Graphene Electrodes



Graphene as a Transparent and Conductive Electrode for Organic Optoelectronic Devices

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Graphene is emerging as one of the most useful electrode materials for various organic optoelectronic devices because of its outstanding properties such as high optical transparency, excellent mechanical flexibility, good electrical conductivity, and environmental stability. Numerous synthesis and transfer techniques used to obtain large-area and high-quality graphene materials are demonstrated, aiming at high-performance graphene-based organic optoelectronic devices such as solar cells, light-emitting diodes, and field-effect transistors. The properties, synthesis, and transfer processes of graphene are first introduced. Recent research progress on organic optoelectronic devices with graphene bottom, top, and full electrodes is then reviewed. Finally, graphene composite electrodes integrated with other conductive materials are also summarized. All these advanced works represent important steps in the evolution of graphene electrodes and indicate a bright future for their application in organic optoelectronic devices.

1. Introduction

As a 2D material formed by carbon atoms arranged in hexagonhoneycomb-liked lattice structure, monolayer graphene possesses single-atomic thickness. Since Novoselov et al. firstly separated monolayer graphene from highly oriented pyrolytic graphite (HOPG) in 2004,^[1] plentiful explorations and efforts have been focused on the practical application of graphene materials. Among these applications, both optical transparency and electrical conductivity of graphene make it as an ideal transparent and conductive electrode (TCE) in optoelectronic devices. Commercially, TCEs market is mainly dominated by mature materials like indium tin oxide (ITO). A thin layer of ITO exhibits low sheet resistance of ≈15 Ω sq⁻¹, favorable optical transparency above 90% and satisfied work function (WF) of ≈4.8 eV.^[2]

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However, the drawbacks of ITO related to high cost, acid/temperature sensitivity, and mechanical brittleness should not be ignored. Therefore, alternative TCEs, such as conductive polymer,^[3,4] metal film/grid/nanowire,^[5–8] carbon nanotubes (CNTs),^[9,10] and graphene,^[11,12] have been explored as replacement of ITO. Among these materials, conductive polymer like poly(3,4-ethylenedioxythiophene):poly-(styrene-sulfonate) (PEDOT:PSS) shows promising flexibility, but its intrinsic acidic and hygroscopic properties (damaged to adjacent layers) have limited its applications. Metal films include Au, Ag, Al, and Cu materials normally deposited by thermal evaporation or sputtering exhibit low resistance and acceptable transmittance. In fact, Au and Ag precious metals are costly; other common materials like

Al and Cu are easily oxidized in atmospheric environment. As for metal grid and nanowire, complicated photolithography or spinning process is required. CNT conducting film formed by CNTs network has been realized in commercialization, but its rough surface morphology has hindered its specific applications in thin-film devices. In this way, graphene is regarded as the most promising TCEs due to its balanced and unique properties of outstanding transmittance, low sheet resistance, high carrier mobility, thermal/chemical stability, and flexibility.

Organic optoelectronic devices, mostly including organic solar cells, dye-sensitized solar cells (DSSC), organic lightemitting diodes (OLEDs), and organic field-effect transistors (OFETs), paly the important roles in clean energy generation, future display/lighting, and electronic switch devices.^[13-18] Graphene as TCEs in these organic optoelectronic devices has been widely investigated due to its potential advantages over other electrode materials. Up to now, numerous graphene synthesis methods have been explored. The mature graphene production techniques mainly cover the reduction of graphene oxide (GO), liquid phase exfoliation (LPE), and chemical vapor deposition (CVD).^[19-26] Among these synthesis methods, CVD is considered as the most efficient process to produce large-area, high-quality, and layer-controlled graphene on catalytic metal (Cu, Ni) foils. For device fabrication, graphene grown by CVD usually needs to be transferred from metal foils to other desired substrates. To obtain damage-free and nonpollution transferred graphene, numerous transfer strategies including polymersupported wet transfer,^[27] roll-to-roll,^[28-30] lift-off,^[31,32] and electrochemical delamination^[33,34] have been demonstrated. As a result, organic optoelectronic devices fabricated with CVD



graphene TCEs have shown excellent device performance compared with that of ITO-based devices. Furthermore, flexible devices based on graphene electrodes offer outstanding stability and reliability.

Here, we will firstly introduce the properties of graphene, as well as graphene synthesis and transfer methods, pointing at the recent progress in graphene fabrication and transfer strategies. Different from recent reviews, the progress of graphene materials applied for organic optoelectronic devices is systematically described according to the types of graphene bottom, top, and full electrodes.^[35,36] As the electrode optimization, graphene combined with other conductive materials as composite electrodes are simultaneously exhibited. In addition, the latest researches related to the performance of organic optoelectronic devices with graphene electrodes are summarized. The excellent performance of graphene-based organic devices promotes graphene being prospective in future flexible and foldable electronic and optoelectronic devices.

2. Graphene Properties, Synthesis, and Transfer Methods

2.1. Properties of Graphene

Monolayer graphene possesses a single-atomic thickness of \approx 0.34 nm and the material sizes can be tuned from nanodots to wafer-scale according to different synthesis methods.[37,38] Thanks to the ultrathin thickness of monolayer graphene, its theoretical transmittance reaches to 97.7% in visible wavelength.^[39] In the adjacency of the Fermi energy Dirac point, the charge carriers in graphene possess linear electronic dispersion due to its zero bandgap feature.^[40,41] The carrier mobility in graphene exceeds 2×10^5 cm² V⁻¹ S⁻¹, higher than any other semiconductors ever reported.^[42] Graphene also exhibits excellent mechanical strength and thermal conductivity due to its π -network structure. Corresponding Young's modulus of graphene reaches up to 1 TPa,^[43] and its thermal conductivity is calculated to be around 5×10^3 W mK⁻¹ which thermal conductive ability is better than graphite.^[44] Hexagonal honeycomb graphene structure formed by C=C bonding also provides high thermal/chemical stability and flexibility. Therefore, graphene is also a superexcellent candidate as blocking layer for materials which are hygroscopic and easily oxidized in atmospheric condition.^[45,46]

The sheet resistance of graphene is mainly depended on its internal continuity and crystalline quality. Indeed, the synthesis methods determine the electrical properties of as-fabricated graphene. Reduction of GO is widely used to prepare graphene films due to its solution processing capacity and smooth surface morphology, but its sheet resistance is higher than 3 k Ω sq⁻¹ with the transmittance of around 65%.^[47] Liquid phase exfoliation of graphite is another efficient method to produce pure graphene in solution. However, its high resistance is comparable to reduced GO (RGO) due to the large interlayer contact resistance between graphene sheets.^[48,49] Up to now, CVD is the most reliable method to synthesize high-quality and large-area conductive graphene film. The sheet resistance of pristine CVD monolayer to five layers graphene varies from 560 to







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120 Ω sq⁻¹ while corresponding transmittance only deceases from 97.4% to 85.1%.^[50] However, the electrical conductivity of pristine CVD graphene is still inferior to ITO electrode. Besides, pristine graphene suffers from low WF of ≈4.4 eV, which mismatches with most organic transport layers. Commonly, chemical dopants including small molecules (HNO₃, AuCl₃)^[51,52] and transition metal oxides (MoO₃, WO₃)^[53,54] have been used to modify the electrical qualities of pristine graphene by charge transfer. Recently, Kwon et al. have proposed that nonvolatile polymeric acid (PFSA) as dopants for graphene p-type doping.^[55] PFSA-doped 4LG exhibits low sheet resistance of 91.4 \pm 30.1 Ω sq⁻¹ and high WF of \approx 5.1 eV, extraordinary graphene doping stability under high temperature and chemical conditions are also observed.

Even lately, Cao et al. reported the new electronic ground states in twisted bilayer graphene with their lattices rotated out of alignment.^[56–58] At a very low rotation angles, the misaligned lattices forms a moiré pattern. Additional states in twist graphene are regarded as Mott insulating states. Carriers in these states are motionless due to their mutual repulsion, and strong insulating property of bilayer graphene is observed. Interestingly, charge carriers filling in Mott insulating states process zero electrical resistance below a critical temperature of around 1.7 K, forming a 2D superconductor. This finding is promising for exploration and design of unconventional graphene-based superconductors.

2.2. Synthesis of Graphene

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So far, plentiful methods were employed to prepare graphene materials. To balance high quality and easy fabrication of graphene, including reduction of GO, LPE, and CVD are widely applied. Among them, CVD method has been recognized as the most efficient strategy to prepare high-quality continuous graphene film, which is particularly critical for its application in organic optoelectronic devices. Besides, graphene derived from solid organic materials is arising as an innovative strategy to produce transfer-free and naturally doped graphene. **Table 1** summarizes the electrical and optical characteristics of graphene films obtained by various synthesis methods on different substrates.

2.2.1. Reduction of Graphene Oxide

Electrically insulating GO is usually synthesized by Hummers or modified Hummers methods which refers to that graphite reacts with potassium permanganate (KMnO₄) and concentrated sulfuric acid (H₂SO₄) under proper conditions.^[59-61] Therefore, GO possesses a crowd of oxygen functional groups on its surface and edge.^[62] The large proportion of oxygen content in GO decreases its conductivity by breaking the C sp² structure. Up to now, many reduction methods have been applied to achieve highly conductive and uniform RGO, such as thermal reduction.^[63–66] chemical reduction.^[67–70] photochemical reduction,[71-73] plasma-assisted reduction,[74-76] and electrochemical reduction.^[77-79] Among them, thermal and chemical reduction are currently efficient and convenient approach to produce conductive RGO films. As shown in Figure 1a, the intrinsic purpose of GO reduction is removing the oxygen functional groups and repairing the C sp² structure.^[80] Our group has applied femtosecond (Fs) laser to directly reduce GO into patterned RGO electrodes. Figure 1b,c shows the thickness of RGO film decreases by 15 nm due to the mass loss and rearrangement of atoms in GO. Corresponding X-ray photoelectron spectroscopy (XPS) in Figure 1d,e further demonstrates the removal of C–O and C=O bonds after GO reduction.^[81]

Graphene sheets in solution can achieve large-scale and uniform conducting film by simple spin coating or inkjet printing, thus the thickness of as-prepared graphene film could be tuned by different spin revolutions and solution concentrations. For example, Yin et al. obtained RGO films with the thickness change from 4 to 28 nm by controlling the spincoating conditions.^[47] The sheet resistance decreases from 16 to 0.72 k Ω sg⁻¹ while the transmittance degrades from 88% to 40% at 550 nm, causing twofold light loss. In this way, how to balance the electrical and optical properties of RGO film seems like an urgent problem to be solved. It is considered that poor connection between separated graphene microscale sheets causes poor electrical conductivity of RGO film. In this way, conductive strip-liked materials including metal nanowires (MNWs) and CNTs are combined with RGO as the charge pathway.^[82-87] Aliprandi et al. recently reported that the sheet resistance of hybrid copper nanowire-RGO film reaches to 40 Ω sq⁻¹ with only 10% loss of transmittance, which performance is comparable to ITO.^[88] Besides, this hybrid conducting film shows great potential for severing as TCEs in high-performance flexible organic optoelectronic devices.

2.2.2. Liquid Phase Exfoliation

LPE is a simple and low-cost method to manufacture monolayer and few-layer graphene from bulk graphite. In addition, other 2D materials such as MoS₂, WS₂, and WSe₂ also could be exfoliated from their bulk counterparts by LPE method.^[23,89] Figure 2a exhibits the schematic representation of graphene exfoliated from graphite by LEP method.^[22] Graphene exfoliated from bulk graphite commonly composed of chemical dispersion, ultrasonication and centrifugation processes.[90] N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) are the popular organic solvents used to produce high concentration of monolayer graphene, while graphene always suffers from toxic and residual pollution due to the high boiling points of solvents. Aqueous dispersion of graphene solution is environment-friendly and pure for preparing conducting graphene films. However, the insolubility of graphite limits the degree of LEP. To solve this difficulty, surfactants have been applied to facilitate its solubility and exfoliation.^[91-93] For instance, Lotya et al. have reported that ≈3% monolayer of <5 layers (40%) exfoliated graphene sheets dispersed in water-surfactant solution, and this result is comparable with exfoliation in organic solvents.^[94] Atomic resolution transmission electron microscopy (TEM) and Raman spectra in Figure 2b,c show that as-prepared graphene flakes are free of defects. Graphene sheets absorbed by surfactant could be steadily dispersed into water without any reaggregation due to their Coulomb repulsion.

For electrodes manufacture, spray coating is an efficient technique to prepare thin conducting film from LPE graphene and the film thickness can be easily tuned by controlling its concentration.^[48,95] Blake et al. demonstrated that spray-coated pristine graphene dispersion in DMF possesses high transparency of

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 Table 1. The comparison of sheet resistance and transmittance of various graphene films on different substrates.

Graphene films	Substrate	Sheet resistance [k $\Omega \square^{-1}$]	Transmittance/at wavelength [nm]	Ref.
RGO (thermal)	Quartz	≈0.8	≈82%/550 nm	[19]
N-doped RGO (thermal)	Glass	0.3	80%/550 nm	[20]
RGO (hydrazine)	Soda lime glass	19	72.7%/550 nm	[21]
RGO (thermal)	PET	16-0.72	88–40%/550 nm	[47]
RGO (hydrazine)	Glass/plastic	0.1–1	80%/550 nm	[63]
RGO (HI)	PET	0.84	78%/550 nm	[68]
RGO (Na-NH ₃)	PET	0.35	80%/-	[70]
RGO (plasma-assisted)	PET	47.7	-	[75]
N-doped LPE graphene	SiO ₂ /Si	0.4	98%/-	[48]
LPE graphene	Filter paper	1	-	[90]
ECE graphene	PET	24.2	≈91%/–	[92]
LPE graphene	Fritted glass holder	0.97	≈ 6 2%/632 nm	[94]
LPE graphene	Glass	0.668	80%/550 nm	[95]
LPE graphene	Glass	≈]	≈40%/550 nm	[97]
3L-CVD graphene (UVO)	Fused silica	0.91	>98%/THz	[11]
4L-CVD graphene	Glass	0.35	≈90%/550 nm	[27]
4L-CVD graphene (HNO ₃)	Quartz	≈0.08	≈90%/550 nm	[28]
1L-CVD graphene	PET	0.56	≈97.4%/550 nm	[50]
1L-CVD graphene (AuCl ₃)	Glass	0.5–0.7	93%/550 nm	[51]
ML-CVD graphene (HNO3)	Glass or PET	0.45	>98%/400–1400 nm	[52]
1L-CVD graphene (Cul)	PET	0.539	96.5%/550 nm	[54]
1L-CVD graphene (HNO ₃)	Glass	≈0.4–0.5	≈ 97%/550 nm	[116]
1L-CVD graphene (CYTOP)	PET	≈0.32	-	[117]
ML-CVD graphene	Quartz	≈0.28	≈80%/550 nm	[118]
1L-CVD graphene	EVA/PET	≈5.2	97.5%/550 nm	[119]
1L-CVD graphene (HNO3)	PET	≈0.26	96.8%/550 nm	[121]
Polarized ML-CVD graphene [P (VDF-TrFE)]	Ferroelectric polymer	≈0.07	87%/550 nm	[123]
4L-CVD graphene (SOCl ₂)	Glass	0.03	88.1%/550 nm	[124]
ML-CVD graphene (HNO3)	PET	0.23	72%/550 nm	[125]
3L-CVD graphene	Glass or PET	0.305	92.9%/550 nm	[128]
1L-CVD graphene (HNO ₃)	Glass	≈0.5	≈97%/–	[134]
2L-CVD graphene	PET	≈0.42	≈90%/–	[135]
4L-CVD graphene (HNO ₃)	Glass	0.084	-	[136]
2L-CVD graphene (TiO ₂)	PET	≈0.29	87.3%/550 nm	[137]
1L-CVD graphene (AuCl ₃)	PET	≈0.095	≈90%/500 nm	[138]
1L-CVD graphene (TFSA)	Glass	≈0.11	≈96%/550 nm	[140]
4L-CVD graphene (HNO ₃)	PET	≈0.058	>91%/550 nm	[152]
1L-CVD graphene (AuCl ₃)	Glass or PET	0.16	82%/550 nm	[154]
4L-CVD graphene (HNO ₃)	PET	0.054	90%/550 nm	[155]
1L-CVD graphene (PEDOT/MoO ₃)	PET	<0.2	>95%/-	[156]
4L-CVD graphene (MoO ₃)	Glass	≈0.03	86%/550 nm	[158]
1L-CVD graphene (WO ₃)	SiO ₂ /Si	<0.3	-	[159]
1L-CVD graphene (CsCO ₃)	SiO ₂ /Si	<0.5	-	[160]
1L-CVD graphene	Al ₂ O ₃ /ITO	≈0.465	-	[164]
1L-CVD graphene (MoO ₃)	SU-8/glass	≈444	97.4%/550 nm	[168]
4L-CVD graphene (benzimidazole)	SiO ₂ /glass	≈0.065	-	[169]



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Table 1. Continued.



Graphene films	Substrate	Sheet resistance $[k\Omega \square^{-1}]$	Transmittance/at wavelength [nm]	Ref.
1L-CVD graphene	Plastic	≈0.5	97.6%/-	[173]
8L-CVD graphene	Glass	≈0.12	≈82%/550 nm	[183]
1L-CVD graphene (PEDOT:PSS)	-	≈0.26	≈94%/500 nm	[184]
1L-CVD graphene (HAuCl₄)	Glass	≈0.325	≈92%/550 nm	[186]
8L-CVD graphene (AgNW)	-	≈0.741	≈80%/535 nm	[193]
1L-CVD graphene (TFSA and TETA)	PET	0.185 and 0.22	>85%/>500 nm	[194]
$PMMA \rightarrow graphene$	SiO ₂ /Si	1.2	94.3%/550 nm	[112]
$HAT-CN \rightarrow graphene$	Glass or quartz	0.55	91.2%/-	[113]
Food, insects, waste $ ightarrow$ graphene	Quartz	1.5–3	-	[114]

90% and acceptable sheet resistance of ${\approx}5~k\Omega~sq^{-1.[48]}$ In contrast, Tung et al. have reported that GO nanosheets as surfactant to exfoliate graphite into graphene-GO composite materials and steadily disperse in water.^[95] During the sonication process, GO

shielded graphene from the damage of ultrasonic cavitation thus resulting in high-quality graphene with large lateral size over 5 μ m. The sheet resistance and transmittance at 550 nm of spray-coated graphene thin film are 668 Ω sq⁻¹ and 80%,



Figure 1. a) Schematic of the preparation of surfactant-stabilized reduced graphene oxide. Reproduced with permission.^[80] Copyright 2011, The Royal Society of Chemistry. b) AFM images of the edge of GO films and the height profile along the white line. c) AFM images of the edge of FsLDW-reduced GO films and the height profile along the white line. d,e) C 1s XPS spectra of pristine GO films and FsLDW-reduced GO films, respectively. Reproduced with permission.^[81] Copyright 2014, American Chemical Society.







Figure 2. a) Schematic representation of the liquid-phase exfoliation process of graphite with and without surfactant molecules. Reproduced with permission.^[22] Copyright 2014, The Royal Society of Chemistry. b) High-resolution TEM images of surfactant exfoliated graphene flakes. Intensity analysis along the left white dashed line shows a hexagon width of 2.4 Å, and intensity analysis along the right white dashed line shows a C-C bond length of 1.44 Å. c) Raman spectrum of a graphene film (thickness \approx 300 nm) deposited on an alumina membrane by filtration from an SDBS-based dispersion. Spectra associated with both large flakes (diameter \approx 3–6 μ m, top) and small flakes (diameter \approx 1 μ m, middle) are shown. For comparison, a spectrum collected from the starting graphite powder is included (bottom). Reproduced with permission.^[94] Copyright 2009, American Chemical Society. d) Comparison of the transparent conductive film performance with previous experiment reports which presented optical transmittance at wavelength of 550 nm higher than 80% versus sheet resistance. e) A digital image of transparent conductive electrodes containing few-layer graphene films patterned on glass substrates by spray coating showing decreased trend in both resistance and transparence when increased spaying volume of graphene inks. Reproduced with permission.^[95] Copyright 2016, American Chemical Society.

respectively. By adjusting the concentrations of graphene solution from 0.05 to 1.5 mg mL⁻¹, the sheet resistance and transmittance decrease from 2.15×10^5 to $3.32 \times 10^2 \Omega$ sq⁻¹ and 93%

to 68%, respectively (Figure 2d,e). In addition, vacuum-assisted filtration is also a widely used method to produce nanoscale controlled graphene film by controlling the concentration or



the filtrated volume of graphene dispersion.^[96–98] Better than spray-coating, vacuum-assisted filtration process can effectively remove the surfactant and organic solvents molecules on the filter membrane.

Although graphene produced by LPE possesses the nature of high crystalline structure, the resistance of corresponding film is still quite high. We consider that the large contact resistance between graphene flakes and organic solvents residue are the main reasons. Therefore, fabricating large-size and pure exfoliated graphene sheets are key factors to prepare graphene film with high electrical conductivity.

2.2.3. Chemical Vapor Deposition

The growth of high-quality and large-area graphene on Ni and Cu metal substrates by CVD method were firstly reported in 2008 and 2009, respectively.^[99,100] **Figure 3**a schematically shows the CVD system, carbon precursors like methane decompose on catalytic metal substrates at around 1000 °C in hydrogen and argon sealed atmosphere.^[101] There are two totally different growth mechanisms of graphene synthesized on Ni and Cu catalytic metal substrates. As shown in Figure 3b, Ni or Ni/Cu alloy possess a high solubility of carbon, ¹²C and ¹³C will firstly dissolve



Figure 3. a) Illustration of graphene synthesis by CVD. Reproduced with permission.^[101] Copyright 2015, Elsevier Ltd. b,c) Schematic diagrams of the possible distribution of C isotopes in graphene films based on different growth mechanisms for sequential input of C isotopes. b) Graphene with randomly mixed isotopes such as might occur from surface segregation and/or precipitation. c) Graphene with separated isotopes such as might occur by surface adsorption. Reproduced with permission.^[102] Copyright 2009, American Chemical Society.



and mix into the metal bulk up to the solubility limit. During the cooling process of Ni foil, most of the dissolved carbon separates out to its surface and forms graphene, which thickness is related to the cooling rate and carbon concentration in metals. In this way, graphene film grown on Ni foils is difficult to yield uniform monolayer graphene. On the other hand, carbon atoms are extremely difficult to diffuse into the internal Cu bulk. Graphene synthesized on Cu foils is dominated by the "surface-adsorption" mechanism (Figure 3c), and ¹³C appears in the center of graphene domain spatially separated with ¹²C due to the successive injection of carbon isotopes.^[102] Due to the "self-limited" process of graphene grown on Cu foils, it will lose catalytic ability to decompose methane once the surface of Cu is fully covered by graphene. Therefore, Cu is an excellent candidate for producing large-area, high-quality, and homogeneous monolayer graphene.^[24,103,104]

Graphene grown by CVD exhibits a polycrystalline quality due to the numerous active sites on Cu substrate; the high density grain boundaries of microscale graphene domains degrade its electrical and mechanical properties. Ruoff's group has introduced controllable oxygen on Cu surface to control the amount of nucleation sites, and produced centimeter-sized graphene single crystals.^[105] As shown in Figure 4a, Lin et al. also developed a second passivation route to rapidly grow large single-crystalline graphene.^[106] During the interval between the nucleation (low carbon supply) and growth (high carbon supply) stages, inserted oxygen furnish ensures overproduced active carbon attaching to the growth frontier of the original graphene nucleation instead of forming new nucleation sites. This method obtains a high graphene synthesis rate of $\approx 100 \ \mu m \ min^{-1}$, corresponding monolayer graphene exhibits large crystalline domain varied from ≈1 to 4 mm (Figure 4b,c). Recently, Vlassiouk et al. produced foot long monolayer single-crystal-like graphene on polycrystalline metal foils at a high growth rate of 2.5 cm h^{-1} .^[107] As shown in Figure 4d, a local feed of carbon precursor on translational substrate is used to achieve evolutionary selection. This method could self-select the fastest graphene growth domain orientation, which ultimately eliminates the slower growth domains and results in single-crystal-like homogeneous graphene film (Figure 4e). As-prepared 1-foot-long single crystal in Figure 4f shows highly oriented nature with the direction of growth about 20°, Raman intensity ratio maps in Figure 4e indicate the monolayer nature and low defect concentration of synthetic single crystal graphene. Actually, this evolutionary selection growth method is also suitable for producing other 2D materials such as boron nitride (BN) and transition metal disulfide compounds (MoS₂, WSe₂, WS₂).

At present, CVD growth of large-area and high-quality graphene is a relatively mature technique. Both the fundamental understanding and process development of the method have made remarkable progress in the past few decades. However, further works are still needed to improve the growth rate and quality of graphene, satisfied to the demands for high performance optoelectronic devices.

2.2.4. Graphene Grown from Solid Organic Materials

Many works have proved that high-quality and continuous graphene film synthesized from solid carbon sources, such





Figure 4. a) Schematic illustration of strategy for rapid growth of large-single-crystalline graphene (LSCG). Specifically, oxygen was introduced to initiate second passivation after the nucleation step for the suppression of new nucleation. The improvement of the CSS in the second growth step promises a rapid growth of LSCG. b) Photographs of graphene grains with domain sizes of around 1 and 4 mm, respectively. c) Graphene growth rate statistics with varying domain size obtained by using multistage CSS (red) or constant CSS (black). Inset: Photograph image of wafer-sized graphene films transferred onto 4 in. SiO₂/Si substrate. Reproduced with permission.^[106] Copyright 2016, Wiley-VCH. d) An illustration of the set-up for ALC CVD used for graphene growth. e) Single-crystal growth is achieved upon realization of the conditions for "evolutionary selection." f) Longitudinal and transverse maps of 1-footlong single-crystal graphene, showing its highly oriented nature with a growth direction at about 20° with respect to ZZ. g) Raman intensity ratio maps (1.5 mm steps) for single-crystal graphene transferred onto a quartz wafer. Reproduced with permission.^[107] Copyright 2018, Nature Publishing Group.

as evaporated small organic molecules or spin-coated polymers.^[108-111] Sun et al. reported high-quality and thicknesscontrolled graphene grown from poly(methyl methacrylate) (PMMA) film with underneath Cu catalyst (Figure 5a).^[112] During the growth process, hydrogen plays dual roles of both reductant and carrier gas for C atoms decomposed from PMMA. Unlike traditional CVD growth method always terminated with monolayer graphene on Cu foils, PMMA-converted graphene could result in multilayer nature with lower hydrogen flows. TEM image exhibits the edge of PMMA-derived graphene and selected area electron diffraction (SAED) pattern has demonstrated its well crystalline nature (Figure 5b). N-doped graphene can be prepared by simply mixed PMMA with melamine $(C_3N_6H_6)$ as the precursor, and n-doped graphene exhibits defect-related D and D' peaks in Raman spectra due to the heteroatoms break the graphene symmetry (Figure 5c). N-doped graphene field-effect transistors (FETs) also possess the n-type behavior (Figure 5d). Besides, Zhuo et al. directly fabricated graphene on dielectric substrates by annealed dissolution of an overlying stack of polycyclic aromatic hydrocarbons (PAHs) with e-beam evaporated Cu layer (Figure 5e), further transfer process is needless.^[113] The main growth mechanism of graphene derived from PAHs is dehydrogen and surface-mediated

nucleation process rather than the decomposition of PMMA polymer, thus graphene synthesized from PAHs requires temperature as low as 600 °C. Patterned graphene can be obtained by using shadow mask during the deposition process of Cu or PAHs layers. Due to the nitrogen dopant element contained in PAHs, n-type doped graphene could be achieved simply. The transmittance and sheet resistance of graphene directly synthesized on glass substrate is 550 Ω sq⁻¹ and 91.2%, respectively.

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Sustainable solid carbon sources, even food, insects, and waste also have been applied to grown graphene.^[114] *Melaleuca alternifolia* extracted from tea tree plants as the carbon source to synthesize homogeneous graphene film without any catalyst of metal has been presented by Jacob et al. (Figure 5f).^[115] Compared with PMMA and PAHs, *Melaleuca alternifolia* is a natural and renewable precursor to produce high-quality graphene. The scanning electron microscope (SEM) image in Figure 5g exhibits 3D rough graphene surface due to the strains induced by fast growth process. In this way, as-grown graphene materials attained a hydrophobic contact angle of 135°, exhibiting a great application prospect for very high hydrophobic coatings. Graphene derived from solid organic material is an innovative and promising strategy which provides a controllable transferfree and doped graphene synthesis route. Also, multifunctional







Figure 5. a) Monolayer graphene is derived from solid PMMA films on Cu substrates by heating in an H₂/Ar atmosphere at 800 °C or higher (up to 1000 °C). b) HRTEM images of PMMA-derived graphene films. c) Raman spectra of pristine and n-doped PMMA-derived graphene. d) Room temperature $I_{DS}-V_G$ curves ($V_{DS} = 500$ mV) showing n-type behavior obtained from three different n-doped graphene-based back-gated FET devices. Reproduced with permission.^[112] Copyright 2010, Nature Publishing Group. e) Schematic of the direct synthesis of patterned graphene on SiO₂ without transfer. Reproduced with permission.^[113] Copyright 2014, American Chemical Society. f) Schematic of graphene grown from *Melaleuca alternifolia*, showing potential application in very high hydrophobic coatings. g) SEM images of samples fabricated on 1 × 1 cm² silicon substrates. Reproduced with permission.^[115] Copyright 2015, American Chemical Society.

graphene can be fabricated by applying various solid carbon sources and adjusting the growth conditions.

The features of different graphene synthesis methods are compared in **Table 2**, both the advantages and disadvantages are exhibited. We consider this comprehensive comparison as a guidance of the following graphene synthesis techniques, aiming at more balanced route for graphene production which is satisfied with future industrial fabrication.

2.3. Transfer of CVD-Grown Graphene

Unlike graphene synthesized by reduction of GO or LPE method in solutions, the application of CVD-grown graphene

on metal foils demands an essential step for transfer of asgrown graphene onto transparent substrates, such as glass, quartz, and poly(ethylene terephthalate) (PET).^[27–36] PMMA is a widely used polymer supporting layer for graphene wet transfer process due to its prominent features of wetting resistance, flexibility, low viscosity and dissolubility in several organic solvents. As shown in **Figure 6**a, PMMA-supported wet transfer process can be divided as following steps: i) PMMA is deposited on the top of graphene/Cu substrate, then the other side graphene is destroyed by plasma treatment; ii) Cu foil is removed by etchant, leaving PMMA/graphene membrane floating on the solution surface; iii) PMMA layer is removed by hot organic solvents. In general, PMMA polymer ADVANCED SCIENCE NEWS _____

Table 2.	Comparison	of different	graphene	synthesis	methods.
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Synthesis methods	Advantages	Disadvantages
Reduction of GO	Low-cost; mass-production	High defect density; nonenvironmental friendly reduction processes
Liquid phase exfoliation	Highly crystalline; low defects; solution-processed	Low production rate; small lateral size; organic solvent pollution
Chemical vapor deposition	High-quality; large-area; layer-controlled	Relatively high temperature (≈1000 °C); complicated transfer processes
Anneal of solid organic materials	Transfer-free; intrinsically doped	High defect density; relatively high temperature

is difficult to be fully removed from graphene surface due to its large adsorption energy and relatively low solubility. Here, we applied a subsequent thermal anneal process to further



remove PMMA residue, after that, HNO₃ was applied as p-type dopant to improve the electrical conductivity and wettability of graphene.^[116] A smooth and uniform surface morphology of annealed graphene is observed in atomic force microscope (AFM) images (Figure 6b,c). Innovatively, Lee et al. used fluoropolymer (CYTOP) for simultaneously transferring and doping of CVD-grown graphene onto the desired substrates (Figure 6d).^[117] The blue shifts of G and 2D bands as well as decrease of I_{2D}/I_G in Raman spectra (Figure 6f) confirms that residual CYTOP plays p-type dopant for as-transferred graphene, and the average sheet resistance of doped graphene is only \approx 320 Ω sq⁻¹ (Figure 6g).

Earlier works have demonstrated that Raman spectra applied to monitor the doping of graphene.^[23,25] For both electron and hole doping, the G position of graphene Raman spectra increases to higher wave number. Besides, the G peak full width at half maximum and intensity ratio of I_{2D}/I_G simultaneously decreased. While the position of 2D peak shows a different response to holes (increase) and electrons (decrease),



Figure 6. a) Schematic of the wet transfer process for PMMA-supported graphene. An additional thermal annealing process is applied to further clean the graphene surface in a CVD furnace, and annealed graphene is doped by HNO₃ on a spin coater. b,c) AFM image comparison of as-transferred graphene and 500 °C annealed graphene. Reproduced with permission.^[116] Copyright 2016, Elsevier B.V. d) Chemical structure of CYTOP. e) Schematic of the graphene-transfer process with a CYTOP supporting layer. f) Photographs of the graphene film on a PET substrate transferred with a CYTOP supporting layer. g) Raman spectra of the graphene films transferred onto SiO₂/Si substrates with PMMA (black) or CYTOP (red) as the supporting layer. h) Sheet resistances of graphene films transferred using PMMA or CYTOP. Reproduced with permission.^[117] Copyright 2012, American Chemical Society.

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Figure 7. a) Synthesis, etching, and transfer processes for large-scale and patterned graphene films. b–d) Graphene films on a PDMS substrates are transparent and flexible. The PDMS stamp makes conformal contact with a silicon dioxide substrate. Reproduced with permission.^[118] Copyright 2009, Nature Publishing Group. e) Roll-to-roll "green" transfer process of graphene and illustration of the roll-to-roll delamination of copper and graphene onto an EVA/PET substrate. Reproduced with permission.^[119] Copyright 2015, Wiley-VCH. Electrochemical exfoliation of graphene from Cu foil. f) Schematic diagram of the electrochemical cell used for the electrochemical exfoliation. g) Optical images showing the "whole film" peeling of PMMA-covered graphene from the copper foil. h) Graphene film was transferred onto a 4 in. wafer by a wetting transfer process. i) Electrochemical exfoliation times are controlled by the cathode voltage and the electrolyte concentration. Reproduced with permission.^[120] Copyright 2011, American Chemical Society.

making Raman spectroscopy as ideal strategy to analyze the doping type and doping level of graphene.

Polydimethylsiloxane (PDMS) possesses a low surface free energy, thus the substance on PDMS prefers to adhere to the target substrate rather than the PDMS. Kim et al. reported a dry-transfer process for CVD grown graphene on Ni film using PDMS stamp (**Figure 7**a).^[118] When graphene on PDMS is brought onto SiO₂/Si substrate after Ni film is completely etched away, graphene released from PDMS and attached to SiO₂/Si due to its relatively higher surface free energy. By using prepatterned Ni film, various sizes and shapes of graphene can be transferred to arbitrary substrates (Figure 7b–d). Roll-to-roll is a time-effective and low-cost production strategy for large-area

and damage-free graphene transfer, and 30 in. graphene transferred by this method was firstly reported in 2010.^[28] For further exploration, Chandrashekar et al. demonstrated a green roll-to-roll transfer method for large-area graphene and flexible ethylene vinyl acetate/poly(ethylene terephthalate) (EVA/PET) composite film serves as target substrate.^[119] As the schematic illustration described in Figure 7e, the stacked Cu/graphene/ EVA/PET films can be mechanically delaminated into graphene/EVA/PET films and Cu foil in hot water. This green transfer process is metal etchant-free, eco-friendly and without polymer residue. Additionally, the mechanically delaminated Cu foil could be reused for latter graphene growth, which shows excellent economic efficiency and cyclic utilization.

Wang et al. firstly proposed electrochemical delamination of CVD-grown graphene for recycling the Cu foils.^[120] PMMA was precoated onto Cu/graphene as protecting layer before the electrochemical delamination process. As shown in Figure 7f, electrochemical reaction generates hydrogen bubbles at graphene/Cu interface, and the hydrogen bubbles offer temperate and indispensable force to separate the graphene on Cu foil (Figure 7g). Graphene delaminated from Cu foils is transferred onto target substrate and subsequently removing PMMA in organic solvent. Electrochemically delaminated 4 in. graphene film on SiO₂/Si substrate is homogeneous over 95% of its surface and exhibits excellent electrical conductivity (Figure 7h). Generally, the efficiency of the electrochemical exfoliation could be adjusted by the concentration of electrolyte as well as cathode voltage (Figure 7i). Besides, the electrochemical delamination method can also realize the transfer process of graphene grown on noble metal substrates (such as Au and Pt), while graphene on these substrates cannot be transferred by traditional wet transfer process due to the chemical stability of noble metal in normal etchant. However, the hydrogen bubbles on graphene surface could cause serious mechanical damage especially during its transfer process. To solve this problem, Cherian et al. demonstrated a bubble-free electrochemical delamination of CVD graphene films.^[35] A thin layer copper oxide was inserted between graphene and Cu foils by air-oxidized treatment, and copper oxide would be etched away during electrochemical delamination process because of its relative low potential (-0.8 V) compared to that electrolysis of water (-1.5 V). The crack area of graphene transferred by bubble-free method is only $0.32 \pm 0.2\%$, much lower than the sample transferred with hydrogen bubbles (6.9 \pm 5.7%). It is obvious that the bubblefree electrochemical delamination is more efficient to reduce defects of graphene transferred onto desired substrates.

The transfer of graphene is of great significance for its application as clean and high-quality electrical conductive electrodes. There are still many challenges to transfer graphene films: i) Ensuring the integrity of transferred graphene without forming cracks and wrinkles during the transferred process; ii) Obtaining graphene with clean surface and avoiding the surface residual contaminants; iii) Simplifying the transfer process to make it low-cost and time-effective. We are firmly convinced that reliable, large-scale synthesis and transfer of industrial scale graphene is becoming mature in the near future.

3. Graphene as TCEs for Organic Optoelectronic Devices

As already mentioned, graphene is an ideal candidate to replace commercially available ITO as TCEs for optoelectronic devices due to its excellent conductivity, ultrahigh transmittance, low cost, and mechanical stability. Here, we focus on the latest advances of graphene as TCEs applied for organic optoelectronic devices including organic solar cells, dye-sensitized solar cells, organic light-emitting diodes, and organic field effect transistors, illustrating the advantages and drawbacks of graphene TCEs as well as stressing the highlighted researches. The performance of various organic optoelectronic devices with graphene electrodes are summarized in **Tables 3–5**.



3.1. Graphene as TCEs

3.1.1. Graphene Bottom TCEs

Organic Solar Cells: Organic solar cells (OSCs) are emerging as low-cost green energy-converted devices which can be simply fabricated via solution process on cheap substrates. Until now, numerous groups have attempted to use graphene as TCEs in OSCs.^[121-124] Thermal reduction of GO with a thickness of 16 nm as bottom electrode in OSC with device structure of RGO/PEDOT:PSS/P3HT:PCBM/TiO₂/Al only shows a power conversion efficiency (PCE) of 0.78%.[47] The relatively low efficiency of the graphene-based device is mainly blamed for the low transmittance and electrical conductivity of RGO film (3.2 k Ω sq⁻¹ and 65% at 550 nm). Usually, there are several approaches to enhance the PCEs of OSCs based on graphene TCEs. One is to enhance the intrinsic transparency and conductivity of graphene electrodes, and the other is to introduce modified layer for graphene. In addition, the active layer itself and device structures also play the key roles for highly efficient OSCs.

To this end, Arco et al. firstly applied CVD grown graphene as transparent conductive anodes in flexible OSCs with a configuration of TCEs/PEDOT:PSS/CuPc/C₆₀/BCP/Al (Figure 8a).^[125] Graphene grown on Ni film then transferred onto PET substrate possesses low sheet resistance of 230 Ω sg⁻¹ and high transmittance of 72%, and the sheet resistance is much lower than RGO films with similar transmittance. The best PCE of OSCs incorporated with CVD graphene anodes is 1.18%, which is nearly same as the performance of commonly used ITO electrodes (1.27%). Furthermore, flexible OSCs based on graphene TCEs exhibit stable solar cell performance under the bending angle of 138°, while device with ITO shows poor performance and completely failed after being bent to only 60° (Figure 8b-d). Optical images in Figure 8e prove that ITO forms cracks perpendicular to the bending direction due to its brittleness nature while no such cracks are observed on CVD graphene film. Inverted OSCs with a bottom cathode provide longer device lifetime due to the moisture-sensitive electron injection layer can be kept beneath the other organic layers and top electrode.^[126,127] Recently, Jung et al. reported annealing-free and solution processed zinc oxide nanoparticles (ZnO-NP) as an n-type dopant for graphene cathode used in inverted OSCs (Figure 8f,g).^[128] As shown in Figure 8h, graphene is effectively doped by ZnO-NP and corresponding WF of pristine graphene decreased from 4.27 to ≈4.0 eV. The n-doped effect of graphene can be further confirmed by Raman spectra in Figure 8i, the upshifted G band of ZnO-NP on graphene film reveals an electron doping effect. The decreased WF of n-doped graphene would lower the energy barriers for carriers transport from active layer to graphene electrode. J-V characteristics in Figure 8j show notable PCE of 8.16% and 7.14% of graphene based devices on rigid and flexible substrates, respectively. After 100 bending cycles under a radius of 3 mm, graphene based flexible OSCs still maintain 80% of its initial PCE. While the PCE of ITObased device decreases to 30% only after 20 bending cycles (Figure 8k). All of the aforementioned researches have exhibited the superior mechanical performance of graphene as TCEs over ITO electrode.



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Table 3. Previous works on organic, perovskite and dye-sensitized solar cells with graphene electrodes.

Devices	Material	Electrode	Substrate	Device structure	PCE [%]	Ref.
Organic solar cells (OSCs)	CVD Gra	Bottom anode	quartz	4L-graphene/MoO ₃ + PEDOT:	2.5	[28]
				PSS/P3HT:PCBM/LiF/Al		
	RGO	Bottom anode	PET	RGO/PEDOT:PSS/P3HT:PCBM/TiO ₂ /Al	0.78	[47]
	CVD Gra	Bottom anode	glass	ML-graphene/PEDOT:PSS/P3HT:PCBM/Ca/Al	2.6	[52]
	CVD Gra	Bottom anode	glass	1L-graphene/v-WO ₃ /PEDOT:PSS/PTB7:	5.3	[53]
			0	PC ₇₁ BM/TiO _x /Al		. ,
	CVD Gra	Bottom anode	PET	1L-graphene/MoO _x /CuI/ZnPc/C60/BCP/Al	0.84	[54]
	CVD Gra	Bottom anode	glass	1L-graphene/PEDOT:PSS/MoO ₃ /	2.43	[116]
			-	SubPc/C60/BCP/Ca/Ag		
	CVD Gra	Bottom anode	PET	3L-graphene/GraHEL/PCDTBT:PC70BM/LiF/Al	4.33	[121]
	CVD Gra	Bottom anode	PVDF	5L-graphene/PEDOT:PSS/P3HT:PCBM/Ca/Al	2.07	[123]
	CVD Gra	Bottom cathode	glass	4L-graphene/ZnO/PEIE/PffBT4T-2OD:	3.13	[124]
			0	PC ₇₀ BM/V ₂ O ₅ /Ag		
	CVD Gra	Bottom anode	PET	CVD graphene/PEDOT/CuPc/C60/BCP/Al	1.18	[125]
	CVD Gra	Bottom cathode	glass	1L-graphene/ZnO/PTB7:PC71BM/MoO2/Ag	7.51	[126]
	CVD Gra	Bottom cathode	glass	1L-graphene/ZnO-NPs/PTB7-Th:PC71BM/MoO2/Ag	8.16	[128]
	CVD Gra	Top anode	عدام	ITO/7nO/P3HT·PCBM/CO/101-graphene	25	[187]
			giass		2.5	[107]
	CVD Gra	Top anode	glass	ITO/ZnO/P3HT:PCBM/PEDOT:PSS/1L-graphene	1.98	[190]
	CVD Gra	lop anode	PI	Ag/ZnO/P3H1:PCBM/PEDO1:PSS/1L-graphene	3.2	[191]
	CVD Gra	Full electrodes	glass	graphene/PEDOT:PSS/PTB7:PCBM/ZnO/PEDOT:PSS/	3.35	[196]
		F	DET	graphene		[] 0.01
	CVD Gra	Full electrodes	PEI	IL-graphene/PEDOI:PSS/P3H1:	3.3	[198]
		F H L .		PCBM/ZnO/IL-graphene		(3.0.0)
	CVD Gra	Full electrodes	glass	IL-graphene/PEDOI:PSS/ZnO/PDTP:	4.1	[199]
				PCBM/MoO ₃ /2L-graphene		
Perovskite solar cells (PSCS)	CVD Gra	Bottom anode	glass	1L-graphene/MoO ₃ + PEDOT:	17.1	[134]
				PSS/perovskite/C60/BCP/LiF/Al		
	CVD Gra	Bottom anode	PET	1L-graphene/MoO ₃ + PEDOT:	11.48	[135]
				PSS/perovskite/C60/BCP/LiF/A		
	CVD Gra	Bottom cathode	PET	1L-graphene/TiO ₂ /PCBM/perovskite/	11.9	[137]
				Spiro-OMeTAD/CSCNTs		1
	CVD Gra	Bottom anode	PFN	11-graphene/MoO ₂ + PEDOT	16.8	[] 39]
				PSS/perovskite/C60/BCP/LiE/Al		[]
		Bottom anode	ماعدد	11 graphene/DEDOT:DSS/perovskite/DCBM/Al	18.0	[] 40]
	CVD Gra	Top anode	glass	FTO/TiO. /perovskite/Spiro-OMeTAD/	12 37	[1 9 9]
		top anoue	giass	PEDOT:PSS/11-graphene	12.57	[100]
		<u> </u>			5 70	
Dye – sensitized solar cells (DSSCs)	Gra sheets	Counter	glass	FIO/IiO ₂ /N-/I9/2946/graphene	5.73	[143]
. ,	N-GF	Counter	glass	FTO/TiO ₂ /dye/N-GF	7.07	[144]
	RGO	Anode	quartz	RGO/TiO ₂ /dye/Spiro-OMeTAD/Au	0.26	[145]
	Gra sheets	Counter	_	FTO/TiO ₂ /dye/FGS ₁₃	4.99	[146]
	Gra sheets	Counter	-	FTO/TiO ₂ /dye/NSG	6.19	[147]

Hybrid organometal halide perovskites possess the properties of high carrier mobility, long carrier diffusion length, and intense light absorption coefficient.^[129-132] In this way, perovskite solar cells (PSCs) are appearing as the most promising photovoltaics with the highest reported PCE of 22.1%.^[133] In order to realize PSCs with both high efficiency and excellent mechanical flexibility, graphene has been applied in PSCs as efficient and robust transparent flexible electrodes.[134-138] Yoon et al. reported flexible PSCs based on graphene TCEs obtained a best PCE of 16.8% without any hysteresis, the device structure is shown in Figure 9a.[139] A thin layer of MoO₃ is thermally evaporated on graphene for p-type doping. Besides, the MoO₃ layer on hydrophobic graphene surface makes it better wettability to PEDOT:PSS solution, thus forming a smooth and homogeneous interface between PEDOT:PSS and graphene. The graphene-based PSCs exhibit superb stability and maintain 85% of its initial PCE after 5000 bending cycles (Figure 9b,c). For efficiently stable doping of graphene, bis(trifluoromethanesulfonyl)-amide (TFSA) is used as dopant to achieve high conductivity and modified WF of graphene electrodes.^[140] When the doping concentrations of TFSA is 30×10^{-3} M, the sheet resistance of pristine graphene decreases from \approx 650 to \approx 108 Ω cm⁻² and WF elevates from ≈4.52 to ≈4.92 eV. Due to the proper band alignment between PEDOT:PSS and TFSA-doped graphene (Figure 9e), hole carriers generated in perovskite layer are easily transporting to graphene electrode for collection. Flexible PSCs based on TFSA-doped graphene possess the high PCE of 18.3%. Unencapsulated PSC with TFSA-doped graphene TCE maintains ≈95% of its original efficiency under a persistent 1 Sun light illumination for 1000 h, which stability is better than that of AuCl₃-doped graphene (Figure 9g,h).





Table 4. Previous works on organic light-emitting diodes with graphene electrodes.

Devices	Material	Electrode	Substrate	Device structure	Luminance [cd m ⁻²]	Current efficiency [cd A ⁻¹]	Ref.
Organic light-emitting diodes (OLEDs)	Gra sheets	Bottom anode	Glass	Graphene/PEDOT:PSS/NPD/Alq3/LiF/Al	300 @ 11.7 V	-	[19]
	RGO	Bottom cathode	Glass	Graphene/ZnO/Cs2CO3/F8BT/MoO3/Au	19 020 @ 27 V	7 @ 24.2 V	[20]
	CVD Gra	Bottom anode	PET	3L-graphene/GO/MoO ₃ /TAPC/ emission layers/Bphen/Li/Al	1000 @ 5.5 V	89.7 (max)	[50]
	CVD Gra	Bottom anode	Glass	4L-graphene/GraHIL/TAPC/ emission layers/TPBi/Li/Al	≈6200 @ 7 mA cm ⁻²	≈91.9 (max)	[152]
	CVD Gra	Bottom anode	Glass	TiO2/graphene/GraHIL/OS1/LiF/Al	≈500 @ 5 V	≈168.4 (max)	[153]
	CVD Gra	Bottom anode	Glass	3L-Graphene/PEDOT:PSS/HAT-CN/TAPC/ emission layer/BmPyPB/Li/Al	≈10 000 @ 8 V	56.42 (max)	[154]
	CVD Gra	Bottom anode	Glass	4L-Graphene/GraHIL/NPB/ emission layers/Bebq ₂ /BaF ₂ /Al	≈100 @ 4 V	16.3 (max)	[155]
	CVD Gra	Bottom anode	Plastic	1L-Graphene/PEDOT:PSS/MoO ₃ / MoO ₃ :CBP/CBP/emission layers/ TPBi/LiF/Al	>10 000 @ 5V	>250	[156]
	CVD Gra	Bottom anode	Glass	1L-Graphene/MoO ₃ /MoO ₃ :CBP/CBP/ emission layers/TPBi/LiF/Al	>2000 @ 6 V	55 @ 1000 cd m ⁻²	[157]
	CVD Gra	Bottom anode	Glass	1L-Graphene/WO3/MoO3:CBP/CBP/ emission layers/TPBi/Liq/Al	≈2000 @ 6 V	64 @ 1000 cd m ⁻²	[158]
	CVD Gra	Bottom anode	Glass	1L-Graphene/WO ₃ /WO ₃ :CBP/CBP/ emission layers/TPBi/Liq/Al	≈1000 @ 4V	-	[159]
	CVD Gra	Bottom cathode	Glass	1L-Graphene/Bphen:Cs2CO3/TPBi/ CBP:Ir(ppy)/CBP/MoO3/Al	3000 @ 6 V	≈40 (max)	[160]
	CVD Gra	Bottom anode	PET	Graphene/GO/MoO₃/TAPC/emission layer/ Bphen/LiF/Al	-	82 (max)	[162]
	CVD Gra	Bottom cathode	Glass	1L-Graphene/Sm/Bphen:Cs ₂ CO ₃ / Alq3:C545T/NPB/MoO ₃ /Al	≈3000 @ 6 V	7.9 (max)	[163]
	CVD Gra	Bottom anode	SU-8/NOA63	2L-Graphene/MoO ₃ /PEDOT:PSS/ MoO ₃ /NPB/Mcp:Ir(ppy) ₃ /TPBi/ Ca/Ag	≈5000 @ 25 mA cm ^{-2}	31.4 (max)	[168]
	CVD Gra	Bottom anode	SiO ₂ /glass	Graphene/HAT-CN/TAPC/emission layer/ BmPyPB/LiF/Al	≈1000 @ 5 V	-	[169]
	CVD Gra	Top anode	Glass	ITO/TRE:Li/TRE/Ir(ppy) ₂ (m-bppy): PGH02/TcTa/TAPC/HAT-CN/ ML-graphene	≈20 000 (max)	_	[193]
	CVD Gra	Top cathode	Glass	ITO/HAT-CN/VB-FNPD/ PVK:Firpic:OXD-7/PFN/graphene	1034 (max)	3.1 (max)	[194]

 Table 5. Previous works on organic field-effect transistors with graphene electrodes.

Devices	Material	Electrode	Substrate	Device structure	Mobility [cm ² V ⁻¹ S ⁻¹]	On/off ratio	Ref.
Organic field-effect transistors (OFETs)	Gra sheets	Source/drain	Si/SiO ₂	Graphene/N2200/graphene	≈0.01	$3 imes 10^3$	[172]
	CVD Gra	Source	Si/SiNx	Si/SiNx/graphene/P3HT/Au	_	>103	[173]
	CVD Gra	Source	Doped Si/SiO ₂	Si/SiO ₂ /graphene/pentacene/Au	-	>103	[174]
	CVD Gra	Source/drain	PAR	PEDOT:PSS/PVP: PMF/Pentacene/graphene	0.12	>107	[180]
	RGO	Source/drain	Doped Si/SiO ₂	Si/SiO ₂ /MPS-SAMs/Pentacene/RGO:PVA	0.23	-	[179]
	CVD Gra	Source/drain	Doped Si/SiO ₂	Si/SiO ₂ /PTCDI-C13/graphene	0.11 ± 0.05	-	[175]
	CVD Gra	Source/drain	Doped Si/SiO ₂	Si/SiO ₂ /Pentacene/graphene	1.2	>108	[176]

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Figure 8. a) Schematic representation of the energy-level alignment (top) and construction of a heterojunction organic solar cell fabricated with graphene as the anodic electrode: CVD graphene/PEDOT/CuPc/C₆₀/BCP/Al. b,c) *J*–V characteristics of CVD graphene and ITO photovoltaic cells with different bending angles. Insets show the experimental setup. d) Fill-factor dependence on the bending angle for CVD graphene and ITO devices. e) Photographs of CVD graphene (top) and ITO (bottom) films on PET before and after being bent. Reproduced with permission.^[125] Copyright 2010, American Chemical Society. f,g) Schematic of an inverted-structure graphene-based OSC and the corresponding energy level diagram. h,i) Cut-off regions of the UPS and Raman spectra from pristine graphene, graphene/ZnO-NP-AF, and graphene/ZnO-NP-A. j) *J*–V characteristics of ITO- and graphene-based PTB7-Th:PC₇₁BM OSCs on glass and PET substrates. k) Normalized PCE of PET/graphene and PET/ITO devices with bending cycles at a bending radius of 3 mm. Reproduced with permission.^[128] Copyright 2018, American Chemical Society.

Many groups have reported graphene as blocking layer for water/air sensitive hybrid perovskites passivation by utilizing its chemical stability and protection from moisture and oxygen.^[46,142] By inserting a monolayer CVD grown graphene between Au electrode and spiro-OMeTAD in PSCs, corresponding device maintains 94% of its initial PCE after storing in 45% humidity condition for 96 h.^[46] Graphene blocking layer also hinders Au atoms diffusing into perovskite layer under thermally annealing, PSCs without graphene layer maintain only 57% PCE after annealing at 80 °C for 12 h due to the Au doping into perovskite layer. Besides, Hadadian et al. mixed perovskite material with n-doped RGO (N-RGO) to optimize the device performance of PSCs.^[141] N-RGO slows down the crystallization rate of perovskite film thus enlarges its grain size, which is attributed to the higher fill factor and short circuit current. Graphene sheets also exhibits passivated effect to the surface of perovskite, and the recombination of electron and hole pairs is effectively suppressed thus leading to an enhanced open-circuit voltage. The PSCs with N-RGO modified perovskite layer possess a PCE of 18.7% without obvious hysteresis, higher than 17.3% of the reference device.







Figure 9. a) Device structure of graphene-based flexible perovskite solar cell (inset image: Photograph of a complete device). b) Normalized PCEs as a function of bending cycles at a fixed bending radius of 4 mm for the Gr-Mo/PEN and ITO/PEN devices c) Normalized PCEs of the Gr-Mo/PEN and ITO/PEN devices measured after 1000 bending cycles with various bending radii: flat, 6, 4, and 2 mm. Reproduced with permission.^[139] Copyright 2017, The Royal Society of Chemistry. d–f) Schematic of device structure, energy band diagram, and SEM cross-sectional image of TFSA-doped graphene TCE-based perovskite solar cells composed of glass/PEDOT:PSS/perovskite/PCBM/Al. g,h) Photostability of unencapsulated TFSA-doped graphene TCE-based perovskite solar cells and AuCl₃-doped graphene TCE-based solar cells at 30% relative humidity and 60 °C under continuous one-sun (xenon lamp) illumination. Reproduced with permission.^[140] Copyright 2018, The Royal Society of Chemistry.

Dye-Sensitized Solar Cells: DSSCs are another type of photovoltaic devices which have been widely investigated because of its capability for high energy conversion efficiency and low-cost production.^[143,144] The DSSCs usually consist of dve sensitized mesoscopic TiO₂ photo-anodes, Pt counter electrodes, and liquid electrolyte with I3-/I- redox couples. The electron carriers are firstly injected from the dye excited state into the conduction band of TiO₂, then the electron goes through an external circuit and arrives at the counter electrode.^[17] Thermally reduced GO film shows an electrical conductivity of 550 S cm⁻¹ and transmittance above 70% over 1000-3000 nm, DSSC based on RGO transparent anode (as replacement for fluorine-doped tin oxide (FTO)) only shows a efficiency of 0.26%.^[145] As a comparison, the solar cell based on FTO gives an efficiency of 0.84%. RGO electrode has a WF of 4.42 eV, which is closed to the 4.4 eV of FTO (Figure 10a,b). Therefore, the low transmittance of RGO electrode and high series resistance of device might be responsible to the lower efficiency of graphene-based DSSCs. Beyond that, graphene has been applied as catalytic counter electrodes in DSSCs to replace traditional Pt electrode. Roy-Mayhew et al. applied functionalized graphene as catalytic counter electrodes in DSSCs, showing an efficiency of 5.0%.[146] To obtain better conversion efficiency of graphene-based DSSCs, a simple hydrothermal method was applied to synthesize highly efficient nitrogen and sulfur co-doped graphene (NSG) (Figure 10c).^[147] The NSG material shows homogeneous distribution of nitrogen and sulfur atoms over the graphene nanosheets (Figure 10e). DSSCs based on NSG counter electrodes exhibit high conversion

efficiency of 7.42%, which is closed to that of Pt electrode (7.56%) (Figure 10d). It is considered that the charge polarization induced by structural distortion and difference in electronegativity makes NSG electrode possessing high catalytic activity.

Apart from pure graphene, graphene composite counter electrodes integrated with carbon nanotube and conductive polymer in DSSCs also exhibit promising performance compared to that of Pt electrode.^[148–150] For example, Chen et al. applied n-doped graphene decorated with PEDOT as counter electrode to fabricate high performance DSSCs. N-doped graphene microscale flakes built the matrix of composite electrode to provide high conductivity and porous PEDOT attached to graphene enlarges the active area of composite film. Besides, PEDOT provides strong adhesion between the counter electrode and substrate. In this way, graphene and PEDOT composite electrode possesses an increased electrical conductivity and electrocatalytic ability. The transparent DSSCs with n-doped graphene and PEDOT composite electrode show PCEs of 8.3% and 6.1% as the sun light illuminated from front and back sides, respectively. Corresponding PCEs are higher than the referenced DSSCs with Pt counter electrode (8.17% and 5.76%). All these aforementioned results indicate that graphene-based materials possess great potential to take the place of expensive Pt as lowcost catalytic counter electrode in DSSCs.

Organic Light-Emitting Diodes: OLEDs are devices which convert electrical energy into light, and exhibit great potential for lighting area and display electronics with high contrast ratio, low power consumption, and flexibility. As an essential







Figure 10. a) Illustration of a dye-sensitized solar cell using graphene film as electrode. The four layers from bottom to top are Au, dye-sensitized heterojunction, compact TiO_2 , and graphene film. b) The energy level diagram of a graphene/ TiO_2 /dye/spiro-OMeTAD/Au device. Reproduced with permission.^[145] Copyright 2008, American Chemical Society. c) Schematic illustration of the synthesis of N and S dual-doped graphene (NSG) nanosheets from GO and thiourea using a simple hydrothermal method. d) Photocurrent–voltage curves of DSSCs with different counter electrodes under one-sun illumination. e) Elemental mapping of NSG nanosheets. Reproduced with permission.^[147] Copyright 2014, the Royal Society of Chemistry.

component of OLEDs, low-cost, flexible, and chemically stable TCEs are crucial for production of next-generation OLEDsbased flexible display devices. Similar to the solar cells based on graphene electrodes, graphene also offers an excellent choice as flexible and efficient TCEs in OLEDs.^[50,55,151-154] For the first time, Han et al. demonstrated extremely efficient flexible OLEDs with modified graphene electrode, which current efficiency is superior to that of ITO reference.^[155] Here, the authors applied polymeric conducting polymers (PEDOT:PSS+PFI) with tunable WF as hole injection layer to facilitate hole carriers injecting from graphene electrode into the adjacent layers (Figure 11a,b). Four-layer graphene doped by HNO₃, with a sheet resistance of 54 Ω sq⁻¹ at high transmittance of 90%, is comparable to the properties of ITO electrode. The white OLEDs based on graphene anode exhibit a much higher current efficiency of 16.3 cd A^{-1} compared to 10.9 cd A^{-1} of ITO anode (Figure 11c). Flexible white OLED lighting device with graphene anode further proved its promising prospect in future flexible and efficient OLEDs (Figure 11d). Soon after, Li et al. also demonstrated efficient OLEDs based on p-doped monolayer graphene anode.^[156] The p-doped graphene is obtained by dipping monolayer graphene in triethyloxonium hexachloroantimonate (OA)/dichloroethene solution (Figure 11e). Compared with

un-doped graphene, the WF of OA-doped graphene elevates from 4.7 to 5.1 eV and sheet resistance decreases from ≈1 to $<200 \Omega \text{ sg}^{-1}$ (Figure 11f). In order to further enhance the WF of graphene, a thin layer transition metal oxide is uniformly deposited on the surface of PEDOT:PSS modified graphene electrode. The pure hole device with graphene/PEDOT:PSS/MoO₃ composite anode exhibits an extremely low turn-on voltage due to the matched WF of MoO₃ (≈6.7 eV) with the HOMO level of CBP layer (6.1 eV), suggesting a more efficient hole carriers injection from graphene anode to adjacent organic layers. By introducing the light-coupling structures on transparent substrate, the external quantum efficiency of phosphorescent white OLEDs with modified graphene anode exceeds 45% under the luminance of 10^4 cd m⁻². Corresponding devices also exhibit high power efficiency of 80 lm W^{-1} at 3×10^3 cd m⁻², which is closed to the most efficient white OLEDs ever reported.

Other transition metal oxides as dopants for graphene electrode in OLEDs are also widely investigated by Meyer and his group.^[157–159] Similar to MoO₃, the electronic structures of WO₃ and V₂O₅ usually result in large WF exceeding 6 eV. The electrons in graphene are strongly attracted by transition metal oxides and resulting in charge transfer doping for graphene electrode.^[158] Innovatively, Meyer et al. applied patterned







Figure 11. a) Schematic illustration of the hole-injection process from a graphene anode to a conventional HTL (NPB) used in OLEDs. b) Schematic illustration of the hole-injection process from a graphene anode via a self-organized HIL with work-function gradient (GraHIL) to the NPB layer. c) Device structure and current efficiency as a function of voltage for flexible white OLED devices with graphene (doped with HNO₃) and ITO anodes. d) Flexible OLED lighting device with a graphene anode on a 5×5 cm PET substrate. Reproduced with permission.^[155] Copyright 2012, Nature Publishing Group. e) Charge-transfer complex formation process between graphene and OA. f) An energy level diagram for the SLG anode/ PEDOT:PSS/MOO₃/CBP structure. Reproduced with permission.^[156] Copyright 2013, Nature Publishing Group.

WO₃ as both p-type dopant and masking layer for graphene electrode.^[159] WO₃ on graphene surface causes the alignment of Fermi level due to the charge transfer process, and the sheet resistance of monolayer graphene doped by 5 nm WO3 decreased to around 300 Ω sq⁻¹. Phosphorescent green OLEDs with 5 nm WO₃ on patterned monolayer graphene electrode exhibits a power efficiency of 50 lm W^{-1} at 10³ cd m⁻². Apart from transition metal oxides as p-type dopants for graphene, alkali metal compound like Cs2CO3 has been demonstrated as efficient n-type dopant.^[160] It is considered that a small amount oxygen or water vapor would cause oxidation to alone Cs₂CO₃ layer, therefore, 10 vol% Cs₂CO₃ is co-evaporated with Bphen matrix for higher doping stability. The WF of Cs₂CO₃:Bphen co-doped graphene shifts from ≈4.6 to ≈3.6 eV. OLEDs with inverted device structure show a low on-set voltage of \approx 3 V, and the maximum current efficiency (40 cd A^{-1}) is superior to that of ITO electrode (37 cd A⁻¹).

Large-area, uniform and efficient flexible OLED based on graphene electrode is difficult to be achieved because of graphene rough morphology induced by polymer residue during the transfer process. Previous reported lighting areas of graphene-based OLEDs are usually less than 1 cm².^[161–163] Lately, Zhang et al. reported large-area flexible OLEDs with ultraclean and damage-free graphene anode successfully achieved by a rosin-enabled transfer process.^[50] As one of natural organic small molecules, rosin (C₁₉H₂₉COOH) has super solubility in organic solvent, adequate mechanical strength and week interactive force with graphene, which enables clean and damage-free graphene transfer compared to conventional PMMA (**Figure 12a**–f). The current efficiency of OLEDs with rosintransferred graphene anode reaches to 89.7 cd A⁻¹, higher

than that of PMMA-transferred graphene and ITO electrodes (Figure 12g,h). Even better, a 4 in. monolithic flexible green OLED with a lighting area of 8×7 cm² based on a rosin-transferred four layer graphene is achieved (Figure 12i). The turn-on voltage of the whole large-area and flexible OLEDs is around 5 V, showing uniform luminescence over the 4 in. lighting area. This highlighted work has demonstrated that clean, damage-free, and large-area transferred graphene as TCEs for OLEDs-based commercial lighting sources and displays.

It is an essential and imperative demand for microscalepatterned graphene as electrodes in OLEDs-based highresolution displays, as well as integrated field-effect transistor array,^[164] electric circuits,^[165] and printed electronics.^[166,167] Our group has used Fs laser reduced GO as patterned electrode to fabricated microscale OLEDs (Figure 13a).^[81] Fs laser direct writing is a mask-free technique to reduce GO into graphene with arbitrary patterns. GO reduced by Fs laser possesses high resolution and good conductivity; corresponding devices show excellent characteristics of uniform electroluminescence and well-defined patterns. Recently, we demonstrated a simple transfer-patterned method by utilizing positive photoresist of S1805G as both supporting layer and plasma etching mask layer to obtain transferred and microscale-patterned graphene films.^[168] Transfer-patterned graphene films exhibit clean surface morphology and high graphic accuracy, ≈ 2 in. large-area patterned bilayer graphene can be fabricated by this transferpatterned strategy (Figure 13b). OLEDs based on 5 nm MoO3 doped bilayer graphene electrode exhibit the maximum current efficiency of 33 and 31.4 cd A⁻¹ for rigid and flexible substrates, respectively. Furthermore, 100, 50, and 25 µm line width of OLEDs arrays with microscale-patterned graphene electrodes

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Figure 12. a) HMMA and d) rosin molecules on graphene with the most stable adsorption configuration. 3D AFM images of b) HMMA- and e) rosintransferred graphene films. High-resolution C1s XPS spectra of graphene on SiO₂/Si transferred with c) HMMA and f) rosin. g) Device structure (left) and energy level diagram (right). h) Current efficiency versus luminance characteristics of OLEDs with rosin-transferred 3-layer graphene, PMMAtransferred 3-layer graphene and ITO films as anodes. i) A 4 in. monolithic flexible green OLED with a rosin-transferred five-layer graphene anode, showing uniform luminance and excellent flexibility. Reproduced with permission.^[50] Copyright 2017, Nature Publishing Group.

are achieved. The lighting areas of microscale OLEDs arrays possess the excellent characteristics of high contrast, bright and uniform electroluminescence (Figure 13c). Our work has demonstrated the great potential of transfer-patterned microscale graphene as electrode for high resolution panel displays. Shin et al. also reported OLEDs-based static display with prepatterned graphene bottom electrodes (Figure 13d).^[169] Patterned graphene film is fabricated by traditional photolithography process, and bottom graphene electrodes are separated with electrical contact pads by a passivation layer to prevent the electrical shorts. OLEDs module with two color emission (red and orange) are encapsulated by glass and derived by a control board. The fine operation shown in Figure 13e demonstrates its promising application for displays at the commercial level. This work actually proves the practical application level of graphenebased displays.

Organic Field-Effect Transistors: OFETs are indispensable elements for plastic optoelectronic devices such as flexible displays based on OLEDs. The performance of OFETs is governed by two significant factors: one is intrinsic property of organic materials, while the other one is the interface contact of source/drain (S/D) electrodes with organic semiconductor as well as their WF difference. In this way, OFETs with gold S/D electrodes are widely fabricated due to its favorable WF.^[170,171] As an ideal replacement for metal film, graphene has been demonstrated as excellent S/D electrodes in OFETs.^[172-174] Towards high-performance graphene-based OFETs, Park et al. controlled the WF of graphene by functionalizing the substrate with electron-donating NH2-terminated self-assembled monolayers (SAMs).^[175] The WF of SAMs-doped graphene decreases from 4.5 to 3.9 eV, therefore, electron injection is facilitated due to the low injection barriers between graphene electrode and organic semiconductor (Figure 14a,b). OFETs based on modified graphene exhibit an improved field-effect mobility of $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, much higher than that of graphene on bare SiO_2 (0.01 cm² V⁻¹ S⁻¹). Apart from the tunable WF of D/S electrodes, the interface contact between graphene and organic semiconductor is also crucial for efficient OFETs. Lee et al. reported that the molecular assembly orientation of pentacene grown on graphene is affected by surface polymer residues.^[176] Pentacene tends to be lying-down structure on clean graphene due to the π - π interaction between graphene film and pentacene. While polymer residues on graphene result in stand-up orientation growth of pentacene. The morphological difference of pentacene deposited on clean graphene and channel region would cause high resistance at the interface of graphene and pentacene. As a result, OFETs based on polymer residual monolayer graphene exhibit an average field-effect mobility of 1.2 cm² V⁻¹ S⁻¹, while the devices with thermally treated clean graphene electrodes are only 0.4 cm² V⁻¹ S⁻¹.







Figure 13. a) Illustration of the preparation procedure of FsLDW, involving reducing and patterning the GO films, and optical microscopy images of operating micro-OLEDs based on the patterned RGO electrodes. Reproduced with permission.^[81] Copyright 2014, American Chemical Society. b) Photograph of a ≈ 2 in. bilayer graphene pattern fabricated by the simple transfer-patterned method. c) Optical microscopy images of OLEDs based on microscale-patterned monolayer graphene anodes with 100, 50, and 25 µm lighting line width. Reproduced with permission.^[168] Copyright 2018, Wiley-VCH. d) Graphene-pixel electrode OLED with addressing metal line. e) Addressable two-color OLED module with pixelated graphene films as transparent electrodes. Reproduced with permission.^[169] Copyright 2018, IOP Publishing Ltd.

In order to improve the driving current and stability of OFETs, Liu et al. demonstrated high performance OFETs with a vertical device structure (Figure 14c).^[173] Without any lithography processes, the vertical design achieves ultrashort channel lengths of 100-200 nm by controlling the thickness of spincoated organic thin films. The vertical current density passed through heterojunction formed between monolayer graphene and organic thin film is greater than 3.4 A cm⁻², on/off ratio exceeds 10³ (Figure 14d). Besides, the organic thin film is sandwiched between D/S electrodes due to this vertical architecture, n-type vertical OFETs maintains good switching behavior after storing in air for 1 week (Figure 14e). The doping of graphene source electrode could effectively tailor the carrier injection at heterojunction and improve the performance of vertical OFETs. However, normal graphene topside doping strategy induces deterioration of its surface morphology, which further causes poor crystalline structures of the overlying organic semiconductors. According to this challenge, Kim et al. reported high performance vertical OFETs with underside-doped graphene source electrode (Figure 14f).^[174] The Dirac voltage of graphene doped by underside PEI and TFSA shifts to -24 and +108 V corresponding to strong n-type and p-type doping, respectively

(Figure 14g). Furthermore, pentacene deposited on undersidedoped graphene exhibits regular crystalline structures compared to that grown on topside-doped graphene surfaces (Figure 14h). The p-type and n-type vertical OFETs with underside-doped graphene electrodes obtained a high current density and on/off current ratio exceeding 10 mA cm⁻² and 10³.

Due to the remarkable application of transparent OFETs as pixel driving units of future transparent active matrix displays and up-to-date optoelectronic devices, flexible and transparent graphene electrode has been widely applied.^[177,178] Cho's group reported inkjet-printed RGO and CVD-grown graphene as electrodes for flexible transparent OFETs, which are compatible with plastic substrates.^[179,180] Corresponding devices exhibit high carrier mobility and on/off ratio, OFETs with high flexibility and transparency are compatible with next-generation electronic devices. Besides serving as the S/D electrodes, graphene flakes mixed with organic materials are also applied to improve the performance of OFETs.^[181–183]

On the other hand, graphene is also qualified as the blocking layers for air-stable OFETs because of its abilities to prevent oxygen and water.^[184–186] Kim et al. developed a water-free method to transfer graphene from Cu foils onto flexible

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Figure 14. a) Chemical structure of *N*,*N*'-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide (PTCDI-C13) and schematic FET structure using PTCDI-13 as active layer and graphene as source/drain (S/D) electrodes. b) Schematic band diagrams of PTCDI-C13 and graphene on different SAMs. Reproduced with permission.^[175] Copyright 2011, American Chemical Society. c) Schematic of the cross-sectional view of the device, with the graphene and top gold thin film functioning as the source and drain electrodes. The P3HT layer is the vertically stacked semiconducting channel with its thickness defining the channel length. d) graphene-P3HT-Au p-type OVTFTs at various gate voltages from -30 to +30 V (15 V steps). The transfer curve is semi-log-plotted in the insets with various bias voltages where $V_{ds} = -1$ V (blue), -2 V (red), and -4 V (black). e) Air stability of the OVTFTs.^[173] Copyright 2015, American Chemical Society. f) Cross-sectional structure of VFETs fabricated with graphene–organic semiconductor heterostructures prepared using underside-doped graphene source electrodes. g) Transfer characteristics of graphene transistors prepared using pristine graphene and underside-doped graphene using PEI and TFSA dopants. h) Atomic force microscopy images of pentacene films deposited onto the topside-doped and underside-doped graphene surfaces.^[174] Copyright 2016, Wiley-VCH.

OFET substrates by using PMMA and polybutadiene (PBU) supporting layers.^[184] The PMMA/PBU bilayer provides sufficient support during graphene transfer process and protects graphene from the damage caused by the pattern technique of reactive ion etching (RIE). Besides, OFETs covered by PMMA/PBU/graphene can effectively resist the ambient impurities, and the device maintains stable operation in a highly humid condition (a relative humidity of 80%) for 5 h. Recently, Hsieh et al. have used solution-processed graphene flakes integrated with organic polythiophene polymer active channel to increase the transistor mobility.^[186] Simultaneously, graphene covered on OFETs acts as air and moisture barrier films to extend its effective work time up to 1700 h, while OFETs without graphene passivation layer cannot switch after only 800 h.

3.1.2. Graphene Top TCEs

Since there are various methods for transferring large-area graphene onto the top of desired substrates, graphene has also been developed as the transparent conductive top electrodes for organic optoelectronic devices, especially for the semitransparent devices. As a promising replacement of metal top electrodes, graphene has unique nature of ultrahigh transparency, excellent flexibility, and air stability with impermeability to gas and liquid.^[187-189] For the first time, Lee et al. reported semitransparent OSCs with top laminated graphene anode.[187] The graphene top anode is transferred by a simultaneous thermally annealing/releasing method, and thermal release tape is applied as the supporting mediator. The resulting semitransparent OSC with ten layers graphene top electrode exhibits a PCE of 2.5% lower than 3.3% of standard nontransparent device with Ag top electrodes. For highly transparent and conductive top electrodes, monolayer is suitable for its excellent transmittance compared with multilayer graphene films. Yan and his group have demonstrated semitransparent OSCs with highly doped monolayer graphene electrodes.^[190] The conductivity of PEDOT:PSS and Au nanoparticles co-doped monolayer graphene increases more than 400% with a high transmittance above 90% (Figure 15a). Semitransparent OSCs with graphene top anode, ITO bottom cathode, and P3HT:PCBM active material are exhibited in Figure 15b,c. The OSCs based on highly doped graphene top electrode exhibit a PCE of 3.04% when the active area is 6 mm², and the device still maintains a PCE







Figure 15. a) Schematic diagram of the two approaches for the fabrication of graphene/PEDOT:PSS top electrodes in organic solar cells. b) Photograph of semitransparent solar cell with graphene top electrode. c) Schematic diagram of a semitransparent organic solar cell with the structure glass/ITO/ ZnO/P3HT:PCBM/PEDOT:PSS/graphene. d) Photovoltaic parameters of short circuit current (J_{SC}) and PCE (η) of organic solar cells with different active areas illuminated from graphene electrodes. Reproduced with permission.^[190] Copyright 2012, American Chemical Society. e) Schematic diagram of an OPV with the inverted structure: PI/Metal/ZnO/P3HT:PCBM/PEDOT:PSS (Au)/Graphene/PMMA. f) Schematic diagram of single- and double-layer graphene films as air (H₂O, O₂) barrier. g) PCE of package-free OPVs with 1 to 4 layers of graphene or Au top electrodes measured in air. Reproduced with permission.^[191] Copyright 2013, Wiley-VCH.

of 2.3% as the active areas increased to 50 mm² (Figure 15d). Furthermore, Yan et al. also reported this kind of graphene as top electrodes for semitransparent PSCs with a device structure of FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/Spiro-OMeTAD/PEDOT:PSS/ graphene. PEDOT:PSS is used as both hole transport layer and adhesion layer between graphene and Spiro-OMeTAD, PSCs with average PCEs of 12.02% (FTO side) and 11.65% (graphene side) are obtained.^[188]

As mentioned above, graphene is impermeable to liquids, vapors, and gases. According to this important property, Yan et al. have fabricated environmentally stable OSCs with highly doped multilayer graphene top TCEs on flexible polyimide (PI) substrate (Figure 15e).^[191] As shown in Figure 15f,g, monolayer graphene inevitably possesses a few broken holes, and these areas act as channels for the diffusion of air into the active material and result in a high speed device degradation ($\alpha = 0.94\%$ h⁻¹). As for bilayer to four layer graphene top electrodes, the degradation speed (α) of OSCs is only about 0.1% h⁻¹ with indistinguishable difference (Figure 15g). It is demonstrated that oxygen or moisture diffused into the pores of first layer graphene need to cross from the space between

the bilayer graphene then pass through the pores in another layer of graphene. However, the space between is too narrow to transport oxygen or moisture. As a result, bilayer graphene top electrode is an efficient packaging film as well as the excellent flexible TCE for organic optoelectronic applications.

Transparent OLEDs are candidates for future lighting and display devices for their potential use in smart windows, retail advertising and head-up displays.^[192-195] Lim et al. applied multilayer graphene as top electrode for transparent OLEDs with flexion patterns (Figure 16a) and corresponding device performance are comparable to that of OLED with a semitransparent thin-Ag top electrode.^[193] Here, methacryloxypropyl terminated polydimethylsilo-xanes (DMS-R22) severs as bonding layer (BL) between multilayer graphene and PET substrate, the low Young's modulus of DMS-R22 leads to entire attachment of graphene electrode without any air gaps. The irregular thickness of graphene grown on Ni films might be responsible for the microscopically inhomogeneous luminescence of top graphene based OLEDs (Figure 16b). In addition, a large OLED segment panel with graphene top electrode is also fabricated (Figure 16c), proving the great potential of multilayer graphene







Figure 16. a) Schematic planar image (left panel), an optical image (right panel), and schematic cross-sectional view (bottom panel) of a glass/ITO/EGBS with bank patterns. b) Top and bottom pixel images during operation of a G-TOLED with active size of $1.5 \times 1.5 \text{ mm}^2$. c) "ETRI" logo displayed from an OLED segment panel with an MLG top electrode (the area of MLG is $23 \times 23 \text{ mm}^2$. Reproduced with permission.^[193] Copyright 2015, Nature Publishing Group. d) The schematic illustration of a CsF-doped graphene multilayer. e) The device structure: ITO/HAT-CN/VB-FNPD/PVK:Firpic/PFN:CsF/multi-layer graphene. f) Photographs showing the device during operation with active size of $2 \times 3 \text{ mm}^2$. The inset shows a photograph of a working blue-light polymer OLED in front of a mirror, showing emission from both surfaces. Reproduced with permission.^[194] Copyright 2015, Nature Publishing Group.

as top electrode to replace metal films in large-area optoelectronic devices. Chang et al. also demonstrated transparent solution-processed blue OLEDs with n-doped multilayer graphene top cathode.^[194] Here, CsF was applied as n-type dopant for multilayer graphene during the transfer/doping process (Figure 16d). The WF of n-doped graphene reduced from 4.2 to 3.2 eV. The device structure of fully solution-processed OLEDs with graphene top cathode is shown in Figure 16e. Without any vacuum process, the device exhibits uniform and doubleside light emission (Figure 16f). Moreover, this transfer/doping method is suitable for a wide range of optoelectronic devices which satisfies with simple transfer and efficient doping.

3.1.3. Graphene Full TCEs

For the purpose of fully taking advantage of the transparent flexible graphene materials, several works have applied graphene as both bottom and top electrodes for organic optoelectronic devices.^[197–199] Yan and his group demonstrated neutral-color semitransparent OSCs with full graphene electrode. The bottom graphene cathode on glass substrate was doped by PEDOT:PSS and ZnO nanoparticles, then PTB7:PCBM was subsequently coated onto modified graphene anode as active layer. As for graphene top anode, graphene/PMMA film was attached to a thin layer PDMS and conformally laminated on the surface of PTB7:PCBM layer. A weight ratio of 5% D-sorbitol mixed with PEDOT:PSS is inserted between graphene top anode and active layer to increase the interface adhesion, and corresponding OSCs exhibit improved stability. To modify the WF of graphene applied for proper anodes and cathodes, Shin et al. controlled the WF of graphene by doping triethylene tetramine (TETA) and TFSA, respectively (**Figure 17**a).^[198] The WF of pristine graphene (4.56 \pm 0.04 eV) changes to 4.88 \pm 0.02 and 4.49 \pm 0.03 eV due to the charge transfer between graphene and doped materials, which energy levels are matched with the adjacent PEDOT:PSS and ZnO NPs (Figure 17b). Transparent OSCs integrated with graphene anode and cathode exhibit a maximum optical transmittance of 70% at ~650 nm and its best PCE reached to 3.12% and 3.30% with the light illuminated from graphene cathode and anode sides, respectively (Figure 17c). Besides, the PCE of OSCs with graphene full electrodes is further elevated to 4.23% by applying metal reflective mirror.

For visibly transparent OSCs with all graphene electrodes, Song et al. applied highly transparent organic active layer that principally absorbs in the near-UV and near-IR wavelength (Figure 17d,e).^[199] Flexible OSCs based on graphene full electrodes achieve PCEs of 2.8–3.8% and the transmittance of whole device reach up to 54–61% across the visible wavelength (Figure 17f,g). Furthermore, this work also demonstrated that OSCs with all graphene electrodes could be prepared on various flexible substrates such as paper and plastic. These devices based on graphene TCEs are more stable to bending compared to device with ITO electrode.

3.2. Graphene Composite Electrodes Integrated with Other Materials

Large-area graphene grown by CVD method commonly exhibits polycrystalline characteristic with local defects such as grain boundaries or dislocations. The sheet resistance of www.advancedsciencenews.com

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Figure 17. a) Schematic of the device architecture for a typical solution-processed semitransparent FOSC of PEDOT:PSS, ZnO, and P3HT:PCBM. b) Energy band structure and c) *J*–V curves of the FOSCs obtained through illumination from the TETA/GR and TFSA/GR TCE sides. Reproduced with permission.^[198] Copyright 2017, American Chemical Society. d) Device structure with approximate layer thicknesses. e) Cumulative absorption spectra of a PDTP:PC₆₀BM device as each layer is added from the bottom (cathode) to the top (anode). f) Photograph taken through a PC₆₀BM device. Dotted lines outline the corners of the device. g) *J*–V curves of PC₇₀BM Gr/Gr devices when illuminated from the glass (cathode) side versus the PDMS (anode) side. *J*–V curve of a PC₇₀BM ITO/Gr device illuminated from glass/ITO side is included as a reference. Lower-right bar-chart shows the average J_{SC} values for these configurations. Reproduced with permission.^[199] Copyright 2016, Wiley-VCH.

pristine monolayer graphene grown by CVD method is usually around 1 k Ω sq⁻¹, whose value is dramatically higher than ITO TCEs.^[116,157–159] Although there are numerous methods for graphene doping to improve its conductivity, the sheet resistances of most doped monolayer graphene are still around 200 Ω sq⁻¹.^[51,52] Besides, graphene composite electrodes combined with other conductive materials such as conducting polymer,^[200–202] metal film/nanowires,^[203–207] and carbon nanotubes^[208] are efficient strategies for elevating the electrical properties of graphene. For instance, Xu et al. prepared graphene and PEDOT composite film from their hybrid solution exhibiting high transmittance greater than 80% and conductivity of 0.2 S cm⁻¹.^[200] Kholmanov et al. reported that monolayer graphene films integrated with Ag nanowires obtained decreased sheet resistance of ≈64 Ω sq⁻¹ at the transmittance of 93.6%, much better than that of pristine graphene (≈1.05 k Ω sq⁻¹).^[203]

For organic optoelectronic devices, Lee et al. applied highly flexible and stable silver nanowire and graphene composite

TCEs in OSCs.^[205] The sheet resistance and transmittance of silver nanowires covered by monolayer graphene are \approx 34.4 Ω sq⁻¹ and 92.8% at 550 nm, respectively. Furthermore, silver nanowire-graphene hybrid TCE shows long-term stability at 70% RH and 70 °C for a few days. While the sheet resistance for singular silver nanowires increases more than 300% due to the silver oxidization under the direct exposure to air (Figure 18a). Comparing with ITO and silver nanowire TCEs, OSCs based on silver nanowire-graphene hybrid film exhibit the highest PCE of 3.30% (Figure 18b). Even better, the OSCs with hybrid TCEs could remain over 61% of the original efficiency after they were stored in atmospheric environment for 480 h (Figure 18c). Recently, Li et al. fabricated single-layer graphene composite electrode combined with several nanometers silver film.^[206] The single-layer graphene and 8 nm silver film shows extremely low sheet resistance of 8.5 Ω sq⁻¹ and high transmittance of 74% at 550 nm. Simultaneously, the graphene/Ag composite electrode exhibits high







Figure 18. a) SEM images of AgNW and AgNW–graphene hybrid TCEs after a long-term stability test. b) *J*–*V* characteristics of inverted bulk-heterojunction organic solar cells with ITO, AgNW, and AgNW–graphene hybrid TCEs. c) Device performance of inverted bulk-heterojunction organic solar cells with AgNW and AgNW–graphene hybrid TCEs as a function of exposure time under ambient conditions without encapsulation. Reproduced with permission.^[205] Copyright 2013, The Royal Society of Chemistry. d) Energy-band diagram of device. e) The sheet resistance variation trend of three composite electrode samples. f) Luminance versus voltage characteristic curve. Reproduced with permission.^[206] Copyright 2017, IOP Publishing Ltd. g) Digital image of EG/PH1000 hybrid ink and molecular structures of EG and PH1000. h) *I*–*V* characteristics of the ultrathin photodetectors. i) The on/off characteristics of the ultrathin photodetectors. Reproduced with permission.^[209] Copyright 2014, Wiley-VCH.

mechanical stability and low energy barrier compared with ITO TCEs (Figure 18d,e). Furthermore, OLEDs with graphene/ Ag composite anode delivers a turn-on voltage of 2.4 V, and the maximum luminance is over 40 000 cd m⁻² at only 9 V (Figure 18f). Apart from metal films and nanowires, conducting polymer also plays an important role for graphene composite electrodes. Liu et al. demonstrated an innovative solution-processed method of large-area graphene film by spin coating hybrid ink of exfoliated graphene and PEDOT:PSS formulation in DMF (Figure 18g).^[209] The thickness of graphene/ PEDOT:PSS composite film could be tailored from 10 to 20 nm by spray-coating method, yielding high electrical conductivity of 1000 S cm⁻¹ and transmittance of 80%. Ultrathin organic photodetectors fabricated with graphene/PEDOT:PSS composite electrodes and P3HT:PCBM photoactive layer exhibit a short-circuit current density of 0.61 mA cm⁻² and open-circuit voltage of 0.58 V (Figure 18h). A remarkably high $I_{\rm on}/I_{\rm off}$ ratio of 2 × 10⁵ could be obtained (Figure 18i).

Because of the extremely high conductivity, tunable WF, and environmental stability, we anticipate that graphene composite electrodes integrated with other conducting materials present exciting opportunities for advanced electronics with high performance and stability.

4. Conclusion and Outlook

Numerous remarkable progresses of graphene synthesis, transfer, and application have been made over the past few years. As the relatively young transparent conductive electrodes, graphene acts as the promising candidates for replacement of the conventional electrode materials such as ITO, metal



film/grid/nanowire, conducting polymer, and carbon nanotube. Up to now, graphene materials have already been broadly applied in various organic optoelectronic devices as efficient electrodes due to their high transparency/conductivity, flexibility, excellent chemical/thermal stability, and impermeability to gas/liquid. Despite the significant advances in graphenebased organic optoelectronic devices, there are still many challenges for graphene-based application in industry level. Unlike experiments operated in lab level, graphene-based technique satisfied for industry needs to demonstrate enough advantages in device performance, cost, reproducibility, and stability. To overcome these challenges, high-quality production and largearea transfer method for graphene films with high conductivity and long-term uniformity need to be further developed. Besides, excellent stability in air as well as clean and smooth graphene morphology is required for devices with perennial lifetime and high performance.

According to this review, some of these mentioned challenges have been partly solved. Roll-to-roll method enables large-area damage-free transfer of CVD grown high-quality graphene; PFSA-doped graphene exhibits extraordinary doping stability at high temperature and chemical conditions; 1-foot-long single crystal graphene is achieved by a local feed of carbon precursor on translational metal substrate. Although there are still many barriers need to be climbed over, we are optimistic that new techniques will be developed to overcome these challenges in near future and commercialized organic optoelectronic devices with graphene TCEs such as OSCs-based transparent glass wall, augmented reality displays and even foldable/stretchable electronics are coming into our life.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrodes, graphene, organic optoelectronic devices

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