Superior Electrochemical Performance of Graphene *via* Carboxyl Functionalization and Surfactant Intercalation

YU Jian-Hua[1,2], XU Li-Li[1], ZHU Qian-Qian[1], WANG Xiao-Xia[1], YUN Mao-Jin[3], DONG Li-Feng[1]

(1. College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China; 2. Key Laboratory of Inorganic Coating Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China; 3. College of Physics Science, Qingdao University, Qingdao 266071, China)

Abstract: Superior capacitance of carboxyl functionalized and surfactant-intercalated graphene were prepared by a relatively simple with two-step solution-based processing technique. In comparison to pristine graphene, surface carboxyl functionalization and surfactant intercalation can tailor its specific capacitance from 50 F/g to 230 F/g. Meanwhile, the modified materials retain more than 95% of their capacitance after 800 charge-discharge cycles, demonstrating good cyclic stability. Surfactant itself cannot improve the performance of pristine graphene as graphene intercalated with surfactant has a specific capacitance of 45 F/g, however, carboxyl groups can dramatically enhance specific capacitance to 130 F/g. The excellent performance of functionalized graphene emphasizes the importance of controlling its surface chemistry.

Key words: graphene; functionalization; electrochemical performance

Supercapacitors, which are also called electrochemical capacitors (ECs) or ultracapacitors, have attracted much attention in recent years because of their pulse power supply, long cyclic life (>100,000 cycles), simple operational mechanism, and high dynamics of charge propagation[1]. Furthermore, in comparison with batteries, ECs usually have much higher rate capabilities suitable for special requirements in electronics, AC-line filtering, aircraft, energy storage devices, uninterrupted or emergency power supplies, and electric vehicles[2]. A unit cell of an electrical double-layer capacitor (EDLC) displays the characteristics of a double-layer capacitor at the electrode/electrolyte interface, where electric charges are accumulated on the electrode surfaces and ions of opposite charge are arranged in the electrolyte side[3]. In order to improve the performance of supercapacitors, most research is focused on using innovative electrode materials, appropriate electrolytes, and tuning electrode/electrolyte interface properties.

Graphene, the two-dimensional (2D) unit of three-dimensional (3D) bulk material graphite, has received significant attention due to its extraordinary properties[4-5]. It has captured the imagination of engineers for a variety of electronics, optical, sensing, microfluidics, manufacturing, and clean energy device applications[6-7]. In this study, a Wurtz-type reductive coupling (WRC) reaction was utilized as a bottom-up method for rapid preparation of high-quality pristine graphene, and the samples obtained were labeled as PG[8]. However, the availability of as-prepared graphene is confined to high cohesive van der Waals energy (5.9 kJ/mol carbon)[9] adhering graphitic sheets to one another. Thus, pristine graphene-based materials actually exhibit unsatisfactory capacitance because of inevitable aggregation of graphene sheets. The oxidation chemistry of graphene is similar to that used to functionalize single-walled carbon nanotubes (SWCNTs)[10], which yields a variety of oxygen functionalities (–OH, –O–, and –COOH), primarily at "defect" sites on SWCNT ends. These surface functionalities of graphene can inhibit graphene sheets from aggregation and thereby, improve their electrochemical properties. Pristine graphene has tiny amount of oxygen functionalities on their surface. Surfactant intercalation can inhibit graphene sheet aggregation, enhance surface wettability, and thus improve their specific capacitance. Lomeda, *et al*[11] employed aryl diazonium salts to enhance the solubility of graphene

nanosheets in organic solvents. Zhang, *et al*[12] used different surfactants to improve electrochemical performance of chemically reduced graphene oxide, and reported that surfactants were connected to graphene by oxygen functionalities. Herein, we firstly functionalized the surface of graphene by nitric acid treatment and then used surfactant to stabilize functionalized graphene, and the samples obtained were labeled as PGC and PGCS, respectively. In order to distinguish effects of carboxyl functionalization and surfactant intercalation, only surfactant intercalation procedure was conducted on some samples, and they were labeled as PGS.

1   Experimental

1.1   Preparation of Graphene-based materials (PG, PGS, PGC and PGCS)

Pristine graphene (PG) was synthesized by a solvothermal method[8]. For the synthesis of carboxyl-functionalized graphene, 80 mg of graphene was dispersed in 50 mL of nitric acid solution (68%). The solution was then sonicated for 30 min and refluxed at 90℃ for 16 h. The obtained sample (labeled as PGC) was washed completely with distilled water and dried in a vacuum at 60℃ for 12 h. For the preparation of surfactant-intercalated graphene (labeled as PGCS), 25 mL of PGC solution (2 mg/mL) and 25 mL of surfactant solution (SDBS: sodium dodecyl benzenesulfonate, 23 mg/mL) were added to a 500 mL flask. The mixture was stirred at room temperature for 3 d, and then washed completely with distilled water. For comparison, the same intercalation procedure was also conducted on pristine graphene, and the samples obtained were labeled as PGS.

1.2   Characterization

Fourier-transformed infrared spectra (FTIR, Nicolet 510P) were measured using pressed KBr pellets. Brunauer-Emmet-Teller (BET) specific surface area was determined from N_2 adsorption by using a Micromeritics ASAP 2020 (USA) analyzer at liquid nitrogen temperature.

1.3   Electrochemical measurement

The electrochemical measurements were carried out on a conventional three electrode cell setup. The working electrode was prepared by casting a Nafion-coated sample onto a glassy carbon electrode having a diameter of 5 mm. Typically, 10 mg of active material was dispersed in a 2 mL ethanol solution by sonication for 1 h. Then, 3 μL of the solution (The mass of active material deposited is about to 15 μg) was dropped onto the glassy carbon electrode and dried in air; subsequently, 7 μL of Nafion solution was dropped onto the glassy carbon electrode and dried in air

prior to the electrochemical test. A platinum wire served as the counter electrode, Ag/AgCl with saturated KCl solution was the reference electrode, and a 1.0 mol/L H_2SO_4 solution served as the electrolyte. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge–discharge (GCD) were performed on a CHI760D electrochemical workstation (CH Instruments). The potential range for CV and GCD was from 0 V to 1.0 V. The frequency for the EIS tests ranged from 100 kHz to 1 Hz, and the applied amplitude was 5 mV.

2   Results and discussion

FTIR spectroscopy was used to characterize surface functionalization of pristine graphene. As shown in Fig. 1, the FTIR spectrum of PG exhibits representative peaks at 3439, 1629, and 1121 cm^{-1} corresponding to O–H stretch, C=O stretch of the –COOH, and epoxy C–O stretch, respectively. After nitric acid treatment, the FTIR spectrum of PGC demonstrates three broad peaks at 3446, 1633, and 1175 cm^{-1} corresponding to O–H stretch, C=O stretch of the –COOH, and epoxy C–O stretch, respectively, which is consistent with previous reports[13-14]. In comparison to PG, the C=O absorption is enhanced, an observation that confirms the surface oxidation of PG *via* acid treatment. The linkage of SDBS to PG surfaces modifies the C=O stretching of the –COOH, in which the absorption band is blue shifted to 1634 cm^{-1} from 1629 cm^{-1} for the PG. This shift arises from the weaker π–π and hydrophobic interactions between carboxyl and SDBS functional groups. The linkage of SDBS to PGC modifies the O–H stretch and C=O stretching of the –COOH, in which the absorption band is red shifted to 3435 cm^{-1} from 3446 cm^{-1} and to 1625 cm^{-1} from 1633 cm^{-1} for PGC. This shift arises from the hydrogen bonding and π–π interaction between carboxyl and SDBS functional groups.
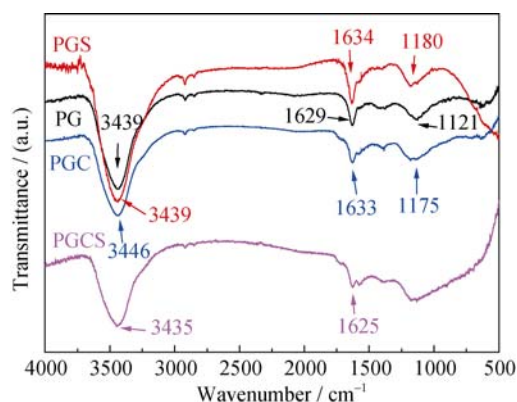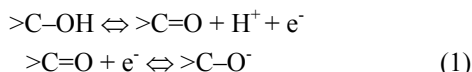

Fig. 1   FTIR spectra of various graphene-based samples (PG, PGS, PGC, and PGCS)

The N$_2$ adsorption-desorption isotherms and the pore size distribution of samples are shown in Fig. 2. Nitrogen adsorption isotherms of all graphene-based composites exhibit a typical type-I curve at low relative pressure and a hysteresis loop at relative pressure from 0.4, indicating the presence of microporosity and mesoporosity[15]. The BET surface areas, pore volumes, and average pore sizes of all samples are shown in Table 1. After surface carboxyl functionalization, the BET surface areas and pore volumes of the obtained PGC and PGCS displayed obvious increases. In contrast, after surfactant intercalation, the BET surface areas and pore volumes of the obtained PGS and PGCS decreased compared with PG and PGC.

Figure 3(a) displays CV curves of PG, PGS, PGC, and PGCS. At a scan rate of 50 mV/s, curves of both PG and PGS show a clear capacitive behavior with a rectangle-like CV curve, while Faradic peaks are observed at 0.4 V of anodic scan and 0.35 V of cathodic scan in curves of PGC and PGCS. The redox peaks on the CV plots can be ascribed to oxygenated groups attached to the surface of graphene, such as –COOH[16-17]. The redox reaction (Faradic process) can be considered as below:

$$>C–OH \Leftrightarrow >C=O + H^+ + e^-$$
$$>C=O + e^- \Leftrightarrow >C–O^- \qquad (1)$$

Obviously, PGCS exhibits the largest capacity; whereas, PGS demonstrates only a minimal capacitance due to the decrease in surface area (poorer than pristine graphene material). The representative galvanostatic charge/discharge plots in Fig. 3(b) have consistent outcomes. The average specific capacitance was estimated from the discharge slope according to the following equation:

$$C = I \Delta t / (\Delta V \times m) \qquad (2)$$

Where C is specific capacitance, I is the current loading (A), Δt is the discharge time (s), ΔV is the potential change during discharge process, and m is the mass of active material in a single electrode (g). The specific capacitances of PG, PGS, PGC, and PGCS are 50, 45, 130, and 230 F/g, respectively, at a current density of 1 A/g. Carboxyl functionalized graphene (PGC) and surfactant-intercalated graphene (PGCS) also have a little increase of double-layer capacitance, which can also be calculated from Fig. 3(a). The capacitance of carbon-based electrochemical supercapacitors depends on two kinds of accumulated energy: the electrostatic attraction in electrical double-layer capacitors (EDLCs) and Faradic reactions induced pseudocapacitance. The much higher specific capacitance of PGC (130 F/g) compared with PG (50 F/g) mainly emanates from oxygenated groups attached to the surface of graphene generated by nitric acid treatment. SDBS is combined on graphene sheets through oxygenated groups and defects accrued on the surface of graphene. Surfactant cannot directly improve the capacitance of pristine without nitric acid treatment, and the introduction of ions decreases the capacitance of pristine graphene instead. The much higher specific capacitance of PGCS (230 F/g) compared with PGC (130 F/g) without surfactant intercalation may be ascribed to surfactants enhancing the wettability of the electrode surface in the electrolyte. We reach the conclusion that nitric acid treatment is a crucial step in whole experiments.

EIS data were analyzed using Nyquist plots, which display frequency response of electrode/electrolyte system. As shown in Fig.3c, nearly vertical Nyquist plots are observed for PG, PGS, PGC, and PGCS at low frequency, indicating a nearly ideal capacitor response. The cycle stability of PGC and PGCS electrodes was examined and the results are shown in Fig. 3(d). The capacitance decreases slightly during the first 10 cycles, yet remains constant thereafter, retaining more than 95% charge after 800 charge-discharge cycles, thus demonstrating good cyclic stability.
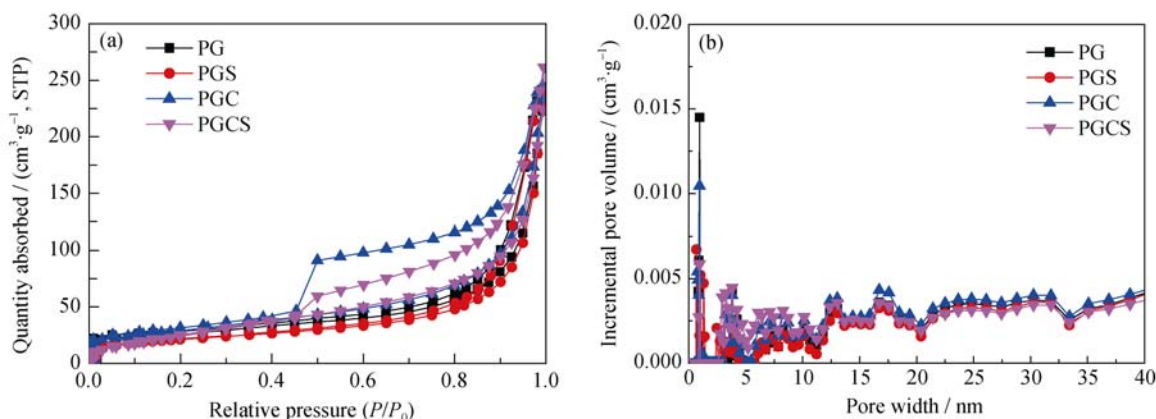

Fig. 2 The N$_2$ adsorption-desorption isotherms (a) and the pore size distribution (b) of the samples

Table 1   BET surface areas, pore volumes, and average pore sizes of obtained samples.

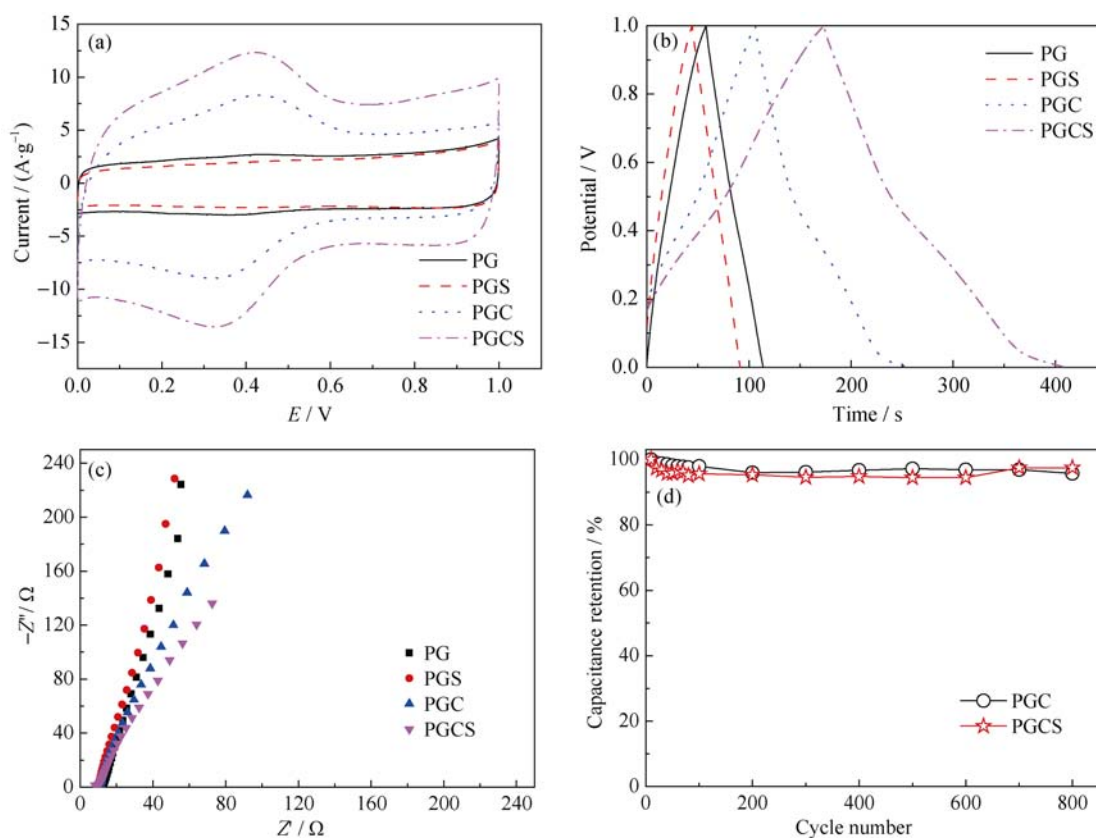| Samples	BET surface area/$(m^2 \cdot g^{-1})$	Pore volume/$(cm^3 \cdot g^{-1})$	Average pore size/nm
PG	88.7	0.37	16.8
PGS	74.6	0.37	19.8
PGC	104.6	0.38	14.5
PGCS	102.1	0.40	15.8

Fig. 3   (a) CV curves (at 50 mV/s, b) galvanostatic charge/discharge curves (at current density of 1 A/g), (c) nyquist plots of PG, PGS, PGC, and PGCS, and (d) cyclic stability of PCS and PGCS electrodes at current density of 1 A/g (1 mol/L H_2SO_4 being used as electrolyte)

3   Conclusions

In summary, a solution-based processing technique was used to prepare carboxyl functionalized, surfactant-intercalated pristine graphene. The functionalized surfactant-treated graphene demonstrates specific capacitance up to 230 F/g at 1 A/g in a 1 mol/L H_2SO_4 electrolyte with good rate performance and cycling stability. The superior capacitive performance of carboxyl functionalized, surfactant-intercalated pristine graphene demonstrates the importance of controlling the surface chemistry of graphene for supercapacitor applications.

References:

[1] CHENG Q, TANG J, MA J, *et al*. Graphene and carbon nanotube composite electrodes for supercapacitors with ultra-high energy density. *Physical Chemistry Chemical Physics*, 2011, **13(39):** 17615–17624.

[2] CHEN J, LI C, SHI G. Graphene materials for electrochemical capacitors. *The Journal of Physical Chemistry Letters*, 2013, **4:** 1244–1253.

[3] XING W, QIAO S, DING R, *et al*. Superior electric double layer capacitors using ordered mesoporous carbons. *Carbon*, 2006, **44(2):** 216–224.

[4] GEIM A K. Graphene: status and prospects. *Science*, 2009, **324:** 1530–1534.

[5] GEIM A K, NOVOSELOV K S. The rise of graphene. *Nat. Mater.*, 2007, **6:** 183–191.

[6] ZHU Y, MURALI S, STOLLER M D, *et al*. Carbon-based super-

capacitors produced by activation of graphene. *Science*, 2011, **332(6037):** 1537–1541.

[7] ZHU Y, MURALI S, CAI W, *et al.* Graphene and graphene oxide: synthesis, properties, and applications. *Advanced Materials*, 2010, **22:** 3906–3924.

[8] ZHU Q, YU J, ZHANG W, *et al.* Solvothermal synthesis of boron-doped graphene and nitrogen-doped graphene and their electrical properties. *Journal of Renewable and Sustainable Energy*, 2013, **5(2):** 021408.

[9] ZACHARIA R, ULBRICHT H,HERTEL T. Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons. *Physical Review B*, 2004, **69(15):** 155406.

[10] CHEN J, HAMON M A, HU H, *et al.* Solution properties of single-walled carbon nanotubes. *Science*, 1998, **282:** 95–98.

[11] LOMEDA J R, DOYLE C D, KOSYNKIN D V, *et al.* Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. *Journal of the American Chemical Society*, 2008, **130(48):** 16201–16206.

[12] ZHANG K, MAO L, ZHANG L L, *et al.* Surfactant-intercalated, chemically reduced graphene oxide for high performance supercapacitor electrodes. *Journal of Materials Chemistry*, 2011, **21(20):** 7302–7307.

[13] PARK S, AN J, JUNG I, *et al.* Colloidal suspensions of highly reduced graphene oxide in a wide variety of organic solvents. *Nano Letters*, 2009, **9(4):** 1593–1597.

[14] NETHRAVATHI C, RAJAMATHI M. Chemically modified graphene sheets produced by the solvothermal reduction of colloidal dispersions of graphite oxide. *Carbon*, 2008, **46(14):** 1994–1998.

[15] BOURLINOS A, STERIOTIS T A, KARAKASSIDES M, *et al.* Synthesis, characterization and gas sorption properties of a molecularly-derived graphite oxide-like foam. *Carbon*, 2007, **45(4):** 852–857.

[16] PAN H, POH C K, FENG Y P, *et al.* Supercapacitor electrodes from tubes-in-tube carbon nanostructures. *Chemistry of Materials*, 2007, **19(25):** 6120–6125.

[17] FRACKOWIAK E, METENIER K, BERTAGNA V, *et al.* Supercapacitor electrodes from multiwalled carbon nanotubes. *Applied Physics Letters*, 2000, **77(15):** 2421–2423.

羧基功能化和表面活性剂修饰对石墨烯电化学性能的影响

于建华 [1,2]，许丽丽 [1]，朱倩倩 [1]，王晓霞 [1]，云茂金 [3]，董立峰 [1]

(1. 青岛科技大学 材料科学与工程学院, 青岛 266042; 2. 中国科学院 上海硅酸盐研究所, 特种无机涂层重点实验室, 上海 201899; 3.青岛大学 物理科学学院, 青岛 266071)

摘 要: 通过简单的两步溶液法对石墨烯进行羧基接枝和表面活性剂修饰, 并研究其电化学性能。研究结果表明, 与纯石墨烯(比电容 50 F/g)相比, 表面活性剂本身并不能有效提高石墨烯的比电容(45 F/g), 羧基功能化可以将石墨烯的比电容提高至 130 F/g。而羧基功能化和表面活性剂修饰双处理工艺能够将石墨烯的比电容提高到 230 F/g, 且经 800 次充放电循环后其比电容仍然具有 95%的保持率, 表明该材料具有良好的循环稳定性。因此, 调控石墨烯的表面化学特性对提高其电化学性能具有重要的意义。

关 键 词: 石墨烯; 功能化; 电化学性能

中图分类号: TQ174 **文献标识码:** A