Electronic Supplementary Information (ESI)

High-performance flexible fibre-shaped electrochemical capacitor based on electrochemically reduced graphene oxide

Yingru Li, Kaixuan Sheng, Wenjing Yuan and Gaoquan Shi*
Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China.

1. Experimental Section

Synthesis and purification of GO. GO was prepared by the oxidation of natural graphite powder (325 mesh, Qingdao Huatai Lubricant Sealing S&T Co. Ltd., Qingdao, China) according to a modified Hummers' method.[S1] Typically, graphite powder (3.0 g) was added to concentrated sulfuric acid (70 mL) under stirring at room temperature. Then, sodium nitrate (1.5 g) was added, and the mixture was cooled to 0°C. Under vigorous agitation, potassium permanganate (9.0 g) was added slowly to keep the temperature of the suspension lower than 20 °C. Successively, the reaction system was transferred to a 35 ± 5 °C water bath and stirred for about 0.5 h, forming a thick paste. 150 mL of water was added, and the solution was stirred for 15 min at 90 ± 5°C. Additional 500 mL water was added and followed by a slow addition of 15 mL H_2O_2 (30%), turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions followed by washing with 200 mL water to remove the acid. The resulting solid was dried in air and diluted to make a GO aqueous dispersion (0.5% w/w).

Finally, it was purified by dialysis for one week using a dialysis membrane (Beijing Chemical Reagent Co., China) with a molecular weight cut off of 8,000 to 14,000 g mol^{-1} to remove the remaining metal species.

Fabrication of ErGO electrodes. The ErGO electrodes were prepared by electrolyzing 3, 6, 9 or 12 mg mL^{-1} GO aqueous suspension containing 0.1 M lithium perchlorate ($LiClO_4$) at a potential of −1.2 V (vs. SCE) for 2, 5, 10, 20 or 40 s. The counter electrode was a platinum pipe. The working electrode was an Au wire, which was placed in the centre of the Pt pipe to provide a relatively uniform electric field during electrolysis (**Figure S1)**. After electrodeposition, the ErGO electrodes were immersed in de-ionized water to remove residual salts and electrolyte.

Characterization. GO dispersion, ErGO were freeze-dried and used for morphological and structural characterizations. Raman spectra were recorded on a Renishaw Raman microscope with a 514-nm laser at a power density of 4.7 mW. X-ray photoelectron spectra (XPS) were taken out by using an ESCALAB 250XI photoelectron spectrometer (ThermoFisher Scientific, USA). Scanning electron micrographs (SEM) were performed on a field-emission scanning electron microscope (Sirion-200, Japan).

Precursor solution of H_3PO_4/PVA/H_2O gel electrolyte. The gel electrolyte was prepared according to the method described in literature.[S2] Briefly, polyvinyl alcohol (PVA) (molar mass = 80,000 g, 99% hydrolyzed, Sinopharm Chemical Reagent Co. Ltd. Shanghai, China) powder was put into de-ionized water (1 g PVA/ 10 g H_2O). Then, the mixture was heated at ~90^{o}C under stirring until the solution turned clear.

After cooling to room temperature, 0,8 g phosphoric acid solution (85%, Beijing Chemical Works, Beijing, China) was added and the system was stirred to form a viscous homogenous solution.

Assembly of ECs: The as-prepared fiber-shaped electrodes were immersed in the H_3PO_4/PVA/H_2O precursor solution described above for 2 h to ensure them to be completely wetted. Then, the electrodes covered with the gel electrolyte were put into a dryer at room temperature until the formation of a viscous gel. Two electrodes covered with the gel electrolyte were assembled in a parallel manner and then wrapped with a poly(tetrafluoroethylene) film carefully. The ECs were kept undisturbed overnight to ensure the electrodes to be bound together with the solid electrolyte.

Electrochemical tests: All of the electrochemical tests were performed in a two-electrode system. Each EC was pre-treated by CV cycling in the potential range of 0 to 1 V at a scan rate of 500 mV s^{-1} for 100 cycles to get a stable performance. The electrochemical impedance spectra (EIS) were taken out using a CHI 760D potentiostat-galvanostat (CH Instruments Inc. Shanghai, China) in the frequency range of 0.05 Hz to 100 kHz with a 5 mV ac amplitude. Cyclic votammograms and galvanostatic charge/discharge curves were recorded between 0 and 1.0 V using a CHI 440D potentiostat-galvanostat (CH Instruments Inc. Shanghai, China).

2. Calculation of Specific Capacitances

The specific capacitance, C_s (μF cm^{-1}), of a FSS-EC was calculated by the use of following equation:

$$C_s = \frac{I_D}{dV/dt} \quad (1)$$

where I_D is the current density (μA cm^{-1}), dV/dt is the slope of the discharge curve (V s^{-1}).

Capacitance per unit area, $C_{s,A}$ (mF cm^{-2}), was calculated by the use of following equation:

$$C_{s,A} = \frac{C_s}{\pi d/2} \quad (2)$$

where *d* is the diameter of the electrode.

Supplementary References

S1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

S2 M. Kaempgen, C. K. Chan, J. Ma, Y. Cui and G. Gruner, *Nano. Lett.*, 2009, **9**, 1872.

3. Supplementary Figures

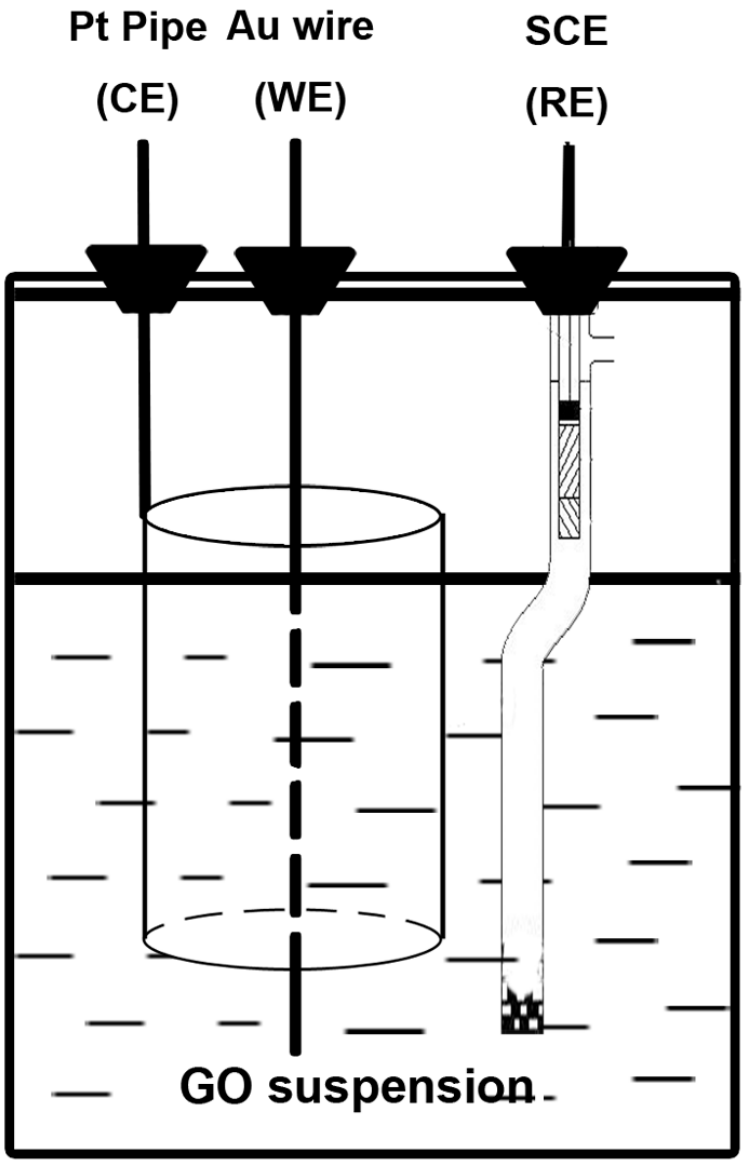

Figure S1. Schematic illustration of the electrochemical cell.

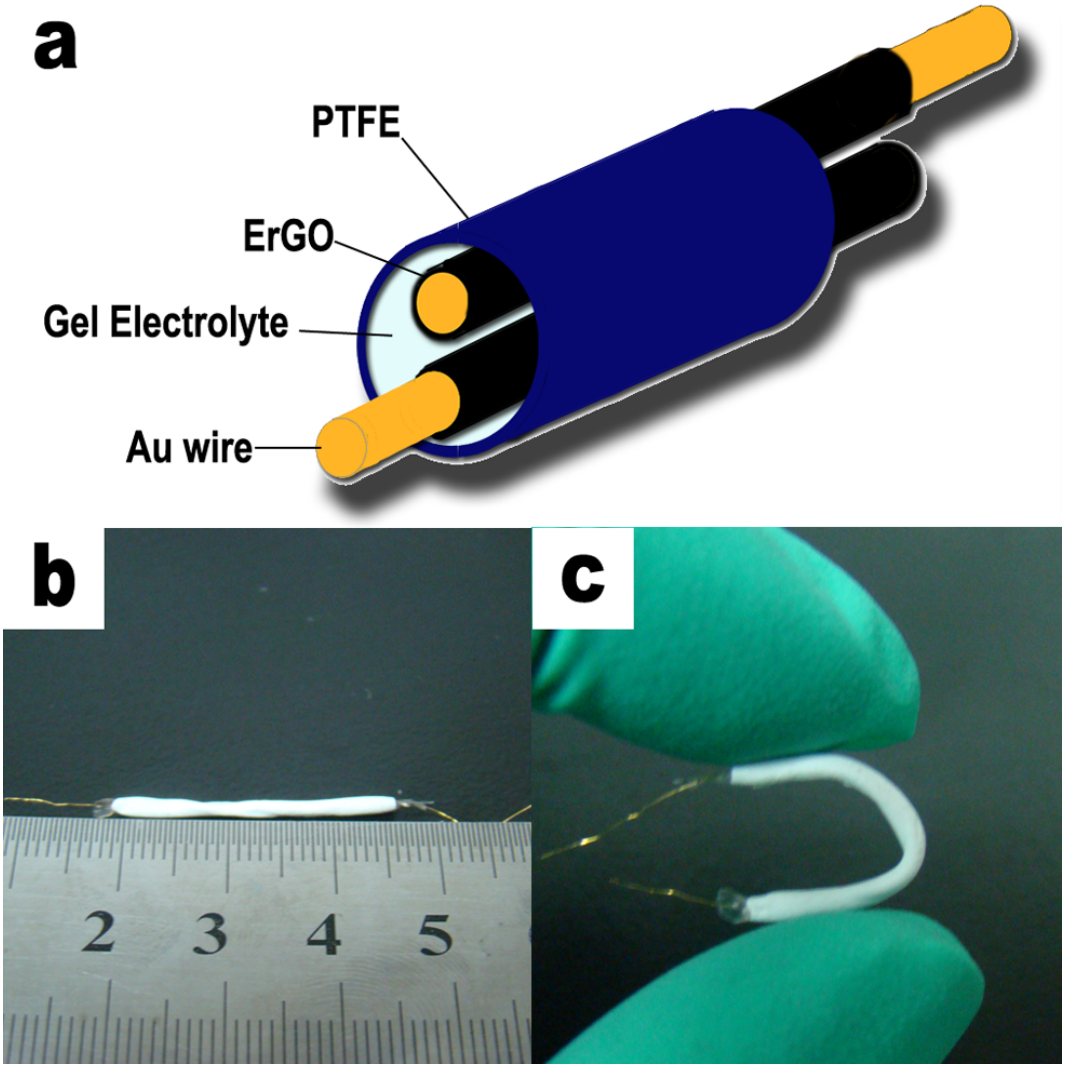

Figure S2. (a) The structure of a FSS-EC. (b, c)Photographs of a FSS-EC in (b) straight and (c) bent states.

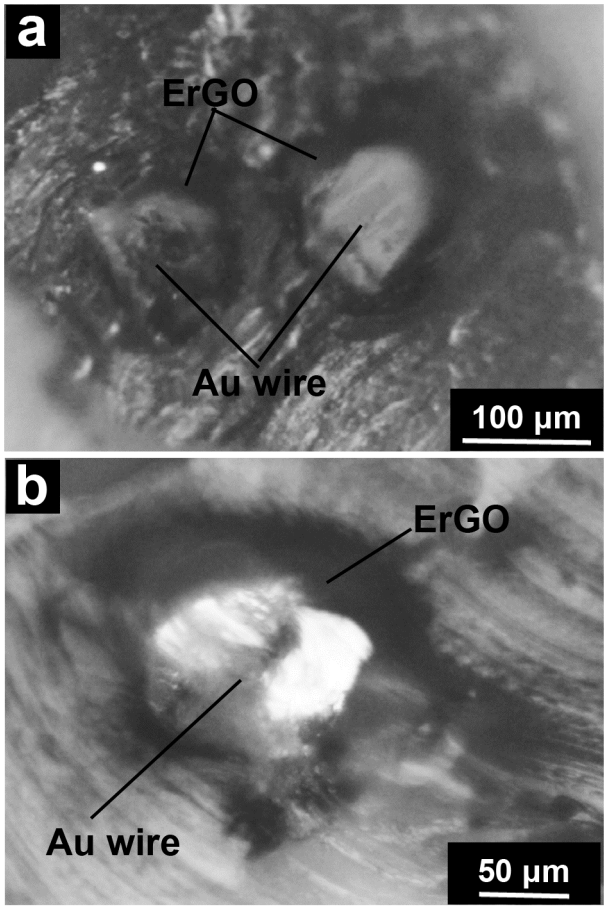

Figure S3. Cross-sectional photographs of the typical FSS-EC and an ErGO electrode in the device after repeated bending to 90^{o} for 1,000 cycles.

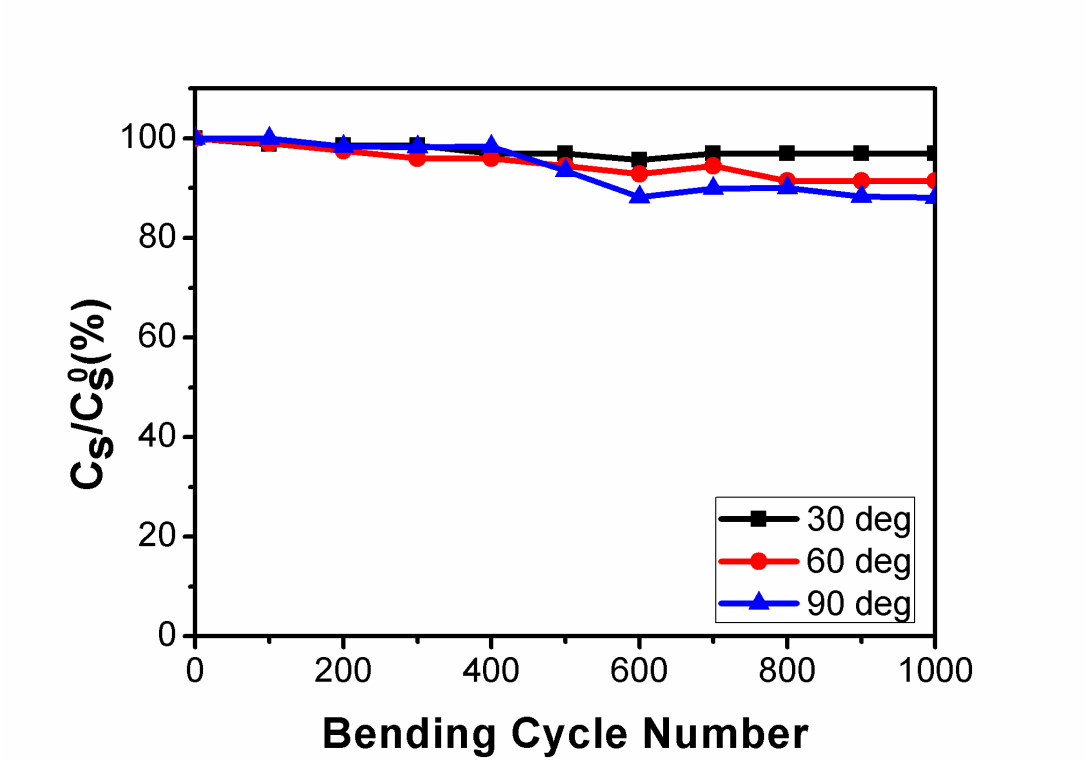

Figure S4. The capacitance retention of the typical FSS-EC after repeated bending to 30^o, 60^o or 90^o for 1,000 cycles,

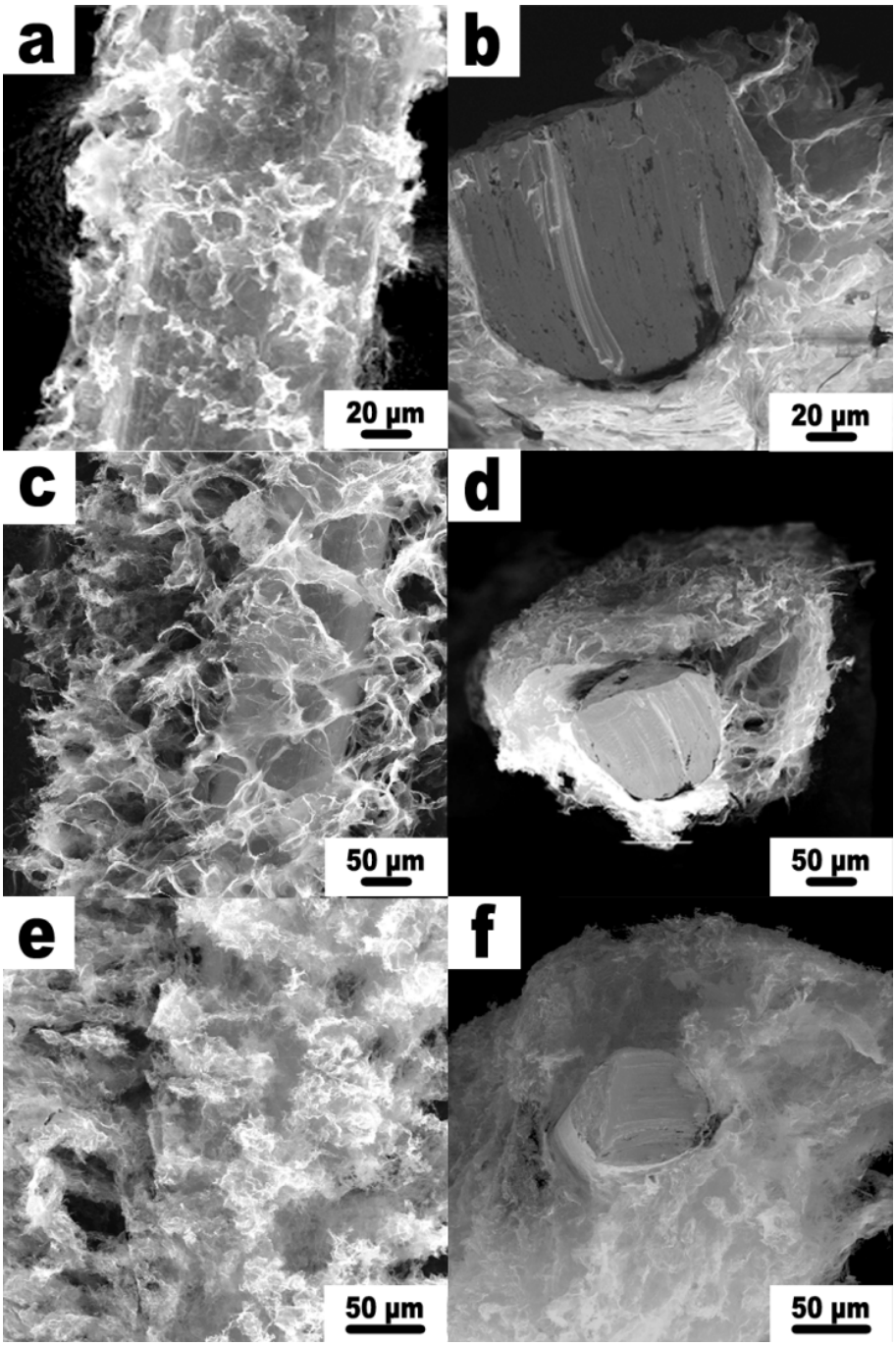

Figure S5. SEM images of the fibre electrodes prepared by electrolysis of a 3 mg mL^{-1} GO suspension for different T_E. a, b) 5 s, c, d) 20 s, e, f) 40 s.

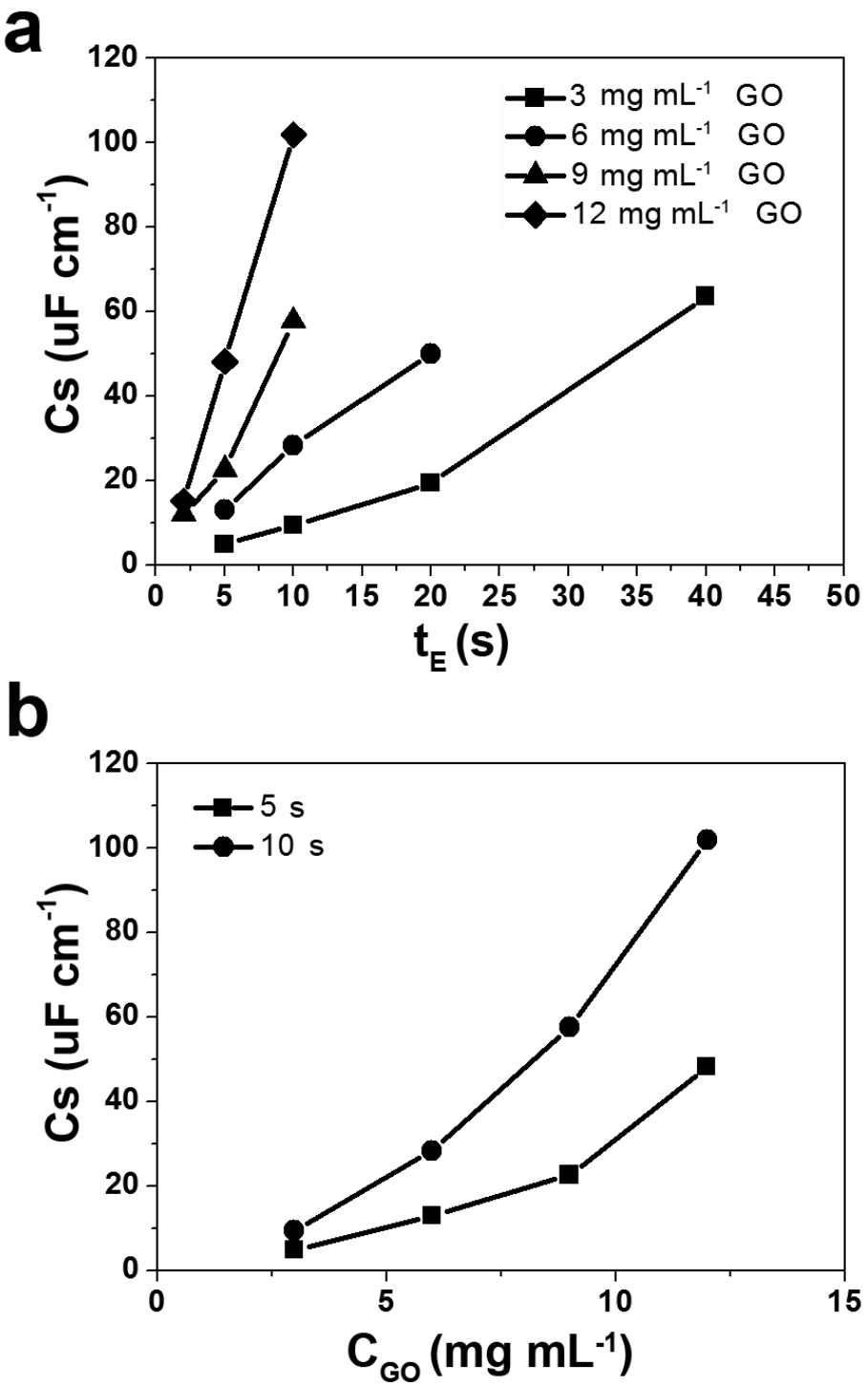

Figure S6. a) Plots of Cs versus t_E for the FSS-ECs with the electrodes prepared from GO suspensions with different C_{GO}; b) Plots of Cs versus C_{GO} for the FSS-ECs with the electrodes prepared by electrodeposition for 5 or 10 s.

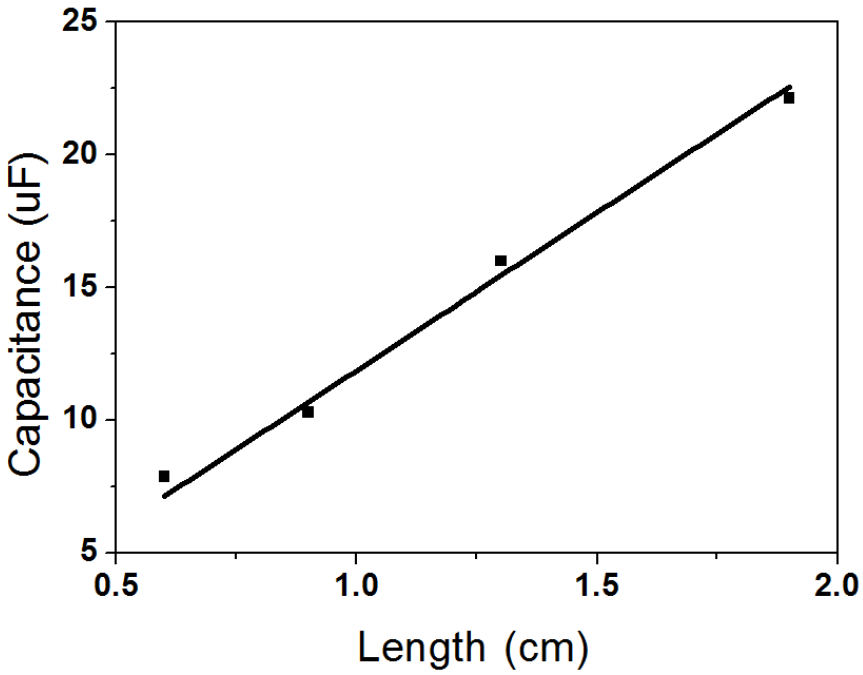

Figure S7. Plot of capacitance of a FSS-EC versus its electrode length (C_{GO}=3 mg mL^{-1}, t_E=10 s).