

Application of Photo-Reduced Graphene for Supercapacitors: Synthesis, Characteristic and Properties

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Abstract

Photo-irradiation reduction of graphene oxide to produce graphene is a simplified, rapid, energy efficient and poisonous material free alternative to the most commonly used chemical reduction method. This process not only can be used to produce large quantities of high quality graphene for large-size supercapacitors usable in automotive and stationary energy storage, but also can be used to prepare small amount of graphene used for printable, portable and flexible supercapacitors. The main advantage of the photo-irradiation process is that it does not rely on the use of chemicals or high temperature. Specifically, it can shorten the reaction time from several hours to a few minutes. In addition, photo-irradiation reduction has significant advantages for the design and fabrication of graphene-based micro-devices since graphene layers can be structured by direct patterning of graphene oxide films. With the rapid progress of photo-irradiation reduction methodology, low cost and high volume industrial production of graphene by this method could become a vital process. In this paper, the recent advances of using the photo-irradiation reduction process to produce graphene will be reviewed. The paper will also describe the characteristics of photo-reduced graphene and its performance when it is used as the active electrode materials for supercapacitors.

Keywords: *Electrochemical capacitor; Supercapacitor; Photo-irradiation reduction; Photo-chemical reduction; Photo-thermal reduction; Laser reduction; Graphene; Graphite oxide; Specific capacitance of photo-reduced graphene*

Introduction

Graphene is a form of carbon material that made up of one single atomic layer. In order to create high quality and sufficient quantities of graphene for industrial applications such as energy storage, catalysis, sensors and printable electronics, simple and cost effective fabrication methods are greatly needed. Currently, the most common and vital process to form graphene is by reducing graphite oxide chemically. Hummers and Offeman's method [1] is the most common ways for producing graphite oxide, in which graphite is treated with oxidising agents such as a mixture of sulphuric acid, sodium nitrate and potassium permanganate. However, other modified chemical reduction methods have been developed recently that are shown

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to be more efficient [2,3]. The oxidising agents react with graphite, resulting in increasing the inter-planar spacing between the layers of graphite and forming graphite oxide. When graphite oxide is dispersed uniformly in a solution such as water by sonication or stirring, graphene oxide is produced. Mechanically stirring causes much less damage to graphene oxide sheets than sonication, but it can take much longer to accomplish the dispersion. Sonication could cause heavy damage of the graphene oxide flakes by reducing their sheet size from microns to nanometres.

Graphene oxide was then reduced by reducing agents such as hydrazine and NaBH₄. Reducing graphene oxide by using chemical reduction is a very scalable method, but unfortunately, the graphene produced has often resulted in relatively poor yields in terms of surface area and electronic conductivity. The use of toxic agents could not only bring some risks to the environment and safety of production, but also introduce impurities in the reduced graphene [4]. Thermal or electrochemical means can also be used to reduce graphene oxide to produce graphene. Graphene produced by thermal treatment at temperature of 1000°C or above produces graphene that has been shown to have surface area similar to that of pristine graphene. Thermal reduction has unique advantages of short reaction time and avoiding uncontrollable aggregation in solvents [5], the heating process could damage the structure of the graphene platelets creating imperfections and vacancies, and potentially affect the mechanical strength of the graphene produced. The thermal process also requires huge energy consumption which limits its widespread commercialization. Electrochemical reduction of graphene oxide can produce graphene that has almost identical structure to pristine graphene. Electrochemically reduced graphene was found to have a very high carbon to oxygen ratio with electronic conductivity readings higher than that of silver (8500 S/m, higher than that of silver). This technique has not used any hazardous chemicals, however, only a very thin layer of graphene oxide that needs to be coated on conductive substrates such as indium tin oxide coated glass can be reduced; therefore, the scalability of the electrochemical technique is an issue due to the difficulty in depositing graphene oxide onto the electrodes in bulk form. It is very clear that the methods selected for reducing graphene oxide to produce graphene have a large impact on the quality of the graphene produced, in terms of surface area, electronic conductivity and structure.

Most recently, it has been demonstrated that graphene oxide can be reduced by a photo-irradiation reduction process [6-10]. The main advantage of the photo-irradiation process is that it does not rely on the use of chemicals or high temperature. In some cases, photo-reduction takes only a few minutes instead of several hours by the chemical reduction. In addition, photo-irradiation reduction has significant advantages for the fabrication and integration design of graphene-based micro-devices, and for direct patterning for micro-device fabrication of flexible electronic devices [8,11]. With the rapid progress of photo-irradiation reduction methodology, low cost and high volume industrial production of graphene by this method could become a vital process. In this paper, the recent advances of using the photo-irradiation reduction process to produce graphene will be reviewed. The paper will also describe the characteristics of photo-reduced graphene and its performance when it is used application as the active electrode materials for supercapacitors.

Fabrication of Graphene by Photo-Irradiation Reduction Process

The photo-irradiation reduction of graphene oxide to produce graphene can be accomplished with different light sources, including solar light, UV, visible and IR lights generated by different types of lamp, and lasers operating at different wavelengths. Photo-irradiation reduction processes include variety mechanisms such as photo-thermal reduction, photochemical reduction, and catalyst assisted photochemical reduction. By adjusting the energy, power, irradiation time,

wavelength length of the light source, as well as the surrounding medium and atmosphere, the conductivities, residual oxygen contents, porosity, surface area and wettability of the reduced graphene can be controlled and optimized for specific applications. By mixing graphene oxide with various chemical compounds before photo-irradiation reduction, doped and composite graphene with various functionalities can be produced; thereafter to fit towards a wide range of applications, such as supercapacitors and Li-ion batteries. In this section, recent development on photo-irradiation reduction of graphene oxide to form graphene by various light sources at different condition parameters will be briefly overviewed and discussed.

Mohanapriya et al. [12] reported the use of focused solar light to irradiate graphene oxide paper to make graphene. The graphene oxide paper was formed by drying the solution of graphene oxide suspension on a Petri dish at atmospheric conditions. The graphene oxide was synthesized according to the Hummers method. A convex lens was used to focus the solar radiation to irradiate the graphene oxide paper to exfoliated and reduced graphene oxide simultaneously. Reduction of graphene oxide was induced by suddenly rising in temperature up to 204°C under focused solar irradiation and the thermal reduction process is accompanied by a color change and volume expansion. Graphene oxide was then decomposed into graphene along with releasing CO₂ and H₂O gases. Typically the reduction and exfoliation process takes less than two minutes to complete. Concentrated solar radiation obtained by focusing a large area of sunlight into a small beam using lenses or mirrors can be used as a heat source for photo-thermal reduction of large quantities of graphite oxide. Since a wide range of concentrating technologies already exists to provide process heat for commercial and industrial applications, the process of using solar radiation for reducing graphene oxide to produce graphene could be low cost, rapid, and scalable process for the large scale preparation of graphene for energy storage in automotive, transportation and stationary applications in whose applications low cost and large quantity of graphene is needed. The challenge would be on how to control the quality of large quantities of graphene produced by this process as limited process parameters can be controlled and optimized.

To produce small quantities of graphene by the photo-irradiation reduction method, a simple camera flash lamp or a mercury lamp can be used to generate the light beams. Wang et al. [13] used an ordinary camera flash to photo-reduce freeze-dried graphene oxide and produce highly interconnected 3D structured graphene having a high surface area and good conductivity. Cote et al. also reported the use of flash light reduction of free-standing graphene oxide films with a Xenon lamp equipped on a common digital camera to trigger instantaneous deoxygenation of graphene oxide by the photo-thermal heating [8]. They found that the sheet resistance of flashed area was decreased from 2.108 kΩ/sq for the pure graphene oxide to 9.5 kΩ/sq for the graphene with a significant decrease in hydrophilicity. Chen et al. [14] prepared phosphomolybdic acid (PMoA)-graphene nanocomposites by photo-reduction using a high-pressure mercury lamp. In their method, an alcoholic solution containing graphene oxide, PMoA and isopropanol was irradiated by an IR lamp. The PMoA was excited by the photons and then reduced by the electron donors, isopropanol. The reduced PMoA subsequently reacted with graphene oxide (acting as an electron acceptor), forming graphene and regenerating PMoA. Guo et al. [15] used a common bathroom IR lamp with a power of 275 was the light source to reduce graphene oxide. Although the energy of IR photon is lower and adsorption of IR light by graphene oxide films is also less than that of UV and visible light, adsorption of intensive IR light by graphene oxide can increase its temperature very rapidly to induce the thermal reduction. Guo et al. also found that the power density of the IR light has great influence on the structure and properties of graphene. At high IR power densities, the reduction reaction was fierce and the graphene produced was highly porous due to rapid degassing and exfoliation of graphene oxide sheets. At relatively low IR power intensities, the reduction process was relatively slow and the produced graphene was less porous.

Although photo-irradiation reduction of graphene oxide by various lamps is a simple, rapid, chemical-free, and energy efficient process, it is only suitable at producing a small quality of graphene for applications in thin film devices or micro-devices such as sensors, printable electronics and small energy storage devices for portable electronics.

To increase the degree and percentage of graphene oxide that was reduced, photo-catalysts such as TiO_2 , BiVO_4 , were added into the graphene oxide solution or films. Under UV/visible light irradiation, the photo-catalysts in the solutions or films absorb photon and become excited. The excited photo-catalysts give up the electrons which are accepted by graphene oxide inducing its reduction to form graphene. The photo-catalyst assisted reduction process also provides a new way to make graphene-metal oxide composites that can be used as active materials for energy storage devices. Williams et al. [16] used TiO_2 as the photo-catalyst and an Oriel 450 W xenon arc lamp as the light source to carry out UV-induced photocatalytic reduction of graphene oxide in a TiO_2 -graphene oxide colloidal suspension. To ensure uniform irradiation of the TiO_2 /graphene oxide suspension, nitrogen gas was bubbling through the suspension solution to induce agitation. Due to the existing TiO_2 particles, the degree of reduction of graphene oxide was improved and collapse of exfoliated sheets of graphene was avoided. Yang et al. [16] also synthesized reduced graphene oxide/ TiO_2 composites by combining TiO_2 and graphene oxide under UV irradiation (254 nm, 18 W, Philips) based on a modified version of Williams's method. They investigated the influences of TiO_2 content on the reduction degree of graphene oxide during synthesis of the graphene/ TiO_2 composites by varying the weight ratios of graphene oxide: TiO_2 at 1:0, 1:1, 1:1.5, 1:2, and 1:2.5. They found that with the increasing amount of TiO_2 , the percentage of graphene oxide that was reduced was increased. At a graphene oxide: TiO_2 ratio of 1:2, the OH, carboxylic and carbonyl functional groups, on the edge of the graphene oxide were completely removed. Akhavan and Ghaderi investigated the light-induced photocatalytic reduction of the graphene oxide films deposited on the TiO_2 substrate in an ethanol solution [7]. Different irradiation times was used to prepared the graphene films, after 4 h of photocatalytic reduction, the concentration of the C–OH, C=O, and O=C–OH bonds was found to decrease to 73%, 85%, and 72%, respectively, which is good indication of effective reduction of graphene oxide to form graphene. Besides the most commonly used photo-catalyst, TiO_2 , which absorbed UV light, other photo-catalysts can also be used. For example, Ng et al. [17] use bismuth vanadate (BiVO_4) as the photo-catalyst to reduce graphene oxide. They reported that BiVO_4 can use the visible light instead of the UV light as by TiO_2 to reduce graphene oxide. These authors attributed this finding to the larger band gap energy and longer electron lifetime of excited BiVO_4 compared to TiO_2 , which can better utilize visible light and minimize photoelectron recombination.

Nitrogen has comparable atomic size to carbon and it has five valence electrons available to form strong valence bonds with carbon atoms, therefore chemical doping of graphene with N can effectively modify its intrinsical electronic and chemical properties. N-doping can result in a higher positive charge on a carbon atom adjacent to the nitrogen atoms in graphene. It has been proved that nitrogen doped graphene (N-graphene) has higher electro-catalytic activity for the reduction of hydrogen peroxide and oxygen than graphene [18] and better performance in Li ion battery applications [19]. Huang et al. [20] synthesized N-graphene by simple photo-reduction of graphene oxide deposited on nickel foam under NH_3 atmosphere. In their experiments, graphene oxide was first coated on nickel foam framework without any binder, and then, the graphene oxide deposited on nickel foam was irradiated by a high-pressure Hg lamp (500 W) under NH_3 (99%) atmosphere as shown schematically in FIG. 1.

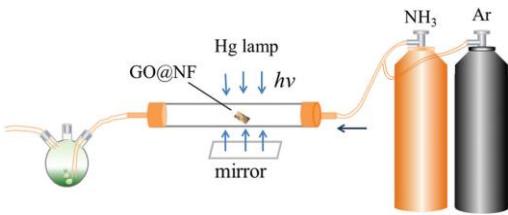


FIG. 1. Schematic illustration of the photo-reduction apparatus for producing N-graphene from the GO deposited on nickel foam (GO@NF), Reproduced with permission from ref [20].

This method shown in the FIG. 1 can reduce graphene oxide to graphene together with inducing nitrogen doping. The nitrogen-doped content can reach up to 5.99 at a % with only 15 min of irradiation. The nitrogen-doped graphene deposited on Ni foam can be directly used as an electrode for supercapacitors, without adding any conductive agents such a carbon black and polymer binders such as PTFE. Li et al. [21] also used the simple irradiation method to synthesize N-graphene thin films from graphene oxide thin films. The reduction and nitrogen doping of graphene were simultaneously achieved by irradiation in NH_3 atmosphere, and the nitrogen content of N-graphene could reach as high as 12.34 at a % within only 5 minutes of irradiation. With longer irradiation time to 120 minutes, the N content could reach a very high value of 17.21%. Compared to the irradiation of graphene oxide films in Argon atmosphere, irradiation in NH_3 atmosphere is much more effective at improving its electrical conductivity. This is attributed to nitrogen doping and oxygen reduction, both of which can effectively enhance the electrical conductivity. The mechanism for photo-induced N-doping of graphene was believed to relate to photo-dissociation of the NH_3 gas to generate nitrogen radicals. Nitrogen radicals then react with the graphene oxide via free radical addition reactions. Electrons generated under irradiation can be captured by graphene oxide leading to its reduction.

Compared to other light sources used for photo-reduction of graphene oxide, laser has a number of distinguishing properties: (i) laser beams can be focused on very tiny spots, achieving a very high energy density, and therefore, can be very effective for the reduction of graphene oxide; (ii) wavelength of laser can be selected to cover UV, visible and IR ranges, therefore graphene oxide can be reduced by photo-thermal or photochemical reduction or both mechanisms depending on the needs; (iii) laser beams can be concentrated and travelled at a great distance due to their low divergence and temporal coherence, therefore they can be used to directly reduce/pattern graphene oxide layer for thin film devices so their power. Lasers with short pulse and strong peak power, such as femtosecond and picosecond laser, also enable a nonlinear multiphoton interaction with the graphene oxide within the focal point that could result in more completely de-oxygenation of graphene and create graphene with more porous and curved structures. Huang et al. [22] used a KrF excimer laser operating at 248 nm, 200 mJ and 5 Hz to irradiate a graphene oxide solution contained in a quartz tube. They found that the majority of oxygen-containing functional groups in graphene oxide were removed by the irradiation of the pulsed excimer laser onto the solution. The graphene film prepared from the irradiated solution has a sheet resistance of 53.8 k Ω /sq. Yang et al. [23] also used a KrF excimer laser to irradiate a graphite oxide solution formed by dispersing graphene oxide in Milli-Q water by the sonication treatment. The graphite oxide solution in a quartz vial was irradiated by the KrF excimer laser at 300 mJ or 530 mJ beam energy with 10 Hz repetition for 1 hour, or 2 hours, respectively. The color of the graphite oxide solution was found to changes from brownish yellow color to black after prolonged irradiation. The results again confirmed that excimer laser radiation at UV wavelength (248 nm) can reduce graphite oxygen to graphene in fast rates in the aqueous solution. Yang et al. then evaluated the laser reduced graphene prepared at different laser conditions in a two-electrode supercapacitor cell in

order to understand the effect of laser parameters on the supercapacitive behaviors of laser reduced graphene. Wang et al. [24] also used focused laser beam to fabricate a few layers graphene through simultaneous exfoliation and reduction of graphite oxide. In their experiment, a piece of graphene oxide foam was pressed at 0.2~0.5 MPa to form a relatively dense graphene oxide flake for the laser reduction experiment. The laser used is a continuous wave semiconductor laser with wavelength of 808 nm. In their laser reduction experiment, the laser power was ~1 W (the corresponding power density is about 127 W cm^{-2}), the graphene oxide flake was put onto the quartz tube directly at ambient conditions, and irradiated with the laser for around 1 s. Laser reduction of graphene oxide film to form graphene film was also reported by Romualdas Trusovas et al. [25,26]. They first formed graphene oxide films of around 20 nm by filtration of aqueous graphene oxide suspensions through the polycarbonate membrane filters in an aqueous medium. Reduction of graphite oxide films to graphene were performed by scanning focused laser beam that induces photo-thermal decomposition of graphene oxide. A picosecond laser (PL10100, 10 ps, 100 kHz, Ekspla) and the nanosecond laser (NL15100, 10 ns, 20 kHz, Ekspla) were used for the reduction. The picosecond laser used both 1064 nm and 532 nm wavelengths while the nanosecond laser has the 532 nm wavelength. The optimal laser power was in the range of 10-100 mW (corresponding to the laser fluence in the range of $F = 0.01\text{-}0.3 \text{ J/cm}^2$), depending on the sample thickness. Resistance of the graphene oxide films was decreased by 4-5 orders after they were irradiated with the picosecond 1064 nm laser indicating the formation of graphene. By conducting experiments in nitrogen and argon atmosphere, Romualdas Trusovas et al., have achieved the higher I_{2D}/I_D ratio in Raman spectra indicating higher degree of deoxygenation. In order to understand the fundamentals of the laser photo-reduction process in solutions, Gengler et al. [27] performed a series of transient absorption experiments. They observed an ultrafast photo-induced chain reaction, which is initiated by femtosecond ultraviolet laser pulse. The laser pulse first photo-ionizes the solvent, and then liberating solvated electrons, which trigger the reduction of graphene oxide.

Two dominant mechanisms were accounted for photo-reduction of graphene oxide: photochemical and photo-thermal reductions, in the absent of any photo-catalyst. In the photochemical events, absorption of photons by the graphene oxide leads directly to covalent bond breaking. The threshold of photon energies for photo-reduction of graphene oxide was found to be larger than 3.2 eV ($\lambda < \approx 390 \text{ nm}$) in order for a photochemical process to proceed [28]. In photo-thermal events, photons energy was absorbed by the electrons in graphene oxide. When the photon/electron energy transfer efficiency is high enough, the excited electrons can heat up the lattice to raise the localized temperature and induce bond breaking which results in reduction of graphene oxide. When different laser sources are used for photo-reduction of graphene oxide, reduction can undergo either photochemical or photo-thermal processes, or proceed through a combination of both [29] depending on the wavelength, energy and pulse duration. In principle, reduction by a laser with a wavelength smaller than 390 nm would mainly undergo a photochemical process; whereas for lasers with wavelengths larger than 390 nm, the reduction proceeds through the photo-thermal process mainly. However, in the case of some tightly focused ultrafast lasers, two-/multiphoton absorption may occur and laser-induced thermal relaxation commonly exists. Laser reductions may use both photo-thermal and photochemical effects. For multiphoton ionization to occur, the laser intensity needs to be in the range of 1012 W/cm^2 to 1016 W/cm^2 [30].

Photo-reduction of graphene oxide by laser is an easy way to produce high quality graphene in a fast manner and has demonstrated its exciting potential, however, the small spot size and poor penetration depth of a laser beam has limited its application mainly for deoxygenation of thin films of graphene oxide (typically in several layers), rather than for producing large quantity of graphene. High power and large beam size lasers such as excimer lasers, however, could be exploited to

produce relatively large quantities of graphene using configurations such as a flowing cell in which graphene oxide solution continuously flows through a quartz cell where excimer laser irradiation convert the graphite oxide to graphene. The thus produced graphene can be collected in a receiving reservoir located downstream.

Characterization of Photo-Irradiation Reduced Graphene

XRD Transmission electron microscopy (TEM), Scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman, and X-ray photoelectron spectroscopy (XPS) are the most common techniques to evaluate the graphene oxide and photo-reduced graphene. High-resolution TEM and SEM can clearly exhibit the surface morphology of graphene oxide and photo-reduced graphene samples. They can be used to confirm the degree of exfoliation and preservation of the sheet-like structures after the photo-reduction process. Any photo-induced folding, wrinkling or restacking of graphene sheets can be clearly seen by the two techniques. TEM and SEM results are used to guide the selection of photo-reduction processing parameters in order to create desired structures to match the specific application needs. As an example, FIG. 2, shows the SEM micrographs of the graphite oxide and reduced graphene (rGO) /TiO₂ composited materials of various weight ratios prepared by Yang et al. [16] by combining TiO₂ and graphene oxide under UV irradiation. The 2-dimensional GO sheets are clearly visible in FIG. 2a. At a graphite oxide: TiO₂ ratio of 1: 1, only a small amount of TiO₂ is attached to the graphite oxide surface as shown in FIG. 2b. Upon increasing the graphite oxide: TiO₂ ratio to 1:1.5, increasing amount of TiO₂ was observed to deposit on the graphite oxide surface as shown in FIG. 2c, however, at this ratio, reduction of graphene oxide does not complete and TiO₂ fails to intercalate into the graphene layers. On further increasing the graphite oxide: TiO₂ ratio to 1: 2 FIG. 2d, the amount of graphene oxide that was reduced increases, allowing more TiO₂ to intercalate into the space between graphene sheets. As the graphite oxide: TiO₂ ratio increases to 1:2.5 FIG. 2e, even more TiO₂ particles are inserted into graphene sheets, resulting in a high degree of exfoliation and less chance for restacking of graphene sheets. TEM image of as-prepared rGO/TiO₂ composite materials in FIG. 2f shows that granular TiO₂ particles were placed on the rGO surface after the UV photo-reduction process.

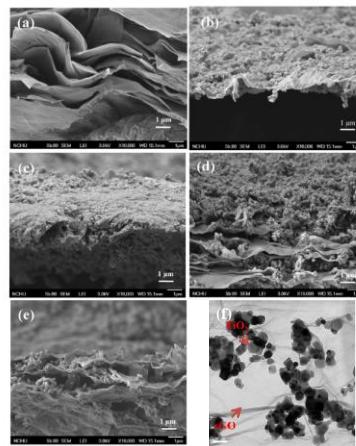


FIG. 2. The SEM micrographs of the GO and the as-prepared rGO/TiO₂ from various weight ratios of raw materials.

(a) GO, (b) GO: TiO₂ weight ratio of 1:1, (c) GO:TiO₂ weight ratio of 1:1.5, (d) GO:TiO₂ weight ratio of 1:2, and (e) GO:TiO₂ weight ratio of 1:2.5. The TEM image of the as-prepared rGO/TiO₂ composite materials is given in (f),

Reproduced from with permission from ref [16].

Confirmation of making graphene by photo-reduction of graphene oxides was done by X-Ray diffraction patterns that were typically measured using CuK α radiation ($k = 1.54 \text{ \AA}$). Graphene oxide displays a peak at 2θ around 10° which is due to diffraction patterns from the it's (002) plane with d-spacing around 0.9 nm, while graphite has a diffraction peak at $2\theta = 27.5$ corresponding to the d-spacing of 0.340 nm which is multiple times smaller than that of graphene oxide. The increase in the d-spacing (i.e. distance between consecutive carbon layers) for graphene oxides is due to the introduction of oxide functional groups to the carbon basal plane via chemical oxidation reaction. Typically, after the photo-irradiation reduction of graphene oxides, the intensity of the XRD peak located at 10° will be decreased or completely disappeared. The two characteristics broad peaks will then appear at 24° and 43° that are arising from the (002) and (100) planes of graphene.

The smaller the intensity of the 10° peak remains, the more complete the graphene oxides is reduced, therefore this XRD peak can be used to confirm the degree of photo-reduction of graphene oxides. The broadness of peaks appears at 24° and 43° in photo-reduced graphene can be attributed either due to small sizes of layers or short domain order of stacked sheets, so the degree of broadness can reveal the size of the photo-reduced graphene. Lack of any graphite peak in a XRD pattern is a good indication of photo-reduced graphene staying exfoliated and packed disorderly despite their strong π - π interaction. Yang et al. [23] has shown that excimer laser irradiation can completely remove the XRD peak located peak at 2θ of 12° corresponding to the (001) diffraction peak of graphite oxide with a larger d-spacing of 7.38 \AA as shown in FIG. 3. In FIG. 3, XRD patterns were measured from graphite oxide and graphene films prepared by drop-casting either graphite oxide or graphene aqueous solutions on a Si(100) wafer.

Graphene aqueous solutions were fabricated by excimer laser irradiation reduction of graphite oxide solutions at 300 mJ and 1 h, 300 mJ and 2 h and 530 mJ and 2 h. Following the 248 nm excimer laser irradiation at 300 mJ and 1 h, 300mJ and 2 h and 530 mJ and 2 h, the peak at 2θ of 12° disappears. Therefore, the XRD results confirm that the deoxygenation of the graphite oxide sheets occurs almost completely for all laser irradiation conditions studied here. Mohanapriya et al. [12] has also shown that focused solar light irradiation can completely remove the XRD peak located at 9.68° confirming the reduction of graphene oxides by solar irradiation. The two characteristic broad peaks appear at 23.7° and 42.7° after solar reduction.

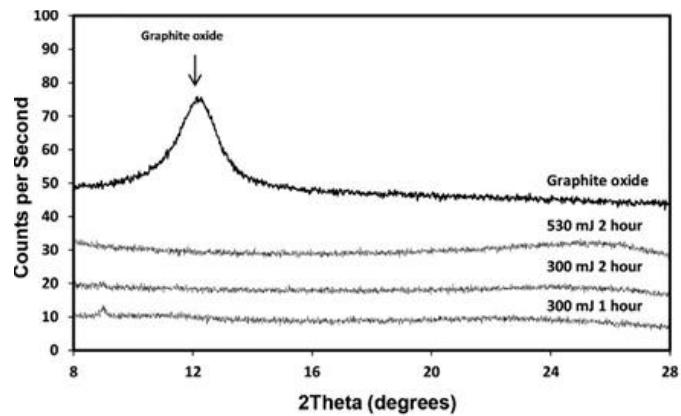


FIG. 3. XRD patterns of graphite oxide, and graphene prepared by laser irradiation of graphite oxide solution at 300 mJ for 1 h, 2 h and at 530 mJ for 2 h. Reproduced with permission from ref [23].

Camera lamp flash reduction of free-standing graphene oxides films reported by Cote et al. [8] also show graphene oxide peak disappearing from the XRD pattern and a broad peak centered at 22.5° emerged, which is at a slightly lower angle than the peak for solar reduced graphene, indicating larger d-spacing of the graphene sheets. Since flash irradiation of graphene oxides in this study occurred *in situ* in the solid state, the reduced graphene stayed exfoliated with larger d-spacing resulting from the microscopically explosive reduction which IR-irradiation employed by Guo et al. [15] to reduce graphene oxides in N_2 and air to form graphene that give rise to broad and much lower intensity peaks at $20 = 24.6^\circ$ and 24.3° . Those 2θ angles of IR reduced graphene are larger than graphene prepared by solar light and camera lamp flash. Those XRD results indicate that the IR reduced graphene oxides sheets are small sizes and more disorderly stacked. The XRD pattern of nitrogen-doped graphene prepared by Huang et al. [20] using Hg lamp irradiation is not different than the un-doped graphene and the weak broad peak located at around 24.5° can also be seen indicating N doping does not affect the structure of photo-reduced graphene using Hg lamp. Laser irradiation reduction has also been shown to be able to remove the graphene oxide peak at $20 = 10^\circ$. Wang et al. [24] showed that after continuous wave laser irradiation under ambient conditions, the sharp characteristic peak of graphene oxide around 11° disappeared while a new broad peak centred at $20 = 24.1^\circ$ was observed, corresponding to an interlayer spacing of 3.69 \AA . The broad and weak intensity implies that the graphene oxides are effectively exfoliated and they are randomly aggregated to form disordered solid. Very weak and broad peak around at $20 = 24^\circ$ was also observed by Huang et al. [22] and Yang et al. [23] when they used an excimer laser to reduce graphene oxides to form graphene in aqueous solutions. The broadness and very low intensity of the 24° peak in laser-reduced graphene oxides indicate that laser irradiation can break down the graphene oxide sheet into very small sizes of layers or create a very short domain order of stacked sheets due to high energy of the laser beam compared to other incoherence light sources.

Infrared spectroscopy is another important method to characterize bond vibrations of various functional groups in graphene oxide before and after the photo-irradiation reduction. In a typical IR spectrum of graphene oxide, the absorption bands due to O-H, C=C and C-O are observed. O-H at $\sim 1396\text{ cm}^{-1}$ (carboxyl) and at $\sim 3223\text{ cm}^{-1}$ (broad coupling) are originated from carboxylic acid group vibrations, while C=C at $\sim 1631\text{ cm}^{-1}$ is attributed to the skeletal vibration from un-oxidized sp^2 C=C bonds. The stretching bond of C-OH (phenyl hydroxyl) then appears around $\sim 1100\text{ cm}^{-1}$. Sometimes, due to the moisture present in the sample, the O-H stretching vibrations at 3423 cm^{-1} were also found. When graphene oxide is reduced to graphene after photo-irradiation, the adsorption bands relating to oxygen functionalities such as O-H, C-O either become weaker or total disappear in the IR spectrum. The band due to C=C skeletal vibration at 1631 cm^{-1} remains. Mohanapriya et al. [12] has shown that focused solar light irradiation can completely remove all the adsorption bands relating to oxygen functionalities confirming the total reduction of graphene oxide by solar irradiation. Camera lamp flashing of free-standing graphene oxide films [8] can eliminate almost all the IR bands corresponding to carboxylic acid ($1630\text{-}1730\text{ cm}^{-1}$), phenyl hydroxyl (around 1100 cm^{-1}), and epoxide groups (around 930 cm^{-1}). The flashed film also showed much decreased transmission in the IR spectra, which is characteristic of electrically conducting graphene. However, when IR light is used to reduce graphene oxide by Guo et al. [15], the bands for C-O (carboxyl C-O at 1410 cm^{-1} and epoxy C-O at 1223 cm^{-1}) and C=O (carbonyl C=O at 1730 cm^{-1}) groups are only decreased but not completely removed. This indicates the deoxygenation reaction was not completed by the IR radiation. The band at $1575\text{-}1625\text{ cm}^{-1}$ for the aromatic C=C groups of un-oxidized graphitic skeleton remains strong as shown in the FT-IR spectra of FIG. 4.

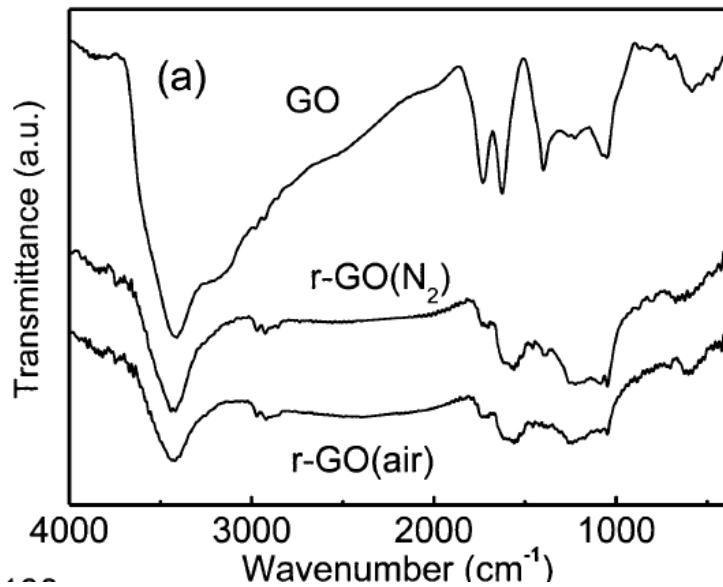


FIG. 4. FT-IR spectra of graphene oxide, graphene reduced in air and in N₂ by IR lamp irradiation. Reproduced with permission from ref [15].

The incomplete reduction of graphene oxide by IR light may be due to the lower photon energy of IR light than UV and visible light. The reduction of oxygen-containing groups in graphene oxide by pulsed laser irradiation using an UV excimer laser was also confirmed by FTIR spectroscopy [22]. After the graphene oxide was reduced by the excimer laser, all the characteristic absorption bands of oxygen-containing groups (C=O at 1726 cm⁻¹, O—H at 1402 cm⁻¹, and C—O at 1104 cm⁻¹) were nearly eliminated, indicating that UV laser can be very effective at reducing graphene oxide.

To determine the information such as disorder, edge and grain boundaries, thickness, doping, and strain of photo-reduced graphene, Raman is an excellent technique of choice. Raman spectroscopy is typically used in the range 1000 cm⁻¹ to 3000 cm⁻¹ with laser excitation at wavelength of 514.5 nm, 532 nm or 632.8 nm. Raman spectra of carbon (i.e. graphite, graphene oxide and graphene) display two major peaks corresponding to D and G bands, respectively. The D band is associated with the defects, while G band corresponds to the vibration of sp² bonded atoms in a two dimensional hexagonal lattice. The intensity ratio (ID/IG) of D and G peaks was always used to determine the degree of disorder in the structure of the graphene oxide and graphene. Typically, G band of graphite is sharp and appears at around 1570 cm⁻¹ while the broad D band appears at 1340 cm⁻¹. After graphite was oxidized chemically to form the graphene oxide, various oxygen-containing functional groups were introduced into the structure of graphite. The structural change caused the D and G bands shifted towards a higher frequency with respect to graphite accompanied with broadening of the G band. The intensity (ID/IG) ratio is also higher than that of graphite. After photo-irradiating reduction of graphene oxide, the position of the G band shifted towards lower frequencies with relation to graphene oxide and the ID/IG ratio of graphene also becomes lower, which is attributed to the restoration of sp² network after the photo-reduction. Raman spectroscopic studies of solar irradiation reduced graphene oxide by Mohanapriya et al. [12] showed that the ID/IG ratio of solar reduced graphene is reduced from 1.25 to 0.79 (the value for graphite is 0.21) and the position of the G band shifted towards lower frequencies. When IR light is used to reduce graphene oxide [15] at 0.64 W/cm² for 5 min in air and N₂, the G band located at around 1599 cm⁻¹ for graphene oxide shifts to around 1590 cm⁻¹, which is closer to that of pristine graphite as shown in FIG. 5, which is an

indication of reduction of graphene oxide by the IR irradiation. The I2D/IG area ratio increases from 0.093 for graphene oxide to 0.143 for IR reduced graphene under N₂ and 0.128 under air. Similar to ID/IG ratio, I2D/IG ratio is also related to the degree of recovery for sp² C=C bonds in graphitic structures. The increase in I2D/IG instead of decrease (like in the case of solar reduction) may indicate that IR irradiation breaks down the graphene oxide into smaller pieces even although de-oxygenation of graphene oxide does restore the graphitic structure which should increase the I2D/IG ratio.

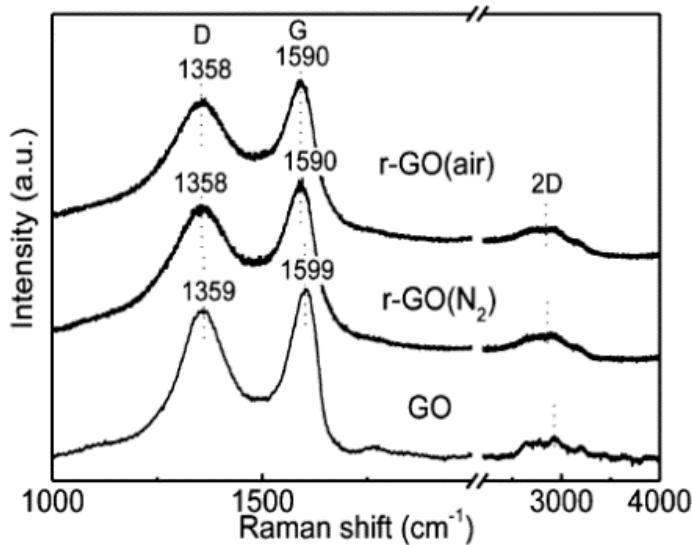


FIG. 5. Raman spectra of Raman spectra of graphene oxide, graphene reduced in N₂ and in air by IR lamp irradiation. Reproduced with permission from ref [15].

Similar phenomena were observed in the excimer laser reduced graphene as reported by Huang et al [22], the ID/IG ratio of graphene oxide after pulsed laser irradiation increased from 1.03 to 1.08. By using the empirical Tuinstra-Koenig relation, which relates the ID/IG ratio to the sp² cluster size [31], the authors concluded that the sp² cluster size is slightly reduced from ~4.3 nm to ~4.1 nm after 5 min of pulsed laser irradiation. When a continuous laser operating at 808 nm was used to reduce graphene oxide, however, the ID/IG of laser reduced graphene is decreased from 0.97 to 0.91 indicating restoration of the graphitic structure. In comparison to the 248 nm pulsed excimer laser, the 808 nm continuous semiconductor laser has low energy photons, which may be a less destructive way to break down the graphene sheet to smaller size.

XPS is a very useful method to reveal the changes of various functional groups before and after the photo-reduction which are very useful information to help in the understanding of the mechanisms of the photo-irradiation reduction processes. XPS detects C, O and N (for N-doped graphene) elements within a depth of 7 - 10 nanometres of graphene oxide or graphene samples with the detection limits ranging from 0.1 - 0.5 atomic percent depending on the element. Typically, a survey scan analyses are carried out with an analysis area of hundreds of microns to determine the atomic percentages of consisting elements. Then a high resolution analysis is performed for C1s, O1s and N1s (for N-doped graphene) to determine the percentages of different functional groups such as O-C=O, C=O, C-OH, C-O-C, C-NC-C, C-H, C=C, -NH₂, and R=N-R by

curve fitting. XPS analysis of the solar irradiation reduced graphene oxide by Mohanapriya et al. [12] showed the peak intensity of C-C increases dramatically while C-O (epoxy and hydroxyl groups) and C=O (carbonyl groups) decrease sharply in high resolution C1s spectra. XPS results clearly indicate the efficient removal of oxygen containing functional groups and restoration of C-C graphitic structure after solar reduction of graphene oxide. The C/O atomic ratios were found to be 2.7 and 6.1 for graphene oxide and solar reduced graphene, respectively. When an IR light was used to reduce graphene oxide [15], the C/O atomic ratio increases from 2.7 for graphene oxide to 8.3 for graphene reduced in N₂ and 7.7 for graphene reduced in air, respectively, confirming more effective de-oxygenation of graphene reduced by IR light than solar light. The high resolution XPS spectra showed elimination of most of the C–O and C=O groups after IR irradiation. The C–O band (286.2 eV) had a more apparent decrease for graphene reduced in N₂ than in air which indicates the reduction of graphene oxide in nitrogen is more completed. Excimer laser reduction of graphene oxide reported by Huang et al [22] also show that the oxygen-containing functional groups (C–OH, C–O and C=O) have been significantly decreased after the pulsed laser irradiation. High-resolution XPS spectra shows that the C–O (epoxy and alkoxy) and C=O peaks in the C1s spectra area of the pulsed laser reduced graphene reduced from the 38.1% and 14.3% values for graphene oxide to 8% and 7.6%, respectively. These results suggest that most of the oxygen-containing functional groups have also been removed after the pulsed laser irradiation. Wang et al. [24] also used XPS to characterize continuous laser reduced graphene and showed that the C/O atomic ratio increased to 7.47 for the laser reduced graphene from 2.91 for the graphene oxide, confirming the partial reduction of graphene oxide during the laser irradiation process. The high-resolution C1s spectra show that the intensities of C–OH, and C–O bonds were reduced greatly, while the peak intensities for C=C/C=C increased significantly, suggesting that the conjugated graphene networks are partially restored and some oxygen containing functional groups still retained on the surface of the graphene after laser reduction. Huang et al. [20] used XPS to characterize the elemental composition of graphene oxide coated Ni foam samples after Hg lamp irradiation under NH₃ atmosphere as shown in FIG. 6. The C1s and O1s peaks of graphene oxide are shown in the XPS full scan spectrum of FIG. 6a. After irradiation under NH₃ atmosphere, N signals in the XPS spectrum appeared indicating the introduction of N to reduced graphene. The C/O atomic ratio for N-graphene increased from 4.64 to 7.26 as irradiation time increased from 15 min to 90 min FIG. 6b, indicating more oxygen containing functional groups were eliminated. To understand the role of NH₃ during the photo-irradiation reduction process, the graphene oxide was irradiated for 30 min under Ar atmosphere for comparison. XPS spectra under both NH₃ and Ar atmosphere are shown in FIG. 6c. The C/O atomic ratio of graphene is 4.51 when irradiated under Ar atmosphere while it is 5.80 under NH₃. The results in FIG. 6c, indicate NH₃ facilitated the reduction of graphene oxide in addition to nitrogen doping. The high-resolution C1s XPS spectrum of the graphene oxide FIG. 6d, shows two main peaks, which can be fitted to C=C/C–C (284.6 eV) and C–O (hydroxyl and epoxy, 286.7 eV), C=O (carbonyl, 287.7 eV) and O–C=O (carboxyl, 288.9 eV) functional groups. After photo-irradiation under NH₃ atmosphere, the high-resolution C1s XPS spectrum FIG. 6e, shows only a mainly single peak with a small tail in the higher binding energy region. FIG. 6e reveal that after photo-irradiation, the C=C/C–C bonds become dominant and the hydroxyl and epoxy species of C–O, and C=O reduce significantly. A new peak appears at 285.8 eV was attributed to the C–N bond, originating from doping of nitrogen atoms. Curve fitting of the high-resolution XPS spectrum of N1s in FIG. 6f revealed four possible peaks located at 398.4, 399.5, 400.4, and 401.3 eV. This could suggest that the doped nitrogen may exist in four possible functional groups, namely pyridine-like, amino-like, pyrrolic-like, and graphitic-like nitrogen, respectively.

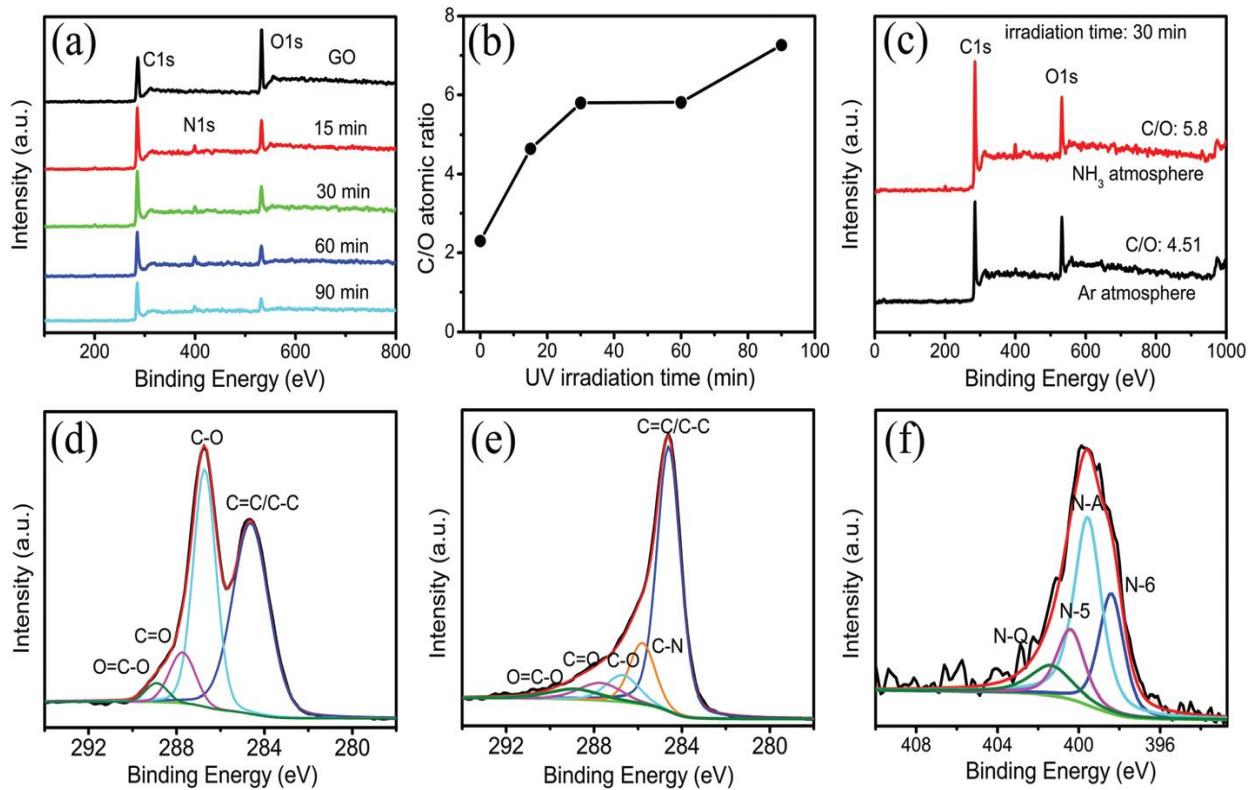


FIG. 6: (a) XPS full scan spectrum of graphene oxide and N-graphene prepared by irradiating under NH_3 for 15 min to 120 min with a Hg lamp, (b) the C/O atomic ratio, (c) The comparison of XPS full scan spectrum of graphene under NH_3 and Ar atmosphere, respectively, (d) High resolution C1s XPS spectra of graphene oxide, (e) High resolution C1s XPS spectra of N-graphene, (f) High resolution N1s XPS spectra of N-graphene. Reproduced with permission from ref [20].

The surface area of photo-reduced graphene oxide is an important parameter to determine how much charge can be stored in a supercapacitor. Typical nitrogen gas was used to determine the adsorption/desorption isotherm of photo-reduced graphene. The BET specific surface area of photo-irradiation reduced graphene can be calculated from the adsorption/desorption isotherm. The theoretical surface area of graphene is around $2630 \text{ m}^2 \text{ g}^{-1}$.

The solar reduced graphene prepared by Mohanapriya et al. [12] was found to be $273.2 \text{ m}^2 \text{ g}^{-1}$, and the value is much lower than theoretical one, indicating that the solar reduced graphene is not completely exfoliated and some stacked graphitic layers are still existent. In comparison, the laser reduced graphene reported by Dewei Wang et al. [24] shows an impressively high specific surface area up to $520.086 \text{ m}^2 \text{ g}^{-1}$. The BET surface area of flash lamp reduced graphene was found to be $733 \text{ m}^2 \text{ g}^{-1}$, which is higher than that of solar light and laser reduced graphene [13]. The low energy flash lamp seems causing less damage to the produced graphene.

To evaluate the electrochemical properties of photo-reduced graphene when it is used as the active electrode material for supercapacitors, cyclic voltammetry (CV) and galvanostatic charge/discharge measurements are typically carried out using either two electrode or three-electrode systems with aqueous, organic or ionic liquid electrolytes. CV measurements were carried out at different potential ranges depending on the stability of solvents used.

The CV scan rates are varied from a few mV/sec to a few V/sec. The appearance of an approximate rectangular shape is a characteristic of the electrical double layer capacitors. Distortion of the ideal rectangular shape is typically due to the redox processes of the oxygen-containing functional groups left on photo-reduced graphene. Galvanostatic charge/discharge curves are obtained with various current densities from $< 1 \text{ A g}^{-1}$ to a few tenths of A g^{-1} . Symmetric triangle features are a good indication of electrical double layer capacitor behaviours.

Specific capacitance is determined from the slope of discharge curves. High values of charge storage capacitance are good indicators of large surface area, optimum porosity and high electrical conductivity. For lifetime and durability evaluation, galvanostatic charge/discharge measurement at a fixed current density is taken up to tenths thousands of cycles. Electrical Impedance spectrum measurements are also carried out and the Nyquist plots of graphene electrodes in the selected frequency range such as from 0.1 Hz to 1000 kHz are typically recorded.

In a Nyquist plot, the solution resistance (R_s) can be obtained as the real axis intercept at a high-frequency region. The semicircle represents the interfacial charge-transfer resistance (R_{ct}) and interfacial capacitance (C_s) connected in parallel at the electrode/electrolyte interface. The more vertical the plot is at a low-frequency region, the more closely the supercapacitor behaves as an ideal capacitor. The transition region from a high-frequency semicircle to the middle-frequency semicircle is related to Warburg resistance (W).

Applications of Photo-Irradiation Reduced Graphene for Supercapacitors

Supercapacitors, ultracapacitors or electrochemical capacitors (ECs), are energy storage devices that store energy as charge on the electrode surface. As one of the most promising energy storage devices, supercapacitors have unique features of high power density, short recharging times, long cycle life, as well as environmental friendliness. Supercapacitors with increased energy density are greatly needed for practical applications such as plug-in hybrid electric vehicles, wind turbine energy storage, regenerative breaking, cold starting of trucks and space exploration applications [32,33].

The class of supercapacitors can be divided in two types. The first one is the electrical double-layer capacitor (EDLC), in which the capacitance comes from pure electrostatic charge accumulation at the electrode/electrolyte interface. EDLC uses high surface-area carbons, such as activated carbon, carbon fibre, carbon nanotubes and graphene, as the electrode active materials; the energy storage capacity is strongly dependent on the surface area of the electrode active material that is accessible to the electrolyte ions.

The second type of supercapacitors use pseudo-capacitive and electrochemical active materials, such as metal oxides or conductive polymers, in which rapid and reversible Faradaic processes take place at the surface and inside the materials. FIG. 7 provides the schematic illustration of an EDLC using porous electrode materials [34].

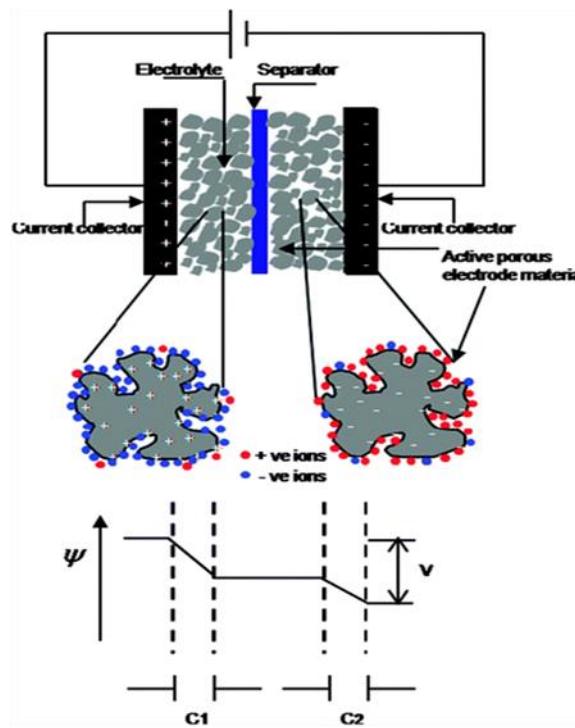


FIG. 7: Schematic illustration of an Electrical Double-Layer Capacitor (EDLC). Reproduced with permission from ref [34]

Although, the specific pseudo-capacitance values of metal oxides and conductive polymers typically exceed the double layer capacitance of carbon materials due to involving Faradaic charge transfer reactions, the poor cyclic stability and relatively slow Faradaic charge transfer reactions of the pseudo-capacitive materials prohibit their application for situations where high power, long lasting and reliable energy devices are needed. Therefore, high surface area carbon materials are still the research and development focus for supercapacitors. Graphene is a form of carbon that has a high theoretical surface area, i.e., substantially higher than activated carbon which is the more common electrode active material, thus potentially allows more storing of electrostatic charge. In addition, the conductivity of graphene is close to that of pristine graphite, which is $2\text{--}3 \times 10^5 \text{ S/m}$, and it is much higher than activated carbon which is only $10\text{--}100 \text{ S m}^{-1}$. The planar structure of graphene also allows fast charging and discharging because the electrolyte ions can easily move in and out of the large surface areas of the sheets. Graphene is also ecologically friendly, unlike most other forms of energy storage such as batteries. The theoretical upper limit for graphene-based supercapacitors is 550 F g^{-1} if the entire theoretical surface of graphene can be utilized. Although relative high specific capacitance of 205 F g^{-1} for graphene materials was reported [35], values around 150 F g^{-1} are more commonly achieved. The low specific capacitance of graphene compared to its theoretical value is mainly due to high restacking tendency of graphene sheets due to the $\pi\text{--}\pi$ electron interactions between adjacent sheets. After restacking, graphene is converted back into graphite like structure and no longer possesses the high surface area of a single layer graphene. This will result in reducing its charge storage capabilities [36].

Graphene synthesized using chemical reduction methods normally shows low charge storage performance due to the irreversible agglomeration and restacking of graphene sheets, which is undesirable for high energy and good durability supercapacitor practical applications [37]. As a cost effective alternative to the chemical and thermal reduction methods, photo-irradiation reduction method creates a disordered corrugated graphene structure in which adjacent sheets are no longer oriented parallel to each other. This process not only can be used to produce large quantities of graphene for large supercapacitors usable in automotive and stationary energy storage, but also can be used to prepare small amounts of graphene for portable and flexible small or thin film supercapacitors. Besides, the photo-reduction of graphene oxide in solution makes it particularly attractive for producing graphene composites by premixing with other materials such as metal nanoparticles, metal oxides and conductive polymers. In this section, the unique properties and performance of graphene produced by the photo-irradiation reduction process for supercapacitor application will be reviewed and discussed.

Graphene reduced by solar radiation of graphite oxide was used as an electrode active material and evaluated in the supercapacitors. K. Mohanapriya et al. [12] measured the specific capacitance of the solar reduced graphene in both 6M KOH aqueous electrolyte and EMIBF₄ ionic liquid electrolyte at room temperature. Specific capacitance values of 265.9 F g⁻¹ at 1 A g⁻¹ and 211 F g⁻¹ at 10 A g⁻¹ were determined for solar reduced graphene in 6M KOH. In comparison, the specific capacitance of 187.1 F g⁻¹ was obtained in EMIBF₄ electrolytes. The performance of the focused sun light reduced graphene was compared to that of graphene materials synthesized by other reduction techniques. For example, graphene prepared by flame reduction has a specific capacitance value of 212 F g⁻¹ at 1 A g⁻¹ in 6M KOH [38], while graphene produced by chemical reduction using hydrazine hydrate has the value of 135 F g⁻¹ at 0.01 A g⁻¹ in 5.5 M KOH [39], and chemical reduced graphene using hydrazine gas has the value of 205 F g⁻¹ at 0.01 A g⁻¹ in 30% KOH [40]. This high value of specific capacitance can be attributed to the high surface area, low degree of restacking and high conductivity of the solar reduced graphene.

Wang et al. [13] investigated the performance of camera flashing reduced graphene in a coin cell supercapacitor. Two procedures were used to flash convert graphene; i.e., pre-FCG, in which bulk graphene oxide (Freeze-dried) is first converted to graphene and then cast onto a current collector, and post-FCG in which the graphene oxide solution is first cast onto the current collector and then converted to graphene. Graphene that exhibit high specific power, response time, and rate capabilities was produced by both methods. Specific energies of 7 Wh kg⁻¹ and 9 Wh kg⁻¹, and very high power (5 × 105 W kg⁻¹ and 7 × 105 W kg⁻¹) and rate capabilities (900 A g⁻¹ and 500 A g⁻¹) were demonstrated for pre-FCG and post-FCG, respectively. The specific power and rate capabilities of pre-FCG and post-FCG were found to be ten times higher than that of carbon-based commercial supercapacitors. The authors believe that flashing reduced graphene possesses low-density, high surface area with a porous network. Freeze-drying the aqueous graphene oxide dispersion was believed to be able to preserve the graphene oxide molecular configuration. Oxygen functional groups in graphene oxide were converted to gases such as CO₂, and H₂O after camera light flashing. This results in slightly morphology expansion and 55% mass decrease. Due to thinner casted film before flashing treatment, post-FCG was reduced more completely than pre-FCG. The simple and low cost camera light flashing method has the potential for commercial production of graphene used in coin cell supercapacitors for a wide range of applications [13]. The electrochemical performance of the laser reduced graphene prepared by Wang et al. [24] using a continuous wave semiconductor laser at the wavelength of 808 nm to irradiate graphene oxide at 127 W cm⁻². The laser reduced graphene was mixed with acetylene black, and poly(tetrafluoroethylene) binder to form electrode active materials and evaluated in a symmetrical two-electrode supercapacitor cell in aqueous 6M KOH electrolyte solution. The

specific capacitances of the laser-reduced graphene were found to be 236.5 F g^{-1} , 226 F g^{-1} , 220 F g^{-1} , 208 F g^{-1} , and 201 F g^{-1} at current densities of 0.25 A g^{-1} , 0.5 A g^{-1} , 1 A g^{-1} , 2 A g^{-1} , and 3 A g^{-1} , respectively, and the laser reduced graphene supercapacitor cell delivered an energy density of 8.21 Wh kg^{-1} at a power density of 62.5 W kg^{-1} . In comparison, commercial activated carbon only delivered an energy density of 5.26 Wh kg^{-1} at the same power density using the same cell. Wang et al.'s results demonstrate excellent electrochemical performance of laser induced graphene, which they attributed to its unique curved and crumpled graphene sheets that can effectively prevent the aggregation and restacking of graphene sheets and allow more surfaces to absorb electrolyte ions. They also believed that laser reduced graphene has a mesoporous structure and a uniform pore size distribution which facilitates fast electrolyte ion adsorption/desorption and transportation. They also believed that the presence of residual oxygen containing functional groups can not only improve the wettability of laser reduced graphene, but also can participate in Faradic redox reactions in alkaline aqueous solutions to provide additional pseudo-capacitance; therefore enhance the charge-storage capability. The improvement in electrical conductivity of laser reduced graphene after partially restoring π -conjugated graphene networks is also favourable for charge transportation as they suggested. Graphene prepared by photo-reduction using a KrF excimer laser was also evaluated as the electrode active material for supercapacitors [23]. Specific capacitance of the laser-reduced graphene was evaluated in either a $0.5\text{M Na}_2\text{SO}_4$ aqueous or a 1M Tetraethylammoniumtetrafluoroborate acetonitrile (ACN) based electrolyte using the two electrode cell. FIG. 8a shows CVs of graphene prepared by laser irradiation at 300 mJ and 2 h at potential scan rates ranging from 10 to 500 mV/s in the aqueous $0.5 \text{ M Na}_2\text{SO}_4$ electrolyte. The specific capacitance is seen to increase with decreasing scan rates for the graphene film indicating that there is resistance for ions to transport into and out of the graphene films during the charge-discharge process. FIG. 8b, gives the galvanostatic charge/discharge cycles of the graphene films obtained at various constant current/weight densities of: 1.04 A/g , 5.20 A/g and 11.4 A/g . The specific capacitance, calculated from these charge/discharge curves, for graphene fabricated by laser irradiation at 300 mJ and 2 h are 141 F/g at 1.04 A/g , 121 F/g at 5.20 A/g and 120 F/g at 11.4 A/g , respectively. The cell resistance calculated from the linear voltage drop observed immediately after discharging, illustrated in the insert of FIG. 8b, is $0.64 \Omega/\text{cm}^2$. FIG. 8c, shows the CVs at scan rates ranging between 50 and 500 mV/s and FIG. 8d, the galvanostatic charge/discharge cycles at constant currents of 1.46 A/g , 7.28 A/g and 14.6 A/g of graphene prepared under the same conditions in the $1 \text{ M TEABF}_4/\text{ACN}$ electrolyte. The specific capacitance, calculated from the charge/discharge curves for graphene are 84 F/g at 1.46 A/g , 80 F/g at 7.28 A/g and 77 F/g at 14.6 A/g . The cell resistance calculated from the linear voltage drop immediately after discharging is $1.2 \Omega/\text{cm}^2$. The specific capacitance at the low discharging current density is only slightly higher than that at the high current density.

Photo-irradiation reduction of graphene oxide in NH_3 atmosphere can produce N-doped graphene with better electrical conductivity. It is very interesting to evaluate the performance of N-doped graphene as electrode active material for supercapacitors. Huang et al. [20] evaluated N-doped graphene coated nickel foam in a supercapacitor cell. The electrochemical performance of N-doped graphene was found to be very good in term of high power densities, high rate capability performance and excellent cycle stability. The maximum specific capacitance was determined to be 252.3 F g^{-1} at the current density of 0.29 A g^{-1} in the KOH electrolyte. The excellent performances was attributed to the continuous and interconnected 3D network of the Ni foam, high electronic conductivity of nitrogen-doped graphene, and good contact N-doped graphene and the nickel foam even without any binder. The authors also discovered that long enough irradiating time ($\geq 30 \text{ min}$) is necessary for good electrochemical performance, but too long of irradiation time will not further improve the specific capacitances of the graphene. The optimized irradiation time was found to be around 45 min . Long irradiation time

caused expansion of the N-doped graphene film that induces delamination of the graphene sheets from the metal substrate and result in poor electrical contact between N-doped graphene sheets and the metal current collector.

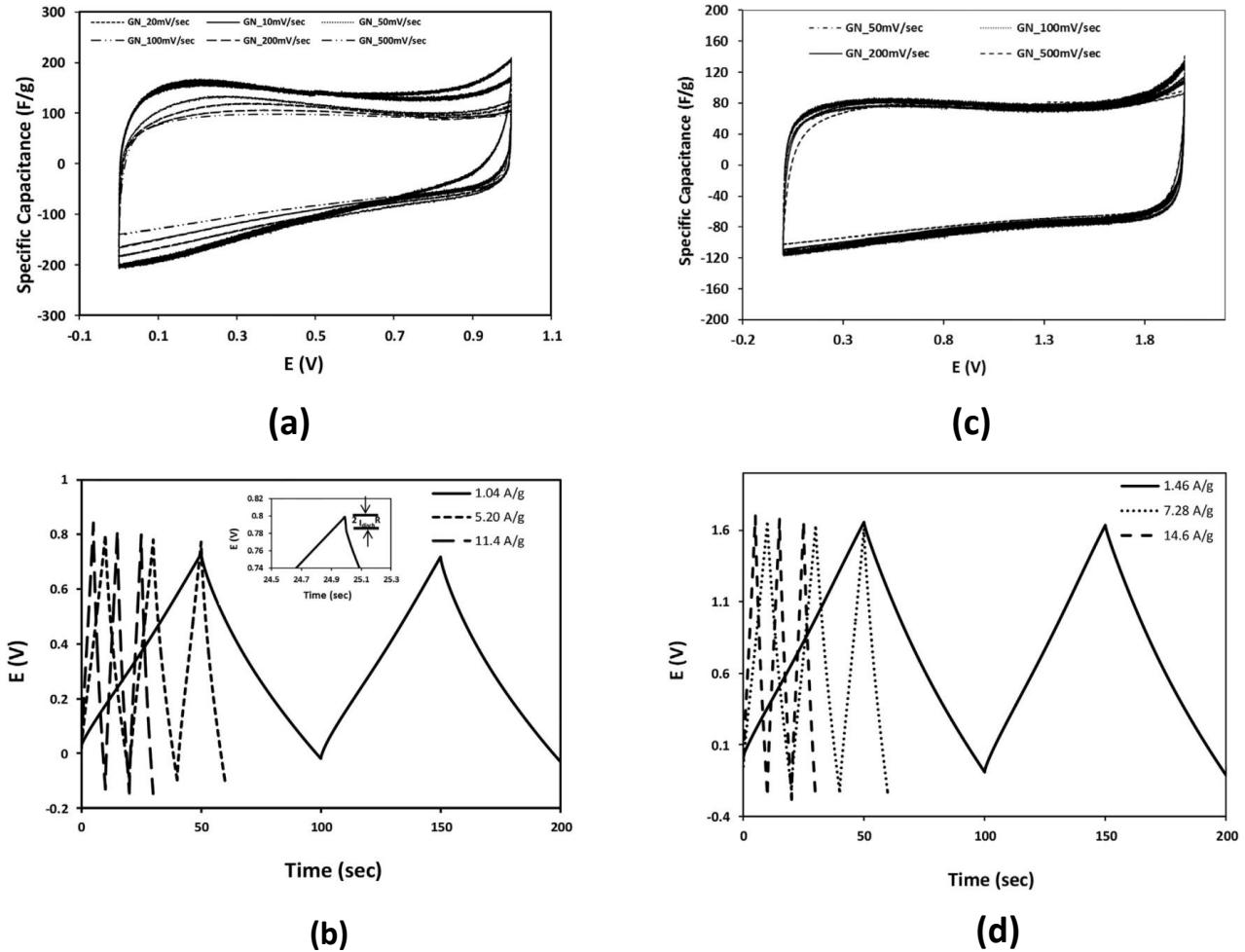


FIG. 8: Cyclic voltammograms (CVs) at various potential scan rates, (b) galvanostatic charge/discharge cycling at constant currents for the graphene electrode prepared by laser irradiation of graphite oxide solution at 300 mJ for 2 h in 0.5 M K₂SO₄ aqueous solution (a, b) and (c, d) in 1 M Tetraethylammoniumtetrafluoroborate [TEABF₄] ACN solutions. Reproduced with permission from ref [23].

The application of the photo-catalysts such as TiO₂ to assist photo-reduction of graphene oxide is a very interesting method that can quickly remove oxygen functional groups to produce graphene having high degree de-oxygenation. UV Photo-irradiation reduced graphene/TiO₂ composites synthesized by Yang et al. [16] was also evaluated its performance in a supercapacitor. In the composite, TiO₂ was used as a photo-catalyst to assist the reduction of graphene oxide and also helps to reduce restacking of graphene sheets. The pseudo-capacitive/ faraday behaviour of TiO₂ can contribute to the specific capacitance of the composite because of the contribution from reversible conversion of proton and cation between TiO₂ and

the electrolyte [41,42]. The as-prepared graphene/TiO₂ with weight ratios of graphene oxide to TiO₂ at 1: 2.5 showed a specific capacitance of 226.45 F g⁻¹ at a scan rate of 10 mV s⁻¹ in 1 M H₂SO₄ electrolyte solution. At high ratio between TiO₂ and graphene oxide, the degree of de-oxygenation of graphene oxide increases (as illustrated in FIG. 2). In addition, restacking of graphene sheets can be greatly avoided due to intercalation of more TiO₂ into the space between the graphene sheets at high TiO₂ loading.

Thin Film Graphene Supercapacitors

Graphene films produced by photo-irradiation reduction of graphene oxide films are typically very thin (a few tenth to hundred nm) due to the small penetration depth of light and therefore, are only suitable for thin film supercapacitor or micro-supercapacitors. Supercapacitors used thin films of photo-reduced graphene provide a variety of applications, including mobile electronic devices, sensors, actuators and printable devices. Although thin film supercapacitors can be manufactured using a number of conventional printing and lithography techniques, direct photo-patterning/reducing is an emerging technique in term of cost and scalability, and the full potential of the technique needs to be realized. Optimization of the photo-irradiation reduction method to fabricate high-quality graphene films with a more porous structure, higher conductivity and larger surface area is a key to achieve higher performance in term of energy, power and durability of thin film supercapacitors. The photo-reduction methods have been demonstrated to better prevent restacking of graphene nano-sheets due to the smaller size and curved graphene sheets, and therefore allow more surface area for charge storage in thin film supercapacitors. Pioneering studies by El-Kady et al. [43] that reported on the performance of graphene based supercapacitors fabricated by employing the laser scribing technique using a standard LightScribe DVD optical drive have stimulated great interest worldwide. In this subsection, more recent development of photo-irradiation reduced graphene thin film supercapacitors or micro-supercapacitor will be briefly reviewed.

When a substantial amount of water is entrapped in the layered graphene oxide structure, graphene oxide can become a anisotropic ionic conductor. Since laser direct irradiation can reduce graphene oxide and produce high surface area and conductive graphene, laser can be used to create graphene-graphene oxide-graphene patterns in various configurations with micro-meter resolution to build thin film supercapacitors, in which graphene acts as the active electrode material and graphene oxide as separator and electrolyte. Gao et al. [44] demonstrated the fabrication of such supercapacitors by laser reduction and patterning of graphite oxide films. They patterned both in plane and conventional graphene electrodes, between which graphene oxide serves as a solid electrolyte. The resulting micro-supercapacitor devices show good cyclic stability, and energy storage capacities comparable to existing thin-film supercapacitors. However, they found that the in plane structure has a much higher ESR value than that of the conventional sandwich structure. Although direct laser patterning/reducing of graphene oxide in plane configuration can create high surface area porous graphene for fast ion diffusion, the high porosity could also increase the electrical resistance of graphene due to poor electrical contact among graphene sheets. The challenges of relatively low conductivity, limited rate capability and low time constant of laser patterning/reduced graphene electrodes still needed to be addressed. R.-Z. Li et al. [45] reported an interesting approach by incorporating laser patterning of graphene oxide electrodes with the fabrication of Au current collectors in a single step. They employed a method to simultaneously reduce hydrated graphene oxide and chloroauric acid (HAuCl₄) by a femtosecond laser (operating at 1030 nm central wavelength, and 400 fs pulse duration at a repetition rate of 120 kHz) to form Au-graphene nanocomposite.. The process for fabricating flexible micro-supercapacitors using Au-graphene nanocomposite is displayed in

FIG. 9. Graphene oxide /HAuCl₄ mixture was first coated on a photo paper, then direct laser patterning of graphene/Au electrodes was followed, and the next step was to remove the unreacted HAuCl₄ and finally apply the H₂SO₄/PVA hydrogel solid state electrolyte. Such flexible micro-supercapacitors show greatly enhanced in-plane conductivities up to two orders-of-magnitudes higher than that of the pure graphene electrodes. The Au-graphene micro-supercapacitors was found to demonstrate high rate capability and high frequency responses, and large specific capacitances of 0.77 mF cm⁻² (17.2 F cm⁻³ for volumetric capacitance) at 1 V s⁻¹, and 0.46 mF cm⁻² (10.2 F cm⁻³) at 100 V s⁻¹.

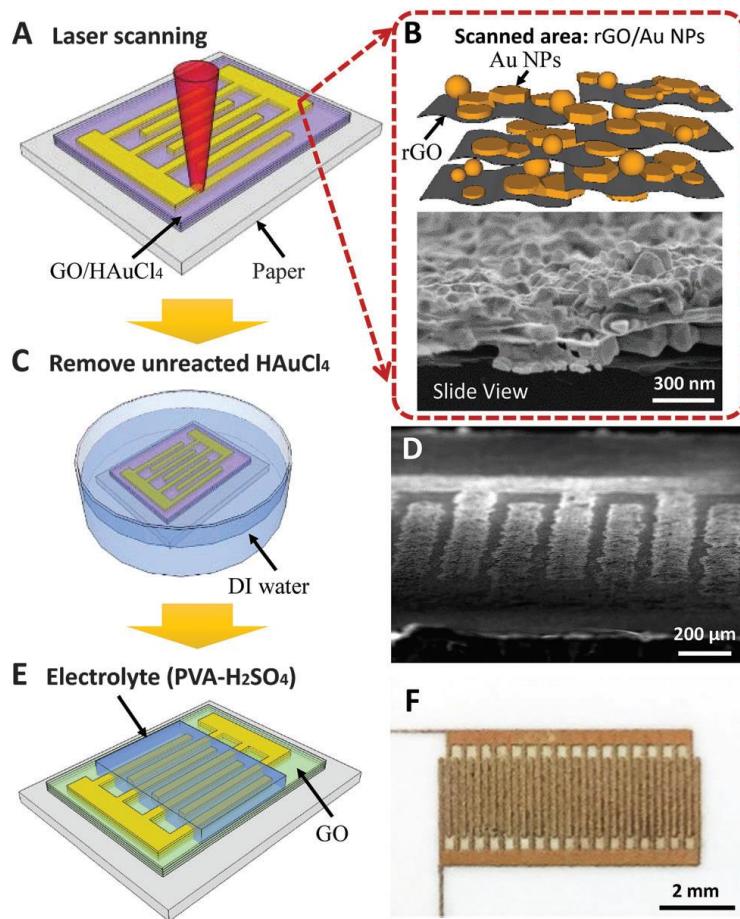


FIG. 9. Schematic illustration of the fabrication process for a graphene/Au micro-supercapacitor on a paper substrate and photo-images of the graphene and the micro-device. The fabrication process includes: (A) direct FS laser patterning of the graphene/Au microelectrode, (B) the SEM image of the graphene/Au microelectrode, (C) removal of unreacted HAuCl₄ by rinsing in DI water, (D) SEM image of the interdigitated graphene/Au microelectrode, (E) spreading the PVA/H₂SO₄ electrolyte onto the microelectrode, and (F) the optical image of the final graphene/Au micro-supercapacitor. Reproduced with permission from ref [45].

The performance of thin film supercapacitors using laser patterning/reducing graphene has been improved recently; however, the energy density is still very low compared to thin film batteries if only carbon based materials such as graphene is used. In incorporation of transition-metal oxides and conducting polymers into photo-irradiation reduced graphene is an effective strategy to increase the capacitance of thin film supercapacitors and also prevent graphene from aggregating and restacking. Manganese dioxide (MnO_2) is a suitable metal oxide due to its low cost and environmentally friendliness. Chen et al. [46] produced high-performance supercapacitor electrode films on flexible substrates using laser scribed graphene decorated with MnO_2 . The MnO_2 nanospheres are directly synthesized on the surface of graphene oxide. Then, flexible graphene oxide/ MnO_2 composite film is reduced in a standard laser-scribing DVD burner. Synergistic effect of the excellent electrical conductivity of laser scribed graphene and pseudocapacitance of the homogeneously dispersed MnO_2 particles results in achieving a volumetric capacity of 202.98 F cm^{-3} (882.52 F g^{-1}) at a current density of 0.3 A cm^{-2} in $1.0 \text{ M Na}_2\text{SO}_4$ electrolyte. The device also exhibits excellent charge/discharge rate and good cycling stability, retaining 91.2 % of its initial charge after 5500 cycles. These performance improvements are attributed the conductive network and unique structure formed by laser scribed graphene and MnO_2 nanoparticles in which the diffusion distance of electrolyte to the interior surfaces was shorten, allowing better penetration of the electrolyte into graphene active material.

Although laser beam ablation/reduction is the most common method for patterning/reducing of graphene oxide to fabricate graphene thin film supercapacitors or micro-supercapacitors, the strong intensity of the laser beam can often causes structural damages to the graphene oxide film. In addition, laser equipment is expensive and not easy to operate. Xue et al. [47] developed a simple and facile method that used UV light instead of laser to pattern graphene oxide films without causing serious structural damage. In their experiments, a graphene oxide film supported on PET was exposed to the UV irradiation through a photomask with an interdigital electrode pattern for 24 h. After removal of the photomask, the $\text{H}_3\text{PO}_4/\text{PVA}$ gel electrolyte was then spin-coated on the in-plane patterned graphene oxide-graphene film and the two edge-sides of the graphene oxide-graphene patterned film was sputter-coated with Au as the current collectors. Although the concept of building such a planar thin film supercapacitor has been proved, the high resistance of such a supercapacitor cell gave a non-ideal CV curve indicating further improvement of the device structure and quality of materials are needed.

Discussion

The methods used to reduce graphite oxide significantly affects the morphology, surface area, pore size and electronic conductivity of the resulting graphene nano-sheets, which are critical to its electrochemical performance in supercapacitors. Although solution-based chemical reduction methods are the most common process to produce large quantities of graphene from graphite oxide, graphene synthesized using chemical reduction methods still delivers low charge storage performance due to the irreversible agglomeration and restacking of graphene sheets, which limits its practical applications for supercapacitor. As an alternative to the chemical reduction method and other methods such as thermal reduction, the photo-irradiation reduction process has many advantages. It is a simplified, rapid, energy efficient and poisonous material free alternative to the chemical and high temperature thermal methods. The ability of photo-reducing graphite oxide in solution makes it particularly attractive for producing graphene composites by premixing it with other materials such as metal, metal oxides and conductive polymers. This process not only can be used to produce large quantities of high quality graphene for large-size supercapacitors usable in automotive and stationary energy storage, but also can be used to prepare small amount of graphene used for printable, portable and flexible supercapacitors

Light sources that can be used for photo-irradiation reduction of graphite oxide include solar light; UV, visible and IR lights generated by lamps, and laser beam operating at different wavelength. Solar light is an eco-friendly light source and the solar radiation reduction process could be further developed for the low cost, rapid, and scalable production of large quantities of graphene for supercapacitors used in automotive and transportation sectors. The challenge of the solar reduction method lies in lacking quality control of graphene, as limited process parameters can be optimized. Light generated from a simple camera flash lamp or mercury lamp can be used to produce small quantities of high quality graphene that is suitable for micro-supercapacitor and thin film supercapacitor applications. Compared to other light sources, laser has unique advantages of spatial coherence, high irradiance, and available wavelengths covering UV, visible and IR ranges. Although laser irradiation reduction is typically used for patterning/reducing graphite oxide film to form thin film supercapacitors.

The successful use of laser to reduce graphite oxide in aqueous solution opens a new venue for the production of high quality and relatively large quantities of graphene for large supercapacitors applications. The photo-irradiation reduction processes typically include various mechanisms such as photo-thermal reduction, photochemical reduction, and catalyst assisted photochemical reduction. Light sources with low energy photons, such as IR and visible light, photo-thermal reduction would be the dominant process, while high energy photons such as UV light can induce photochemical reduction, in addition to the photo-thermal reduction process. Short pulse and strong peak power lasers such as femtosecond picosecond laser enables a nonlinear multiphoton interaction with the graphite oxide, and induces both photo-thermal and photochemical reduction processes, therefore could lead to a more complete de-oxygenation of graphene and produce more porous and curved structures. During the photo-irradiation process, photo-catalysts can be used to absorb photons and generate electrons to reduce graphite oxide. With the assistance of photo-catalysts, graphite oxide can be reduced with high degree of deoxygenation. Chemical doping with nitrogen is an effective way to intrinsically modify the electronic and chemical properties of graphene. Synthesis of N-doped graphene can be completed by simple photo-irradiation reduction of graphene oxide under NH₃ atmosphere.

TEM, SEM, XRD, FTIR, Raman, and XPS are the most common techniques used to characterize the structures and properties of the photo-reduced graphene. High-resolution TEM and SEM can be used to evaluate the degree of exfoliation, the size and structures of the graphene sheets. The decrease in intensity of the XRD peak at 10° can provide the percentage of graphite oxide that was reduced. UV light and high intensity laser were found to be more capable to totally remove this XRD peak. FTIR can further provide the information about the functional groups that have been removed or reduced after the photo-irradiation reduction process. The peak intensity change for C–O and C=O groups is good indication of the degree of completion of deoxygenation reaction after the photo-process. Similar information about functional groups before and after the photo-process can be obtained by high-resolution XPS analyses of C1s, O1s and N1s (for N-doped graphene) peaks through the curve fitting. The BET surface area of photo-irradiation reduced graphene was found to be varying significantly depending on the light sources used.

The unique properties and high performance of photo-reduced graphene for supercapacitor application have been thoroughly demonstrated. The photo-irradiation reduction can create a disordered corrugated graphene structure in which adjacent sheets are no longer oriented parallel to each other. Other unique features include a high degree of exfoliation, small sheets and curved like structures. Direct photo-patterning/reduction of graphene–graphite oxide structures with customized geometries

in plane or in 3D structures to create thin film supercapacitors is an emerging technique in term of cost and scalability. These photo-reduction methods have been demonstrated to better prevent restacking of graphene nano-sheets due to its smaller size and curved graphene sheets, and therefore allow more surface area for charge storage in thin film supercapacitors.

Conclusion

In conclusion, photo-irradiation reduction of graphene oxide is a simplified, rapid, energy efficient and poisonous material free alternative to the most commonly used chemical reduction method. This process not only can be used to produce large quantities of high quality graphene for large-size supercapacitors usable in automotive and stationary energy storage, but also can be used to prepare small amount of graphene used for printable, portable and flexible supercapacitors. The unique properties and high performance of graphene produced by the photo-irradiation reduction process has great potential for supercapacitor application.

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