Siloxene-Reduced Graphene Oxide Composite Hydrogel for Supercapacitors

Qin Meng, Cuicui Du, Zhenyang Xu, Jianhang Nie, Min Hong, Xiaohua Zhang, Jinhua Chen

PII: DOI: Reference:	S1385-8947(20)30675-6 https://doi.org/10.1016/j.cej.2020.124684 CEJ 124684 <i>Chemical Engineering Journal</i>		
To appear in:			
Received Date:	18 November 2019		
Revised Date:	15 February 2020		
Accepted Date:	5 March 2020		



Please cite this article as: Q. Meng, C. Du, Z. Xu, J. Nie, M. Hong, X. Zhang, J. Chen, Siloxene-Reduced Graphene Oxide Composite Hydrogel for Supercapacitors, *Chemical Engineering Journal* (2020), doi: https://doi.org/10.1016/j.cej.2020.124684

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier B.V.

Siloxene-Reduced Graphene Oxide Composite Hydrogel for Supercapacitors

Qin Meng, Cuicui Du*, Zhenyang Xu, Jianhang Nie, Min Hong, Xiaohua Zhang* and

Jinhua Chen*

State Key Laboratory of Chemo/Biosensing and Chemometrics, Provincial Hunan Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing Carbon-dioxide Emissions, College of Chemistry and Chemical Engineering, Hunan

University, Changsha, 410082, P.R. China.

Abstract

The electrochemical properties of graphene-based supercapacitor electrode materials are closely related to their architecture and chemical nature. Herein, the siloxene-reduced graphene oxide composite hydrogel (SGH) with modified three-dimensional (3D) hierarchical architecture and increased oxygen-containing functional groups are developed via intercalating small amount of layered siloxene between the reduced graphene oxide sheets by a one-step hydrothermal process. Siloxene serves as the "spacers" to form a three-dimensional structure with graphene, resulting in increased specific surface area. More importantly, siloxene is used to modify the surface chemical nature of graphene sheets by introducing additional oxygen-containing functional groups. The abundant oxygen-containing functional groups on SGH contribute to the pseudocapacitance and improve the wettability.

^{*} Corresponding author. Tel.: +86-731-88821848

E-mail address: chenjinhua@hnu.edu.cn, ducc@hnu.edu.cn, mickyxie@hnu.edu.cn

Consequently, the proposed SGH exhibits a high specific capacitance of 520 F g⁻¹ at 1 A g⁻¹ in a three-electrode system in 1 M H₂SO₄ electrolyte, which can be maintained for 76.9% even as the discharging current density increases up to 100 A g⁻¹. Moreover, excellent stability is achieved for SGH with approximately 96.3% retention of the initial specific capacitance value after 15000 cycles at a high current density of 50 A g⁻¹. Furthermore, the assembled symmetrical supercapacitor of SGH//SGH delivers a high energy density of 24.5 Wh kg⁻¹ at the power density of 399.6 W kg⁻¹. These imply that the siloxene-reduced graphene oxide composite hydrogel may be a promising electrode material for high-performance supercapacitors.

Keywords: Siloxene; Graphene; Oxygen-containing functional groups; 3D architecture; Supercapacitors

1. Introduction

To meet the future global demands for hybrid electric vehicles and portable electronic devices, research on developing the eco-friendly energy storage devices of solar cells, lithium-ion batteries and supercapacitors etc., has been actively pursed currently [1]. Among them, supercapacitors have achieved great interest and tremendous efforts because of higher power density and longer cycling life compared to other electrochemical energy-storage devices [2-4]. As one of the key issues on the supercapacitor performance, many supercapacitor electrode materials have been developed [5,6]. In the past decades, graphene, as one of the most promising candidates, has received great attention due to excellent electronic conductivity, large theoretical specific surface area (2630 $m^2 g^{-1}$) and high chemical stability [7]. Theoretically, it has been predicted that the specific capacitance can reach up to 550 F g^{-1} for graphene [8]. Nevertheless, the actual specific capacitance for most reported graphene are limited within the scope of 100-300 F g⁻¹ [9]. This is due to the $\pi - \pi$ stacking originated from the van der Waals interactions between graphene sheets, consequently generating unsatisfactory porous structure and low specific surface area, which causes serious limitations for mass transport and thus non-satisfactory capacitor performance [10,11].

In this concern, great effort had been made to overcome these bottlenecks by inserting active materials between graphene sheets, serving as "spacers" to store charges via faradaic reactions. However, the inserted pseudocapacitive materials, such as metal oxides, metal hydroxides, and conducting polymers, will suffer from

structural change during the charging and discharging processes because of the repeated reduction-oxidation reactions, leading to poor cycling stability and rate capability of the supercapacitor electrode [12].

Another alternative approach is to construct two-dimensional/three-dimensional (2D/3D) structures based on the sole graphene, like crumpled graphene balls [13], porous graphene [14] and 3D intercalated graphene sheet-sphere microstructure [15], or to combine graphene with other 2D structures such as boron carbon nitride nanosheets [16] and MXene nanosheets [17]. The increased accessible surface area of these hybrid structures would facilitate the transportation of electrolytic ions, thus favoring the formation of double layer. Besides, the interconnected mesopores are anticipated to be generated in the graphene-based architectures in order to accelerate the mass transfer via providing transport channels for electrolyte ions [12]. For example, 3D graphene hydrogel or aerogel self-assembled and partially overlapping with flexible graphene sheets were achieved to form interconnected porous architectures, which not only prevent excessive stacking of graphene sheets, but also allow free species diffusion inside the framework [18,19].

Besides the architecture, the chemical nature is equally important to affect the supercapacitor performance of the electrode materials. In this respect, the oxygen-containing functional groups attached to graphene sheets can contribute to the pseudocapacitance and improve the wettability in aqueous electrolyte, which hence increase the charge storage capacity [20]. For example, Bai et al. [21] have studied the effect of pH-induced chemical modification on supercapacitor performance for

hydrothermally reduced graphene oxide. Krishnamoorthy et al. [12] have introduced the oxygenated functional groups on porous graphene by nitric acid treatment under solar radiation for electrochemical capacitors, resulting in a promising capacitance of 354 F g⁻¹ at 1 A g⁻¹. Ma et al. [22] have tailored the oxygenated groups of graphene hydrogels by phosphoric acid, which serves as the protective agent of phenol hydroxyls on graphene oxide during hydrothermal process, finally displaying a capacitance of 260 F g⁻¹ at 1 A g⁻¹. Therefore, graphene-based electrode materials with high specific surface area, suitable pore structure and surface functionalities are expected to surpass other carbon-based electrode materials for the energy storage devices.

On the other hand, since the advent of graphene, 2D materials have received more and more consideration for the development of next-generation energy storage devices [23,24]. Recently, siloxene, 2D layered sheets consisting of Si₆ rings connected through Si–O–Si bridges and surface-functionalized with oxygen, hydrogen, and hydroxyl groups, which can be considered as an analogue to graphene oxide, receives increasing attention in supercapacitor application [25,26]. It was reported that the chemically prepared siloxene sheets could be used as high-performance electrode materials for supercapacitors, in which the siloxene symmetric supercapacitor device reveals a specific capacitance of 2.18 mF cm⁻² (8.1 F g⁻¹) in the tetraethylammonium tetrafluoroborate electrolyte [25]. Even so, the specific capacitance is still too low to meet the practical applications. However, few studies have been conducted on the utilization of siloxene as an additive to improve

the capacitive performance of the graphene materials. This inspires us to develop siloxene-graphene hybrids as a high-performance electrode material for supercapacitors.

Herein, we synthesized 3D siloxene-reduced graphene oxide composite hydrogel (SGH) via a one-step hydrothermal method using the graphene oxide (GO) sheets and the layered siloxene as precursors. In SGH, siloxene as a planar inserted active material forms three-dimensional structures with graphene, which improves the specific surface area and promotes the structural stability, thus significantly facilitating the capacitive performance. More importantly, siloxene can also be used to modify the surface chemical nature of graphene sheets by introducing additional oxygen-containing functional groups during the hydrothermal process, leading to oxygen-rich siloxene-reduced graphene oxide composite hydrogel. Via the dehydration reaction of siloxene and GO, new oxygen-containing functional groups of C-O-Si bonds will be generated at the interfaces to contribute to the pseudocapacitance [27,28]. Meanwhile, the abundant oxygen-containing functional groups can greatly improve the wettability of SGH, which is beneficial to the charge storage behavior in aqueous electrolytes [22]. Thus, the proposed SGH electrode material is anticipated to show high specific capacitance and power characteristics with good long-term cycling stability.

2. Experimental Section

2.1. Synthesis of GO and siloxene

GO was synthesized from oxidative exfoliation of graphite powder by the

modified Hummers' method, as reported previously [29].

Siloxene was prepared according to the following procedure [25]: CaSi₂ was pretreated with KOH solution to remove the residual crystalline silicon for further use. Then, the treated CaSi₂ was incubated with the concentrated HCl solution (37 wt.%) under continuously stirring at 0 °C. The dispersions slowly changed from black to yellowish-green, demonstrating that siloxene was formed. After the reaction was completed, the product was collected by centrifugation, washed with acetone and water, and then freeze-dried to obtain the siloxene sheets.

2.2. Synthesis of 3D SGH and GH

A simple one-step hydrothermal method was used to synthesize 3D SGH. Briefly, siloxene (50 mg, 33 mg or 25 mg) and GO (100 mg) with a mass ratio of 1:n (n = 2, 3, 4) were separately dispersed into 25 mL deionized water by ultrasonication. After that, the dispersions of siloxene and GO were mixed in a beaker and magnetically stirred for 30 min. Then, the mixture was transferred into a sealed Teflon-lined stainless steel autoclave and heated at 140 °C for 12 h. After the temperature was cooled down to room temperature, the 2D nanosheets of siloxene and GO self-assembled into 3D siloxene-reduced graphene oxide composite hydrogel (SGH). Finally, the products of SGH were washed with deionized water and freeze-dried. The SGH materials synthesized by siloxene and GO with a mass ratio of 1:n (n = 2, 3, 4) were named as SGH (1:n) (n = 2, 3, 4). As a control, the reduced graphene oxide hydrogel (GH) was also synthesized by similar synthetic method without the addition

of siloxene.

2.3. Characterization

Scanning electron microscope (SEM) (Hitachi S-4800, Japan) and transmission electron microscope (TEM) (Tecnai G2 F20 S-TWIN, Holland) were employed to investigate the morphology and structure of the as-prepared materials. The crystalline structure and chemical composition were characterized by X-ray diffraction (XRD) (D/MAX-RA, Japan) and X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, USA). The functional groups of the materials were examined via FT-IR spectroscopy collected on a Thermo Scientific FT-IR spectrometer (Nicolet 6700). Raman spectra were obtained by using a Laser confocal inverted microraman spectrometer (invia-reflex, England) with a 532 nm laser. The contact angle measuring instrument (JC2000D2(RT-400)) was employed to test the contact angles. The N₂ adsorption–desorption isotherms of GH and SGH were measured using an automatic micropore and chemisorption analyzer (ASAP 2020, USA) and the pore size distributions were calculated using the Barret–Joyner-Halenda (BJH) method.

2.4. Electrochemical measurements

The electrochemical measurements in a three-electrode system were conducted in 1 M H₂SO₄ aqueous solution on an electrochemical workstation (CHI 660E, China). A platinum sheet and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. A modified glassy carbon (GC) electrode with a diameter of 5 mm was used as the working electrode. After the pre-treatment of polishing and rinsing, the GC electrode was coated with 10 µL suspension of active materials (2 mg mL⁻¹, in Nafion (5.0 wt.%): water: ethanol (v/v) = 2: 99: 99) and dried at room temperature. The cyclic voltammetry (CV) and galvanostatic charge and discharge (GCD) measurements were tested in the potential ranged from -0.2 to 0.8 V (vs. SCE) at different scan rates and current densities, respectively. Electrochemical impedance spectroscopy measurements were operated at the open circuit potential from 10^{-2} to 10^{5} Hz with a 5.0 mV amplitude. The specific capacitances of the electrode materials were calculated from the galvanostatic discharge process according to the following equation: $C = I\Delta t/(m\Delta V)$, where C is the specific capacitance (F g⁻¹), I is the discharge current (A), Δt is the discharge time (s), ΔV is the voltage change during the discharge process, and m is the mass of the active materials on the electrode (g). For the electrochemical tests in the two-electrode system, the symmetric supercapacitor was fabricated in Swagelock cells by using two identical electrodes with a glass fiber separator in 1 M H₂SO₄ solution. To prepare the electrode with a mass loading of 1 mg for active materials, the conductive carbon paper was coated by the mixed slurry of SGH (1:3) (80 wt.%), carbon black (10 wt.%) and poly(tetrauoroethylene) (10 wt.%) in dimethyl formamide and then dried under vacuum at 60 °C. The cyclic voltammetry and charging/discharging measurements were performed in the potential range of 0-1.6 V. The specific capacitance (C_s) of the samples were calculated using eq. 1 given below.

$$C_{s} = 4 (I \times \Delta t) / (m \times \Delta V)$$
⁽¹⁾

Energy density (E) and power density (P) were calculated using eqs. 2 and 3:

$$E = 1/2 C \times (\Delta V)^2$$
⁽²⁾

$$\mathbf{P} = \mathbf{E}/\Delta t \tag{3}$$

where I is the constant discharge current (A), Δt is the total discharge time (s), m is the mass of active materials on both electrodes (g), and ΔV is potential window during the discharge process (excluding the IR drop).

3. Results and discussion

As illustrated in Scheme 1, 3D SGH were facilely synthesized via one-step hydrothermal reaction between GO and siloxene. During this process, GO is transformed into reduced graphene oxide (rGO) and the siloxene sheets are inserted between the rGO sheets through π - π interaction, hydrogen bonding and C-O-Si bonding.



Scheme 1. Schematic illustration for the preparation of the 3D oxygen-rich SGH via a hydrothermal self-assembly process.

The morphologies of siloxene, GO, GH and SGH were examined by SEM. The SEM image of siloxene (Figure 1a) reveals a sheet-like structure with densely packed layers, which is one of the potential reasons of the low specific capacitance and in agreement with that reported previously [30]. The SEM image of GO (Figure 1b) indicates that GO also forms a dense agglomerate consisting of layered structure. In comparison, the GH reveal typical 3D porous networks, which are composed of crumpled and entangled lamellas as shown in Figure 1c. Furthermore, the SEM image of SGH in Figure 1d also shows a similar 3D porous architecture but with slightly flatter lamellas. This is resulted from that the layered siloxene sheets with flat surface are inserted between the rGO sheets during hydrothermal process.



Figure 1. SEM images of (a) siloxene, (b) GO, (c) GH and (d) SGH (1:3).

TEM was further applied to characterize the microstructures of the siloxene, GO, GH and SGH samples. The TEM image of siloxene in Figure 2a illustrates its flat sheet morphology identified with the SEM result (Figure 1a). Figure 2b shows a TEM image of the exfoliated graphene oxide by ultrasonic, indicating the typical attributes of crumpled ultrathin structure with some folds [31]. As expected, the TEM image illustrates that GO is exfoliated into thin layers. After hydrothermal reaction, the thin and crumpled sheets are randomly entangled to form the reduced graphene oxide hydrogel and the siloxene-reduced graphene oxide composite hydrogel as shown in Figure 2c-d, resembling rippled silk waves [32]. However, compared with GH (Figure 2c), SGH (Figure 2d) presents more interlaced edges due to the alternant stack of GO and siloxene sheets. Figure 2e-h depict the elemental mapping images of C, O and Si in SGH. It is noted that C, O and Si elements distribute uniformly, which means that the siloxene sheets are successfully incorporated into the graphene skeleton after the hydrothermal reaction. The resulted intercalated structure would prevent the stack and accumulation of rGO sheets, forming a 3D hierarchical network for fast ion and electron transfer, which is beneficial to boosting the electrochemical capacitive properties of SGH [33].

Nitrogen adsorption-desorption measurements were employed to explore the specific surface area and porous nature of GH and SGH. As shown in Figure 3a, the type IV nitrogen adsorption/desorption isotherms indicate the presence of mesopores for the samples [34]. The specific surface area of SGH (1:3) analyzed by the Brunauer–Emmett–Teller (BET) method is 395 m² g⁻¹, which is higher than that of GH (351 m² g⁻¹), indicating that the insertion of siloxene contributes to improving the specific surface area of graphene hydrogel. The pore size distribution curves of GH

and SGH (1:3) are obtained according to the BJH method (Figure 3b), revealing the existence of meso-pores and macro-pores. The high specific surface area and abundant pore channels of SGH (1:3) can facilitate the diffusion of electrolyte ions as well as enhance the electric double layer capacitance [35].



Figure 2. TEM images of (a) siloxene, (b) GO, (c) GH and (d) SGH (1:3); (e) The corresponding EDS elemental mappings of (f) carbon, (g) oxygen and (h) silicon for SGH (1:3).

The surficial functional groups of siloxene, GO, GH and SGH were further probed by Fourier transform infrared (FT-IR) spectroscopy, as shown in Figure 3c. The broad bands observed at 3417-3430 cm⁻¹ indicate the presence of hydroxyl

groups for all samples. Besides, the typical absorption bands assigned to C=O bonds and carboxylic acid at 1735 and 1626 cm⁻¹, C-OH bonds at 1405cm⁻¹, C-O-C bonds at 1219 cm⁻¹ and C-O bonds at 1053 cm⁻¹ are clearly seen in the spectrum of GO [36]. For the GH, the intensity of above-mentioned bands obviously decrease or disappear but with C=C bonds emerging at 1567 cm⁻¹, indicating the removal of oxygen-containing functional groups and the increase of graphitization degree during the hydrothermal process [37]. In the spectrum of siloxene, the absorption bands are observed at 433, 879, 1060, 1635 and 2123 cm⁻¹, respectively corresponding to the vibrations of Si-Si, Si-H, Si-O-Si, Si-OH, and OSi₂=Si-H [25]. In contrast, the FT-IR spectrum of SGH (1:3) visibly changes as follows: (1) the bands attributed to OSi₂=Si-H and Si-H groups disappear, suggesting their thermolysis during hydrothermal process [26]; (2) a new band is observed at 943 cm⁻¹, which is assigned to C-O-Si, demonstrating that the hydroxyl groups on GO and siloxene dehydrates to form new oxygen-containing functional groups at the interfaces, which achieve the reservation of oxygen [38]; (3) meanwhile, the band at 1623cm⁻¹ for SGH (1:3) weakens, further revealing that part of Si-OH groups on siloxene change to C-O-Si bonds and some residual Si-OH groups are still held after the dehydration reaction; (4) another new band can be also seen at 805 cm⁻¹ due to the formation of Si–O bond, resulting from the suffered thermal shock for the oxygen-incorporated hexagonal silicon rings. Consequently, above analysis demonstrates the successful incorporation of siloxene into the reduced graphene oxide sheets accompanied by additional oxygen-containing functional groups including the newly generated C-O-Si bonds,

Si-O bonds, and residual Si-OH bonds, resulting in the oxygen-rich graphene-based materials after hydrothermal process [27].

Generally, the introduction of oxygen-containing functional groups can improve the hydrophilicity. As shown in Figure 3d, the water contact angle obviously decreases from 53.9° for GH to 36.2° for SGH (1:3), indicating that the additional oxygen-containing functional groups greatly improve the wettability of the siloxene-reduced graphene oxide composite hydrogel. Good wettability for an electrode material is beneficial to not only the increase of effective active specific surface area for charge storage, but also the decrease of ion diffusion resistance [39,40].



Figure 3. (a) N₂ adsorption-desorption isotherms, (b) pore size distribution curves, (c) FT-IR spectra and (d) water contact angle measurements for different samples.

The structure of the as-prepared samples was further investigated by XRD. Figure S1 shows the presence of two diffraction peaks centered at 13.5° and 27° for the

siloxene sheets, respectively attributed to the (001) and (100) planes of 2D silicon sheets derived from layered calcium disilicide via a topochemical reaction [25]. The XRD patterns of GO, GH and SGH (1:n) are presented in Figure 4a. The characteristic (002) diffraction peak of GO sheets appears at $2\theta = 9.06^{\circ}$, corresponding to an interlayer distance of 9.75 Å. The significantly higher interlayer distance of GO compared to the natural graphite is ascribed to the abundant oxygen-containing functional groups intercalated into the interlayer space [41]. After hydrothermal process, the typical peak at $2\theta = 9.06^{\circ}$ completely disappears for GH and SGH (1:n), and instead broad peaks located at around $2\theta = 24.15^{\circ}$ appear, corresponding to a decreased interlayer spacing of 3.68 Å [42]. The substantial shift of (002) reflection and the decreased interlayer spacing confirm the formation of the reduced graphene oxide [43-44].

The chemical composition and structure were also characterized by Raman spectra. Figure S2 manifests the characteristic bands of siloxene sheets at 370, 495, 506, 640, 730 and 1090 cm⁻¹, respectively attributed to the vibrations of Si-Si, Si–O, Si–Si, Si–H, Si–H and Si–O bonds, confirming the presence of Si-Si, Si-O and Si-H groups [25,34,45]. In the Raman spectra of GO and GH (Figure 4b), two bands at 1347 and 1596 cm⁻¹ for D band and G band can be clearly observed, which are signatures of graphitic carbon materials, respectively. By comparison, the Raman spectra of SGH (1:n) presented in Figure 4b indicates the successful introduction of siloxene into GH, based on two additional bands observed at 554 and 1087 cm⁻¹ for SGH (1:n) corresponding to Si–O vibrations [46]. Generally, the relative intensity

ratio between D and G band (I_D/I_G) declares the amount of disorder or defects in the carbon structure [47]. The I_D/I_G values of GO, GH, SGH (1:4), SGH (1:3) and SGH (1:2) were measured to be 1.13, 1.30, 1.21, 1.20 and 1.17, respectively. Compared with GO, the enhanced I_D/I_G values of GH and SGH (1:n) indicate that more defects were generated in graphene sheets after the hydrothermal reduction process. Interestingly, the I_D/I_G ratio of SGH (1:n) decreases with the increase of siloxene. This result illustrates that the incorporation of siloxene leads to less structural defects on rGO sheets, potentially due to the formation of new oxygen-containing functional groups at the potential sites of defect by integrating with siloxene during the hydrothermal reduction process [48].

Furthermore, XPS measurements were used to investigate the oxygen contents and the surface functionalities on siloxene, GH and SGH (1:n). For siloxene, the Si 2p spectrum (Figure S3) can be deconvolved into two peaks located at 99.9 eV and 103.5 eV, respectively assigned to Si-Si and Si-O bonds. The O 1s peak at 532.5 eV in Figure S4 corresponds to Si-O bonds of siloxene, which is consistent with that shown in previous report [25]. The survey spectra (Figure 4c) of SGH (1:n) further indicate the presence of C, O and Si elements. Accordingly, Table 1 presents the atomic contents (at.%) of carbon, silicon and oxygen in SGH (1:n), along with GH and siloxene based on XPS measurements. According to the atomic ratios of different samples in Table 1, the mass content of the reduced graphene oxide in SGH (1:3) is approximately calculated to be 86%. Apparently, the oxygen contents of SGH are improved successively by introducing siloxene, resulting in an oxygen-rich graphene-based materials. To explore the valence state and composition of oxygen species, the high-resolution O 1s spectra of SGH (1:n) were further studied as contrasted with GH. As shown in Figure 4d, the O 1s spectra of SGH (1:n) can be divided into four types of oxygen-containing bonds: O-C=O bonds (536.0±0.2 eV), C-O-C, C-OH and/or C-O-Si bonds (533.2±0.2 eV), Si-O bonds (532.5±0.2 eV) and C=O bonds $(531.5\pm0.2 \text{ eV})$ [22,25,27]. Generally, the peaks centered at $533.2\pm0.2 \text{ eV}$ in O 1s spectra were assigned to C-OH and/or C-O-Si bonds due to the easy transformation of epoxy groups (C–O–C) into hydroxyl groups (C–OH) for graphene in acidic medium via ring opening reactions. With respect to that of the C=O bonds, the distinctly enhanced intensity of the signal at 533.2±0.2 eV for SGH (1:3) further confirms the formation of C-O-Si bonds at the interfaces of graphene and siloxene sheets. It can be seen that the content of the dominated C-O functional groups (C-OH/C-O-Si) is improved with the increase of siloxene in the composite, which is ascribed to the increase of interface functional groups of C-O-Si. To further confirm the state of oxygen-containing functional groups, the C 1s spectrum of SGH (1:3) is fitted and shown in Figure S5. The C-C/C=C, C-O, C=O and O-C=O groups are located at 284.8 eV, 286.1 eV, 288.5 eV and 290.4 eV, respectively [49], which is consistent with the results shown in the O 1s spectrum (Figure 4d). The resulted siloxene-reduced graphene oxide composite hydrogel with increased oxygen-containing functional groups would optimize the pseudocapacitance and wettability and thus enhance the capacitor performance [27-28,50].

siloxene.				
	C (at.%)	Si (at.%)	O (at.%)	
SGH (1:2)	72.6	4.6	22.8	
SGH (1:3)	76.0	3.5	20.5	
SGH (1:4)	78.8	2.1	19.1	
GH	84.2	_	15.8	
siloxene	-	39.4	60.6	

Table 1. The atomic contents of carbon, silicon and oxygen in SGH (1:n), GH and



Figure 4. (a) XRD patterns, (b) Raman spectra, (c) XPS surveys for different samples, and (d) high-resolution O 1s spectra for the GH and SGH (1:n).

The electrochemical performance of siloxene, GH and SGH (1:n) were tested in a three-electrode system and 1 mol L^{-1} H₂SO₄ was used as the electrolyte. Figure 5a describes the cyclic voltammetry (CV) curves of siloxene, GH and SGH (1:n) at a

scan rate of 20 mV s⁻¹. For siloxene, a small-area rectangular curve and thus very-low capacitance are observed. Except for siloxene, a rectangular-like shape with a couple of redox peaks at a voltage range of 0.2-0.4 V is exhibited for the CV curves of other samples, indicating a combination of electronic double layer capacitive and pseudocapacitive behaviors [51]. In which, the pseudocapacitances are attributed to the Faradaic redox reactions of electrochemically active oxygen-containing functional groups on the surface of the electrode materials [52]. According to above composition and structural analysis, we know that abundant oxygen-containing functional groups such as C-OH, C=O and C-O-Si exist on GH and SGH (1:n), which play an important role in contributing the pseudocapacitance by Faradic redox reactions in the aqueous electrolyte [22,27,41]. The possible oxidation/reduction reactions [22,27-28] are proposed as shown in Scheme 2. Compared with GH, SGH (1:n) demonstrate a greatly enhanced capacitance with significantly larger area of the rectangular-like CV curves. Particularly, SGH (1:3) shows an optimal capacitance. Figure 5b shows the CV curves of SGH (1:3) at different scan rates ranging from 5 to 200 mV s⁻¹. The peak current and area of the CV curves gradually increase with the increase of scan rate. Especially, the CV curves still maintain a rectangular-like shape with the symmetrical anodic and cathodic peaks even at a high scan rate of 200 mV s⁻¹, indicating outstanding electrochemical reversibility and excellent rate capability of the SGH (1:3) electrode. Based on the CV curves, the specific capacitances of SGH (1:3) are calculated to be 463, 453, 439, 419, 400 and 372 F g⁻¹ at 5, 10, 20, 50, 100 and 200 mV s⁻¹, respectively. Figure 5c depicts the galvanostatic charge/discharge

(GCD) profiles of siloxene, GH and SGH (1:n) at a current density of 1 A g⁻¹. Due to the Faradaic redox reactions of oxygen-containing functional groups, the GCD curves of GH and SGH (1:n) slightly deviate from ideal triangular shape. The SGH (1:3) exhibits a superior specific capacitance of 520 F g⁻¹, which is much higher than that of siloxene (23 F g⁻¹), GH (283 F g⁻¹), SGH (1:4) (364 F g⁻¹) and SGH (1:2) (431 F g⁻¹) under the same conditions, further indicating a satisfactory improvement of the electrochemical supercapacitor performance by incorporating siloxene into graphene hydrogel. According to the specific capacitance values of GH and siloxene, it can be inferred that the reduced graphene oxide may contribute most of capacitance of the SGH composite. Certainly, the specific capacitance of SGH (1:n) are electronic double layer capacitance coupled with pseudocapacitance. The enhanced capacitive performance can be reasonably attributed to the improved pseudocapacitance and wettability resulted from the increased oxygen-containing functional groups, as well as the modified 3D hierarchical structure with increased specific surface area. Figure 5d presents the GCD curves of SGH (1:3) at different current densities. Based on the discharge curves, the specific capacitances of SGH (1:3) were calculated to be 520, 488, 461, 445, 428, 410 and 400 F g⁻¹ at the current densities of 1, 2, 5, 10, 20, 50 and 100 A g⁻¹, respectively. For comparison, the specific capacitance values at different current densities for SGH (1:n) and GH are shown in Figure 5e. Even at a high current density of 100 A g⁻¹, SGH (1:3) still remain an impressive capacitance of 400 F g⁻¹ with 76.9% capacitance retention of the original capacitance (at 1 A g^{-1}), which are higher than that of GH (64.7%), reflecting a superior rate capability. The excellent

rate performance of SGH (1:3) are potentially related to good wettability, large specific surface area, 3D interconnected pore structure and high electronic conductivity, which are beneficial to accelerating the multidimensional electron diffusion transport and the electrolyte ion [12,22,53]. а high-rate As discharge-recharge is required in practical applications, the proposed SGH (1:3) with outstanding rate performance is promising as a high-performance electrode material for supercapacitors.

$$\sum_{c \to 0} C \longrightarrow OH \xleftarrow{-H^+ -e^-}{+H^+ +e^-} \sum_{c \to 0} C \Longrightarrow O$$

$$(1)$$

$$CO_x Si_y + H^+ + e^- \longleftrightarrow CO_{x-1} Si_y(OH) \qquad (2)$$

Scheme 2. The redox processes of oxygen-containing functional groups in H_2SO_4 electrolyte.

Electrochemical impedance spectroscopy (EIS) measurements were further employed to investigate the kinetic feature of ion and charge transport within the porous network of SGH. As shown in Figure S6, an ideal capacitive behavior of SGH (1:3) is revealed by the nearly vertical Nyquist plot in low frequency region. The Warburg region and semicircle (inset in Figure S6) in the magnified region respectively represents the ion diffusion and charge transfer resistance [54]. The large slope of the ideal straight line in the low frequency range corresponding to the Warburg impedance declares fast ion diffusion. Meanwhile, the small diameter of the semicircle indicates a low charge transfer resistance (1.81 Ω) for SGH (1:3), revealing

good charge transfer properties. Consequently, the fast ion diffusion and charge transport deliver greatly positive effect on the electrochemical capacitance properties of SGH (1:3). Despite a larger charge transfer resistance of the siloxene electrode (Figure S7), the incorporation of siloxene at a small proportion has little effect on the charge transfer properties of the graphene-based hydrogels (Figure S8).



Figure 5. (a) CV curves of different samples measured at the scan rate of 20 mV s⁻¹. (b) CV curves of SGH (1:3) at different scan rates (5-200 mV s⁻¹). (c) GCD curves of different samples at the current density of 1 A g⁻¹. (d) GCD curves of SGH (1:3) at different current densities (1-100 A g⁻¹). (e) Specific capacitances of GH and SGH

(1:n) at different current densities. (f) Cycling stability and coulombic efficiency of SGH (1:3) measured at 50 A g⁻¹.

Cycling stability is crucial for the practical applications of the electrode material in supercapacitors. Thus, we conducted the cycling life tests for SGH (1:3) by repeating the galvanostatic charge-discharge process for 15000 cycles at a current density of 50 A g⁻¹. As shown in Figure 5f, the specific capacitance remains as high as 96.3% of the initial value after 15000 cycles, delivering an admirable long-term cycling stability. On the other hand, the coulombic efficiency of SGH (1:3) is maintained at around 100% throughout the whole cycling process. The proposed siloxene-reduced graphene oxide composite hydrogel exhibits superior supercapacitance performance in three electrode system compared with other graphene-based materials as presented in Table S1.

In order to further demonstrate the superior electrochemical capacitive performance and the potential of the SGH electrode in practical energy storage applications, we assembled symmetric supercapacitor using the proposed sample of SGH (1:3) in 1 mol L⁻¹ H₂SO₄ aqueous electrolyte. Figure 6a shows the CV curves of the symmetric supercapacitor of SGH//SGH operated at 20 mV s⁻¹ in different voltage windows. No obvious increase of anodic current is observed even at 1.6 V, demonstrating the stability of the electrolyte. Besides, the CV curves at different scan rates of 5, 10, 20, 50, 100 and 200 mV s⁻¹ for the symmetric supercapacitor are presented in Figure 6b. It is noted that each CV curve displays a rectangular-like shape, further proving good capacitive behavior of the SGH electrodes. Even at the

high scan rate of 200 mV s⁻¹, there is no obvious distortion, delivering fast charge/discharge stability and excellent rate capability. By calculating from the galvanostatic discharge curves (Figure 6c), the specific capacitance of the assembled symmetric supercapacitor is 276 F g⁻¹ at the current density of 0.5 A g⁻¹. The corresponding power density is 399.6 W kg⁻¹, accompanying with an energy density of 24.5 Wh kg⁻¹. Impressively, the energy density can be still maintained at 19.4 Wh kg⁻¹ even when the power density reaches up to 1600.2 W kg⁻¹. Both of energy density and power density for the assembled SGH//SGH symmetric supercapacitor are significantly higher than that of other reported devices based on graphene materials (Figure 6d) [55-62]. On the other hand, the assembled SGH//SGH symmetric supercapacitor exhibits an excellent cycling stability with a capacitance retention of 96.5% after 10000 charge/discharge cycles at a current density of 10 A g⁻¹ (Figure S9). These results demonstrate that the siloxene-reduced graphene oxide composite hydrogel is an excellent electrode material for supercapacitors.



Figure 6. Electrochemical performance of SGH (1:3) in a two-electrode symmetrical supercapacitor (1 M H_2SO_4): (a) CV curves with different potential windows. (b) CV curves at different scan rates (5-200 mV s⁻¹). (c) Galvanostatic discharge curves at various current densities (0.5-5 A g⁻¹). (d) Ragone plot of the device in comparison with the other reported data.

4. Conclusions

The oxygen-rich siloxene-reduced graphene oxide composite hydrogel is successfully achieved via interface engineering. By intercalating small amount of siloxene between the reduced graphene oxide sheets to introduce additional oxygen-containing functional groups and to form a three-dimensional structure with graphene, the surface chemical nature and the 3D hierarchical architecture of graphene sheets are tailored. In which, the abundant oxygen-containing functional groups on SGH can contribute to the pseudocapacitance and improve the wettability,

thus enhancing the capacitive properties. On the other hand, the modified 3D hierarchical architecture with increased specific surface area can also facilitate the capacitance performance. Consequently, the electrode materials of siloxene-reduced graphene oxide composite hydrogel shows high gravimetric specific capacitance, good rate capability and excellent cycling stability. This work provides an effective method of preparing high-performance graphene-based materials for supercapacitors by tailoring the architecture and regulating the chemical nature.

Declaration of interest

The authors have no competing interests to declare.

Acknowledgments

This work was financially supported by the NSFC (21727810).

References

[1] C. Long, X. Chen, L. Jiang, L. Zhi, Z. Fan, Porous layer-stacking carbon derived from in-built template in biomass for high volumetric performance supercapacitors, Nano Energy 12 (2015) 141-151.

[2] Y. Gogotsi, P. Simon, True performance metrics in electrochemical energy storage, Science 334 (2011) 917-918.

[3] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, Supercapacitors based on flexible graphene/polyaniline nanofiber composite films, ACS nano 4 (2010) 1963-1970.

[4] Y. Xu, Z. Lin, X. Zhong, X. Huang, N. O. Weiss, Y. Huang, X. Duan, Holey graphene frameworks for highly efficient capacitive energy storage, Nat. Commun. 5 (2014) 4554.

[5] X. Li, L. Zhi, Graphene hybridization for energy storage applications, Chem. Soc.Rev. 47 (2018) 3189-3216.

[6] W. Raza, F. Ali, N. Raza, Y. Luo, K. H. Kim, J. Yang, S. Kumar, A. Mehmood, E.E. Kwon, Recent advancements in supercapacitor technology, Nano Energy 52 (2018)441-473.

[7] V. Chabot, D. Higgins, A. Yu, X. Xiao, Z. Chen, J. Zhang, A review of graphene and graphene oxide sponge: material synthesis and applications to energy and the environment, Energy Environ. Sci. 7 (2014) 1564-1596.

[8] C. Liu, Z. Yu, D. Neff, A. Zhamu, B. Z. Jang, Graphene-based supercapacitor with an ultrahigh energy density, Nano Lett. 10 (2010) 4863-4868.

[9] S. Rasul, A. Alazmi, K. Jaouen, M. N. Hedhili, P. Costa, Rational design of reduced graphene oxide for superior performance of supercapacitor electrodes, Carbon 111 (2017) 774-781.

[10] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, Graphene and graphene oxide: synthesis, properties, and applications, Adv. Mater. 22 (2010) 3906-3924.

[11] Y. Sun, Q. Wu, G. Shi, Graphene based new energy materials, Energy Environ.Sci. 4 (2011) 1113-1132.

[12] M. Krishnamoorthy, N. Jha, Oxygen-Rich Hierarchical Porous Graphene as an

Excellent Electrode for Supercapacitors, Aqueous Al-Ion Battery, and Capacitive Deionization, ACS Sustain. Chem. Eng. 7 (2019) 8475-8489.

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

[14] A. Amiri, M. Shanbedi, G. Ahmadi, H. Eshghi, S. Kazi, B. Chew, M. Savari, M.

N. M. Zubir, Mass production of highly-porous graphene for high-performance supercapacitors, Sci. Rep. 6 (2016) 32686.

[15] Z. U. Khan, T. Yan, L. Shi, D. Zhang, Improved capacitive deionization by using3D intercalated graphene sheet–sphere nanocomposite architectures, Environ. Sci.Nano 5 (2018) 980-991.

[16] S. Wang, G. Wang, T. Wu, Y. Zhang, F. Zhan, Y. Wang, J. Wang, Y. Fu, J. Qiu, BCN nanosheets templated by gC_3N_4 for high performance capacitive deionization, J. Mater. Chem. A 6 (2018) 14644-14650.

[17] H. Li, Y. Hou, F. Wang, M. R. Lohe, X. Zhuang, L. Niu, X. Feng, Flexible all-solid-state supercapacitors with high volumetric capacitances boosted by solution processable MXene and electrochemically exfoliated graphene, Adv. Energy Mater. 7 (2017) 1601847.

[18] M. Foroutan, L. Naji, Systematic evaluation of factors influencing electrochemical and morphological characteristics of free-standing 3D graphene hydrogels as electrode material for supercapacitors, Electrochim. Acta 301 (2019) 421-435.

[19] Y. Xu, X. Huang, Z. Lin, X. Zhong, Y. Huang, X. Duan, One-step strategy to

graphene/Ni(OH)₂ composite hydrogels as advanced three-dimensional supercapacitor electrode materials, Nano Res. 6 (2013) 65-76.

[20] N. Subramanian, B. Viswanathan, Nitrogen-and oxygen-containing activated carbons from sucrose for electrochemical supercapacitor applications, RSC Adv. 5 (2015) 63000-63011.

[21] Y. Bai, R. Rakhi, W. Chen, H. N. Alshareef, Effect of pH-induced chemical modification of hydrothermally reduced graphene oxide on supercapacitor performance, J. Power Sources 233 (2013) 313-319.

[22] H. Ma, Q. Zhou, M. Wu, M. Zhang, B. Yao, T. Gao, H. Wang, C. Li, D. Sui, Y. Chen, Tailoring the oxygenated groups of graphene hydrogels for high-performance supercapacitors with large areal mass loadings, J. Mater. Chem. A 6 (2018) 6587-6594.

[23] X. Zhang, L. Hou, A. Ciesielski, P. Samorì, 2D Materials Beyond Graphene for High-Performance Energy Storage Applications, Adv. Energy Mater. 6 (2016) 1600671.

[24] A. H. Khan, S. Ghosh, B. Pradhan, A. Dalui, L. K. Shrestha, S. Acharya, K.
Ariga, Two-dimensional (2D) nanomaterials towards electrochemical nanoarchitectonics in energy-related applications, Bull. Chem. Soc. Jpn. 90 (2017) 627-648.

[25] K. Krishnamoorthy, P. Pazhamalai, S. J. Kim, Two-dimensional siloxene nanosheets: novel high-performance supercapacitor electrode materials, Energy Environ. Sci. 11 (2018) 1595-1602.

[26] P. Pazhamalai, K. Krishnamoorthy, S. Sahoo, V. K. Mariappan, S. J. Kim, Understanding the Thermal Treatment Effect of Two-Dimensional Siloxene Sheets and the Origin of Superior Electrochemical Energy Storage Performances, ACS Appl. Mater. Interfaces 11 (2018) 624-633.

[27] C. H. Kim, B. H. Kim, Effects of thermal treatment on the structural and capacitive properties of polyphenylsilane-derived porous carbon nanofibers, Electrochim. Acta 117 (2014) 26-33.

[28] S. Y. Kim, K. Yang, B. H. Kim, Enhanced electrical capacitance of heteroatom-decorated nanoporous carbon nanofiber composites containing graphene, Electrochim. Acta 137 (2014) 781-788.

[29] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev,L. B. Alemany, W. Lu, J. M. Tour, Improved synthesis of graphene oxide, ACS nano4 (2010) 4806-4814.

[30] W. Zheng, P. Zhang, W. Tian, Y. Wang, Y. Zhang, J. Chen, Z. Sun, Microwave-assisted synthesis of SnO_2 -Ti₃C₂ nanocomposite for enhanced supercapacitive performance, Mater. Lett. 209 (2017) 122-125.

[31] C. Hu, F. Chen, T. Lu, C. Lian, S. Zheng, R. Zhang, Aqueous production of TiO₂–graphene nanocomposites by a combination of electrostatic attraction and hydrothermal process, Mater. Lett. 121 (2014) 209-211.

[32] W. Ai, W. Zhou, Z. Du, Y. Du, H. Zhang, X. Jia, L. Xie, M. Yi, T. Yu, W. Huang, Benzoxazole and benzimidazole heterocycle-grafted graphene for high-performance supercapacitor electrodes, J. Mater. Chem. 22 (2012) 23439-23446.

[33] 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 (2014) 4720-4729.

[34] Y. Zou, W. Zhong, S. Li, J. Luo, C. Xiong, W. Yang, Structure of functionalized nitrogen-doped graphene hydrogels derived from isomers of phenylenediamine and graphene oxide based on their high electrochemical performance, Electrochim. Acta 212 (2016) 828-838.

[35] M. M. Sk, C. Y. Yue, Layer-by-layer (LBL) assembly of graphene with p-phenylenediamine (PPD) spacer for high performance supercapacitor applications, Rsc Advances 4 (2014) 19908-19915.

[36] Y. Li, M. Zhou, Y. Wang, Q. Pan, Q. Gong, Z. Xia, Y. Li, Remarkably enhanced performances of novel polythiophene-grafting-graphene oxide composite via long alkoxy linkage for supercapacitor application, Carbon 147 (2019) 519-531.

[37] C. Yang, N. Hu, W. Wang, B. Cao, Surface-crumpled graphene hydrogels with macro-and microporous structures for ultrahigh-volumetric energy storage, J. Power Sources 399 (2018) 115-124.

[38] N. Hassan, A. Jalil, N. Khusnun, M. Ali, S. Haron, Role of reduced graphene oxide in improving interfacial charge transfer of hybridized rGO/silica/zirconia for enhanced Bisphenol A photodegradation, J. Alloy. Compd. 789 (2019) 221-230.

[39] J. Zhao, H. Lai, Z. Lyu, Y. Jiang, K. Xie, X. Wang, Q. Wu, L. Yang, Z. Jin, Y. Ma, Hydrophilic hierarchical nitrogen-doped carbon nanocages for ultrahigh supercapacitive performance, Adv. Mater. 27 (2015) 3541-3545.

[40] Z. Song, W. Li, Y. Bao, Z. Sun, L. Gao, M. H. Nawaz, D. Han, L. Niu, A new route to tailor high mass loading all-solid-state supercapacitor with ultra-high volumetric energy density, Carbon 136 (2018) 46-53.

[41] Y. Zhang, G. Wen, P. Gao, S. Bi, X. Tang, D. Wang, High-performance supercapacitor of macroscopic graphene hydrogels by partial reduction and nitrogen doping of graphene oxide, Electrochim. Acta 221 (2016) 167-176.

[42] H. Huang, G. Luo, L. Xu, C. Lei, Y. Tang, S. Tang, Y. Du, NH₃ assisted photoreduction and N-doping of graphene oxide for high performance electrode materials in supercapacitors, Nanoscale 7 (2015) 2060-2068.

[43] J. Shen, B. Yan, M. Shi, H. Ma, N. Li, M. Ye, One step hydrothermal synthesis of TiO₂-reduced graphene oxide sheets, J. Mater. Chem. 21 (2011) 3415-3421.

[44] N. A. Kumar, H. J. Choi, Y. R. Shin, D. W. Chang, L. Dai, J. B. Baek, Polyaniline-grafted reduced graphene oxide for efficient electrochemical supercapacitors, ACS nano 6 (2012) 1715-1723.

[45] C. Li, X. Kang, D. Luan, Q. Zhu, W. Zheng, Laser-irradiation-driven formation of oxygen-related defects and performance degradation in fused silica with nanosecond pulsed laser at 355 nm, Opt. Laser Technol. 111 (2019) 727-733.

[46] N. Wójcik, S. Ali, D. Möncke, N. Tagiara, E. Kamitsos, H. Segawa, M. Eriksson,B. Jonson, The influence of Be addition on the structure and thermal properties of alkali-silicate glasses, J. Non-Cryst. Solids 521 (2019) 119532.

[47] Z. J. Jiang, Z. Jiang, W. Chen, The role of holes in improving the performance of nitrogen-doped holey graphene as an active electrode material for supercapacitor and

oxygen reduction reaction, J. Power Sources 251 (2014) 55-65.

[48] B. Rajagopalan, J. S. Chung, Reduced chemically modified graphene oxide for supercapacitor electrode, Nanoscale Res. Lett. 9 (2014) 535.

[49] Y. Zou, Z. Zhang, W. Zhong, W. Yang, Hydrothermal direct synthesis of polyaniline, graphene/polyaniline and N-doped graphene/polyaniline hydrogels for high performance flexible supercapacitors, J. Mater. Chem. A 6 (2018) 9245-9256.

[50] S. Y. Kim, B. H. Kim, K. S. Yang, K. Oshida, Supercapacitive properties of porous carbon nanofibers via the electrospinning of metal alkoxide-graphene in polyacrylonitrile, Mater. Lett. 87 (2012) 157-161.

[51] Q. Zhou, M. Wu, M. Zhang, G. Xu, B. Yao, C. Li, G. Shi, Graphene-based electrochemical capacitors with integrated high-performance, Mater. today energy 6 (2017) 181-188.

[52] C. Liu, G. Han, Y. Chang, Y. Xiao, H. Zhou, G. Shi, High-performance supercapacitors based on the reduced graphene oxide hydrogels modified by trace amounts of benzenediols, Chem. Eng. J. 328 (2017) 25-34.

[53] H. Zhang, K. Wang, X. Zhang, H. Lin, X. Sun, C. Li, Y. Ma, Self-generating graphene and porous nanocarbon composites for capacitive energy storage, J. Mater. Chem. A 3 (2015) 11277-11286.

[54] Z. Bo, W. Zhu, W. Ma, Z. Wen, X. Shuai, J. Chen, J. Yan, Z. Wang, K. Cen, X. Feng, Vertically oriented graphene bridging active-layer/current-collector interface for ultrahigh rate supercapacitors, Adv. Mater. 25 (2013) 5799-5806.

[55] F. Li, X. Wang, R. Sun, A metal-free and flexible supercapacitor based on

redox-active lignosulfonate functionalized graphene hydrogels, J. Mater. Chem. A 5 (2017) 20643-20650.

[56] H. Banda, D. Aradilla, A. Benayad, Y. Chenavier, B. Daffos, L. Dubois, F. Duclairoir, One-step synthesis of highly reduced graphene hydrogels for high power supercapacitor applications, J. Power Sources 360 (2017) 538-547.

[57] N. Q. Tran, B. K. Kang, M. H. Woo, D. H. Yoon, Enrichment of Pyrrolic Nitrogen by Hole Defects in Nitrogen and Sulfur Co-Doped Graphene Hydrogel for Flexible Supercapacitors, ChemSusChem 9 (2016) 2261-2268.

[58] W. Zhang, Z. Chen, X. Guo, K. Jin, Y. Wang, L. Li, Y. Zhang, Z. Wang, L. Sun,T. Zhang, N/S co-doped three-dimensional graphene hydrogel for high performance supercapacitor, Electrochim. Acta 278 (2018) 51-60.

[59] N. An, Y. An, Z. Hu, B. Guo, Y. Yang, Z. Lei, Graphene hydrogels non-covalently functionalized with alizarin: an ideal electrode material for symmetric supercapacitors, J. Mater. Chem. A 3 (2015) 22239-22246.

[60] R. Liu, L. Wan, S. Liu, L. Pan, D. Wu, D. Zhao, An interface-induced Co-assembly approach towards ordered mesoporous carbon/graphene aerogel for high-performance supercapacitors, Adv. Funct. Mater. 25 (2015) 526-533.

[61] Y. Qing, Y. Jiang, H. Lin, L. Wang, A. Liu, Y. Cao, R. Sheng, Y. Guo, C. Fan,
S. Zhang, Boosting the supercapacitor performance of activated carbon by constructing overall conductive networks using graphene quantum dots, J. Mater.
Chem. A 7 (2019) 6021-6027.

[62] K.O. Oyedotun, T.M. Masikhwa, S. Lindberg, A. Matic, P. Johansson, N.

Manyala, Comparison of ionic liquid electrolyte to aqueous electrolytes on carbon nanofibres supercapacitor electrode derived from oxygen-functionalized graphene, Chem. Eng. J. 375 (2019) 121906.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- 1. 3D oxygen-rich graphene-based hydrogel is developed for supercapacitors.
- 2. Layered siloxene is used to tailor the architecture and chemical nature of graphene.
- 3. Superior capacitance performance with excellent cycling stability is achieved.

Graphical Abstract

