683.002 lm W⁻¹), $E_{\rm e,\lambda}$ (λ) stands for the spectral irradiance (in W m⁻² nm⁻¹) of light source, $V(\lambda)$ presents the CIE photopic curve (the relative spectral responsivity of the human visual system), and λ_1 and λ_2 are the wavelength limits for the illuminance encompassing 380–780 nm. For the T5 fluorescent light, the limits of integration λ_3 and λ_4 could be identical to the terminals for the illuminance.

However, for other light sources (such as incandescent bulbs) having the spectrum beyond the visible regime, λ_3 and λ_4 should be defined individually.

The conventional solar reference cells applied widely for the STCs to evaluate the total irradiance of solar simulators (or natural sunlight) are not appropriate for use under the diffused indoor lighting because of the limited angular response.³⁸ Theoretically a spectroradiometer should be sufficient to obtain simultaneously the illuminance as well as the spectral and total irradiance of any light source. However, the state-of-the-art designs and calibrations of the spectroradiometers to satisfy both the photometry and radiometry measurements (for obtaining the absolute values) cannot be achieved at this moment. Hence our suggestion, inspired by the cavity radiometer applied in the primary calibration of solar reference cells,³⁹ is to use an illuminometer as a prime standard to meet the requirements for the practical indoor applications. A spectroradiometer is applied in the meantime for the conversion of the light intensity from illuminance to total irradiance. From eq 2, the $E_{e,\lambda}$ (λ) measured with the spectroradiometer can be adjusted proportionally to reach the absolute illuminance. Therefore, the total irradiance estimated with eq 3 can correlate well with the illuminance, and the effects caused by the imperfect wavelength resolution and nonlinear response of the spectroradiometers on irradiance of the indoor dim light can be reduced.

For correctly measuring the absolute illuminance, the relative spectral response of the illuminometers should match the CIE standard photopic curve (<3% of the difference from the standard spectral luminous efficiency (f1')). The calibration, linear dynamic range, and angular response of the illuminometers should also be considered.⁴⁰ For measuring the P_{in} , three additional key items need to be taken care of according to the correlation between instability of illuminance and ambient temperature, relative deviation in illuminance versus distance, and the spatial power distribution under various illuminance, as presented, respectively, in Figures S8-S10: (1) The ambient temperature should be stable because it is inversely proportional to the light intensity, (2) the reference planes of light detectors and samples should be aligned in the same direction and at the same distance because the incident light intensity depends on the distance toward the light source and the test planes, and (3) the nonuniformity of illumination must be seriously considered for measuring large PV samples because it may vary with the illuminance. Our recommendation is selecting the average value of light intensity according to the data of the spatial power distribution for light source.

For obtaining the "true" $P_{\rm max}$ of PV samples under indoor lighting, the easiest way should be measuring the I-V curve with a wide range of the sampling delay time and both sweeping directions (the forward and reverse ways). The data presented in Figures S6 and S7 show that the slope of curves near $I_{\rm sc}$ changes significantly when an inadequate sampling delay time is adopted. Such reverse-biased I-V characteristics can be an excellent indicator to qualify the sampling delay time. If the hysteresis cannot be diminished even when using an extremely long sweeping time (such as 30 min), then additionally tracking the current at a fixed voltage nearby the $V_{\rm max}$ is suggested to obtain the stable $P_{\rm max}$. Then, a corresponding I-V curve (gives the nearest $P_{\rm max}$) will be acceptable for reporting the efficiency. These recommendations of measuring photometrically and radiometrically the light intensity as well as the I-V curves of devices under dim light

are highly important to the performance and indoor applications of the new-generation photovoltaics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b00515.

Experimental procedures, additional photovoltaic results of samples, normalized T5 fluorescent spectra of collaborators, and performance of T5 fluorescent light source measured by the PVEVL. (PDF)

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Notes

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ACKNOWLEDGMENTS

We thank Pi-Tai Chou from National Taiwan University (NTU) and Sanekazu Igari and Yoshihiro Hishikawa from National Institute of Advanced Industrial Science and Technology (AIST) for valuable suggestions. Financial support from the Ministry of Science and Technology (MOST), Taiwan, R.O.C. (Grant Nos. 104-2731-M-008-005-MY2, 104-2119-M-008-001, and 104-2731-M-008-002) and the Advanced Laboratory of Accommodation and Research for Organic Photovoltaics (AROPV), MOST, Taiwan, R.O.C. is gratefully acknowledged.

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