

Graphene-Based Interconnects for Stable Dye-Sensitized Solar Modules

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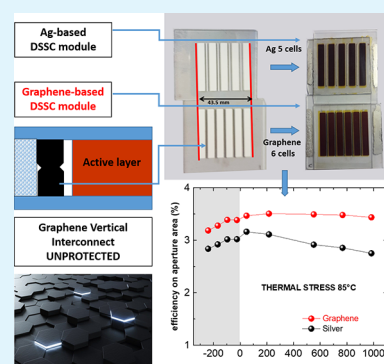


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ABSTRACT: We present Z-Type Dye Sensitized Solar Modules (DSSMs) with screen printed graphene-based vertical interconnects. This prevents corrosion of interconnects in contact with electrolytic species, unlike conventional Ag interconnects. By enlarging the width of single cells, or by increasing the number of cells, we get an enhancement of the aperture power conversion efficiency $\sim +12\%$ with respect to Ag-based modules, with 1000 h stability under 85 °C stress test. This paves the way to original design layouts with decreased dead area and increased generated power per aperture area.



KEYWORDS: graphene, dye sensitized solar modules, vertical contact, large area deposition, stability

1. INTRODUCTION

The installation rate of photovoltaic (PV) technologies has increased by 2 orders of magnitude over the past 15 years,¹ from ~ 1 GW/year in 2004,² to ~ 100 GW/year in 2018.² This fostered the development of new PV technologies that better suit specific applications, when compared to conventional Si cells. Dye Sensitized Solar Cells (DSSCs)^{3,4} are photo-electrochemical cells,⁵ ideal for Building Integrated Photo-Voltaics (BIPVs)^{6–8} and for energy harvesting in indoor-light conditions.⁹ They have better response to diffuse light compared to traditional semiconductor PV technology,¹⁰ due to the mesoporous structure of the cell allowing omnidirectional light harvesting,¹¹ an almost constant Power Conversion Efficiency, PCE, i.e., the ratio between incident solar photon energy and electrical energy output,¹² as a function of inclination angle¹³ (i.e., the angle of the PV plane with respect to the horizontal),¹⁴ transparency $>50\%$ ^{15,16} and one of the highest ($>60\%$) transmission rate percentage of the solar radiation through the PV unit,¹⁷ amongst TPV (Transparent Photovoltaic) technologies.

Typically, DSSCs are made of two conductive transparent glass substrates:¹⁸ (1) photoelectrode (PE) coated with mesoporous TiO_2 ; (2) counter-electrode (CE) coated with Pt clusters,¹⁹ or carbon-based materials.²⁰ Dye molecules are adsorbed on TiO_2 by immersing the PE into a dye solution.^{21,22} The electrons of these molecules, excited by light, are injected in the conduction band of TiO_2 ^{23,24} and subsequently transferred to fluorine-doped Tin Oxide (FTO), the most common

Transparent Conductive Oxide (TCO) covering the glass substrates for DSSCs.¹⁰ Oxidized dyes can recover electrons via a redox reaction with the electrolytes (typically iodide/triiodide, I^-/I_3^-) inserted into the cell.^{23,25,26} The reduction of the electrolyte occurs at the CE, catalyzed by Pt. DSSCs are scalable to large ($>10 \text{ cm}^2$) area by employing sheet-to-sheet printing.²⁷ In large area modules (from 100 to 1000 cm^2),²⁷ a reduction of PCE is observed,²⁸ due to the impact of substrate resistivity. This is counteracted by printing conducting grids,²⁹ or by making cells of smaller dimensions connected in various ways.³⁰ The cells of a Dye-Sensitized Solar Module (DSSM) can be either connected in parallel (currents summed) or series (voltages summed), with 4 possible module architectures: (i) parallel,^{29,31,32} (ii) series monolithic,^{33,34} (iii) series W-type (where the polarity of adjacent cells is inverted),^{35,36} and (iv) series Z-type (where adjacent cells have the same polarity).^{37–39} In the latter configuration, the module is composed by identical cells sandwiched between two scribed conducting glass plates, with conducting vertical interconnections (typically Ag) connecting adjacent cells.^{40–42}

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A Z interconnection guarantees uniform and reliable output over large areas in different illumination and temperature (T) conditions, such as orientation with respect to the sun⁴³ and a T range = -40° – 85° C,³⁷ and achieves the best PCE amongst the different DSSMs architectures.^{40,44} The Active Area (AA) of a module⁴⁵ is dedicated to solar energy conversion, while the dead area (DA)^{40,45} is needed for the interconnects and their protection. The aperture ratio is defined as $AR = AA/(AA + DA)$, where the sum of AA and DA is the aperture area (APA).^{40,45} One of the major drawbacks of DSSMs is the electrolyte corrosive action on the metal grids.^{46,47} Thus, a rugged encapsulation is needed to isolate the electrolyte chamber from metal connections and to mechanically keep firm the two electrodes.⁴⁸ This safety area surrounding the Ag grids is greater than the surface occupied by the same Ag grids. However, this layout unavoidably reduces AR.

Ref 39 first reported a Z-type DSSM and connected 64 DSSMs (100 cm^2) in series to form a large panel. It performed an outdoor stability test comparing the DSSMs power with a crystalline Si module of similar power rating over 6 months. The major issue during fabrication was the DSSM sealing, which resulted in performance degradation.⁴⁸ This was overcome by refs 37 and 49, where glass frit was used as the sealant, processed at $T > 600^{\circ}$ C in atmosphere, giving a PCE $\sim 3.5\%$ on $\sim 30\text{ cm}^2$, showing a low ($<55\%$) Fill Factor, FF, i.e., ratio of cell maximum power output to the product of its open-circuit voltage, V_{OC} , and its short-circuit current, I_{SC} ⁵⁰ and low ($<0.5\text{ mA/cm}^2$) short circuit density current (J_{SC}).⁴⁸ 100 cm^2 modules were reported⁵¹ with PCE $\sim 6.3\%$. In ref 51, a significant enhancement in FF and J_{SC} was achieved by decreasing the width of each individual strip ($\sim 0.8\text{ cm}$). FF and J_{SC} depend on the width of each TiO_2 cell and much less on their lengths.^{41,52} Following this approach, ref 40 realized a DSSM using a reflective/diffusive CE, with $\sim 6.9\%$ PCE on APA $\sim 43\text{ cm}^2$, and $\sim 9.4\%$ on AA $\sim 31\text{ cm}^2$, using a multilayer TiO_2 in combination with TiCl_4 treatment.⁵³ As of July 2020, the certified record, but without information on stability, is $\sim 8.8 \pm 0.3\%$ on 400 cm^2 (26 cells in series) and $\sim 10.7 \pm 0.4\%$ on 26 cm^2 (7 cells in series, mini-module).⁴⁴

Z-type modules have 3 main problems:⁴⁸ (i) liquid electrolytes corrode Ag-based electrical contacts (which reduces the options for scaling up DSSCs to module size),⁵⁴ (ii) AA is reduced with respect to APA, due to the need of additional sealing to protect the vertical connections, i.e., three layers of seal/conductor/seal for each interconnect,^{36,55} (iii) the fabrication process is more complex (more steps) with respect to other configurations, such as W (not requiring a connection grid).^{36,56}

Vertical connections can create difficulties when assembling the electrodes, since tolerances in variations in height of the vertical connections and sealants are tight ($\sim 5\text{ }\mu\text{m}$).²⁸ Corrosion of Ag connections significantly affects stability.⁵⁷ Thus, interconnects need to be protected from electrolyte corrosion via sealing. In DSSMs, sealant is also used to prevent electrolyte leakage,²⁶ evaporation of solvents,⁵⁸ delamination of substrates,^{59,60} electrolyte bleaching,⁶¹ and to fix the distance between the electrodes (typically ~ 20 – $60\text{ }\mu\text{m}$).^{55,59,62,63} The most common sealants are thermoplastics, such as Surlyn,^{64,65} Bynel,^{55,64,66,67} or glass frit.⁶⁸ Ref 65 reported that large area devices (10 modules of 15 cm^2 , arranged in a panel) assembled with a glass frit retained $\sim 86\%$ of the initial PCE, after an outdoor test of 47 days in the summer. Ref 65 also showed that glass frit sealed small area cells ($<0.2\text{ cm}^2$) lost only $\sim 2.3\%$ of the initial PCE compared to $\sim 34\%$ of Surlyn. However, glass frit

requires an immersion of PE in the dye solution after assembling the device, because the dye would be destroyed at the T needed to process glass frit ($\sim 600^{\circ}$ C).^{37,49} Very low PCEs ($<2\%$) were reported for large area ($\sim 23\text{ cm}^2$) devices⁶⁹ with glass frit, without using any Ag grid. To the best of our knowledge, accelerated and outdoor tests on sealants for Z-type DSSMs are lacking, hampering the industrialization of this technology.⁴⁶

The interconnection strategy to obtain efficient and stable Z-type modules, according to ISOS (International Summit on Organic Photovoltaics Stability) tests⁷⁰ based on IEC (International Electrotechnical Commission) International Standards⁷¹ is still an open technological issue. Ref 72 replaced Ag interconnects with a Ti-based compound ($\sim 45\text{ }\mu\text{m}$ Ti particles and $5\text{ }\mu\text{m}$ W particles in a polymer matrix) less sensitive to electrolyte corrosion. Although the resulting vertical connections are less conductive than those based on Ag, implying a reduction of module PCE (due to FF reduction), a new design without additional sealant for interconnections could be used. Ref 73 applied a layer of nonmetallic material, such as TiN, ZrN, boron carbide, to protect the metallic (e.g., stainless steel) conductors from the electrolytic species (e.g., tri-iodide/iodide). These nonmetallic materials are chemically inert to the conductors, which act as a vertical connection. This introduces an additional complexity when manufacturing the nonmetallic grids, leading to loss of module bifaciality, i.e., the possibility to be illuminated from both sides.^{74,75}

Graphene and related materials (GRMs) can be used in several solar cell technologies^{76,77} such as Si,^{78,79} polymer/organic,^{80,81} and Perovskite (PSC).^{82,83} In PSC, few-layer graphene (FLG) was combined with mesoporous TiO_2 (mTiO_2),^{84–86} and lithium neutralized graphene oxide (GO-Li) was employed as the interlayer at the mTiO_2 /perovskite interface,⁸⁷ while GO was used as a hole transport material (HTM) to replace standard spiro-OMeTAD.⁸⁸ GRMs have been incorporated into DSSCs with a variety of roles.^{89,90} Ref 91 reviewed the use of graphene-based composites as CE in DSSCs, replacing, or in combination with, Pt. This strategy was demonstrated on small area cells ($\sim 0.38\text{ cm}^2$) showing a lower charge-transfer resistance, R_{CT} , of the CE based on graphene-flakes used in combination with an ionic liquid electrolyte, when compared to traditional electrolytes in methoxypropionitrile (MPN).⁹² A CE prepared from a graphene ink was used on large area modules achieving $\sim 3.5\%$ PCE on $\sim 43.2\text{ cm}^2$ AA.⁶⁶ Ref 93 combined a stable aqueous dispersion of graphene flakes, prepared by noncovalent functionalization with 1-pyrenebutyrate (PB^-), with PEDOT-PSS as catalyst, in small area $\sim 0.072\text{ cm}^2$ cells, achieving PCE $\sim 4.5\%$. Ref 94 incorporated GO, obtained by a modification of the procedure of ref 95, in the TiO_2 film, to obtain higher light harvesting in the visible region. A typical DSSC has a ~ 6 – $15\text{ }\mu\text{m}$ thick layer of TiO_2 .⁹⁶ Electrons photogenerated in the inner part of the photoelectrode have to percolate through TiO_2 particles and be collected at the photoelectrode ($\sim 100\text{ }\mu\text{m}$ length assuming a random walk).⁹⁷ Ref 98 proposed the use of GO as an electron bridge in the photoanode, shuttling electrons to the current collector and lowering recombination. In ref 98, GO was found to induce macropores in the TiO_2 films, acting as scattering centers and improving J_{SC} and PCE. Polycrystalline FLG deposited by Chemical Vapor Deposition (CVD), covering homogeneously $\sim 1\text{ cm}^2$, was used to replace the transparent conductive film (TCF).⁹⁹ FLG nanoribbons, produced by catalytic CVD on Si, either attached to the CE, or dispersed into the electrolyte, induced optical transparency of an iodide/

triiodide redox couple in a DSSC, resulting in a $\sim 22\%$ increase in PCE, when measured from the CE side.¹⁰⁰ In ref 101, the TiO_2 surface was modified with ~ 2 nm Graphene Quantum Dots (GQDs) to promote light absorption, enhancing $J_{\text{SC}} \sim 30\%$ and PCE $\sim 27\%$ with respect to cells with pristine TiO_2 .

Here, we use graphene-based screen-printed vertical interconnects in Z-type DSSMs as alternative to the common Ag paste. The superior stability and PCE on APA of our graphene-based interconnects against electrolyte-induced degradation is demonstrated by removing the sealant and increasing AA $\sim 25\%$. The resulting modules show an improvement in PCE on APA up to $\sim 12\%$ with respect to Ag-based ones. We also show that graphene can be used in DSSMs to overcome grid corrosion. Our work can be applied to any combination of active materials within Z-type modules, such as TiO_2 , Pt (or any carbon-based CE), dye, and electrolyte, already shown to improve J_{SC} , V_{OC} , and FF.

2. RESULTS AND DISCUSSION

Graphene is prepared by microfluidization of graphite (Timrex KS25) in water and sodium deoxycholate (SDC).¹⁰² Microfluidization applies high pressure (up to ~ 207 MPa)¹⁰³ to a fluid, forcing it to pass through a microchannel (diameter < 100 μm).^{102,103} The key advantage over sonication^{104,105} and shear-mixing¹⁰⁶ is that a high shear rate $> 10^6$ s^{-1} is applied to the whole fluid volume,¹⁰⁷ not just locally, resulting in a uniform processing and no material waste.¹⁰² The lateral size of the exfoliated flakes dispersed in deionized (DI) water (graphene-ink concentration ~ 9 g/L) is ~ 1 μm .¹⁰² A representative Raman spectrum of the processed flakes after 70 cycles is shown in Figure 1, acquired at 514 nm. The 2D band line shape shows two

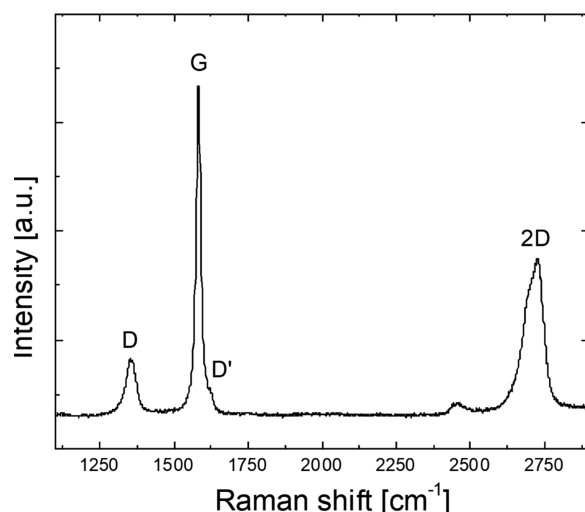


Figure 1. Representative Raman spectrum at 514.5 nm for microfluidized flakes after 70 cycles.

components (2D_2 , 2D_1). Their intensity ratio $I(2\text{D}_2)/I(2\text{D}_1)$ changes from ~ 1.5 for starting graphite to ~ 1.2 for 70 cycles, indicating exfoliation, but not complete to single layer.^{102,108}

The DSSMs are then assembled. First, we describe the fabrication process for standard devices with Ag vertical interconnects. Two 2.2 mm-thick FTO/glass substrates are cut and prepared to act as PE (65 or 60 mm in width) and CE (65 or 60 mm in width). The glasses are cleaned in an ultrasonic bath first with acetone, then with ethanol, and finally UV- O_3 treated to remove organic contaminations¹⁰⁹ and improve

wettability.¹¹⁰ The two glasses are then etched (Figure 2a) by means of a Nd:YVO₄, $\lambda = 1064$ nm, raster scanning laser⁴⁵ to separate the cells within each substrate.⁴⁵ On both electrodes, Ag paste is screen-printed (Figure 2b) to realize the vertical contact. The thickness of this vertical contact is ~ 20 μm for each electrode. Then, we deposit two layers of TiO_2 paste, based on 20 nm TiO_2 particles, onto the PE (Figure 2c1) by screen printing. The first layer is dried at 120 $^\circ\text{C}$ for 20 min before printing the second one.

The PE is then sintered at 480 $^\circ\text{C}$ for 30 min to decompose the organic binders in the paste and to promote electro-mechanical bonding between the TiO_2 nanoparticles.¹¹¹ The final thickness is ~ 11 – 12 μm , as measured via profilometry. This is the optimum value to obtain the best PCE and J_{SC} for a DSSC.^{112,113} On the CE (Figure 2(c2)) a double layer of Pt is screen-printed. The first is dried at 120 $^\circ\text{C}$ for 10 min before printing the second one. Then, the CE is fired at 480 $^\circ\text{C}$ for 30 min, i.e., baked in an oven to ensure the complete volatilization (i.e., conversion to CO_2) of all organic components, such as terpeneol, of the Pt paste.^{114,19} The PE is then immersed overnight (Figure 2(d1)) in a dye N719 solution in Ethanol (0.3 mM), to sensitize (i.e., put the PE in condition to react to light by the mediation of a light-absorbing molecule, i.e., the dye)^{21,24} the TiO_2 film, and then rinsed in ethanol. We consider N719 as a benchmark dye. However, the stability of N719 upon a light soaking stress (at 1 SUN, 1000 h) is limited, since it loses $> 30\%$ of its initial PCE, while organic dyes maintain $> 88\%$ of their initial efficiency.¹¹⁵ N719 is also a Critical Raw Material (CRM) since it contains Ru.¹¹⁶ Thus, we opt for the organic dye DN-F05 for stability analysis, even though both N719 and DN-F05 have similar efficiency in DSSMs. DN-F05 is not a CRM,¹¹⁶ and allows us to get similar PCE to N719, increasing the sustainability and the greenness of the resulting devices. Then, the two electrodes are thermally (at 150 $^\circ\text{C}$) sealed (Figure 2(e)) with a thermoplastic foil already placed onto CE (Figure 2(d2)) and shaped to protect the grids, by the pressure applied with an automatic pneumatic heat press. An electrolyte is then injected (Figure 2(f)) by vacuum backfilling¹¹⁷ through the channels, one for each cell, realized in the thermoplastic foil (Figure 2(d2)). These are subsequently sealed with a commercial acrylic resin or closed with a pneumatic heat press.

The fabrication process for the devices with graphene-based vertical contacts is the same as that for the standard ones, except for step (b) in Figure 2. In this case, we use the graphene-based ink to realize the vertical contacts. Via screen printing, we deposit 6 superimposed layers, which reach 25 μm thickness, on each of the two electrodes. Each is dried with N_2 for few seconds to ensure a better adhesion of the subsequent layer.

For TLM (Transfer Length Method)^{118–120} measurements, we print six, equally dimensioned in width (W) and length (L) (Figure 3a), Ag (1 layer, as in Ag-based devices) and graphene (6 superimposed layers, as in graphene-based devices) contacts on 2 FTO/glass substrates, at increasing distances (d_i), and insulate single contact stripes by raster scanning a 15 ns Nd:YVO₄ laser at 1064 nm with a fluence 12 J/cm². The resistance, R , between different contacts is then measured and plotted as a function of d_i , in Figure 3b.

We derive the transfer length (L_T), i.e., the effective length over which the current that flows in a layer sitting under a metal contact is transferred into the latter, from¹¹⁹

$$L_T = \sqrt{\frac{1}{R_{\text{SH}} G_C}} = \sqrt{\frac{\rho_C}{R_{\text{SH}}}} \quad (1)$$

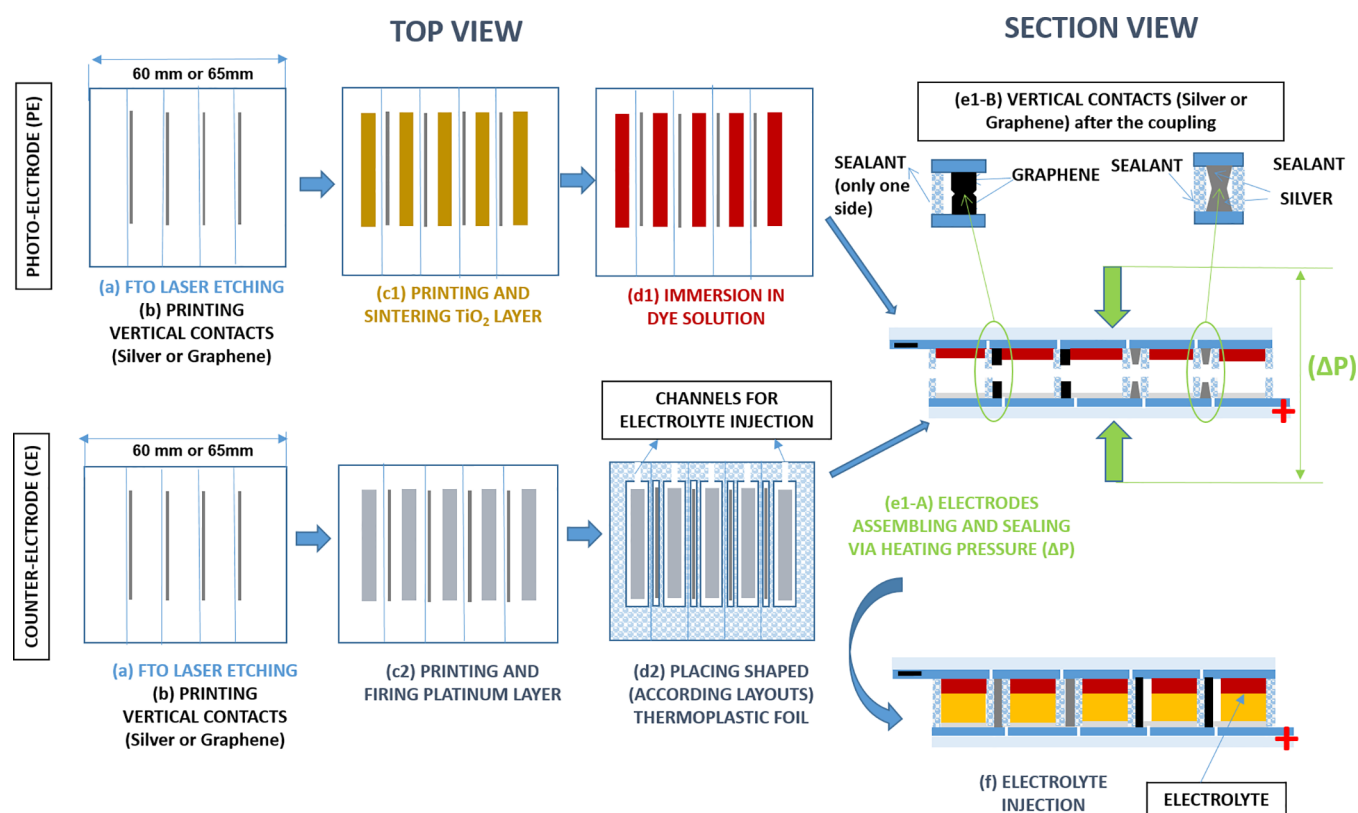


Figure 2. Fabrication process of a Dye Sensitized Solar Module with vertical contacts (Z-Type). (a) Laser etching of FTO (blue) both on PE and CE, (b) deposition of vertical contacts, (c1) deposition and sintering of TiO_2 (ochre yellow), (c2) deposition and firing of Pt (gray), (d1) PE immersed in dye solution (red), (d2) placing shaped thermoplastic foil (textured blue) on CE, (e1-A) assembling and sealing PE and CE by heat pneumatic press, (e1-B) zoom of vertical interconnects for graphene and Ag-based modules, and (f) electrolyte (yellow) injection by vacuum backfilling.

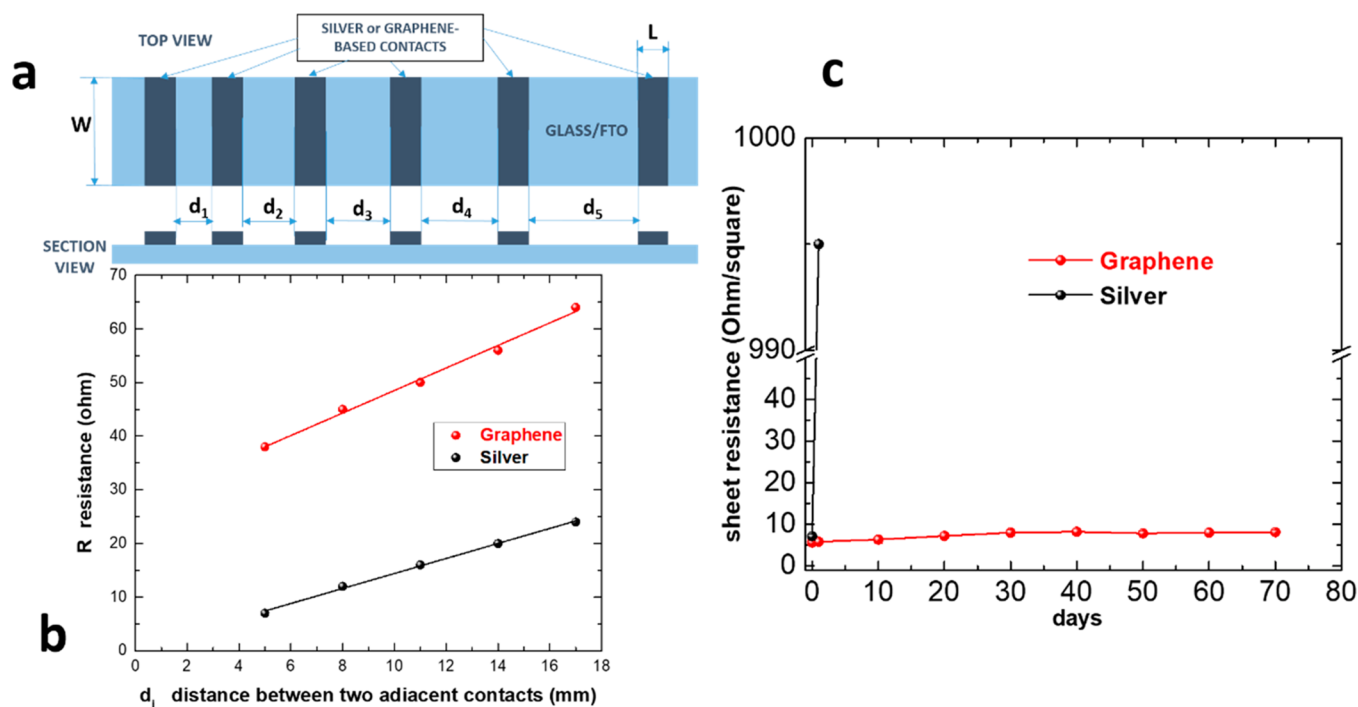


Figure 3. (a) TLM measurement setup. (b) TLM experiments on graphene and Ag contacts. (c) R_{SH} of screen-printed graphene and Ag immersed in HSE electrolyte over 10 weeks.

where R_{SH} is the sheet resistance of the layer sitting under the contact, G_C is the conductance of the contact between metal and underneath layer, and ρ_C is the contact resistivity.

A test on electrolyte corrosion resistance of the graphene-based printed fingers is then carried out. A 5 cm^2 , $6 \mu\text{m}$ thick, film is deposited and annealed on a nonconductive glass. The

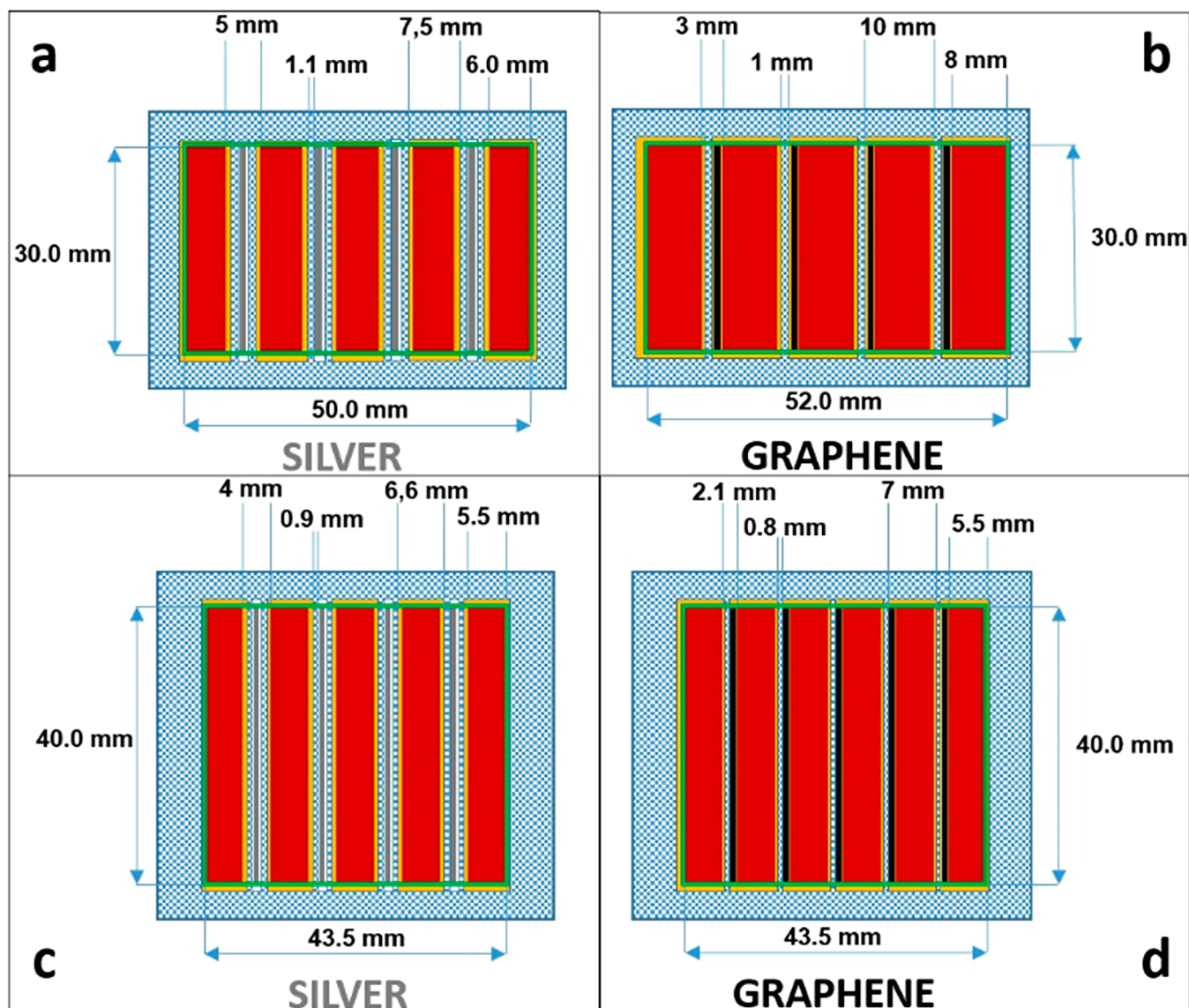


Figure 4. DSSMs layouts. (a,b) Modules (top view of PE) with the same number of cells: (a) Ag-based, (b) graphene-based. The reduction of the sealing area in graphene-based DSSMs allows us to increase the cell width with respect to Ag (Layout A). (c,d) Two modules (top view of the PE) having (c) 5 cells (Ag-based) and (d) 6 cells (graphene-based). Due to the reduction of sealing area, a larger number of cells can be accommodated in the graphene-based module (Layout B). The gray lines in (a,c) depict the Ag contacts, the black lines in (b,d) depict the graphene-based contacts. In (a–d) the sealant is shown as a textured blue grid, the AA ($\text{TiO}_2 + \text{dye}$) is in red, the electrolyte in yellow, and the surface corresponding to APA is shown by green boxes.

resulting $R_{\text{SH}} \sim 5\text{--}9 \, \Omega/\text{sq}$ is similar to FTO-covered glass ($\sim 7\text{--}8 \, \Omega/\text{sq}$). This is then immersed in HSE (High Stability Electrolyte). R_{SH} measurements are then carried out in 9 sites of the square sample surface. Figure 3c shows that, when starting from $R_{\text{SH}} \sim 5 \, \Omega/\text{sq}$, this reaches $\sim 7 \, \Omega/\text{sq}$ after 20 days and remains almost constant over the following days (measurements done every 10 days). After 70 days, R_{SH} is still $\sim 8 \, \Omega/\text{sq}$.

For the Ag film, after 1 day Ag sheets are seen floating in the electrolyte, and R_{SH} goes from $\sim 7 \, \Omega/\text{sq}$ to $\sim 1 \, \text{k}\Omega/\text{sq}$. This shows that the graphene-based ink is less affected by electrolyte than Ag, paving the way to the fabrication of devices in which the contact between electrolyte and interconnects is allowed. Refs 94 and 121 showed that the dye can attach onto graphene. However, in our case, this is not responsible for the chemical sturdiness with respect to the electrolyte, because the graphene fingers are also stable when immersed into the electrolyte, as in Figure 3c.

By definition, AR can be improved by decreasing DA. DA is mainly occupied by the sealant needed both to assemble the device and to protect the vertical contact from the electrolyte corrosive action. It is possible to reduce the surface dedicated to the sealant by increasing the width of the cells and their number. In this way, AA increases. The layout based on Ag-interconnects comprises a finger surrounded by two sealant stripes, to avoid the electrolyte corrosion action, Figure 4a,c. The graphene-interconnects allow us to remove one sealant strip because of the chemical resistance to the electrolyte. We thus gain space, and increase AA for the same APA, thus increasing AR.

The Ag-based DSSM comprises 5 cells (Figure 4a), each 6 mm wide and 30 mm long, with 1 mm wide fingers, 5 mm wide interdistance between two subsequent cells, and 2 mm sealant stripes (1.1 mm at the right of the Ag finger and 1.1 mm at its left, Figure 4a). In this configuration $\text{AA} = 9 \, \text{cm}^2$, $\text{DA} = 6 \, \text{cm}^2$, thus $\text{APA} = 15 \, \text{cm}^2$, and $\text{AR} = 0.60$. By removing the part of the

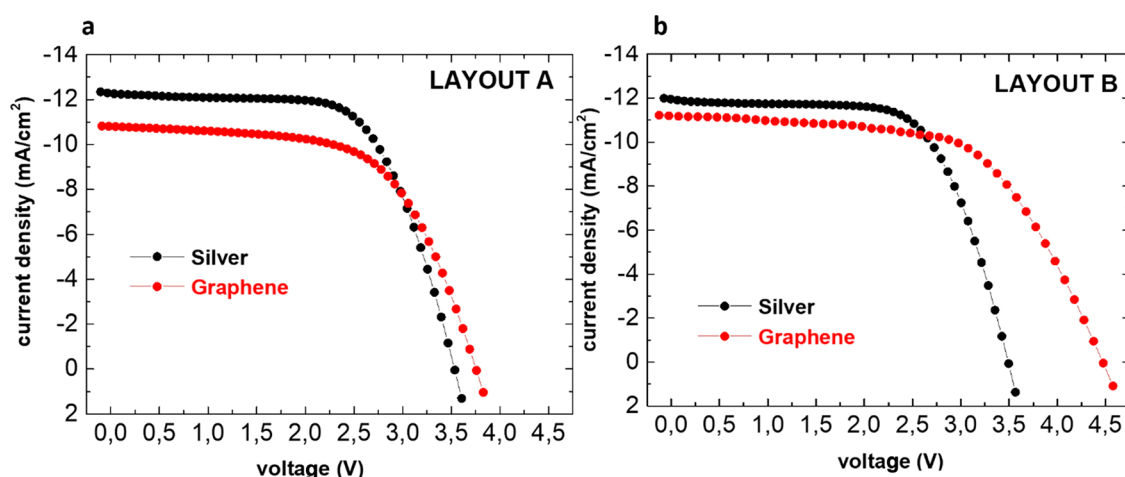


Figure 5. Representative J - V curves for (a) DSSMs layout A and (b) DSSMs layout B.

Table 1. Comparison between Photovoltaic Parameters of Ag-Based DSSMs and Graphene Based-DSSMs for Layout A (Figure 4a,b) and Layout B (Figure 4c,d)

layout	material	AR	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE _{AA} (%)	PCE _{APA} (%)
A	silver	0.60	3.54	-12.3	64.8	5.62	3.37
A	graphene	0.77	3.76	-11.2	61.1	4.96	3.82
B	silver	0.63	3.50	-11.9	65.3	5.45	3.43
B	graphene	0.76	4.47	-11.3	60.0	4.98	3.78

sealant at the right of each finger, it is possible to accommodate both the graphene finger (1 mm wide, as in Ag-based devices) and the AA of the cell in the same gasket (increased from 7.5 to 10 mm, Figure 4b) filled by the electrolyte.

In this first approach (Layout A, Figure 4a,b), we increase the cell width to 8 mm and, consequently, we get $DA = 3 \text{ cm}^2$, $AA = 12 \text{ cm}^2$, $APA = 15.6 \text{ cm}^2$, $AR = 0.77$. The sealant layout is easier to fabricate. We need only 4 areas within the green box in Figure 4b (corresponding to APA) to protect the cells, instead of the 8 of the Ag layout in Figure 4a. The interdistance width between two subsequent cells is now 3 mm, for the same substrate size as Ag-based modules.

In the second approach (layout B, Figure 4c,d), we increase the number of cells. The Ag-based DSSM has 5 cells, 5.5 mm wide and 40 mm long, and 0.8 mm finger width. The interdistance between two subsequent cells is 4 mm, 1.8 mm sealant stripes (0.9 mm at the right of the Ag finger, and 0.9 mm at its left, Figure 4c). In this configuration, $AA = 11.1 \text{ cm}^2$, $DA = 6.4 \text{ cm}^2$, $APA = 17.40 \text{ cm}^2$, $AR = 0.63$. In graphene-based devices, the cell width is 5.5 mm, and that of a finger is 0.8 mm. As in the first approach, by removing the part of the sealant at the right of each finger it is possible to enclose the graphene finger (0.8 mm width) and the AA of the cell in the same gasket (increased from 6.6 to 7 mm, Figure 4d), filled by the electrolyte. The change in sealant layout exploits the resistance of the graphene ink to the electrolyte. In the overall gained space, we can add one cell. Thus, we get $AA = 13.2 \text{ cm}^2$, $DA = 4.2 \text{ cm}^2$, $APA = 17.40 \text{ cm}^2$, $AR = 0.76$. In this case, we need only 5 areas within the green box in Figure 4d (corresponding to APA) to protect the cells, instead of the 8 of the Ag layout in Figure 4c. The interdistance width between two subsequent cells is now 2.1 mm, and we maintain the same substrate size as the Ag-based modules.

We then prepare and characterize 8 devices employing both graphene and Ag-based vertical interconnects. For layout A

(Figure 4a,b), we make two graphene-based devices and two Ag-based ones. The best J - V curves are in Figure 5a.

Layout A (Figure 4a,b) increases AR from 0.60 to 0.77, leading an increment of PCE_{APA} from 3.37% to 3.82% (relative increase $\sim 12\%$). The slight difference (see Table 1) between the two values of J_{SC} ($\sim 1\%$) is due to the difference in cell width (2 mm) between Ag and graphene-based devices.

I_{SC} is $\sim 22.1 \text{ mA}$ for Ag-based devices and $\sim 26.9 \text{ mA}$ for graphene-based ones. This significant improvement ($\sim 18\%$) of I_{SC} is related to the AA increase (from 9 to 12 cm^2), while maintaining the same number of cells (5).

For the 6-cells format (layout B, Figure 4c,d) we fabricate two graphene-based devices and two Ag-based, and we report the J - V curves for the best performing modules in Figure 5b. In this configuration, AR increases from 0.63 to 0.76 with respect to Ag-based devices, with PCE_{APA} raising from 3.43% to 3.78% (with a relative increase $\sim 10\%$). J_{SC} is similar because the cell width is the same. The coupling of electrodes is easier and faster than with Ag. Graphene-based vertical interconnects give a smoother upper surface, requiring lower pressure ($\Delta P \sim -35\%$) and less time ($\Delta t \sim -33\%$) for assembling, compared to Ag-based ones.

We detect a systematic difference in V_{OC} that does not depend on module layout, as shown in Figure 6. Ag and graphene have different work functions (WF). For Ag, $WF = 4.26 \text{ eV}$,¹²² for FLG, $WF = 4.7 \text{ eV}$.¹²³ Thus, the interface FTO/Ag or FTO/FLG could induce a different voltage drop, consistent with the V_{OC} difference. The SEM images in Figure 7 show a more interconnected matrix in the case of graphene. The largest J_{SC} difference between graphene and Ag-based modules is for the A configuration. These cells have different widths: 6 mm for Ag and 8 mm for graphene. Thus, nonuniformity could have a larger impact for graphene modules, reducing the shunt resistance. This, combined with the increase of series resistance (wider cell), could explain the reduced current with respect to Ag. For the B configuration, statistics on J_{SC} show overlapping data.

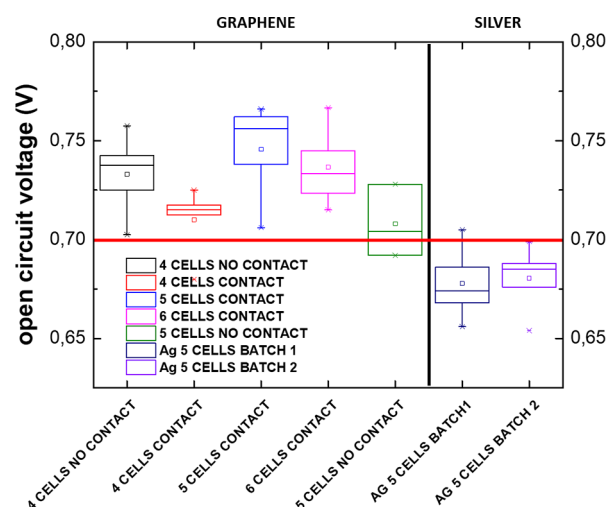


Figure 6. V_{OC} of different module layouts for graphene interconnects (4 cells in contact with electrolyte, 4 not in contact, 5 in contact (as for the layout in Figure 4b), 5 not in contact and 6 in contact (as for the layout in Figure 4d), and Ag interconnects (as for the layout in Figure 4a,c). To compare different configurations, V_{OC} is that of the module divided by the number of cells. The V_{OC} of modules with graphene interconnects is always higher than for Ag ones.

Taking into account one standard deviation, we have $J_{sc} \sim 11.7 \pm 0.4 \text{ mA/cm}^2$ for Ag-based devices and $\sim 11.2 \pm 0.3 \text{ mA/cm}^2$ for graphene-based devices.

Owing to the catalytic activity of graphene,¹²⁴ we could expect some contribution to the cell current from the graphene interconnects. When these are immersed in the electrolyte, they act as an additional surface for electrolyte reduction, as the cell CE with the Pt catalyst. This, in principle, could impact the current. However, the graphene surface in contact with the electrolyte is very small, with a ratio between the two surfaces $\sim 1/200$. Thus, the contribution to the current due to graphene is negligible. The graphene electrode is porous and the electrolyte can penetrate it, thus the equivalent surface (i.e., the surface contacting the electrolyte) is larger than the corresponding surface in the Ag case. The distance between graphene and PE is almost 1 order of magnitude larger ($150\text{--}200 \mu\text{m}$ instead of $40 \mu\text{m}$) than between CE and PE. This results in a larger diffusion resistance, which further reduces the impact of the graphene electrode on the electrocatalysis.

For the design of a DSSM it is necessary to consider the losses due to ρ_c between FTO and printed graphene-contacts. In order to evaluate ρ_c we measure L_T . This relates to ρ_c as^{120,125,126} $\rho_c = R_{FTO} \times L_T^2$. L_T is $\sim 0.14 \text{ mm}$ for Ag and $\sim 6.5 \text{ mm}$ for graphene. Considering the low current densities (typically $\sim 9\text{--}15 \text{ mA/cm}^2$ for a large area series connected device)^{37,40,127,128} and the

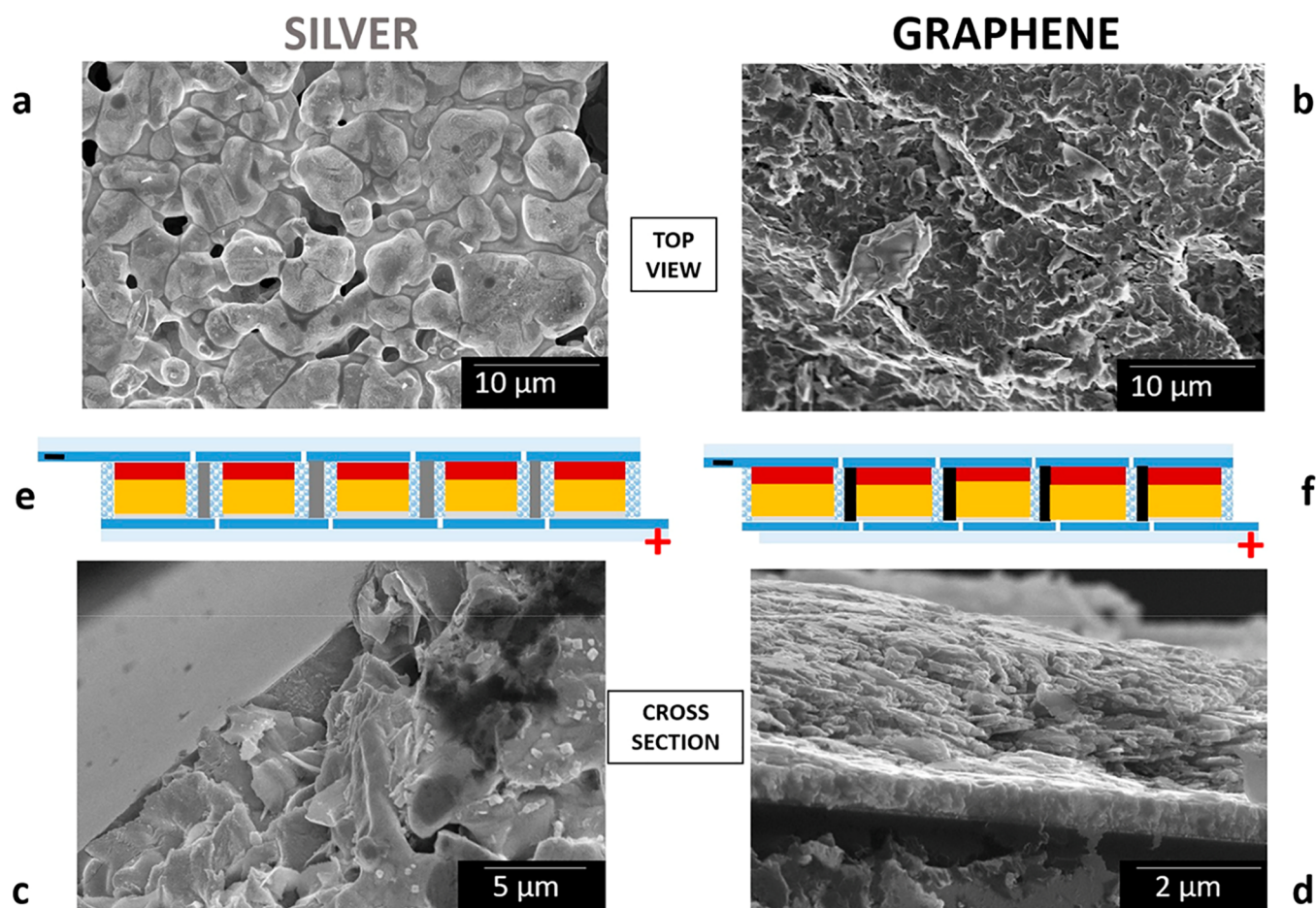


Figure 7. SEM images of (a) Ag layer, (b) graphene coating, (c) cross section of Ag layer, (d) cross section of graphene coating, (e) schematic cross view of Ag-based device. The structure for each vertical Ag contact is depicted in gray: cell/sealant/contact/sealant/cell.^{36,55} (f) Schematic cross view of graphene-based device. The structure for each vertical graphene-based contact is depicted in black: cell/sealant/contact/cell. In (e,f) the TiO_2 + dye layer is in red, the electrolyte in yellow, the Pt layer in clear gray, the sealant in textured blue, and the FTO in simple blue.

width of the vertical interconnects ~ 1 mm, the photovoltaic parameters (Table 1) of graphene-based DSSMs on AA are not penalized by the higher L_T and are comparable with those of Ag-based devices. The conductivity of graphene could be improved through lithium intercalation, as discussed in ref 129.

The complexity of fabrication of a Z-type DSSM lies mainly in the vertical contact.^{28,48,54,55} The higher Ag resistance to localized deformation with respect to the thermoplastic polymer-based material used as sealant (Bynel 60, Dupont), could weaken the contact between upper and lower finger, affecting J_{SC} and FF. The presence of spikes in the printed Ag layer, or the volume expansion of the electrolyte,⁶⁰ could affect the sealing, separating the electrodes. At $T \sim 85$ °C, the distance between the two electrodes can increase because of expansion of the sealing material. If this occurs, the vertical contact could be interrupted.

In order to avoid these issues, it is possible to deposit a layer of low T Ag paste (curing $T \sim 130$ °C,¹³⁰ e.g., PV412 Dupont) onto the already sintered Ag layer.⁴² The deposition via screen-printing, or via dispensing, on one or both substrates, and curing during sealing ensure a better contact. Mechanical pressure allows one to fill the empty spaces deriving from the roughness of the sintered Ag layers. The low T Ag paste deposition and the subsequent assembling steps must be realized very quickly (<10 min) to avoid Ag drying in air. This further step in manufacturing empathizes the complexity of fabrication. Figure 7 compares a sintered layer of Ag paste (1710, Dupont) at 480 °C and a graphene based-ink annealed at the same T . The SEM images from top of the layers show a different agglomeration. The graphene contact appears more compact than Ag and looks quite similar to screen-printed films for other applications, such as printed circuits.¹⁰² SEM cross section images (Figure 7c,d) show two features for graphene layers: compactness and smoothness, when compared to Ag. The smoothness of graphene with respect to Ag is reflected into the lower pressure needed to assemble the graphene-based modules compared to Ag ones. The morphology of graphene-based interconnects mimics the effect of the vertical contact made with the low- T Ag paste of ref 42.

These fabrication differences impact the device's long-term stability. We thus perform a stability test in an oven for 1000 h at 85 °C, following the thermal stress approach of refs 96, 131, 132, since DSSC technology has not yet developed its own certification protocols (this corresponds to ISOS-D-2 tests).⁷⁰ This is useful to assess the different behaviors of graphene and Ag-based devices, and to check the DSSM's structural stability, i.e., their robustness in terms of delamination and subsequent electrolyte leakage. For this, we fabricate and characterize 10 devices with layout B: 5 with the Ag-layout of Figures 4c and 5 with graphene-based interconnects, with the 6-cells format in Figure 4d. In the layout of Figure 4d, the vertical interconnects are not protected with an encapsulant. We use this layout to compare modules with larger AA (11.1 cm² for Ag-based devices and 13.2 cm² for graphene-based ones) and greater number of cells (in the case of graphene), in order to maximize the number of interdistances (in the case of graphene). The graphene-based devices have a width of the strip of sealant between one gasket (containing cell and one finger) and the next gasket ~ 0.8 mm, Figure 4d. The number of these strips is 5. For the Ag-based devices, the strip of sealant between two gaskets, one containing only the cell, and the other containing only the finger, is ~ 0.9 mm wide. The number of these strips is 8. The surface area related to these strips is ~ 2.88 cm² for Ag and ~ 1.6 cm² for graphene. This

means that the encapsulation is more rugged for Ag-based devices. The cell width is the same: 5.5 mm. The electrolyte involved is HSE. Before starting the thermal stress in the oven, we test the devices under shelf life conditions, as detailed in the ISOS-D-1 protocol,⁷⁰ for 240 h.

After 1000 h at 85 °C, the PCE of all graphene-based devices remains stable, Figure 8, and no structural defects, such as

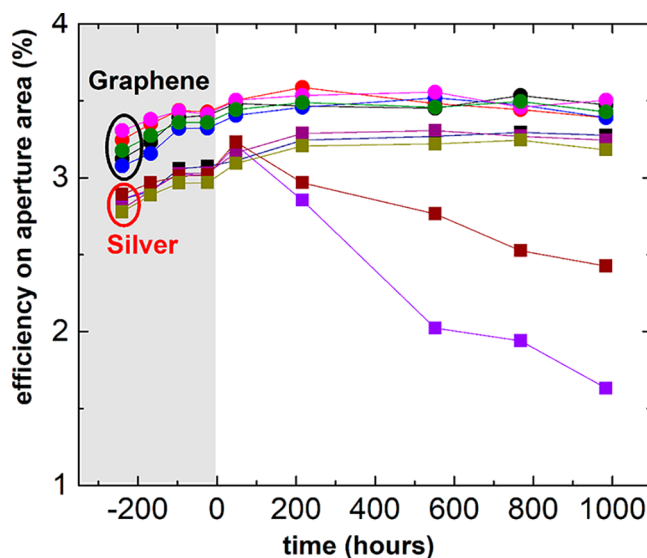


Figure 8. Stability test at 85 °C comparing 5 DSSMs with Ag-vertical interconnects and 5 with graphene ones. Layout B (Figure 4c,d) is used. The gray region is related to the shelf-life time at ambient T .

delamination between the two substrates, are observed. Two out of five Ag-based devices have sealant delamination and subsequent electrolyte bleaching (due to contact with Ag) and leakage. Thus, graphene-based interconnects improve the structural stability of the devices.

3. CONCLUSIONS

We prepared graphene-based interconnects overcoming degradation due to the corrosion of Ag grids in Z-type DSSMs. These improve the aperture area efficiency and decrease the dead area by up to ~ 3 cm² (halving this value), raising the aspect ratio related to the substrate by 0.17, with respect to devices with Ag-based interconnects. By enlarging the width of single cells, or by increasing the number of cells within the same area, we achieve an enhancement of the aperture area efficiency up to +12% with respect to Ag-based devices. Our approach solves the main issues of DSSC technology: grid corrosion and electrolyte bleaching. The graphene-based vertical interconnects increase the number of devices passing the dry heat test by 40% (1000 h @ 85 °C), highlighting their effectiveness and mechanical stability, due to their intrinsic morphological characteristics, with no spikes, unlike Ag-based ones. Our work paves the way to the roll-out of DSSC technology in BIPV and for indoor applications.

4. MATERIALS AND METHODS

4.1. Graphene-Ink. The ink is formulated as follows: 80 g/L of microfluidized flakes are mixed in deionized (DI) water with ~ 9 g/L of SDC and then processed for 70 cycles with a Microfluidic processor (M-110P, Microfluidics).¹⁰² The dispersion is then stabilized by adding 10 g/L of carboxymethylcellulose sodium salt (CMC) as rheology modifier at room T , while stirring.¹³³ This allows us to reach a shear

thinning viscosity as required for screen printing (~ 0.2 Pa·s at shear rate of 1000 s^{-1}).¹⁰²

4.2. Dye Sensitized Solar Modules (DSSMs) and TLM. Conductive substrates for DSSMs are from “NSG-Pilkington”. Their R_{SH} is $7\ \Omega\text{-sq}^{-1}$. They are cleaned with brushing, without scratching the FTO surface, using a “Hellmanex” cleaning solution diluted with water in a 2:98 v/v ratio. Acetone and ethanol for the ultrasonic bath (10 min for each of the two) are from “Sigma-Aldrich”. Substrates are then rinsed in ethanol and quickly dried with a strong air flow. The UV- O_3 treatment is performed using a PSD Pro Series Digital UV Ozone System from Novascan. Both etching of substrates and ablation of Ag and graphene-based contacts for TLM are performed using a BrightSolutions, Luce 40 laser. The Ag interconnects and the graphene-based ones, as well as the TiO_2 and Pt layers, are deposited with a highly automated Screen Printer (SP) from “Baccini-Applied Materials”. All the depositions are performed in double squeegee mode, with an applied force ~ 110 N on the screen, except for the graphene-based interconnects (in this case, the applied force is ~ 80 N). In order to screen-print both Ag and graphene-base interconnects, we use a screen with mesh 77T (i.e., 77 threads in the polyester screen/cm). The mesh is 48T for TiO_2 and 100T for Pt. The Ag paste is 7713 from Dupont, the TiO_2 paste is 18 NR-T from Greatcell Solar, and the Pt precursor paste is from 3D-nano. Sintering, firing, and drying are performed in an oven, Lenton WHT6/60 (Hope Valley, U.K.). The thermal stress test is carried out in a Lenton WHT 4/30 oven. The dye N-719 (Ditetra-butylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)) from Sigma-Aldrich is prepared in ethanol solution (0.3 mM). The dye DN-F05 (also known as D35CPDT, 3-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b']dithiophene-2-yl)-2-cyanoacrylic acid) form Dyenamo is prepared in ethanol solution (0.2 mM). They are left to stir overnight before use. The electrolyte, HSE from Greatcell Solar is left to stir at $\sim 50\text{ }^\circ\text{C}$ for ~ 20 min before use. Assembling and sealing DSSMs is performed by an automated pneumatic heat press (model 50 speciale from “Memo s.r.l.”), composed by two opposite heated plates. T of both plates is set at $\sim 150\text{ }^\circ\text{C}$. The coupling between PE and CE is obtained using a thermoplastic foil (Bynel 60 from “Dupont”) between the two electrodes. The difference of pressure between the two plates is set at ~ 1.1 bar for Ag and ~ 0.8 bar for graphene-based devices. The time of coupling is ~ 60 s for Ag and ~ 40 s for graphene-based ones. Channels for electrolyte injection (Figure 2(d2)) are sealed with UV-curable resin Threebond 3035B.

4.3. Measurements Setup. The Raman spectrum in Figure 1 is measured using a Renishaw InVia spectrometer equipped with 50 \times objective. The thickness of Ag, graphene, and TiO_2 is measured via profilometry (Deektat Veeco 150). R_{SH} is measured with a 4-point probe system integrated in Arkeo System from Cicci Research. The J - V curves of DSSMs (Figure 5) and their electrical parameters (PCE , J_{SC} , V_{OC} , and FF) are acquired in air using a Keithley 2420 source meter coupled with a solar simulator (ABET Sun 2000, class A), calibrated by a thermopile pyranometer (Pyranometer MS-602, EKO) at AM (Air Mass) 1.5 and 100 mW cm^{-2} illumination conditions. The voltage step is 70 mV. The SEM images (Figure 6) are acquired in a FEI Magellan-400 XHR SEM at 15 kV, 0.2 nA, with magnification $\sim 15\ 000$ – $35\ 000$.

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Notes

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