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Reduced Graphene Oxide Hydrogel Film with a Continuous Ion Transport Network for Supercapacitors

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Stacking of Graphene usually results in a close packing of graphene nanosheeets corresponding to a low specific surface area and pore volume. A new simple method to prepare reduce graphene oxide (rGO) film has been developed using an in situ electrochemical reduction of the as-formed GO hydrogel film in aqueous solution electrolyte. The as-obtained rGO hydrogel film has highly specific surface area and was

10 used directly as the electrodes for a supercapacitor, where the ion channels were remained with excellent capacitance, even at high current density. The as-obtained rGO hydrogel film has also been used to prepare a flexible belt-like supercapacitor, which may light up a LED lamp for more than two minutes. Electrochemical in situ reduction provides a simple method to prepare novel graphene based supercapacitors for a wide application in the near future.

15 ## Introduction

As a class of energy storage devices with high power density and long lifespan, supercapacitors are of interest to a wide range of application from commercialized pocket electronics, hybrid vehicles to military devices.[1, 2] However, the low energy density
20 of traditional electrochemical capacitors has limited their applications.[3, 4] New nanostructured electrode materials should be developed to improve the specific capacitance and increase the operating voltage.[5, 6] The storage of electrostatic energy is based on the formation of an electric double layer of electrolyte ions on
25 the surface of conductive electrodes,[7] and the porous carbon has been paid much attention to its highly reversible ion adsorption on the surface of high-surface-area electrodes.[8]

As a famous star of carbon family, graphene has been actively investigated for supercapacitors for its high theoretical surface
30 area (2630 m^2 g^{-1}), excellent electrical conductivity and chemical stability,[9] and various types of graphene based materials have been reported for their application as supercapacitor electrodes. However, the surface areas of graphene derived from graphene oxide (GO) were low and far below the theoretical value due to
35 the stacking of GO/rGO nanosheets, and it is necessary to develop new method to fabricate graphene electrodes having a high surface area with higher pore volume.

The ion diffusion and adsorption in carbon materials are highly sensitive to pore size, surface wettability, and the pore
40 interconnectivity.[10] So the packing density of graphene materials is a key factor needed to be controlled.[11] Generally, graphite is a highly compact conductive carbon material with a packing density of about 2.2 g cm^{-3} in the ambient condition, and most ions cannot access the interplanar space, resulting in poor energy
45 storage capacity.[12] GO nanosheets has been used to prepare graphene electrodes by reduction and controlling its structures.[13-15] However, the reduction or drying of GO nanosheets maybe

results in serious stacking, which makes it very difficult to obtain a higher specific surface area and pore volume.[16, 17] Therefore, it
50 is very important to make non-stacked or less-stacked graphene materials as electrodes for supercapactiors. Recently. Lee et al. reported using an anti-solvent method to fabricate non-stacked reduced graphene oxide for supercapacitors.[18] They utilized hydrophobic hexane as an anti-solvent for the fabrication of
55 hydrophilic GO materials to give highly crumpled non-stacked GO nanosheests with a high surface area of 1435 cm^3 g^{-1} and simultaneously ultrahigh pore volume of 4.11 cm^3 g^{-1}, providing a high capacitance. Li et al. reported the fabrication of a chemically converted graphene (CCG) hydrogel film by filtration
60 of CCG dispersion, which was exchanged with a miscible mixture of volatile and nonvolatile liquids and was then subjected to removal of the volatile liquid by vacuum evaporation.[12, 19] The ions channel was remained by the nonvolatile liquid, which makes it a controllable packing density from 0.13 to 1.33 g cm^{-1}.
65 In their study, they found that the effect of packing density on the capacitance is limit when the hydrogel film remained its wet state, and the capacitance changed just from 203.2 to 191.7 F g^{-1} when the packing density increased from 0.13 to 1.33 g cm^{-3}. However, if the CCG film was completed dried, the capacitance
70 was only 155.2 F g^{-1}, indicating the importantace of the remaining of the wet state of the material. Similarly result has been also found by our previous studies on the 3D hydrogel with interconnected pores as potential electrode materials for supercapactors.[20, 21] So it is still necessary to develop a simple
75 method to prepare graphene electrode using GO nanosheets as feedstock for supercapacitors.

As stated above, one key point for the nano-stacked graphene preparation is preventing the collapse of the GO architecture during reduction due to the increasing of hydrophobicity of the
80 as-fromed rGO nanosheets. In addition, the homogeneous

reduction is also important to achieve a highly electrical conductivity. In situ reduction in the wet state under mild condition will be the best method. Here, a hydrogel film of GO nanosheets were prepared at first by filtration of the GO aqueous 5 suspension, and the hydrogel film was then directly reduced by electrochemical method to remain its ions channels and highly specific surface area, and the as-formed electrochemical reduced GO film (ERGO) was directly used in wet state as the electrodes for supercapacitors. High performance of supercapacitor was 10 achieved.

Experimental Materials

Materials

Graphite powder, natural briquetting grade, ~8000 meshes, 99.95% (metals basis) was purchased from Aladdin. Graphite 15 powder (~400mesh), analytical grade $NaNO_3$, $KMnO_4$, 98% H_2SO_4, 30% H_2O_2 aqueous solution, NH_4Cl, KOH, were purchased from Shanghai Chemical Reagents Company, and were used directly without further purification. Ultra-pure water (18 MΩ) was produced by a Millipore System (Millipore Q, 20 USA).

Preparation of GO hydrogel film

GO is prepared from graphite by a modified Hummers method.[22, 23] The obtained sediment was dispersed into water and treated by 25 mild ultrasound for 30 min to get GO solution (0.5 mg ml^{-1}). The GO hydrogel films were prepared by following the method reported by Li et al.[19] In brief, 30 ml of the as-prepared GO suspension was vacuum filtrated through a mixed cellulose ester filter membrane, and the as-obtained GO hydrogel film was then 30 carefully peeled off from the filter membrane and immersed in ultrapure water in a Petri dish to remain its wet state. The water content of the GO hydrogel film is 275% by a thermal mass losing analysis.

35 **Electrochemical reduction of the GO hydrogel film**

The electrochemical reduction of the GO hydrogel film was carried out in a three-electrode system, where an Ag/AgCl electrode worked as a reference electrode, Pt electrode was employed as the auxiliary electrode, and the GO hydrogel film 40 was directly used as the working electrodes, respectively (Figure 1c). 1M NH_4Cl aqueous solution was used as the electrolytes. Constant electrochemical reduction was carried under amperometric *i-t* curve with -1.2V with a CHI 660C potentiostat-galvanostat (CH Instruments Inc.).

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Fabrication of supercapacitors and their performances

ERGO hydrogel films deposited on Ti meshs (1 cm × 1cm, as collector) was directly used as electrodes to fabricate supercapacitors, and the electrochemical properties and 50 capacitance of the supercapacitors were studied in a two-electrode setup by cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy. The mass of the ERGO active material is 2.75 mg. The two electrodes were separated by a filter paper, and aqueous KOH 55 solution (5 M) was used as the electrolyte, and the voltammetric

testing was carried out at potentials between 0 and 1.2 V. The specific capacitance (C_{wt-sp}) of the supercapacitor was calculated using the equation $C_{wt-sp} = 2I\Delta t/m\Delta V$, where I is the constant discharge current, Δt is the discharging time, m is the mass of 60 graphene in one electrode, and ΔV is the voltage drop upon discharging. The volume specific capacitance (C_{vol}) was calculated using the equation $C_{vol} = C_{wt-sp} \times \rho$. The specific energy density (E_{wt-sp}) of the supercapacitor cells was calculated using the equation of $E_{wt-sp} = C_{wt-sp} \times \Delta V^2/8$. The volume specific 65 capacitance (E_{vol-sp}) was calculated using the equation $E_{vol-sp} = E_{wt-sp} \times \rho$.

Characterization

A commercial atomic force microscope (AFM, Nanoscope IIIa; 70 Digital Instruments, Santa Barbra, CA), equipped with a J scanner was used to measure the morphologies and thicknesses of the samples. Si_3N_4 tip (Nanoprobes, Digital Instruments Inc.) was used by the contact mode. The scan rates were between 1.0 and 2.4 Hz. Wide-angle X-ray diffraction (XRD) analyses were 75 carried out on an X-ray diffractometer (D/MAX-1200, Rigaku Denki Co. Ltd., Japan). C, H, and N contents of the samples were measured on an element analyzer (Elementar Analysensyeteme GMBH -vatio EL III, Germany). The XRD patterns with Cu Ka radiation (λ= 1.5406) at 40 kV and 100 mA were recorded in the 80 range of 2θ= 5-65°. X-ray photoelectron spectroscopies (XPS) were recorded on an Escalab MK II photoelectron spectrometer (VG Scientific Ltd., United Kingdom). The structures of the films were measured using a Sirion 200 FESEM at an accelerating voltage of 10 kV. For the electrical conductivity measurement, 85 the reduced GO film was patterned silver conductive paste through a shadow mask, and then the sheet resistance was measured using a semiconductor parametric analyzer (Keithley 2420, Keithley Instruments Inc., Cleveland, OH). The electrical properties the samples were measured by a CHI 660C 90 electrochemical workstation (CH Instruments Inc.).
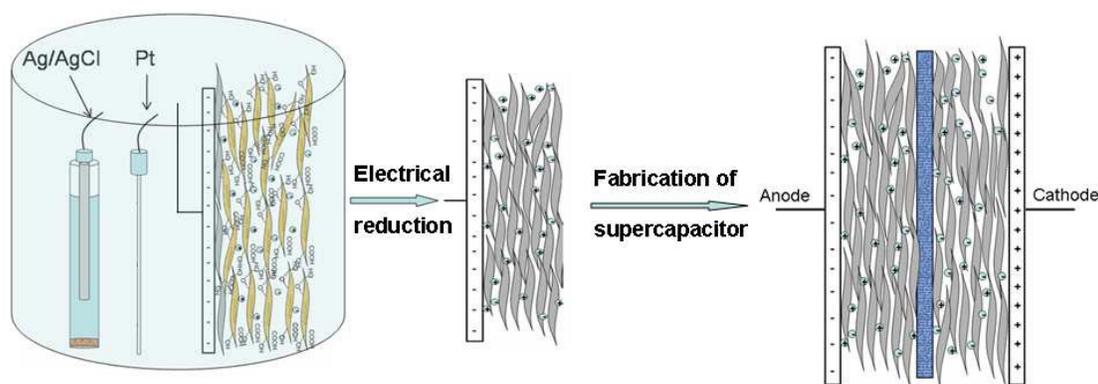
Results and Discussion

The advantage of electrochemical reduction is the high diffusion of electrons that can diffuse anywhere the electrolyte exists, 95 which maybe plays a significant role in the preparation of non-stacked graphene architectures. In addition, electrochemical reduction can carry out at room temperature, even at low temperature. For the GO hydrogel film, ions can easily access and attach to the surface of GO nanosheets, and ion channels should 100 be retained during the electrochemical reduction. As shown in Scheme 1, the oxygen-containing groups of GO nanosheets should be removed by electrons, and an ERGO hydrogel film can be obtained retaining the network structure, which can be used as electrodes for the fabrication of a supercapacitor directly.

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Figure 1 shows the formation of an ERGO hydrogel film by an electrochemical reduction at room temperature. At first, a GO film was prepared by filtration of GO aqueous suspension, and after drying a close packing GO film in yellow color was 110 obtained (Fig.1a). Figure 1b shows a photo image of an as-formed GO hydrogel film in its wet state, and clearly it was

swollen by the aqueous solution. The electrochemical reduction was carried out in a Petri dish full of 1M NH4Cl aqueous solution by a three-electrode process while the GO hydrogel film was contacted with Ag wire by multi-line contact (Fig. 1c), and a
[5] black ERGO hydrogel film was obtained after the reduction for 30 min. Figure 1d shows its SEM cross-sectional image of the as-obtained ERGO hydrogel film after it was freezing drying, and a rather uniform structure with thickness of 7.84 μm can be found, and the specific surface area of the wet ERGO hydrogel film is
[10] 1085 m^2 g^{-1} measured by methylene blue adsorption, indicating the ion channels was well remained after reduction. However, the value of specific surface area was only 504 m^2 g^{-1} if the hydrogel film was completed dried, and the thickness is about 3.72 μm (inset in Fig.3d), indicating the irreversible stacking of the GO

[15] nanosheets once the solvent was removed. The result also reveals that the as-obtained ERGO hydrogel film is in non-stacked state. Figure 1e shows the SEM cross-sectional image of the ERGO hydrogel film after it was compressed under 1 MPa pressure, and clearly the thickness of the film decrease from 7.84 μm to 4.6
[20] μm, also indicating the porous structure of the as-obtained ERGO hydrogel film. The packing density of the compressed rGO film is 1.12 g cm^3, close to that of the rGO film reported by Li et al.,[12] indicating that it is a potential material as electrode for supercapactiors. Figure 1f shows the SEM image of the surface of
[25] the as-obtained ERGO film, and the surface is flat while many wrinkles appear, indicating the overlap of the graphene nanosheets during the reduction and drying processes.[24]

[30] **Scheme 1**. Schematic diagram showing in situ electrochemical reduction of the as-formed GO hydrogel film and the fabrication of a supercapactior using the obtained ERGO hydrogel film in 1M KOH aqueous solution.
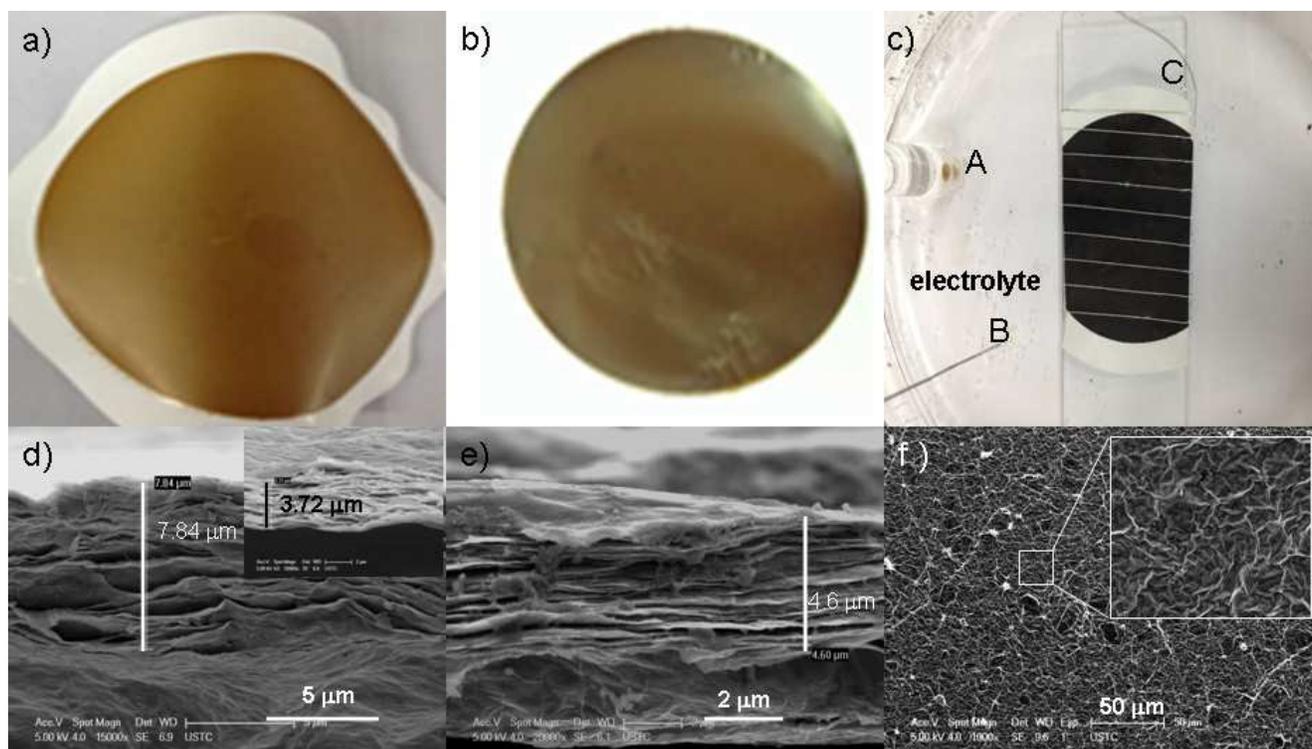

Figure 1. Photographies of the GO film in dry state (a), GO hydrogel film in wet state (b), the as-formed ERGO hydrogel film by electrochemical
[35] reduction with multi-lines contact (c). SEM images of the cross-sections of the as-formed ERGO hydrogel film before (d, inset is for the dried GO film) in d is the) and after (f) compress under 1 MPa pressure , and the SEM image of the surface of the ERGO film (f).
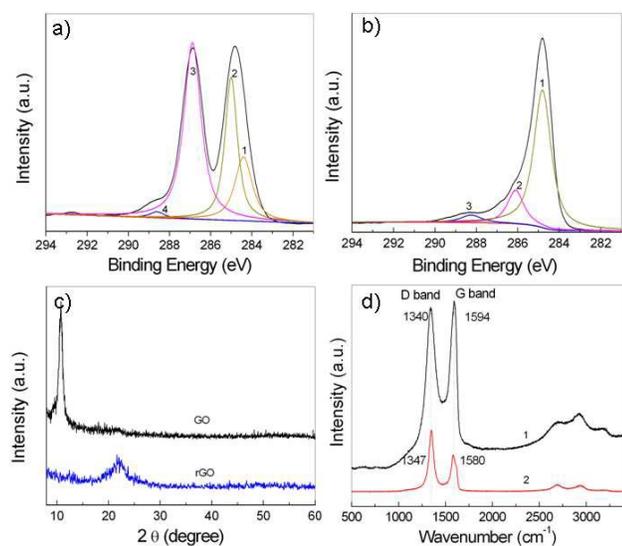
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Figure 2. XPS C1s profiles of GO film (a) and the as-formed ERGO film (b), and XRD patterns (c) and Raman spectra (d) of the as-formed ERGO
5 film.

XPS measurements could provide direct evidences of the reduction of the GO film. Figure 2a and 2b show the C1s XPS spectra of the dried GO hydrogel film and the relative ERGO
10 film, respectively. For GO film the curve was fitted as below: C=C (sp2; peak 1; 284.4eV), C-C (sp3; peak 2; 285eV), C-O/C-O-C (hydroxyl and epoxy groups; peak 3; 286.8eV), O-C=O (carboxyl groups; peak 4; 288.5eV).[25] After the electrochemical reduction, the oxygen species of C-O (hydroxyl and epoxy, 286.8
15 eV) reduced significantly, and the minor oxygen specie remaining was O-C=O (carboxyl groups; peak 3). In addition, element analysis studies revealed that the film consists of 85.68% C, 1.77% H, 0.19% N, indicating the efficient reduction of the ERGO hydrogel film. The X-ray diffraction (XRD) experiment
20 was used to measure the interlayer spacing of both the GO and ERGO films, and the results were shown in Fig.2c. For GO film, a sharp peak at 10.2°of 2θ corresponds to interlayer spacing along the c-axis of 0.87 nm. After electrochemical reduction, the layer structure became denser, and the peak of ERGO appears at
25 22.7° correspond an interlayer spacing of 0.39 nm. Figure 2d shows the typical Raman spectra of GO and the ERGO films. All the spectra indicate the existence of the D, G and 2D bands. For GO film, the G band is located at 1594 cm^{-1}, while for the ERGO film the G band moved to 1580 cm^{-1}, indicating the reduction of
30 GO nanosheets.[26] However, the existence of the D band at 1340 or 1347 cm^{-1} indicates the defect of the sample and the size of the in-plane sp^2 domain.[27] The intensity ratio of the D and G band (I_D/I_G), varies from 0.97 to 1.59, and Stankovich et al.[28] suggested that reduction GO increases the number of aromatic
35 domains of smaller average size in graphene, which could lead to

an increase of the I_D/I_G ratio.

The in situ electrochemical reduction of the GO hydrogel film in wet state can also be recorded by multiple cyclic voltammetries of GO hydrogel film electrode, and the
40 electrochemical double layers (EDLs) capacity can be recorded at the same time. EDLs currents increased with cycling times as shown in Fig.3a, and a high specific capacity up to 287 F g^{-1} was calculated for fully reduced GO film electrodes (three-electrode). Peaks appeared at -0.6V/0.6V are generally attributed to the
45 reversible oxygenated functionalities such as quinone/hydroquinone transformation, and similar result was also found by Shivakumara et al.[29] The performance of graphene based supercapacitors is highly dependence on the specific area, pore structure and electrical conductance of the electrode
50 materials, and the as-obtained ERGO hydrogel film can be directly worked as non-stacked graphene electrodes for fabrication a two-electrode supercapacitor (Scheme 1). The galvanostatic charge/discharge curves of the ERGO hydrogel film based supercapacitor in 5M KOH electrolyte were observed
55 at a current density of 0.5A g^{-1} (Fig.3b), and as a control the performance of the supercapacitor using a dried ERGO film as electrodes was also studied. The charging curves were almost symmetric with respect to the relative discharging curves within the potential range of 0 to 1.2 V, indicating a high performance of
60 the supercaptior. The specific capacitance was 206 F g^{-1}, which is close to the value of the non-stacked ERGO reported by Lee et al.[18] In addition, for the dried ERGO film the specific capacitance was just 109 F g^{-1}, indicating that the drying process result in serious stacking of ERGO nanosheets. Figure 3c shows the
65 electrochemical characteristics of the wet and dried ERGO films electrodes in 5M KOH solution at a scan rate of 10 mV s^{-1}, respectively. The CV curves are near rectangular shapes, indicating the ideal supercapacitor properties for the charge/discharge process. The specific capacitance were
70 measured of 210 F g^{-1} and 109 F g^{-1} for wet and dried ERGO films, which is similar to the results reported by Li et al.[12] The specific surface area of wet and dried ERGO films was 1085 and 504 m^2 g^{-1}, respectively, well agreed with the results, and it also reveals the advantage of using the in situ prepared wet ERGO
75 film for supercapacitor. Besides, after 10000 cycles of charge/discharge at a current density of 10 A g^{-1}, 89% of capacitance retention remained, indicating the stability of supercapacitor (Fig.3d). Volume energy density of the supercapacitors were also calculated and they were listed in
80 Table S1, accompany with the other ever reported values of porous carbon materials. Clearly, the ERGO or compressed ERGO films showed the highest Evol values, indicating the high performance of the new supercapacitors, and the maximum E_{vol} is 15.78 Wh L^{-1}.
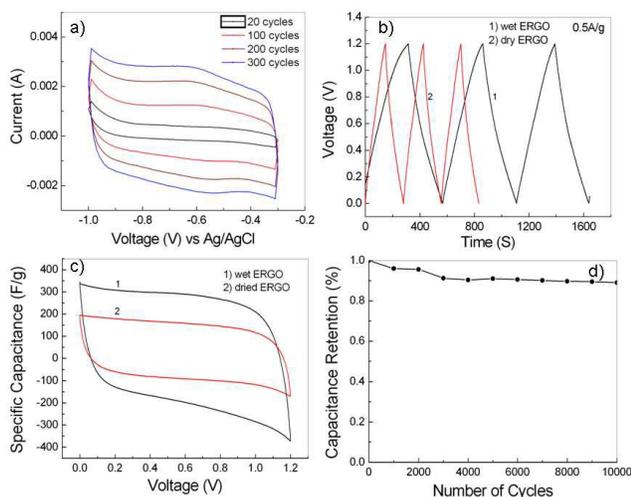
Figure 3. a) multiple cyclic voltammetry (CV) curves during the electrochemical reduction of GO hydrogel film where GO hydrogel film as working electrode in a three-electrode system: 10 mV s^{-1}, from 20-300
5 cycles. b) Galvanostatic charge/discharge curves of both the wet and dried ERGO films at a current density of 0.5A g^{-1} in a two-electrode system. c) CV curves of ERGO film at both the wet and dried states at a scan rate of 10 mV s^{-1} in a two-electrode system. d) Cycle performance of the supercapacitor using the ERGO hydrogel film as electrode in 5M
10 KOH over 10000 cycles of charge/discharge at a current density of 10A g^{-1} in a two-electrode system.

The above results showed that the highly specific surface area and the remaining of ion channels in the ERGO hydrogel film allow the pre-incorporation of electrolytes, which ensured a high
15 rate performance of the compact ERGO film. Figure 4 shows the Nyquist plots of the wet and dried ERGO film supercapacitors over the frequency range of 0.1 Hz to 10 kHz. As expected, at a low frequency, the imaginary part increased sharply and a nearly vertical line is observed, indicating an ideal capacitive behavior
20 for both the wet and dried ERGO films. Of magnified data in the high-frequency range, a transition between the RC semicircle and the migration of electrolyte was observed at a frequency of about 31.5 Hz, corresponding to a resistance of 8 ohms for the wet ERGO film and 3.8 ohms for the dried ERGO film, indicating the
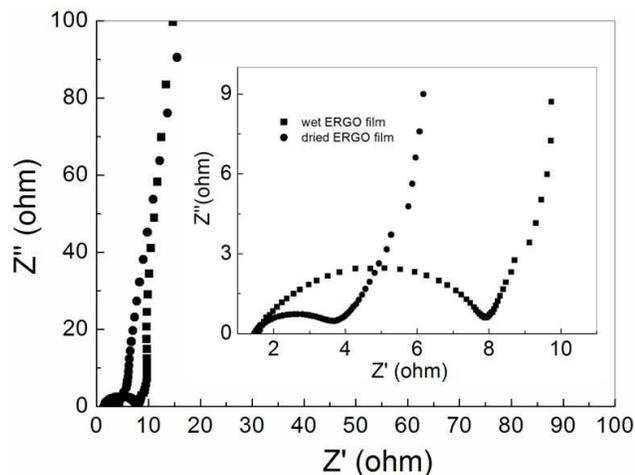25 dried film is in higher conductivity due to the stacked packing.

Figure 4. Nyquist plots of the wet and dried ERGO films and magnified data in the high frequency region (inset).

30 Figure 5 shows the rate performance curves of specific capacitance versus current density of both the wet and dried ERGO films. The wet ERGO film electrode gave a specific capacitance of up to 206 F g^{-1} at a current density of 0.5 A g^{-1}, which was higher than that of the dried ERGO film (109 F g^{-1}).
35 Furthermore, the capacitance showed only a slight decrease to 122 F g^{-1} even at a current density of 32 A g^{-1}, while the dried ERGO only showed a capacitance of 16 F g-1 at the same current density, indicating that the wet ERGO film has a high rate capability than that of the dried one.
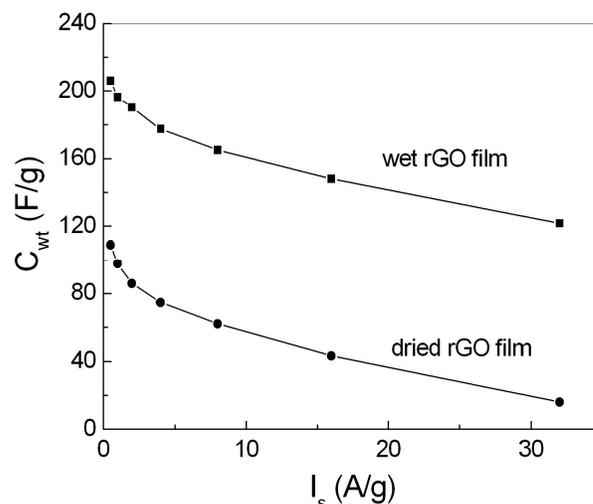

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Figure 5. Dependence of specific capacitance on current density in ERGO (dry and wet films) based supercapacitors in 5M KOH.

Graphene shows impressive potential applications in flexible and wearable electronic devices. Here, we fabricated a belt-like
45 packed flexible capacitor in size of 1.5 cm × 20 cm with two pieces of ERGO electrodes using titanium mesh as current collector, as shown in Fig.6a. 200 F g^{-1} specific capacity was reached when the charge/discharge current density was 0.5A g^{-1} (Fig.6b). The target is to develop a wearable leather belt-like
50 EDLs capacitor, so the capacitance retention under bending was also studied, and 91.5% capacitance remained after 1000 times bending, indicating excellent flexibility of the device (Fig.6c). In addition, the belt-like capacitor was employed as a power source for an external LED lamp (Fig.6d), and it lasted 150 seconds
55 before it was dark, indicating that the wearable EDLs capacitor has practical applications in the near future.
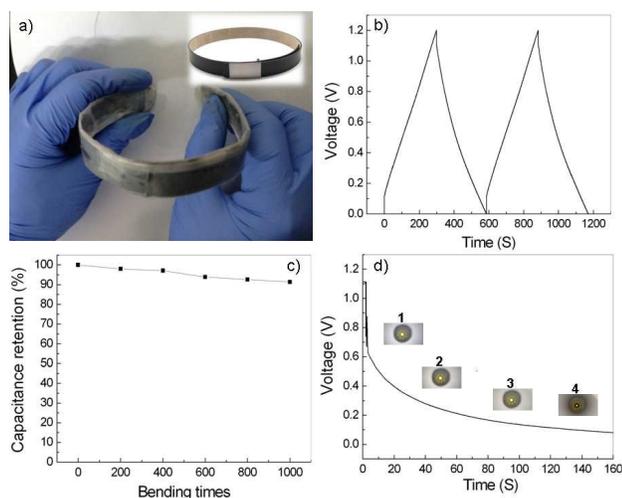
Figure 6. a)A belt-like flexible capacitor device with 0.05g electrochemical reduced ERGO on each side. b) Galvanostatic charge/discharge curve of the capacitor at 0.5A g^{-1}. c) Capacitance retention after 1000 bends. d)Voltage-time curve of the belt-like capacitor while a LED lamp was lighted; insets were images of LED at different time.

Conclusions

Non-stacked reduced graphene oxide hydrogel film has been prepared by an in situ electrochemical reduction, and the as-obtained film was porous with highly specific surface area that remains the ion channel. Without drying, the as-obtained ERGO film can be used directly as the electrodes for a supercapacitor. The specific gravimetric/volume capacity of wet ERGO reached 206 F g^{-1} or 231 F cm^{-3}, similar to the best result of the reported rGO systems. In addition, a flexible belt-like capacitor device was designed and fabricated, and it can provide electrical energy for a LED lamp for more than two minutes. The easy processing made the electrochemical reduction a facile method for the preparation of ERGO architectures and capacitor electrodes in a large scale.

Acknowledgements

References

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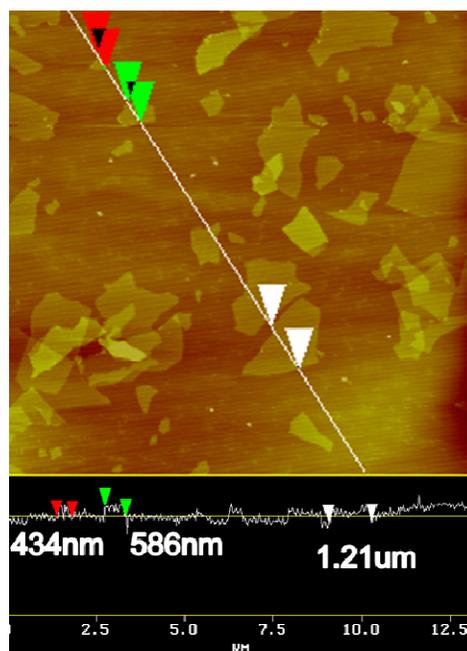2. Y. P. Zhai, Y. Q. Dou, D. Y. Zhao, P. F. Fulvio, R. T. Mayes and S. Dai, *Adv. Mater.*, 2011, 23, 4828-4850.
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Supporting materials for:

Reduced Graphene Oxide Hydrogel Film with a

Continuous Ion Transport Network for Supercapacitors

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10 Figure S1. Typical AFM image of the GO nanosheets used in this study.

The GO nanosheets used in this studied is in size of about 1 μm, as shown in Fig.S1, AFM image

shows the typical morphology of the GO nanosheets, and most of them is in single layer.
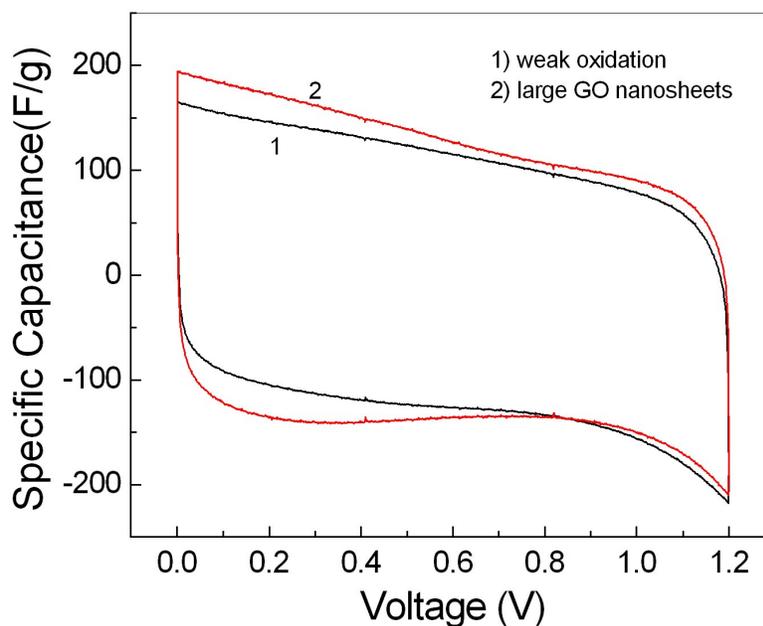
Figure S2. CV curves of supercapacitors based on large area GO or weakly oxidized GO at scan rate of

10 mV s^{-1}.

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The capacity of ERGO is also determined by two factors: oxidation degree of GO and the size of GO sheets. Here, weakly oxidized GO (w-GO) prepared from 8000 mesh graphite powder showed a specific capacity of 119 F g^{-1}. For strongly oxidized GO from 400 mesh graphite, with larger sheets size (L-GO), it showed a specific capacity of 133F g^{-1}.

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Table S1. Performance of selected porous materials carbon for ECs

Materials reported	Packing density (g cm^{-3})	Structure of the capacitor	Electrolyte	Test condition I_s/ A g^{-1}	C_{wt-c} (F g^{-1})	C_{vol} (F cm^{-3})	E_{vol} (Wh L^{-1})	Ref.
Carbide derived carbon	N/A	three-electrode	H_2SO_4	N/A	N/A	160	5.56	[30]
Laser scribed graphene	0.048	two-electrode	H_3PO_4	1.0	202	9.7	0.45	[31]
Graphene hydrogel	0.05	three-electrode	H_2SO_4	0.3	258	12.9	0.45	[32]
Oriented graphene hydrogel	0.069	two-electrode	H_2SO_4	0.1	215	14.8	0.51	[11]
Curved graphene	0.3	two-electrode	$EMIMBF_4$	1.0	154	N/A	N/A	[33]
Carbon onions	0.5	two-electrode	Et_4NBF_4/PC	N/A	N/A	9.0	1-2	[34]
Chemically modified graphene	0.5	two-electrode	KOH	1.33	135	67.5	2.34	[35]
Commercial activated carbon	0.7	two-electrode	KOH	0.2	160-200	80-110	2.78	[36]
EM-CCG film	1.25-1.33	two-electrode	BMIM BF$_4$/TEA BF$_4$/AN	0.1 1.0 10.0	191.7 170.6 146.3	255.5 226.9 194.6	8.87 7.88 6.76	[37]
ERGO film	0.7	three-electrode two-electrode	KOH	0.5	287 206	200.9 144.2	10.05 7.21	This work
Compressed ERGO film	1.1	three-electrode two-electrode	KOH	0.5	285 203	315.7 226.6	15.78 11.33	This work

a., b.

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