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Structural evolution during annealing of thermally reduced graphene nanosheets for application in supercapacitors

Cheng-Meng Chen ^{a,d,*}, Qiang Zhang ^{b,*}, Mang-Guo Yang ^{a,d}, Chun-Hsien Huang ^c, Yong-Gang Yang ^a, Mao-Zhang Wang ^a

^a Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 Taoyuan South Road, Taiyuan 030001, China

^b Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

^c Department of Biomedical Engineering and Environmental Sciences, National Tsing-Hua University, Hsinchu 30013, Taiwan

^d Graduate University of the Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China

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ABSTRACT

The surface functional groups of thermally reduced graphene nanosheets (TRG) prepared by vacuum promoted thermal expansion of graphene oxide are tailored by progressive carbonization. The residual carbon ratios after annealing at various temperatures from 250 to 1000 °C increase progressively from 44.3 to 84.8%. The oxygen containing functional groups are intensively removed at higher annealing temperature. The thermally stable phenols, ethers, and carbonyls become the major components in 1000 °C annealed TRG. Though the starting material G250 owns a high specific capacitance of 170.5 F/g, the value decreases to only 47.5 F/g when the annealing temperature is increased to 1000 °C. The oxygen containing functional groups can enhance the capacitance performance of TRGs by introducing abundant pseudocapacitance active sites through reversible Faradic redox reactions. The correlation between the structural evolution and electrochemical performance of TRGs provides new insight for designing graphene based electrodes with controllable properties for advanced supercapacitors.

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1. Introduction

Supercapacitor, also called electrochemical capacitor or ultracapacitor, is a type of energy storage device that store charges at the electrode/electrolyte interface [1,2]. Compared to the battery devices, it is not limited by the electrochemical charge transfer kinetics of batteries and thus owns unique advantages in high power density (10 kW/kg), short charge/discharge duration (in seconds), and long cycle life (over a million cycles). These features have generated great interest in the applications of supercapacitors in consumer electronics, hybrid electric vehicles, and industrial power management [3]. Carbon is the electrode material most frequently used for supercapacitors [4,5]. On one hand, charge storage on carbon electrodes is predominantly capacitive in the electric doublelayer capacitor (EDLC) through physical electrostatic accumulation. On the other hand, contributions from surface functional groups can also be charged and discharged through Faradic redox reactions so as to give rise to pseudocapacitance (PC) [6].

Among various carbon allotropes, graphene, a two-dimensional single layer crystal of sp² hybridized carbon atoms, is the basic building block of various carbon materials. Owing to its unique two-dimensional structure, high electronic

^{*} Corresponding authors: Fax: +86 10 6277 2051.

E-mail addresses: ccm@sxicc.ac.cn (C.-M. Chen), zhang-qiang@mails.tsinghua.edu.cn (Q. Zhang). 0008-6223/\$ - see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.carbon.2012.03.029

conductivity, huge surface area, and good chemical stability, it has attracted tremendous attention and research interest towards electrochemical energy storage applications such as supercapacitors and Li ion batteries [7-11]. Since the thermally reduced graphene (TRG) can be reliably produced by thermal exfoliation of graphite oxide (GO), the chemical method became the strategic starting point for scale-up production of graphene [12-17]. As inherited from the precursor GO, TRG is instinctively decorated by various active sites (e.g. heteroatoms and lattice defects), which provides a fertile ground for surface chemistry of carbon. The functionality, microtexture, polarization, acid/basic as well as electronic properties of graphene can be easily tuned by adjusting the degree of thermal annealing [18]. The promising properties together with the ease of processability and functionalization make graphene an ideal candidate for developing high performance supercapacitors [19-29]. It is clear that the ultimate performance of graphene based supercapacitors will be closely linked to the physical and chemical characteristics of graphene electrodes [22-24,28]. Thus, an understanding of the structural evolution of graphene during annealing is desirable for matching chemical surface properties with supercapacitor applications, which provides further new insights into the design of advanced energy storage devices in industry.

In this contribution, the TRG was prepared by vacuum promoted thermal expansion of GO at relatively low temperatures, and the surface chemistry of which was further tailored by progressive annealing at various temperatures. An intensive investigation on the structural evolution (microtexture, pore structure, type and density of residue functionalities) of TRGs was carried out, while the electrochemical performance of which as supercapacitor electrodes was also evaluated.

2. Experimental

2.1. Preparation of TRG

The TRG was obtained by rapid heating up of GO under high vacuum [14]. GO was prepared by a modified Hummers' method [30]. As the precursor, the as-prepared GO was grounded into fine powder (~100 mesh), and air dried at 100 °C for 3.0 h. Then it was loaded into a quartz tube (Φ , 80 mm and L, 1200 mm), with one end sealed while the other end connected to a vacuum pump through a valve. The tube was pre-evacuated to pressure of less than 2.0 Pa, and then a heating schedule with a heating rate of 30 °C/min was executed. An abrupt expansion of GO was observed with mass fluffy black powder generated at about 200 °C. The above expanded GO was further annealed, and dwelled at 250, 600, 800, and 1000 °C for 20 min, respectively. Finally, a family of graphene samples with different surface functionalities were obtained, which are denoted as G250, G600, G800, and G1000, respectively. During the whole exfoliating and annealing process, a high vacuum in the quartz tube with a pressure of less than 5.0 Pa was maintained, as the vacuum pump was kept onto suck the desorbed gas out of the tube.

2.2. Sample characterization

The morphology of the samples was characterized using a JEOL JSM 7401F scanning electron microscope (SEM) operated at 2.0 kV and a JEOL JEM 2010 transmission electron microscope (TEM) operated at 200.0 kV. The samples were ultrasonically dispersed in ethanol, and a drop of the solution was deposited on a Lacey carbon film grid for TEM characterization; X-ray diffraction (XRD) measurements were performed at room temperature using specular reflection mode (Cu K_a radiation, $\lambda = 0.15406$ nm, D8 Advance, BRUKER/AXS, Germany); Laser Raman spectroscopy was performed on powder samples by using an ISA LabRam instrument equipped with an Olympus BX40 microscope. The excitation wavelength was 632.8 nm and a spectral resolution of 0.9 $\rm cm^{-1}$ was used; The isotherm of N₂ physisorption was obtained at 77 K using a Micromeritics 2375 Brunauer-Emmett-Teller (BET) apparatus, the specific surface area (SBET) was determined by the BET method, the pore size distribution was deduced from the desorption isotherm by the Barret-Joyner-Halenda (BJH) method, and the surface area of micropores (Smicro) was calculated by the t-plot approach (plot range from 3.5 nm to 5 nm); Fourier transform infrared spectroscopy (FTIR) spectrums were collected on a Thermo Nicolet IR200 spectrometer and the sample was pre-pressed with KBr into pellets before test; X-ray photoelectron spectroscopy (XPS) was performed on the Thermo VG ESCALAB250 surface analysis system with parameters: Al K_{α} = 1486.6 eV, Power = 150 W (HV = 15 kV and I = 10 mA), spot size = 500 μ m, pass energy 50.0 eV and energy step size 0.1 eV. The X-ray photoelectron spectrums were calibrated for both beam intensity and charging (reference the binding energy at 284.4 eV of C1s peak). Prior to fitting, a Shirley background was subtracted. Peak areas were normalized with theoretical cross-sections to obtain the relative surface elemental compositions; The as-obtained graphene samples were further characterized using thermal gravimetric analysis (TGA) system (STA 409 PC Luxx, Netzsch, Germany) equipped with a sweep gas mass spectroscopy appliance (ALZERS OmniStar 20, Switzerland).

2.3. Electrochemical measurements

Electrochemical properties of TRGs were measured in an aqueous system (electrolyte: 6.0 M KOH). A three-electrode system was employed in the measurements, whereas Ni foam coated with electrode materials served as the working electrode, a platinum foil electrode as the counter electrode, and a reversible hydrogen electrode (RHE) as the reference electrode. In order to prepare a working electrode, a mixture of the active material, carbon black, and poly(tetrafluoroethylene) (PTFE) with a weight ratio of 80:5:15 was ground together to form a homogeneous slurry. The slurry was squeezed into a film and then punched into pellets (area \sim 0.8 cm²). The punched pellets with a piece of nickel foam on each side were pressed under 2.5 MPa and dried overnight at 110 °C. Each electrode was quantified to contain \sim 3.5 mg active materials. The electrodes were saturated with the electrolyte by vacuum enhanced impregnation for 2.0 h prior to the electrochemical evaluation. Cyclic voltammetry (CV) curves (scan rates at 3, 10, 50, 100, 200, and 500 mV s^{-1}),

galvanostatic charging/discharging (GC) curves (current density under 1, 3, 5, 10 and 20 A g^{-1}) and electrochemical impedance spectroscopy (EIS) profiles (frequency from 200 kHz to 10 mHz) were measured with a BioLogic electrochemistry workstation. The specific capacitances (C_F , F g⁻¹) were calculated from CV curves by equation: $C_F = S_{int}/(2V_sm)$, where S_{int} (mAV) is the integrated area of CV curves, V_s (mV s⁻¹) is the sweep rate, and m (g) is the weight of active materials in the electrode. The Nyquist plots were fitted by the EC-Lab software with the equivalent circuit as $R_c + C_c/(R_i + W) + C_d$, the Randomize plus Levenberg-Marquardt method was employed for the fitting. The Ragone plot was calculated from GC results, the energy density (E, Wh kg^{-1}) was calculated by equation: $E = 1/2 * (C_F/4) * U^2$, where U is the potential window employed for GC (1.0 V in this work). While power density (P, W kg⁻¹) was calculated by: P = E/t, whereas t (s) is the current drain time of discharging.

3. Results and discussion

3.1. Structural evolution

The TRG was prepared by vacuum promoted thermal exfoliation of GO. As shown in Fig. 1a, a huge volume expansion can be observed during the transformation from GO to TRG. In a typical procedure, ~0.6 g of TRG (G250) was obtained by exfoliating 1.0 g of GO dry powder. As shown in Fig. 1b-d, GO exhibits compact bulk morphology, while G250 owns a 3D honeycomb-like nanostructure. Numerous exterior macropores can be clearly identified among the lateral edges of graphene sheets. After high temperature annealing, G1000 still maintained a honeycomb-like structure. The microstructures of individual graphene sheets were further examined by TEM. A typical waving and curving 2D structures was shown in Fig. 1e and f. However, a basal plane with a quite irregular edge is identified in G250 (Fig. 1e inset), while a more graphitic texture with a trimming edge can be found in G1000 (Fig. 1f inset).

XRD, Raman spectroscopy, and N_2 physical adsorption were employed to investigate the morphological and structural evolution from graphite to TRG. As shown in Fig. 2a, the interlayer space (d_{002}) is increased from 0.334 nm of graphite to 0.698 nm of GO due to the efficient chemical intercalation by functional groups and water. As an indicator for efficient transformation from GO to graphene, all TRG samples exhibit very weak diffraction peaks, due to the dissociation of long-range ordered stacking of GO by random interlayer expansion and exfoliation [31].

The nature of disorder in GO and TRG is further studied by Raman spectroscopy (Fig. 2b). The in-plane vibration of unmodified graphitic lattice (G band) as well as the disorder band aroused from amorphous carbon and edges (D band) are identified, respectively. The peak positions and I_D/I_G ratios as calculated from Raman spectra (Fig. 2b) are given in Table 1. Along the graphite–GO–TRG path, both the D and G band undergo significant changes upon amorphization of graphite, as amorphous carbon contains a certain fraction of sp³ carbons. Firstly, from graphite to GO, the G band broadens significantly with a blue shift to higher frequencies of peak position and an increasing in I_D/I_G ratio, for the reason that some inplane sp² carbons in graphitic domain transform into distorted sp³ carbons in amorphous domain. Thus, these amorphous domains may divide a pristine graphitic region into several isolated sp² domains and double bonds, which resonate at higher frequencies than the G band of graphite. Besides, the newly introduced amorphous domains will also cause the increase in I_D/I_G ratio [32–35]. Secondly, a gradual sharpening of G band as well as increasing of I_D/I_G ratio (1.4–1.5) are observed from GO to G1000. During annealing, the desorption of oxygen bonded saturated sp³ carbons as CO_2 and CO would generate various topological defects and vacancies in the graphene lattice, while a simultaneous "self-healing" of graphitic lattice ("re-graphitization") will take place due to the continuous deoxygenation.

The N₂ physical adsorption is carried out to investigate the pore structure of the TRGs at different annealing stages. As shown in Fig. 2c, all the isotherms exhibit a similar type III adsorption with H3 hysteresis loop in IUPAC classification, which indicates a unique adsorption behavior in the slitshaped macropores raised from aggregates of plate-like particles. The specific BET surface area (SBET), t-plot micropore surface area (Φ < 2 nm) (S_{micro}), and total pore volume (V_P) of TRGs are shown in Table 1. It is noteworthy that the S_{BET} is dramatically expanded from $46.4\,m^2\,g^{-1}$ of precursor GO to $308.8\ m^2\,g^{-1}$ of G250, and the value keeps steady around $300\ \text{m}^2\,\text{g}^{-1}$ for G600 and G800, however increases to 434.1 $m^2\,g^{-1}$ for G1000. Besides, all the TRGs afford large pore volumes (V_P) of \sim 3 mL g⁻¹, which are higher than most of the ordered porous carbon materials (usually less than 1 mL g^{-1}) [36-39]. The BJH adsorption pore size distribution of G250 and G1000 (Fig. 2d) and t-plot micro-pore data (Table 1) indicate that the surface area and pore volume are mainly contributed by the pores with larger diameters (Φ > 2 nm).

FTIR spectrum is employed to characterize the surface functionalities of graphene qualitatively. As shown in Fig. 3, GO shows a wide hydroxyl stretching vibration mode in carboxyl, phenol, and/or intercalated H_2O (v O–H) at 3400 cm⁻¹, and the C=O stretching vibration from carbonyl and carboxyl groups (v C.O) at 1710 $\rm cm^{-1}.$ The adsorption peak at 1620 $\rm cm^{-1}$ is assigned to the components from the skeletal vibrations of un-oxidized graphitic domains (δ C=C). While the peaks at 1370, 1220, and 1050 cm^{-1} are attributable to the carboxyl C–O deformation vibrations (δ O–H), epoxy and/or ether type C-O-C (v C-O-C), and alkoxy C-O stretching vibrations (v C-O), respectively [40-42]. Upon thermal reduction of GO in high vacuum at different temperatures, the oxygen-containing groups are diminishing progressively. For G250 and G600, the v O–H peak is blue shifted to 3340 cm^{-1} with a weaker intensity, while the ν C–O–C is red shifted to 1280 cm⁻¹ with a relative higher intensity.

Such phenomenon is attributed to the dehydration of some neighboring —OH species, which not only weaken the intramolecular hydrogen bonding but also introduce more thermally stable C—O—C species. The v C=O peak was significantly diminished due to the decomposing of thermally unstable –COOH species. The remained peak, up shifted to 1740 cm⁻¹, can be a trace of C=O groups in quinones, ketones, and lactones [43]. The vanishing of v C—O peak implies the removal or transformation of oxygen saturated sp³ carbon sites,

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Fig. 1 – (a) Digital images of the GO precursor (1.0 g) and resulted G250 (\sim 600 mg); SEM images of (b) GO, (c) G250, and (d) G1000; TEM images of (e) G250 and (f) G1000. Inserted figures are the high resolution TEM images of (e) G250 and (f) G1000.

whereas the remained strong δ C=C mode is ascribed to the effective repairing of conjugated C=C in sp² graphitic regions. Finally, G1000 shows a characteristic of infrared inert, due to the increase of structural symmetry by intensive deoxygenation and thermal healing of graphitic domains at higher temperature.

XPS analysis is carried out to obtain the relative abundance of each oxygen component on the surface of GO and TRGs (Fig. 4). The atomic percentage of C, O heteroatoms, as well as the C/O atomic ratio are calculated and summarized in Table 1. After thermal expansion of GO in high vacuum at 250 °C, the oxygen content significantly decreases to 10.30 at.% of G250 from 27.82 at.% of GO. As the annealing temperature increases, oxygen on the surface of TRGs are

progressively removed with a final value of only 2.94 at.% for G1000 (Table 1), indicating a high degree of carbonization. As shown in Fig. 4a and b, various C (C1–C5) and O (O1–O5) components in GO, G250 and G1000 are further determined by fitting the C1s and O1s fine scan spectra. The summary of XPS fitting results, which quantitate the relative abundance of each species, are listed in Table 2 and 3. C1 (284.4 eV), C2 (285.9 eV), C3 (287.4 eV), C4 (289.3 eV), and C5 (290.8 eV) components are assigned to C–C, C–O, C=O, C(O)O related groups and graphitic shake-up satellites, respectively. O1 (530.4 eV), O2 (531.2 eV), O3 (531.9 eV), O4 (532.8 eV) and O5 (533.4 eV) components are assigned to quinone-type, C(O)O, –C=O, –C–O, and –OH groups, respectively [35,44,45].



Fig. 2 – (a) XRD pattern and (b) Raman spectrum evolution from GO to TRG; (c) N_2 physical adsorption isotherm and (d) BJH adsorption pore size distribution of G250 and G1000.

As shown in Table 2, the amounts of C—C components are significantly increased from 33.75 at.% (GO) to 73.13 at.% (G1000), with a simultaneous enhancement in the intensity of graphitic shake-up satellites. Meanwhile, the abundance of C—O and C=O related species are correspondingly reduced. Correlated with the Raman spectra and FTIR curves, the C1s peak fitting results indicate that the oxygen heteroatoms are gradually removed from the basal plane of graphene during the thermal exfoliation and further annealing process. This will benefit the restoration of sp² conjugated carbon lattice so as to improve the electronic conductivity of final products. Moreover, the fitting results of O1s spectrum are more reliable in quantitating the relative accurate composition of different oxygen components in GO and TRGs. As shown in Table 3, the C=O components (mainly contributed by carboxyls and carbonyls) are dramatically decreased from 8.71 (GO) to 1.40 at.% (G250), while the C(O)O related components (mainly ascribed to anhydrides and lactones) are simultaneously increased from 0.66 (GO) to 1.52 at.% (G250). Thus, it is deduced that, during the vacuum promoted thermal expansion at 250 °C, a vast majority of unstable carboxylic groups in GO is either eliminated by thermal decarboxylation, or rather transformed into more thermally stable anhydrides and lactones. What worth mentioning is that, about 1.41 at.% of quinone-type oxygens are also introduced to graphene after the thermal-induced exfoliation. As some unadulterated free

Table 1 – Summary of pore structure and elemental composition of TRG.										
Sample	D band ^a (cm ⁻¹)	G band ^a (cm ⁻¹)	I_D/I_G^a	${{S_{BET}}^{b}}$ (m ² g ⁻¹)	${\stackrel{b}{\operatorname{Smicro}}}^{b}$ (m ² g ⁻¹)	V_P^b (mL g ⁻¹)	C ^c (at.%)	O ^c (at.%)	C/O atom ratio ^c	Residual carbon ^d (%)
Graphite	1348.9	1574.5	0.16	-	-	-	-	-	-	-
GO	1336.7	1588.7	0.97	46.4	-	-	72.18	27.82	2.59	44.3
G250	1331.1	1591.5	1.42	308.8	8.34	3.578	89.70	10.30	8.71	62.2
G600	1330.7	1587.9	1.47	293.1	NA	2.905	91.19	8.81	10.35	71
G800	-	-	-	302.2	NA	3.192	95.34	4.66	20.46	79.7
G1000	1331.1	1594.8	1.44	434.1	NA	3.138	97.06	2.94	33.05	84.8
a Obtained from Raman spectroscopy.										

b Calculated from N₂ physisorption isotherm.

c Quantified by XPS.

d Obtained from TGA (from room temperature to 1000 °C with rate of 10 °C/min in Ar).



Fig. 3 – The FTIR spectra of GO and TRG (G250, G600, and G1000).

radicals will generate on the edge and basal plane of graphene during the elimination of functionalities, the oxygen atoms in the circumstance are tend to adsorb on these radicals to form the carbene-type coordinate intermediates. Then the rearrangement reactions occur between the delocalized π electrons from the basal plane of graphene and these coordinate intermediates, so as to give thermodynamically stable quinones [46,47]. At the same time, a majority of C–O and O–H components are also removed through the intramolecular dehydration between hydroxylic and/or carboxylic groups. After carbonized at 1000 °C, most of the thermally unstable oxygen components in graphene have been thoroughly removed. As a result, the O–H, C–O, and C=O related functional groups, which are respectively attributed to thermally more stable isolated phenols, ethers, and carbonyls, finally become the major components in G1000.

The thermochemistry of GO and TRGs are further analyzed by the thermogravimetric analysis–mass spectrometry (TG– MS) experimental in Ar atmosphere (Fig. 5). As shown in Table 1, the residual carbon ratios after annealing at various temperatures from 250 to 1000 °C, are increased progressively from 44.3% of G250 to 84.8% of G1000, which implies the stabilization effect on graphene by thermal annealing. The sweep gases from TG are further analyzed by mass spectrometry, various fragments with m/z = 12.3 (radical C), 16.26



Fig. 4 - (a) The C1s and (b) O1s XPS fine scan spectrum of GO, G250, and G1000.

Table 2 – Fitted results (at.%) of C1s XPS spectra of TRG.								
B.E. (eV)	C1 (284.4)	C2 (285.9)	C3 (287.4)	C4 (289.3)	C5 (290.8)			
Assignment GO G250 G1000	C—C 33.75 64.98 73.13	C—O 22.57 14.82 14.19	C=O 14.70 3.81 2.07	C(O)O 1.16 4.04 4.49	Graphitic shake-up 0.00 2.26 2.60			

Table 3 – Fitted results (at.%) of O1s XPS spectra of TRG.							
B.E. (eV)	O1 (530.5)	O2 (531.2)	O3 (531.9)	O4 (532.7)	O5 (533.5)		
Assignment GO G250 G1000	Quinone 0.00 1.41 0.11	C(O)O 0.66 1.52 0.27	C=O 8.71 1.40 0.90	C—O 11.66 3.09 1.09	O—H 6.79 2.28 1.13		





(radical O), 18.16 (H₂O), 28.18 (CO) and 44.09 (CO₂) are assigned (Fig. 4b–f). From GO to G1000, all the evolved gases fragments are dramatically decreased with the blue shifts of decomposing temperature, which indicates the improved stability of graphene at higher carbonization stages.

The surface chemistry and the accompanying structural evolution of carbons have been widely investigated in the past several decades [47–49]. However, Graphene, as an allotrope of carbon with unique 2-dimensional structure, is bringing new insights towards the surface chemistry of carbon materials [18,46,50,51]. The surface properties of carbon are

primarily dependent on the maximum temperature employed in the annealing process, as different oxygen-containing functional groups exhibit distinct decomposing behavior during carbonization [52,53]. It is reported that the sequence of thermal stability for various oxygen containing groups on carbon surface and corresponding gases evolved during the decomposing are: carbonyl/quinones (CO) > lactones (CO₂) > phenols (CO) > anhydrides (CO and CO₂) > carboxylic acids (CO₂) [18,52]. Herein, according to the FTIR, XPS, and TG–MS results, several evolution pathways for surface oxygen functionalities are proposed in Fig. 6. The deoxygenation and CARBON 50 (2012) 3572-3584



Fig. 6 – Proposed pathway for transformation and evolution of oxygen containing functional groups during thermal expansion of GO into TRGs.

reduction during annealing process is roughly divided into five stages: (I) from 30 to 150 °C, the physically adsorbed and intercalated water is evaporated ("physical" water); (II) from 150 to 400 °C, the intermolecular dehydration takes place between neighboring carboxylic and/or hydroxyl groups, to generate thermally stable lactones, anhydrides, ethers, and carbonyls as well as release abundant H_2O ("chemical" water). Meanwhile, the decarboxylation of individual carboxylic groups release abundant CO_2 [49]; (III) from 400 to 600 °C, the anhydrides decompose to evolve both CO_2 and CO, while the individual phenols decompose to release CO; (IV) from 600 to 800 °C, the lactones and individual ether desorb as CO_2 and CO, respectively and (V) from 800 to 1000 °C, the most stable carbonyls and quinones will decompose to evolve CO [52].

3.2. Electrochemical performance

The TRG based supercapacitor electrodes were fabricated and characterized in a three-electrode system with 6.0 M KOH aqueous solution as the electrolyte. As indicated in Fig. 7a, the CV curves for all TRGs at a potential sweep rate of 3.0 mV s⁻¹ exhibit the prominent capacitive behaviors, as the sign of current reverse immediately upon reversal of the potential sweep. The capacitive current (i_M , A g⁻¹) drops quickly from G250 to G1000, while the CVs approach nearly ideal rectangular shape for G1000, indicating an increased proportion of EDLC within the total electrode capacitance of the electrode. The specific capacitance G_F (F g⁻¹) and C_S (F m⁻²) as calculated from CVs (Fig. 7a) and S_{BET} (Table 1) are shown in Fig. 7b, the initial C_F and C_S of G250 reach 170.5 F g⁻¹ and 0.56 F m⁻² at a slow

sweep rate of 3 mV s⁻¹. However, this value drops quickly for the further annealed TRGs. The G1000 presents a very poor capacitance ($C_F = 47.5$ F g⁻¹, $C_S = 0.11$ F m⁻²). On one hand, most of the PC is eliminated due to the intensive removal of PC-active oxygen-containing functional groups at higher temperature; On the other hand, the electronic conductivity of the electrode is significantly enhanced with the progressive re-graphitization of the carbon lattice in graphene basal plane.

In order to evaluate the fast charge/discharge abilities of the materials, the CVs at different sweep rates from 3 to 500 mV s^{-1} are examined, and the CV evolution for G250 and G1000 are shown in Fig. 7c and d, respectively. As the sweep rate increases, the CVs of G250 distort quickly to a willow-leaf-like shape with a voltage delay (ΔU) of ~ 0.2 V at 500 mV s^{-1} . This is ascribed to the relatively slow charge/discharge kinetics from redox reactions of surface functionalities compared to EDLC. Meanwhile, the CVs of G1000 retain a rectangular-like shape with much less distortion ($\Delta U \sim$ 0.06 V) at 500 mV s⁻¹, for the quick response of EDLC with a pure electrostatic character. The specific capacitance values as calculated from CVs at different sweep rates are shown in Fig. 7e. Among the TRGs, G250 exhibits the highest capacitive value within the whole range of potential sweep rate. Though the initial C_F at 3 mV s^{-1} is remarkably decreased for the higher temperature annealed TRGs, the retention of C_F at a high sweep rate of 500 mV s⁻¹ is gradually improved from 33.2% of G250 to 55.6% of G1000. With the increase of sweep rates, the EDLC becomes the primary electrochemical manner of the electrodes due to the delay of potential during



Fig. 7 – (a) Evolution of CVs at 3.0 mV s⁻¹ from G250 to G1000; CVs of (b) G250 and (c) G1000 with sweep rates from 3.0 to 500 mV s⁻¹; (d) specific capacitance C_F (F g⁻¹) and C_S (F m⁻²) for G250 to G1000 at 3.0 mV s⁻¹; (e) C_F versus sweep rates for G250 to G1000.

reversing the potential sweep, which is connected with a kinetically slow process involved during charging/discharging the PC [1].

Fig. 8a shows the GC curves at the current density of 1.0 Ag^{-1} . The C_F was calculated from the discharge curves with values of 167.3, 98.3, 49.4, and 42.6 F g⁻¹ for G250, G600, G800, and G1000, respectively, while the voltage drop (IR_{drop}) at the initiation of the discharge is 9.6, 9.9, 8.1, and 8.7 mV, respectively, suggesting a very low equivalent series resistance (ESR) in the test cell. A frequency response analysis (FRA) of the frequency range from 200 kHz to 100 mHz yields the Nyquist plot shown in Fig. 8b. An equivalent circuit model (inset of Fig. 8b) is introduced to simulate the capacitive and

resistive elements of the cells under analysis. These elements include the internal resistance of the TRG based electrode (R_i), the capacitance and resistance due to contact interface (C_c and R_c), a Warburg diffusion element attributable to the ion migration through the graphene (Z_w), and the capacitance inside the pores (C_d) [54]. The fitting results are shown in Table 4. In accordance with the micro-structural and chemical evolution of graphene, the internal resistance (R_i) of G1000 (0.89 Ω) is remarkably lower than that of G250 (1.93 Ω). This is attributed to the increased charge carrier density aroused from the sp² conjugated carbon lattice, which is significantly restored during the annealing process. Moreover, comparing with G250 ($Z_w = 1.07 \Omega \text{ s}^{-1/2}$), G1000 exhibits a slightly higher



Fig. 8 – (a) Galvanostatic charge/discharge curves and (b) Nyquist plot of G250 and G1000; Inserted figure show the enlarged Nyquist plot and equivalent circuit model.

Table 4 – Fitting results of internal components for graphene based electrodes.								
Sample	R _i (Ω)	R _c (Ω)	C _c (F/g)	W ($\Omega \text{ s}^{-1/2}$)	C _d (F/g)			
G250 G1000	1.93 0.89	0.43 0.34	0.39 0.23	1.07 1.12	135.14 34.47			

Warburg diffusion resistance ($Z_w = 1.12 \Omega s^{-1/2}$), which is due to the hamper of ion transfer between the inner channel of honeycomb and the aqueous electrolyte, as the wettability of the graphene surface is remarkably tampered after removal of most hydrophilic oxygen groups. Finally, the inner-porous capacitance of G1000 (34.5 F g⁻¹) drops to only about a quarter of the value of G250 (135.1 F g⁻¹), which suggest the crucial role of oxygen functional groups in both introducing abundant peseudocapacitance as well as improving the surface efficiency of graphene during electrochemical cycling. The introduction of pseudocapacitance from oxygen functional groups is based on a reversible Faradic redox mechanism [1,3]. The basal plane of a TRG sheet is composed of numerous sp² graphitic domains and distorted sp³ carbons decorated by various oxygen-containing functional groups [50]. The delocalized electrons within the sp² domains provide a low resistant channel for charge transfer within the electrode, while the inductive effects aroused from the oxygen atoms will cause the polarization of some C—C bonds. As a result, the reversible redox reactions are likely to take place on



Fig. 9 – Proposed reversible pseudo-capacitive reactions of various oxygen-containing functional sites with its acid-base property in the aqueous electrolyte.



Fig. 10 – Energy storage performance of TRGs: (a) Ragone plot as calculated from GC results under current density of 1, 3, 5, 10 and 20 A g^{-1} and (b) cycling performance of G250 and G1000. Inset shows the 1 and 3000 cycle CV of G250 at a scan rate of 50 mV s^{-1} in 6.0 M KOH.

these polarized sites during charging/discharging process (Fig. 9).

Comparing with basic functional groups (Fig. 9a and d), it is believed that the acidic sites (Fig. 9b and c) on carbon play a more dominant role in the alkaline KOH electrolyte. The abundant carboxylic and phenolic groups, which are usually thermally unstable, can be well maintained at a mild annealing temperature. However, as the temperature increases, these oxygen-containing functional groups will be eliminated or transferred into basic sites, which are unfavorable for the pseudo-capacitive reactions. This is the reason that the mild annealed G250, which not only holds the highest oxygen content, but also own abundant acidic sites, exhibits the best performance as supercapacitor electrode materials.

A Ragone plot of TRGs is exhibited in Fig. 10a. The energy and power densities are calculated by means of GC curves of a supercapacitor using a cell-voltage window of 1.0 V. In accordance with the capacitance performance as calculated by CV curves, G250 owns the best performance in energy storage among the TRGs based electrodes, with a maximum energy density of 11.6 Wh kg⁻¹ corresponding to power density of 250 W kg⁻¹. As the power density reaches as high as 5000 W kg⁻¹, it still holds an energy density of no less than 7.8 Wh kg⁻¹.

The cycle life of G250 and G1000 based electrode was tested by repeating CV charge/discharge process at a scan rate of 50 mV $s^{-1}\!.$ As shown in Fig. 10b, after 3000 times of cycling, the specific capacitance of G250 was reduced to 94.7% of the initial cycle, while G1000 still hold a high capacitive retention of as high as 99.5%. The disparity of cycling stability between G250 and G1000 is attributed to the difference in surface chemistry for TRGs carbonized at different stages. Comparing with G1000, G250 hold a much higher density of oxygen functional groups, especially for the unstable acidic carboxyls which may be neutralized and diminished by alkaline KOH during repeating charging/discharging cycles, so as to cause the loss of PC. Overall, comparing with the other energy storage devices which often suffer from a short cycle life due to irreversible physical and/or chemical changes; TRGs based supercapacitor is still very attractive for its prominent durability and stability.

4. Conclusions

In conclusion, thermally reduced graphene (TRG) with tailored surface chemistry was prepared by vacuum promoted thermal expansion of GO, followed by annealing at different temperatures. In one aspect, the C=O components (mainly contributed by carboxyls and carbonyls) are dramatically decreased from 8.71 at.% (GO) to only 1.40 at.% (G250), while the C(O)O related components (mainly ascribed to anhydrides and lactones) are simultaneously increased from 0.66 at.% (GO) to 1.52 at.% (G250) during annealing at 250 °C. After carbonization at 1000 °C, most oxygen components in TRG have been removed. The O-H, C-O, and C=O related functional groups, which are respectively attributed to thermally more stable isolated phenols, ethers, and carbonyls, finally become the major components in G1000. In another aspect, the desorption of oxygen bonded carbons as CO2 and CO generates large amount of topological defects and vacancies in the graphene lattice, with a simultaneous "self-healing" of graphitic lattice ("re-graphitization"). The TRGs were further fabricated into and characterized as supercapacitor electrodes; it is found that the thermal annealing induced structural evolution play a key role in determining the electrochemical performance of TRGs towards supercapacitor applications. The oxygen functional groups can significantly enhance the capacitance performance of TRGs by introducing abundant PC-active sites through reversible Faradic redox reactions. These results, which correlate the surface chemistry and structural properties of TRGs to the supercapacitor performances, provide a reliable experimental and theoretical model for the development of graphene based electrode materials with controllable properties, and will benefit the application of graphene in advanced energy storage.

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