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Synthesis, transfer and application of graphene as a transparent conductive film: a review

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Abstract. Transparent conductive films (TCFs) have been widely used as transparent electrodes in nanoelectronic and energy storage devices. An ideal electrode should have high optical transparency, electrical conductivity and carrier mobility to increase the performance and efficiency of devices. Graphene is introduced as a promising new-generation material for the fabrication of transparent electrodes because of its unique electrical, optical and mechanical properties. Consistent efforts, such as the synthesis and transfer of graphene, have been exerted to produce excellent transparent electrodes. This article presents the methods that have been used to produce graphene, such as chemical vapour deposition, solution processing and chemical reduction. In addition, the benefits and drawbacks of several transfer techniques, such as chemical etching from a metal substrate, roll-to-roll process, spin coating, dip coating, drop casting and spray coating, are briefly discussed. For instance, the transfer of graphene for TCF preparation remains challenging. The potential applications of graphene-based TCFs, such as in flexible displays, solar cells, supercapacitors, transistors and electrochromic films, are also discussed.

Keywords. Graphene; coating; transparent conductive film; nanoelectronic; energy storage.

1. Introduction

Owing to high electrical conductivity and good optical transmittance, transparent conductive films (TCFs) have been widely used in (i) energy storage devices, such as solar cells [1–5], field-effect transistors [6] and supercapacitors [7–10], and (ii) optoelectronic devices, such as displays [11], touch screens, organic light-emitting diodes (OLEDs) [12], smart windows and electrochromic devices. Metal oxide-based composite materials, such as indium-doped tin oxide (ITO) [13,14], fluorine-doped tin oxide (FTO) [15,16], tin(IV) oxide (SnO_2), zinc peroxide (ZnO_2), Al-doped ZnO_2 [17], titanium dioxide (TiO_2) nanotubes and In-doped ZnO_2 [18], are the most common materials used in TCF fabrication. ITO has received considerable attention because of its low electrical resistivity (18 Ω cm^{-2}), high optical transmittance ($\sim$80%) within the visible region (550 nm) and high stability under normal conditions [13]. However, the application of ITO in TCF fabrication is limited by its sensitivity/instability at high temperatures, high manufacturing cost, low performance due to brittleness and easily damaged condition [19,20]. FTO is a good replacement of ITO because of its resistance to harsh chemical and thermal treatments (up to 700°C), low cost and sheet resistance stability after sintering (remains $\sim$8.5 Ω cm^{-2}) [13,21]. Recently, a new TCF fabrication method utilizing crackle lithography resulted in lower sheet resistance of the fabricated TCF compared to ITO or FTO. The crackle template improve the electrical conduction thus decrease the films' sheet resistance. Low sheet resistance value of $\sim 5\ \Omega\ \mathrm{sq}^{-1}$ was obtained when the TCF was fabricated by utilizing inexpensive copper (Cu) deposited on the crackle template (Cu mesh/glass) [22]. Lower sheet resistance was further achieved ($\sim 3.5\ \Omega\ \mathrm{sq}^{-1}$) when hybrid electrode was used by coating Al-doped ZnO (AZO) on Cu mesh/glass [23].

Platinum (Pt) is a good catalyst for producing TCF and usually used as a thin film for electrode materials because of its high efficiency. However, the application of Pt in TCF fabrication is limited by its scarcity and high cost. The development of new electrode materials with high transparency, low cost and high conductivity is important for Pt replacement [24,25]. Graphene, a new-generation carbon nanomaterial with 2D honeycomb lattice, is a good replacement for TCF because of its flexibility, high surface area (2360 $\mathrm{m}^2\ \mathrm{g}^{-1}$ of a single graphene sheet (GS)), high optical transparency (97.7%), high carrier mobility (2×10^5 $\mathrm{cm}^2\ (\mathrm{Vs})^{-1}$), superior electrical conductivity ($10^6\ \Omega^{-1}$ cm^{-1}) and excellent mechanical strength (Young's modulus > 1 TPa) [26–29].

Many studies reported on the fabrication of graphene-based TCF. In general, graphene-based TCF exhibits less efficiency than commercial transparent conductive oxides because of the aggregation between graphene layers, less active area ($\sim 100\ \mu\mathrm{m}^2$) and difficulties to produce uniform deposition over the desired substrate. Therefore, the fabrication of large, homogenous and agglomerated-free graphene films is important. Top-down and bottom-up methods are generally used to synthesize graphene. Mechanical exfoliation [29], electrochemical exfoliation/cleavage [5,30] and chemical synthesis based on Brodie, Staudenmaier and Hummers' method [31,32] belong to the top-down method. Meanwhile, epitaxial growth from silicon carbide [29] and thermal- and plasma-assisted chemical vapour deposition (CVD) [33,34] are classified in the bottom-up method. Mechanical cleavage and CVD techniques yield few layers of graphene with a high carrier mobility up to 10,000 cm^2 $(\mathrm{Vs})^{-1}$. However, these methods produce less quantity of graphene films with a small area in the order of a few tens of micrometres. Chemical reduction methods can produce a large quantity of graphene. However, its electrical properties are weaker than those of mechanically exfoliated graphene.

Nowadays, graphene is used in medical, sports, water desalination, gas separation, anticorrosion, sensors and so on [35]. These facts prove that graphene is a rising star in research development. Therefore, a simple and cost-effective method to produce graphene needs to be developed for mass production. Conversely, transferring the as-grown graphene into the desired substrate (usually an insulator) for applications in optoelectronic devices is challenging. The transferred graphene should remain pure, clean, free of contamination from another material and high in quality. An ideal transfer process should yield a uniform and continuous graphene, i.e., without folds, cracks or holes in the substrate [36]. Thus, the main problem is the transfer of as-grown graphene to large-area graphene films with compatible methods applicable to industrial use. Finding a transfer method of graphene to a target substrate is an important issue to be addressed. The separation and transfer of large-area single-layer graphene is another problem in TCF fabrication.

This article briefly discusses the various transfer techniques of graphene synthesis, such as chemical etching from a metal substrate, roll-to-roll process, spin coating, dip coating, drop casting and spray coating, for TCF fabrication. The studies in this field are still widely open to obtain high-quality and low-cost graphene materials. This review is used to understand the transfer of graphene materials and to realize highly efficient TCF fabrication.

2. Synthesis of graphene

CVD, Hummers' method, exfoliation of graphite in aqueous solutions and its reduction are promising methods to produce graphene with high quality and quantity. Figure 1 illustrates the schematic diagram of graphene synthesis.

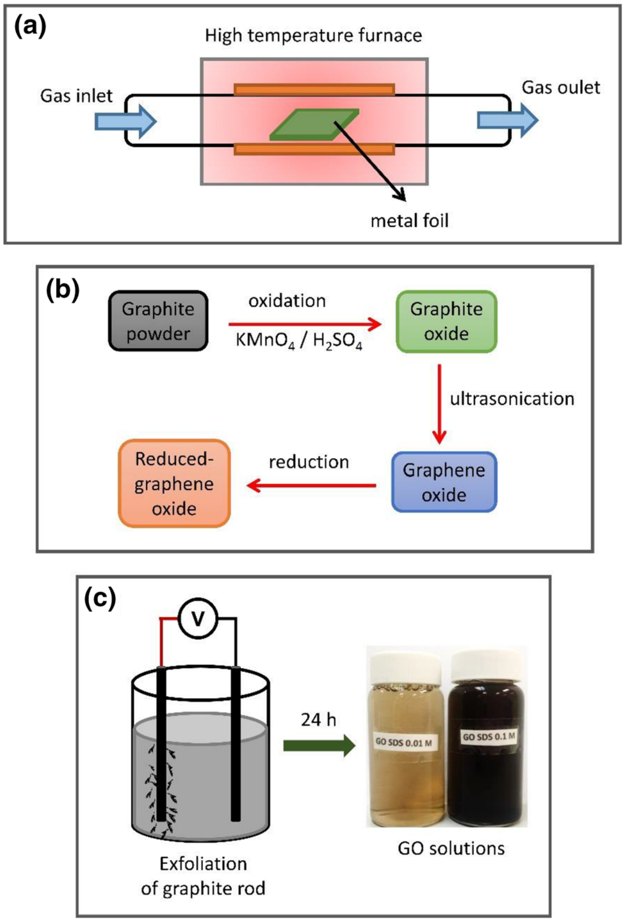


Figure 1. Schematic diagram of graphene synthesis: (**a**) CVD, (**b**) Hummers' method and (**c**) electrochemical exfoliation.

2.1 *CVD technique*

CVD is a favourable technique to produce graphene with high conductivity. CVD is a technique of thin solid film deposition on substrates from the vapour species through chemical reactions. Some variants of CVD techniques include the use of reactors, pressures, carrier gases and temperatures. The unique aspect of CVD techniques is the presence of a catalyst (usually metals). Metals with finite carbon solubility are used to achieve heterogeneous precursor decomposition on the substrate surface through chemical reaction. The catalyst usually used in CVD is copper (Cu) with zero carbon solubility and nickel (Ni). The catalyst controls the chemical reactions by lowering the energy barrier to achieve high-quality films [37].

The first successful graphene deposition via CVD was achieved using Ni by Ni/SiO_2/Si structure [38]. The graphene film grown on Ni is not uniform in thickness over a large area of the deposited sample. The non-uniformity of the thickness is caused by the carbon nature solubility in Ni. The different temperatures between deposition time and cooling process result in the non-uniform arrangement of the precipitated carbon atoms. The challenge of graphene synthesis on Ni is the pyrolysis of the precursor species, commonly hydrocarbon species. Hydrocarbon is not preferred for graphene deposition, except for methane (CH_4), because of the high pyrolysis rates at high temperatures. CH_4 is relatively stable and has simple atomic structure. However, the thermal decomposition of CH_4 is still poorly understood. Therefore, alternative catalysts are needed to replace Ni because it promotes the deposition rate that forms the uniformity of graphene film [37].

Given the problems related to Ni, a new catalyst Cu with almost zero carbon solubility even at 1000°C is introduced to replace it. Li *et al* [39] showed that graphene has good uniformity when grown on Cu foil at 1000°C using a mixture of methane and hydrogen as a precursor. Continuous graphene film is obtained with the wrinkle structure because of the difference in thermal expansion between Cu and graphene. A similar synthesis process to produce graphene using CVD was reported elsewhere using PET and silicon (Si) substrate [40–42].

Other CVD variations are the involvement of plasmas, ions, photons, lasers, hot filaments and combustion reactions [43]. Some modifications of CVD have been carried out to reduce temperature and shorten deposition time. Kim *et al* [44] reported the low-temperature synthesis of large-area graphene by using surface wave plasma CVD (SWP-CVD). They obtained a few layered graphene at 300–400°C using methane gas mixed with argon and hydrogen. The graphene film produced from this SWP-CVD technique exhibits a transmittance above 80% with a low resistivity about 2.2 $k\Omega\ sq^{-1}$. Similarly, Vlassiouk *et al* [45] introduced the atmospheric pressure CVD technique to produce large-scale graphene materials on Cu foils. This procedure eliminates the difficulties of low-pressure CVD and produces large-area (100 μm) graphene films on Cu. The as-grown graphene film is then transferred to the desired substrates by using a suitable transfer process explained in the next section.

The advantages of this technique are the utilization of low vacuum, high yield and deposition rate with high purity and controllable film thickness of the deposited material. However, the synthesis process of graphene using CVD also possesses several drawbacks. The CVD technique requires high-cost equipment and precursor (such as metal–organic precursor). The CVD precursor can be highly toxic ($Ni(CO)_4$), explosive (B_2H_6) and corrosive ($SiCl_4$). CVD also requires very high temperatures up to 1600°C, which makes some restrictions to the coated substrates. In addition, the heating and cooling processes are time consuming because of the high-required temperature. Another drawback is a complex transfer process, which involves a wet chemical technique. The by-products of CVD reactions, such as carbon monoxide (CO), dihydrogen (H_2) and hydrogen fluoride (HF), can also be hazardous [43]. These several drawbacks become the limitation of this method, and solution processing of graphene offers an easier method to produce graphene.

2.2 *Solution processing of graphene*

Solution-based graphene can be obtained from the dispersion of graphene powder produced from the reduction of the exfoliated graphene oxide (GO) based on Brodie, Staudenmaier and Hummers' method or some modifications of these methods [46–49]. The initial GO based on Brodie method needs 3 or 4 days of synthesis time, which is then improved by Staudenmaier. However, both methods producing highly toxic and explosive gas need to be replaced by other methods [50]. Hummers' then proposed an alternative oxidation method to avoid that. In brief, graphite flakes were placed in a flask along with sodium nitrate and sulphuric acid and stirred in an ice bath to cool down its temperature. Potassium permanganate was then added and maintained the temperature at <20°C. After diluting the mixture with distilled water, hydrogen peroxide is added to stop the oxidation process, and the resultant slurry is washed with distilled water to obtain graphite oxide. Finally, the as-prepared graphite oxide is dispersed in distilled water and ultrasonicated, filtered and dried to produce GO powder [31]. Many modifications of this method (modified Hummers' method) are usually carried out on the second step of oxidation [32,47,48]. The synthesized GO based on Hummers' method presents good properties. However, the utilization of toxic chemicals and the complex synthesis process limits this method for large-scale production.

GO can also be synthesized by exfoliating graphite as a starting material in aqueous solution by the presence or absence of a surfactant and offers a simpler synthesis process than Hummers' method [51–56]. Nitric acid, sulphuric acid, sodium sulphate and lithium sulphate are usually used as electrolytes in the absence of a surfactant. Meanwhile, water is usually used as an electrolyte in the presence of a surfactant. The two types of surfactants usually used are (i) ionic surfactants, such as sodium dodecylbenzene sulphonate and lithium dodecyl sulphate, and (ii) non-ionic surfactants, such as Triton X-100, Tween-80, Tween-60, Tween-40 and Tween-20 [57]. The natural properties of surfactants help to form stable graphene dispersion because of the ability of the hydrophobic chain of surfactants to link up with graphene particles. Alanyalioglu *et al* [51] showed the effect of surfactant and the applied intercalated potential on the structure, size and number of graphene layer. They successfully produced several sizes of graphene (average of 500 and 1 nm) when they use intercalated potential from 1.3 to 2 V.

GO has a wide range of oxygen functionalities, such as 1,2-epoxide and alcohol groups on the basal planes and carboxyl and ketone groups on the edge planes [58]. Unfortunately, the utilization of GO for electrical applications is less desirable because of the high oxygen (O) content in GO structure and its low conductivity. The chemical or thermal reduction of GO is usually performed to produce high-quality graphene with increased conductivity and low GO agglomeration [50]. Several factors that influence the oxygen atomic ratio and electrical conductivity of reduced GO (rGO) are the chemical identity of the reductants, particle size of graphite, oxidation methods for preparing GO, reaction temperature and solvents [59]. Several reductants known for GO reduction are hydrazine hydrate, 1,1-dimethylhydrazine, hydroquinone and sodium borohydride ($NaBH_4$). Among many reducing agents, hydrazine hydrate is a common material for GO reduction [59,60]. Hydrazine hydrate is the preferable reductant to produce thin and fine rGO [61].

Park *et al* [59] reported the reduction of GO by adding hydrazine solution. In this process, 3 mg ml^{-1} GO solution is prepared by ultrasonication and then 1 μl of hydrazine is added to the GO solution under constant stirring. The solution is heat treated in an 80°C oil bath for 12 h under moderate stirring. Lee *et al* [60] reported another reduction process, wherein 3 g of GO is directly mixed with 0.6 g of solid hydrazine and ground by mortar, which is then stored in a glass pressure bottle to perform the reduction process. Meanwhile, Suriani *et al* [62] utilized 1 ml of hydrazine for a 100 ml GO solution, which is stirred for 24 h with the maintained temperature of ~95°C. The major problem in this technique is the optimization of reduction parameters, such as hydrazine concentration, reduction temperature and time.

However, hydrazine is a hazardous chemical. Hence, it requires high precautionary during experiments. Thermal reduction offers a green and easy route for GO reduction. Unfortunately, the high temperature (up to 1100°C) required during the process has become the limitation of this technique, especially in applications using low heat-resistant substrates. Poorali and Bagheri-Mohagheghi [63] compared the thermal and chemical (by utilizing $NaBH_4$ and hydrazine hydrate) reduction processes of GO, which was initially synthesized by Hummers' method. On the basis of several characterizations, 3 ml of hydrazine hydrate was added to 100 mg ml^{-1} GO still it results in higher crystallinity, wrinkled graphene layers and lower bandgap energy as compared with other samples. In addition, hydrazine hydrate presents high performance to remove oxygen content in GO.

3. Transfer of graphene

Several transfer processes of graphene to prepare TCF are chemical etching from metal substrate, roll-to-roll process, spin coating, dip coating, drop casting, vacuum filtration transfer, screen printing, Langmuir–Blodgett (LB) and spray coating.

3.1 *Chemical etching from metal substrate*

Chemical etching is widely used to separate the CVD-grown graphene from the catalyst substrate and transfer it to a desired substrate. In this process, the as-grown graphene film with metal foil (Ni or Cu) substrate is immersed in a suitable solvent and the metal foils are allowed to dissolve in the solvent. After being completely dissolved, the graphene layers are then recovered from the solution. For example, graphene film grown on Cu foil is removed by chemical etching treatment using a 0.05 g ml^{-1} iron nitrate solution and transferred to a substrate. Two methods are used to transfer CVD-grown graphene films. One is the direct transfer using etching and scooping. After the catalyst is dissolved by immersing it in an etchant, the floating GS is then scooped and placed on the substrate. The simple process with few steps is the advantage of this technique. However, the low quality caused by the cracked GS possibly occurs during scooping. The etchant is also possibly involved during the transfer process, which degrades the electrical properties of graphene [37]. Therefore, this simple technique is not preferable because of the low-quality end product, which is easily damaged.

The other method is the initial coating of polydimethylsiloxane (PDMS) or polymethyl methacrylate (PMMA) on the as-grown graphene film before the etching of Cu. The PDMS or PMMA layer is then washed and placed on SiO_2/Si and glass substrates. Then, the PDMS or PMMA layer is removed with acetone. A better graphene film is obtained from this technique. Somehow, defects such as cracking and low attachment between graphene and target substrate are observed. The metal surface (Cu foils) is rough at high temperatures during the grown/deposition of graphene. As a consequence, the as-grown graphene follows the metal surface. When graphene is transferred to another substrate, it does not lie flat on top of the substrate surface. Some small gaps appear between them, and cracks make graphene break easily.

Li *et al* [64] improved that technique by introducing a second deposition of PMMA coating after the PMMA–graphene is placed on the target substrate. This additional process is meant to reduce the stiffness of graphene, thus improving contact with the target substrate. The film has a thickness uniformity, although some wrinkles are observed from this method. Copper is a common substrate used for CVD graphene growth, and it is also usually removed by using popular aqueous chemical etchants, such as iron nitrate, iron chloride and ammonium persulphate. Even if these etchants effectively remove the copper substrate, the resultant graphene films with oxidized metal particles are hard to remove by normal washing. The PMMA-mediated transfer technique slightly reduces the formation of metal oxide particles, but the amount of metal oxide must be further reduced to obtain high-quality graphene films.

Liang *et al* [36] introduced a new transfer process, such as 'modified Radio Corporation of America (RCA) clean' transfer technique. In this modified RCA clean process, the metal particles are removed by using $H_2O/H_2O_2/HCl$ (standard clean 2), and $H_2O/H_2O_2/NH_4OH$ solution is intended to remove organic contaminants (standard clean 1), which are reversible steps of the standard RCA clean process. Furthermore, they diluted the solution concentration from 5:1:1 to 20:1:1 and cleaned at room temperature to prevent the graphene from aggressive H_2O_2 solution. In general, chemical etching from metal substrate can produce high-quality graphene. However, the application of this transfer method is limited by the high cost of equipment and material, high experiment skills needed and inability to produce large-area graphene.

3.2 *Roll-to-roll process*

Roll-to-roll transfer offers a highly transparent large-area graphene film at very low cost [65,66]. In general, the roll-to-roll transfer process is similar to the polymer-assisted chemical etching transfer method in which polymer support is attached to the as-grown graphene on Cu foil. Then, the copper layers are electrochemically removed by using 0.1 M ammonium per sulphate ($(NH_4)S_2O_8$) solution. Finally, graphene layers are recovered from the solution and transferred to a target substrate [65]. A temperature gradient exists during this process, which leads to the formation of inhomogeneous graphene films. However, it can be minimized by altering the radial position of the roller by wrapping a copper foil over the quartz tube in hydrogen atmosphere.

Bae *et al* [65] used a thermal release tape as a polymer support and attached to the graphene film grown on copper foil by applying pressure of ~0.2 MPa between two rollers. A PET substrate is then rolled between the rollers at ~90–120°C to make contact with the graphene–polymer sheet. The polymer support is then detached by thermal treatment leaving the graphene film only on PET substrate. Then, graphene films are transferred to the desired substrate with a transfer rate of 150–200 mm min^{-1}. On the basis of Raman spectroscopy, the graphene films produced from this technique are composed of monolayer graphene. However, bilayer and multilayer graphene are observed using atomic force microscopy and transmission electron microscopy. This process produces 30 inches (in the diagonal direction) graphene films with a low resistance (125 Ω sq^{-1}) and high transparency (~97.5%).

Juang *et al* [67] synthesized few-layered graphene (FLG) on Ni foil by CVD. In this process, ethylene-vinyl acetate copolymer (EVA)-coated transparent polyethylene terephthalate (PET) polymer sheets are used as the target layer and pressed on the FLG/Ni sheet to form a double-sided PET/EVA/FLG/Ni sheet by using hot rollers at 150°C. Then, the PET/EVA/FLG/Ni sheet is allowed to enter the cold roller at room temperature to remove the Ni layer. As a result, they obtained 2×3 cm^2 transparent flexible FLG/EVA/PET films and they found that the transmittance of the films is inversely proportional to the FLG layer thickness. The roll-on-roll process has the potential to produce large-area graphene. However, these methods require high-cost and sophisticated equipment.

3.3 *Spin coating*

Spin coating is a simple method to prepare paper-like graphene films with excellent mechanical, electrical and optical properties [46,68]. Chemically reduced few layered graphene films usually have the sheet resistance of ~4 MΩ sq^{-1}. However, this high resistance is unsuitable for transparent electrode fabrication. Thus, injection of intensive charge or other modifications are needed to improve the conductivity of solution-processed graphene films. Wu *et al* [69] applied thermal and chemical reduction steps to deoxygenate the graphene films and restore conductivity. As a result, they achieved the conductivity in the order of 10^2 S cm^{-1} with 80% optical transparency.

Kymakis *et al* [46] developed spin-coated graphene films on a glass substrate as TCF in organic photovoltaic devices. Initially, GO powder is synthesized using modified Hummers' method and further dispersed in water with a concentration of 15 mg ml^{-1}. Then, the GO solution is spin coated on a preheated (200°C) glass substrate at 500–1000 rpm for 10 s followed by 5000 rpm for 30 s. The coated film is then dried in a nitrogen-filled glove box at 80°C, hydrazine treated to obtain rGO film and then annealed in argon ambient at 400, 800 and 1000°C. Important findings from this study are as follows: (i) the transparency and sheet resistance of graphene film reduce with increasing film thickness and (ii) sheet resistance and film transparency decrease with increasing annealing temperature. Another study reported on the deposition of colloidal GO (1.0 mg ml^{-1}) on ITO substrate at 800 rpm. In this spin coating transfer process, the graphene film thickness can be easily controlled by the concentration of solution, rotating speed, gas condition and number of coating [68].

Chang *et al* [70] tried to reduce the sheet resistance below 100 Ω sq^{-1} by doping the chemically derived GO with conducting polymers and spin coated on PET substrates. Finally, they achieved a PET/graphene-poly (3,4-ethyldioxythiophene) (PEDOT):poly 3-styrene sulphonate (PSS) sheet resistance of 80 Ω sq^{-1} with 80% optical transparency. Interestingly, Eda *et al* [71] prepared phenyl isocyanate-treated functionalized GO and spin coated on degenerately doped Si for field-emission studies. In this work, they obtained 10–50 nm-thick graphene composite films. The thickness of the films is varied by altering the spin coating speed. They also found the relation of the spin coating speed to the resistivity of the composite film. They concluded that 600 rpm is suitable to obtain highly conductive films. Similar results were also obtained by Vorotilov *et al* [72]. Results from this study are as follows: (i) the higher the spin coating speed, the thinner the film thickness obtained, (ii) the higher the spin coating speed, the higher the percentage of film uniformity obtained, and (iii) the higher the spin coating speed, the less film conductivity obtained.

Hong *et al* [73] also prepared a graphene/PEDOT:PSS composite material and spin coated on ITO substrate at 7000 rpm for 30 s. In this study, they achieved ~90% of transmittance and used it as a counter electrode (CE) for DSSC fabrication. Meanwhile, Lee *et al* [74] prepared highly controllable transparent conductive rGO films by layer-by-layer deposition. Prior to the deposition process, positively and negatively charged rGO was prepared by chemical method, and it was spin coated over piranha-treated quartz/Si substrate. During the deposition process, they coated the graphene material (first layer) at 3000 rpm of spin coating speed for 30 s and waited for 2 min to make another deposition (second layer). This was then represented as a single bilayer, in this way they achieved number of bilayers. The resultant multi-layered graphene film showed 75% optical transmittance with an electrical resistivity of 2.5 kΩ sq^{-1}. However, the uniformity of the graphene film produced using this method is relatively low, and the coating deposition can only cover a small area of the substrate.

3.4 *Dip coating*

In dip coating, a substrate is immersed into a solution containing uniformly distributed graphene material and then pulled out with a certain constant speed under controlled temperature and atmosphere. Dip coating is the easiest and most favourable economical technique to produce low-cost GO films. Liu *et al* [47] reported the dip coating of graphene on aluminium (Al) substrate as an anticorrosion barrier. First, GO powder is synthesized from Hummers' method and then 0.015 g GO powder was dispersed in 50 ml of deionized (DI) water and sonicated for 10 h at room temperature to obtain GO solution with a concentration of 0.3 mg ml^{-1}. Al foil substrate is then immersed in the GO solution. Prior to immersion, Al foils are etched in NaOH solution and then immersed in nitric acid and rinsed with DI water. Dip coating of graphene was carried out at rise rate of 2 cm s^{-1} at room temperature and air dried for 4 h. This process can be adopted for the deposition of graphene on other flexible transparent substrates.

Wang *et al* [75] reported the deposition of GO sheets on pre-treated quartz substrate by dip coating of hot GO dispersion, and film thickness is controlled by varying the solution temperature and dipping iterations. Then, the GO film was reduced into graphene using thermal annealing at 1100°C under Ar and/or H_2 flow. They concluded that the conductivity of graphene film depends on the annealing temperature and film thickness. As a result, the electrical conductivity of graphene film increases from 550 to 727 S cm^{-1} when the film thickness is increased three times from ~10 nm. Wöbkenberg *et al* [76] demonstrated the patterning of chemically derived graphene onto a glass substrate by LB dip coating. In this process, the partially oxidized graphene monolayer (~1 nm thickness) is deposited and then annealed at 500°C to induce thermal reduction. This contact transfer deposition is repeated for four times to form a four-layered film with thickness ~4 nm and exhibits an optical transparency of 95% and electrical resistivity of 30 kΩ sq^{-1}.

Zheng *et al* [77] introduced LB-coupled dip coating to prepare graphene-based transparent conducting films. In this process, GO synthesized from Hummers' method forms a monolayer GO by LB, which is then compressed by moving barriers at a speed of 10 mm min^{-1}. Then, the monolayer GO is transferred into a quartz substrate at various compression stages by dip coating. The quartz substrate is vertically dipped into the solution and pulled out at a speed of 0.1 mm min^{-1}. Thus, this LB-coupled dip coating process produces gram-scaled ultra-large (50–200 μm) GO films with a transmittance of 90% and a sheet resistance of 459 Ω sq^{-1}. This dip coating technique is simple and does not require sophisticated equipment. Unfortunately, the inconsistent film thickness and large volume of graphene solution limit the industrial-scale application of this method.

3.5 *Spray coating*

Spray coating transfer is a simple, fast and low-cost technique to prepare large-area graphene films. Prior to this transfer process, the synthesized GO materials are ultrasonically dispersed in a suitable solvent. Then, the dispersion is sprayed on a preheated substrate using an airbrush system. Pham *et al* [78] achieved high transmittance (84%) with low sheet resistance (2.2 kΩ sq^{-1}) by transferring chemically converted graphene using spray deposition. They mixed GO with an excess amount of hydrazine monohydrate solution in a ratio of 1:3. A spraying rate of 3 ml min^{-1} and an N_2 inlet pressure of 2 bar are used in this method. They use quartz as a substrate, and the spraying distance between the substrate and the tip of the nozzle is 12 cm. Various preheating temperatures (190–295°C) were used to investigate the effect of temperature. Surprisingly, the preheating temperature significantly affects the sheet resistance and transmittance of the film. The sheet resistance decreases with temperature when the preheating temperature is below 240°C, and *vice versa*. Moreover, the spray volume of the solution affects the transmittance. The transmittance increases slightly with temperature and decreases with spray volume.

Cruz *et al* [24] investigated the effect of GO and rGO before and after annealing with the transmittance to produce graphene film by spraying. They used FTO as a substrate to deposit graphene films. Their results showed that the film transmittance decreases after annealing. The thin film can be produced by electrophoretic deposition, but this technique is time consuming and requires expensive equipment. Beidaghi *et al* [79] prepared graphene by electrostatic spray deposition (ESD). The thickness of film is controlled by the spraying time and concentration of the solution. A high voltage (3–5 kV) can be applied between the nozzle and the heated substrate to obtain uniform film with an open pore structure. This high potential atomizes the solution at the tip of the nozzle. During the deposition process, the solution lands on the surface and forms a thin film upon the evaporation of the solvent. The thickness and morphology of the graphene films can be controlled by adjusting the flow rate, substrate temperature, applied voltage and solution concentration. This ESD deposition offers the combination of small-size droplet and rapid evaporation of the solvent, which allows the formation of porous films which provide high ion accessibility in electrochemical energy systems.

Wang *et al* [80] introduced superhydrophilic-assisted electro-hydro dynamic spraying deposition (SH-ESD) to achieve partially unfolded graphene coating without ring-shape aggregation. They modified borosilicate glass used as a substrate with superhydrophilic surface treatment. The applied high voltage and the flow rate were $\sim$3 kV and 1 ml h^{-1}, respectively. The distance between the nozzle and the substrate was 9 cm, and the deposition time varied from 1 to 20 m. The optimized substrate temperature was obtained at 140–160°C. Uniform deposition without ring-shape aggregation and 63% coverage surface is obtained from this technique. Meanwhile, Kim *et al* [81] developed a unique kinetic spray deposition technique with 6 bar air jet pressure attached with the syringe. This supersonic acceleration system provides a large amount of energy, and the precursor is atomized upon high-speed gas stream. As a result, the graphene is stretched, and the defects on films are healed. They obtained the graphene film with a transmittance of about 72.7% and sheet resistance of 19 kΩ sq^{-1} by using this supersonic kinetic spraying technique. They also demonstrated that the concentration of precursor directly influences the film transmittance. For instance, 10–33 wt% rGO in the suspension reduces the transmittance from 70 to 30%.

Blake *et al* [82] also employed this simple spray deposition technique. They prepared graphene suspension by chemically exfoliating graphite rather than graphene/graphite oxide. This graphene suspension is spray deposited on preheated glass substrate and annealed for 2 h at 250°C in Ar/H_2 (9:1) atmosphere. The calculated film thickness is $\sim$1.5 nm, which is about 4–5 layers of graphene, the resultant optical transmittance is 90% and the sheet resistance is in the order of 5 kΩ sq^{-1}. Overall, the spray deposition transfer technique is promising for large-area graphene coating on various substrates without the aggregation between GO sheets and for obtaining uniform film thickness.

3.6 *Drop casting*

Drop casting transfer is an effective method for the self-assembly of rGO by solution evaporation to produce flexible, transparent and conductive graphene films. This drop casting technique is quite similar to spray coating; in this process, the graphene-suspended solution is dropped onto the preheated substrate instead of spraying. It is a facile method to transfer a single-layer GS into a desired substrate for device fabrication [83]. Li *et al* [84] transferred a single-layer graphene by drop casting the diluted solution of chemically converted graphene into a Si wafer substrate.

Xu *et al* [85] prepared a graphene/PEDOT composite material by polymerization and drop casted on the various substrate. The film thickness and transparency can be controlled by varying the solution concentration. Films with thicknesses of 33, 58, 76 and 103 nm exhibit 96, 76, 51 and 36% transmittance, respectively. By contrast, the film thickness does not influence the resistivity; for example, films show a conductivity of $\sim$0.2 S cm^{-1} when the film thickness is increased from 35 to 119 nm. The conductivity of the film was measured under the application of some bending forces. When the bending force is increased, the resistance of the film is gradually increased and its conductivity returns to the original value when the force is released. Yin e*t al* [86] also studied the conductivity of graphene thin film under the application of mechanical bending force. Prior to this experiment, graphene solution is drop cast on the PET film and vacuum dried, producing 65% transparency with 670 kΩ sq^{-1} sheet resistivity. Finally, they found that the film retains its conductivity after being bent at an angle of 45° for more than 1500 times. Kavan *et al* [87] fabricated CE by using commercially available graphene by drop casting. Without any annealing process, they achieved a film transmittance of ~85% and an efficiency of 9.6%, which is relatively higher than that of Pt-based CE. Apart from being simple and material saving, this method cannot control the film uniformity. Moreover, only a small-area coverage is produced through this method, and GO sheet surface reduces the evaporation path of the solvent, thereby prolonging the evaporation time.

3.7 *LB technique*

The LB technique is used to transfer GS dispersed on the water surface to the substrate by immersion or dip coating. The first step of LB technique is preparing GS suspension, which can be produced by exfoliation or modified Hummers' method and further transferred by vertical dipping. The GS suspension is dispersed on the subphase surface, and then the substrate is slowly pulled out from the aqueous solution. The substrate is then annealed, and one layer of graphene film is already formed. Li *et al* [88] reported that the smallest sheet resistance can be obtained from three layers of LB films with a transparency of 83%. Meanwhile, Sutar *et al* [89] successfully obtained a single-layer graphene with average thicknesses of (1.16 ± 0.09) and (0.9 ± 0.13) nm for GO and rGO sheets, respectively. The size of graphene sheets in their research was 20–40 μm. Qing-bin *et al* [90] obtained 86% film's transparency and 605 Ω sq^{-1} of sheet resistance by utilizing this method.

The LB technique offers a simple, low-cost and tuneable method for the mass production of graphene films. Unfortunately, some parameters required in the LB technique limit the applications of this method. The first one comes from surface pressure during the deposition. A high-enough surface pressure is needed to ensure the cohesion in the monolayer and obtain a homogeneous deposition of multilayer graphene films. The pulling speed during deposition also needs to be considered to achieve homogeneous and good-quality films. Other parameters include the nature of the spread film, the type and nature of the solid substrate and subphase properties (composition, pH and temperature).

Several transfer methods of graphene with its advantages and drawbacks are summarized in table 1. Meanwhile, the resistivity and transmittance value of the fabricated TCF utilizing different synthesis and transfer method are tabulated in table 2.

4. Graphene for transparent conductive film application

TCF is now a leading component in nanoelectronic field because of its wide range applications, such as in solar cell devices, displays, sensors, transistors, supercapacitors, lasers and light-emitting diodes. A great demand is also addressed on flexible TCF, such as for flexible touch screen panel and displays. Apart from being flexible, transparent, conductive and light, TCFs should also satisfy the market requirements by considering the large-scale and low-cost fabrication process. Here, we discuss the role of graphene-based TCF in various nanoelectronic and energy storage devices.

4.1 *Flexible displays*

One of the most popular applications of graphene-based TCF is its use as flexible displays. Many replacements of ITO have been introduced for TCF applications, such as metals (Ag, Au), metal oxides (ZnO, TiO_2) or alloy-based (Ag/Au) materials, with high electrical conductivity and transmittance [91–94]. However, they are not as flexible, stretchable and robust as graphene. A large area of 30-inch flexible graphene-based TCF transferred on PET substrate using roll-to-roll process has been applied as a touch-screen panel device with a high optical transmittance of 90% and a low sheet resistance of 30 Ω sq^{-1} [65]. Han *et al* [41] used graphene as an anode to replace ITO for OLED, resulting in reduced sheet resistance and low work function. The current efficiency (CE = 30.2 cd A^{-1}) and luminous efficiency (LE = 37.2 lm W^{-1}) of the graphene film were also studied. The efficiency of graphene-based OLED device is higher than those of ITO (CE = 13.7 cd A^{-1}, LE = 16.1 lm W^{-1}) and carbon nanotube (CNT) (CE of 15.8 cd A^{-1} and LE of 14.5 lm W^{-1}) based devices.

Graphene sheets vertically aligned on various substrates (Si, ITO and stainless steel) possess good field electron emission characteristics with low turn-on and threshold fields, high field enhancement factor and good stability [95–97]. Thus, graphene sheets show a promising application of graphene for flexible field-emission display. The hybrid structures of graphene/CNTs have been studied and show potential applications in transparent and flexible field-emission devices. Graphene is initially grown using CVD on a Cu foil and then transferred to PET substrate using hot press lamination. A CNT solution is further spin coated on the transferred graphene to obtain the graphene/CNTs cathode. It was reported to have low turn on (2.05 V μm^{-1} at 1 μA cm^2) and threshold fields (2.2 V μm^{-1} at 10 μA cm^2) and excellent stability for 10 h of measurement [98]. Viskadouros *et al* [99] explored another route to study the field emission of rGO by compositing it with poly(3-hexylthiophene) (P3HT)-conducting polymer. However, the field-emission performance is still lower than those in previously mentioned studies. Studies in this field are still widely open to fabricate high-performance flexible displays.

4.2 *Solar cells*

Rising demand for energy gives a positive impact on the rapid increment of research related to alternative energy

Table 1. Several transfer method of graphene with its advantages and drawbacks.

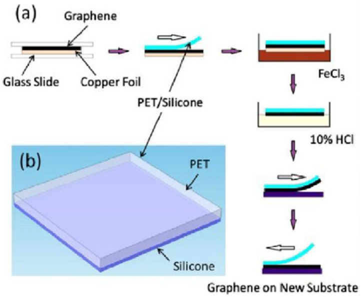
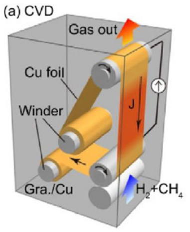
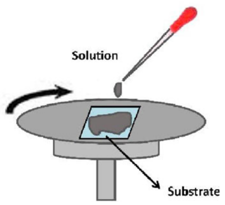
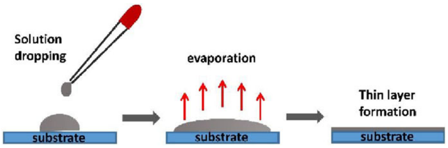
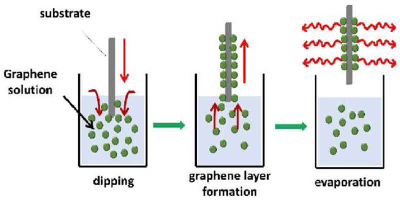
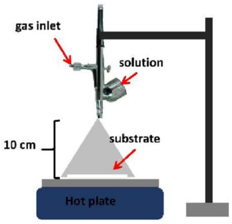
Transfer method	Schematic diagram	Advantages	Drawbacks
Polymersupported chemical etching		– High quality	– High cost – Complex handling skill – Not suitable for large area transfer
Roll-to-roll		– Potential for large area transfer	– High cost – Sophisticated equipment
Spin coating		– Simple – Low cost – Easily controlled	– Low uniformity – Cover limited coating area
Drop casting		– Simple – Material saving	– Hard to control the thickness – Not suitable for large area coating
Dip coating		– Simple – Cheap – Potential for large-scale	– Need a large volume of solution
Spray coating		– Promising for largescale coating – Easy controlled – Suitable for various materials and shape of substrates	– Aggregation of solution droplets often occur

Table 2. Comparison of resistivity and transmittance values of the fabricated TCF utilizing different synthesis and transfer methods.

Synthesis–transfer method–substrate	Resistivity (Ω sq^{-1})	Transmittance (%) at 550 nm	References
Hummers'–drop casting–quartz	200	70	[83]
CVD–chemical etching–glass	2.1×10^3	90	[64]
Hummers'–drop casting–PET	21.75×10^3	82	[101]
Hummers'–spray coating–glass	2.2×10^3	84	[78]
Hummers'–spray coating–glass	20×10^6	96	[84]
Exfoliation–transfer printing–quartz	1.598×10^3	~80	[77]

sources. The popular one is the utilization of solar energy, which is sustainable, environmental friendly, inexpensive and renewable. The first generation of Si-based solar cells has been widely used and showed a high conversion efficiency up to ~20% [100]. However, it requires a high fabrication cost, resulting in expensive Si-based solar cells, especially for large-scale applications. Meanwhile, the second and third generations based on hybrid materials and dye-sensitized solar cells (DSSCs) offer cheaper fabrication cost. Many studies reported on graphene-based hybrid solar cells and DSSCs [102–105]. Graphene can act as either a CE or active material in a photoanode.

Liu *et al* [102] prepared hybrid organic/inorganic solar cells by using carbolic acid (COOH)-functionalized GO composited with TiO_2. Their result shows that P3HT/GO-COOH-TiO_2 is a good acceptor used in hybrid solar cells. The GO-COOH-TiO_2 composite was mixed with P3HT and spin coated on PEDOT:PSS-coated ITO substrate. A 100 nm-thick Al layer was deposited on the top of sandwich structure and tested under 100 mW cm^{-2} UV irradiation. Short current density and power conversion efficiency of the GO-COOH-TiO_2 were obtained to be 1.83 mA cm^{-2} and 0.367%, respectively, which are higher than those of P3HT/TiO_2 only (short current density of 0.127 mA cm^{-2} and efficiency of 0.015%). Here, the addition of functionalized GO sheets successfully increases the connection of TiO_2 nanorods and hence improves the electron transfer in the P3HT/TiO_2 structure.

Yun *et al* [1] used transparent electrode-based rGO for organic photovoltaic cell (OPV) application. The GO was initially synthesized via modified Hummers' method and reduced with a *p*-toluenesulphonyl hydrazide-reducing agent. The rGO solution was then spin coated on a UV/O3-treated glass substrate. The film thickness was controlled by coating cycles (1–7 cycles). For OPV fabrication, a 80 nm-thick Al layer is deposited followed by PEDOT:PSS coating on the rGO substrate (5000 rpm, 40 s). The film is then annealed at various temperatures (100–200°C) for 10 min followed by the deposition of the P3HT/phenil-C61-butyric acid methyl ester-active layer and Ca/Al top electrode. The rGO-7 cycles annealed at 200°C produce the lowest sheet resistance and best device performance with the highest short current density, fill factor and efficiency of 2.26 mA cm^{-2}, 25.67 and 0.33%, respectively. However, these values are still lower than those of ITO-based cell prepared with a similar procedure in this study (short current density of 8.93 mA cm^{-2}, fill factor of 61.09 and efficiency of 3.19%). This study noted that the electrical conductivity of the film plays a significant role in the performance of the solar cell device. A highly conductive graphene-based TCF must be fabricated to obtain a high-performance solar cell device.

Meanwhile, DSSCs have become a promising alternative device for energy storage because of the easy processing, environmental friendliness, low-cost and relatively high-energy conversion efficiency. TiO_2 is commonly used as a photoanode, but several highly electrically conductive carbon materials, such as fullerene, CNTs and graphene, are introduced into TiO_2 to improve the performance of DSSCs. Zhu *et al* [106] investigated graphene–TiO_2 composite as a photoanode. Their result shows that DSSCs based on the graphene–TiO_2 composite photoanode exhibits higher energy conversion efficiency (4.28%) than DSSCs based on pure TiO_2 photoanode (3.11%). Similar studies were also performed by Bkakri *et al* [107] and obtained higher power conversion up to 6.3% from DSSCs based on graphene/TiO_2. The graphene/TiO_2 photoanodes are coated on FTO substrate via a doctor blade method and the dye-adsorbed photoanodes are sandwiched with platinum (Pt)-coated FTO CE. The cell performance was then measured using a solar simulator with a 150 W Xenon lamp source (100 mW cm^{-2}). High short current density was obtained to be 15.08 mA cm^{-2}. By the introduction of highly conductive graphene into TiO_2 network, the electron transport was improved and the charge recombination which usually lowers the DSSC performance was reduced.

Pt is commonly known as CE for high-efficiency DSSCs. However, given their high cost, several carbon-based materials were widely investigated including graphene as Pt replacement. Owing to the large surface area and high electrical conductivity of graphene, it can help improve the electron transfer in DSSCs and hence increase the energy conversion efficiency of the cell. Li *et al* [108] deposited graphene film on FTO substrate by introducing polyvinyl pyrrolidone as a wrapping agent. They used a simple doctor blade method and obtained a uniform and smooth thin film. The film then used as CEs and exhibits 3.01% conversion efficiency. The hybridization of graphene with multi-walled CNTs (MWCNTs) was also done to improve CE performance. Their hybridization results in higher efficiency as compared with pure film [104,109]. However, its efficiency is still lower as compared with the Pt as CE. The challenge to produce low-cost and large-area graphene-based TCF is still a main motivation for the researchers to fabricate high-performance solar cell devices as comparable as Si-based solar cell.

4.3 *Supercapacitor*

Supercapacitor as energy storage offers fast and high power capability, long life cycle, wide thermal operation range, simple charging circuit, no memory effect, safety and low-cost maintenance [110,111]. Supercapacitors have two energy storage mechanisms, i.e., electrical double-layer (EDL) capacitance and pseudocapacitor. EDL capacitance contains activated carbon with a high surface area as the electrode material. Graphene is a promising candidate for electrode material for supercapacitor applications owing to its high surface area and electrical conductivity. The specific capacitance of graphene-based supercapacitors is in the range of $\sim$99–550 F g^{-1} [9,10]. However, graphene sheets are easily agglomerated and stacked because of the strong van der Waals interaction between the layers [112]. This phenomenon often leads to the reduction of active area, electrical conductivity and capacitance of graphene, which are not preferable for supercapacitor applications. Hence, many efforts have been exerted to improve the performance of graphene-based supercapacitors. Such efforts include the use of hybrid graphene-conducting polymer [8] and graphene/metal oxide composites [112,113].

The combination of graphene and metal oxide semiconductors can reduce the aggregation of graphene sheets and thus improve the active surface area and electrical conductivity of graphene/metal oxide nanocomposites. The nanocomposite structure of graphene and metal oxide semiconductor can complement and cover the shortage of each other and result in high-performance supercapacitors. As well as flexible displays, flexible transparent supercapacitors have also recently gained great attention for future applications in energy storage devices. Sarker and Hong [114] fabricated a PANi-RGO flexible transparent electrode on PET substrate and achieved a specific capacitance of 529 F cm^{-3}. Without any metal current collector, the sample exhibits a good cycling stability and rapid charge/discharge rate. The capacitance performance can be enhanced by various routes, such as the use of other composite materials, electrolytes and the improvement in device fabrication technique.

4.4 *Transistor*

A transistor is an important basic component in semiconductor field and electronic devices. Owing to its excellent electrical properties, such as high carrier concentration, high thermal conductivity and high transparency, graphene is a promising material for transistor application [115]. High-performance transparent flexible graphene-based transistors and inverters were fabricated with low voltage operation (<2 V), high on-current and mobility of 628 cm^2 (Vs)$^{-1}$ and $\sim$84% transparency at 550 nm [116]. Flexible transparent films of graphene heterostructures such as with tungsten disulphide (WS$_2$) [117] and hexagonal boron nitride (hBN) [115] were also applied. The presence of WS$_2$ and hBN layers overcomes the barrier between graphene and substrate or avoids the charge trapping effect by the substrate, which often lowers the mobility of graphene.

4.5 *Electrochromic films*

Electrochromic materials show many potential applications in optical, displays, electronic devices and architecture [118,119]. Electrochromism is characterized by colour changes induced by heat and light due to electric field application. It occurs due to the electron-transfer (electrochemical redox) reaction in the active material. One of its interesting applications is electrochromic smart window, which has been applied in the building and aeroplane industries for energy savings and sun protection. The window application design consists of five thin film layers sandwiched between two glass substrates or just layered on a single glass substrate. These thin films are transparent conductors, CEs, ion conductors and electrochromic layers. Transition metal oxides, conducting polymers, carbon-based materials and their composites are common materials used for electrochromic film applications. However, the low conductivity of polymers and natural brittleness and low chemical stability of metal oxides often degrade the device performances. Graphene is a promising material for electrochromatic TCF applications because of its high transparency, conductivity, optical tunability and mechanically flexibility.

CVD-grown multilayer graphene on metal foils was transferred onto a flexible and transparent polyvinyl chloride substrate via lamination. The electrochromic device was fabricated by attaching two graphene films with an ionic liquid electrolyte spacer. The transmittance of device at 900 nm is increased from 8% at 0 V to 55% at an applied voltage of 5 V. Raman spectroscopy showed no significant change in the disorder-(D) and graphitic-(G) bands of the device when the applied voltages are less than 2.5 V. Meanwhile, the intensity of G-band increases at applied voltages above 2.5 V. This result suggests that the threshold voltage of the device is around 2.5 V. This study offers a simple and scalable process to fabricate graphene-based electrochromic films. It can be easily adopted with other transparent substrates, and the device performance can be enhanced by improving the active material properties or selecting a proper electrolyte.

5. Conclusions and perspectives

Owing to its outstanding properties, graphene is a promising material for various future applications. Several methods have been introduced to synthesize graphene and its derivatives. Hummers' method is the most common and promising route to produce a large quantity of graphene. However, this method involves many hazardous chemicals and a complex preparation. Meanwhile, CVD can produce high-quality graphene. However, high production cost and complex etching and transfer processes limit the application of CVD in industrial-scale graphene production. Most applications require graphene to be deposited on certain substrates. Solution processing of graphene offers various simple transfer processes, such as spin coating, dip coating and spray coating. Hence exfoliation of graphite in solvent-based solutions is a promising method for the mass production and transfer process of graphene. Moreover, this method involves less chemical and relatively low-cost production, although further reduction is needed to improve the properties of graphene. The mass production and large area of transferred graphene with high quality, uniformity, easy process and low-cost production are still challenging and need further exploration to meet the industrial and market demands.

Graphene utilized as a TCF offers many potential future applications in solar cells, displays, transistors, supercapacitors and electrochromic films. Graphene-based TCF with high conductivity, transmittance, flexibility and mechanical strength must be fabricated to obtain high-performance devices. The hybridization of graphene with polymers, metal oxides and other nanostructured materials can enhance the performance of graphene-based TCFs. However, considerable efforts are still needed to improve the current and future technology based on flexible TCF for electronic devices. In addition, a cheap TCF-based technology that is easily accessible is not yet established.

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