Abstract
The use of graphene-based electrodes is burgeoning in a wide range of applications, including solar cells, light emitting diodes, touch screens, field-effect transistors, photodetectors, sensors and energy storage systems. The success of such electrodes strongly depends on the implementation of effective production and processing methods for graphene. In this work, we take advantage of two different graphene production methods to design an advanced, conductive oxide- and platinum-free, graphene-based counter electrode for dye-sensitized solar cells (DSSCs). In particular, we exploit the combination of a graphene film, produced by chemical vapor deposition (CVD) (CVD-graphene), with few-layer graphene (FLG) flakes, produced by liquid phase exfoliation. The CVD-graphene is used as charge collector, while the FLG flakes, deposited atop by spray coating, act as catalyst for the reduction of the electrolyte redox couple (i.e. $I_{3}^{-}/I^{-}$ and $Co^{2+/3+}$). The as-produced counter electrodes are tested in both $I_{3}^{-}/I^{-}$- and $Co^{2+/3+}$-based semitransparent DSSCs, showing power conversion efficiencies of 2.1% and 5.09%, respectively, under 1 SUN illumination. At 0.1 SUN, $Co^{2+/3+}$-based DSSCs achieve a power conversion efficiency as high as 6.87%. Our results demonstrate that the electrical, optical, chemical and catalytic properties of graphene-based dual films, designed by combining CVD-graphene and FLG flakes, are effective alternatives to FTO/Pt counter electrodes for DSSCs for both outdoor and indoor applications.

1. Introduction
Dye-sensitized solar cells (DSSCs) [1, 2] represent an affordable photovoltaic (PV) technology (production costs below 0.5 USD/Wp [3]), which recently achieved power conversion efficiency (PCE) > 14% [4] (certified PCE of 14.1% [5]). These solar cells also offer several advantageous properties [6, 7], such as lightweight [8], flexibility [9–11], low toxicity [12–14], and the possibility to efficiently work under weak and indirect illumination [15–17], (e.g. in cloudy [18, 19] and artificial light conditions) [20, 21]. The DSSCs can be fabricated with on-demand color [22–25] and transparency level [26], and be thus integrated in buildings [27] or used for indoor energy generation [28–30]. Typically, a DSSC has a layered structure [2, 31] composed of a conductive photoanode coated with a few-µm-thick semiconductor (e.g. $TiO_{2}$ [12, 32, 33], $ZnO$ [34–36], $SnO_{2}$ [37, 38], $In_{2}O_{3}$ [34, 39], $Nb_{2}O_{5}$ [40, 41], and $SrTiO_{3}$ [40]), a dye sensitizer (organic [14, 42–46] or inorganic [12, 47], e.g. ruthenium...
bipyridyl derivatives \cite{48,49}, such as N719 \cite{49} and N3 \cite{49}, an electrolyte (liquid \cite{50,51} or solid \cite{50,52}) containing a redox system (e.g. $I^-_3/I^-_1$ and Co$^{2+}$/Co$^{3+}$ complexes \cite{53,54}) and a counter-electrode (CE) (e.g. platinized transparent conductive oxide –TCO– \cite{55–57} and nanocarbon-based electrodes \cite{58–65}). More in details, CEs are composed by two components, namely the current collector (e.g. TCO \cite{55–57} or metal grid electrode \cite{66,67}) and a catalytic film made of Pt particles \cite{55–57} or nanocarbons \cite{58–65}). The current collector gathers the electrons through the external circuit, while the catalysts generates the electrolyte species \cite{2,31}. In most cases, fluorinedoped tin oxide (FTO) is used as current collector due to a high electrical conductivity (i.e. sheet resistance \(R_{\text{sheet}} \leq 10 \ \Omega \ \square^{-1} \ [68,69]\)) combined with optical transparency (transmittance \(T_r \geq 80\%\) in the visible wavelength range \cite{69,70}). Traditionally, platinized-FTO (FTO/Pt) have been adopted to catalyze the regeneration of the electrolyte species for the standard $I^-_3/I^-_1$ redox couple (i.e. $I^-_3 + 2e^- \rightarrow 3I^-$) \cite{2,31}. Recently, both platinized-FTO (FTO/Pt) \cite{71} or graphene nanoplatelets-coated FTO \cite{46,72} have been exploited to reduce Co-based redox mediator \cite{55,56}. Noteworthy, polypyridine complexes of Co$^{2+}$/Co$^{3+}$ (coupled with donor-$\pi$-bridge-acceptor sensitizers) \cite{73,74} show redox potential (>0.4 V versus NHE \cite{75,76}) more positive than the $I^-_3/I^-_1$ couple (0.35 V versus RHE \cite{76–80}), allowing PCE over 12% to be achieved \cite{4,46,71,72} (up to 14.3% \cite{4}). However, such results have been obtained by using current collectors of FTO, which are brittle \cite{81} and whose fabrication requires high-temperature processes \cite{82–84}. These undesired properties arise severe challenges for the FTO deposition on plastic substrates, as needed for flexible solar cells \cite{85,86}. In addition, Pt-based CE can account for the 50% of the overall cell price \cite{3}, due to the high cost of Pt (~800 USD oz$^{-1}$) \cite{87}. Pt-based CEs also tend to degrade when exposed to the liquid electrolytes \cite{88,89}, affecting the lifetime stability of the cells \cite{88,89}. In this context, carbon-based materials have been successfully demonstrated as reliable alternative catalyst to replace Pt in CE. The list includes activated carbons \cite{90}, carbon nanotubes (CNTs) \cite{91,92}, hard carbon spherules \cite{61}, graphite \cite{93–95}, graphene flakes \cite{96}, graphene nanoplatelets \cite{46,72,97}, graphene oxide (GO) \cite{98}, anthraquinone, and graphite \cite{99,100}. Specially, graphene nanoplatelet deposited onto FTO have been reported as excellent catalyst for DSSC based on the Co$^{2+}$/Co$^{3+}$ redox couple \cite{46,101}, outperforming FTO/Pt CE \cite{101} and reaching PCE as high as 13% \cite{46}. However, to date the development of (semi)transparent CEs entirely based on nanocarbons acting both as current collector and catalysts has been scarcely investigated \cite{64,102,103}. For example, a CE based on CNT fibers has been recently proposed as dual-functional current-collectors/catalysts in DSSCs with PCE up to 8.8% \cite{64}. However, the bottleneck regarding the use of ‘bulky’ CNTs fibers is the loss of transparency, which limits the possibility of illuminating the DSSCs from both sides in a conventional configuration \cite{64}, as well as the fabrication of DSSCs with on-demand color \cite{22–25} to be integrated in buildings \cite{27}.

In this context, graphene appears to be the ideal candidate to fulfill multiple functions \cite{104,105} as it uniquely combines high charge carrier mobility (\(\sim 200 \ 000 \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}\)) \cite{106,107} optical transparency \cite{108} (transmittance \(T_r = \sim 97.7\%\) \cite{109}), excellent thermal conductivity (\(\sim 5000 \ \text{W} \ \text{m}^{-1} \ \text{K}^{-1}\)) \cite{110,111}, outstanding mechanical properties \cite{112} (e.g. Young’s modulus \(\sim 1 \ \text{TPa}\) \cite{113}), and catalytic activity \cite{46,72,96,97,114–118}. These properties refer to single graphene flakes and it is still difficult to match them in large-area samples; however, recent reports demonstrated the application of graphene-based electrodes in a wide variety of devices \cite{119–123}, such as solar cells \cite{124–128}, light emitting diodes \cite{129–131}, touch screens \cite{132–134}, field-effect transistors \cite{135,136}, photodetector \cite{137} (electro)chemical sensors \cite{138–140} and energy storage system \cite{141–146}.

The success of such graphene-based electrodes, especially if compared to those based on others carbon allotropes, crucially originates from the implementation of effective production \cite{147–149} and processing techniques \cite{150–154}. In this context, large-area growth of pristine single-layer graphene (SLG) can be obtained via chemical vapor deposition (CVD) \cite{155–158}. Subsequently, it can be transferred onto arbitrary substrates \cite{159} by both wet \cite{147,160–164} and dry \cite{121,132,147,165} methods. This allows for the realization of flexible electrodes with \(T_r \geq 85\%\) and \(R_{\text{sheet}} \leq 30 \ \Omega \ \square^{-1} \ [132,166,167]\), which are both comparable to those of conventional TCO \cite{168,169}, e.g. indium tin oxide –ITO– \cite{170,171} and FTO \cite{69,172}. Meanwhile, the production of graphene-based materials in high volumes have been achieved through liquid-phase exfoliation (LPE) methods \cite{147,148,151,173–175}. These methods are based on top-down approaches which permit to exfoliate bulk graphite into SLG and few-layer graphene (FLG) in a liquid environment \cite{147,148,151,173–175}. This process is performed by exploiting techniques such as ultrasonication \cite{176–180}, ball milling \cite{181,182} shear mixing \cite{183–186} and wet-jet milling \cite{174,187} to break the van der Waals bond between the adjacent planes of the graphite. The possibility to produce and process graphene in a liquid phase allows functional inks with on-demand rheological and morphological properties to be formulated \cite{172–174,188}. This represents a step forward towards the development of industrial-scale, reliable and inexpensive printing/coating processes of graphene \cite{113,188–193}.

Based on the advantages offered by the aforementioned graphene production and processing methods, we demonstrated a novel TCO and noble metal-free CE based on CVD-graphene/graphene flakes dual-film.
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(figure 1). By taking advantages of different graphene production and processing methods, we successfully eliminated the drawbacks typically related to the use of (i) Pt as catalyst and (ii) FTO as current collector. Specifically, low-resistance graphene film produced by CVD (figure 1(a)) acts as charge collector, while high-surface area graphene flakes with abundant sharp edges, produced by liquid phase exfoliation (LPE) (figure 1(b)) and spray-coated onto CVD-graphene (figure 1(c)), work as catalysts for the reduction of the electrolyte redox couple (figure 1 (d)). Chemical vapor-deposited graphene exhibited a high optical transparency ($T_r > 97\%$ for visible wavelength ranging between 500–800 nm) and low $R_s$ ($\sim 1.2 \Omega \square^{-1}$), while submicron-sized graphene flakes provided high specific surface area –SSA– ($123 \pm 25 \ m^2 \ g^{-1}$ and sub-μm size (lateral dimension ranging between 200–900 nm), resulting in abundance of catalytic edge sites. The as-produced CE were tested in both $I_{3}^{-}/I^{-}$ and $Co^{2+}/Co^{3+}$-based electrolyte have been tested, together with C106 and Y123 dye, respectively.

2. Methods

2.1. Production of materials

2.1.1. Chemical vapor deposition and transfer of graphene

Continuous films of graphene were synthesized on Cu foil (Sigma Aldrich, thickness 20 μm, 99.999%) by CVD by using a cold-wall reactor with methane as a carbon precursor [199]. The Cu foil was loaded into the CVD reactor, which was then heated to 1060 °C in Ar atmosphere to anneal the foil for 10 min. After this annealing step, the graphene growth was performed at 1060 °C for 10 min (pressure of 25 mbar) by flowing CH$_4$ (2 sccm), H$_2$ (20 sccm) and Ar (1000 sccm). The CVD reactor was then cooled down to 120 °C before removing the samples to prevent substrate oxidation. Samples of CVD-graphene of $1 \times 1 \ cm^2$ size were transferred to glass or SiO$_2$ substrates using wet transfer technique with poly(methyl methacrylate) (PMMA) as support medium [200]. Briefly, a thin layer of PMMA (2% solution in acetyl lactate, All resist GmbH) was deposited onto Cu/graphene by spin coating, and dried for 1 h at ambient conditions. The as-obtained samples were immersed in a 0.05 M solution of iron(III) chloride (FeCl$_3$, Sigma-Aldrich) for 16 h to etch the Cu and release the graphene/PMMA membrane. Once the Cu was completely etched away, the graphene/PMMA membrane was removed from...
the FeCl₃ solution using a glass slide and transferred to deionized water several times to remove the etchant residue. Subsequently, the membrane was removed from the water using glass or SiO₂ substrates, and dried at ambient conditions. Finally, the PMMA support film was removed by immersing the sample in acetone (Sigma Aldrich) for 4 h and then rinsed in 2-propanol (Sigma Aldrich).

2.1.2. Graphene flakes production via LPE of graphite

The graphene flakes were produced by the LPE [114, 147, 148, 191], followed by SBS [114, 188, 191] of pristine graphite (≥100 mesh, 75% min, Sigma Aldrich) in N-Methyl-2-pyrrolidone (NMP) (99.5% purity, Sigma Aldrich). Experimentally, 1 g of graphite was dispersed in 100 ml of NMP and ultrasonicated in a bath sonicator (Branson 5800 cleaner, Branson Ultrasonics) for 6 h. The resulting dispersion was then ultracentrifuged at 4500 g (in Beckman Coulter Optima XE-90 with a SW32Ti rotor) for 30 min at 15 °C, exploiting SBS to remove thick flakes and unexfoliated graphite [201, 202]. Subsequently, the supernatant (~80% of the dispersion) was collected by pipetting.

2.2. Characterization of materials

Scanning electron microscopy (SEM) images of CVD-graphene were taken with a FE-SEM (Jeol JSM-7500 FA). The acceleration voltage was set to 5 kV.

Transmittance spectra of the CVD-graphene on glass were taken with a Cary Varian 6000i UVvis–NIR spectrometer, using a 1 mm pinhole holder. The pristine glass substrate was used as baseline. Each sample was measured five times and the averaged values were reported.

Optical absorption spectroscopy (OAS) measurements of the LPE-produced graphene flake dispersion in NMP were performed with a Cary Varian 6000i UVvis–NIR spectrometer. The absorption spectra were acquired using a 1 ml quartz glass cuvette. The inks were diluted to 1:100 in NMP, to avoid scattering losses at higher concentrations. The corresponding solvent baseline was subtracted to each spectrum. The concentration of graphitic flakes is determined from the optical absorption coefficient at 660 nm, using $A = \alpha l c$ where $l$ is the light path length, $c$ is the concentration of dispersed graphitic material, and $\alpha$ is the absorption coefficient, with $\alpha \sim 1390 \text{ l g}^{-1} \text{ m}^{-1}$ at 660 nm [179, 203].

Raman spectroscopy measurements on CVD-graphene (transferred on glass and Si/SiO₂) and LPE-produced graphene flakes were carried out by using a Renishaw inVia confocal Raman microscope using an excitation line of 532 nm (2.33 eV) with a 50 × objective lens, and an incident power of ~1 mW on the samples. The LPE-produced flakes were obtained by drop-casting their dispersion in NMP onto a Si wafer with 300 nm of thermally grown SiO₂ (LDB Technologies Ltd.). The samples were then dried under vacuum before the measurement. The spectra were fitted with Lorentzian functions. Statistical analysis was carried out by means of OriginPro 9.1 software.

Transmission electron microscopy (TEM) measurements of the LPE-produced graphene flakes were carried out with a JEM 1011 (JEOL) transmission electron microscope operating at an acceleration voltage of 100 kV. The samples were obtained by depositing 1:100-diluted graphene flake dispersion in NMP onto holey carbon (200 mesh grids). Subsequently, the samples were dried under vacuum overnight.

Atomic force microscopy (AFM) images of the LPE-produced flakes were taken using an Innova AFM (Bruker, Santa Barbara, CA). The measurements were taken in tapping mode with a NTESPA 3.75 mm cantilever (Bruker, 300 kHz k: 40 N m⁻¹), in air at room temperature, with a relative humidity less than 30%. The software used for image analysis was Gwyddion version 2.43. Statistical analysis was carried out by means of Origin 9.1 software, using different AFM images of the sample. The sample for the measurements was prepared by drop-casting 1:30 diluted graphene flake dispersion in NMP onto mica sheets (G250-1, Agar Scientific Ltd., Essex, U.K.) and drying them under vacuum overnight.

2.3. Fabrication of graphene-based CEs

Glass/CVD-graphene were produced according to the protocols described in section 2.1. Subsequently, the LPE-produced graphene flakes dispersions (see section 2.1 for the details regarding the dispersion production) were deposited onto glass/CVD-graphene samples by spray coating. The dispersions were sprayed using a flux of N₂ at 1 bar, and keeping the substrates at a temperature of 150 °C. By controlling the amount of sprayed dispersion, three different mass loadings of the graphene flakes (0.16, 0.32 and 0.48 mg cm⁻²) were deposited onto the CVD-graphene. After the deposition of the graphene flakes film, the substrates were annealed in glove box at 350 °C for 2.5 h in order to remove solvent residuals.

2.4. Characterization of graphene-based CEs

SEM images were acquired with a FE-SEM (Jeol JSM-7500 FA). The acceleration voltage was set to 5 kV.

Atomic force microscopy and Raman spectroscopy measurements were acquired with the same instrumentalations and parameters reported in section 2.2.

Transmittance spectroscopy measurements of the graphene-based CEs were acquired with an integrating sphere-supported UV–vis Shimadzu Spectrophotometer. A glass/CVD-graphene substrate was used as baseline. Each sample was measured five times and the average values were reported.

Sheet resistance measurements were performed with a Keithley Model 2612A Dual-channel System Source Meter in four-point probe configuration, using in line gold-plated probes of constant spacing (2 mm) contacting the surface of the films.
Specific surface area measurements of electrodes were carried out in Autosorb-iQ (Quantachrome) by Kr physisorption at temperatures of 77 K. The specific surface areas were calculated using the multi-point Brunauer-Emmett-Teller (BET) model [204], considering equally spaced points in the P/P0 range from 0.009–0.075 to. P0 is the vapour pressure of Kr at 77 K, corresponding to 2.63 Torr [205–208]. Before the measurements, the samples were degassed for 1 h at 60 °C under vacuum conditions to eliminate weakly adsorbed species.

2.5. Fabrication of DSSCs and symmetrical dummy cells

Fluorine-doped SnO2-coated glass (soda lime) substrates (8 Ω□−1, Pilkington Tec) were cleaned using successive ultrasonic baths in acetone (Sigma Aldrich) and ethanol (Sigma Aldrich). Two types of DSSCs using C106 and Y123 as dye sensitizer, respectively, were fabricated using specific protocols. For C106-based DSSCs, films of nanocrystalline TiO2 (0.5 × 0.5 cm2) were deposited onto FTO-glass via screen-printing, using a TiO2 paste (Dyesol 18NR-T). Subsequently, the substrates were dried in an oven for 20 min at 120 °C in order to evaporate the solvent. The thickness of TiO2 layers was 6 µm thick, as measured by Dektak Veeco 150 profilometer. The as-obtained samples were then exposed to a sintering procedure at 525 °C for 30 min. Then, the samples were soaked in the C106 solutions for 16 h, washed with ethanol and blown with compressed air, obtaining the photoanodes. Graphene-based CEs were prepared as described in section 2.3. Reference counter electrodes based on FTO-Pt were also fabricated. Briefly, a Pt layer was deposited onto FTO by screen-printing an as-purchased paste containing Pt precursor (Platisol, Soralonix). Subsequently, the substrates were dried in an oven at 120 °C for 20 min, and sintered for at 480 °C 30 min. The devices were laminated with a 25 µm-thick thermoplastic resin (Surlyn, Solaronix) filled with I3−/I− electrolyte (HSE, Dyesol). An active area of 1.44 cm2 was made with a thermoplastic mask.

2.6. Characterization of DSSCs and dummy cells

The PV performance of DSSCs was determined by current density versus voltage (JV) measurement in air under a solar simulator (ABET Sun 2000, class A) at 1 SUN and 0.1 SUN, calibrated with a certified reference Si Cell (RERA Solutions RR-1002). The incident power was measured with a Skye SKS 1110 sensor. The class of the sun simulator was measured with a BLACK-Comet UV–VIS Spectrometer.

Electrochemical impedance spectroscopy (EIS) measurements of dummy cells were taken in dark conditions at room temperature using an Autolab 302N Modular Potentiostat (Metrohm) in two-electrode configuration under short circuit condition (0 V of electrical bias). The ac perturbation was set at 10 mV with frequencies ranging from 100 kHz to 0.1 Hz.

3. Results and discussion

The CVD-graphene and the LPE-produced graphene flakes (see Experimental, section 2.1, for the material production details) were first characterized separately before the fabrication of the graphene-based CE. The morphology of the materials was evaluated by electron microscopy and AFM measurements. Figure 2(a) shows a representative SEM image of the CVD-graphene grown on Cu foil by using a cold-wall reactor (see additional detail in Experimental, section 2.1) [199]. The sample is overall a continuous polycrystalline film without any tears or holes, in agreement with previous studies [199]. Such morphology resulted in a Rsheet of ~1.2 kΩ□−1. Partial coverage experiments with a growth time of 5 min revealed a high nucleation density (25,000 grains mm−2) with an average grain size of a ~10 µm (figure 2(b)). The nucleation of
graphene on Cu occurs primarily on the surface irregularities such as the rolling grooves and crystal terraces acting as energetically favorable spots for the nucleation of graphene [199, 210]. Figures 2(c) and (d) show representative bright field TEM and AFM images, respectively, of the LPE-produced sample, consisting of irregularly shaped (figure 2(c)) and nm-thick flakes (figure 2(d)). The corresponding electron diffraction pattern of the TEM image is also shown (inset in figure 2(c)), proving that the flakes are crystalline [211]. Statistical analysis (figures 2(e) and (f)) indicate that the lateral size and the thickness of the flakes follow a lognormal distribution, peaked at ~190 nm and ~2 nm, respectively. These data indicate that the sample obtained by LPE of graphite is mostly composed by FLG flakes (experimental SLG thickness measured by AFM is typically between 0.4 and 1 nm [104, 212–214] depending on tip-surface interactions and image feedback settings [213, 214]).

Raman spectroscopy analysis was carried out to evaluate the structural properties of the as-produced materials. A typical Raman spectrum of graphene shows, as fingerprints, G, D and 2D peaks (see Supplementary material for more details) [191, 215–217]. For SLG the 2D band is roughly four times more intense than the G peak [215, 216]. Multi-layer graphene (>5 layers) exhibits a 2D peak, which is almost identical, in term of intensity and lineshape, to the graphite case (intensity of the 2D2 band is twice the 2D1 band) [216–218]. Instead, FLG (<5 layers), has a 2D1 peak more intense than the 2D2 [219]. Taking into account the intensity ratios of the 2D1 and 2D2, it is possible to estimate the flake thickness [145, 174, 191, 192, 219]. Figure 3(a) shows the Raman spectrum of the CVD-graphene transferred onto Si/SiO2. The absence of the defect-related D peak and the ratio between the intensity of 2D and IG peak –I(2D)/I(G)– of ~3 indicate that a high-quality SLG has been obtained [220], in
agreement with previous studies [199]. The analysis of the 2D peak, a single and sharp Lorentzian band centered at ~2683 cm\(^{-1}\), also confirm that the sample is SLG [191, 215, 217]. Figure 3(b) displays a representative Raman spectrum of LPE-produced graphene flakes. The Raman spectrum of the native bulk graphite is also shown for comparison. The LPE-produced flakes exhibit an enhancement of the D and D\(^\prime\) bands compared to those of the pristine graphite, in agreement with previous discussion [191, 215, 217, 221–224]. For graphite, the G peak is more intense of D, while the Raman statistical analysis for LPE-produced graphene flakes (figure S1 (stacks.iop.org/TDM/6/035007/mmedia)) shows that the ratio between the intensities of the D and G peaks –I(D)/I(G)– ranges between 0.35 and 0.75, with an average values of ~0.55 (figure S1(a)). However, the plot of I(D)/I(G) versus FWHM(G) (figure 3(c)) does not show a linear correlation, which means that the defects mainly originate from the flake edges without altering the structure of the basal plane [225, 226]. The analysis of I(2D\(_1\))/I(2D\(_2\)) (figure 3(d)) demonstrates that the LPE-produced sample has a few-layer flakes enriched composition [209, 216, 219].

After the preparation and characterization of the CVD-graphene and LPE-produced graphene flakes, the CEs were fabricated by spraying the LPE-produced graphene flakes dispersion onto the CVD-graphene previously transferred onto the glass substrate, as detailed in section 2.3. The concentration of graphene flakes in the LPE-produced dispersion (~0.36 gl\(^{-1}\)) was estimated by OAS measurements (figure S2) [203], and served to adjust the amount of deposited graphene flakes. Three different batch of graphene-based CE (named as graphene-A, graphene-B, graphene-C) were prepared with graphene flakes mass loading of 0.16, 0.32, 0.48 mg cm\(^{-2}\), respectively. The morphology of the CEs was analyzed by SEM and AFM measurements. Figure 4(a) reports a SEM image of a representative graphene-based CE (graphene-B). The electrode surface is completely covered by a film of graphene flakes. Figure 4(b) shows the AFM images of the surface of the same electrode. The root means square roughness (R_{rms}) of the sample is 42 ± 2 nm and the average roughness (R_{a}) is 15 ± 2 nm. The SSA of the electrode was estimated by BET analysis [204] of physiosorption measurement with Kr at 77 K [205, 207, 208], obtaining a value of ~123 ± 25 m\(^2\) g\(^{-1}\). Figure 4(c) shows the transmittance spectra of the CVD-graphene/FLG flakes dual film CEs, in comparison to those measured for both the CVD-graphene and conventional FTO/Pt CE (see fabrica-
As previously reported, CVD-graphene shows an excellent optical transparency ($T > 97\%$ for visible wavelengths ranging between 400 and 800 nm). After graphene flakes deposition, graphene-A and graphene-B retain $T \approx 25\%$ and $\sim 14\%$, respectively, at 700 nm, while graphene-C exhibit low $T$ ($<5\%$ for all the visible wavelength) due to the high mass loading of the graphene flakes (i.e. $0.48\; \text{mg cm}^{-2}$).

The graphene-based CEs were used to fabricate DSSCs by using commercial $\Gamma^-/I^-$-based electrolyte, and C106 dye (see detail of the DSSCs’ fabrication in the Methods section), which are simply named the corresponding CEs (i.e. graphene-A, graphene-B and graphene-C). Figure 5(a) shows the IV measurements of the devices under 1 SUN and in dark (inset to panel), respectively. Table 1 summarizes the main PV parameters of the fabricated DSSCs (as estimated by the IV curves). DSSCs with CE based on FTO and CVD-graphene are also shown for comparison. DSSCs based on only graphene flakes have been preliminary discarded because of the high $R_{\text{sh}}$ of their films ($>100\; \text{k}\Omega\; \square^{-1}$ for a mass loading of 0.16 mg cm$^{-2}$ and $>10\; \text{k}\Omega\; \square^{-1}$ for both mass loadings of 0.32, 0.48 mg cm$^{-2}$), which resulted in poor PV performances.

Graphene-A exhibits a short circuit current $J_{sc}$ of 5.67 mA cm$^{-2}$, an open circuit voltage $V_{oc}$ of 740 mV, and a fill factor $FF$ of 37.2%, leading to a PCE of 1.62%. By increasing the mass loading of the graphene flakes, the PCE of graphene-B (2.13%) improves by 51% compared to graphene-A. This is mainly attributed to the higher $J_{sc}$ and FF of graphene B (5.97 mA cm$^{-2}$ and 54.9%, respectively) compared to those of graphene-A. However, a further increase of the mass loading of graphene flakes (graphene-C) decreases the PCE to 1.2%. The IV results can be tentatively explained by considering that the catalytic activity depends both by the amount of the catalytic materials and its electrical resistance. In absence of resistive effects, the increase of the mass loading of the catalytic materials enhances the catalytic activity of the CEs for the electrolyte regeneration reaction ($\Gamma^-\text{ reduction}$ in our case), as typically observed for conventional FTO/Pt CE [227, 228]. However, an excessive mass loading of graphene flakes can increase the electrical resistance of the corresponding layer, negatively affecting the catalytic activity of the superficial (i.e. more exposed)
flakes, which interact more effectively with the electrolytes than the inner flakes. The IV curves in dark (inset in figure 5(a)) show that current density at forward bias polarity for graphene-A and graphene-C (maximum current density of 2.1 mA cm$^{-2}$ and 1.7 mA cm$^{-2}$, respectively) is lower than that of graphene-B (maximum current density of 12.0 mA cm$^{-2}$). Differently from the reference cell adopting FTO/Pt CE, the current density for the graphene-based DSSCs does not saturate, which means that the diffusion limiting current density is not reached in the investigated voltage window (where corrosion effects can be excluded) [229], and resistive losses occur.

In order to elucidate the origin of such losses in presence of graphene-based CEs, EIS measurements were carried out on dummy cells consisting of two identical CEs sandwiching the $I^-_3/I^-_3$-based electrolyte used for DSSCs (see detail of dummy cell fabrication in Experimental, section 2.5). EIS is a perturbative techniques, which measures the current response of an electrochemical system when AC voltages are applied with difference frequency, thus computing the electrochemical impedance (Z) [230]. The analysis of Z allows the kinetics of the (photo)electrochemical processes [230], including the electronic and ionic ones occurring in the DSSCs, to be studied [229, 231–233]. In particular, by performing EIS on symmetrical dummy cells it is possible to elucidate both the electrochemical activity and the electrical resistance of CEs in simulated DSSC operating conditions, eliminating the photo-anode contribution [101, 234, 235]. The Z data can be expressed graphically in a Nyquist plot (imaginary part of Z – Im[Z]– versus real part of Z – Re[Z]–), which is typically composed of two semicircles for symmetrical
dummy cells [231, 236]: the first one (at frequency in the kHz–MHz range) is associated to the catalyst/electrolyte interface [231, 236], the second one (at lower frequency, <100 Hz) is connected with ionic diffusion processes occurring in the electrolyte [231, 236]. The intercept with the x-axis of the first semicircle represents the ohmic series resistance ($R_s$) given by both the electrolyte resistance and the resistance of external circuit, including the electrical resistance of the CE's [231, 236–239]. The diameter of the first semicircle is proportional to the electrode-electrolyte charge transfer resistance ($R_{ct}$) [231, 236–239], which is related to catalytic activity of the CE towards the electrolyte redox reactions (low $R_s$ corresponds to a high catalytic activity) [96, 230]. Figure S3 reports the equivalent electrical circuit used to model the symmetrical dummy cells impedance, together with its description, in agreement with previous literature [230, 239]. Figure 5(b) reports the Nyquist plots obtained for the symmetric dummy cells adopting different electrodes, i.e. graphene-B and FTO/Pt. FTO and graphene flakes-covered FTO (FTO/graphene flakes) were also characterized to ascertain the impedance contribution of each layer, i.e. the current collectors (FTO or CVD-graphene) and the catalytic films (Pt or graphene flakes). The FTO-based dummy cell has a low $R_s$ ~ 20 Ω cm$^2$, mainly ascribable to the $R_{sheet}$ of FTO (8 Ω□$^{-1}$), and a high $R_{ct}$ (>10 kΩ cm$^2$), which indicates the absence of catalytic activity [240]. The FTO/graphene flakes-based dummy cell exhibits the same $R_s$ of pristine FTO, while $R_{ct}$ (~650 Ω cm$^2$) decreases by one order of magnitude compared to that of FTO. For graphene-B-based dummy cell, $R_s$ is higher than 500 Ω cm$^2$ due to high $R_{sheet}$ of CVD-graphene (~1.2 kΩ□$^{-1}$), as measured by four-point probe. Interestingly, the $R_{ct}$ of graphene-B-based dummy cell (~250 Ω cm$^2$) decreases by ~62% compared to that of FTO/graphene flakes-based dummy cell. This indicates that the coupling between CVD-graphene and graphene flakes is effective for increasing the overall CE catalytic activity of the same graphene flakes. However, the $R_{ct}$ measured for graphene-B-based dummy cell is still significantly higher than that of FTO/Pt (~<2 Ω cm$^2$), which indicate that graphene-based CEs have an insufficient catalytic activity with $I_-^3/I_+^3$-based electrolyte for practical DSSCs operating under solar illumination, in agreement with previous studies [235, 241].

Figure 6. (a) IV curves of the DSSC based on Y123 dye adopting Co(bpy-pz)$_{2+}/3^+$ (bpy-pz = 6-(1H-pyrazol-1-yl)-2,2'-bipyridine)-based electrolyte and using graphene-based CE (graphene-B) or conventional FTO/Pt CE, at 1 SUN. (b) IV curve of the same DSSCs reported in panel at low intensity illumination (0.1 SUN).
Table 2. Photovoltaic parameters of our DSSCs (data extrapolated by IV curves in figure 6) in comparison to literature data about cells based on Y123 dye and Co(bpy-pz)$_2^{2+/3+}$ (bpy-pz = 6-(1H-pyrazol-1-yl)-2,2'-bipyridine)-based electrolyte. Our DSSCs with all-graphene CEIs were fabricated using CVD-graphene and graphene flakes (graphene-B), as described in the text. PEDOT:PSS stands for poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), GNPs for graphene nanoplatelets, and PProDOT for poly(3,4-propylenedioxythiophene).

| CE                                | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) | Illumination intensity (SUN) | Ref. |
|-----------------------------------|-------------------------|--------------|--------|---------|-------------------------------|------|
| FTO/Pt                            | 13.68                   | 1.010        | 57     | 7.96    | 1                             | This work |
| CVD-graphene/graphene flakes (graphene-B) | 11.23                  | 0.958        | 47     | 5.09    | 1                             | This work |
| FTO/Pt                            | 13.40                   | 0.802        | 63     | 6.90    | 1                             | [243] |
| Ag/PEDOT:PSS                      | 13.40                   | 0.790        | 66     | 7.00    | 1                             | [243] |
| FTO/Pt                            | 12.10                   | 1.047        | 63     | 8.10    | 1                             | [237] |
| FTO/GNPs                          | 12.70                   | 1.030        | 70     | 9.30    | 1                             | [237] |
| FTO/Pt                            | 13.45                   | 1.015        | 69     | 9.52    | 1                             | [242] |
| FTO/PProDOT                       | 13.06                   | 0.998        | 77     | 10.08   | 1                             | [242] |
| FTO/Pt                            | 1.47                    | 0.930        | 66     | 9.00    | 0.1                           | This work |
| CVD-graphene/graphene flakes (graphene-B) | 1.28                   | 0.865        | 62     | 6.87    | 0.1                           | This work |
| FTO/Pt                            | 1.31                    | 0.934        | 77     | 9.93    | 0.1                           | [242] |
| FTO/PProDOT                       | 1.35                    | 0.914        | 81     | 10.56   | 0.1                           | [242] |
| FTO/Pt                            | 1.37                    | 0.984        | 74     | 10.00   | 0.1                           | [237] |
| FTO/GNPs                          | 1.34                    | 0.956        | 76     | 9.70    | 0.1                           | [237] |

In order to exploit CVD-graphene/graphene flakes as CE for efficient DSSC under simulated 1 SUN for outdoor application, we tested them into DSSCs based on Y123 dye and Co(bpy-pz)$_2^{2+/3+}$ (bpy-pz = 6-(1H-pyrazol-1-yl)-2,2'-bipyridine)-based electrolyte. It has been demonstrated that graphene-based materials exhibit a catalytic activity for reducing the redox mediator of polymeric complexes of Co$^{2+}$/Co$^{3+}$ comparable to that of Pt [55, 56, 235, 237, 242].

Figure 6(a) shows the comparison between the IV curves obtained for a Co$^{2+}$/Co$^{3+}$-based DSSC adopting the optimized graphene-B (i.e. the best graphene-based CE in I$_{sc}$/I$^{-}$-based DSSCs) and FTO/Pt. In particular, the PCE of graphene-based DSSC achieved a PCE of 5.09%, which is much higher than the one reached with I$_{sc}$/I$^{-}$-based electrolyte (2.1%). We further extended the study and validation of our graphene-based DSSCs for indoor applications, by testing them under low illumination intensity conditions (< 1 SUN). In this case, the photocurrent densities are lower than those generated under 1 SUN, and consequently the PV performances are less affected by the CE series resistance. Under 0.1 SUN illumination, the graphene-based DSSC reached a PCE of 6.87% (figure 6(b)), i.e. an increase of ~35% in comparison to the PCE measured at 1 SUN. This PCE increase at 0.1 SUN is mainly attributed to a higher FF (up to 0.62), which is instead limited at 1 SUN illumination (up to 0.47) due to the high $R_s$ of the CVD-graphene current collector.

Table 2 summarizes the PV parameters of innovative DSSCs using Y123 dye and Co$^{2+}$/Co$^{3+}$-based electrolytes. At 1 SUN illumination, our graphene-based DSSCs have shown PV parameters approaching those of cells based on Ag/PEDOT:PSS CEs, showing an overall PCE of ~5.1% versus 7% [243]. The main difference here is related to the Ag electrode, which clearly provide lower $R_s$ than CVD-graphene, as demonstrated by the higher FF (66% versus 47%). This effect is further confirmed by the PV performances of the cells that used GNPs or PProDOT catalysts in combination with FTO. In these cases, the low $R_s$ of the TCO contributes in bringing the FF up to 70% and 77%, respectively, leading to PCE beyond 9%. Overall, our graphene-based CEs can be used in high-performance TCO/Pt-free DSSCs, which can compete with state-of-the-art DSSCs made with glass/FTO in combination with various kinds of carbon- and polymer-based catalysts [244]. This indicates the potential of the CVD-graphene/graphene flakes dual-films as CEs in DSSCs, providing a viable alternative to be experimented also in the context of flexible devices.

4. Conclusions

In this work, we demonstrated advanced Pt- and transparent conductive oxide (TCO)-free counter electrodes (CEs) for DSSCs based on dual films of graphene materials. In particular, single-layer graphene, produced by chemical vapor deposition (CVD) using a cold-wall reactor, has been used as current collector, while graphene flakes produced by liquid phase exfoliation (LPE) effectively acted as catalyst for reducing the electrolyte. The graphene-based DSSCs have been tested in configuration using both I$_{sc}$/I$^{-}$- and Co$^{2+}$/Co$^{3+}$-based electrolytes. In the first case, the optimized DSSCs using ruthenium complex dye (C106) reached a power conversion efficiency (PCE) of 2.1% at AM 1.5 G illumination (1 SUN). In the second case, [Co(bpy-pz)$_2^{2+/3+}$ (bpy-pz = 6-(1H-pyrazol-1-yl)-2,2'-bipyridine) was selected as redox couple, and cyclopentadithiophene-bridged donor-acceptor dye (Y123) as organic dye [71]. The graphene-based DSSCs achieved a PCE of...
5.09% at 1 SUN. Noteworthy, the DSSCs have shown even better performance under low illumination intensity condition, reaching a PCE of 6.87% at 0.1 SUN. To the best of our knowledge, these PCE values, compete with record-high values reported for DSSCs using Pt- and TCO-free CEs [237, 242]. In perspective, the replacement of conventional FTO/Pt CE with all-graphene-based CEs is promising for lowering the manufacturing costs of DSSCs, as well as for developing flexible solar cell designs. Our results, coupled with the recent progress on the synthesis of metal-free organic sensitizer [14, 42–45], quantum-dot sensitizer [194, 195], perovskite-based sensitizer [196–198], and natural dyes [14, 45], confirm DSSCs as an important branch within the current PV panorama.

Acknowledgments
This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement no. 696656–GrapheneCore1 and no.785219–GrapheneCore2. The authors also thank IIT Electron Microscopy for the access to carry out TEM and SEM measurements, and Alberto Portone for his help with transmission measurements. A Di Carlo gratefully acknowledges the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Megagrant N°14. Y26.31.0027.

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