Solar reduction of graphene oxide in large scales for high density electrochemical energy storage

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S1. A Brief Review on the Reduction of Graphene oxide

Graphene oxide sheets are insulating in nature and contain oxygen functional groups. To get graphene from GO, reduction of the oxygen functional group is required and the graphene obtained from reduction is also referred as reduce graphene oxide [1]. There are two major routes for reduction of GO: chemical and thermal reduction.

1.1 Chemical reduction of Graphene oxide

Chemical reduction is solution-based procedure of reducing graphene oxides and can be used for making large scale quantities. Normally in this process GO is dispersed in water for making homogenous suspension to facilitates the efficient reduction of individual sheet. GO containing different oxygen functional groups bonded to the edge and basal plane are reduce by partially restoring the aromatic structure of graphite. This reduction occurs due to different chemical reactions depending upon the chemicals used. As GO is converted to rGO, it settles down to bottom due to hydrophilic nature and is further cleaned from impurities [2]. Different types of chemical used to reduce GO include phenyl, sodium borohydride, hydrazine hydride, hydrazine, glucose, ascorbic acid, pyrrole, hydroquinone, amino acid, hydroxylamine, strong alkaline solution, and urea. Although the chemical reduction is

efficient process for reducing the GO, but due to use of chemicals it is consider as non-eco-friendly and hazardous for nature and at the same time it is time consuming process [3, 4].

1.2 Thermal reduction of Graphene oxide

Alternate to chemical reduction is thermal reduction in which GO is reduced by agitating the oxygen functional group with the help of heat sources. Thermal source, exfoliate and reduce GO by inducing pressure at graphene oxide layer, consequently removing oxygen groups by generating CO_2 and CO [5]. In thermal annealing normally GO powder is exposed to high temperature in air or inert atmosphere. At high temperature functional groups are removed while at the same time exfoliation occurs and high surface is generated. Thermal annealing some time also introduces defects which can largely affect the properties. Also extended time is required for complete removal of functional groups for GO surface [6].

Apart from direct thermal annealing microwave radiations are also used for reduction of GO sheet, microwave radiation can rapidly increase the temperature up to 400 centigrade in 2 seconds and instantly converting GO into rGO. During reduction process volume expansion at large scale is observed which indicates the simultaneous exfoliation and reduction. The microwave reduction is rapid and fast reduction procedure and can be used for large scale reduction of GO [7].

LASER is also another effective method for producing GO at large scale. Exposing laser beam to GO can cause local heating at exposed part ultimately breaking the oxygen bonds and exfoliating the sheets along with storing the graphitic structure of graphene. The whole process occurs in two steps, firstly breaking of carbon oxygen bonds and secondly restoring of the sp2 structure of graphene. The efficient and desirable reduction process mainly depends upon the laser parameter and environment. GO can be reduce with laser radiation in different forms including films, fibers and powder [8, 9].

Wang et al. reported reduction of GO by using gas phase hydrazine reduction and its supercapacitive performance. GO was placed in vacuum desiccator. While filter paper wet with hydrazine was placed near to GO powder. In 72 hours GO was reduce with the assistant of hydrazine vapors. The resulted reduce powder was tested in symmetric device using 6 M KOH electrolyte. Charge discharge was used to calculate the capacitance, energy density and power density. Total capacitance calculated was 205 F/g with minimum energy density of 28 Wh/kg. 90% of the capacitance was retained till 1200 charge-discharge cycle [10].

Zhu et al. reported very simple method of reduction of graphene oxide by using commercially available microwave oven, GO powder was placed in microwave and exposed to microwaves of 700W. In 1 minutes GO was immediately converted to rGO with the release of carbon specious with very large volume expansion. rGO powder was assembled as an electrode and tested in symmetric system. Cyclic voltammetry and charge discharge tests are carried out in 6 M of KOH to check super capacitor performance. Capacitance calculate from charge discharge test was 191 F/g at 150 mA/g [7].

Peng et al. reported reduction of GO by using electrochemical technique and also its use in supercapacitor. The GO aqueous solution was dropped costed on gold coated polyethylene terephthalate sheet (PET). Electrochemical reduction was carried out using GO film in sodium nitrate solution for 4.5 hour at -1.1 V across Ag/AgCl electrode. Reduced GO film was tested as super capacitor device by making symmetric electrode system. The testing was carried out using charge discharge test in 1M of $NaNO_3$. Device exhibits capacitance of 128 F/g at voltage window of 1V. The energy and power densities values were 17.8 Wh/kg and 106 KW/kg. Over 14% drop was observed after 3500 cycles [11].

Zhang et al. reported superior performance of chemical activated porous rGO in supercapacitor. In two step process, the KOH powder was first intercalating in the sheet of GO and transformed into film. In second step activation and reduction of KOH intercalated GO sheets was carried out at high temperature in inert atmosphere. Resulting porous rGO powder was tested in symmetric electrode system. Higher voltage organic electrolyte was used to check the performance of porous material. Specific capacitance calculated by using CDC at 10 A/g was 120 F/g. Superior energy density of 26 Wh/kg was observed at same current density [12].

Luo et al. reported the use of rGO crumble balls in supercapacitor application. Crumble balls were synthesis by spraying GO sheets using nebulizer into preheated furnace at 800oC. Due to repaid evaporation of solvent and high temperature, GO was reduce and transformed into crumble balls. The material was tested in symmetric system by assembling electrode in coin cell. The specific capacitance was calculated to be 150 F/g at low current density of 0.1 A/g [13].

Niu et al. reported thin microsupercapacitor fabricated from rGO integrated with solid state electrolyte. Microsupercapacitor were prepared by patterning GO on the gold coated

sheet using photoresists. After patterning insulating GO, electrode was converted to conductive electrode using hydrazine. To make flexible device, solid state electrolyte of polyvinyl alcohol and phosphoric acid was prepared and coated on the rGO electrode. Electrochemical characterization was carried out of above microsupercapacitor using CDC test. Capacitance calculated was 285 F/g and 90% of capacitance was retained after 1000 cycles [14].

Yoon et al. reported use of non-stacked crumble rGO sheets prepared by hexane in supercapacitor application. Hexane was added to ethanol dispersed GO which immediately crumbled the sheets. After evaporation of ethanol and hexane crumbled GO powder was dried and thermally reduced to get crumbled rGO. Crumbled rGO was tested in two electrode system using 6M of KOH. The supercapacitor showed capacitance of 236.8 F/g at 1 A/g. This initial value was stable up to 103.5 % after charge-discharge cycles of 16000 [15].

Sun et al. reported reduction of graphene oxide paper by flame induced reduction and its utilization as supercapacitor. Vacuum filtration was used to make graphene oxide paper. Reduction was carried out using flame of commonly available cigarette lighter. Reduced graphene oxide paper was crushed into powder and assembled in the form of electrode. Symmetric cell configuration was used to test the material in 2 M of KOH. CDC test carried out at 1 A/g showed that cell can achieve the capacitance of 175 F/g. Energy density and power density of the device were 6 Wh/kg. Device retained the capacity up to 91% after 2000 cycles [16].

Yan et al. reported metal template method for preparation of restacking free rGO. GO was disperse with magnesium hydroxide metal which act as templated and spacer. Sheets were thermally reduced by slow heating up to 300 centigrade. The reduced GO sheets with magnesium hydroxide template were washed with HCl to remove the template. Resultant powder was transformed into electrode and electrochemical performance was evaluated in two electrode system using 1 mole of sodium sulphate. At 2 mV/s the symmetric supercapacitor was charged up to 2V which achieved the capacitance of 58.6 F/g. The energy density calculated was 26.4 Wh/kg while the device showed stable capacitance till 10,000 cycles with no degradation [17].

Li et al. reported the use of zinc oxide nanostructures treated rGO for the supercapacitor application. GO was precipitated with zinc nitrate solution and heated up to 350 centigrade to

form rGO-ZnO edge composite. In next step ZnO at edges was dissolved in hydrochloric acid to obtain non-aggregated rGO. Supercapacitive performance of the prepared rGO was checked in 6M of KOH using CDC method. Specific capacitance of 182 F/g was calculated at 1 A/g current density while cycle stability was observed up to 1000 cycle without losing any significant capacitance. Energy density and power density calculated were 44 Wh/kg and 2.5 KW/kg respectively [18].

Ali et al. reported the use of hydrazine reduced GO in supercapacitive application. GO was treated with hydrazine mono hydrate which act as reducing agent. rGO obtained was tested for supercapacitive performance in symmetric electrode system using 5 M of KOH. The specific capacitance calculated was 140 F/g at current density of 0.025 A/g while the energy density calculated was 5 Wh/kg at 0.05 A/g. the device showed stability of 85% after 1100 cycles [19].

Johra et al. reported the use of hydrothermal reduce GO in supercapacitor application. The hydrothermally rGO was prepared by placing GO solution in stainless steel autoclave and heating it for 6 hours at temperature of 180 centigrade. Capacitance calculated at 1 A/g was 367 F/g while the columbic efficiency was almost 100 %. The capacitance value was stable up to 1000 cycles at 10 A/g current density. Energy and the power densities of the devices were 44.4 Wh/kg and 40 KW/kg respectively in 1 M of sulfuric acid [20].

Ramadoss et al. reported the concept of thermally reduce GO carbon fabric for using as supercapacitor application. Flexible fabric of carbon was coated with GO and thermally reduced at 160 centigrade for 2 hour. Solid state supercapacitor was fabricated using phosphoric acid and polyvinyl gel. The capacitance calculated from charge and discharge curve at 0.1 mAcm^2 was 42 F/g. the energy density of solid state device was 5.8 Wh/kg while power density reached to 27.7 kw/kg [21].

Shivakumara et al. reported the use of low temperature reduced GO in non-aqueous electrolyte based supercapacitor. Rapid reduction route was adopted using ambient conditions to prepare rGO. Two electrodes symmetric system was used to test the supercapacitive performance in 1 M of Lithium hexafluorophosphate. CDC test showed that device exhibit capacitance of 140 F/g at current density of 0.2 A/g. The energy density and power density calculated were 44 Wh/kg and 15 Wh/kg respectively. 84% charge was retained after 3000 cycles [22].

Yang et al. reported the laser reduction of GO in aqueous suspension with different laser exposing time and energies. GO powder reduce at 30 mJ for 2 hours, was checked for supercapacitive properties using two electrode symmetric system in neutral and organic electrolyte. In 0.5 M of sulfuric acid the capacitance was calculate as 141 F/g at current density of 1.04 A/g. After 2000 cycle this value was reduce to 54.3 F/g, more than 47% of the capacitance loss was observed [23].

Mohanpriya et al. reported the reduction of GO using focused solar radiation and utilization in supercapacitor application. rGO was prepared by focusing solar light using optical lens. Solar radiation immediately convert GO to rGO by raising the temperature up to 200 centigrade. rGO was tested as supercapacitor in two electrode symmetric system using 6M of KOH and 1-Ethyl-3-methylimidazolium tetrafluoroborate ionic liquid. Supercapacitance device exhibits capacitance of 265.9 F/g in 6M of KOH while for EMIMBF$_4$ electrolyte the capacitance value was 187.1 F/g. The energy density for KOH was calculated as 9.23 Wh/kg at 1016 W/kg. While for ionic liquid with high voltage window, the energy density was increase up to 5 fold. In ionic liquid the stable value of capacitance was observed till 1000 cycles [24].

kumar et al. used 310 mw laser for the reduction of GO film. GO film was prepared by vacuum filtration and exposed to 355 mm laser. Low power laser efficiently reduced the exposed area by irradiating the thick GO film. Reduce GO was checked for the supercapacitive properties using two electrodes system in sodium hydroxide, sodium suphate and potassium chloride solution. The capacitance calculated for Na$_2$SO$_4$, NaOH, KCl is 2.23, 2.40, 1.620 μF/cm2 respectively at 50 mV/s. NaOH showed the stable value of capacitance 3600 cycles. No energy or power densities values were reported [25].

Ye et al. developed rGO paper for supercapacitor application. Firstly GO/acetic acid/hydrogen iodide mixed suspension was prepared for making GO paper. In second step this suspension was coated on teflon block to prepare the above mentioned paper and transfer to the oven. Resultant reduced paper was tested for supercapacitor application. Flexible supercapacitor made with KOH/PVA solid electrolyte showed high areal capacitance of 152.4 mF/cm^2 at 2 mA/cm^2 current density. The capacitance was stable up to 96.9% after 10,000 charge discharge cycles. The energy density calculated was 0.13 mWh/cm^3 while power density was 9.92 mW/cm^3 [26].

Zhu et al. reported rGO/nickel foam electrode prepared by ammonia reduction for supercapacitor. GO was coated inn the nickel foam micropores to prepare rGO/nickel foam framework. GO/nickel foam framework was converted to rGO/nickel foam framework by heating at 90 centigrade in the ammonia solution. Two identical pieces of rGO/nickel foam were used to prepare supercapacitor for testing in two electrode system. The supercapacitor showed specific capacitance of 230 F/g at current density of 0.33 A/g in 6 M of KOH. 96.7 % of capacitance was retained after 2000 cycles of charge-discharge [27].

Wang et al. reported low temperature nanocellulose assisted synthesis of rGO and use it in supercapacitor application. Aqueous solutions of nanocellulose and GO were mixed and freeze dried to make aerogel which was further annealed to 350 centigrade. The two electrode symmetric test was carried out to check performance of the material. The capacitance calculated for the rGO symmetric capacitance was 224 F/g with the 74% of the original value of capacitance was retained for 1000 cycles [28].

Yag et al. prepared rGO by rapid thermal annealing of 70-80 centigrade/s in inter gas atmosphere in quartz tube and showed its performance as supercapacitor electrode material. The two electrode setup was used to evaluate the performance of the material in 1-Ethyl-3-methylimidazolium tetrafluoroborate ionic liquid. The specific capacitance calculated from charge discharge test was 279 F/g at current density of 1 A/g [29].

Han et al. reported 3D interconnected reduced graphene oxide prepared by the assistance of sugar blowing. During synthesis process small amount of glucose was added to the suspension. Glucose can assist in bubble burst and crosslinking of graphene oxide. Material was thermally annealed at 1000 centigrade to reduce GO perfectly. Two electrodes setup was used to test the performance of material in 1M of sulfuric acid. The capacitance calculate at 10 mV/s was 115 F/g. No visible degradation capacitance was observed up to 10,000 cycles [30].

Solar reduction of graphene is another cost effective green process of reduction of GO. Normally solar radiation are focused on powder by any converging source ultimately raising the temperature and reducing the GO to rGO [31]. Also direct sunlight exposure partially reduce the GO but it takes hour of exposure [32, 33]. Apart from above methods different other mechanisms are also reported which include flame reduction, hot plate reduction, soldering iron reduction etc. [34-36]. Although different methods are proposed for reduction

of GO but still more improvement is required like in case of chemical reduction process mostly graphene is partially restacked in the form of graphite in the water reducing media. Due to reduce surface area of GO obtained by chemical rout show lower performance as compared to thermally reduce graphene oxide where high surface area is achieved.

S2: Synthesis of Graphene oxide

Synthesis of graphene oxide (GO) was carried out using improved method by modifying cleaning process which is essential and crucial step for getting good quality of GO [37]. In synthesis process 3 g of graphite, 18 g of Potassium permanganate, 360 ml of sulphuric acid, 90 ml of phosphoric acid, 9 ml of hydrogen peroxide and 4000 ml of deionized water were used. The above process gives advantage of eliminating the emission of nitrogen oxide which is by product in other synthesis process due to use of sodium nitrate, where as in this process no sodium nitrate was used [38]. In typical synthesis process sulphuric acid and phosphoric acid were mixed together in synthesis pot which was placed in ice bath. Temperature of the mixture slowly came down to ~5 ℃. Potassium permanganate was added slowly to above mixture with the rate of 2g for5 minutes in order to ensure that the temperature of the pot does not increase rapidly which may lead to explosion or fire. After addition of potassium permanganate mixture was stirred for 30 minutes and graphite according to above mentioned amount was added to pot. The temperature of the mixture was further raised to 50℃ and was kept at stirring for 74 hours in order to insure the complete oxidation of graphite into graphene oxide. After oxidation process hydrogen peroxide was added to the above suspension in order to stop further oxidation and terminate the reaction process. At this stage the suspension consists of contaminated graphene oxide, graphite oxide, by product salts and acid. The above suspension was centrifuge at 8,000 rpm for 20 minutes in order to take out the primary acid followed by one time washing with deionized water. The graphene oxide mixture was suspended in 1 M of hydrogen chloride in order to remove the metal particles and then centrifuge at 8000 rpm for 10 minutes in order to remove contaminated hydrogen chloride. Metal free GO was suspended in 4000ml of water in order to reduce the traces of acid and was again centrifuge at 8,000 rpm to get clean GO. Cleaned GO was stored at minus 50 ℃ and put into freeze drier for one day for drying. Light weight and clean GO were stored in seal container and stored in desiccator for reduction process.

S3. Geometry of the Fresnel Lens used in this work

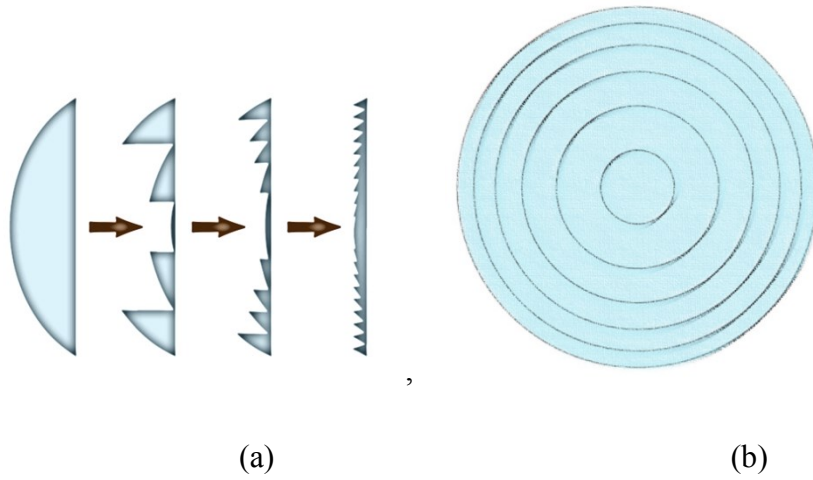(a)   (b)

Figure S1: (a) Transformation to thin Fresnel lens from conventional bulky lens.   (b) Front
view of Fresnel lens.

Table S1: Shows detail specification of Fresnel lens.

Appearance	Square
Size	350 X 350 mm
Thickness	3mm
Material	PMMA
Focal length	370 mm
Concentrated multiple	1000 times
Magnification times	4-5 times
Optical transmittance	92%

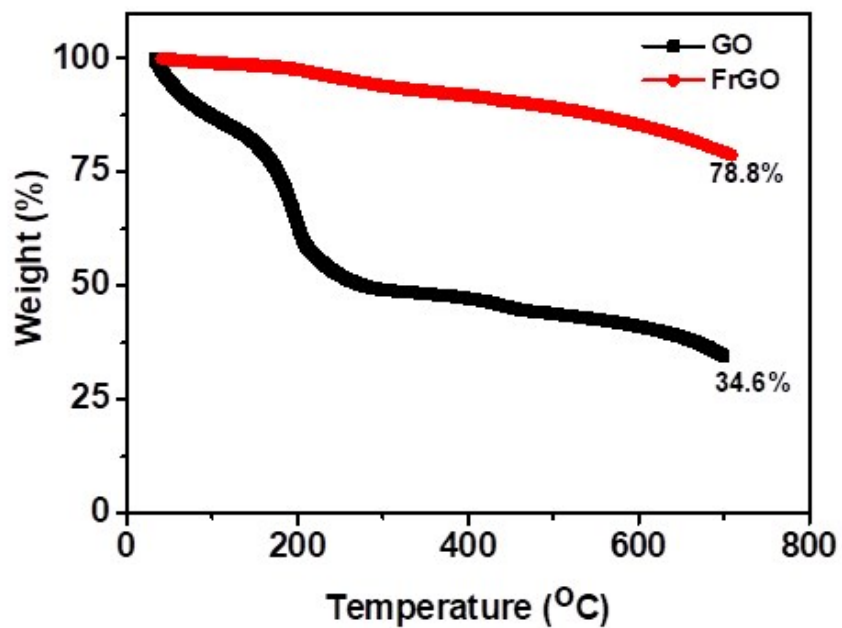S4 Thermogravimetric Analysis

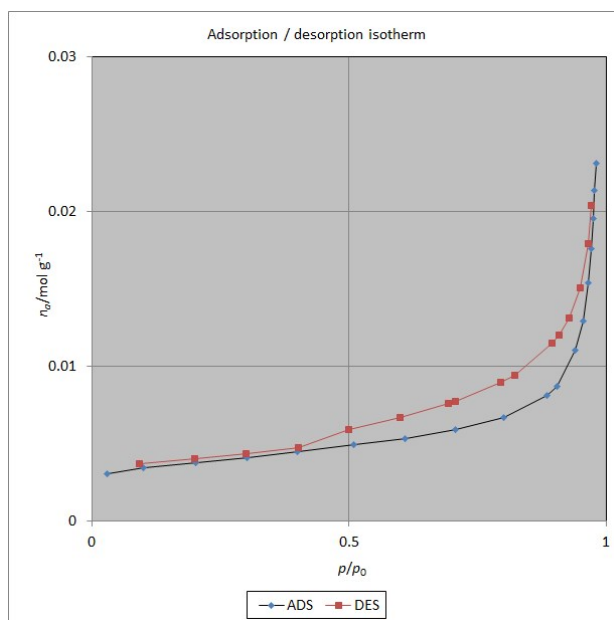Figure S2: TGA curves of GO and FrGO

S5: Surface area data

Figure S3: Adsorption isotherm of FRGO

Table 1: BET Surface area, pore volume, pore diameter of FrGO

Starting point			1	
End point			2	
Slore			0.014092	
Intercept			0.000028145	
Correlation coefficient			1	
Vm			70.822	$[cm^3(STP)\ g^{-1}]$
$a_{s,BET}$			308.25	$[m^2\ g^{-1}]$
C			501.69	
Total pore volume(p/p_0=0.980)			0.8017	$[cm^3\ g^{-1}]$
Average pore diameter			10.403	[nm]

S6: Optimization of potential window in the aqueous electrolyte.
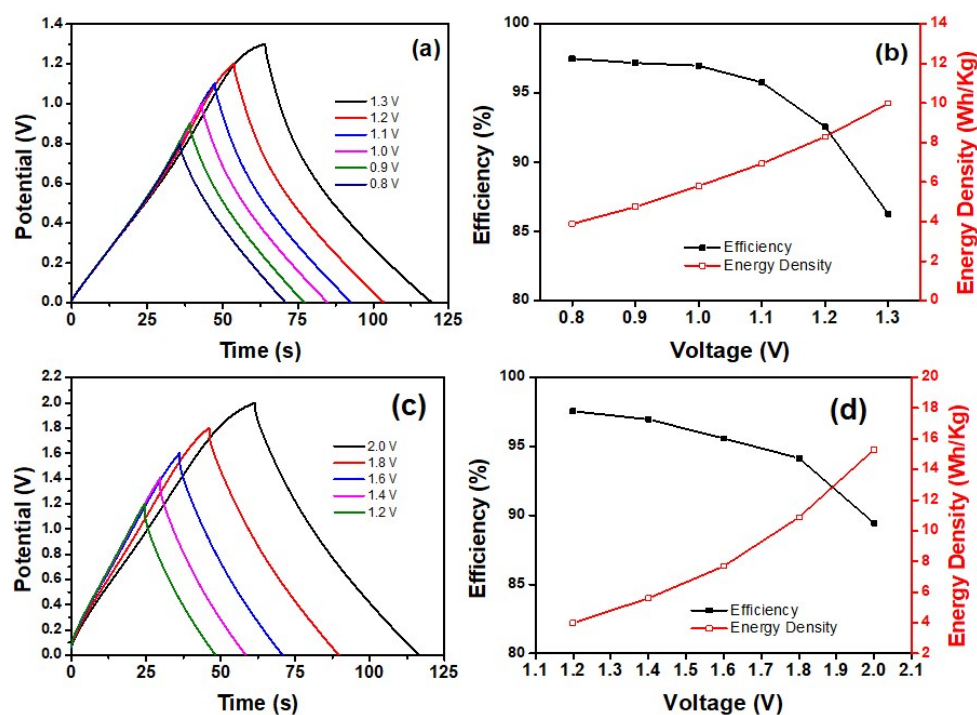

Figure S4: (a &c) Charge discharge curves at varying voltages in KOH and Na_2SO_4 electrolytes; (b & d) variation of coulombic efficiency and energy density in KOH and Na_2SO_4 electrolytes.

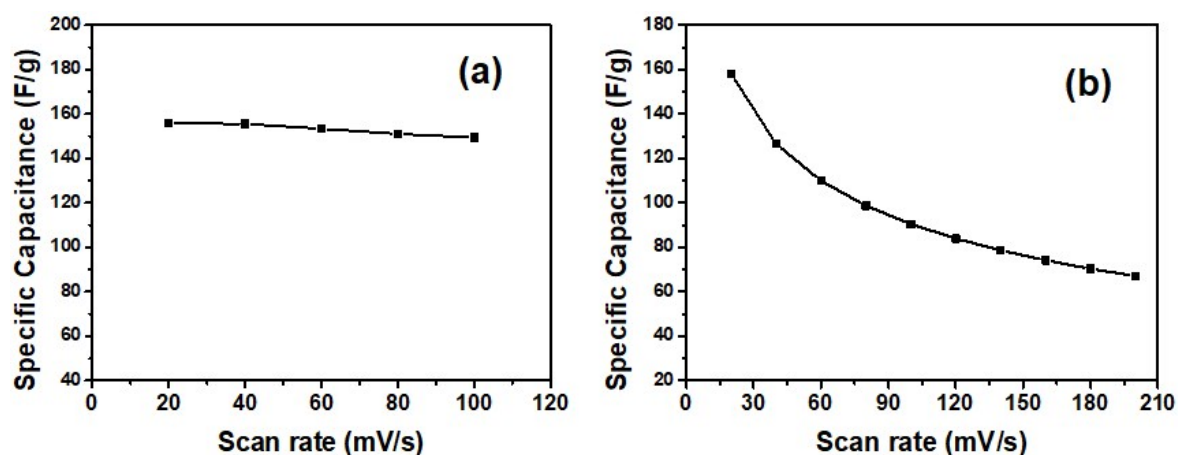## S6: Variation of specific capacitance with scan rate

Figure S5: Variation of specific capacitance with scan rate o (a)KOH and (b) EMIMBF$_4$ electrolytes.

References:

[1] D. Krishnan, F. Kim, J. Luo, R. Cruz-Silva, L.J. Cote, H.D. Jang, J. Huang, Energetic graphene oxide: challenges and opportunities, Nano today 7(2) (2012) 137-152.

[2] A. Alazmi, S. Rasul, S.P. Patole, P.M. Costa, Comparative study of synthesis and reduction methods for graphene oxide, Polyhedron 116(2016) (2016) 153-161.

[3] S. Thakur, N. Karak, Alternative methods and nature-based reagents for the reduction of graphene oxide: A review, Carbon 94(2015) (2015) 224-242.

[4] K. De Silva, H.-H. Huang, R. Joshi, M. Yoshimura, Chemical reduction of graphene oxide using green reductants, Carbon 119(2017) (2017) 190-199.

[5] Y. Qiu, F. Guo, R. Hurt, I. Külaots, Explosive thermal reduction of graphene oxide-based materials: mechanism and safety implications, Carbon 72(2014) (2014) 215-223.

[6] H. Saleem, M. Haneef, H.Y. Abbasi, Synthesis route of reduced graphene oxide via thermal reduction of chemically exfoliated graphene oxide, Materials Chemistry Physics 204(2018) (2018) 1-7.

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

[8] R. Kumar, R.K. Singh, D.P. Singh, E. Joanni, R.M. Yadav, S.A. Moshkalev, Laser-assisted synthesis, reduction and micro-patterning of graphene: recent progress and applications, Coordination Chemistry Reviews 342(2017) (2017) 34-79.

[9] R. Trusovas, G. Račiukaitis, G. Niaura, J. Barkauskas, G. Valušis, R. Pauliukaite, Recent advances in laser utilization in the chemical modification of graphene oxide and its applications, Advanced Optical Materials 4(1) (2016) 37-65.

[10] Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, Y. Chen, Supercapacitor devices based on graphene materials, The Journal of Physical Chemistry C 113(30) (2009) 13103-13107.

[11] X.-Y. Peng, X.-X. Liu, D. Diamond, K.T. Lau, Synthesis of electrochemically-reduced graphene oxide film with controllable size and thickness and its use in supercapacitor, Carbon 49(11) (2011) 3488-3496.

[12] L.L. Zhang, X. Zhao, M.D. Stoller, Y. Zhu, H. Ji, S. Murali, Y. Wu, S. Perales, B. Clevenger, R.S. Ruoff, Highly conductive and porous activated reduced graphene oxide films for high-power supercapacitors, Nano letters 12(4) (2012) 1806-1812.

[13] J. Luo, H.D. Jang, J. Huang, Effect of sheet morphology on the scalability of graphene-based ultracapacitors, ACS nano 7(2) (2013) 1464-1471.

[14] Z. Niu, L. Zhang, L. Liu, B. Zhu, H. Dong, X. Chen, All-solid-state flexible ultrathin micro-supercapacitors based on graphene, Advanced Materials 25(29) (2013) 4035-4042.

[15] Y. Yoon, K. Lee, C. Baik, H. Yoo, M. Min, Y. Park, S.M. Lee, H. Lee, Anti-Solvent Derived Non-Stacked Reduced Graphene Oxide for High Performance Supercapacitors, Advanced materials 25(32) (2013) 4437-4444.

[16] D. Sun, X. Yan, J. Lang, Q. Xue, High performance supercapacitor electrode based on graphene paper via flame-induced reduction of graphene oxide paper, Journal of Power Sources 222(2013) (2013) 52-58.

[17] J. Yan, Q. Wang, T. Wei, L. Jiang, M. Zhang, X. Jing, Z. Fan, Template-assisted low temperature synthesis of functionalized graphene for ultrahigh volumetric performance supercapacitors, Acs Nano 8(5) (2014) 4720-4729.

[18] Y. Li, D. Zhao, Preparation of reduced graphite oxide with high volumetric capacitance in supercapacitors, Chemical Communications 51(26) (2015) 5598-5601.

[19] G.A. Ali, S.A. Makhlouf, M.M. Yusoff, K.F. Chong, Structural and electrochemical characteristics of graphene nanosheets as supercapacitor electrodes, Rev. Adv. Mater. Sci 41(2015) (2015) 35-43.

[20] F.T. Johra, W.-G. Jung, Hydrothermally reduced graphene oxide as a supercapacitor, Applied Surface Science 357(2015) (2015) 1911-1914.

[21] A. Ramadoss, B. Saravanakumar, S.J. Kim, Thermally reduced graphene oxide-coated fabrics for flexible supercapacitors and self-powered systems, Nano Energy 15(2015) (2015) 587-597.

[22] S. Shivakumara, B. Kishore, T.R. Penki, N. Munichandraiah, Symmetric supercapacitor based on reduced graphene oxide in non-aqueous electrolyte, ECS Electrochemistry Letters 4(8) (2015) A87-A89.

[23] D. Yang, C. Bock, Laser reduced graphene for supercapacitor applications, Journal of Power Sources 337(2017) (2017) 73-81.

[24] K. Mohanapriya, G. Ghosh, N. Jha, Solar light reduced Graphene as high energy density supercapacitor and capacitive deionization electrode, Electrochimica Acta 209(2016) (2016) 719-729.

[25] R. Kumar, E. Joanni, R.K. Singh, E.T. da Silva, R. Savu, L.T. Kubota, S.A. Moshkalev, Direct laser writing of micro-supercapacitors on thick graphite oxide films and their electrochemical properties in different liquid inorganic electrolytes, Journal of colloid interface science 507(2017) (2017) 271-278.

[26] X. Ye, Y. Zhu, Z. Tang, Z. Wan, C. Jia, In-situ chemical reduction produced graphene paper for flexible supercapacitors with impressive capacitive performance, Journal of Power Sources 360(2017) (2017) 48-58.

[27] Y. Zhu, H. Huang, W. Zhou, G. Li, X. Liang, J. Guo, S. Tang, Low temperature reduction of graphene oxide film by ammonia solution and its application for high-performance supercapacitors, Journal of Materials Science: Materials in Electronics 28(14) (2017) 10098-10105.

[28] J. Wang, R. Ran, J. Sunarso, C. Yin, H. Zou, Y. Feng, X. Li, X. Zheng, J. Yao, Nanocellulose-assisted low-temperature synthesis and supercapacitor performance of reduced graphene oxide aerogels, Journal of Power Sources 347(2017) (2017) 259-269.

[29] H. Yang, S. Kannappan, A.S. Pandian, J.-H. Jang, Y.S. Lee, W. Lu, Rapidly annealed nanoporous graphene materials for electrochemical energy storage, Journal of Materials Chemistry A 5(45) (2017) 23720-23726.

[30] F. Han, O. Qian, B. Chen, H. Tang, M. Wang, Compounds, Sugar blowing-assisted reduction and interconnection of graphene oxide into three-dimensional porous graphene, Journal of Alloys 730(2018) (2018) 386-391.

[31] V. Eswaraiah, S.S.J. Aravind, S. Ramaprabhu, Top down method for synthesis of highly conducting graphene by exfoliation of graphite oxide using focused solar radiation, Journal of Materials Chemistry 21(19) (2011) 6800-6803.

[32] N. Todorova, T. Giannakopoulou, N. Boukos, E. Vermisoglou, C. Lekakou, C. Trapalis, Self-propagating solar light reduction of graphite oxide in water, Applied Surface Science 391(2017) (2017) 601-608.

[33] N.N. Nyangiwe, M. Khenfouch, F.T. Thema, K. Nukwa, L. Kotsedi, M. Maaza, Free-green synthesis and dynamics of reduced graphene sheets via sun light irradiation, Graphene 4(03) (2015) 54.

[34] H.-B. Jiang, Y.-L. Zhang, Y. Zhang, Y. Liu, X.-Y. Fu, Y.-Q. Liu, C.-D. Wang, H.-B. Sun, Flame treatment of graphene oxides: cost-effective production of nanoporous graphene electrode for Lithium-ion batteries, Scientific Reports 5(2015) (2015) 17522.

[35] A. Hussein, S. Sarkar, B. Kim, Technology, Low Temperature Reduction of Graphene Oxide Using Hot-plate for Nanocomposites Applications, Journal of Materials Science 32(5) (2016) 411-418.

[36] F. Kim, J. Luo, R. Cruz-Silva, L.J. Cote, K. Sohn, J. Huang, Self-propagating domino-like reactions in oxidized graphite, Advanced Functional Materials 20(17) (2010) 2867-2873.

[37] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M.J.A.n. Tour, Improved synthesis of graphene oxide, 4(8) (2010) 4806-4814.

[38] J. Chen, B. Yao, C. Li, G.J.C. Shi, An improved Hummers method for eco-friendly synthesis of graphene oxide, 64 (2013) 225-229.