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Organic solar cells and fully printed super-capacitors optimized for indoor light energy harvesting

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ABSTRACT

Flexibility, lightness and printability make organic solar cells (OSC) strong candidates to power low consumption devices such as envisioned for the Internet of Things. Such devices may be placed indoors, where light levels are well below typical outdoors level. Here, we demonstrate that maximizing the efficiency of OSC for indoor operation requires specific device optimization. In particular, minimizing the dark current of the solar cells is critical to enhance their efficiency under indoor light. Cells optimized for sunlight reach 6.2% power conversion efficiency (PCE). However when measured under simulated indoor light conditions, the PCE is to 5.2%. Cells optimized for indoor operation yield 7.6% of PCE under indoor conditions. As a proof-of-concept, the solar cells are combined with fully printed super-capacitors to form a photo-rechargeable system. Such a system with a 0.475 cm^2 indoor-optimized solar cell achieved a total energy conversion and storage efficiency (ECSE) of 1.57% under 1-sun, providing 26 mJ of energy and 4.1 mW of maximum power. Under simulated indoor light the system yielded an ECSE of 2.9%, while delivering 13.3 mJ and 2.8 mW. Those energy and power levels would be sufficient to power low-consumption electronic devices with low duty cycles.

1. Introduction

Organic solar cells (OSC) currently achieve more than 10% of power conversion efficiency (PCE) under 1-sun conditions [1,2] and can be stable over several years [3,4]. The materials involved in their fabrication require low processing temperatures, compatible with many plastic substrates [5,6]. They can also be completely printed [7,8], allowing the use of large-area, high-throughput, low-cost manufacturing processes such as roll-to-roll printing. As a result, full-scale outdoors demonstrations have already been successfully performed [9,10].

The combination of flexibility, low-cost and short energy payback time makes OSC particularly interesting as an energy harvester for autonomous low-power devices, such as wearables or wireless sensor nodes (WSN) for the Internet of Things. In these new applications, lightness and flexibility become highly desirable and milder operating conditions alleviate materials stability concerns. Typically, WSN are designed as very low-power systems able to gather data from their environment, connect to a network and perform minimal computation tasks, and are self-powered [11,12]. In order to minimize energy consumption WSN operate in cycles, alternating long periods of sleep with very short active periods (of the order of hundreds of milliseconds) during which they perform their tasks. Typically, 10–100 mW are needed under active mode, while this range falls to 1–100 μW during the sleeping mode [13–15].

WSN are expected to operate in a wide variety of environments, including indoors, where the available light differs significantly from the conventional 1-sun illumination for which solar cells are usually designed. In contrast to outdoors, there are no clearly defined standards to test solar cells in low or indoor lighting conditions, which are typically more varied both in terms of spectrum and intensity. Outdoors, the spectrum is always that of the sun and the intensity usually ranges between 100 mW cm^{-2} and 1 mW cm^{-2}. For indoors, it has been reported that, near windows, the light is dominated by the daylight sun spectrum [16]. In places with no access to sunlight, the spectrum of indoor light depends largely on the type of light source used. Earlier work by Minnaert et al. [17] suggests that artificial indoor lighting can be sorted into three categories of spectra, corresponding to incandescent light bulbs, sunlight-type light bulbs such as high

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temperature compact fluorescent lights (CFL) and all other light sources such as LEDs. Indoor light intensity varies greatly, depending on the type of room, the position, orientation and proximity to the light source. While the intensity right below a lamp or through a window can exceed 1 mW cm^{-2}, the intensity in poorly lit rooms can fall under 10 μW cm^{-2} [18]. Indoor light intensity is usually described by its illuminance, a measure relating the human eye's sensitivity to the light's spectrum. Conversion of illuminance (φ, in lux=lm m^{-3}) to irradiance (P, in W m^{-3}) per unit wavelength λ is given by:

$$\varphi(\lambda) = K_m.\ V_m(\lambda).\ P(\lambda) \tag{1}$$

Where K_m, the maximum photopic luminous efficacy, equals 683 lm/W and V_m is the spectral luminous efficiency function (Fig. S1). Thus, the illuminance is very dependent on the light spectrum. Previous studies on solar cells for indoor conditions have used 400–500 lx as a reference illuminance [17,19] or light intensity ranging from ~1 mW cm^{-2} to below 60 μW cm^{-2} [18,20]. Several countries establish standards regarding the minimum indoor lighting requirements (such as the IESNA illuminance recommendations in the U.S. or the European Norm 12464-1). In Europe and America, the lowest legal illuminance in buildings (transit areas) is 50–100 lx, and the minimum allowed in offices and commercial buildings usually ranges between 200 and 500 lx. From these considerations, three ranges of indoor illuminances are defined: poor lighting (from 0 to 200 lx), typical lighting (200–500 lx) and excellent lighting (superior to 500 lx). Converted to irradiance with the AM1.5 spectrum, those illuminance categories correspond respectively to 0–180 μW cm^{-2}; 180–450 μW cm^{-2} and > 450 μW cm^{-2}. To generate the 100 μW needed for the sleep mode operation of a WSN in an environment with 450 μW cm^{-2} of light power available, 2.2 cm^2 of a solar cell with 10% of PCE would be enough. To power the active mode of WSN (10–100 mW), the area of the solar cell would need to be 0.22–2.2 m^2. Such a big area is not practical for most indoor applications.

To overcome that limitation, one strategy is to take advantage of the cyclical operation of WSN by storing excess energy produced during their sleep period and using it to power the active mode. Super-capacitors are able charge and discharge very rapidly, can withstand many cycles of operation and do not require charge/discharge management electronics. They can be fully printed and made mechanically flexible, thus presenting the same manufacturing advantages as OSC [21,22]. OSC and super-capacitors can be combined to form a system able to simultaneously generate and store energy, called a photo-rechargeable system [23]. Such combinations have previously been demonstrated as part of a complete electronic system [24], as two separate devices connected together [25–27], or as a stack forming a single device [28–34]. Single-stacks reduce the footprint and the internal series resistance of the system compared to separated solar cells and super-capacitors externally connected [28]. Most of the earlier reports on photo-rechargeable systems use dye-sensitized solar cells (DSSC),[26,30–32,35] while a few groups investigate organic solar cells [27,28]. Moreover, all these reports dealt exclusively with outdoor light conditions, with only one [33] investigating intensities between 10% and 100% of 1-sun. A metric to consider for photo-rechargeable systems is the energy conversion and storage efficiency (ECSE) of the system. Measured during a charge-discharge cycle, the ECSE is defined as the ratio between the electrical energy that can be extracted from the super-capacitor and the total light energy received by the solar cell during the charging step. To the best of our knowledge, the highest reported ECSE of photo-rechargeable systems to date is 5.12% with DSSC and 0.82% for organic solar cells [23].

In this work, we demonstrate that an OSC integrated with a super-capacitor can provide enough energy to power the active mode of WSN operating under indoor-light. In addition, we show that optimization of OSC for low light intensity is different from the 1-sun case and we establish that the ratio of the 1-sun short-circuit current over the dark current – the current flowing through the cells when biased in the dark – is a critical parameter to control. The best solar cells for 1-sun achieve 6.2% of PCE under 100 mW cm^{-2} and 5.2% under 310 μW cm^{-2} (typical indoor light), while the solar cells optimized for low light reach 5.7% under 100 mW cm^{-2} and 7.6% under 310 μW cm^{-2}. Fully-printed super-capacitors are developed with a maximum capacitance of 130 mF cm^{-2}, maximum power of 9.8 mW cm^{-2}, and maximum energy of 31 μW-hr cm^{-2}. A photo-rechargeable system comprising a 0.475 cm^2 OSC (optimized for indoor conditions) externally connected with a super-capacitor achieves an ECSE of 1.57% under 1-sun light, and an ECSE of 2.92% under simulated indoor light (310 μW cm^{-2}).

2. Experimental

2.1. Solar cell fabrication

ITO-covered glass (from Thin Film Devices) were sequentially cleaned in acetone, isopropanol and water, then passed under UV-ozone plasma treatment for 30 min. PEDOT:PSS (Heraeus Clevios VPAI 4083, 40 nm) was spin-coated and baked at 180 °C for 10 min. After transfer in a glovebox, an active layer of poly[N- 9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4,7-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) in solution (1:3.7 in ortho-dichlorobenzene with 5% dimethyl sulfoxide) was spin-coated above (80 nm). PCDTBT was purchased from Saint-Jean Photochimie and PC71BM from Solaris. Finally, PEIE (Sigma Aldrich) diluted to 0.048 wt% or 0.024 wt% in ethanol was also spin-coated and the whole device was annealed at 70 °C for 10 min. All PEIE layers were too thin to be accurately measured with conventional profilometry methods, suggesting a thickness value below 5 nm. 200 nm of aluminum were thermally evaporated to complete the devices.

2.2. Supercapacitor fabrication

The super-capacitor are fully dispenser printed. First the polymer binder is dissolved in N-Methyl-2-pyrrolidone (NMP) and the carbon powder mixture is suspended in the resulting gel, producing the electrode ink. Then, a 1 cm^2 layer of electrode ink is deposited on a stainless steel foil substrate. This wet ink layer is briefly dried in an oven at 60 °C for 15 min. This does not cure the ink completely, but thickens it in preparation for deposition of the next layer. The gel polymer electrolyte layer is deposited next, with its dimensions extending beyond the region covered by the first electrode layer to ensure adequate electrical isolation between electrodes. Both the electrode and electrolyte inks are deposited wet, but solidify once their common NMP solvent is removed. This two layer stack is therefore partially dried in an oven at 60 °C for 30 min again to thicken the top layer in preparation for the final electrode layer. The final electrode is deposited on top of the GPE layer shadowing the dimensions of the bottom electrode. This stack is dried in the oven at 60 °C for 15 min and finally cured at 20 °C for 96 h until all the NMP is fully evaporated. The resulting wafer readily separates from the stainless steel substrate and is soaked in BMIMBF4 until saturated. The supercapacitor electrode surfaces are coated in a thin layer of AB powder to reduce interfacial resistance. Stainless steel foils are applied to the AB coated electrode surfaces to act as current collectors during experiments. All super-capacitors in this work have a 1 cm^2 area.