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Graphene and the related conductive inks for flexible electronics

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Fabrication of electronic components or circuits by depositing conductive inks on organic or inorganic substrates is a preferred method in manufacturing of flexible electronics due to low cost and versatility. In the recent years considerable research has been carried out to synthesize graphene and graphene related hybrid inks for various applications in components and circuits for flexible electronics. In this paper the development of graphene and graphene hybrid inks is reviewed, with particular attention on their formulation, properties and applications. The challenges are also discussed and further development should be focused on ink formulation and preparation methods for low cost, eco-friendly manufacture, easy patterning and processing with good film conductivity. The rational combination of ink formulation and pattern deposition methods would be a direction to follow in future development of graphene and the related inks for commercial application in flexible electronics.

1. Introduction

In recent years fabrication of conductive patterns on flexible substrates such as paper,¹⁻³ textile,⁴ glass⁵ and polymer⁶ substrates, has been of significant research interest as a simple method to achieve flexible and low-cost devices. The flexible electronics market is estimated to exceed \$300 billion over the next 20 years.⁷ Clearly, flexible electronics will play a major role in meeting the key challenges in future electronic devices and systems in the coming decades. One major challenge of flexible electronics is to formulate suitable inks that can be printed using inkjet, screen, flexographic, or gravure based methods, while providing the required electrical and mechanical performance.

Up to now, numerous kinds of conductive ink with different fillers such as polymer,⁸ carbon nanotube,^{9,10} and metal nanoparticles or organic metal complex,¹¹⁻⁴² have been developed for the formation of conductive patterns. Among these, silver based inks have been the currently favoured metal inks and are under rapid development for applications in flexible electronics. Different kinds of silver ink with nanosilver fillers or organic silver fillers have been used for inkjet printing of conductive traces. However, the high cost, low content as well as electromigration behaviour of silver limit their wide industrial applications. Copper is an attractive alternative material to silver and exhibits the highest bulk conductivity. Copper inks are typically synthesized using a suspension of copper nanoparticles (NPs).⁴³⁻⁴⁹ However, copper NPs are easily oxidized. The presence of copper oxides increases the sintering

temperature of NPs and reduces the conductivity. Copper coordination compounds are desirable ink materials as they are inexpensive, easy to prepare and process, compatible with a range of different printing methods and have excellent electrical properties. The thermal decomposition ink of amine complexes of copper formate is an innovation in the development of copper compound based inks,⁵⁰⁻⁵⁶ but this is the only example of this ink system so far. Moreover, the relatively high temperature required for decomposition can cause the polyethylene terephthalate (PET) substrate to deform or simply alter its optical transmission thereby limiting their use as a low cost substrate material. Thus there is still need to develop new types of conductive ink to solve the above mentioned problems.

Graphene has many unique properties, such as high carrier mobility at room temperature, large specific surface area, high Young's modulus and excellent thermal conductivity.⁵⁷ To exploit these properties in various kinds of applications, versatile synthetic routes have been developed to prepare graphene and its derivatives.⁵⁸⁻⁶⁴ Among these methods, chemical reduction of graphene oxide (GO) is the most versatile approach, which incorporates many reactive oxygen-containing groups for further functionalization and tuning of the properties of GO or reduced GO (rGO) sheets. With the additional **attributes**, it is desirable to harness the useful properties of graphene **and its derivatives** in conductive inks. To date, several graphene based conductive inks have been produced successfully and are applied in different electronic applications such as sensors, conductive patterns, supercapacitors, electrodes and so on.

In this review, after introducing the synthetic and modification methods of graphene, graphene-based inks are discussed, with particular emphasis on their synthesis, types, properties and applications. Further development of graphene based inks will be focused on the relevant materials, ink preparation, film deposition and optimization of conductivity.

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The rational combination of formulation and patterning of graphene based inks would be a direction.

2. Synthesis of Graphene Inks

2.1 Preparation of Graphene

Up to now, tremendous efforts have been made to synthesize graphene and its derivatives, not only to achieve a high yield of production, but also to develop graphene-based composites. These methods can be generally categorized into bottom-up and top-down processes.^{65, 66}

The bottom-up approaches are based on deposition of graphene materials from carbon sources, such as chemical vapour deposition (CVD), which can produce defect free graphene sheets with large size on metal substrates. For example, large area monolayer graphene has been obtained on Cu films.⁶⁷ Plasma enhanced CVD is able to grow single-layer graphene with high throughput under shorter reaction time and lower deposition temperature conditions than the CVD process.⁶⁸ Besides epitaxial growth of graphene on SiC substrate is also a commonly used technique in which decomposition of SiC results in the formation of graphene layers. This process has several advantages, for example there is no transition or transportation of the resulting material from the metal substrate to the dielectric type substrate; the resultant graphene film is free from impurities; and controlled initiation and growth of the product can be tailored through the correct choice of substrate. Moreover, graphene can also be obtained via wet chemical reaction of ethanol and sodium followed by pyrolysis or through an organic synthesis process.⁶⁹

Although the bottom-up approaches can produce graphene with less defects, these methods are not widely used because of their complexity, limited scaling-up capability and the high cost of metal substrates.

The top-down approaches produce graphene using an existing form of a bulk material, which are advantageous in terms of high yield, solution based processability and ease of implementation. In these methods, graphene is produced by means of intercalation, chemical functionalization, and/or sonication of the bulk graphite. Various methods have been reported to obtain graphene sheets, such as chemical reagent reduction,⁷⁰ photochemical reduction,⁷¹ thermal reduction,⁷² photothermal reduction,⁷³ sonolysis,⁷⁴ microwave-assisted reduction and electrochemical reduction.^{75,76} Among these methods, chemical reduction of GO is the most versatile approach and it offers the greatest ease for functionalization and potential for large scale production of graphene.

Usually, chemical reduction of GO involves two steps. Graphite is first oxidized to graphite oxide using the Staudenmaier or Hummers' method.⁷⁷ Subsequently, the graphite oxide is exfoliated to graphene oxide through ultrasonication and then reduced using various reducing agents such as hydrazine, sodium borohydride, and lithium aluminium hydride etc. Despite that these reducing agents have been used extensively towards obtaining graphene sheets, some of them are not very convenient for large scale usage. For example,

lithium aluminium hydride requires an inert atmosphere and hydrazine is a highly toxic and potentially explosive chemical. Therefore it is necessary to find natural substitutes to replace the toxic reducing agents to address the above problems.

Fernandez-Merino et al.⁷⁸ compared the deoxygenation efficiency of graphene oxide suspensions by different reductants (sodium borohydride, pyrogallol, and vitamin C, in addition to hydrazine), as well as by heating the suspensions under alkaline conditions. Only vitamin C was found to yield highly reduced suspensions in a way comparable to those provided by hydrazine. Stable suspensions of vitamin C reduced graphene oxide can be prepared not only in water but also in common organic solvents, such as N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP) (Fig. 1). **As for the reduction mechanism of graphene oxide suspensions by vitamin C and the reason why complete reduction does not appear to be possible under the selected conditions, further studies are necessary.**

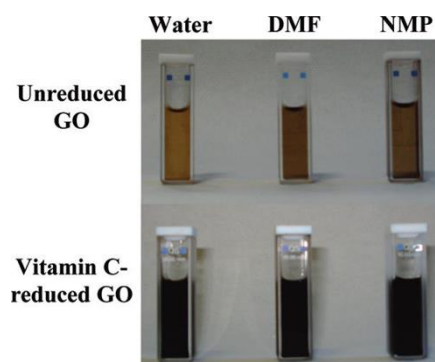


Fig. 1. Optical pictures of unreduced graphene oxide suspensions in water, DMF, and NMP (top), together with their deoxygenated counterparts 4 weeks after reduction with vitamin C (bottom)⁷⁸

He et al.⁷⁹ described a green and efficient solution-phase chemical reduction method to prepare high quality, reduced GO using L-ascorbic acid (L-AA) as the reductant. The reduction was rapid and essentially completed within 10 minutes. L-AA was more effective than D-fructose, glucose, sucrose, or Na₂SO₃. **During the reduction process, L-AA is oxidized to dehydroascorbic acid, 2,3-keketogulnol acid, oxalic acid and threonic acid to provide a large number of hydroxyl groups and carboxyl groups that can form hydrogen bonds with the residual oxygen functionalities, such as hydroxyl groups and periphery carboxylic groups on the reduced GO. Such interactions bring charged groups and steric bulk to the surface of both the GO and the reduced GO, hindering π - π stacking between graphene sheets and preventing the formation of aggregates, and thus result in the ultra-stability of reduced GO suspension. Interestingly, the reduced GO could form very stable suspensions in a variety of nonpolar and polar solvents (Fig.2), which enable the material to be easily modified for a broad range of potential applications, such as composites, biomedicine, conductive inks, and energy storage and conversion.**

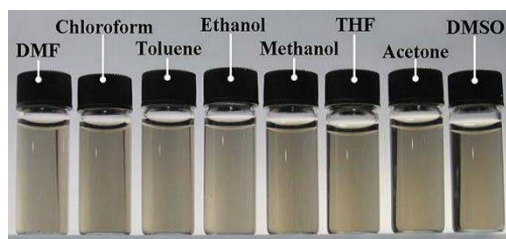


Fig. 2. Optical images of as-prepared reduced GO dispersed in eight types of polar and nonpolar organic solvents⁷⁹

More details of synthesis of graphene via various processes, can be found in reference [65] and [80].

2.2 Modification of Graphene

Pristine graphene is so hydrophobic that it is difficult to disperse in water for ink application. To make full use of the excellent electrical and mechanical properties of graphene and to realize the full potential of graphene inks, surface functionalization of graphene is essential.

To improve its solubility or electrical conductivity, modified graphenes have been obtained by adding functional groups to the surface through either covalent bonding or non-covalent interactions.^{81, 82} The former was achieved by techniques such as atom doping or reaction with residual functional groups on graphene while the latter is more versatile such as through van der Waals force, electrostatic interaction, hydrogen bonding, coordination bonds or p-p stacking interactions. In comparison, the interactions resulting from non-covalent modifications are relatively weak than that of covalent ones but multiple noncovalent bonds working in concert can yield highly stable modifications. Furthermore, they are easy to achieve over the entire graphene surface. When the graphene's electrical conductivity and large surface are required, non-covalent modification methods are typically preferred. Likewise, when the stability and the strong mechanical properties of a modified graphene are expected covalent methods are usually the preferred approaches.

Using different modification media such as ionic liquid, polyaniline, polyelectrolyte and poly(styrenesulfonate) (PSS), Wei et al.⁸³ prepared several kinds of graphene inks stabilized by different functional groups (Fig. 3). The dispersions can be easily cast into high-quality, free-standing films but with very different physicochemical properties such as surface tension and adhesion. Organic functional groups with different polarities impact on the wettability of the graphene inks. Surfactant (PSS anions) modified graphene inks are stable and have the best wettability and thus very good adhesion to the substrate.

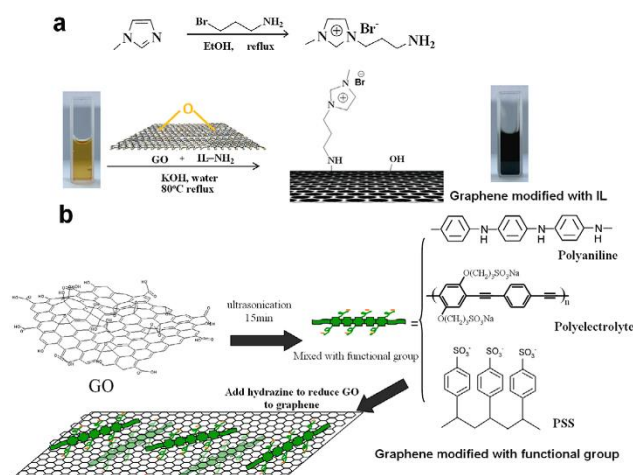


Fig. 3. Two different methods of graphene functionalization: (a) graphene functionalized by ionic liquid (IL) and (b) graphene modified by different functional groups of polyaniline, polyelectrolyte and PSS anions⁸³

3. Graphene Related Conductive Inks and Patterning

3.1 Ink Formulation and Patterning

With high charge carrier mobility, superlative thermal and chemical stability and intrinsic flexibility, graphene is considered to be a very promising ink material for flexible electronics. Usually, graphene based inks are composed of graphene or its derivatives (GO or graphene/metal or polymer composites), organic solvents and some surfactants. The characteristics of graphene or its derivatives are a critical factor because it determines the electrical and mechanical properties of the resultant conductive patterns.

There are several challenges which should be noted while using graphene or its derivatives as the functional component of conductive inks. First, graphene or its derivatives in the ink should be stable against aggregation and precipitation in order to provide reproducible performance. The resulted ink should also possess proper fluidic properties, in particular viscosity and surface tension. The printable ink requires a low viscosity and high surface tension, so it is easy to flow through the nozzle or pen but does not leak, dry out, break away or coagulate within the nozzle or pen. The recommended values of these properties for inkjet printing should be within the range of 1-25 mPa·s and 25-50 mN·m⁻¹.²³ Second, the patterned features from the graphene based inks should achieve good electrical conductivity with good adhesion to the substrates upon annealing at low temperature. Third, the ink synthesis procedure should be simple with high yield. Therefore, ink formulation should be well designed.

Two processes are generally involved in graphene ink patterning. One is transfer of the inks to flexible substrate and the other is the conductive network formation in the printed ink traces. The former involves fabrication methods such as inkjet printing, spinning, and flexographic printing; the latter is a process of sintering the particles together at a suitable

temperature. All types of graphene related inks require sintering treatment to form well conducting tracks, after transferred to substrates.

The most used method for sintering is heating on a hotplate or in an oven. The required temperature varies from ink to ink depending on the boiling points of the organic solvents used, the dissociation temperatures of the salts and the degree of conductive network formation. Sometimes the treatment temperature is higher than 300 °C and the sintering time is over 3 hours, which is not practical to implement on flexible substrates.

Sintering is commonly carried out by heating and can be also realised using other heating techniques including laser sintering,⁸⁴ intense pulsed light annealing,⁸⁵ UV radiation^{86,87} and IR treatment.⁸⁸ All of these techniques can provide the desired temperature for the conversion of the ink traces to become conductor tracks.

3.2 Graphene Related Inks

3.2.1 Graphene Ink

Currently, two routes are taken to prepare stable graphene inks. The first one is to use stabilizers in the ultrasonic exfoliation process of pristine graphene sheets. The second one is to use stabilizers in the chemical reduction process of GO, which can wrap around the graphene and may sterically or electrostatically hinder restacking. The kinds of stabilizers mainly involve polycyclic aromatic hydrocarbons, surfactants (sodium dodecyl sulphate), polymers (PVP, PVA) and ethyl cellulose. Water or organic solvents such as terpineol, ethanol, DMF, NMP and dimethyl sulfoxide (DMSO) are used as the main solvents in ink formulation.

Li and co-workers⁸⁹ developed a simple method to formulate stable graphene inks with high concentration and compatible fluidic characteristics based on the combination of solvent exchange and polymer stabilization techniques. Graphene is first exfoliated from graphite flakes in DMF, and then a small amount of polymer (ethyl cellulose) is added into the above dispersion to protect the graphene flakes from agglomeration. Last, the DMF is exchanged with terpineol through distillation. Benefiting from the polymer stabilization, the graphene/terpineol dispersions with a concentration around 1 mg·mL⁻¹ can be stable for at least several weeks. Ethanol was added to tailor the viscosity and surface tension to make the dispersions compatible with inkjet printing. The inks provided well-directed and constant jetting for printing. Del et al.⁸⁴ also prepared a graphene ink with multiple graphene layers using the solvent exchange technique, where graphite powders were first exfoliated in DMF and then stabilized with ethyl cellulose. DMF was replaced with terpineol to increase the graphene concentration, as well as to adjust the ink viscosity and to reduce solvent toxicity.

Torrisi et al.⁹⁰ produced a stable graphene-based ink by liquid phase exfoliation of graphite in N-methylpyrrolidone (NMP) and used it to print thin film transistors, with mobilities up to 95 cm²V⁻¹s⁻¹, as well as transparent and conductive patterns, with transmittance of 80% and sheet resistance of 30

kΩ/□. The Liquid phase exfoliated graphene turned out to be an ideal low-cost material for making printable inks. **But NMP is still not environmentally benign, which is not good for ink-jet printing process.**

Secor et al.⁹¹ developed a novel graphene ink using a graphene/ethyl cellulose (EC) powder that was produced using only room temperature processing methods. The graphene inks were produced by the exfoliation of graphite in ethanol and EC. The processing steps are illustrated in Fig.4. The graphene/EC powder allowed the ink to achieve stable inkjet printing of features on a variety of substrates with excellent morphology. The graphene features showed low resistivity of 4 mΩ·cm after thermal annealing at 250 °C for 30 minutes while showing uniform morphology, compatibility with flexible substrates, and excellent tolerance to bending stresses. **However, this method involved repeated and complicated process of salt flocculation and redispersion in solvent to obtain the graphene/EC powder, which limits its application.** Recently, by changing the EC composition in the graphene exfoliation step, they obtained graphene/EC powders with a graphene composition ranging from 25 to 65 wt% as precursors for graphene inks [85]. These inks are suitable for intense pulsed light annealing and were prepared by dispersion of the graphene/EC in a solvent system composed of cyclohexanone/terpineol (85:15, v/v).

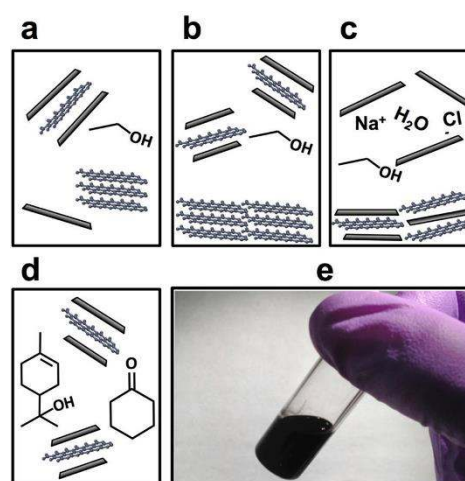


Fig. 4. Schematic illustration of the ink preparation method. (a) Graphene is exfoliated from graphite powder in ethanol/EC by probe ultrasonication, (b) centrifugation-based sedimentation to remove residual large graphite flakes, (c) salt-induced flocculation of graphene/EC, (d) An ink for inkjet printing is prepared by dispersion of the graphene/EC powder in 85:15 cyclohexanone/terpineol, and (e) Vial of the prepared graphene ink⁹¹

Gao et al.⁹² formulated a pristine graphene based ink with high concentration and stability using a simple and practical method and fabricated electrodes with high electrical conductivity. The pristine graphene was prepared by exfoliating graphite using an ultrasound-assisted supercritical CO₂ based method as shown in Fig.5. The graphene ink was formulated using cyclohexanone and ethyl cellulose (EC) as the solvent and the stabilizing agent, the ink was stable for more than 9 months. This long stability is mainly because of the strong hydrophobic

interactions between ethyl cellulose and the graphene sheets, thereby inhibiting the aggregation of the graphene. The sheet resistance of the printed films after 30 printing passes was only $0.81 \pm 0.2 \text{ k}\Omega/\square$, and the films had a transmittance of approximately 60% after annealing at 300°C for 30 minutes. The electrical resistivity of the printed electrodes on flexible substrates increased only slightly despite 1000 bending or folding cycles. **But the annealing temperature is still high for the other flexible substrates such as PET.**

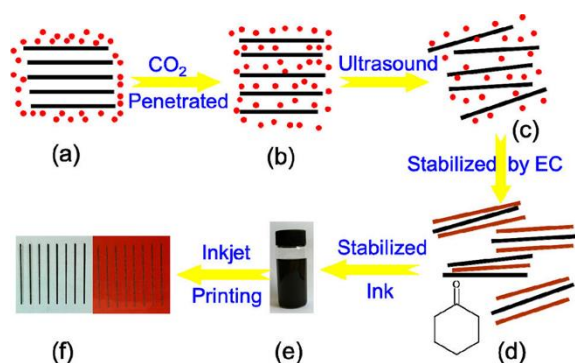


Fig.5. Schematic illustration of the preparation process of pristine graphene ink and inkjet printing. (a) Layered graphite was immersed in supercritical CO_2 , (b) CO_2 molecules penetrated and intercalated in the interlayer of graphite, (c) forming single or few layer thick graphene sheets, (d) Graphene sheets were stabilized by EC in cyclohexanone, (e) formed stable graphene ink, and (f) printing graphene electrodes on PET and PI substrates⁹²

Lee et al. prepared⁹³ a highly stable graphene ink by the adsorption of sodium n-dodecyl sulphate (SDS) and adjusting the pH value to 10. The SDS can yield multiple charged layers, hemi-cylinders, or multiple hemi-spheres, and further it can prevent graphene powder from aggregation. The effect of pH adjustment is to change the charge density of the graphene surface. The graphene dispersions can be stable for more than one month and meet the requirements for inkjet printing. Conductive features were fabricated on a flexible PI film by inkjet printing the stable ink directly on the substrate. The loading of graphene on the PI film showed linear increase with printing time. The conductivity of the sintered film was improved to $121.95 \text{ S}\cdot\text{m}^{-1}$ via a post-heating process, **but it is still too low for flexible electronics.**

Capasso et al.⁹⁴ prepared graphene and few layer graphene based inks suitable for inkjet printing processes on flexible substrates using a low boiling point and environmentally-friendly solvent, ethanol/water mixture. The stable ink formulations were obtained by investigating various rheological properties such as density (ρ), surface tension (γ) and Viscosity (ν). These inks were used to print conductive stripes with sheet resistance of $13 \text{ k}\Omega/\square$.

3.2.2 Graphene Oxide Ink

Graphene oxide (GO) has a similar structure as graphene but with oxygen containing groups which results in expansion of interlayer distance in the GO structure, and as a consequence, it makes GO hydrophilic. The abundant oxygen-containing functional groups enable GO to have excellent solution

processability and allow efficient assembly of large area films from solution. GO can be easily dispersed in water and polar organic solvents such as DMF, NMP, tetrahydrofuran, and ethylene glycol. Preparation of stable GO dispersions does not require addition of stabilizing agents which is an advantage over graphene inks.

Shin et al.⁹⁵ synthesized a GO ink using a modified Hummers and Offeman method. Exfoliated GO aqueous solution was used as conductive ink, and thermal annealing for the reduction process was performed under vacuum conditions. Graphene nanosheets that consisted of a few atomic layers were successfully patterned on a PET film using this ink after the subsequent thermal reduction. The patterned graphene lines had a much higher resolution compared to other conducting polymers. The graphene-based thin film exhibited sustained electrical conductivity. **One disadvantage is that hydrazine vapor was used in the reduction process, which is not desirable due to its high toxicity.**

Le et al.⁹⁶ produced electrically conductive graphene electrodes using a GO dispersion and the subsequent thermal reduction under N_2 at 200°C for 12 hours (Fig.6). Hydrophilic GO dispersed in water was found to be a stable ink for inkjet printing. At room temperature, the viscosity and surface tension of the GO ink were $1.06 \text{ mPa}\cdot\text{s}$ and $68 \text{ mN}\cdot\text{m}^{-1}$ respectively. In order to jet spherical GO ink droplets, the waveform function of the piezoelectric nozzle operation was adjusted to compensate for the low viscosity and high surface tension of the water-based ink.

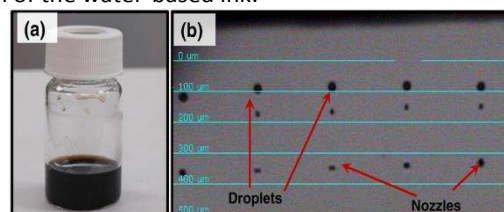


Fig.6. GO ink and morphology. (a) GO dispersed in water at 0.2 wt% as a stable ink, (b) spherical ink droplets generated by piezoelectric nozzles⁹⁶

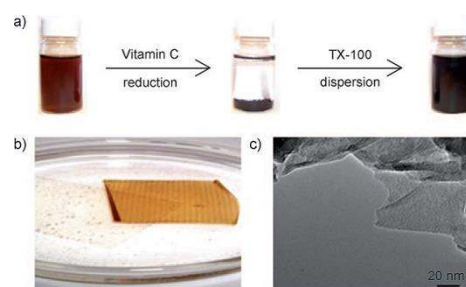


Fig.7. (a) Optical pictures of vials containing GO and rGO dispersions. (b) Inkjet-printed graphene oxide film after lift-off from the PET surface. (c) TEM image of the RGO powder.⁹⁷

Dua et al.⁹⁷ printed rGO platelets by using aqueous surfactant-supported dispersions of GO powder and ascorbic acid as a mild and green reducing agent (Fig.7). The resulting film has electrical conductivity property and has fewer defects

compared to RGO films obtained using a hydrazine based reduction process.

Lim et al.⁹⁸ found that PVA blended with graphite oxide can enhance exfoliation of the graphite sheets and produce a stable solution for inkjet printing. A homogeneous RGO/PVA colloidal suspension was prepared (Fig.8), PVA played an important role in maintaining the long-term stability of the RGO/PVA suspension required for inkjet printing.

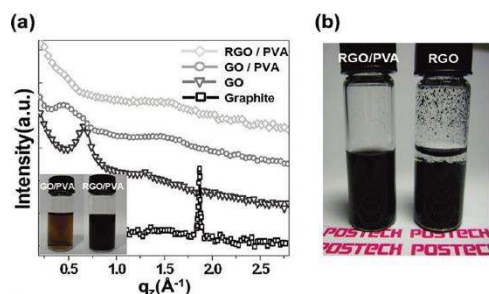


Fig.8. (a) XRD patterns of graphite, graphite oxide (GO), GO/PVA, and RGO/PVA composite, insert showing photographs of well-dispersed GO/PVA (left) and RGO/PVA (right) suspensions, (b) RGO/PVA composite stably dispersed in a mixed solvent with DMF and water for three months (left) and RGO precipitated from the same medium (right)⁹⁷

Porro et al.⁸⁷ prepared a water-based, environmentally friendly graphene oxide/acrylic ink. The possibility of inkjet printing and subsequently polymerizing the composite resin by irradiation with UV light was presented. The graphene oxide filler, which was strongly hydrophilic due to its heavily oxygenated surface for easy dispersion in water, was reduced by UV irradiation during photo-curing of the polymeric matrix. The network clusters of reduced graphene oxide inside the polymer matrix act as preferential pathways for the mobility of charge carriers, thus leading to an overall decrease of the material's resistivity.

Although the solution processability of GO offers a unique advantage in spin-coating or inkjet printing onto substrates for large-scale production of graphene based electronic circuits, the graphene reduced from GO by chemical reduction and thermal annealing is reported usually to have more defects and poor conductivity resulting from low carrier mobility, which restricts its use in electronic applications.

3.2.3 Graphene/Polymer Hybrid Ink

Conducting polymers are promising materials for supercapacitors due to their high pseudocapacitance. As a typical conducting polymer, polyaniline has long been a widely used material for supercapacitor electrodes due to its ease of synthesis, processability, and special redox activity. However, one of the drawbacks of polyaniline as supercapacitor electrodes is its poor cycling stability. Additionally, polyaniline exhibits only moderate electrical conductivity.

Graphene/polyaniline hybrid materials can address the shortcomings of polyaniline and can also form a stable and underlying conductive network due to the incorporation of graphene. Thus it is attractive to formulate

graphene/polyaniline inks to harness these excellent synergistic capacitive properties. Xu et al.⁹⁹ formulated graphene/polyaniline inks and produced graphene/polyaniline thin film electrodes from these inks. Nano graphene platelets (NGPs), SDBS surfactant, polyaniline (PAIN) and water were used to form the inks. In inkjet printing, good control over a number of key film properties including pattern geometry, pattern location, film thickness, and electrical conductivity was achieved.

Liu et al.¹⁰⁰ developed a hybrid ink of exfoliated graphene (EG) and poly (3, 4-ethylenedioxy thiophene) : poly (styrenesulfonate) (PEDOT:PSS) formulation (Clevios PH1000) in DMF. PH1000 was selected as the surfactant due to its conjugated aromatic chains that can strongly anchor onto the graphene surface via π - π interactions without disrupting the electronic structure of graphene. Meanwhile PH1000 was used also due to its superior electronic properties and solution compatibility with EG. The resulting hybrid ink was stable for at least 1 month without apparent precipitation (Fig. 9a). The significant π - π interactions between the EG basal plane and PH1000 are believed to produce charge-transfer effects, which can be confirmed by Raman spectroscopy (Fig. 9c). The fabricated graphene films exhibited excellent mechanical properties. The hybrid ink of EG/PH1000 may pave the way to the future development of transparent electrodes for optoelectronics, and other emerging flexible devices such as wearable supercapacitors and electronic skins.

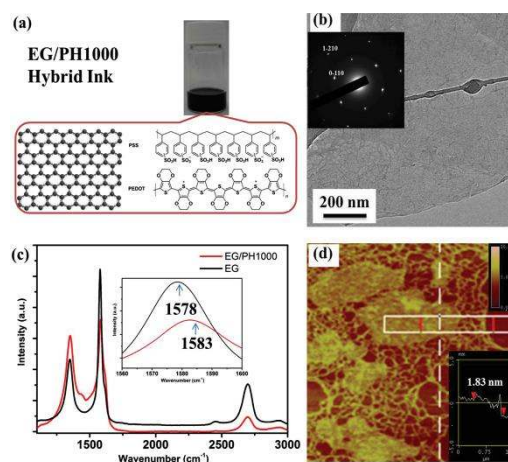


Fig.9. (a) Optical image of EG/PH1000 hybrid ink and molecular structures of EG and PH1000, (b) TEM image of a single graphene sheet from EG/PH1000 hybrid ink, inset showing the SAED pattern of the single graphene sheet, (c) Raman spectra of graphene flakes from EG and EG/PH1000 hybrid ink (Inset shows the shift of the G peak), and (d) AFM image of graphene sheets from EG/PH1000 hybrid ink¹⁰⁰

3.2.4 Graphene/Metal Ink

Recent research has focused on the graphene/metal based composite materials for improving the conductivity of pure graphene ink. It is promising to mix metal nanoparticles and graphene nanosheets together to produce a hybrid ink and thus take full advantage of these two materials to enhance the conductivity and reduce the concentration of metal particles.

Some new approaches using metal nanoparticles and graphene or GO/rGO as their fillers have been developed. So far the work has been focussed on Ag based hybrid systems since the Ag based inks are more cost effective than Pt and Au based metal inks, and they are more stable than Cu based on inks - less prone to oxidation. Therefore Ag nanoparticles have been widely used to decorate graphene and its derivatives in graphene/metal inks.

Li et al.¹⁰¹ prepared inks of Ag and rGO, one based on a mixture of Ag nano-triangle particles (NTPs) and rGO platelets, and the other containing polyhedral Ag and rGO nanoparticles (Fig.10). They used a process starting from graphene oxide exfoliation, ink formation, printing, to final reduction. Central to this approach was that the ink solvent was only water. The monodispersed Ag nano-triangle platelets (Ag NTPs) and Ag polyhedral nanoparticles (Ag NPs) could self-assemble on rGO platelets which were also used as the dispersant and stabilizer. Compared with rGO, (Ag NP)-rGO and other rGO-based materials previously reported, the Ag NTP-rGO pattern showed a low sheet resistance of 170 Ω/\square after reduction with a transmittance of 90.2%. The inkjet printing and reduction process can also be used to obtain other metal-graphene patterns and devices. However the reduction process of this method is not ideal because of the long thermal treatment time of 3 hours at 110°C in a vacuum oven after the ink printing process.

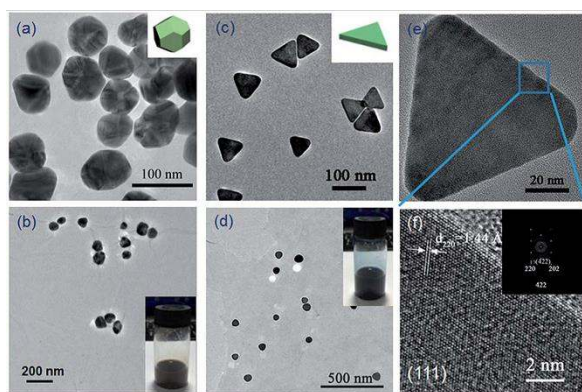


Fig.10. The TEM images of the as-synthesized (a) Ag NPs, (b) Ag NP-GO (the inset is a photograph of the Ag NP-GO ink), (c) Ag NTPs, (d) Ag NTP-GO (the inset is the photograph of the Ag NTP-GO ink) and the HRTEM images of the as-synthesized Ag NTPs (e and f), the inset in (f) is a high resolution fast Fourier transform diffraction pattern of Ag NTPs.¹⁰¹

Annealed graphene nanosheets coupled with Ag organic complex inks have been developed by Chen's group¹⁰², by dispersing an as-purchased silver based complex and the annealed graphene nanosheets in a mixture of cyclohexanone and terpeneol. A resistivity of $4.62 \times 10^{-4} \Omega\text{m}$ was achieved after baking at 300°C for 40 minutes after film deposition. The Ag nanoparticles (NPs) were uniformly distributed on graphene nano-sheets after the post annealing process, which could act as superiorly conductive bridge to further decrease the contact resistance of graphene flakes and the resistivity of the inkjet printed track. The interwoven graphene nanosheets with Ag

NPs formed a three-dimensional conductive network in the film with good mechanical robustness. The results provide a possible pathway for future bendable inkjet printed electronic devices.

Xu et al.¹⁰³ prepared a hybrid conductive ink composed of Ag NPs and graphene-Ag nanocomposites for writing electronics. The Ag NPs and graphene-Ag nanocomposites were dispersed in a mixture of ethanol, ethylene glycol and glycerol to form the ink. Owing to the electrical pathway effect of graphene and the decreased contact resistance of graphene interfaces by depositing Ag nanoparticles onto graphene sheets, the concentration of Ag NPs was significantly reduced while maintaining high conductivity at a curing temperature of 100°C. A typical resistivity value measured was $1.9 \times 10^{-7} \Omega\text{m}$, which is 12 times the value for bulk silver. Even after thousands of bending cycles or rolling, the resistance values of the written tracks only increased slightly.

Recently Zhang et al.¹⁰⁴ synthesized a Ag/RGO composite with good conductivity and dispersivity as a conductive ink filler for inkjet printing (Fig.11). The conductivity of the Ag/RGO filler could be controlled by changing the reaction time to anchor Ag nanoparticles onto the surface of RGO nanosheets. The Ag NPs served as spacers to prevent the reduced graphene sheets from agglomerating and causing nozzle jam. Multifarious regular patterns with an optimum conductivity of $2.0 \times 10^3 \text{ S/m}$ and a sheet resistivity of 0.5 $\text{k}\Omega/\square$ were fabricated using a standard commercial inkjet printer. The Ag/RGO composite was attested to be a suitable material for fabricating printable flexible electronics at 100°C and developing graphene-based functional electronic devices.

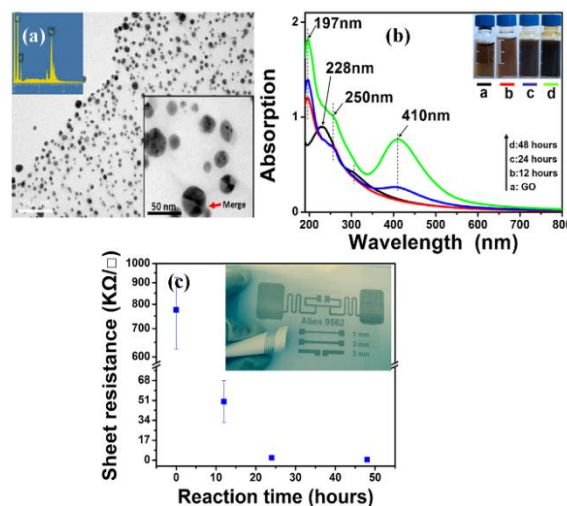


Fig.11. (a) TEM image of Ag/RGO hybrid with reaction time of 48 h (inset: enlarged TEM view of Ag NPs and EDS of Ag/RGO composite), (b) UV-vis absorption spectra of synthesized Ag/RGO composites from GO after reaction times of 12 h, 24 h and 48 h, and (c) sheet resistance as reaction time (inset: Patterns obtained by inkjet printing on office paper and photo paper)¹⁰⁴

3.2.5 Challenges for Graphene Related Inks

Although various kinds of graphene based inks have been created and deposited onto different substrates and conductive

patterns have been obtained, there are still some distinct shortcomings to be overcome for commercial applications.

First, graphene loading is low in the current graphene inks, which is usually in the range of 0.002-1 wt% and therefore poor electrical conduction of the resultant circuit patterns for applications in flexible electronics. Second, GO inks require a thermal reduction process or an alternative method (chemical or photo or thermal) to make the ink tracks conductive, which has cost and safety implications and thus not ideal for industrial applications. Third, there is a compatibility problem between the existing graphene based inks and the production methods as well as the flexible substrates. The important properties of inks, such as viscosity, surface tension and wettability, should be considered. What's more, most of these synthetic methods are not economically feasible because of the low throughput and agglomeration in the process of preparation and storage. Last, although some research has been done to improve the conductivity of graphene by decorating it with silver particles, little work has been conducted successfully in view of the feasibility (both dispersivity and conductivity) of Ag-decorated graphene for printable ink to fabricate flexible electronics. Among the successful cases in which printable Ag/graphene inks were obtained, the synthetic methods are still complicated and time-consuming, and hydrazine was usually used which is a highly toxic substance. Some new approaches need to be developed. A possible idea is to synthesize Ag-graphene inks in one step by chemically reducing the Ag^+ and GO simultaneously.

Thus much effort is still required to obtain highly stable, reliable and high throughput graphene based inks and patterns with good conductivity for commercial applications.

4. Applications of Graphene Based Ink

4.1 Electronic Devices

The electronic devices fabricated using graphene based inks range from various sensors, conductive patterns or lines, electrodes and transistors.

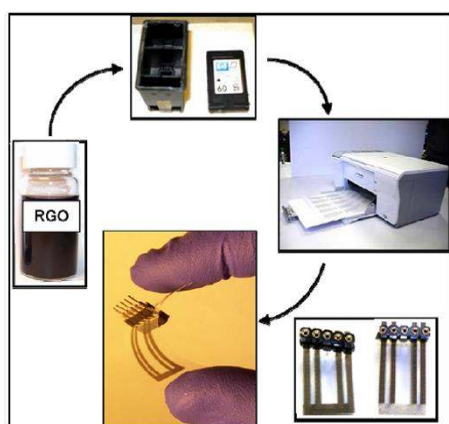


Fig.12. Sensor fabrication procedure. Inset: Digital images of thick and thin (right) bottom strips of inkjet printed sensors.

Dua et al.⁹⁷ fabricated a rugged and flexible sensor using inkjet-printed films of rGO on poly-(ethylene terephthalate) (Fig.12). The rGO films were achieved by the reduction of printed GO using ascorbic acid as a mild and green reducing agent and the sensor could reversibly detect NO_2 and Cl_2 vapors within an air sample at the ppb (parts per billion) level. The large available surface area of rGO makes it an attractive candidate for chemical detection.

Huang et al.¹⁰⁵ printed high image quality patterns with controllable line width and thickness on paper and plastic substrates using both GO and few-layered graphene oxide (FGO) inks. The printable graphene-based inks were prepared by sonicating GO or FGO in deionized water followed by centrifugal filtration to remove the large particles. Inkjet printing was carried out using a standard commercial office printer at room temperature. The printed graphene pattern worked rather well as a normal electronic circuit connected in series with a battery and an LED (Fig.13). Moreover, the brightness of the LED was identical, irrespective of whether the printed graphene electronic circuit was flat or bent. The graphene based ink has also been used to fabricate a novel enzyme-free electrochemical hydrogen peroxide (H_2O_2) sensor using this simple process which has the advantages of low cost, flexibility, ease of mass fabrication and usage under harsh experimental conditions. One problem of this method is that the patterns printed on PI need to be reduced at 400°C for 3 hours in a mixture of 95 vol% argon and 5 vol% hydrogen to make them conductive, which is a high temperature and not efficient approach.

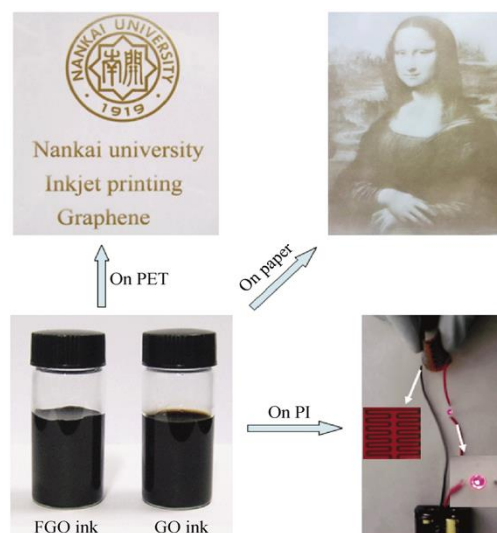


Fig.13 Patterns printed on various substrates by using GO or FGO inks with high resolution¹⁰⁵

Sinar et al.¹⁰⁶ printed microcircuits on a flexible substrate using the prepared GO inks. Using thermal reduction or laser irradiation, the electrical conductivity of the microcircuitry could be restored.

Shin et al.⁹⁵ demonstrated patterns of graphene nanosheets, derived from the reduction of GO using hydrazine

vapor deposition and mild thermal annealing, on a PET film with high resolution. The graphene-based thin film track exhibited sustained electrical conductivity and used successfully as an electrode for a wideband antenna with 500 MHz of bandwidth and a high transmission power efficiency of 96.7% (Fig.14).

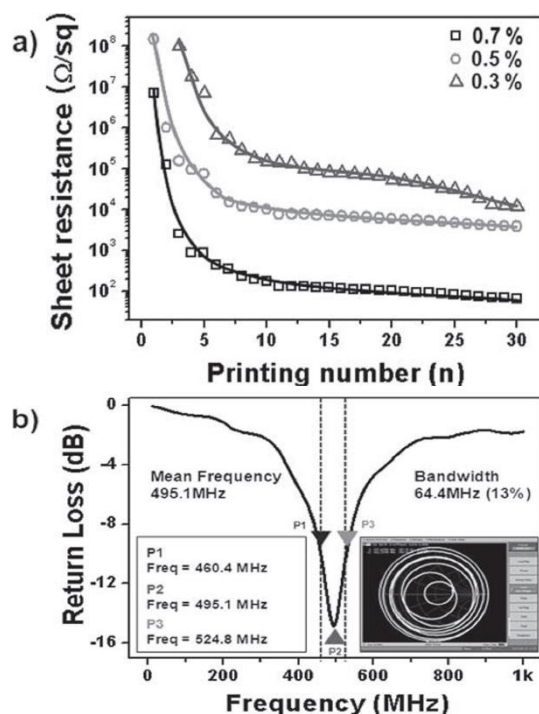


Fig.14. (a) Sheet resistance of printed films from solutions of different GO concentrations as a function of printing number. The graphene-based thin film has a minimum sheet resistance of $65 \Omega/\text{sq}$, (b) The return loss curve of a dipole antenna fabricated using a printed graphene pattern. Inset: Smith chart impedance diagram of the designed dipole antenna⁹⁵

Liu et al.¹⁰⁰ fabricated transparent conductive electrodes using graphene/PEDOT:PSS hybrid inks for ultrathin organic photodetectors (OPD). Conductive graphene films with thickness between 10 to 20 nm were obtained by spray-coating of the ink, yielding a conductivity of about $1000 \text{ S}\cdot\text{cm}^{-1}$ with a transmittance of 80% at 500 nm and were used as the bottom electrode in ultrathin OPD devices with performance comparable to that of the state-of-the-art Si-based inorganic photodetectors. The work shows the potential for future development of transparent electrodes for optoelectronics, and other emerging flexible devices.

Kong et al.⁸⁸ fabricated micro-patterns of graphene electrodes by inkjet printing of GO dispersion ink onto flexible polymeric substrates and the subsequent photothermal reduction using an IR heat lamp in the ambient environment (Fig.15a, b). Spacing between the adjacent ink droplets and the number of printing layers were used to tailor the electrode's electrical sheet resistance as low as $0.3 \text{ M}\Omega/\square$ and optical transparency as high as 86% (Fig.15c). The graphene electrode was found to be stable under mechanical flexing and it behaved as a negative temperature coefficient material. This finding suggests the potential use of the inkjet-printed graphene

electrode as a writable, very thin, mechanically flexible, and transparent temperature sensor.

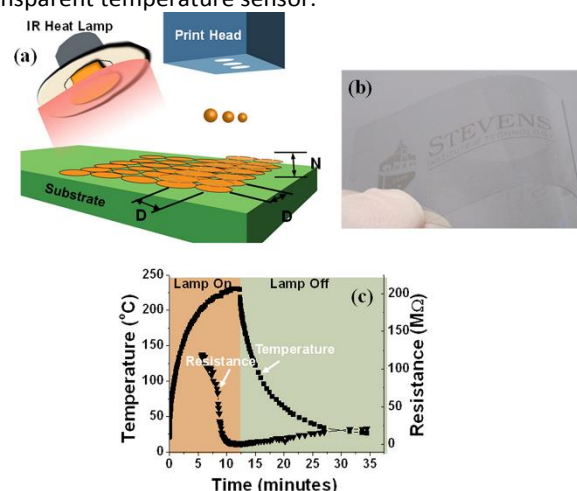


Fig.15. Flexible graphene micropatterns produced by inkjet-printing of GO sheets and photothermal reduction using an IR heat lamp in ambient environment. (a) illustration of the overall processing concept with the spacing between adjacent ink droplets (D) and the number of printed layers (N) as the major printing variables, (b) micropatterns printed on a transparent PET substrate, and (c) electrical resistance and temperature changes measured in real-time during the photothermal reduction step of the inkjet-printed graphene produced at $D = 30 \mu\text{m}$ and $N = 3$.⁸⁸

Casaluci et al.¹⁰⁷ produced a graphene based ink by liquid phase exfoliation of graphite in dimethylformamide. By using a spray based coating method they deposited the graphene ink on a transparent conductive oxide substrate to realize a large area (90 cm^2) counter-electrode with a transparency of 44% (Fig.16). The graphene based counter-electrode was successfully integrated in a large-area (43.2 cm^2 of active area) dye-sensitized solar cell module achieving a power conversion efficiency of 3.5%. The work demonstrates the potential application of graphene based inks in the development of all printed, flexible, transparent, large-area and cost-effective photovoltaic devices on arbitrary substrates.

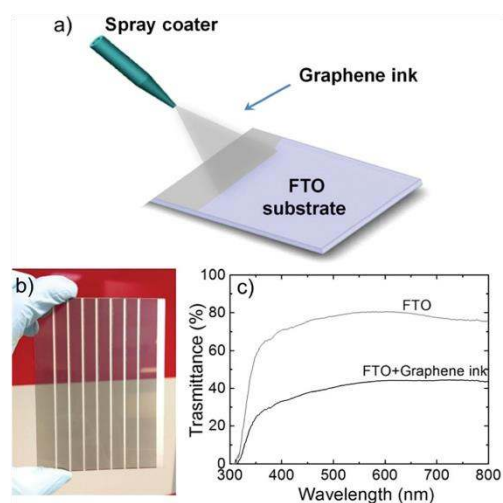


Fig.16. (a) Spray coating of graphene ink. The graphene ink was deposited onto a FTO coated glass substrate by a spray gun, (b) Optical image of graphene-

based counter electrode, and (c) Optical transmittance of FTO and graphene-coated FTO substrates.¹⁰⁷

Gao et al.⁹² fabricated highly conductive pristine graphene electrodes by inkjet printing using ethyl cellulose as the ink stabilizer. The sheet resistance of the printed films after 30 printing passes was only $0.81 \pm 0.2 \text{ k}\Omega/\square$, and the films had a transmittance of approximately 60% after annealing at 300°C for 30 minutes (Fig. 17b). The electrical resistivity of the printed electrodes on flexible substrates increased only slightly after 1000 bending or folding cycles (Fig. 17a). The formulated pristine graphene ink is expected to have significant potential applications in fabrication of flexible electronic devices.

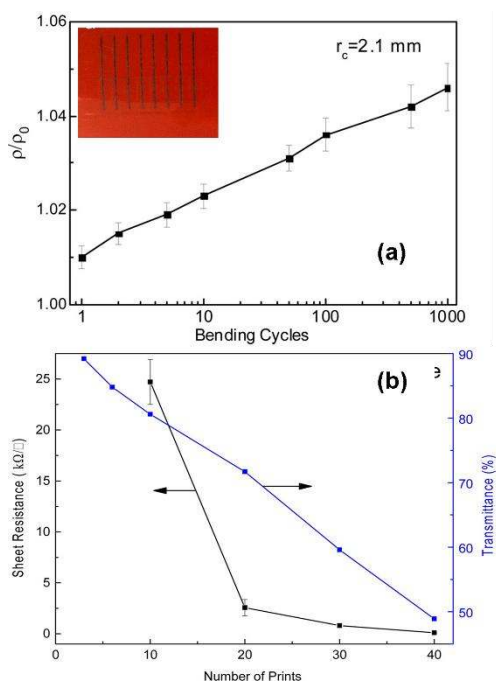


Fig. 17 (a) Relative resistivity of the original graphene electrodes after repeated bending (inset is photograph of printed electrodes of 25-mm of length on a PI substrate), (b) Sheet resistance and transmittance (at $\lambda = 550 \text{ nm}$) of the printed patterns with the number of printing passes.⁹²

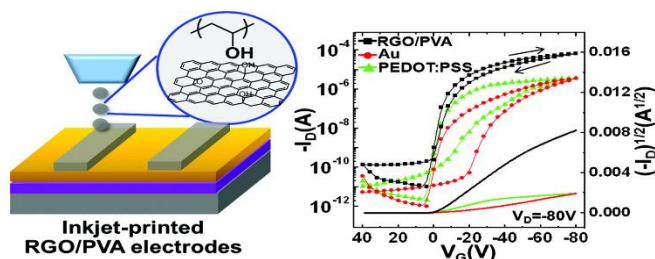


Fig. 18. Inkjet-printed rGO/PVA electrodes and the transfer characteristics at $V_D = -80 \text{ V}$.⁹⁸

Lim et al.⁹⁸ fabricated organic field-effect transistors using inkjet-patterned rGO and poly(vinylalcohol) (PVA) composite electrodes (Fig. 18). The rGO/PVA composite was easily patterned by inkjet printing. A multistep reduction approach based on the combination of chemical and thermal reduction was conducted to increase the conductivity. The inkjet-

patterned rGO/PVA electrodes increased the field-effect mobility of the bottom-contact pentacene FETs to $0.23 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which was significantly enhanced relative to that of the FETs with Au or PEDOT:PSS electrodes. Moreover, they successfully prepared all-organic flexible transparent FETs using inkjet-patterned rGO/PVA electrodes on a plastic substrate.

Labroo et al.¹⁰⁸ demonstrated graphene ink based biosensor arrays on a microfluidic paper for the multiplexed detection of different metabolites (Fig. 19). The sensor arrays performed sensitive, specific, and rapid detection of different metabolites, including glucose, lactate, xanthine and cholesterol. The approach may open new avenues for a variety of applications in healthcare, pharmaceuticals, food science, and environmental monitoring.

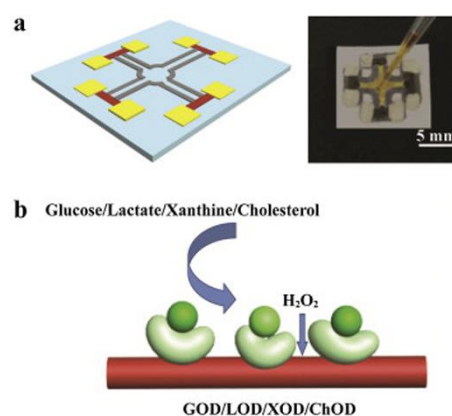


Fig. 19 (a) Schematic illustration (left) and camera image (right) of the multiplexed graphene-based electrical biosensor arrays on a microfluidic paper, (b) biosensor detection principle. In (a) left: red is graphene; yellow is silver paste; blue is paper; grey is microfluidic channel and in (b): light green is enzyme; dark green is analyte.¹⁰⁸

Torresi et al.⁹⁰ and Han et al.¹⁰⁹ used pristine graphene prepared by liquid phase exfoliation (LPE) of graphite in NMP to print thin film transistors (TFTs). However, a low graphene concentration (0.11 mg/mL) reduced the efficiency of inkjet printing, and the residual solvent in the printed patterns also impaired the electrical conductivity.

Shin et al.⁹⁵ developed a simple method to deposit large area and transparent graphene films via inkjet printing and vapour deposition process for fabrication of poly(vinylidene fluoride) based acoustic actuators. The results demonstrated that the graphene based acoustic actuator had much less power consumption compared to the commercial thin film speaker, and it was expected to be used as an extremely thin and lightweight loud speaker.

Bardpho et al.¹¹⁰ developed a graphene/polyaniline (G-PANI) modified carbon electrode to use as a new electrochemical sensor for chromatographic determination of antioxidants in tea samples. The G-PANI conductive ink was deposited on screen-printed carbon electrodes by inkjet printing for providing an enhanced electrochemical performance of the electrodes. Four antioxidants were successfully separated and quantified within 3 minutes with

good recovery and low LOD (limits of detection). The proposed method is an improved approach to the determination of antioxidants in tea samples.

4.2 Energy Devices

Rechargeable lithium batteries have been fabricated using different formulations of graphene inks by Wei et al.¹¹¹ and the performance was compared at room temperature. Electrodes using the anionically-modified graphene inks containing anatase titanate (TiO_2) nanoparticles showed improved performance over those fabricated using a pristine graphene ink as well as the p-type conducting polymer modified ones. In addition, the open circuit voltage of batteries based on the ink with TiO_2 nanoparticles was boosted over 3 V with good cyclability when mixed with the graphene ink. Combined with a polymer electrolyte, the work suggests a feasible route towards fully printable rechargeable lithium batteries.

Supercapacitors have advantages in power density, cycle life, and shelf life, and exhibit rapid charging/discharging capability and good performance over a wide temperature range over batteries for energy storage. Microsupercapacitors (MSC) as miniature energy cells can be used as power sources for a range of emerging applications in microelectromechanical systems (MEMS), portable/wearable devices, wireless sensor networks, piezoelectric nanogenerators, solar cells and thermoelectric cells¹¹⁴. Graphene is being widely studied for supercapacitor applications due to its superior electrical conductivity, transparency and large surface area. Graphene-based materials are especially attractive for printing flexible supercapacitors since graphene is a very strong and flexible material, and its oxidized form (graphene oxide) can be used to make a good inkjet printable ink when dissolved in water.

Li et al.⁸⁹ fabricated microsupercapacitors (MSCs). Silver nanoparticles were first printed as the current collectors in an interdigitated structure (Fig.20a). Then, graphene was printed onto the fingers as the electrodes (Fig.20b). The printed silver current collectors possess considerable capacitance due to the porous nature resulting from the printed nanoparticles. A value of $0.19 \text{ mF}\cdot\text{cm}^{-2}$ at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ was calculated from the cyclic voltammetry curves measured in Na_2SO_4 aqueous electrolytes. With only 8 printed layers of graphene, the capacitance was increased by about a factor of 3 to $0.59 \text{ mF}\cdot\text{cm}^{-2}$. At a lower scan rate ($10 \text{ mV}\cdot\text{s}^{-1}$), the capacitance was even higher ($0.82 \text{ mF}\cdot\text{cm}^{-2}$). The technique provides an efficient, low-cost method for fabrication of a variety of graphene based electronic devices with good performance and it is a promising alternative to the existing approaches for future commercial applications in printed and flexible electronics.

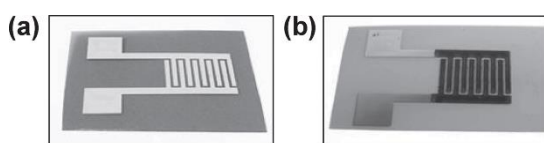


Fig.20. (a) Photograph of pre-annealed silver current collectors for an MSC which can also be considered as an MSC with bare silver electrodes, (b) Photograph of a pre-annealed graphene MSC (graphene is on top of silver current

collectors). In (a) and (b), the fingers are 1.0 mm wide, 9.4 mm long and interspaced by 0.6 mm. The two large silver pads (on the left) are for electrical connections for electrochemical measurements. The total effective electrode area for each MSC is about 1.6 cm^2 ⁸⁹

Xu et al.⁹⁹ formulated NGP/PANI inks and prepared thin film electrodes via inkjet printing of these inks. Homogeneous NGP/PANI thin films were printed on a carbon fabric substrate, with good control over pattern geometry and location. Moreover, as the carbon fabric substrates are electrically conductive, the printed films can be used as electrodes directly for supercapacitor devices. Two as-printed NGP/PANI electrodes on carbon fabric substrate were sandwiched with a separator to form an electrochemical capacitor, using a 1 M H_2SO_4 electrolyte (Fig.21 left). The supercapacitors exhibited good electrochemical performance (maximum specific capacitance of 82 F/g) and a long cycle life (over 1000 cycles, Fig.21 right). Their work offered the possibility of an industrially scalable route to achieving printable energy storage devices.

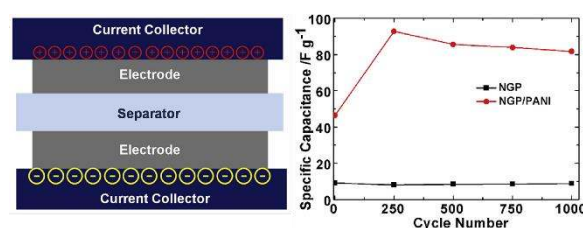


Fig. 21. Supercapacitor device structure (left) and cycling stability over 1000 cycles and measured at a constant current density of 1.4 A/g , with 1 M H_2SO_4 electrolyte.⁹⁹

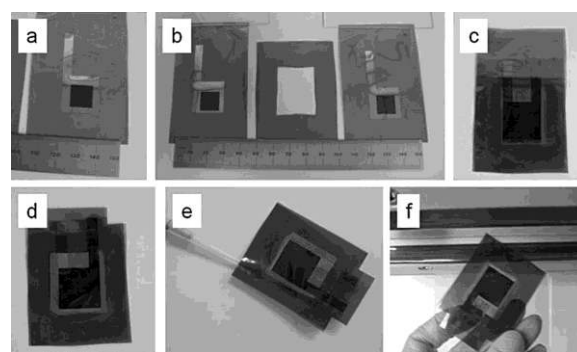


Fig.22. Flexible supercapacitor assembly process. (a) graphene oxide printed on a metal current collector on Kapton film and reduced at 200°C , (b) two electrodes were assembled with an intervening frame of FEP-coated Kapton film, (c) electrodes were heat sealed face to face on three sides, (d) the polypropylene separator was placed between the electrodes, (e) the electrolyte was added, and (f) the final seal was made.⁹⁶

Le et al.⁹⁶ fabricated supercapacitor electrodes by printing GO (0.2 wt%) dispersion on metal foil current collectors combined with thermal reduction. A commercial inkjet printer (Fujifilm Dimatix DMP 2800) was used to print the ink and then thermal reduction was carried out in N_2 environment at 200°C for 12 hours to make the GO film conductive. The supercapacitor prototypes were assembled using the obtained

electrodes, a Celgard separator and a rigid fluoropolymer clamp (Fig.22). The achieved specific capacitance of 132 F/g is similar to that obtained using other electrode fabrication methods. In the subsequent work, they fabricated a supercapacitor by printing graphene electrodes on flexible Kapton substrates.¹¹² Graphene oxide dispersed in water was used as an ink for inkjet printing of the electrode active material onto metal film on Kapton current collector and then was thermally reduced at 200°C to produce conductive graphene electrodes. The supercapacitor was assembled by the obtained electrodes together with added electrolyte and separator. The specific capacitance of the graphene-based flexible supercapacitor was measured to be as large as 192 F/g and the supercapacitor showed very good capacitance retention with bending.

Guo et al.¹¹³ prepared a GO and single-walled carbon nanotube (SWCNT) composite ink and fabricated paper-based electrodes for supercapacitors without using binders, additional current collectors or other additives (Fig.23). The interaction between GO and SWCNT not only provides means to separate SWCNTs but also offers approaches to separate individual GO sheets, which increases the effective active area for electrochemical reaction. SWCNT over 12 mg/ml could be dispersed in water without surfactants, which is the highest reported value so far. The mixture showed high stability and permeability as ink material to prepare paper electrodes. The highest value of specific capacitance was 295 F/g at a current density of 0.5 A/g with a GO/SWCNT weight ratio of 1:5. This approach provides a binder-free ink printing method for large-scale fabrication of electrochemical energy storage devices.



Fig.23. Preparation of supercapacitor electrodes using GO/SWCNT ink and paper.¹¹²

An interdigital MSC based on an ink of template-assisted graphene nanosheets (TAGNs) as the active electrode material was fabricated on a flexible polyimide substrate using a gravure printing process by Zhang et al.¹¹⁴ The ink was prepared by inserting an Mg(OH)₂ template between the GO nanosheets. By successively printing Ag interdigitated electrodes (IDEs), the crumpled graphene active material layer and polyvinyl alcohol (PVA):H₂SO₄ as the solid electrolyte on a PI substrate, a printed interdigital MSC with TAGNs was fabricated, exhibiting a large capacitance of 6.65 mF·cm⁻². Furthermore, printed interdigital MSC arrays were demonstrated by using them to drive a liquid crystal display (LCD).

5. Outlook

Remarkable scientific progress has been made in the synthesis and application of graphene based inks, but considerable future development is necessary before they can be used in practical applications. Large scale, good quality, low-cost and eco-friendly synthetic techniques are required for producing and handling graphene based inks for commercial adoption in flexible electronics.

The ink properties such as viscosity, surface tension as well as volatility are important determining the ink's printability and need to be specifically controlled to meet the requirements of different patterning methods. Meanwhile, the wettability of the ink with flexible substrates, which determines the quality of the formed film, is also an important factor. Therefore further efforts should also focus on the selection of functional components such as solvents and surfactants in the ink formulation process.

The characteristics of graphene or its derivatives are very critical for an ink because they determine the electrical and mechanical properties of the resultant conductive patterns. Although high quality graphene can be fabricated by liquid phase exfoliation without oxidation, pristine graphene still shows poor solubility in common solvents. In order to achieve efficient synthesis of graphene based inks, it is essential to carry out surface functionalization of graphene. The choice of organic surface-modifiers may be a solution, since these surface-modifiers can serve as bridges by attaching onto graphene surfaces with one end and providing accessible functionalities with the other end. Using a mixture of solvents is another promising approach, which can increase the affinity between the solvent and the pristine graphene flakes, thereby increasing the graphene concentration in the ink.

As already discussed, GO is strongly hydrophilic and can be easily formulated into ink. However GO sheets are not electrically conductive. Therefore the GO ink requires an additional step to make the ink tracks conductive after deposition by a thermal, chemical, or photo-thermal treatment which involves cost and safety considerations. In this respect, self-sintering mechanisms, where sintering occurs spontaneously in the patterning process, may be preferred. The rational combination of formulation-processing-sintering of the GO inks is a direction for future development.

Currently the conductivity of films deposited from pure graphene inks remains low and limits their applications. For high conductivity applications, graphene/metal hybrid inks may be a better solution. The graphene nanosheets coupled with metal nanoparticles could increase the electrical conductivity of the resulting films due to the defect free structures and effective electrical pathways produced by graphene between the metal nanoparticles. The work needs to be conducted in this respect is to improve the methods for ink synthesis. An efficient approach would be one step synthesis of Ag decorated graphene inks.

Most of the available ink synthesis methods such as ultrasonic exfoliation or chemical reduction are still not economically feasible because of the low throughput, complex process as well as the utilization of toxic chemicals. To date, the solvents used in synthesis of graphene-based inks, such as NMP,

DMF, DMSO, are not environmentally friendly and have a high boiling point, which is a limitation for the development of a graphene-based printing technology. Non-toxic and low boiling point solvents such as water and alcohols, may be the preferred options for the development of fully environmentally-compatible ink-jet printing processes. Apart from changing the ink solvents, development of new synthesis methods such as the in-suit approach may be a good strategy for practical application of graphene based inks in manufacturing of functional devices and electronic systems on flexible substrates.

Clearly much effort is still required to obtain highly stable, reliable and high throughput ink materials as well as the related patterning methods in order to produce electrode patterns with good resolution and conductivity, sensors and energy storage devices for flexible electronics.

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