

Graphene Films for Flexible Organic and Energy Storage Devices

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ABSTRACT: Graphene and its derivatives have been the subject of extensive research in fundamental science and have viable applications in current and future technology. The exceptionally high electronic and thermal conductivity, optical transparency, and high specific surface area, combined with excellent mechanical flexibility and environmental stability leave graphene poised to be a material of the future. This perspective introduces the importance of graphene electrodes, discusses the synthesis of graphene and transfer onto desired substrates and the role of graphene in electrodes for a broad range of flexible devices such as photovoltaic, electronic, and electrochemical energy storage.

Rectronic devices that can maintain their original electrical and mechanical properties under high strain have the potential for use in many new applications. Examples include more conformable biosensors for health monitoring, microactuators that employ biologically inspired designs, wearable displays, rollable solar cells, and energy storage devices.^{1,2} Flexible electrode materials play a key role in these nextgeneration devices. Substantial research has been undertaken on conductive polymers,³ silver wires,⁴ carbon nanotubes (CNTs) and CNT/polymer composites.⁵ However, they have many obstacles that include incompatibility with other device components and difficulty in micro/nano fabrication. Therefore, many researchers have been seeking alternative materials to overcome such drawbacks. As an alternative, the graphenebased electrode has attracted lots of attention for diverse flexible electronic devices due to its excellent electronic, optical, and mechanical properties. In particular, its strong interfacial cohesion with organic materials make it well suited for use in transparent electrodes for organic optoelectronic devices such as organic light emitting diodes, photovoltaic cells, and field effect transistors. In addition, recent reports highlight the use of graphene as an electrode in flexible power sources, which is one of the essential components of flexible electronic devices. Graphene and its derivatives are the ideal candidates for an electrode material due to their high specific surface area, good chemical stability, and mechanical flexibility, which make them suitable for use in flexible power sources.⁶ Using graphene foam as a support for the cathode of lithium ion batteries (LIBs) improves their specific power density and, as an anode, is also expected to give an even higher specific capacity as lithium adsorption is taking place from both sides of the graphene nanosheets and its high specific surface area.

From this perspective, recent progress in the synthesis and tailoring of electronic properties by doping method of graphene are discussed along with its various application, starting with its



Graphene is the ideal candidate for a flexible and high capacity electrode material due to its high specific surface area and mechanical flexibility.

use as a transparent electrode for organic electronic devices and expanding to that for energy storage devices, depicting graphene's potential utilization in this important technological field.

Synthesis and Transfer Method of Graphene. The properties and size of graphene are strongly influenced by the different synthesis routes. The first ever reported monolayer graphene was obtained by mechanical exfoliation of graphite using scotch tape, which results in excellent structural integrity but is not suitable for device applications due to limited scalability. The epitaxial growth by thermal decomposition of SiC wafers in an ultrahigh vacuum is another way of producing high-quality graphene.⁷ The advantage of this method is to grow graphene directly on an insulating SiC substrate without an additional transfer process. Unlike epitaxial growth and the mechanical exfoliation method, the chemical exfoliation method that produces graphene flakes via a weakening of the interactions between the layers of graphite allows for production upscaling.⁸ This method employs oxidation of graphite using strong acids and oxidants, which contain several functional groups such as epoxide and hydroxyl. These hydrophilic oxygen groups on the graphene layer facilitate the intercalation of water molecules by sonication as shown in Figure 1a. The resulting

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Figure 1. (a) Schematic of chemical method for aqueous graphene dispersion. (b) Chemically converted graphene film on 4 in. quartz wafer by spray coating. (c) Schematic illustration of the graphene synthesis mechanism on Cu foil (left) and roll-to-roll transfer of graphene grown on Cu foil with thermal release tape (right). Reprinted with permission from ref 11. Copyright 2010 Elsevier.

graphene oxide (GO) suspension has an insulating property and is chemically reduced using hydrazine or by thermal reduction over 300 °C in an inert atmosphere to recover the original conductivity. To avoid the relatively high reduction temperature of GO, the electrochemical reduction and plasma method have been preferred.⁹ In addition, a simple production method of graphene flakes by intercalating potassium into graphite was reported. This approach can avoid the reduction and oxidation process that causes serious generation of defects in graphene, and, as a result, the conductivity of graphene flakes can be improved.¹⁰ The uniform and large area deposition of these graphene flakes dispersed in solvents can be achieved by spin-coating, vacuum filtration, Langmuir-Blodgett, and spray techniques, as shown in Figure 1b.11 The resulting graphene films showed a relatively high sheet resistance value over a few kohm/sq with 70% transparency because of the high flaketo-flake contact resistance and defects created during the exfoliation process, which remain a major challenge. Another progressive way for large-area and high-quality graphene growth is chemical vapor deposition (CVD) using a gaseous carbon source and the catalyst metal substrate (Figure 1c).^{12,13} A variety of transition metals with different solubilities of carbon atoms as a catalyst layer have been studied to synthesize graphene in many desired forms, including mono-, bi-, or multilayer sheets for diverse purposes.¹⁴ For example, Ni, Fe, and Co, with a relatively high solubility produces thick graphene films of over 10 layers.¹⁴ On the other hand, Pt and Cu with low carbon solubility can produce a monolayer graphene film with high optical transmittance. Recently, growth methods using polymer sources such as polystyrene (PS), polyacrylonitrile (PAN), and poly(methyl methacrylate) (PMMA) have been receiving attention due to their low cost production and safe tractability.^{15,16} The process enables the production of doped graphene, which allows for the manipulation of the graphene's electronic properties. A similar study also successfully demonstrated graphene growth using sugar and tar.¹⁵ Plasma-assisted CVD approaches have been explored for growth at a low temperature (300 °C).¹⁷ The electrical and optical properties of the resulting graphene films can be easily controlled by varying the growth time and temperature, and plasma power. Furthermore, this low-temperature synthesis method enables the direct growth of graphene on plastic substrates for various electronic applications.

In general, a graphene film grown by CVD method needs to be transferred to the target substrates for device fabrication without defect generation to preserve the original properties. The most accepted transfer method is a wet transfer method that uses spin-coated PMMA and PDMS as a supporting layer. Furthermore, a roll transfer method using a thermal release tape has been demonstrated that allows for a continuous process without size limitations and a layer-by-layer multiple printing to enhance the electrical conductivity of graphene films (the right image of Figure 1c).¹²

Chemical and Electrostatic Doping of Graphene Film. Graphene prepared by the chemical exfoliation and CVD methods described in the previous section do not exhibit enough conductivity for practical applications as transparent electrodes for the touch panel screens, organic light emitting diodes, and photovoltaic cells. To overcome such limitations, various doping methods using chemical dopants and ferroelectric substrates have been explored (Table 1).^{12,18-24} First, the chemical doping method using various dopants such as nitric acid (HNO₃), gold chloride (AuCl₃), bis(trifluoromethanesulfonyl)-amide[((CF₃SO₂)₂NH)] (TFSA) and tetracyanoquinodimethane (TCNO) can effectively reduce the sheet resistance of graphene (Figure 2a). For example, nitric acid, which is p-type dopants, accepts electrons from the surface by the charge transfer described in the reaction below (reaction 1).²⁵ A sheet resistance of monolayer graphene that is as low as 150 Ω /sq can be achieved.

Table 1. Sheet Resistance (R_{sh}) Transparency of Doped Graphene by Chemical or Electrostatic Methods

		$(\Omega/$	sq)					
type	dopant	before	after	transparency (%, at 550 nm)	ref			
chemical	HNO ₃	50	30	90	12			
	TFSA	184	129	86.5	18			
	AuCl ₃	448	150	87	19			
	nitrogen	-	300	80	20			
	TCNQ	-	180	88	21			
	PVA	-	400	98	22			
	FTS	-	65	-	23			
electrostatic	P(VDF-TrFE)	1440	120	95	24			

$$6HNO_3 + 25C \rightarrow C_{25}^+ NO_3^- \cdot 4HNO_3 + NO_2 + H_2O$$
(1)

When nitric acid is used for doping, the G and 2D peaks of graphene are blue-shifted in Raman spectra, and the carbon 1s peak is broadened and red-shifted in X-ray photoelectron spectroscopy (XPS) (Figure 2b). In addition, using AuCl₃ as a dopant reduces the sheet resistance of graphene by 83%.¹² The significant drop in sheet resistance was interpreted as an extraction of electrons from the graphene due to the reduction of Au_{3n} to Au₀. However, the sheet resistance of the sample doped with these chemicals degraded with time due to the adsorption of moisture and other chemical molecules, which limit the applicability of chemically doped graphene. Therefore, recent research efforts have been devoted to stabilize the volatile chemical doping effect. Yan et al. recently reported that encapsulation with a curable polymer coating such as poly(4vinylpyridine) (P4VP) can improve the durability of the doped graphene films (Figure 2c).²⁶

Although the conductivity of graphene can be effectively improved by chemical doping, the adsorption of moisture under environmental conditions can cause serious degradation in electrical conductivity.^{19,26} On the other hand, nonvolatile doping by ferroelectric polarization of piezoelectric materials such as poly(vinylidene fluoride-*co*-trifluoroethylene) (P(VDF-TrFE)) can effectively enhance the conductivity of graphene by heavily doping and to preserve it for a long time with chemical inertness.^{24,27} In addition, a fully polarized P(VDF-TrFE) thin film with proper thickness fulfills both heavy doping and mechanical supporting to graphene owing to its good optical transparency and mechanical flexibility. When an electric field is applied to a P(VDF-TrFE) thin film through graphene, charge carriers accumulate on the graphene surface due to vertically aligned dipoles. The conductance of graphene strongly depends on the maximum polarization (P_{max}) and direction of remnant polarization (P.) of the P(VDF-TrFE) thin film (Figure 3a).



Figure 3. (a) Polarization hysteresis of P(VDF-TrFE) with respect to applied electric field. (b) Principle of electrostatic doping by polymer ferroelectric P(VDF-TrFE). (c) Sheet resistance change of electrostatic doped graphene according to the polarization direction of P(VDF-TrFE). (d) Mechanical flexibility of a graphene-P(VDF-TrFE) film. The inset shows a photograph of the transparent and bendable device. Reprinted with permission from ref 24. Copyright 2012 American Chemical Society.

For the +P_r polarization direction, accumulated electrons provide n-type behavior of the graphene film. In this case, the sheet resistance of the graphene on P(VDF-TrFE) increased because of the large potential barrier. On the other hand, the ferroelectric gating of the $-P_r$ direction makes p-type doping of graphene, which results in much lower sheet resistance due to smooth potential barriers along with the planner direction (Figure 3b). Ni et al. reported that a high sheet resistance of 1440 Ω /sq, due to the large disorder created by randomly oriented dipoles before polarization, which can be reduced to 120 Ω /sq for monolayer graphene after full polarization as



Figure 2. (a) Decrease in sheet resistance of graphene according to various dopants. (b) XPS and Raman spectra (inset) variation after HNO_3 doping process of monolayer graphene film on SiO_2/Si substrate. (c) Stability of doping effect with respect to the existence of an encapsulation layer. Reprinted with permission from refs 12 (copyright 2010 Nature Publishing Group) and 26 (copyright 2011 American Chemical Society).

The Journal of Physical Chemistry Letters

shown in Figure 3c.²⁴ The merit of the graphene/P(VDF-TrFE) multilayer film is long-term stability of the low sheet resistance by nonvolatile doping, even though the applied power is turned off. In addition to the nonvolatile doping effect, this polymer ferroelectric-based doping method can provide high optical transparency and mechanical flexibility, which are critical for the various applications of graphene-based optoelectronics (Figure 3d).

Nonvolatile doping by ferroelectric polarization of piezoelectric materials can effectively enhance the conductivity of graphene by heavily doping and preserve it for a long time with chemical inertness.

Application of Graphene Electrode in Flexible Organic Electronic Devices. As discussed above, graphene is an attractive material as the conductive transparent electrode of flexible organic devices such as organic photovoltaic cells (OPVs), organic lightemitting diodes (OLEDs), and organic thin film transistors (OTFTs). Graphene transparent conductive films can be classified into two groups, reduced graphene oxide (rGO) and CVD-grown graphene, according to the production method. Several examples of organic devices have been demonstrated using these two types of graphene films (Table 2).²⁸⁻⁴³ The first example is an application in the anode of OLEDs for the replacement of ITO. Although graphene films have the advantage of good mechanical properties and easy pattern formation, the relatively lower work function that causes the high injection barrier at the interface between the graphene anode and the overlying organic layers, and higher sheet resistance than ITO electrodes have limited the performance of OLEDs.^{28,29} For instance, the OLED based on the rGO anode exhibited a limited performance because of the higher sheet resistance of nearly 2 orders of magnitude than ITO and a

difference in the work function over 1 eV. Recently, Han et al. reported a promising route to enhance OLED performance using efficient methods to improve the work function and sheet resistance of graphene films to the levels needed for anodes.³¹ They demonstrated highly efficient OLEDs using a conducting polymer mixture to generate a work function gradient for matching work functions between the graphene and the organic hole transport layer, and the layer-by-layer stacking of graphene and chemical doping for the improvement of the electrical conductivity of graphene. Figure 4a shows a schematic illustration of the efficient hole injection mechanism from the graphene anode to the hole transport layer (NPB: N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl) benzidine) via the conducting polymer buffer layer with a work function gradient. As shown in Figure 4b, the fluorescent OLEDs using graphene anodes with lower sheet resistance of 40 Ω /sq and 90% transmittance exhibit extremely high luminous efficiency (37.2 lm/W), which is significantly higher than those of devices optimized with a commercially available best-quality ITO anode (24.1 lm/W); this is attributed to the improvement of two main factors. These remarkable improvements in device efficiencies resulted from removing the underlying cause from serious diffusion of indium and tin atoms from the ITO anode to organic layers, which leads to degradation of hole injection efficiency of OLEDs. In addition to the anode application, Matyba et al. presented the use of a graphene as a cathode of an all-solution processable light emitting device (Figure 4c).⁴⁴ The light-emitting electrochemical cell (LEC) is composed of the rGO film as the transparent cathode, a screen-printable conducting polymer (PEDOT:PSS) as a partially transparent anode, and a micrometer-thick active layer solution-deposited from a blend of a light-emitting polymer and a polymer electrolyte, similar to an OLED. The resulting LEC devices using a graphene cathode exhibited a quantum efficiency of 9 cd/A and luminous efficiency of 5 lm/W at 4 V (Figure 4d).

Furthermore, graphene has been studied for application in electrodes of flexible OPVs owing to its capability to maintain the structural integrity and sheet resistance under the bent state. Initial efforts using rGO in OPVs were not very successful. These cells exhibited a low power conversion efficiency (PCE)

Table 2. Various Organic Devices Based on Graphene (rGO, CVD-G) Electrodes

	device/gra	aphene type	doping	Φ (eV)	emission type	luminous eff. (lm/W)	ref
	OLED	rGO	-	-	fluorescent	~0.35	28
		CVD-G	-	_	phosphorescent	~0.53	29
		CVD-G	HNO ₃	4.6	fluorescent	37.2	30
	device/gra	aphene type	doping	Φ (eV)	substrate	PCE (%)	ref
	OPV	rGO	phenyl isocyanate	-	glass	1.4	31
		rGO	-	-	PET	0.78	32
		CVD-G	AuCl ₃	-	quartz	1.51	33
		CVD-G	HCl, HNO ₃	4.36	glass	2.5	34
		CVD-G	$HAuCl_4$	4.6	glass	2.6	35
		GO/PEDOT gel	-	_	glass	4.14 (tandem)	36
					_		
	DSSC	CNT/rGO	-	-	graphite	6.17	37
		CVD-G	-	-	G-paper	6.05	38
		PEDOT/CVD-G	HNO_3	-	PET	6.26	39
	device/gra	device/graphene type		substrate	on/off ratio	mobility $(cm^2/V \cdot s)$	ref
	TFT	CVD-G	rubrene	SiO ₂	10 ⁷	10.3	40
		CVD-G	pentacene	SiO ₂	10 ⁸	1.2	41
		CVD-G	pentacene	SiO ₂	10 ⁷	1.01	42
		CVD-G	pentacene	polyarylate	10 ⁸	0.12	43



Figure 4. (a) Schematic illustration of hole injection from graphene to a conventional HTL (NPB) via work function gradient HIL. (b) Luminous efficiency of OLED devices as various types of anode (doped graphene or ITO). (c) Schematic structure of metal free light-emitting electrochemical cells based on graphene cathode. (d) Current density and brightness as a function of voltage through the graphene cathode side. Reprinted with permission from refs 30 (copyright 2012 Nature Publishing Group) and 44 (copyright 2010 American Chemical Society).



Figure 5. Current density vs voltage characteristics of OPVs using (a) CVD graphene and (b) ITO electrodes under 100 mW/cm² and AM1.5G spectral illumination for different bending angles, and insets show the experimental setup employed in the experiments. (c) J-V characteristics of bent and pristine DSSCs using graphene/PEDOT as counter electrode, and the inset shows the different layers of DSSC with a graphene/PEDOT counter electrode on a flexible PET. Reprinted with permission from refs 39 (copyright 2012 Wiley) and 47 (copyright 2010 American Chemical Society).

(<0.4%) and a leakage current under dark conditions. The low performance of the cells resulted from poor conductivity of rGO due to the high flake-to-flake contact resistance and incomplete reduction of GO. For instance, Eda et al. demonstrated a PCE of 0.1%, using doped rGO films which has a sheet resistance of 40 k Ω /sq with 64% transparency.⁴⁵ As an alternative, composite films of rGO and CNTs doped by alkali carbonates were used in OPVs. The work function of these composite electrodes was adjusted in the range of 4.6–3.4 eV, due to the formation of interfacial dipoles.⁴⁶ The rGO electrode as a cathode with modulated work function showed an optimal PCE of 1.27%.

CVD-grown graphene films are much more attractive for efficient OPVs fabrication due to their superior electrical and surface properties compared to rGO. Arco et al. demonstrated OPVs with a PCE of 1.18% on flexible PET substrates,⁴⁷ and recently Park et al. presented OPVs with 1.51% using highly

doped multistacked graphene films of ~70 Ω /sq and 89% transmittance.³³ These graphene-based devices showed an outstanding capability to function properly under bending up to 138°; by contrast, the ITO-based devices failed completely at 60° (Figure 5 a,b).⁴⁷ One of the challenges in the integration of graphene electrodes in OPV is the weak adhesion between the graphene electrode and the PEDOT:PSS hole transport layer due to the differences of hydrophilicity, which causes significant device failure. As an alternative, a thin MoO₃ buffer layer on PEDOT:PSS was investigated to address the bonding issue between graphene and PEDOT:PSS.³⁴

Dye-sensitized solar cells (DSSCs) are another kind of photovoltaic device that has also attracted interest due to their low cost production and relatively high energy conversion efficiency. In general, DSSCs are composed of a mesoporous titania nanocrystal electrodes coated with ruthenium-based sensitizers on a transparent conductive oxide (TCO) substrate,



Figure 6. (a) AFM image of the pentacene film on a graphene electrode. (b) Transfer characteristic of flexible/transparent pentacene FETs on plastic substrate. Inset shows bending image of the device. (c) Optical image of stretchable graphene-based TFTs on a PDMS substrate. (d) Schematic dual-doped bilayer graphene transistor structure and chemical structure of NH_2 -functionalized SAMs on a SiO₂/Si substrate (n-doping) and F4-TCNQ (p-doping). (e) Transfer characteristics of bilayer graphene FETs with various thicknesses of the F4-TCNQ layers. Reprinted with permission from refs 41 (copyright 2011 American Chemical Society), 43, 48 (copyright 2011,2012 Wiley), and 50 (copyright 2011 American Chemical Society).

iodine/iodide electrolyte, and platinum on the TCO substrate as a counter electrode. An important issue for commercialization of DSSCs is to find a fabrication method for lightweight, thin, and low-cost DSSCs through roll-to-roll mass production. The development of flexible platinum-free counter electrode materials is an important issue to address. Lee et al. reported platinum-free, low-cost, and flexible DSSCs using graphene film coated with a conducting polymer as a counter electrode (Figure 5c).³⁹ The graphene-conducting polymer based DSSCs showed a PCE of 6.26%, which is comparable to Pt/ITO (6.68%). This is attributed to the low sheet resistance of graphene coated with PEDOT:PSS. Figure 5c shows the cell performance of DSSCs before and after the bending test of counter electrodes. It shows very stable performance without serious degradation.

Recently, organic field-effect transistors (OFETs) have been widely studied because of their potential applications in integrated circuits for large-area, flexible, and low cost electronics. Currently, metals such as gold and platinum have been commonly used as source/drain electrodes. However, the high hole-injection barrier between the organic semiconductors and these metal electrodes are an obstacle that limits the performance of OFETs. Even though conducting polymers such as PEDOT:PSS have been studied as alternative electrodes, its hygroscopic and acidic nature are weak points. Lee et al. presented the charge injection and transport property between pentacene and graphene as conducting electrodes.^{41,43,48} Interestingly, the graphene electrode with a polymer residue showed better performance, compared to that of the FET using a graphene electrode with a clean surface because of a different molecular arrangement of pentacene.⁴¹ Figure 6a shows that the pentacene molecules tend to lie down on the surface of the graphene electrode due to the strong $\pi - \pi$ interaction between the molecules and underlying graphene surface, while the vertical alignment of pentacene molecules is induced because the polymer residue on graphene suppresses

the interactions between them. This continuous vertical orientation through the channel and an electrode region in π -stacks of pentacene molecules results in a minor injection barrier between the electrode and the pentacene (~ 0.6 eV), which is smaller than the commonly used Au electrode.⁴⁹ In addition, the unrecognizable transition regime between channel and electrode owing to the extremely thin nature of graphene also helps in reducing the contact resistance as much as 2 orders of magnitude compared with metal electrodes. These factors induce the superb performance of pentacene OFET using graphene electrodes (0.54 $\text{cm}^2/(\text{V}{\cdot}s))$ than conventional Au electrodes (0.02 $\text{cm}^2/(\text{V}\cdot\text{s})$), even though the sheet resistance of graphene is higher than the Au electrode. Park et al. also fabricated pentacene OFETs with a graphene electrode as shown in Figure 6b.⁴³ By adopting a new process (patterning of graphene on a Cu foil) for the graphene electrode, the flexible OFETs assembled on a plastic substrate, which shows the excellent performance. Recently, Lee et al. reported a stretchable and transparent transistor composed of monolithically patterned graphene films on a PDMS rubber substrate as shown in Figure 6c.50 The monolithic devices displayed several advantages, including good mechanical stretchability as well as improved contact at the channel-toelectrodes interface. As a result, the outstanding electrical properties of the devices are maintained even at a strain level of \sim 5% without a structure especially designed for high stretchability. The graphene shows its potential in outstanding electrical, optical, and mechanical performance that allows for future stretchable electronic applications, which could not be accomplished using conventional electronic materials.

Although graphene has the potential to replace conventional inorganic semiconductors as reported in the literature, the gapless character of the graphene band structure is a major obstacle for its utility in FETs. So it is highly desirable to induce a band gap in graphene for device applications. Various techniques have been suggested to form The unrecognizable transition regime between channel and electrode owing to the extremely thin nature of graphene also helps in reducing the contact resistance as much as 2 orders of magnitude compared with metal electrodes.

the band gap by using bilayer graphene, the edge effects of a nano ribbon, and gap tuning on special substrates. Although graphene nanoribbon FETs exhibited excellent semiconducting behavior $(I_{on}/I_{off}$ ratios >10⁵), it still remains technically challenging to control the fine edge structure of the graphene nano ribbons. The chemical functionalization of graphene by H, OH, and F has been studied for the engineering of the band structure as an alternative approach. Self-assembled monolayers (SAMs) on the substrate are also an attractive method to control the electrical properties of graphene. Recently, the band structure of bilayer graphene was modulated by dual molecular doping as shown in Figure 6d.⁴⁸ The band gap is created by applying a perpendicular electric field to bilayer graphene from amine (NH₂)-functionalized SAMs and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) at the bottom and top of the graphene sheet, respectively. Here, the lone-pair of amine (NH_2) works as an electron donor in the bottom side, while the cyano and fluoro groups of F4-TCNQ provide electron withdrawing characteristics on graphene. This band split has been confirmed by the transport characteristic of bilayer graphene FETs and can be controlled further by the thicknesses of the F4-TCNQ layer as well (Figure 6e). The calculated electrical band gap from the on/off ratio varies from 65 to 124 meV with variation in thickness of F4-TCNQ. The incremental rate is approximately 2.9 to 3.1 meV/Å. These results imply a consecutive opening of the band gap with an increase in p-type doping from the top in combination with stable n-type doping at the bottom.

Application of the Graphene Electrode in Electrochemical Energy Storage. Fully integrated stretchable, flexible, and conformable portable electronic devices cannot be realized until the flexible energy sources that match the energy requirements are developed.^{51,52} There has been significant progress in the development of flexible electronics; however, similar progress is needed in the development of flexible power sources.⁵³ Several issues have been associated with flexible power sources that may arise due to the internal short circuits and compatibility of different layers in the development of a simple and easy method to fabricate bendable and flexible energy sources.

The LIB is one of the most widely used batteries, which has a large energy density of 400 Wh/kg and the highest voltage among all secondary batteries. Recently, flexible, and bendable LIBs have been reported where the cell has been integrated onto paper using conventional electrode materials in which the paper substrate functions as both the mechanical substrate and the separator, and the CNT film serves as a current collector.⁵⁵ The isolated layers of graphite are expected for higher specific capacities as the adsorption of lithium ions can take place on both sides of the graphene layers,⁵⁶ and hence most suitable materials for flexible LIBs due to its excellent mechanical

flexibility, superior electrical conductivity, high surface area, and fast reacting edges.^{7,57} The high chemical diffusivity of Li, $\sim 10^{-7} - 10^{-6}$ cm²/s, on a graphene plane also contributes to its high power applications. The double-layer graphene is more reactive than the single layer, which has clear implications for the use of graphene as an electrode material.⁵⁸ Electrodes made from rGO showed a higher specific capacity of 540 mAh/g, which can further increase by mixing CNTs and C₆₀ creating extra sites for insertion of lithium ions.⁵⁹ However, a problem with rGO-based electrodes is fluctuation in the capacity induced by surface side reactions.⁶⁰ Generally, the charge/ discharge rate of a LIB depends on the diffusion rate of lithium ions and electrons from electrolytes and electrodes to the current collector. The transport rate can be improved by synthesizing new electrode materials with good ionic and electronic conductivity and reduce the diffusion length over which the electron and lithium ion have to move.^{2,61} Graphene foam acts as a conducting network to connect the electrode structure, which helps in fast charge transfer and improves the power density of flexible LIBs. Figure 7a shows a thin, lightweight, and flexible LIB made of a flexible, and conductive interconnected graphene foam soaked with Li4Ti5O12 and $LiFePO_4$ as the anode and cathode, respectively. The graphene foam, which is a very lightweight current collector, serves as a highly conductive pathway for both electrons and lithium ions. The battery using graphene foam as support material for electrodes showed a good flexibility, high capacity, high rate, and long-life cycle even under repeated bending to a small radius of 5 mm (Figure 7b). This new strategy opens up the possibility for large-scale fabrication of flexible batteries with high capacity and high power.⁶² Graphene can also be used directly as an anode and, at the same time, as a supporting material for the cathode of flexible LIB. Figure 7c shows a schematic drawing of the flexible rechargeable LIB where V₂O₅/graphene paper is used as the cathode and graphene paper is used as an anode. The specific capacity of the graphene paper electrode showed a higher value than that of the conventional graphene electrode at higher rates, suggesting the potential of freestanding graphene paper as an anode material with high-rate capabilities for flexible LIBs (Figure 7d). The robust integration of graphene into the electrode ensures not only the capability to operate under full mechanical flexibility, but also superior electrochemical performance.⁶³ Thus flexible batteries using graphene electrodes can be integrated to other functional materials, which could be used in various applications to make complete flexible device systems.

Electrochemical capacitors (ECs) are additional charge storage devices that have attracted much attention due to high power density, longer life cycles than batteries, and higher energy density than dielectric capacitors.⁶⁴ ECs store the charge electrostatically using the reversible adsorption of ions of the electrolyte onto the active electrode materials, which are electrochemically stable and possess a high specific surface area. LIBs suffer from a slow power delivery or uptake, so, where faster and high-power density storage devices are needed, ECs are the best choice. ECs currently fill the gap between batteries and conventional solid state capacitors as they store thousands of times more charge than the latter, because of a much larger surface area (1000–2000 m^2/g) available for charge storage.

Carbon-based materials such as CNTs, carbon fibers, and graphene have been used in ECs as the electrodes, which function through the accumulation of charge at the interface of electrode and electrolyte.⁶⁵ The electrode materials hold the



Figure 7. (a) Flexible electrode prepared by graphene foam. (b) Performance of flexible battery using graphene electrode. (c,d) Flexible energy storage device based on graphene paper and its performance. (e) A schematic diagram of the all-solid-state LSG-EC illustrating that the gelled electrolyte can serve as both the electrolyte and separator. (f) Bending has almost no effect on device performance, as seen in these CVs collected at a scan rate of 1000 mV/s. Reprinted with permission from refs 62 (copyright 2012 National Academy of Science), 63 (copyright 2011 Royal Society of Chemistry), and 70 (copyright 2012 American Association for the Advancement of Science).

key to practical applications in flexible devices due to their mechanical and electrical properties and the effect of their bulk and interfacial properties at the interface of the electrode and electrolyte. Using graphene as the electrode has a advantage over traditional carbon electrodes due to higher surface area and better electrical conductivity. Stoller et al. reported ECs using rGO, which showed a high specific capacitance of 135 and 99 F/g in aqueous and organic electrolyte, respectively.⁶⁶ The functionalized reduced graphene oxide (f-rGO)-based flexible EC was prepared using two f-rGO films, which showed a very high specific capacitance (118.5 F/g) and rate capability (90% retention). This is due to the fast ion and charge transport at the interface, and consistent performance over long periods of device operation under bending conditions as a result of good mechanical integrity.⁶⁷ In addition, high specific capacitances (237 F/g) were obtained in the case of flexible and uniform composites of graphene and polypyrrole, which are attributed to the favorable nucleation of new polymer chains at the defect site of the graphene surface.⁶⁸ Choi et al. have fabricated flexible asymmetric supercapacitors based on a functionalized ionic liquid and chemically modified graphene film, which deliver a high energy density of 19.7 Wh/kg under harsh mechanical conditions including twisting and bending that make such devices suitable for application.⁶⁹ Figure 7e shows the device structure of a flexible supercapacitor made of laser scribed graphene (LSG) and a gelled electrolyte (poly(vinyl alcohol)-H₃PO₄), which serves as both the electrolyte and separator and the inset shows a photograph

demonstrating device flexibility.⁷⁰ The LSG sheets showed a high electrical conductivity of 1738 S/m, large specific surface area of 1520 m^2/g , and good mechanical stability. Additionally, LSG-ECs can deliver a power density of $\sim 20 \text{ W/cm}^3$, which is 20 times higher than that of activated carbon-based ECs. The high rate performance of this device is attributed to the porous electrode, which effectively absorbed the electrolyte and minimized the diffusion length. Further, the binder-free electrode helps in the reduction reaction at the surface by enhancing the reaction rate at the electrode surface. The flexible LSG-supercapacitor showed (Figure 7f) that the bending had almost no effect on capacitive behavior. The flexible device tested for 1000 cycles in the bent state with only 5% change in performance. Thus, the LSG-based electrode and gelled electrolyte, which solidifies during fabrication, serve as an adhesive that holds the device components together, which helps to further improve the mechanical flexibility of the device.

In this Perspective, we review representative recent works in the organic and energy storage device applications of graphenebased electrodes (including OPVs, OLEDs, OTFTs, LIBs, and ECs) for flexible and even stretchable substrates. The CVD-grown graphene film could enable high-performance organic devices on plastic or elastomer substrates, as demonstrated in diverse application examples. Developing new chemistries for high-quality graphene growth as well as work function tuning would provide interesting opportunities for developing next-generation flexible organic electronics. In addition, graphene-based power sources show encouraging results; still there have been some issues, in particular irreversible capacity, volume production, and cost. The mass production of graphene derivatives using bulk graphite will help in industrial-scale production for applications in LIBs and supercapacitors.

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