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# **Photo-reduced Graphene as Electrode Active Materials for Supercapacitor Applications**

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Graphene is a form of carbon that has high electrical conductivity, a planar structure and substantially high surface area, thereby having the potential for more storage of electrostatic charge for high energy supercapacitors (SC). In this paper, the recent developments on the fabrication of graphene by means of photo-reduction of graphene oxide will be overviewed. The main advantage of the photo-process is that it does not rely on the use of chemicals or high temperature. For example, KrF excimer laser irradiation process for the fabrication of N-doped graphene from graphene oxide will be illustrated and the performance of laser reduced N-doped graphene when it is used as electrode active materials in supercapacitors will also be evaluated.

## **Introduction**

Effective fabrication methods that can produce high quality and sufficient quantities of graphene at low cost are greatly needed for industrial applications such as energy storage, catalysis, sensors and printable electronics. Currently, the most common and vital process used to form graphene is by reducing graphite oxide chemically. Graphite oxide is commonly produced by Hummers and Offeman's method [1] or its modified version [2, 3], in which graphite is treated with oxidizing agents such as a mixture of sulfuric acid, sodium nitrate and potassium permanganate. The oxidizing agents react with graphite, resulting in an increased 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 (GO) is produced. GO is then reduced by reducing agents such as hydrazine and  $\text{NaBH}_4$ . Reducing GO by using chemical reduction is a very scalable method, but unfortunately, the graphene produced has often resulting in relatively poor yields in terms of surface area and electronic conductivity. Additionally, the use of toxic agents not only brings some risks to the environment and safety of production, but also introduces impurities into the reduced graphene [4]. Thermal or electrochemical means can also be used to reduce GO to produce graphene. Graphene produced by thermal treatment at a temperature of  $1000^\circ\text{C}$  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]; however, 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. Electrochemical reduction of GO can produce graphene that has almost identical structure to pristine graphene. This technique, however, can reduce only a very thin layer of GO that needs to be coated on conductive substrates; therefore, the scalability of the electrochemical technique is an issue.

Most recently, it has been demonstrated that GO can be reduced by a photo-reduction process [6-10]. The main advantages of the photo-reduction process are that it does not rely on the use of chemicals or high temperature. In addition, photo-reduction has significant advantages for the fabrication and integration design of graphene-based micro-devices, and for direct patterning of flexible electronic devices [8, 11]. In this paper, the recent developments on the fabrication of graphene by means of photo-reduction of GO will be overviewed. For example, an excimer laser irradiation process for the fabrication of N-doped graphene will be illustrated and the performance of laser reduced N-doped graphene when it is used as electrode active materials in supercapacitors will also be evaluated.

### **Overview of photo-irradiation reduction process**

Different light sources, including solar light, lamplight generated by different types of lamps, and lasers operating at different wavelengths can be used to reduce GO to form graphene. Photo-reduction processes can undergo photo-thermal, photo-chemical, and catalyst assisted photo-chemical reduction mechanisms. In the photochemical events, absorption of photons by the GO leads directly to covalent bond breaking. The threshold of photon energies for photochemical reduction of GO was found to be larger than 3.2 eV ( $\lambda < \approx 390$  nm) [12]. In photo-thermal events, photons energy was absorbed by the electrons in GO. 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 GO. By adjusting the 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. In addition, by mixing GO with various chemical compounds before photo-reduction, doped and composite graphene with various functionalities can be produced. The great flexibility of photo-reduction processes allows the produced graphene to be used for a wide range of applications including supercapacitors, Li-ion batteries, electronics and sensors.

#### **Solar light reduction**

Solar is the most abundant energy resource on planet Earth. Solar radiation consists of ultraviolet, visible, and infrared bands, of which, infrared radiation makes up 49.4%, visible light 42.3% and ultraviolet radiation just over 8%. When solar radiation is used for photo-reduction of GO, reduction processes can be under either photochemical or photo-thermal processes, or precede through a combination of both as solar radiation cover bands with wavelengths larger or smaller than 3.2 eV. Since 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 GO, reduction of GO to graphene by solar radiation could be a low cost, rapid, and scalable process for the large scale production of graphene. Reducing the production cost of graphene is critical for its use in energy storage for automotive, transportation and stationary applications. Mohanapriya et al. [13] reported the use of focused solar light to irradiate GO paper to make graphene. A convex lens was used to focus the solar radiation to irradiate the GO paper to exfoliated and reduced GO simultaneously. Reduction of GO 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. GO was decomposed into graphene along with releasing  $\text{CO}_2$  and  $\text{H}_2\text{O}$  gases. Graphene reduced by solar radiation was used as an electrode active material and evaluated in supercapacitors. The specific capacitance of the solar reduced graphene in both 6M KOH aqueous electrolyte and EMIBF<sub>4</sub> ionic liquid electrolyte was measured. The specific capacitance values were determined to be  $265.9 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  and  $211 \text{ F g}^{-1}$  at  $10 \text{ A g}^{-1}$  for solar reduced graphene in 6M KOH. In comparison, the specific capacitance of  $187.1 \text{ F g}^{-1}$  was obtained in EMIBF<sub>4</sub> electrolytes. This high value of specific capacitance was attributed to the high surface area, low degree of restacking and high conductivity of the solar reduced graphene. Although solar reduced graphene shows impressive performance, there are challenges such as how to control the quality of large quantities of graphene produced by this process as limited process parameters can be controlled and optimized. Optical filters could be used to select only certain bands of the solar radiation in either UV, visible or IR ranges to achieve more control over the quality of the reduced graphene.

### Lamplight reduction

Lamplight is light produced from a lamp. It is typically not very bright and only shines over a small area. Lamplight generated by a simple camera flash lamp or a mercury lamp is used to reduce GO to form graphene. Although photo-reduction of GO by various lamps is a simple, rapid, chemical-free, and energy efficient process, it is only suitable at producing small quantities of graphene for applications in thin film devices or micro-devices such as sensors, printable electronics and small energy storage devices for portable electronics. Cote et al. [8] reported the use of flash light reduction of free-standing GO films with a Xenon lamp equipped on a common digital camera to trigger instantaneous deoxygenation of GO by the photo-thermal heating. They found that the sheet resistance of flashed area was decreased from  $2.108 \text{ k}\Omega/\text{sq}$  for the pure GO to  $9.5 \text{ k}\Omega/\text{sq}$  for the graphene with a significant decrease in hydrophilicity. Guo et al. [14] used a common bathroom IR lamp with a power of 275 W as the light source for reducing GO. Although the energy of the IR photon is lower and adsorption of IR light by GO films is also less than that of UV and visible light, adsorption of intensive IR light by GO can increase its temperature very rapidly to induce thermal reduction. They 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 GO sheets. At relatively low IR power intensities, the reduction process was relatively slow and the produced graphene was less porous.

To increase the degree and percentage of GO that was reduced, photo-catalysts such as  $\text{TiO}_2$ ,  $\text{BiVO}_4$ , were added into the GO 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 GO 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. [6] used  $\text{TiO}_2$  as the photo-catalyst and an Oriel 450 W xenon arc lamp as the light source to carry out UV-induced photocatalytic reduction of GO in a  $\text{TiO}_2$ -GO colloidal suspension. Due to the existing  $\text{TiO}_2$  particles, the degree of reduction of GO was improved and collapse of exfoliated sheets of graphene was avoided. Besides the most commonly used photo-catalyst,  $\text{TiO}_2$ ,

which absorbs UV light, other photo-catalysts can also be used. For example, Ng et al. [15] used bismuth vanadate ( $\text{BiVO}_4$ ) as the photo-catalyst to reduce GO. They reported that  $\text{BiVO}_4$  can use visible light instead of the UV light as by  $\text{TiO}_2$  to reduce GO. These authors attributed this finding to the larger band gap energy and longer electron lifetime of excited  $\text{BiVO}_4$  compared to  $\text{TiO}_2$ , which can better utilize visible light and minimize photoelectron recombination.

### Laser light reduction

Compared to other light sources used for photo-reduction of GO, laser has a number of distinguishing properties, such as it can be focused on very tiny spots, achieving a very high energy density. The wavelength of laser can be selected to cover UV, visible and IR ranges, therefore GO can be reduced by photo-thermal or photochemical reduction or both mechanisms. Besides, laser beams can be concentrated and travel a great distance, therefore they can be used to directly reduce/pattern GO layer for thin film devices. Laser reduction of GO film to form graphene film was reported by Romualdas Trusovas et al. [16, 17]. They first formed GO films by filtration of aqueous GO suspensions through the polycarbonate membrane filters. Reduction of GO films to graphene were performed by scanning focused laser beam that induces photo-thermal decomposition of GO. It was found that resistance of the GO films was decreased by 4-5 orders after they were irradiated with the picosecond 1064 nm laser indicating the formation of graphene. Wang et al. [18] also used focused laser beams to fabricate a few layers of graphene through simultaneous exfoliation and reduction of graphite oxide. In their experiment, a piece of GO foam was pressed at 0.2~0.5 MPa to form a relatively dense GO 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  $127 \text{ W cm}^{-2}$ ), the GO flake was put onto the quartz tube directly at ambient conditions, and irradiated with the laser for around 1 s. The laser reduced graphene was then 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, 226, 220, 208, and 201  $\text{F g}^{-1}$  at current densities of 0.25, 0.5, 1, 2, and 3  $\text{A g}^{-1}$ , respectively, and the laser reduced graphene supercapacitor cell delivered an energy density of  $8.21 \text{ Wh kg}^{-1}$  at a power density of  $62.5 \text{ W kg}^{-1}$ . 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. Photo-reduction of GO 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 GO (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 directly in aqueous solution.

## Excimer laser-reduced N-doped graphene for supercapacitor application

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 intrinsically 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 [19] and better performance in Li ion battery applications [20]. In this section, excimer laser irradiation process for fabrication of N-doped graphene will be illustrated and the performance of laser reduced N-doped graphene when it is used as electrode active materials in supercapacitors will also be evaluated.

### Experimental

The procedure to fabricate laser reduced N-doped graphene from graphite oxide is described as the following: Graphite oxide with a carbon contents of 63%, 200 mesh, thickness of 0.8 – 1.2 nm, C:O = 1.5 – 1.7 was purchased from Green Stone Swiss Co. Limited. The graphite oxide powder was then dispersed in Milli-Q water by sonication treatment (300 W, 35 kHz) for 1 h causing exfoliation to produce single-layer GO. A small amount of  $\text{NH}_3$  was then added into the GO solution until pH= 10. The  $\text{NH}_3$  containing GO solution was placed in a quartz vial and was irradiated by a Lambda Physik KrF excimer laser (248 nm) using 300 mJ or 530 mJ beam energies at 10 Hz repetition for either 1 or 2 hours. The experimental procedure for the preparation of graphene from the graphite oxide powder is schematically described in Figure 1. The GO solution changes from brownish yellow to black after prolonged irradiation indicating that excimer laser radiation at UV wavelength (248 nm) can reduce GO to graphene at rapid rates.

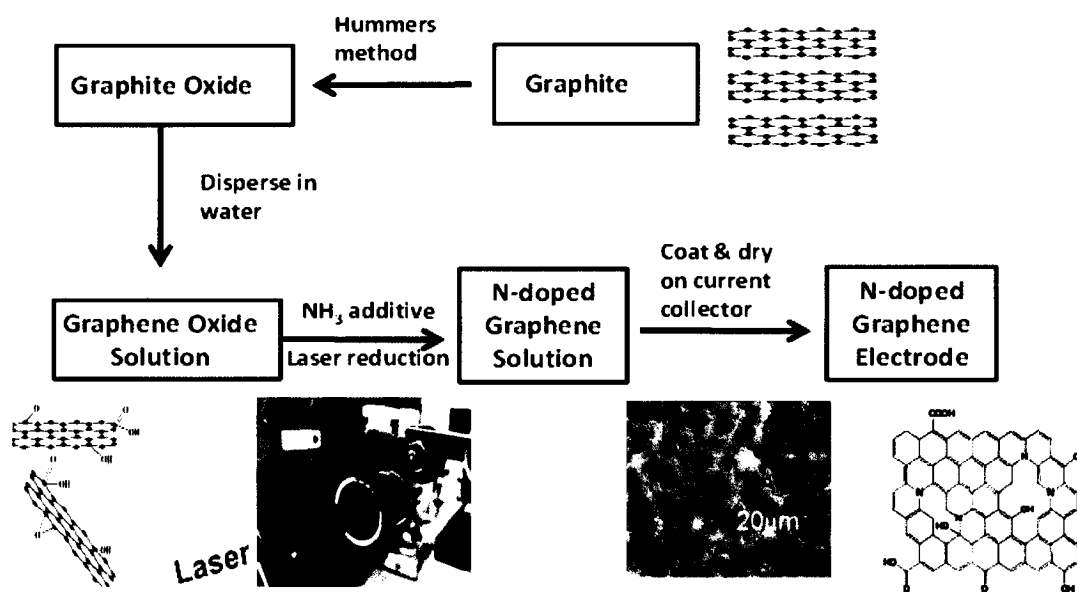


Figure 1 : Experimental procedure for the preparation of N-doped graphene electrode from graphite powder by combining Hummers method and laser irradiation

GO or N-doped graphene films were prepared by drop-casting of GO or N-doped graphene aqueous solutions on Si(100) wafers. The structure of the graphite oxide and laser reduced N-doped graphene were characterized using low angle X-ray diffraction equipment (XRD, Philips, X-Pert MRD) with monochromatized Cu K $\alpha$  in the  $\theta_0$ -2 $\theta$  thin film configuration, where  $\theta_0$  was fixed at 0.5°. Cyclic voltammetry (CV) was used to characterize the specific capacitance of N-doped graphene films coated onto 1 mm thick gold current collectors of 17.8 mm diameter in a two-electrode system. Aqueous 0.5 M Na<sub>2</sub>SO<sub>4</sub> was used as electrolyte solutions. A computer-controlled Gamry (Reference 3000) potentiostat was used to carry out the electrochemical experiments in this work. CV curves were recorded within a range of 0 to 1 V. The following scan rates were used: 5, 10, 20, 50, 100, 200, 500 and 1000 mV/s. The above potential ranges were chosen to ensure that redox processes of water on Au do not occur. The ECC-Aqu electrochemical cell purchased from EL-CELL GmbH was used for all the electrochemical characterization. Gold foils were used as the current collectors to achieve extraordinary low contact resistance between the gold current collector and the graphene. A PTFE film of 25  $\mu$ m thick was used as the separator. The specific capacitance of the N-doped graphene was calculated from the CV data and the weight of the graphene films. The weight of the graphene films were determined by subtracting the weight of the graphene film coated gold substrate by the bare gold substrate. The electrical current and capacitance data were divided by the weight of the film to obtain the specific current and the specific capacitance, respectively.

## Results and discussions

XRD patterns of GO and N-doped graphene films prepared by drop-casting either GO or N-doped graphene aqueous solutions on a Si(100) wafer are shown in Figure 2. N-doped graphene aqueous solutions were fabricated by laser irradiation reduction of GO solutions containing NH<sub>3</sub> at 300 mJ and 1 hour, 300 mJ and 2 hours and 530 mJ and 2 hours, respectively. The XRD pattern of the exfoliated GO is characterized by a peak at 2 $\theta$  of 12° corresponding to the (001) diffraction peak of GO with a larger d-spacing of 7.38 Å (as compared with the typical value of 3.34 Å of graphite). The appearance of the peak results from the insertion of hydroxyl and epoxy groups between the carbon sheets and the carboxyl groups along the terminal and lateral sides of the sheets after the oxidation process. As shown in Figure 2, following the 248 nm excimer laser irradiation at 300 mJ and 1 hour, the intensity of the peak at 2 $\theta$  of 12° decreased but the peak does not totally disappeared. By doubling the irradiating time from 1 hour to 2 hours, the XDR peak only slightly decrease further. When the laser energy increased to 530 mJ, irradiation of 2 hours was able to totally eliminate the peak at 2 $\theta$  of 12° indicating high laser energy is needed to totally remove oxygen-containing groups. In the absence of NH<sub>3</sub> in the GO solution during laser irradiation, it was found that 300 mJ of laser energy was able to eliminate this XRD peak completely after 1 hour of irradiation [21]. The XRD band centered at 2 $\theta$  of 25° which originated from the (002) diffraction peak of graphite becomes more eminent as either laser energy or irradiation time increase. This could indicate a higher stacking of the graphene sheets taking place at longer times of irradiation and higher energy [14]. The structures of laser reduced N-doped graphene were also analyzed by X-ray photoelectron spectroscopy (XPS). As a surface-sensitive analytical technique, XPS provides the chemical environment of C, O and N atoms in either graphite oxide or laser reduced N-doped graphene structures. The percentage of functional groups determined from the high resolution analyses of the N1s regions is

shown in the table 1. The existence of high percentage of alkyl ammonium/ammonium and low percentage of amine in GO may be originated either from chemical residues used in the production of GO from graphite or impurities existed in the graphite. After excimer laser irradiation of the  $\text{NH}_3$  containing GO solution at 530 mJ for 2 hours, the appearance of the  $\text{R}=\text{N}-\text{R}$  (where  $\text{R}=\text{Aromatic}$ ,  $\text{Aromatic Imine}$ ) functional groups (from 0% to 31%) and percentage increase of the amine groups (from 11.3% to 57.6%) indicate that nitrogen atoms were doped into the graphene structure. The percentage of alkyl ammonium/ammonium decreased after laser irradiation may be due to consumption and evaporation of those compounds/functional groups during the laser irradiation process.

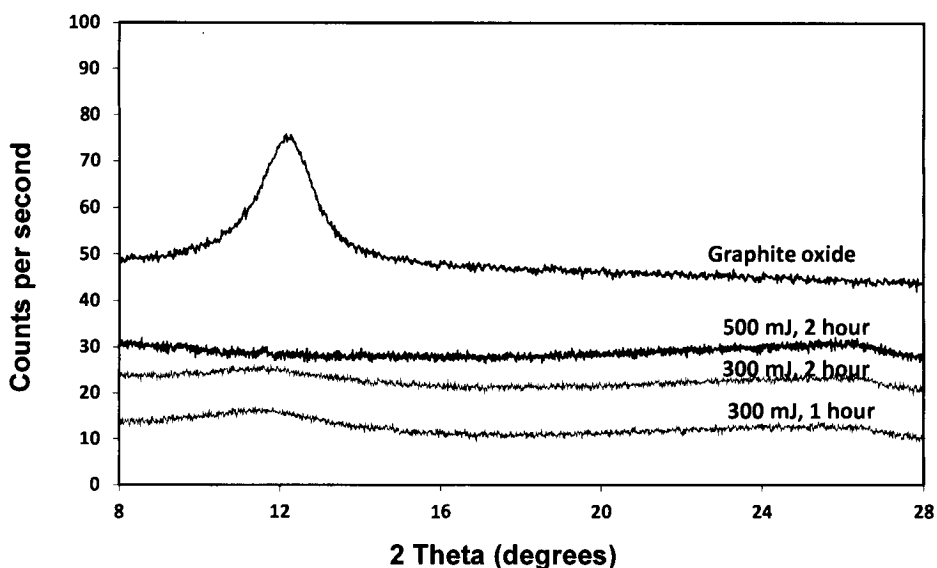


Figure 2 : XRD spectra of GO, and N-doped graphene prepared by laser irradiation of  $\text{NH}_3$  containing GO solution at 300 mJ for 1 hour, 2 hours and at 530 mJ for 2 hours. GO and N-doped graphene samples were prepared by drying drops of GO or graphene aqueous solutions on a silicon wafer.

Table 1: XPS data of graphite oxide and N-doped graphene determined by high resolution analyses of the N1s regions

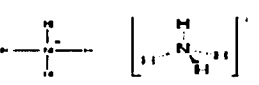
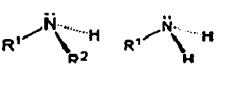
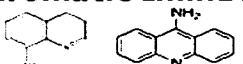
Sample	Alkyl Ammonium, Ammonium 	Amine 	$\text{R}=\text{N}-\text{R}$ ( $\text{R}=\text{Aromatic}$ , Aromatic Imine) 
GO	88.7	11.3	
N-GN	11.4	57.6	31.0

Figure 3(a) shows CVs of N-doped graphene prepared by laser irradiation at 300 mJ and 1 hour at potential scan rates ranging from 10 to 500 mV/sec in the aqueous 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte. The measured currents were normalized by the scan rate and the weight of the films and hence, reported as specific capacitance values. The specific capacitance is seen to increase with decreasing scan rates for the N-doped graphene film indicating that there is resistance for ions to transport into and out of the graphene films



during the charge-discharge process. The CV curves give reasonable rectangle and symmetry shape indicating that charging-discharging of the N-doped graphene film behaves like a double layer capacitor. Figure 3(b) gives the galvanostatic charge/discharge cycles of the graphene films obtained at various constant current/weight densities of: 0.57 A/g, 2.85 A/g and 5.7 A/g. The specific capacitance, calculated from these charge/discharge curves, for N-doped graphene fabricated by laser irradiation at 300 mJ and 1 hours are 99.7 F/g at 0.57 A/g, 90.4 F/g at 2.85 A/g and 85.5 F/g at 5.7 A/g, respectively. The cell resistance calculated from the linear voltage drop observed immediately after discharging, illustrated in the insert of Figure 3(b), is  $2.32 \Omega$  (or  $0.93 \Omega/\text{cm}^2$ ). The specific capacitance of the laser fabricated N-doped graphene is lower than the values of  $\sim 280 \text{ F/g}$  reported in the literature for N-doped graphene by  $\text{N}_2$  plasma treatment [22].

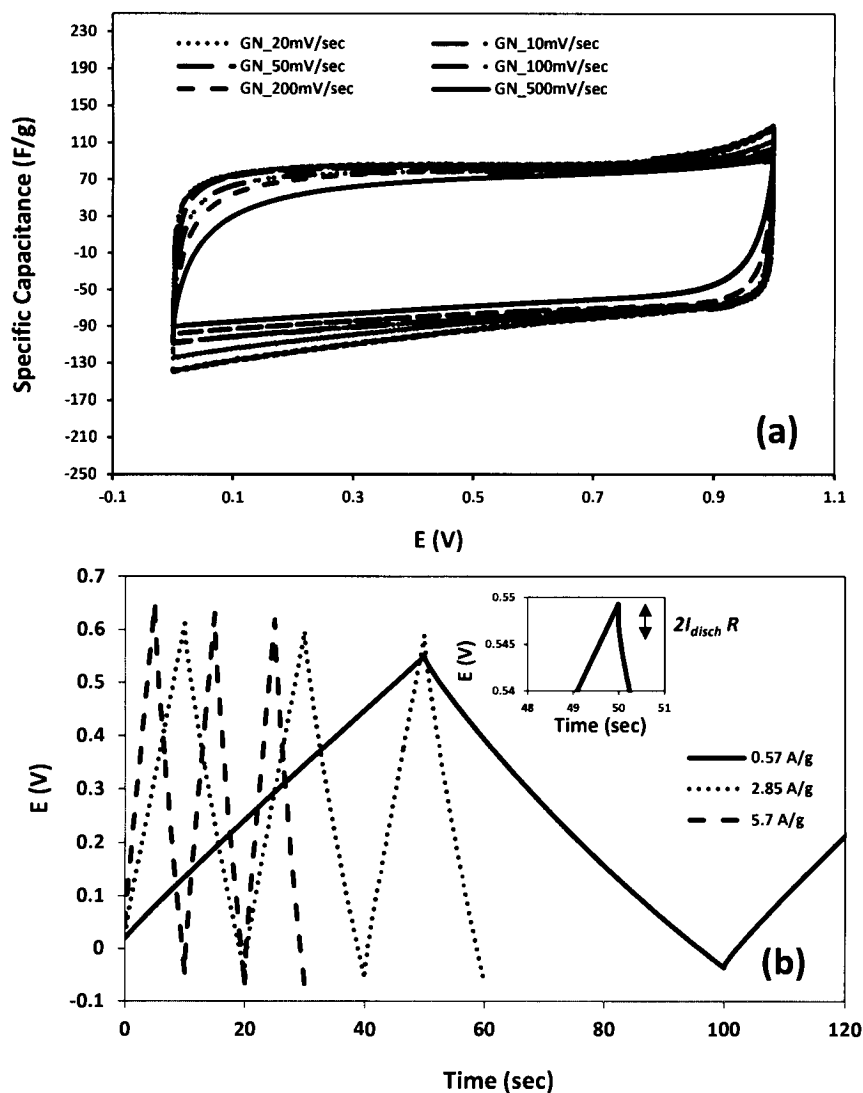


Figure 3 : (a) Cyclic voltammograms at various potential scan rates, and (b) galvanostatic charge/discharge cycling at constant currents of 0.57, 2.85 and 5.7 A/g, for the N-doped graphene electrode prepared by laser irradiation of graphite oxide solution containing  $\text{NH}_3$  at 300 mJ for 2 hours in 0.5 M  $\text{K}_2\text{SO}_4$  aqueous solution.

The curves of specific capacitance vs. the CV scan rate of graphene films prepared at different laser energy and irradiation time are shown in Figure 4. N-doped graphene

prepared at 300 mJ and 2 hours has the highest specific capacitance at all scan rates investigated, while N-doped graphene prepared at 530 mJ and 2 hours has the lowest value. N-doped graphene prepared at 300 mJ and 2 hours has a specific capacitance of 54.8 F/g at 1000 mV/sec and reaches 84.5 F/g at 5 mV/sec. The specific capacitances of N-doped graphene prepared at 530 mJ and 2 hours are 38.9 F/g at 1000 mV/sec and 52.3 F/g at 5 mV/sec, while the specific capacitances of graphene prepared at 300 mJ and 1 hour are 42.4 F/g at 1000 mV/sec and 84.5 F/g at 5 mV/sec. The specific capacitance increases with the decrease in scan rate for the N-doped graphene films indicating that the charge-discharge process of the N-doped graphene films does not behave like an absolutely ideal double layer capacitor, and there is resistance for electrolyte ions to transport into and out of graphene films. N-doped graphene films prepared at 530 mJ show much less decrease in specific capacitance with the increase in the scan rate, particularly, when the scan rate is higher than 200 mV/sec, the specific capacitance almost keeps constant above this scan rate. This could suggest that N-doped graphene prepared at 530 mJ is more electrically conductive and/or easier for ion to transport in and out.

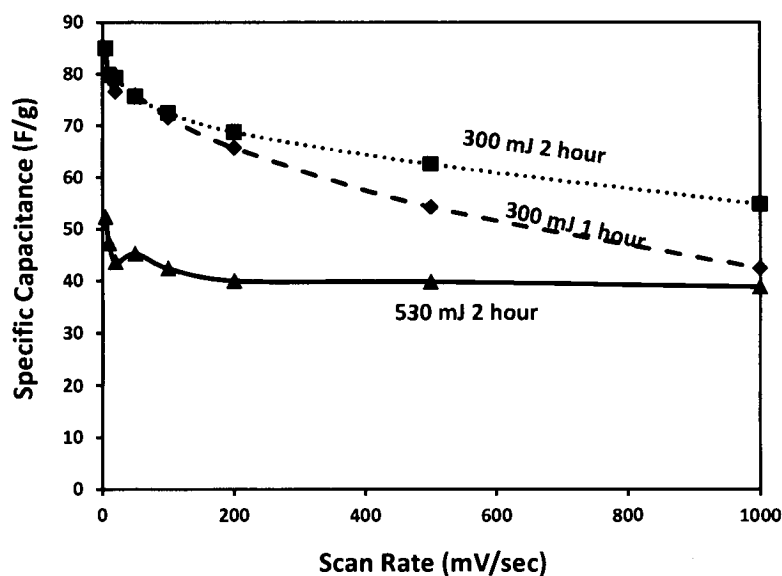


Figure 4 : Specific capacitance versus CV scan rates for N-doped graphene prepared by laser irradiation of graphite oxide solution containing  $\text{NH}_3$  at 300 mJ for 1 hour, 2 hours and at 530 mJ for 2 hours, respectively.

### Summary

The KrF excimer laser irradiation reduction technique has been used in this study to prepare N-doped graphene from GO aqueous solution. By varying the laser irradiation processing conditions such as laser energy and irradiation time, N-doped graphene with different supercapacitive behaviors were successfully grown. The observed different specific capacitance values of n-doped graphene when different laser energy and irradiation time are used may be due to different degrees of deoxygenation, different size and shape of N-doped graphene sheets produced and different levels of re-stacking of N-doped graphene sheets after they are reduced by laser beam irradiation. All those factors will affect the surface area available for charges storage, as well as the electronic and ionic conductivity of laser reduced N-doped graphene.

## Conclusions

The photo-reduction process for producing graphene from graphite oxide is a simplified, rapid, energy efficient and toxic-material-free alternative to chemical, thermal and other reduction methods. Light sources used for the photo-irradiation reduction of graphite oxide can include solar light, lamplight, and laser beam operations at different wavelengths. Solar light is an eco-friendly light source and the solar radiation reduction process could be further developed for low cost, rapid, and scalable production of large quantities of graphene for energy storage device used in the automotive and transportation sectors. Lamplights 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 including 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 in using laser to reduce graphite oxide in aqueous solution opens a new venue for production of high quality and relatively large quantity of graphene for large supercapacitors applications. In this work, unique properties and high performance of N-doped graphene produced by excimer laser photo-reduction process for supercapacitor application have been demonstrated. The specific capacitance of N-doped graphene films prepared at 300 mJ and 2 hours has the highest specific capacitance. It reaches 55 F/g at 1000 mV/sec and 84.5 F/g at 5 mV/sec determined by cyclic voltammetry. N-doped graphene films prepared at 530 mJ is very electrically conductive and/or easier for ion to transport as indicating by specific capacitance independence of scan rate when it is  $> 200$  mV/sec.

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