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Review

Graphene for energy harvesting/storage devices and printed electronics

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ABSTRACT

Graphene-based materials are intriguing from the perspective of fundamental science and technology because they are non-toxic, chemically and thermally tolerant, and mechanically robust. Graphene exhibits superior electrical conductivity, high surface area and a broad electrochemical window that may be particularly advantageous for their applications in energy storage devices. In addition, graphene can be prepared in the form of a colloidal suspension with adjustable solubility and thus is suitable for printing applications and offers both transparency and good conductivity at the same time. In this review, applications of graphene in solar cells, batteries, supercapacitors and fuel cells are summarized with the latest developments. Furthermore, graphene as a conductive ink for printed electronics is also discussed.

Contents

1. Introduction

Graphene is a material which consists of a 2D layer of sp^2 hybridized carbon atoms bonded together and the shape that results from it is a “honeycomb” lattice, notable for its high regularity. It is attracting growing interest from the scientific community (Dresselhaus & Araujo, 2010) due to the recent advancements that have led to the award of the Nobel Prize in Physics in 2010 (Novoselov et al., 2004). Among the possible fields of applications, the use of graphene in energy harvesting and storage devices is particularly interesting due to the number of extremely promising and practical potential uses (Geim & Novoselov, 2007). Graphene exhibits superior electrical conductivity, a high charge carrier mobility ($20\,m^2/(V\,s)$), fascinating transport phenomena such as the quantum Hall effect, high surface areas of over $2600\,m^2/g$ and a broad electrochemical window (Dresselhaus & Araujo, 2010). These features make graphene particularly advantageous for applications in energy technologies. In addition, graphene can be transferred to substrates for transparent electronic applications allowing the fabrication of transparent or semi-transparent energy harvesting and storage devices.

Graphene can be prepared in a number of ways: (i) Mechanical exfoliation from highly oriented pyrolytic graphite (HOPG), which is also indicated as scotch tape peeling. This method is still widely used in many laboratories to obtain pristine perfectly structured graphene layers for basic scientific research and for making

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Abbreviations: CVD, chemical vapour deposition; EDLC, electrochemical double layer capacitor; FTO, fluorine tin oxide; GO, graphene oxide; HOPG, highly ordered pyrolytic graphite; ITO, indium tin oxide; PCE, power conversion efficiency.

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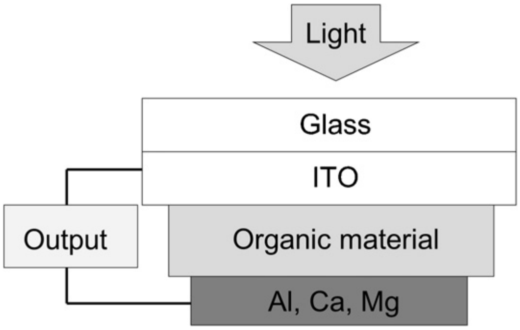

Fig. 1. Mechanism of organic photovoltaic (OPV) cell.
Adapted from Spanggaard and Krebs (2004).

proof-of-concept devices. However, it is not suitable for mass production. (ii) Thermal decomposition of SiC wafer under ultrahigh vacuum conditions (Emtsev et al., 2009). Graphene samples from this method are composed of a multitude of domains, most of them submicrometre in scale, and are not spatially uniform in number or size over larger length scales. (iii) Epitaxial growth through chemical vapour deposition (CVD) on metal substrates. CVD has the potential to enable large scale graphene production for electronic applications such as thin film transistors, solar cells and touch panels which require large area graphene sheets in the order of tens of centimetres but always involve transfer of graphene to a desired substrate. Similar as thermal decomposition of SiC method, CVD is an expensive process. (iv) Exfoliation of graphite in solvents (Zhu, Murali, Cai, et al., 2010).

Graphene oxide (GO) can be obtained through a modification of Hummer's method (Hummers & Offeman, 1958) and the subsequent reduction with $NaBH_4$ or hydrazine can lead to pristine graphene. Due to the toxicity of the reducing agents, green pathways using reducing sugars are also under investigation (Zhu, Guo, Fang, & Dong, 2010). These methods offer the scope to cheaply produce large quantities of graphene. Particularly, chemical reduction of GO is a simple process and sheets as large as 50 μm have been made and then they can be modified chemically. Among the chemical methods, recently developed electrochemical exfoliation is regarded as a green method that allows easy tenability of the obtained products by varying the applied potential. Moreover, in this method, graphene can be prepared in the form of a colloidal suspension with adjustable solubility, suitable for printed electronics applications in an industrial scale. In this review, applications of graphene in solar cells, batteries, supercapacitors and fuel cells are summarized with the latest developments. Furthermore, graphene as a conductive ink for printed electronics is also discussed.

2. Application of graphenes in energy harvesting and storage

2.1. Solar cells

As the economies of scale cut down the production costs, rapid growth of the photovoltaic (PV) industry induces the depletion of the raw materials involved in the production of solar panels. This is particularly true for indium, which is used in the form of indium tin oxide (ITO) as a transparent conducting oxide (TCO) in several electronic applications. Organic photovoltaic (OPV) devices are made of an organic layer sandwiched between two charge collecting electrodes, one of which must be transparent, e.g., ITO or fluorine tin oxide (FTO); while the other is usually aluminium, sometimes coated with LiF or MgO (Spanggaard & Krebs, 2004). As shown in Fig. 1, the organic layer provides exciton dissociation to generate a potential and consequently electrical energy.

OPVs have the advantage over classical solar harvesting devices in that (i) they are flexible and semitransparent; (ii) they can be manufactured in a continuous printing process by coating large areas; (iii) they can be integrated in different devices; and (iv) they are cost effective and environmental friendly. The main challenges are efficiency, lifetime and competitive substitutes for ITO (Brabec, 2004). Graphene was found to be an alternate to ITO in OPVs due to its unique characteristics: single-layer graphene transmits nearly 98% of the total incident light (Nair et al., 2008), while each additional layer contributes approximately 2.3% to the overall opacity. Sheet resistance of a film is expressed as number of Ohms (Ω) of resistance per square of material. Sheet resistance of graphene used in different devices reported is ~6 kΩ/sq (Blake et al., 2008; Lemme, Echtermeyer, Baus, & Kurz, 2007; Tan et al., 2007), whereas ITO has a transmittance of ca. 90% and a resistance of ~20 Ω/sq. The main challenge is how to obtain high quality graphene sheets with less defects or without defects in order to further decrease its sheet resistance. Kalita, Matsushima, Uchida, Wakita, and Umeno (2010) recently synthesized graphene sheets from camphor for use in solar cell applications. Pyrolysis of camphor at 900 °C in argon allows the detachment of methyl carbons from the chemical structure, leaving a transparent graphene-structured carbon films (TGFs) with different thicknesses and with overall resistivity lower than that of ITO. Generally speaking, sheet resistance of graphene from chemical reduction of GO is in range of 1–100 kΩ/sq with transmittance below 80% (Eda, Fanchini, & Chhowalla, 2008; Wang, Zhi, & Mullen, 2008) or from 31 kΩ/sq to 18 MΩ/sq at 95% transmittance (Wu et al., 2008; Zhu, Cai, Piner, Velamakanni, & Ruoff, 2009), while in contrast, sheet resistance of graphene from the electrochemical exfoliation of graphite is in range of 0.015–0.21 kΩ/sq at 96% transparency (Su et al., 2011; Wang, Manga, Bao, & Loh, 2011).

Park, Rowehl, Kim, Bulovic, and Kong (2010) grew graphene sheets by CVD to replace ITO as the negative electrode, with a power conversion efficiency (PCE) comparable to devices containing ITO (1.63% for doped graphene vs. 1.77% for the latter). However, the hydrophobicity of graphene creates some difficulty in adhesion to the organic layer, that is, a mixture of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), is needed to act as a hole-transporting layer. The use of $AuCl_3$ nanoparticles as doping agent proves to be effective in increasing the wettability between the two surfaces, thus improving the device performances. $AuCl_3$ nanoparticles tend to reduce the sheet resistance of the graphene electrodes (Kim et al., 2010), though the success rate is still very low (~10%), probably due to the variability in the $AuCl_3$ particle sizes, which range from 10 to 100 nm.

A vacuum filtration method was used by Wang, Geng, Zheng, and Kim (2010) to produce transparent conducting (TC) graphene films from chemically reduced graphene colloids. The films were then transferred onto quartz substrates for annealing and graphitization at high temperatures (400 °C and 1100 °C respectively). A sheet resistance lower than 2 kΩ/sq and a transparency well over 80% were achieved at a typical wavelength of 550 nm. As indicated in another work by Liu, He, et al. (2010) graphene could be used not only to substitute ITO but also to enhance electron transport and exciton dissociation in the hetero-junction of a solar cell. They questioned the use of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the standard electron acceptor, and combined solution-processable functionalized graphene (SPFGraphene) and functionalized multiwalled carbon nanotubes (f-MWCNTs) to produce a new active layer that was then sandwiched between PEDOT:PSS and LiF. The best result obtained was a PCE of 1.05% (Liu et al., 2008).

Other types of promising, cost effective, flexible solar cells alternative to OPVs are dye-sensitized solar cells (DSSCs), in which, a light-absorbing dye provides electrons, which are collected from the TiO_2 support layer and travel to the external circuit. DSSCs have recently reached efficiencies that are comparable with those of amorphous Si cells (Gratzel, 2007). Wang, Zhi, and Mullen (2008) tried to replace ITO and FTO with graphene as window electrodes in order to simplify fabrication and lower cost of production, even though PCE is still much lower as compared to standard devices.

2.2. *Fuel cells*

Graphene also finds applications in fuel cells (FCs). One of the main issues connected with FCs is the limited availability of platinum (Pt), which is a candidate catalyst for FC reactions. The high surface area of graphene makes it more efficient than carbon black to disperse Pt nanoparticles (Xin et al., 2011). The new Pt/graphene catalyst used in direct methanol fuel cell (DMFC) shows (i) enhanced interactions between Pt and graphene; (ii) additional Pt active sites; (iii) less defects on graphene, thus improving the stability of grapheme; and (iv) better ordered Pt surface morphology, thus introducing more active catalytic sites. Graphene nanosheets (GNS) have also been considered for polymer electrolyte fuel cells (PEFCs), because of their higher carbon monoxide (CO) tolerance (Yoo et al., 2011).

There is also much research on using graphene as metal-free anodes, in order to overcome dependence on noble metals such as Pt, as shown by the first work on metal-free electrodes by Qu, Liu, Baek, and Dai (2010) on the synthesis of nitrogen-doped graphene (N-graphene) anodes via CVD for use in alkaline fuel cells (AFC). The n-type behaviour of N-graphene indicates that substitutional doping can effectively modulate electrical properties (Wei et al., 2009). The new electrode exhibited behaviour similar to the common Pt/C anode, and more importantly proved to be insensitive to CO poisoning. N-graphene can also be used together with Pt in proton exchange membrane fuel cells (PEMFCs) to increase electrical conductivity and improve carbon–catalyst binding (Jafri, Rajalakshmi, & Ramaprabhu, 2010).

2.3. *Batteries*

Graphene proves to be an extremely interesting and innovative material in portable energy storage devices. Conventional lithium ion batteries contain graphite anodes in the form of mesocarbon microbeads (MCMBs) (Scrosati & Garche, 2010). Unfortunately, the specific energy of Li–C batteries is quite low (370 mAh/g) (Liang & Zhi, 2009) since six carbon atoms can host only one lithium ion by forming an intercalation compound (LiC_6). Alternative anodes such as silicon, tin and metal oxides are under development; despite the extremely high specific energy of these electrodes (4200 mAh/g for Li–Si and 990 mAh/g for Li–Sn), they suffer from large volume expansion–contraction during the charge–discharge process, a phenomenon that leads to irreversible cracking and crumbling (pulverization) of the anodes (Ju & Dou, 2010). For this reason, several researchers are trying to use graphene to create silicon or metal oxide composites that show higher specific energy and less variations in their physical properties.

Wang, Zhong, Chou, and Liu (2010), for instance, produced free-standing graphene–Si nanocomposite films by an in situ chemical method. Silicon can reversibly accommodate lithium by forming $Li_{4.4}Si$ alloys, and graphene can minimize volume expansion that leads to pulverization. Electrochemical tests showed that the new electrode had a capacity of about 708 mAh/g even after 100 cycles. The durability of these films is due to the graphene–Si void spaces that buffer the volume change that would normally occur in Si electrodes. Moreover, graphene can also act as a conductive layer for electrons and as an additional source for lithium storage. Silicon nanoparticles have been used in combination with graphene (Lee, Smith, Hayner, & Kung, 2010) to obtain even more outstanding results: with Si particles estimated to be 21–22 nm in size, the measured storage capacity was 2200 mAh/g after 50 cycles and 1500 mAh/g after 200 cycles. It is necessary, however, to ensure good dispersion of the Si nanoparticles in the graphene composite, and that a portion of the graphene sheets reconstitutes graphite to form a continuous, highly conducting 3-D network to sandwich and trap the Si nanoparticles.

Mechanical mixing of nanoparticles with graphene dispersions limits the homogeneity of nanoparticles and the separation of graphene sheets. Therefore, chemical routes are now regarded as more promising. In situ chemical methods were used to insert SnO_2 into graphene layer (Yao, Shen, Wang, Liu, & Wang, 2009). Cyclic voltammetry (CV) measurements showed that the SnO_2–graphene nanocomposite electrode maintained a capacity of 520 mAh/g after 100 cycles. Another oxide that was recently investigated is CuO (Wang, Wu, Shu, Guo, & Wang, 2010); the CuO/graphene nanocomposite, prepared from a liquid solution, exhibited a reversible capacity of 600 mAh/g even after 100 cycles. A promising anode is represented by <20 nm anatase TiO_2 nanoparticles coated on graphene sheets. Used in combination with a $LiFePO_4$ cathode, the battery can deliver a 100% coulombic efficiency even after 700 cycles at 1 C_m (measured C rate) rate (except for the initial few cycles where irreversible loss was observed) (Choi et al., 2010).

Theoretically, it is possible for graphene sheets, ca. 0.7 nm in thickness, to have a Li_4C_6 stoichiometry that would significantly increase its storage performance (Gerouki et al., 1996). There have thus been some attempts to improve the starting quality and regularity of graphene: its specific capacity was increased to up to 1264 mAh/g at a current density of 100 mA/g (Lian et al., 2010). Control of the inter-graphene sheet distance through interacting molecules, such as carbon nanotubes (CNT) or fullerenes (C_{60}), can also be crucial to increase specific energy (Park, Zhang, Chung, Less, & Sastry, 2010). Graphenes from chemical reduction of GO are in a form of colloidal suspension and properties of the ink can be tailored. Ink containing graphene and TiO_2 has been made and directly used as coating of battery electrode (Wei, Andrew, et al., 2011). This battery delivered a specific capacity of 582 mAh/g in the initial discharging, which is approximately 78% of the theoretical capacity (744 mAh/g) of graphene sheets through the formation of Li_2C_6. Cyclability of the electrode made from the graphene ink was examined under longer term cycling for about 100 cycles, which demonstrated a good cyclic performance and reversibility. The graphene electrode still maintained a specific capacity of approximately 250 mAh/g after 100 cycles.

2.4. *Supercapacitors*

There are two types of supercapacitors depending on the charge storage mechanism. In electrochemical double layer capacitors (EDLCs), a pure electrostatic attraction occurs between the ions accumulated at the electrode/electrolyte interface, the electrode usually made of activated carbon. In the second type of capacitors, pseudo-capacitors, electrons are additionally involved in quick Faradic reactions and are transferred to or from the valence bands of the redox cathode or anode reagent when, for example, using conducting polymers. Supercapacitors provide a good complement to Li-ion batteries in applications where both high energy (Li-ion batteries) and high power bursts are required, which reduces the operational voltage dip at the load, extending energy efficiency and lifetime of the battery.

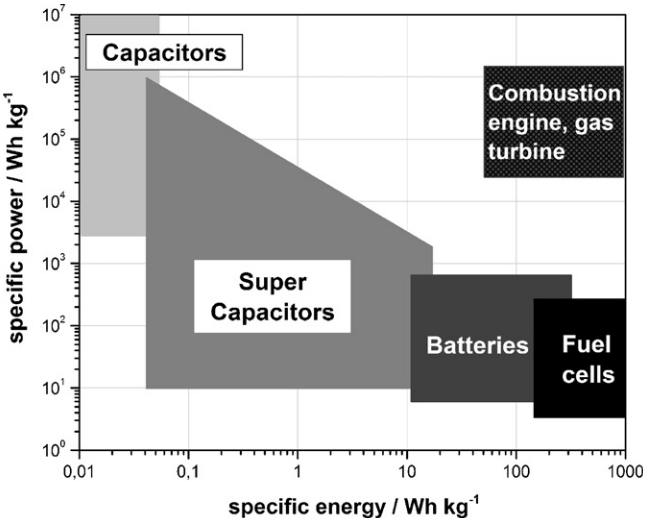

Fig. 2. Ragone plot for energy storage devices.
Adapted with permission from Winter and Brodd (2004).

EDLCs consist of two porous carbon electrodes that are isolated from electrical contact by a porous separator (Pandolfo & Hollenkamp, 2006; Stoller, Park, Zhu, An, & Ruoff, 2008). They differ from batteries in that it is not possible to define a cathode and an anode, though this nomenclature is used for simplicity. EDLCs are increasingly gaining attention because they fill a gap between batteries and ordinary capacitors, as shown in the Ragone plot in Fig. 2 (Winter & Brodd, 2004), which describes the energy density versus power density.

Supercapacitors find commercial applications for devices that need to store energy in the time range $10^{-2}\,\mathrm{s} < t < 10^{2}\,\mathrm{s}$ (Kotz & Carlen, 2000). The advantages electrochemical capacitors (ECs) have over batteries are that (i) most of them are short-circuit proof; (ii) they do not contain hazardous or toxic materials; (iii) they are easily disposable; and (iv) they can withstand many charge–discharge cycles.

The development of novel electrode materials is imperative for the design of high performance ultracapacitors. Graphene is generally used instead of carbon as an EDLC to filter AC current in portable electronics equipment (Miller, Outlaw, & Holloway, 2010). Vertically oriented graphene EDLCs can be used in the miniaturization of AC filtering capacitors by substituting the traditional aluminium electrolyte capacitors. Such ECs can store $\sim$5.5 FV/cm^3 with organic electrolytes, while aluminium electrolytic capacitors have CV/volume values of only up to $\sim$0.14 FV/cm^3.

Conventional EDLCs are essentially DC devices, i.e., they take several seconds to fully charge and then several seconds to fully discharge again. However, at higher frequencies, they become much less efficient and start to behave like resistors rather than capacitors. This is because the devices usually contain porous electrodes made from a high-surface-area conductive material, such as activated carbon, and the pores increase the resistance of devices. EDLC that contains vertically oriented high-surface-area graphene electrodes that are not porous at all can overcome this problem (Miller et al., 2010). The device pushes the operating frequency of an electric double layer capacitor to well beyond 5000 Hz, which is a factor of 105 better than commercial EDLCs. What is more, it is six times smaller than low-voltage aluminium electrolytic capacitors and can be charged and discharged at high efficiency in times much shorter than 1 ms. EDLCs from graphenes can minimize electronic and ionic resistance and produce capacitors with RC time constant of less than 200 ms, in contrast with $\sim$1 s for typical EDLCs.

Integration of graphene EDLCs in electric vehicles (EV) presages a breakthrough in the advancements of transport. EVs are currently limited by the low charge/discharge rate that batteries provide; while the suggested use of supercapacitors is limited by the low specific energy. Liu, Yu, Neff, Zhamu, and Jang (2010) recently showed how supercapacitors based on curved graphene sheets can exhibit a specific energy density comparable to that of modern Ni metal hydride batteries used in hybrid vehicles with the advantage of being rapidly rechargeable in less than 2 min. Moreover, the curved morphology prevents restacking of the graphene sheets, thus assuring a stable mesoporous structure with pore size ranging from 2 to 25 nm.

Moon et al. (2010) synthesized reduced graphene oxide (GO) under microwave (MW) irradiation to obtain high quality graphene layers with a specific capacitance of $\sim$147.5 F/g, which is roughly 1.6 times that of commercial activated carbon (87.8 F/g). MW treatment is quite convenient in a commercial MW oven to obtain microwave exfoliated graphite oxide (MEGO) in about a minute (Zhu, Murali, Stoller, et al., 2010). The highest specific capacitance recorded in this work was 191 F/g with KOH as electrolyte, comparable to what could be obtained with standard methods (205 F/g). Wang et al. (2009) and Yu, Roes, Davies, and Chen (2010) synthesized 25 nm graphene sheets via a vacuum filtration method, realizing a capacitance of 135 F/g. The advantages of such thin sheets are (i) sufficient mechanical strength for the flexible and robust thin films; (ii) transparency for application of the supercapacitor in transparent electronics; and (iii) simplified and lightweight architecture.

Another trend in optimizing the geometry of graphene is the integration of CNT, a good dispersed graphene-based material, with charged soluble poly(ethyleneimine) (PEI) stabilizer to create a good quality hybrid CNT/graphene composite (Yu & Dai, 2010), with an average capacitance of 120 F/g, considerably higher than those of vertically aligned (Futaba et al., 2006) and nonaligned CNT electrodes (Frackowiak & Beguin, 2001; Lu, Qu, Henry, & Dai, 2009).

Hybrid CNT/graphene composite is also used together with polyaniline (PANI), a conducting polymer, which is very attractive due to its easy synthesis, environmental stability, high controllable conductivity, and good electrochemical properties. The performance measured by Wu, Xu, Yao, Liu, and Shi (2010) exhibited a high capacitance of 210 F/g at 0.3 A/g, and about 94% of this value (197 F/g) was maintained as the discharging current density was increased from 0.3 to 6 A/g. Other researchers obtained a value of specific capacitance of 1118 F/g at a current density of 0.1 A/g, even though this figure dropped by 16% after 500 cycles (Kim & Park, 2010). Another conducting polymer that is being used is polypyrrole (PPy) (Han, Ding, & Zhang, 2010), which has some advantages over PANI, and is relatively more stable under ambient conditions and easier to synthesize. Its specific capacitance was found to be 223 F/g at a current density of 0.5 A/g.

Batteries, such as Li-ion batteries, can have high energy densities (up to 180 Wh/kg) with low power densities (up to 1 kW/kg). Supercapacitors can deliver very high power densities ($\sim$10 kW/kg) with a lower stored energy than batteries ($\sim$5 Wh/kg) (Conway, 1999). These characteristics originate from the different mechanisms of energy storage in these devices. Thus energy density and power density usually offset each other. Recent graphene surface enhanced lithium ion exchange cell seems to provide a solution to make an electrochemical energy storage device with both high energy density and power density (Jang et al., 2011). The approach was based on the exchange of lithium ions between the surfaces (not the bulk) of two nanostructured electrodes, completely obviating the need for lithium intercalation or deintercalation. In both electrodes, massive graphene surfaces in direct contact with liquid electrolyte are capable of rapidly and reversibly capturing lithium ions through surface adsorption and/or surface redox reaction. Energy density of 160 Wh/kg was obtained, which is 30 times higher than that (5 Wh/kg) of conventional symmetric supercapacitors and comparable to that of Li-ion batteries. They are also capable of delivering a power density of 100 kW/kg, which is 10 times higher than that (10 kW/kg) of supercapacitors and 100 times higher than that (1 kW/kg) of Li-ion batteries.

3. Feasibility of graphene inks in printable electronics for energy harvesting and storage

In the form of colloidal suspension, graphene is also a non-toxic nanomaterial with adjustable solubility suitable for applications in printable electronics. Development of printable electronics technology has also boosted globally the energy harvesting and storage efforts.

Conductive inks that are now available to print conductive traces directly onto rigid, flexible and relatively cheap substrates, using existing printing technologies such as screen, gravure, flexographic, offset and inkjet (Monie, 2010). This technology can be used to produce transistors, RFID tags, keypads, OLEDS and many more other devices. It has the potential of addressing a multitude of markets, e.g., organic photovoltaics, displays, printed batteries and supercapacitors. The benefits of printed electronics include cost effectiveness, low space, low weight consumption, flexibility, environmental friendliness and robust performances.

Several inks are available for use in printed electronics today (Ag, Cu, Ni, Al, P, Si, C, CNTs, polymer based, etc.). The ideal ink needs to have a combination of low cost, ease of processing and high performance. Table 1 compares some of the inks currently used:

The newest and most exciting entrants to the field are graphene-based inks, for graphene is the most conductive form of carbon and the thinnest material available. The electronic configuration in its hexagonal pattern requires three of each carbon atom's four valence electrons to create the crystal lattice. This allows one electron to float freely released from chemical bonding – delocalized electron. These free electrons create a kind of "sea" which allows them to transfer current with almost no resistance (Lammert, Rozo, & Whittier, 2009). Graphene has also shown to have outstanding dispersibility and stability in a number of solvents (Wei, Li, et al., 2011) and can be manufactured cheaply using the chemical reduction method (Fan et al., 2008; Gilje, Han, Wang, Wang, & Kaner, 2007; Li, Müller, Gilje, Kaner, & Wallace, 2008; Stankovich et al., 2007). Thus it shows considerable promise to offer a low cost and high performance solution for many applications. Graphene inks have already been shown to be compatible with screen, gravure, flexographic and industrial inkjet printers (Vorbeck Materials, n.d.).

These inks are exceptionally conducting, they offer sinter-free curing and can be used across a wide range of substrates, including paper and plastic. In addition, they are extremely flexible, robust and crease-resistant when printed (Monie, 2010; Vorbeck Materials, n.d.), as shown in Fig. 3. They have better surface resistivity than conductive composites and carbon-based inks while being less expensive than metallic inks (Monie, 2010). Graphene inks have also been shown to enhance performance of semiconductor devices (Shah et al., 2010). New patents on graphene inks are also being actively applied for (Jang & Zhamu, 2010).

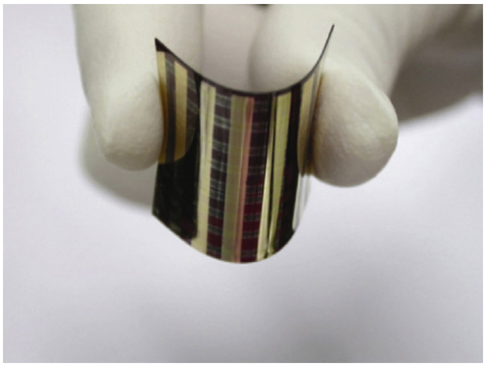

Fig. 3. Graphene inks are highly flexible and lose very little conductivity when folded.

Adapted with permission from Monie (2010).

4. Role of graphene extends beyond inks

It is extremely important to bear in mind the full potential of graphene that extends much further than conductive ink. Graphene transistors are evolving at a rapid pace and graphene-based devices are seen as an option for post-Si electronics (Schwierz, 2010). Graphene is also considered as an outstanding candidate for electrode materials in supercapacitors due to its high surface area, excellent conductivity and high intrinsic capacitance (Liu, Yu, et al., 2010; Stoller et al., 2008). Graphene would also make efficient transparent conducting electrodes because of its high electrical conductivity and excellent transparency (Nair et al., 2008). In other words, besides as replacement of ITO in organic photovoltaics, it could be used for touch-screens in phones, liquid crystal displays, organic photovoltaic cells, and organic light emitting devices (Lammert, Rozo, & Whittier, 2009).

On a larger scale, graphene's most immediate applications lie in composite materials. Graphene can be used to make lighter and more efficient aircraft and automobile parts and also stronger wind turbines (Rensselaer Polytechnic Institute, 2010). Graphene is also cheaper than its carbon nanotube counterpart and does not possess any toxicity issues like CNTs do (Poland et al., 2008). It is also reported to be an excellent material for detection of toxic or harmful gases (Ko et al., 2010).

Table 1
Comparison of different conductive inks available for printed electronics.

Ink	Conductivity	Oxide	Curing	Substrate range	Film cohesion	Substrate adhesion	Process-ability	Reference
Silver	Excellent Expensive	Conductive	High temp. Long time	Limited	Average			Monie (2010)
Carbon	Average				Poor	Poor		Monie (2010)
Copper	Good	Rapid oxidation Insulating layer	High temp. Inert ambience	Limited				Monie (2010), Yaniv (2008, 2009)
Polymer based	Average						Low solubility	Monie (2010)
CNT	Excellent						Low dispersion Toxic	Monie (2010), Ha et al. (2010), Poland et al. (2008)

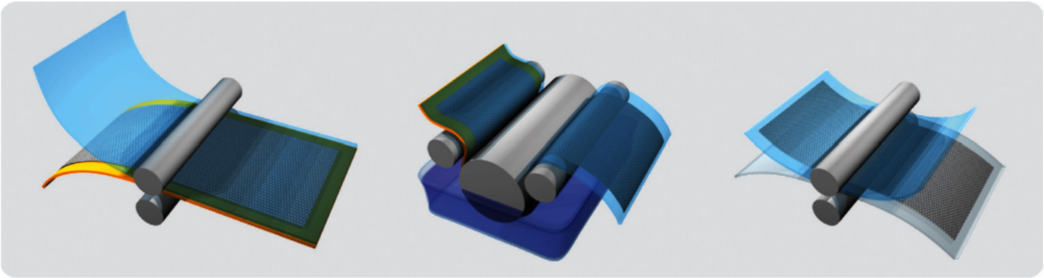

Fig. 4. Schematic of the roll-based production of graphene films grown on a copper foil. The process includes adhesion of polymer supports, copper etching (rinsing) and dry transfer-printing on a target substrate.

Adapted with permission from Bae et al. (2010).

However, to translate all of these applications into reality, large scale and cost-effective manufacturing of graphene is the key. Several methods have already been proposed for large scale production of graphene and its inks. Recent breakthroughs include the large-area deposition of few-layer graphene (FLG) using chemical vapour deposition on catalyst-coated substrates (Kim et al., 2009). Another research thrust involves solution processing of graphene derivatives. Chemical exfoliation methods which produce GO from graphite result in high-yield production of single sheet dispersions (Becerril et al., 2008; Eda & Chhowalla, 2009). The advantage of these solution-processable GOs is that they can be used to create large-scale all-carbon electronics via inkjet printing (Wang, Ang, et al., 2010). Other methods such as graphene exfoliation using a polymer–organic solvent solution have also been proposed (Liang & Hersam, 2010). Recently, roll-to-roll production of 30-in. graphene films by chemical vapour deposition onto ultra large copper substrates was also demonstrated (Fig. 4) (Bae et al., 2010).

5. Conclusions

Graphene-based materials are intriguing from the perspective of both fundamental science and technology because they are nontoxic, chemically and thermally tolerant, and mechanically robust. This review summarized some of the advances of its applications in energy harvesting and storage.

Solar cells and fuel cells can greatly benefit from the introduction of graphene, which is being proven to be a valuable replacement material for the increasingly expensive metals currently employed, such as indium and platinum; in addition, functionalization of graphene sheets could be a breakthrough in achieving even better performances. Though conductivity of materials is generally reversely related to its transparency, the unique property of graphene offers impressive transparency without sacrificing its conductivity. This characteristic can be largely used and even replace the ITO, which lacks the flexibility and robustness in flexible solar cells, LEDs, touch screens and displays. Applications of graphenes in supercapacitors not only improve the specific capacity but also impart the conventional electrochemical double layer capacitor with AC line filtering performance. Graphene in lithium-based batteries can help in the development of high-capacity electrodes based on materials like silicon and tin; in addition, control on the inter-graphene sheet distance can lead to interesting lithium storage properties. It was also reported the reduced charging time by implantation of graphene in battery electrodes, which is not only beneficial to mobile devices but also to the massive deployment of electric vehicles in the car market.

There are numerous ways to produce graphenes, and we focused the discussion on its processing using printing technology, which can easily couple with mass production in an industrial level with cost effectiveness. Roll to roll printing can be used not only in wet-solution based graphene inks but also with transferring graphene made from CVD to conductive substrate. The printing process of graphenes will make it feasible to make energy harvesting and storage devices in the future, which may bring a revolution not only in industry process of manufacturing electronics but also the performance of energy harvesting and storage devices per se.

References

Bae, S., Kim, H., Lee, Y., Xu, X., Park, J.-S., Zheng, Y., et al. (2010). Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature Nanotechnology*, *5*(8), 574–578.

Becerril, H. A., Mao, J., Liu, Z., Stoltenberg, R. M., Bao, Z., & Chen, Y. (2008). Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *ACS Nano*, *2*(3), 463–470.

Blake, P., Brimicombe, P., Nair, R., Booth, T., Jiang, D., Schedin, F., et al. (2008). Graphene-based liquid crystal device. *Nano Letters*, *8*, 1704–1708.

Brabec, C. (2004). Organic photovoltaics: Technology and market. *Solar Energy Materials and Solar Cells*, *83*(2–3), 273–292.

Choi, D., Wang, D., Viswanathan, V. V., Bae, I.-T., Wang, W., Nie, Z., et al. (2010). Li-ion batteries from lifepo4 cathode and anatase/graphene composite anode for stationary energy storage. *Electrochemistry Communications*, *12*(3), 378–381.

Conway, B. E. (1999). *Electrochemical supercapacitors: Scientific fundamentals and technological applications*. New York: Springer.

Dresselhaus, M. S., & Araujo, P. T. (2010). Perspectives on the 2010 Nobel prize in physics for graphene. *ACS Nano*, *4*(11), 6297–6302.

Eda, G., & Chhowalla, M. (2009). Graphene-based composite thin films for electronics. *Nano Letters*, *9*(2), 814–818.

Eda, G., Fanchini, G., & Chhowalla, M. (2008). Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature Nanotechnology*, *3*, 270–274.

Emtsev, K. V., Bostwick, A., Horn, K., Jobst, J., Kellogg, G. L., Ley, L., et al. (2009). Towards wafer-size graphene layers by atmospheric pressure. *Nature Materials*, *8*, 203–207.

Fan, X., Peng, W., Li, Y., Li, X., Wang, S., Zhang, G., et al. (2008). Deoxygenation of exfoliated graphite oxide under alkaline conditions: A green route to graphene preparation. *Advanced Materials*, *20*, 4490–4493.

Frackowiak, E., & Beguin, F. (2001). Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*, *39*(6), 937–950.

Futaba, D. N., Hata, K., Yamada, T., Hiraoka, T., Hayamizu, Y., Kakudate, Y., et al. (2006). Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. *Nature Materials*, *5*(12), 987–994.

Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. *Nature Materials*, *6*(3), 183–191.

Gerouki, A., Goldner, M. A., Goldner, R. B., Haas, T. E., Liu, T. Y., & Slaven, S. (1996). Density of states calculations of small diameter single graphene sheets. *Journal of the Electrochemical Society*, *143*, L262–L263.

Gilje, S., Han, S., Wang, M., Wang, K. L., & Kaner, R. B. (2007). A chemical route to graphene for device applications. *Nano Letters*, *7*, 3394–3398.

Gratzel, M. (2007). Photovoltaic and photoelectrochemical conversion of solar energy. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, *365*(1853), 993–1005.

Ha, M., Xia, Y., Green, A. A., Zhang, W., Renn, M. J., Kim, C.-H., et al. (2010). Printed, sub-3v digital circuits on plastic from aqueous carbon nanotube inks. *ACS Nano*, *4*(8), 4388–4395.

Han, Y., Ding, B., & Zhang, X. (2010). Preparation of graphene/polypyrrole composites for electrochemical capacitors. *Journal of New Materials for Electrochemical Systems*, *13*, 315–320.

Hummers, W. S., Jr., & Offeman, R. E. (1958). Preparation of graphitic oxide. *Journal of the American Chemical Society*, *80*(6), 1339.

Jafri, R. I., Rajalakshmi, N., & Ramaprabhu, S. (2010). Nitrogen doped graphene nanoplatelets as catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell. *Journal of Materials Chemistry*, *20*(34), 7114–7117.

Jang, B. Z., Liu, C., Neff, D., Yu, Z., Wang, M. C., Xiong, W., et al. (2011). Graphene surface-enabled lithium ion-exchanging cells: Next-generation high-power energy storage devices. *Nano Letters*, *11*(9), 3785–3791.

Jang, B. Z., & Zhamu, A. (2010). Nano graphene platelet-based conductive inks. US Patent, US 20100000441 A1.

Ju, S., & Dou, S. (2010). Synthesis of Si/graphene composite as an anode material for lithium-ion battery. In *Meeting abstracts of the 15th international meeting on lithium batteries, ECS, vol. 78* (p. 5878).

Kalita, G., Matsushima, M., Uchida, H., Wakita, K., & Umeno, M. (2010). Graphene constructed carbon thin films as transparent electrodes for solar cell applications. *Journal of Materials Chemistry*, *20*(43), 9713–9717.

Kim, K., & Park, S.-J. (2010). Influence of multi-walled carbon nanotubes on the electrochemical performance of graphene nanocomposites for supercapacitor electrodes. *Electrochimica Acta*, *56*(3), 1629–1635.

Kim, K. K., Reina, A., Shi, Y., Park, H., Li, L.-J., Lee, Y. H., et al. (2010). Enhancing the conductivity of transparent graphene films via doping. *Nanotechnology*, *21*, 285205.

Kim, K. S., Zhao, Y., Jang, H., Lee, S. Y., Kim, J. M., Kim, K. S., et al. (2009). Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*, *457*, 706–710.

Ko, G., Kim, H.-Y., Ahn, J., Park, Y.-M., Lee, K.-Y., & Kim,. J. (2010). Graphene-based nitrogen dioxide gas sensors. *Current Applied Physics*, *10*, 1002–1004.

Kotz, R., & Carlen, M. (2000). Principles and applications of electrochemical capacitors. *Electrochimica Acta*, *45*(15–16), 2483–2498.

Lammert, T., Rozo, L., & Whittier, E. (2009). Graphene-material of the future (in review). Retrieved from http://education.uncc.edu/cmste/summer%20ventures/2010%20Optical%20Engineering/Graphene-%20Material%20of%20the%20future,%20in%20review.%20-%20Taylor%20Lammert,%20Laura%20Rozo,%20Eric%20Whittier.pdf

Lee, J. K., Smith, K. B., Hayner, C. M., & Kung, H. H. (2010). Silicon nanoparticles–graphene paper composites for Li ion battery anodes. *Chemical Communications (Cambridge, England)*, *46*(12), 2025–2027.

Lemme, M. C., Echtermeyer, T. J., Baus, M., & Kurz, H. (2007). A graphene field-effect device. *IEEE Electron Device Letters*, *28*(4), 282–284.

Li, D., Müller, M. B., Gilje, S., Kaner, R. B., & Wallace, G. G. (2008). Processable aqueous dispersions of graphene nanosheets. *Nature Nanotechnology*, *3*, 101–105.

Lian, P., Zhu, X., Liang, S., Li, Z., Yang, W., & Wang, H. (2010). Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries. *Electrochimica Acta*, *55*(12), 3909–3914.

Liang, Y., & Hersam, M. (2010). Highly concentrated graphene solutions via polymer enhanced solvent exfoliation and iterative solvent exchange. *Journal of the American Chemical Society*, *132*, 17661–17663.

Liang, M., & Zhi, L. (2009). Graphene-based electrode materials for rechargeable lithium batteries. *Journal of Materials Chemistry*, *19*(33), 5871–5878.

Liu, Z., Liu, Q., Huang, Y., Ma, Y., Yin, S., Zhang, X., et al. (2008). Organic photovoltaic devices based on a novel acceptor material: Graphene. *Advanced Materials*, *20*(20), 3924–3930.

Liu, C., Yu, Z., Neff, D., Zhamu, A., & Jang, B. Z. (2010). Graphene-based supercapacitor with an ultrahigh energy density. *Nano Letters*, *10*, 4863–4868.

Liu, Z., He, D., Wang, Y., Wu, H., Wang, J., & Wang, H. (2010). Improving photovoltaic properties by incorporating both SPFGraphene and functionalized multiwalled carbon nanotubes. *Solar Energy Materials and Solar Cells*, *94*(12), 2148–2153.

Lu, W., Qu, L., Henry, K., & Dai, L. (2009). High performance electrochemical capacitors from aligned carbon nanotube electrodes and ionic liquid electrolytes. *Journal of Power Sources*, *189*(2), 1270–1277.

Miller, J. R., Outlaw, R. A., & Holloway, B. C. (2010). Graphene double-layer capacitor with ac line-filtering performance. *Science*, *329*(5999), 1637–1639.

Monie, S. (2010). Developments in conductive inks. Retrieved from Industrial Specialty Printing website http://industrial-printing.net/content/developments-conductive-inks?page=0%2C3

Moon, K., Li, Z., Yao, Y., Lin, Z., Liang, Q., Agar, J., et al. (2010). Graphene for ultracapacitors. In *Electronic components and technology conference (ECTC), 2010 Proceedings 60th* Las Vegas, NV, USA, (pp. 1323–1328).

Nair, R., Blake, P., Grigorenko, A., Novoselov, K., Booth, T., Stauber, T., et al. (2008). Fine structure constant defines visual transparency of graphene. *Science*, *320*(5881), 1308.

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., et al. (2004). Electric field effect in atomically thin carbon films. *Science*, *306*(5696), 666–669.

Pandolfo, A. G., & Hollenkamp, A. F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources*, *157*(1), 11–27.

Park, H., Rowehl, J. A., Kim, K. K., Bulovic, V., & Kong, J. (2010). Doped graphene electrodes for organic solar cells. *Nanotechnology*, *21*, 505204.

Park, M., Zhang, X., Chung, M., Less, G. B., & Sastry, A. M. (2010). A review of conduction phenomena in Li-ion batteries. *Journal of Power Sources*, *195*, 7904–7929.

Poland, C. A., Duffin, R., Kinloch, I., Maynard, A., Wallace, W. A. H., Seaton, A., et al. (2008). Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nature Nanotechnology*, *3*(7), 423–428.

Qu, L., Liu, Y., Baek, J.-B., & Dai, L. (2010). Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells. *ACS Nano*, *4*(3), 1321–1326.

Rensselaer Polytechnic Institute. (2010). Three studies highlight benefits of graphene composite structures. Retrieved from Composites World website http://www.compositesworld.com/news/three-studies-highlight-benefits-of-graphene-composite-structures

Schwierz, F. (2010). Graphene transistors – A new contender for future electronics. In *10th IEEE international conference on solid-state and integrated circuit technology (ICSICT)* Shanghai, China.

Scrosati, B., & Garche, J. (2010). Lithium batteries: Status, prospects and future. *Journal of Power Sources*, *195*(9), 2419–2430.

Shah, P., Lettow, J., Nyguen, C., Derenge, M., Jones, K., Batyrev, I., et al. (2010). Graphene containing conductive inks for electrical contacts to power semiconductor devices. In *International semiconductor device research symposium, 2009. ISDRS'09, IEEE* College Park, MD, USA, (pp. 1–2).

Spanggaard, H., & Krebs, F. C. (2004). A brief history of the development of organic and polymeric photovoltaics. *Solar Energy Materials and Solar Cells*, *83*(2–3), 125–146.

Stankovich, S., Dikin, D., Piner, R., Kohlhaas, K., Kleinhammes, A., Jia, A., et al. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, *45*, 1558–1565.

Stoller, M. D., Park, S., Zhu, Y., An, J., & Ruoff, R. S. (2008). Graphene-based ultracapacitors. *Nano Letters*, *8*(10), 3498–3502.

Su, C. Y., Lu, A. Y., Xu, Y., Chen, F. R., Khlobystov, A. N., & Li, L. J. (2011). High-quality thin graphene films from fast electrochemical exfoliation. *ACS Nano*, *5*, 2332–2339.

Tan, Y.-W., Zhang, Y., Bolotin, K., Zhao, Y., Adam, S., Hwang, E. H., et al. (2007). Measurement of scattering rate and minimum conductivity in graphene. *Physical Review Letters*, *99*(24), 246803.

Vorbeck Materials. (n.d.). Retrieved from http://www.vorbeck.com/index.html

Wang, X., Zhi, L., & Mullen, K. (2008). Transparent, conductive graphene electrodes for dye-sensitized solar cells. *Nano Letters*, *8*(1), 323–327.

Wang, Y., Shi, Z., Huang, Y., Ma, Y., Wang, C., Chen, M., et al. (2009). Supercapacitor devices based on graphene materials. *The Journal of Physical Chemistry C*, *113*(30), 13103–13107.

Wang, B., Wu, X., Shu, C., Guo, Y., & Wang, C. (2010). Synthesis of CuO/graphene nanocomposite as a high-performance anode material for lithium-ion batteries. *Journal of Materials Chemistry*, *20*(47), 10661–10664.

Wang, J., Manga, K. K., Bao, Q., & Loh, K. P. (2011). High-yield synthesis of few-layer graphene flakes through electrochemical expansion of graphite in propylene carbonate electrolyte. *Journal of the American Chemical Society*, *133*, 8888–8891.

Wang, J., Zhong, C., Chou, S., & Liu, H. (2010). Flexible free-standing graphene–silicon composite film for lithium-ion batteries. *Electrochemistry Communications*, *12*(11), 1467–1470.

Wang, S., Ang, P., Wang, Z., Tang, A., Thong, J., & Loh, K. (2010). High mobility, printable, and solution-processed graphene electronics. *Nano Letters*, *10*(1), 92–98.

Wang, S., Geng, Y., Zheng, Q., & Kim, J. (2010). Fabrication of highly conducting and transparent graphene films. *Carbon*, *48*(6), 1815–1823.

Wei, D., Andrew, P., Yang, H., Jiang, Y., Li, F., Shan, C., et al. (2011). Flexible solid state lithium batteries based on graphene inks. *Journal of Materials Chemistry*, *21*, 9762–9767.

Wei, D., Li, H., Han, D., Zhang, Q., Niu, L., Yang, H., et al. (2011). Properties of graphene inks stabilized by different functional groups. *Nanotechnology*, *22*, 245702.

Wei, D., Liu, Y., Wang, Y., Zhang, H., Huang, L., & Yu, G. (2009). Synthesis of n-doped graphene by chemical vapor deposition and its electrical properties. *Nano Letters*, *9*(5), 1752–1758.

Winter, M., & Brodd, R. J. (2004). What are batteries, fuel cells, and supercapacitors? *Chemical Reviews*, *104*(10), 4245–4270.

Wu, J., Becerril, H. A., Bao, Z., Liu, Z., Chen, Y., & Peumans, P. (2008). Organic solar cells with solution-processed graphene transparent electrodes. *Applied Physics Letters*, *92*, 263302.

Wu, Q., Xu, Y., Yao, Z., Liu, A., & Shi, G. (2010). Supercapacitors based on flexible graphene/polyaniline nanofiber composite films. *ACS Nano*, *4*(4), 1963–1970.

Xin, Y., Liu, J., Zhou, Y., Liu, W., Gao, J., Xie, Y., et al. (2011). Preparation and characterization of Pt supported on graphene with enhanced electrocatalytic activity in fuel cell. *Journal of Power Sources*, *196*(3), 1012–1018.

Yaniv, Z. (2008). Novel inkjettable copper ink without the need of inert atmosphere and processing temperatures under 100 °C. In *Printed electronics USA, 08* San Jose, CA, USA.

Yaniv, Z. (2009). Nanotechnology and its contribution to technical inks for printed electronics. In *EuroDisplay 2009* Rome, Italy.

Yao, J., Shen, X., Wang, B., Liu, H., & Wang, G. (2009). In situ chemical synthesis of SnO_2–graphene nanocomposite as anode materials for lithium-ion batteries. *Electrochemistry Communications*, *11*(10), 1849–1852.

Yoo, E., Okada, T., Akita, T., Kohyama, M., Honma, I., & Nakamura, J. (2011). Sub-nano pt cluster supported on graphene nanosheets for CO tolerant catalysts in polymer electrolyte fuel cells. *Journal of Power Sources*, *196*(1), 110–115.

Yu, D., & Dai, L. (2010). Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. *The Journal of Physical Chemistry Letters*, *1*(2), 467–470.

Yu, A., Roes, I., Davies, A., & Chen, Z. (2010). Ultrathin, transparent, and flexible graphene films for supercapacitor application. *Applied Physics Letters*, *96*(25), 253105.

Zhu, Y. W., Cai, W. W., Piner, R. D., Velamakanni, A., & Ruoff, R. S. (2009). Transparent self-assembled films of reduced graphene oxide platelets. *Applied Physics Letters*, *95*, 103104.

Zhu, C., Guo, S., Fang, Y., & Dong, S. (2010). Reducing sugar: New functional molecules for the green synthesis of graphene nanosheets. *ACS Nano*, *4*(4), 2429–2437.

Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J. W., Potts, J. R., et al. (2010). Graphene and graphene oxide: Synthesis, properties, and applications. *Advanced Materials*, *22*(35), 3906–3924.

Zhu, Y., Murali, S. D., Stoller, M., Velamakanni, A., Piner, R. D., & Ruoff, R. S. (2010). Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors. *Carbon*, *48*(7), 2118–2122.