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## Tailoring the oxygenated groups of graphene hydrogels for highperformance supercapacitors with large areal mass loadings

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High-performance electrodes with high areal capacitances are highly desired for the practical applications of supercapacitors. Herein, we report such electrodes prepared from hydroxyl-rich graphene hydrogels (HRGHs). The hydroxyl groups on graphene sheets contribute pseudo-capacitance, and improve the wettability of HRGHs to aqueous electrolyte, ensuring fast ions transport within the electrodes, especially for the electrodes with high mass loadings. The supercapacitor based on mechanically compressed HRGHs shows a high gravimetric capacitance ( $260 \text{ F g}^{-1}$ ) and volumetric capacitance ( $312 \text{ F cm}^{-3}$ ) at 1 A g<sup>-1</sup>, good rate capability (~78% at 100 A g<sup>-1</sup>), and excellent cycling stability (~100% after 10,000 cycles). Moreover, an ultrahigh areal capacitance of 2675 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup> is achieved at the mass loading of 10 mg cm<sup>-2</sup>. Even at a high current density of 50 or 100 mA cm<sup>-2</sup>, the areal capacitance still retained at 2140 or 1768 mF cm<sup>-2</sup>, demonstrating the outstanding scalability of HRGH electrodes.

### Introduction

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Supercapacitors have ultrafast charge/discharge rates, high power densities, low maintenance costs, and long cycling lives.<sup>1,2</sup> Therefore, they are promising energy storage devices for electric vehicles, portable electronics, and stationary energy storage devices.<sup>3</sup> Unfortunately, the energy densities of supercapacitors are relatively low because of their surface energy storage mechanism.<sup>4,5</sup> To address this problem, extensive efforts have been devoted to increasing the gravimetric and/or volumetric capacitances of electrode materials, and substantial breakthroughs have been achieved in recent years.<sup>6-11</sup> However, the electrochemical performances of the state-of-the-art supercapacitors remain far from the requirements of practical applications. This is mainly due to the poor scalability of the electrode materials. The excellent gravimetric and/or volumetric performances of the electrodes with low mass loadings are usually lost at high mass loadings.12-14

Graphene is an excellent electrode material of supercapacitors because of its high conductivity, ultrahigh specific surface area (SSA), good flexibility, and tunable heteroatom-doping property.<sup>15–18</sup> Many graphene-based electrode materials have been explored for supercapacitors, including one-dimensional (1D) fibers, 2D films, and 3D frameworks (*e.g.*, hydrogels or aerogels).<sup>19–23</sup> Among them, the 3D graphene hydrogels are the most promising candidates to realize rapid electrons/ions transport at high areal mass loadings

interconnected porous structures.9,12 owing to their Furthermore, compressing the electrolyte saturated graphene hydrogels can largely increase their volumetric capacitances their gravimetric performances.<sup>20,24</sup> without sacrificing However, the gravimetric capacitances of graphene hydrogels are limited by their electrical double layer (EDL) charge storage mechanism; usually < 200 F g<sup>-1</sup>. Introducing redoxactive groups or blending pseudo-capacitive materials can increase the gravimetric capacitances of graphene electrodes. However, these new components usually decrease the electrochemical stability, rate-capability and coulombic efficiency of the electrodes.<sup>7,16,25</sup>

Graphene hydrogels can be easily prepared by hydrothermal treatment of graphene oxide (GO) dispersions.<sup>21,24</sup> The resulting hydrogels are made of reduced GO (rGO) sheets with residual oxygenated groups. Among these groups, the quinone-type oxygen groups are electrochemically active; thus, they can contribute the graphene electrode with pseudocapacitance.4,11,26 Therefore, increasing the content of the quinone-type oxygen groups or their derivatives is an effective route to increase the gravimetric capacitances of graphene hydrogels. In this paper, we developed an effective technique to restrict the elimination of phenol hydroxyls on GO sheets during the hydrothermal process by using phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) as a protecting agent. The phenol hydroxyls in orthopara-positions of 6-memberd carbon rings or can electrochemically convert to 1,2- or 1,4-quinones upon oxidation. Thus, the hydroxyl-rich graphene hydrogels (HRGHs) based supercapacitor showed a high gravimetric capacitance (260 F g<sup>-1</sup>) and volumetric capacitance (312 F  $cm^{-3}$ ) at 1 A  $g^{-1}$ , good rate capability (~78% at 100 A  $g^{-1}$ ), and excellent cycling stability (~100% after 10,000 cycles). Moreover, the residual hydroxyl groups greatly increased the wettability of HRGHs, enabling the HRGH electrodes to keep their performance upon increasing mass loadings. The electrode with a mass loading of 10 mg cm<sup>-2</sup> delivered an ultrahigh areal capacitance of 2675 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>. At a high current

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 $<sup>\</sup>dagger$  Electronic Supplementary Information (ESI) available: Tables S1–S4 and Fig. S1–S19. See DOI: 10.1039/x0xx00000x

density of 50 or 100 mA cm<sup>-2</sup>, the areal capacitance of this electrode still remained at a high value of 2140 or 1768 mF cm<sup>-2</sup>. Such a superior performance demonstrates the well-constructed continuous electron transfer networks and unimpeded ion diffusion channels inside of HRGH electrodes.

#### Experimental

#### **Preparation of HRGHs**

Graphene oxide (GO) was synthesized from 12,000 mesh graphite via the modified Hummers method reported previously.<sup>24</sup> HRGHs were prepared through an improved hydrothermal process by employing H<sub>3</sub>PO<sub>4</sub> as the hydroxyl protecting agent. Typically, a well dispersed GO solution (1 mL, 2 mg mL<sup>-1</sup>) containing a controlled concentration of H<sub>3</sub>PO<sub>4</sub> (0, 0.1, 0.2, or 0.4 mol  $L^{-1}$ ) was sealed in a 10-mL Teflon-lined autoclave and treated at 180 °C for 6 h to yield monolithic HRGH. After the autoclaves naturally cooled to room temperature, the as-prepared HRGHs were taken out and dialysed in deionized water for 24 h to remove the residual H<sub>3</sub>PO<sub>4</sub>. The HRGHs prepared with different concentration of H<sub>3</sub>PO<sub>4</sub> were denoted as HRGH-n (n = 0, 0.1, 0.2, and 0.4), where *n* was the concentration (mol  $L^{-1}$ ) of H<sub>3</sub>PO<sub>4</sub> in GO solution. For comparison, nitric acid-treated graphene hydrogel (NTGH) was prepared by directly immersing conventional graphene hydrogel in HNO3 aqueous solution (20 mL, 12 mol L<sup>-1</sup>) for 2 h, followed by dialysing to remove the residual HNO<sub>3</sub>.

#### Characterizations

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Scanning electron micrographs (SEM) were taken out by using a Sirion-200 field-emission scanning electron microscope at an accelerating voltage of 10.0 kV (FEI, USA). Raman spectra were performed by using a LabRAM HR Evolution (HORIBA Jobin Yvon, France) Raman microscope with a 532 nm laser. X-ray photoelectron spectroscopy (XPS) spectra were collected by using an ESCALAB 250XI photoelectron spectrometer (ThermoFisher Scientific, USA). X-ray diffraction (XRD) patterns were carried out by using a D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm, Bruker, Germany). UV-visible spectra were recorded on a Lambda 35 spectrophotometer (PerkinElmer, USA). Contact angles were tested by using an OCA20 contact angle measuring instrument (Data-Physics, Germany). Electrical conductivities were measured by using a four-point probe technique (KDY-1, Kunde Science and Technology Co. Ltd., China). The SSAs of HRGHs were analyzed by methylene blue (MB) adsorption method.9,24 In detail, a HRGH (1 mg) was put into a MB aqueous solution (5 mL, 0.2 mg mL<sup>-1</sup>) for 48 h at room temperature to achieve an adsorption equilibrium. Then, the MB solution was diluted for 50 times and its concentration was analyzed by UV-visible spectrum. The SSA of the HRGH was calculated by using the following equation: SSA  $(m^2 g^{-1}) =$  $2.54 \times 10^3 \times \Delta M_{\rm MB} / M_{\rm G}$ , where  $\Delta M_{\rm MB}$  (g) is the mass change of MB caused by adsorption, and  $M_G$  (g) is the mass of the HRGH.

#### **Electrochemical measurements**

The as-prepared HRGHs were immersed in 1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte for 12 h, and then mechanically compressed under 1 MPa to form compact HRGH electrodes. The areal mass loadings can be precisely controlled to 1, 5, or 10 mg cm<sup>-2</sup> by adjusting the thick of HRGHs. Two identical compressed HRGHs were directly used as the electrodes and assembled in a sandwich-type two-electrode configuration with

1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> as the electrolyte, filter paper as the separator and gold foils as the current collectors<sub>10</sub> A<sub>39</sub>CHI<sub>A1</sub>GODE electrochemical workstation (CH Instruments Inc. Shanghai) was used to carry out cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests. EIS analyses were performed in the frequency range of  $10^5$  to  $10^{-2}$  Hz with the amplitude of 5 mV. The gravimetric capacitance was calculated from the GCD curves using the formula:

 $C_g$  (F g<sup>-1</sup>) = 2 × I ×  $\Delta t / (m \times \Delta U)$ 

(1)

(2)

(4)

where  $C_g$  (F g<sup>-1</sup>) is the gravimetric capacitance of a single electrode, I (A) is the discharge current,  $\Delta t$  (s) is the discharge time, m (g) is the mass of a single electrode, and  $\Delta U$  (V) is the potential window during the discharge process (excluding the IR drop).

The volumetric capacitance was calculated as:

 $C_v (\mathrm{F} \mathrm{cm}^{-3}) = \rho \times C_g$ 

where  $C_{\nu}$  (F cm<sup>-3</sup>) is the volumetric capacitance of a single electrode,  $\rho$  (g cm<sup>-3</sup>) is the packing density of the electrode material.

The areal capacitance was calculated as:

 $C_a (\text{mF cm}^{-2}) = m_A \times C_g$  (3) where  $C_a (\text{mF cm}^{-2})$  is the areal capacitance of a single electrode,  $m_A (\text{mg cm}^{-2})$  is the areal mass loading of the electrode material.

The volumetric energy density of symmetric supercapacitor was calculated as:

 $E_{vol}$  (Wh L<sup>-1</sup>) = 0.125 ×  $C_v$  ×  $\Delta U^2$  / 3.6

where  $E_{vol}$  (Wh L<sup>-1</sup>) is the volumetric energy density of the symmetric supercapacitor,  $C_v$  (F cm<sup>-3</sup>) is the volumetric capacitance of a single electrode and  $\Delta U$  (V) is the potential window.

The volumetric power density of the symmetric supercapacitor was calculated as:

 $\hat{P}_{vol} \left( \hat{\mathbf{W}} \, \mathbf{L}^{-1} \right) = 3600 \times E_{vol} / \,\Delta t \tag{5}$ 

where  $P_{vol}$  (W L<sup>-1</sup>) is the volumetric power density of the supercapacitor,  $E_{vol}$  (Wh L<sup>-1</sup>) is its volumetric energy density and  $\Delta t$  (s) is the discharge time.

Additionally, the packing density of the HRGHs electrodes were calculated by the following formula:

 $\rho$  (g cm<sup>-3</sup>) =  $m/V = m/(S \times h)$  (6) where  $\rho$  (g cm<sup>-3</sup>) is the packing density of a HRGH electrode, m (g) is the mass of the electrode, V (cm<sup>3</sup>) is the volume of the electrode, S (cm<sup>2</sup>) is the area of the disc and h (cm) is the thickness of the electrode.

#### **Results and discussion**

HRGHs were prepared by hydrothermal treatment of 2 mg mL<sup>-1</sup> GO dispersions containing  $n \mod L^{-1} \operatorname{H_3PO_4}$ , and the resulting hydrogels are called HRGH-*n*. As shown in Fig. 1 and Fig. S1-4<sup> $\dagger$ </sup>, HRGH-*n* have a 3D interconnected porous structure with the pore sizes ranging from sub-micrometers to several tens of micrometers. The pores increased their sizes and structural orderliness upon increasing the concentration of H<sub>3</sub>PO<sub>4</sub> from 0 to 0.4 mol  $L^{-1}$ . This is because GO sheets are amphiphilic and their amphiphilicities can be reversibly tuned by the pH value of solution.<sup>27,28</sup> The added H<sub>3</sub>PO<sub>4</sub> restrained the ionization of the carboxyl groups on GO sheets; thus GO sheets were getting hydrophobic and tended to gather into GO aggregates (Fig. S5<sup>†</sup>). Successively, the GO aggregates were hydrothermally reduced and assembled to form HRGH-n (here n = 0.1, 0.2, and 0.4). It should be noted that the freeze-dried HRGH-n show similar X-ray diffraction (XRD) patterns with

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identical positions of (002) peak and half- peak widths (Fig. S6<sup>+</sup>), indicating that the slight aggregation of GO sheets did not



Fig. 1 a-c) Typical scanning electron microscope (SEM) images of HRGH-0 with different magnifications. d-f) Typical SEM images of HRGH-0.2 with different magnifications.

change the textures of the hydrogels. The SSAs of HRGH-*n* were measured to be 1039, 1011, 998, and 979 m<sup>2</sup> g<sup>-1</sup> for HRGH-0, HRGH-0.1, HRGH-0.2, and HRGH-0.4, respectively (Table S1<sup>†</sup>) by a standard methylene blue adsorption method (Fig. S7<sup>†</sup>).<sup>9,24</sup> This result indicates that the addition of H<sub>3</sub>PO<sub>4</sub> to GO solution induced only a small decrease in the SSAs of HRGH-*n*.

The chemical structures of HRGH-n were analysed by Raman spectroscopy. The Raman spectra of HRGH-*n* show two typical bands: D bands at  $\sim 1350$  cm<sup>-1</sup> and G bands at  $\sim 1590$ cm<sup>-1</sup> (Fig. 2a). The D band is assigned to the structural defects or partially disordered structures of graphitic domains, and the G band is related to the large graphitic domains of carbon materials.<sup>29,30</sup> The intensity ratio of D to G bands  $(I_D/I_G)$  reflects the average distance between the structural defects  $(L_D)$ . For graphene and its derivatives, the value of  $I_D/I_G$  initially increases with the increase of  $L_D$  and reaches a maximum (1 nm  $< L_D < 3$  nm, stage 2), and then gradually decreases ( $L_D > 3$  nm, stage 1).<sup>31</sup> Generally, the L<sub>D</sub>s of GO and rGO belong to the stage 2.<sup>32</sup> The  $I_D/I_G$ s of HRGH-0, HRGH-0.1, HRGH-0.2, and HRGH-0.4 were measured to be 1.11, 1.09, 1.07, and 1.04, respectively (Table S1<sup> $\dagger$ </sup>); their L<sub>D</sub>s were calculated to be 1.52, 1.50, 1.48, and 1.45 nm, correspondingly (Table S1<sup>†</sup>). The smaller L<sub>D</sub> value indicates the smaller graphitic domains and the more structural defects on rGO sheets.<sup>30</sup> Thus, HRGH-0.4 has the most structural defects among HRGH-n. This result indicates that the addition of H<sub>3</sub>PO<sub>4</sub> to GO solution resulted in more structural defects on rGO sheets, and the structural defects increased with the concentration of this acid. This conclusion was further supported by X-ray photoelectron spectral studies (XPS, Fig. 2b). The oxygen atomic contents of HRGH-n increased with the value of n, and they were measured to be 15.5%, 15.8%, 16.4%, and 16.8% for HRGH-0, HRGH-0.1, HRGH-0.2, and HRGH-0.4, respectively (Table S1<sup>†</sup>). Notably, the XPS surveys of HRGH-n do not show any signals of phosphorus element, ruling out the possibility of phosphorus-doping. Therefore, it is reasonable to conclude that the additional structural defects of HRGH-0.1, HRGH-0.2, or HRGH-0.4 compared with those of HRGH-0 are mainly originated from the increased oxygenated groups.

The O 1s XPS core level spectra of HRGH-*n* were further studied to detect the evolution of oxygenated groups. As shown



Fig. 2 a) Raman spectra, b) XPS surveys, and c) O 1s XPS core level spectra of HRGH-n.



in Fig. 2c, the O 1s XPS core level spectrum of each HRGH-n can be divided into three types of oxygenated groups: C=O groups (531.6  $\pm$  0.2 eV), C–OH and/or C–O–C groups (533.2  $\pm$ 0.2 eV) and O–C=O groups (536.0  $\pm$  0.2 eV).  $^{11,33}$  Because epoxy groups (C-O-C) of graphene are easily convered to hydroxyl groups (C-OH) in an acidic medium via ring opening reactions, the peak centered at  $533.2 \pm 0.2$  eV can be assigned only to C-OH groups. After normalizing the spectra with respect to the intensity of the C=O groups, the intesnisty of C-OH groups distinctly increased with *n* value. In the spectrum of HRGH-0.4, the signal of O-C=O groups is also slightly stronger than the bands of other HRGH-n. Therefore, the addition of H<sub>3</sub>PO<sub>4</sub> increased the content of hydroxyl groups on rGO sheets. In this case, H<sub>3</sub>PO<sub>4</sub> acted as a protecting agent to restrict the elimination of hydroxyl groups on GO sheets during the hydrothermal reduction processes (Fig. S8<sup>†</sup>).

The hydroxyl groups on rGO sheets improved the hydrophilicity of HRGH-*n* (Fig. 3). The initial water contact angle (WCA) monotonically decreased from 79.5° for freezedried HRGH-0, to 31.3° for freeze-dried HRGH-0.4 (Table S2†), indicating the residual hydroxyl groups of rGO sheets greatly improved the wettability of HRGH-*n*. This conclusion has also been confirmed by the dynamic WCA tests. Freezedried HRGH-0 can completely adsorb the water droplet within 120 s. By contrast, this time was shortened to 100, 60 or 40 s for freeze-dried HRGH-0.1, HRGH-0.2, or HRGH-0.4. An electrode material with good wettability to electrolyte not only decreases its ion diffusion resistance, but also improves the utilization of its active SSA for charge storage, especially at high areal mass loadings.<sup>2,10</sup>

The electrochemical performances of HRGH-*n* were tested in sandwich-type two-electrode systems by using 1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> as the electrolyte. The mechanically compressed HRGH-*n* were directly used as the electrodes without adding any binders or conductive additives (seeing more details in experimental section). The corresponding supercapacitors are named as HRGH-*n*-SC. The cyclic voltammogram (CV) curve of each supercapacitor shows a rectangular shape with a couple of redox waves at the voltage below 0.4 V, indicating a combination of EDL and pseudo-capacitive behaviors (Fig.

4a).<sup>24</sup> According to the CV profiles at the voltage over 0.8 V, the capacitances contributed by EDLs are nearly identical for these four supercapacitors, which is also confirmed by the tests in a neutral electrolyte (Fig. S9<sup>†</sup>). The redox waves are attributed to the reversible pseudo-capacitances of oxygenated groups.<sup>24</sup> Compared with HRGH-0-SC, the redox waves for HRGH-n-SC (n = 0.1, 0.2 or 0.4) are much stronger, and those of HRGH-0.2-SC are the strongest. Moreover, the CV curves of HRGH-0.2-SC maintain a redox wave-incorported rectangular shape even at a high scan rate of 200 mV s<sup>-1</sup> (Fig. S10<sup>+</sup>), indicating its excellent rate capability for both EDL- and pseudo-capacitances. The CV curves of HRGH-n in threeelectrode system were also tested to further detect the pseudocapacitance behaviors of the quinone-type oxygenated groups (Fig. S11<sup>†</sup>). As reported in our previous work,<sup>11</sup> the redox waves between 0.2 and 0.4 V vs. Ag/AgCl are attributed to the pseudo-capacitive behavior of quinone-type oxygenated groups. Compared with HRGH-0, the redox waves for HRGH-0.2 are much stronger. This result is coincident with that tested in twoelectrode system, further demonstrating that H<sub>3</sub>PO<sub>4</sub> acted as a protecting agent and restricted the elimination of phenol hydroxyls on GO sheets during the hydrothermal reaction. The galvanostatic charge/discharge (GCD) curves of these supercapacitors are slightly distorted from ideal triangular shapes because of the presence of pseudo-capacitances (Fig. 4b). Among them, HRGH-0.2-SC shows the longest discharge time, corresponding to the highest specific capacitance.

The gravimetric capacitances ( $C_g$ s) of the HRGH-*n*-based supercapacitors were calculated according to the GCD curves (Fig. 4c). HRGH-0.2-SC delivers a high  $C_g$  of 260 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>, which is much higher than that of HRGH-0-SC (214 F g<sup>-1</sup> at 1 A g<sup>-1</sup>). Even at a high current density of 100 A g<sup>-1</sup>, HRGH-0.2-SC also retains a  $C_g$  of 203 F g<sup>-1</sup>, with a capacitance retention over 78%, reflecting its excellent rate capability. By contrast, HRGH-0.4-SC delivers a lower  $C_g$  and a worse rate capability than those of HRGH-0.2-SC. This is mainly caused by its large charge transfer restaince (seeing electrochemical impedance spectroscopy, EIS, shown in Fig. S12†). As described above, EDL capacitances of HRGH-*n*-SCs are nearly identical, and they were calcualted to be ~145 F

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**Fig. 4** Electrochemical performances of HRGH-*n*-SCs. a) CV curves at a scan rate of 10 mV s<sup>-1</sup>. b) GCD curves at a current density of 1 A g<sup>-1</sup>. c) Plots of  $C_g$  versus current density. d)  $C_g$ s and  $C_v$ s of HRGH-*n*-SCs. e) Ragone plots of volumetric energy densities versus volumetric power densities. f) Cycling stability and coulombic efficiency of HRGH-0.2-SC at a current density of 10 A g<sup>-1</sup>.

 $g^{-1}$  (Fig. S9†). Therefore, the pseudo-capacitances of HRGH-*n*-SCs were calculated to be 67, 88, 114, and 99 F  $g^{-1}$  as n = 0, 0.1, 0.2 and 0.4, correspondingly. Combining the analyses of XPS, it is reasonable to conclude that these pseudo-capacitances are attributed to the reversible conversions between 1,2- or 1,4-phenol structures and 1,2- or 1,4-quinone structures on rGO sheets (Fig. S13†). The worsened performance of HRGH-0.4-SC is mainly due to the low conductivity of its electrode material caused by the structural defects on rGO sheets (Table S1†).

Nitric acid is an oxidizing acid; it has been often used to introduce oxygenated groups to carbon frameworks.34 Therefore, we also prepared nitric acid treated graphene hydtrogel (NTGH) for comparison. HNO3 introduced a large amount of oxygenated groups to NTGH; however, these groups are electrochemically unstable, and they can be eliminated in the first CV cycle (Fig. S14<sup>†</sup>). Moreover, HNO<sub>3</sub> etched the framework of NTGH, collapsing the porous microstructure of graphene hydrogel. As a result, the NTGH-based supercapacitor exhibited a low gravimetric capacitance (232 F  $g^{-1}$  at 1 A  $g^{-1}$ ) and inferior rate capability (~42% at 100 A  $g^{-1}$ , Fig. S15<sup>†</sup>). This result, in turn, implies the excellent electrochemical performance of HRGH-0.2-SC, and demonstrates the superiorities of the H<sub>3</sub>PO<sub>4</sub> assisted strategy.

Compared with  $C_g$ , volumetric capacitance ( $C_v$ ) is a more reliable parameter to evaluate the practical application potential of an electrode material.<sup>3,16,35</sup> Benefiting from its high  $C_g$  and high packing density (~1.2 g cm<sup>-3</sup>), HRGH-0.2-SC also exhibits a high  $C_v$  of 312 F cm<sup>-3</sup> at a current density of 1 A g<sup>-1</sup> (Fig. 4d). This value is much higher than those of most actived carbons and graphene materials (Table S3†). The Ragone plots further reveal the outstanding volumetric performance of HRGH-0.2-SC (Fig. 4e). A maximum energy density of 11.7 Wh  $L^{-1}$  was achieved at a power density of 30 W  $L^{-1}$ ; at an ultrahigh power density of 34 kW  $L^{-1}$ , a high energy density of 8.5 Wh  $L^{-1}$  was retained. In addition, HRGH-0.2-SC exhibited an excellent cycling stability with a capacitance retention of ~100% after 10,000 charge/discharge cycles at the current density of 10 A g<sup>-1</sup> (Fig. 4f and Fig. S16 † ). The coulombic efficiency was also kept to be around 100% throughout the whole testing process.

The outstanding electrochemical performance of HRGH-0.2-SC is attributed to the following factors. First, the rGO sheets in HRGH-0.2 are highly interconnected and interlocked, providing a continuous electron transfer network as well as large surface areas for charge storage.<sup>36,37</sup> The interconnected porous structure also facilitates the penetration and transportation of electrolyte ions within the whole electrode. Second, the abundant oxygenated groups on rGO sheets generate an additional pseudo-capacitance and simultaneously improve the wettability of HRGH-0.2 to aqueous electrolyte.<sup>2,10,11</sup> Meanwhile, they are chemically and electrochemically stable in acidic electrolyte, enabling HRGH-0.2-SC with excellent cycling stability. Third, the electrolyte saturated HRGH-0.2 can be mechanically compressed to form a compact monolithic electrode with high packing density.10,24 The compressed electrode maintains the initial solvated state, thus achieving a high volumetric capacitance without sacrificing its gravimetric capacitance and rate capability.

A thick electrode with high areal mass loading is highly desired for a supercapacitor to satisfy the requirements of practical applications.<sup>12–14</sup> However, a higher areal mass loading induces longer electrons/ions transport distances in the electrode.<sup>14</sup> Therefore, the good performances achieved at low

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Fig. 5 Electrochemical performances of HRGH-0.2-SCs at high areal mass loadings (mg cm<sup>-2</sup>). a) Nyquist plots. b) CV curves at a scan rate of 10 mV s<sup>-1</sup>. c)  $C_0$ s at current densities ranging from 1 to 100 mA cm<sup>-2</sup>. d)  $C_0$ s of HRGH-0.2-SC in comparison with those of other reported supercapacitors in aqueous electrolytes (Table S4<sup>+</sup>).

areal mass loadings cannot always be inherited into a practical device with a high areal mass loading (or thick electrodes). In our case, the HRGH-0.2 electrode was prepared by mechanically compressing a whole hygrogel (Fig. S17†), thus it has continuous electron transfer networks. Simultaneously, the interconnected porous structure and the outstanding wettability provide HRGH-0.2 electrode with unimpeded ion diffusion channels. Both the good conductivity and rapid ion transport make HRGH-0.2 to be a suitable electrode material for working at high mass loadings.

The electrochemical performances of the HRGH-0.2-SC with a high areal mass loading of 5 or 10 mg cm<sup>-2</sup> are shown in Fig. 5. The nearly vertical Nyquist plots in low frequency region indicate the ideal capacitive behaviours for all HRGH-0.2-SCs (Fig. 5a).<sup>4,38</sup> The magnified middle-to-high frequency region (inset in Fig. 5a) presents a transition from the 45° Warburg region to a semicircle, corresponding to ion diffusion and charge transfer resistances, respectively.<sup>2,11,39</sup> The Warburg regions gradually increased with the areal mass loadings, suggesting the elongated ion diffusion distances in high areal mass loading conditions. This phenomenon indicates that ion diffusion plays a dominate role in controlling the rate capability of HRGH-0.2-SCs in high areal mass loading conditions. By extrapolating the vertical portion to the real axis, the equivalent series resistances of 1.18, 1.46, and 2.11  $\Omega$  were obtained for 1, 5, and 10 mg cm<sup>-2</sup> mass loadings, respectively. The CV curves partially deviated from quasi-rectangular shape and exhibited a small peak separation (Fig. 5b and Fig. S18<sup>†</sup>), mainly due to the increased equivalent series resistances and total capacitance upon increasing areal mass loadings. The areal capacitance  $(C_a)$ of HRGH-0.2-SCs with high areal mass loadings were further calculated according to their GCD curves (Fig. S18<sup>†</sup>). The HRGH-0.2-SC with high areal mass loading of 10 mg cm<sup>-2</sup> delivered an ultrahigh  $C_a$  of 2675 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup> (Fig. 5c), which is significantly higher than those of carbon- or graphene-based symmetric supercapacitors (Fig. 5d and Table S4<sup>†</sup>). At an ultrahigh current density of 50 mA cm<sup>-2</sup>, a high  $C_a$ of 2140 mF cm<sup>-2</sup> was obtained (capacitance retention = 80%).

Further increasing the current density to 100 mA cm<sup>-2</sup>,  $C_a$  still kept at a high value of 1768 mF cm<sup>-2</sup> with a capacitance retention of 66%. Such a superior rate capability has rarely been achieved by a supercapacitor with 10 mg cm<sup>-2</sup> electrode material. The outstanding electrochemical performance of HRGH-0.2-SC with high areal mass loadings were further highlighted in Fig. S19<sup>†</sup>. Compared with those of the supercapacitor based on conventional graphene hydrogel, HRGH-0.2-SC delivered a higher specific capacitance and a better rate capability.

#### Conclusions

Hydroxyl-rich graphene hydrogels, HRGHs, were successfully prepared by precisely controlling the elimination of hydroxyl and/or epoxy groups on GO sheets during hydrothermal reactions. The 1,2- or 1,4-phenol structures on rGO sheets can electrochemically convert to 1,2- or 1,4-quinone structures to contribute pseudo-capacitance. Thus, HRGH-based supercapacitors showed high gravimetric and volumetric capacitances, as well as good rate capability and excellent cycling stability. Simultaneously, the abundant oxygenated groups on rGO sheets greatly improved the wettability of HRGHs to aqueous electrolyte, enabling the HRGH electrodes to keep their performance upon increasing mass loadings. Thus, an ultrahigh areal capacitance of 2675 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup> was achieved when the areal mass loading was increased to 10 mg cm<sup>-2</sup>, demonstrating the outstanding scalability of HRGH electrodes.

#### Conflicts of interest

There are no conflicts to declare.

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Hydroxyl-rich graphene hydrogels, HRGHs, were successfully prepared by precisely tailoring the oxygenated groups and used for a high-performance supercapacitor with high gravimetric, volumetric, and areal capacitances, as well as excellent rate capability and outstanding cycling stability.