Efficient, Flexible, and Ultra-Lightweight Inverted PbS Quantum Dots Solar Cells on All-CVD-Growth of Parylene/Graphene/oCVD PEDOT Substrate with High Power-per-Weight

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Ultra-lightweight and flexible solar cells are desired for many potential applications, such as self-powered aviation, wearable electronics, and the Internet of things. PbS quantum dots (QDs) are good candidates for this purpose due to their low-cost and low-temperature processing. In this work, a thin layer of parylene (1 µm) is deposited on a poly(ethylene teraphthalate) (PET) substrate using chemical vapor deposition (CVD) and is employed as a flexible substrate for PbS QDs solar cell. Here, the commonly used ITO electrode in the QDs photovoltaics (PVs) is replaced by CVD-graphene and its wettability issue is addressed using a thin layer of oxidative CVD poly[3,4-ethylenedioxythiophene] (oCVD PEDOT), which also works as a second hole transporting layer in the device. Inverted PbS QDs device is fabricated on PET/parylene/graphene/oCVD PEDOT stack and finally by removing the PET substrate, an ultra-lightweight PbS QDs solar cell is achieved. Using this architecture, a power conversion efficiency (PCE) of 7.1% and a power-per-weight of 12.3 W g⁻¹ are achieved. Additionally, the QDs device on graphene shows good flexibility as compared to the device on PET/ITO. This work highlights the advantages of oCVD PEDOT and CVD-graphene for the fabrication of flexible and ultralight weight photostatics.

1. Introduction

Colloidal quantum dots (QDs) such as lead sulfide (PbS) are promising semiconductor materials, applicable in photovoltaic (PV) devices thanks to their low-cost and low-temperature solution processing, band gap tunability, and good optical properties.[1–5] Recently, extensive efforts have been devoted to QDs PV technology in terms of synthesis of high-quality QDs, surface passivation, ligand exchanges, and architectural engineering, resulted in a certified power conversion efficiency of 12%.[6–10] Despite other types of thin film technologies such as perovskite and organic semiconductors, QDs materials due to their high crystallinity, do not require any additive or further heat treatment, which is beneficial for flexible PVs.[10,11]

Flexible solar cells with ultra-light weight have attracted tremendous attention recently due to their potential for aircraft, space application, and wearable electronics. Such kinds of applications require highly flexible thin films with superior lightweight.[12] Therefore, thin film materials with strong absorption and low-temperature processing are ideal candidates to be deposited on plastic substrates and more interestingly can be processed by roll-to-roll technique for scale-up. In fact, ultra-light weight solar cells can reduce the transportation and installation costs, resulting in lower energy pay-back time.[13] Among all PV technologies, ultra-thin organic solar cells (OSCs) and perovskite solar cells (PSCs) with good efficiency have been already reported in the literature.[14–19] For instance, Kaltenbrunner et al.[20] reported a flexible PSC with high power-per-weight of 23 W g⁻¹. Besides PSCs and OSCs, PbS QDs PV is also a promising candidate for the fabrication of flexible and lightweight solar cells, due to its tunable and strong absorption up to infrared region, air-stable character and room temperature processing.[21–24] In this regard, Zhang et al.[25] reported a flexible and ultralight weight PbS QDs PV with maximum power-per-weight of 15.2 W g⁻¹ by the fabrication of a conventional device structure, that is, Ag nanowires/aluminum-doped zinc oxide (AZO)/PbS QDs/Au. In fact, most of the reports in the field of PbS QDs PV have been focused on conventional device architecture with zinc oxide (ZnO) as an electron transporting layer (ETL) deposited on indium-doped tin oxide (ITO) glass.[26]
However, developing new device architecture in the QDs PVs is still an open task and could be a solution to further boost the device performance over 12%. There are only two reports in the literature about the inverted design. For instance, Wang et al.\textsuperscript{[27]} demonstrated the inverted architecture for QDs PV by deposition of graded PbS QDs on nickel oxide (NiO) hole transporting layer (HTL) and obtained high efficiency of 9.7%. Lu et al.\textsuperscript{[26]} reported an inverted PbS QDs PV using poly[2,6-(N-(1-pentylhexyl)dithieno [3,2-b:20,30-d]pyrrole)-alt-4,7-(2,1,3-benzothiadiazole)] (PDTPBT) as an HTL and achieved high open circuit voltage ($V_{oc}$) of 0.63 V and thus PCE of 8.45%, due to better band alignment in their devices and lower carrier recombination. Therefore, more efforts using new materials are required in this regard to further improve the performance and flexibility of the PbS QDs PVs.

Monolayer graphene grown by chemical vapor deposition (CVD) is one of the ideal electrodes for the fabrication flexible and ultra-lightweight PV devices due to its great optoelectronic properties, fantastic mechanical property, and ultra-lightweight.\textsuperscript{[28–33]} Basically, deposition of transporting layers on the surface of graphene is challenging due to its hydrophobic nature. Poly(3,4-ethylenedioxythiophene) is the most common conducting polymers (CPs) exploited as the HTL in PV devices. The fabrication of uniform and conformal coating of PEDOT in large-scale production with high throughput roll-to-roll process is of great importance in industrial sectors. To achieve this purpose, oxidative CVD (oCVD) is the promising approaches to expedite the commercialization process of CPs in large-scale applications.\textsuperscript{[34–38]} The formation of uniform spun-cast PEDOT:polystyrene-sulfone (PEDOT:PSS) film onto the graphene surface requires some additional pretreatment and brings an additional cost for the overall process. By contrast, the absence of dewetting effects in the all-dry oCVD process, which derives from the lack of surface tension, provides highly uniform and defect-free PEDOT thin film on graphene.\textsuperscript{[34,39,40]} Both graphene and oCVD PEDOT cannot work properly in a conventional device architecture in terms of efficiency due to their unique band alignment. Consequently, for the fabrication of PbS QDs PVs on graphene and oCVD PEDOT, new architecture such as inverted design is crucial.\textsuperscript{[33]} Since the graphene and oCVD PEDOT films have excellent mechanical properties, they can improve the mechanical properties of the PbS QDs PVs. Therefore, an efficient flexible PbS QDs PV based on graphene and oCVD PEDOT needs to be developed in an inverted PV design.

In this work, we fabricate inverted PbS QDs solar cell on parylene/graphene as a flexible and ultra-lightweight substrate. After transferring the graphene on PET/parylene, we improve the quality of graphene by using toluene as an effective solvent for poly(methyl methacrylate) (PMMA) removal. In order to address the wettability issue in graphene electrode, oCVD PEDOT is deposited on graphene as an HTL with great uniformity. We fabricate inverted PbS QDs on oCVD PEDOT HTL with ultra-lightweight and good flexibility. Finally, we achieve a PbS QDs PV on parylene/graphene with a PCE of 7.1% and a power-per-weight of 12.3 W g$^{-1}$.

2. Results and Discussion

Figure 1 shows the schematics for the fabrication of flexible and lightweight PbS QDs solar cell using parylene and graphene as substrate and bottom electrode, respectively. In this study, we first deposit 1 µm-thick parylene on the PET substrate at room temperature using CVD technique,\textsuperscript{[41,42]} which is lightweight and transparent enough for the fabrication of flexible solar cells (Figure 1a). More details about parylene deposition can be found in Section 4 and literature. Figure S1, Supporting Information, shows the atomic force microscopy (AFM) image of parylene, indicating a smooth layer with an average roughness of 1.2 nm. Afterward, we grow monolayer of graphene with CVD technique on copper foil and transfer

![Figure 1](image-url)
it on PET/parylene substrate using a wet-transfer technique\(^\text{(31)}\) (Figure 1b). To transfer graphene, PMMA was employed as a supporting polymer. In order to improve the quality of transferred graphene and completely remove the residual PMMA from the surface of graphene, we test two different solvents, that is, acetone and toluene. The quality and electrical properties of the graphene cleaned by these solvents are studied by AFM, hall effect measurement and Raman spectroscopy. Figure S2, Supporting Information, depicts the AFM images of the transferred graphene (two layers) after removing the PMMA by acetone and toluene. As seen, the surface of graphene cleaned by acetone has more PMMA residuals with a higher surface roughness of \(7 \pm 2\) nm compared to the one cleaned by toluene (\(4 \pm 1\) nm). This result indicates that toluene is more efficient for removing the PMMA from the graphene surface, improving the quality and electrical properties of the graphene. Figure S3, Supporting Information, shows Raman spectra of the transferred graphene, indicating higher intensity of 2D peak in graphene cleaned by toluene. The electrical properties of the graphene cleaned by both solvents are measured by hall effect method, as shown in Figure S4, Supporting Information. As seen, using both solvents, the carrier density is almost the same since there is not any change in the doping level. However, the average value of sheet resistance is lower in the graphene cleaned by toluene (390 ohm/sq). These results highlight the role of solvent cleaning in the quality of graphene.

To further reduce the sheet resistance of the transferred graphene, we used two layers of graphene with an average sheet resistance of 180 ohm/sq. Then, we transfer graphene on PET/parylene (transparent bottom electrode) and fabricate inverted PbS QDs solar cell using layer-by-layer approach, as explained in Section 4. Basically, deposition of aqueous solutions on the surface of graphene is a big challenge due to its wettability issue and therefore additive engineering or vacuum deposition could help for this issue. Figure S5a, Supporting Information, shows the optical image of PEDOT:PSS, a commonly used HTL for solar cells, deposited on the PET/parylene/graphene substrate via spin-coating. As seen, there are some voids and uncovered areas (indicated by red arrows) in this image, confirming the poor coverage of the PEDOT:PSS layer. To address this issue, we employ vapor phase deposition of PEDOT using CVD approach, as illustrated in Figure 1c. The detailed fabrication process of the PEDOT thin film through versatile CVD deposition technique is reported elsewhere.\(^\text{(37,44,45)}\) Figure S6, Supporting Information, demonstrates the AFM image of the oCVD PEDOT film, indicating a surface roughness of \(\approx 3 \pm 1\) nm. Afterward, PbS QDs are spin-coated on the surface of oCVD PEDOT using a layer-by-layer approach, followed by solid-state ligand exchange. As seen, the active layer is consisted of two layers of 1,2-ethanediolith (EDT)-capped PbS QDs and 12 layers of tetrabutylammonium iodide (TBAI)-capped PbS QDs. We complete the device structure by evaporation of LiF and Al as back contact, as shown in Figure 1d. In order to obtain an ultra-lightweight device, we remove the PET substrate mechanically, as shown in Figure 1e, since there is a weak adhesion between the parylene and PET.

Here, the oCVD PEDOT layer is grown at the deposition temperature of 140 °C using vanadium oxychloride (\(\text{VOCl}_3\)) as a volatile liquid oxidant. The process information including the monomer and oxidant flow rates, saturation ratio (\(P/P_{\text{sat}}\)), where \(P\) and \(P_{\text{sat}}\) are partial pressure and saturation pressure (extracted from Clausius–Clapeyron equation) of reactants, respectively) and deposition rate are presented in Table S1, Supporting Information. The polymerization of conducting polymer (CP) synthesized by the oCVD method occurs in three steps: i) oxidation of monomer to form a cation radical, ii) dimerization of the cation radical, and iii) deprotonation of dimer to form conjugation.\(^\text{(34)}\)

The chemical structure of the oCVD PEDOT film is characterized by attenuated total reflection-Fourier transform infrared (ATR-FTIR). The ATR-FTIR spectroscopy for PEDOT films grown at temperature of 140 °C and oxidant saturation ratio (\(\text{VOCl}_3\), \(P/P_{\text{sat}}\)) of 180 ppm is shown in Figure 2a. The observed FTIR characteristic spectra are in good agreement with the previously reported spectra for the PEDOT film.\(^\text{(38)}\) The characteristic peaks located at 1520 and 1310 cm\(^{-1}\) are assigned to the stretching mode of C=C and C=C bonds in thiophene rings, respectively. The vibrations of the C–O–C bond in the ethyleneoxy group are observed at approximately 1180, 1130, and 1085 cm\(^{-1}\). The vibration at about 1050 cm\(^{-1}\) is ascribed to C–O bond stretching in the ethyleneoxy group. The characteristic peaks at 970, 830, and 690 cm\(^{-1}\) are attributed to C–S bond vibrations in the polymerized PEDOT chains. The characteristic peak at 920 cm\(^{-1}\) is attributed to the deformation mode of ethyleneoxy rings.

The X-ray photoelectron spectroscopy (XPS) analysis (Figure 2b) exhibits the absence of vanadium on the surface of as-grown oCVD PEDOT films at the deposition temperature of 140 °C. The ratio of chlorine/sulfur (Cl/S), which is an indication of Cl-doping level, extracted from XPS elemental analysis is about 0.3 in the film. The Cl-doping in the PEDOT thin film is provided by the vapor phase of \(\text{VOCl}_3\) in the oCVD method. In fact, the amount of doping level affects the optoelectronic characteristics of PEDOT films and can be adjusted by tuning the deposition temperature and oxidant saturation ratio in the oCVD method.\(^\text{(37)}\)

The face-on orientation of as-grown oCVD PEDOT films can be noted from grazing incidence X-ray diffraction (GIXRD) pattern (Figure 2c). The diffraction of (020) plane positioned at \(2\theta = 25.5°\) corresponds to a face-on stacking orientation (0k0). In face-on orientation, as illustrated in the inset of Figure 2c, the conjugated backbone is parallel to the substrate and the \(\pi-\pi\) interchain stacking orientation is perpendicular to the plane of substrate. The b-axis lattice parameter (two times of \(\pi-\pi\) stacking distance) and crystalline size of the PEDOT film (deposited at 140 °C and oxidant saturation ratio of 180 ppm) are approximately 6.97 Å and 3 nm, respectively. Basically, the texture and nanostructural engineering of the PEDOT film control the optoelectronic properties. Therefore, the presence of pure face-on orientation and low b-axis lattice parameter in PEDOT films results in the electrical conductivity enhancement.\(^\text{(37)}\) The pure face-on orientation of PEDOT provides the low energy barrier of intercrystallite charge transport and, as a consequence, yields in high carrier mobility.\(^\text{(37,38)}\) The presence of low b-axis lattice parameter (can be considered as low \(\pi-\pi\) stacking distance) in heavily-doped PEDOT thin films enhances the charge transfer integral among localized sites and induces high carrier mobility and electrical conductivity.\(^\text{(37)}\) As can be noted in Figure 2b, the
as-grown PEDOT film does not exhibit any sign of oxidant by-products. The presence of oxidant by-products in the case of using solid oxidant, such as iron-chloride (FeCl₃), induces carrier mobility scattering and needs a post-deposition acidic rinsing step to enhance the electrical conductivity. The absence of oxidant by-products in PEDOT thin films as a consequence of using highly volatile liquid oxidant (such as VOCl₃) does not need extra and costly post-deposition rinsing step and is more desirable for commercialization. The electrical conductivity of the PEDOT thin film with no post-deposition acid rinsing treatment, as a true one-step all-dry process is in the range of ≈2900 S cm⁻¹.

The ultraviolet-visible-near infrared (UV–vis-NIR) spectra of the PEDOT film (Figure 2d) exhibits a transmittance value of ≈97% at 550 nm. The figure of merit (FOM = σdc/σop; where σdc and σop are DC conductivity and optical conductivity, respectively) are extracted from

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FOM = \frac{\sigma_{dc}}{\sigma_{op}} = \frac{\varepsilon \mu}{\pi R_0 \varepsilon_0} = \frac{\varepsilon \mu}{\pi \varepsilon_0} \left(1 + \frac{Z_0}{2R_{sh}} \right)
\]

where T is the transmittance value at λ = 550 nm, Z₀ = 377 Ω is the impedance of free space, and R_sh is the sheet resistance. The obtained FOM for PEDOT film is approximately 50, which already passes the benchmark indicator of the commercial viability of transparent conductors with the value of 35.

We also investigate the photoluminescence (PL) property of the PbS QDs (EDT-capped) films deposited on glass, oCVD PEDOT and PEDOT:PSS HTLs, as shown in Figure 3a. Figure 3a shows the PL spectra of the corresponding films. As seen, there is a strong PL quenching effect in the QDs film on the oCVD PEDOT layer as compared to the QDs on glass. Additionally, this effect is stronger in oCVD PEDOT/PbS QDs sample as compared to PEDOT:PSS/PbS QDs one. This reveals that the charge carrier can more efficiently transfer from the QDs layer to the oCVD PEDOT and therefore, this layer can work as second HTL in the QDs device. In addition to the steady state PL measurement, we also characterize time-resolved PL (TRPL) spectra of the corresponding samples as shown in Figure 3b. Table S2, Supporting Information, summarizes the fitting parameters of these spectra using biexponential equation. Similar to the PL results, the oCVD PEDOT/PbS QDs sample shows the shortest PL lifetime of 0.73 ns, which is lower than those of PEDOT:PSS/PbS QDs (0.96 ns) and PbS QDs samples (3.3 ns), confirming the quenching effect and thus better charge transfer between the PbS QDs and the oCVD PEDOT film compared with PEDOT:PSS/PbS QDs case.

Figure 3c,d shows the ultra-violet photoelectron spectroscopy (UPS) measurement of the PbS QDs, PEDOT:PSS, and oCVD PEDOT films deposited on ITO glasses. From the UPS results, we estimate the highest occupied molecule orbital (HOMO) level of the PEDOT:PSS and oCVD PEDOT films to be −5.16 eV and −4.95 eV, respectively. The valence band (VB) of the PbS QDs (EDT-capped) is also calculated to be −5.03 eV. Notably,
the optical absorbance of the QDs layer shown in Figure S7, Supporting Information, indicates a bandgap of \( \approx 1.3 \) eV. By considering these values and using the literature\(^{[46,47]} \), we plot the band diagram of the QDs devices using both HTLs, as shown in Figure 3e. From this plot, it is clear that the band offset (80 meV) between the EDT-capped PbS QDs layer and oCVD PEDOT is less than that of PEDOT:PSS/PbS QDs. This can facilitate the hole transfer from the QDs layer to the oCVD PEDOT HTL. In case of PEDOT:PSS, despite the wettability issue, the HOMO level is deeper than the EDT-capped PbS QDs by 130 meV, which is a barrier for the hole transfer. This result indicates suitable band alignment and thus the efficient hole transfer between the oCVD PEDOT film and EDT-capped PbS QDs layer, as verified by the TRPL measurement as well.

In order to investigate the role of oCVD PEDOT on the photovoltaic (PV) properties of PbS QDs solar cells, we fabricate inverted devices on PET /ITO (denoted as reference) and PET /parylene/graphene substrates by deposition of oCVD PEDOT as second HTL. Figure 4a demonstrates the cross-sectional scanning electron microscopy (SEM) image of the device fabricated on the graphene electrode. As seen, the device is consisted of graphene as electrode, oCVD PEDOT and PbS QDs-EDT as HTLs, PbS QDs-TBAI as active layers and LiF/Al as back contact. Figure 4b shows the current-density–voltage \((J–V)\) curves of the PbS QDs PVs fabricated on both parylene/graphene and PET/ITO electrodes. Table 1 summarizes the PV parameters of the corresponding devices. The PET/ITO reference device shows an open circuit voltage \((V_{OC})\) of 0.53 V, a short circuit current density \((J_{SC})\) of 22.5 mA cm\(^{-2}\) and a fill factor (FF) of 57%, resulting in a PCE of 6.8%. While the device on PET/parylene/graphene substrate indicates better \(V_{OC}\) of 0.56 V and higher \(J_{SC}\) of 23.4 mA cm\(^{-2}\) with slightly lower FF of 54%, resulting in a higher PCE of 7.1%. In fact, the device with graphene electrode shows slightly higher PCE, likely due to higher transmittance of the graphene compared with ITO and the better band alignment of graphene with the oCVD PEDOT. As seen in Figure S8, Supporting Information, the transmittance of PET/parylene/graphene substrate is higher than that of PET/ITO one over the entire spectrum. Figure 4c depicts the stabilized PCEs of 6.56% and 6.98% for the reference and PET/parylene/graphene based devices, respectively, under maximum power point condition over 60 s. The statistics of the PV parameters for the corresponding devices are shown in Figure S9, Supporting Information. From these results, the average values of the \(V_{OC}\) and \(J_{SC}\) for the graphene-based PbS QDs devices are 29 mV and 0.8 mA cm\(^{-2}\) higher than those of the reference device, respectively, whereas the average value of FF is 2.4% lower than the reference one. This results in higher efficiency in the graphene-based PbS QDs with an average PCE value of 6.75% as compared to the reference devices (6.32%).

To verify the \(J_{SC}\) of the representative devices, we measure external quantum efficiency (EQE) and estimate the \(J_{SC}\) by

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**Figure 3.** a) Photoluminescence (PL) and b) TRPL spectra of the PbS QDs/glass, PEDOT:PSS/PbS QDs and oCVD PEDOT/PbS QDs samples. UPS measurement of the PbS QDs (EDT-capped), PEDOT:PSS, and oCVD PEDOT samples deposited on ITO glasses, c) the Fermi level and d) the difference between the Fermi level and the HOMO. e) Band diagram of the PbS QDs devices with oCVD PEDOT and PEDOT:PSS HTLs.
integration of the EQE spectra over the solar spectrum (Figure 4d). As shown in Table 1, the integrated $J_{SC}$ for the reference and graphene-based devices are 21.8 and 22.9 mA cm$^{-2}$, respectively, which are in good agreement with the $J$–$V$ results. The higher $J_{SC}$ in the device with graphene is mainly due to its higher transmittance over the visible and infrared ranges as compared to the ITO electrode.[30]

In order to envision the role of electrode on flexibility and mechanical properties of the devices and evaluate their potential applications in the flexible electronics, we perform a bending test for the representative devices. Figure 5a shows the photograph of a bent device with PET/parylene/graphene electrode. In the bending test, we considered a bending radius of 2 mm for both graphene- and ITO-based devices[30] and performed up to 100 cycles for bending test. Figure 5b shows the normalized PCE versus bending cycles. The bending results indicate that the PCE of the reference device with ITO electrode dropped quickly to 21% of its initial PCE value. For the case of graphene electrode, the device maintains 83% of its initial PCE value, highlighting the good mechanical flexibility of graphene in the device as compared to ITO electrode. 

There are several reports in the literature about flexible PbS QDs devices fabricated on different electrodes with good flexibility. From their bending results, their devices retained 75–95% of their initial PCE values after 100 bending cycles.[48–52] Therefore, our device with graphene electrode shows good flexibility as well, which is among the best reported devices in the literature. Notably, the main reason of the PCE loss for the graphene-based QDs device after bending test can be correlated to the poor mechanical properties of the top electrode, that is, LiF/Al. This electrode has lower mechanical properties as compared to graphene and in order to improve the flexibility of such devices, top electrode need to be replaced by other options such as graphene.

We also demonstrate an ultra-lightweight device on parylene/graphene substrates by removing the PET from the device. Figure S10, Supporting Information, shows the photographs of the device before and after removing the PET. Based on parylene/graphene substrate, we achieve a power-per-weight of 12.3 W g$^{-1}$, which is among the best reported value in the literature for PbS QDs PVs.[25]

### 3. Conclusions

In summary, we report ultra-lightweight and flexible inverted PbS QDs solar cell on parylene/graphene substrate. We first improve the conductivity of transferred graphene by effectively

| Device                | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | PCE [%] | $J_{sc}$ from EQE [mA cm$^{-2}$] |
|-----------------------|--------------|--------------------------|--------|---------|-------------------------------|
| ITO/PET               | 0.53         | 22.5                     | 57     | 6.8     | 21.8                          |
| PET/parylene/graphene | 0.56         | 23.4                     | 54     | 7.1     | 22.9                          |
removing the residual PMMA using toluene and obtain smoother graphene surface with lower sheet resistance. To address the wettability issue of graphene and the fabrication of inverted device, the PEDOT film is selected as second HTL and deposited conformally on graphene surface by oCVD technique. PL characterization results reveal that the PbS QDs deposited on the oCVD PEDOT film shows a strong quenching effect and thus an efficient charge transfer at the interface, which further confirms by UPS measurement. By using the oCVD PEDOT film on parylene/graphene, we adjust the band alignment efficiently and obtain an inverted PbS QDs device with PCE of 7.1% and good flexibility as compared to PET/ITO based device (6.8%). Additionally, the QDs device on parylene/graphene substrate shows power-per-weight of 12.3 W g⁻¹, which is among the best reported value in the literature.

4. Experimental Section

Growth of CVD-Graphene: CVD method was used to grow graphene on copper foil (25 µm-thick, Alfa Aesar). The foil was cleaned using acetone and isopropanol and then chemically etched by immersing into a nickel etchant bath (Transene, Nickel Etchant TFB) for 1 min, while sonification, followed by cleaning with deionized (DI) water. Afterward, the copper foil was transferred to a CVD furnace and the growth was performed at 1000 °C by using methane and hydrogen gases as precursors, the details can be found in the authors’ previous publications. The monomer (3,4-ethylenedioxythiophene (EDOT)) and oxidant (vanadium oxytrichloride (VOCl₃)) were purchased from Sigma-Aldrich and placed in a temperature-controlled glass jar. The EDOT and VOCl₃ were vaporized at the temperature of 140 and 30 °C, respectively, and fed simultaneously into the oCVD reactor through a heated line. The temperature of monomer and oxidant delivery lines were kept at 160 and 50 °C, respectively. The flow rates of monomer and oxidant were adjusted by needle-valve and were maintained at the fixed value of at 12 SCCM and 6 SCCM, respectively. The reactor pressure of 1 Torr was controlled through the use of a throttle valve and measured using a baratron capacitance manometer. The PEDOT films were deposited at the growth temperature of 140 °C.

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) was performed on a NICOLET iS50 FT-IR with ATR attachment in order to characterize the oCVD PEDOT films with thickness below 100 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Surface Science Instruments SSX-100. The CasaXPS software was used to extract the atomic percentage (at. %) of elements on the surface of thin film. Grazing incidence X-ray diffraction (GIXRD) was performed using a Rigaku Smart lab diffractometer operated at 45 kV and 200 mA with Cu-Kα radiation of λ = 0.15418 nm. UV-vis-near infrared (UV-vis-NIR) was taken on PEDOT films deposited on microscope glass slides using a Cary 7000 Universal Measurement Spectrometer equipped with an integrating sphere detector.

Device Fabrication: PbS QDs capped with oleic acid were synthesized using a hot injection technique as reported elsewhere in order to deposit the PbS QDs layer, a layer-by-layer deposition technique was employed. After cleaning the PET/ITO/oCVD PEDOT and parylene/graphene/oCVD PEDOT substrates, the PbS QDs was spin-coated from diluted HCl solution (10% vol), the graphene/PMMA was transferred onto the PET/parylene substrate, followed by heating at 70 and 130 °C for 10 and 3 min. In order to remove the PMMA from the graphene surface, acetone and toluene were employed. PET/parylene/graphene/PMMA stacks were immersed into baths of acetone and toluene for 20 min, followed by washing with isopropanol and DI water. To improve the conductivity of the bottom electrode, two layers of graphene were employed. In this regard, first a monolayer of graphene with PMMA support was transferred on an as-grown graphene/copper substrate and then the copper was etched away, followed by transferring the graphene (two-layer) on the target substrates. Then, the PMMA was removed only one time to achieve double-layer graphene electrodes.

oCVD PEDOT Synthesis: The schematic illustration of oCVD reactor adjusted based on using volatile liquid oxidant has been described in previous publications. The monomer (3,4-ethylenedioxythiophene (EDOT)) and oxidant (vanadium oxytrichloride (VOCl₃)) were purchased from Sigma-Aldrich and placed in a temperature-controlled glass jar. The EDOT and VOCl₃ were vaporized at the temperature of 140 and 30 °C, respectively, and fed simultaneously into the oCVD reactor through a heated line. The temperature of monomer and oxidant delivery lines were kept at 160 and 50 °C, respectively. The flow rates of monomer and oxidant were adjusted by needle-valve and were maintained at the fixed value of at 12 SCCM and 6 SCCM, respectively. The reactor pressure of 1 Torr was controlled through the use of a throttle valve and measured using a baratron capacitance manometer. The PEDOT films were deposited at the growth temperature of 140 °C.
a solution of QDs dispersed in octane (50 mg mL$^{-1}$) at 1500 rpm for 30 s. Each layer can make a QDs film with 20–25 nm-thick. After deposition of each layer, the oleic acid ligands were exchanged by short ligands, that is, TBAI and 1,2-EDT. In order to fabricate the inverted architecture of PbS QDs device, the first two layers were exchanged with 1,2-EDT (Sigma-Aldrich) from a diluted solution in acetonitrile (0.01 vol%). The rest of PbS QDs layers (10 layers) were exchanged with TBAI (Sigma-Aldrich) from a solution of TBAI in methanol (10 mg mL$^{-1}$). The ligand exchange was performed by dropping the solution on top of the film with 30 s waiting time, followed by 30 s spin-drying. After ligand exchange, the QDs layer was washed three times with acetonitrile for PbS QDs/EDT and methanol for PbS QDs/TBAI, followed by spin-drying. Notably, all spin-coating steps were performed in ambient condition (40% relative humidity). Finally, the inverted device was completed by thermal evaporation of LiF (0.6 nm) and Al (100 nm) as back contact through a shadow mask at a rate of 1 Å s$^{-1}$.

Film Characterization: Scanning electron microscopy (SEM) images were taken by ZEISS Merlin machine. To measure the optical absorbance and transmittance, Varian Cary 5 machine was used. Band alignment study was performed using AXIS NOVA (Kratos Analytical Ltd, UK) by measuring ultraviolet photoelectron spectroscopy (UPS). In this measurement, the UV source was He I (21.2 eV). The surface of samples was analyzed using atomic force microscopy (AFM, Veeco Digital Instrument Nanoscope III) by using tapping mode. Raman and PL spectra were recorded using a HORIBA Jobin-Yvon HR800 system together with a WITec alpha 300 confocal Raman microscope. The laser used in this measurement and its power were 532.5 nm and 0.1 mW, respectively. A home-made four probe measurement setup was employed to measure Hall parameters and the electrical properties of the graphene samples by using a HP 4156A Precision Semiconductor Parameter Analyzer.

Device Measurement: The J–V curves were measured using a solar sun simulator under AM1.5G standard condition (1000 W m$^{-2}$), which was calibrated with a standard silicon solar cell (Newport). The light source was generated by a xenon lamp (450 W, Oriel, USA).[56,57] The J–V curves were recorded using a digital source meter (Keithley model 2400, USA). The device area in these measurements was 0.04 cm$^2$. For J–V measurement, the scan rate was 10 mV s$^{-1}$ with a dwell time of 15 s. The external quantum efficiency (EQE) was measured by a commercial apparatus (Arkeo-Ariadne, Cici Research s.r.l.).

To evaluate the flexibility test, devices with PET supporting layer were employed and bent. The devices were wrapped around a metal rod with radius of 2 mm and flattened again. This process was repeated 100 times and the PCE of the devices was recorded during the measurement. The light source was provided by a 300 W Xenon lamp. In order to estimate the power-per-weight for the ultra-light weight devices, first the density of substrate was calculated, and then the following equation was used:

$$\text{Power per weight (W g}^{-1}) = \frac{\text{Output power of device (W m}^{-2})}{\text{Device density (g m}^{-2})} \quad (1)$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

flexibility, graphene, oxidative chemical vapor deposition, quantum dots, solar cells, ultra-light weight

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