

## Supporting Information

### **Three-dimensional seamless graphene/carbon nanotubes hybrids for multifunctional energy storage**

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## **Experimental section**

### **Materials**

Nickel foam, ethanol, iron chloride hexahydrate, ammonium persulfate, and phosphoric acid were purchased from Aladdin Reagent, and without further purification before use. Copper wire and polyvinyl alcohol were purchased from Alfa-Aesar. Ferric nitrate nonahydrate and aluminum nitrate nonahydrate were purchased from Adamas Reagent (Co. Ltd). Hydrochloric acid and perchloric acid were purchased from Sinopharm Chemical Reagent (Co. Ltd). Aniline was provided by J&K Chemical. Polydimethylsiloxane was provided by the Dow Chemical Company.

### **Synthesis of multi-layer graphene foam**

Multi-layer graphene foam was grown on nickel (Ni) foam through a typical chemical vapor deposition (CVD) and followed by etching of Ni substrate. Firstly, the Ni foam with 1.2 mm thick was cut into small size (2 cm × 1 cm), followed by ultrasonic cleaned with ethanol for 10 minutes and dried in air. Then, the cleaned Ni foam was put into a tube furnace, and exchanged air in the tube with argon flow (400 sccm). The tube furnace was heated from room temperature to 1000 °C within 40 minutes with a mixture of argon (400 sccm) and hydrogen (80 sccm) as carrier gas. After the furnace was maintained at 1000 °C for 10 minutes to reduce the nickel oxide, the carbon source of methane (flow rate of 60 sccm) was introduced into the tube furnace to grow graphene for 10 minutes. The as-grown graphene on Ni foams was immersed in a mixed aqueous solution of ferric trichloride (1 M) and hydrochloric acid (1 M), and heated to 80 °C for 1 hour. The above process was repeated for three times. The etched graphene foam was washed for several times with deionized (DI) water to remove residual metal salts. The obtained graphene foam was dried at 80 °C.

### **Growing carbon nanotube arrays on graphene layer in the foam**

Typically, the precursor solution of catalyst for growing CNTs was made by resolving ferric nitrate (300 mM), aluminum nitrate (300 mM) and polyvinyl alcohol (0.003 g/mL) in DI water. The graphene foam was pre-treated by nitrogen plasma for five

minutes to improve its hydrophilicity. The graphene foam was fully immersed in the precursor solution for 10 minutes, then taken out and dried at 60 °C for 15 minutes. The catalyst precursor-coated graphene foam was placed in tube furnace, followed by exchanged air in the tube with argon. The tube furnace was heated from room temperature to 750 °C within 15 min with a mixture of argon (200 sccm) and hydrogen (45 sccm) as carrier gas. The tube furnace maintained at 750 °C for 5 min. Then, the carbon source of ethylene (5 sccm) was introduced to grow carbon nanotubes for 10 min. Finally, the ethylene and hydrogen were shut off, G/CNTs hybrid was obtained after the furnace was cooled down to room temperature in Ar.

### **Growth of polyaniline in Graphene/Carbon Nanotube hybrid materials**

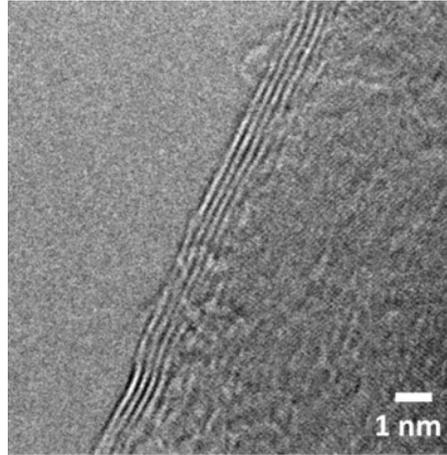
The polymerizing solution was prepared by adding aniline (108  $\mu$ L) into 1M HClO<sub>4</sub> aqueous solution (20 mL) with stirring for 10 minutes, followed by adding ammonium persulfate (30 mg) with stirring for 2 minutes. The whole process was performed in ice bath. Then, G/CNTs hybrid was completely immersed in the above solution for polymerization at 3-5 °C for 24 hours. After polymerization, the G/CNTs/PANI was taken out and washed with DI water for several times, then dried at room temperature.

### **Fabrication of two-electrode supercapacitors**

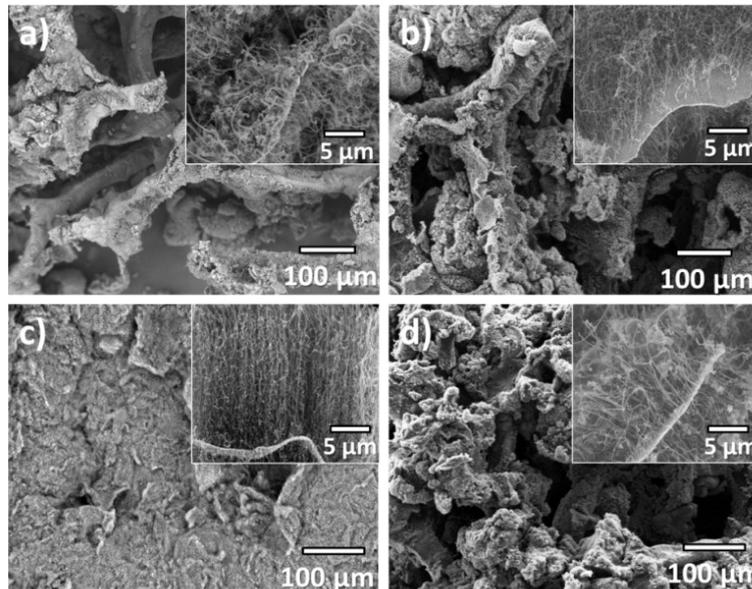
The as-prepared G/CNTs hybrids (or G/CNTs/PANI) were immersed in a mixed solution of ethanol and water, then, all of them was transferred and pressed onto the surface of polydimethylsiloxane (PDMS) films for building of supercapacitors. The electrode materials were treated by nitrogen plasma for 5 min to increase their hydrophilicity. One end of an electrode was connected with a copper wire by silver paste. A gel solution of polyvinyl alcohol and H<sub>3</sub>PO<sub>4</sub> in DI water was used as gel electrolyte, which was infiltrated into electrode materials and dried at room temperature. Finally, two pieces of electrodes coated with gel electrolyte were pressed together and assembled into a supercapacitor.

### **Characterization and measurements**

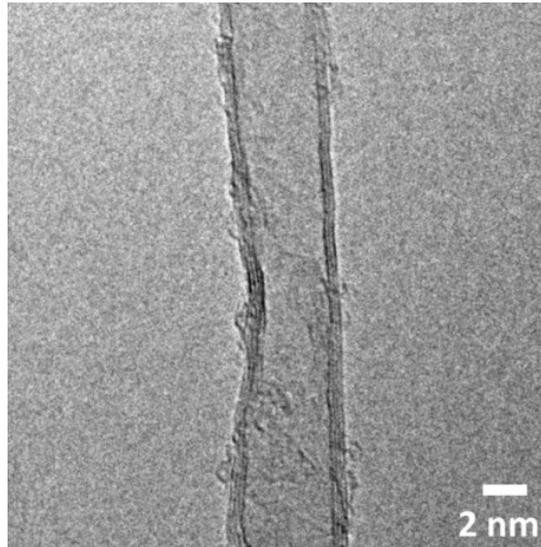
The structure and morphology of the materials were characterized by high-resolution field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL-2010). Raman spectra were recorded on a Renishaw Raman spectrometer equipped with a 514 nm laser. Electrochemical measurements were performed on an electrochemical working station (CHI760E, Chenhua, Shanghai). The photo-sensitive properties of supercapacitors were characterized by recording their electrochemical performance by using electrochemical working station with supercapacitors illuminated under simulated solar light (Oriel-Sol3A) with different intensities (The light intensity was calibrated using a reference Silicon solar cell (Oriel-91150)) coming from a solar simulator. The stretchability of supercapacitors were measured by recording their electrochemical performance by using electrochemical working station as the devices were fixed on a mechanical test machine (HY-0350, Shanghai Hengyi Co. Ltd) and stretched to a certain stain.



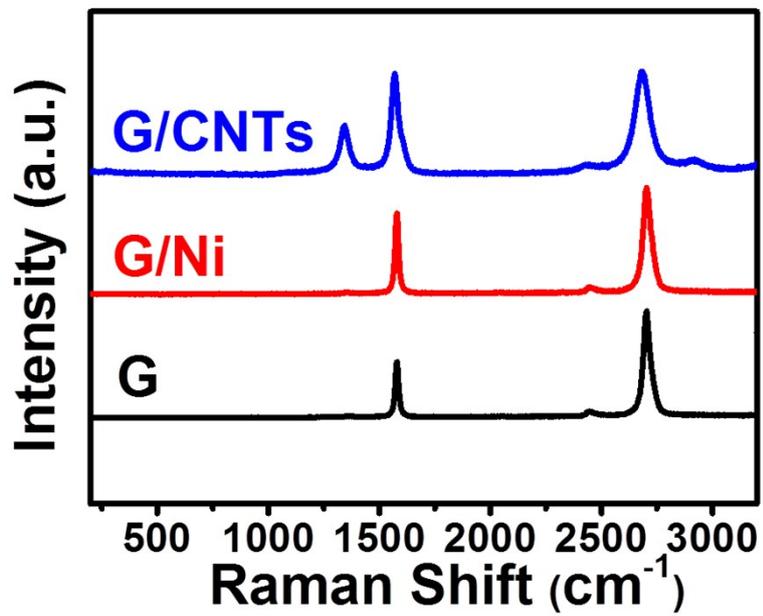
**Figure S1.** TEM image of graphene after etching of nickel.



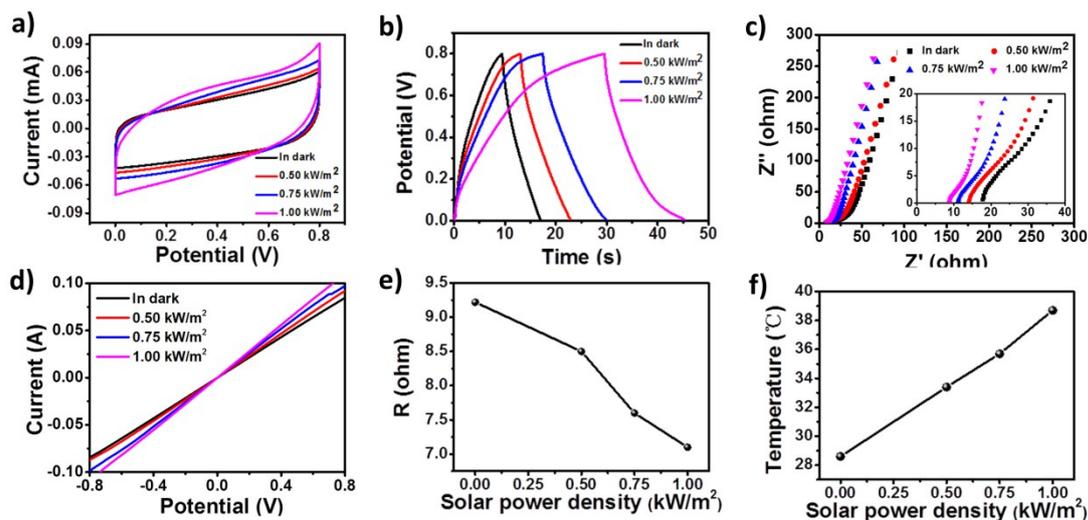
**Figure S2.** SEM images of G/CNTs with CNTs grown from catalyst precursor with different concentrations of ferric nitrate/aluminum nitrate. The concentrations of ferric nitrate/aluminum nitrate were 100 mM/100 mM (a), 200 mM/200 mM (b), 300 mM/300 mM (c) and 400 mM/400 mM (d), respectively.



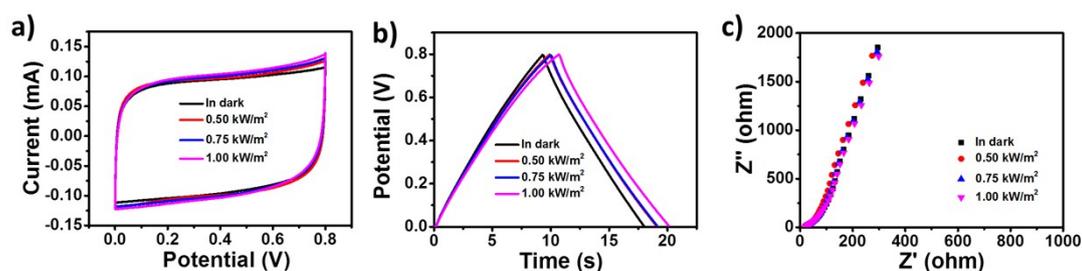
**Figure S3.** TEM image of a carbon nanotube.



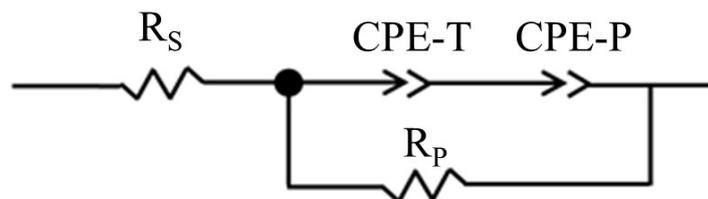
**Figure S4.** Raman spectra of graphene on Ni (G/Ni), graphene foam (G) after etched Ni and as-grown G/CNTs hybrid.



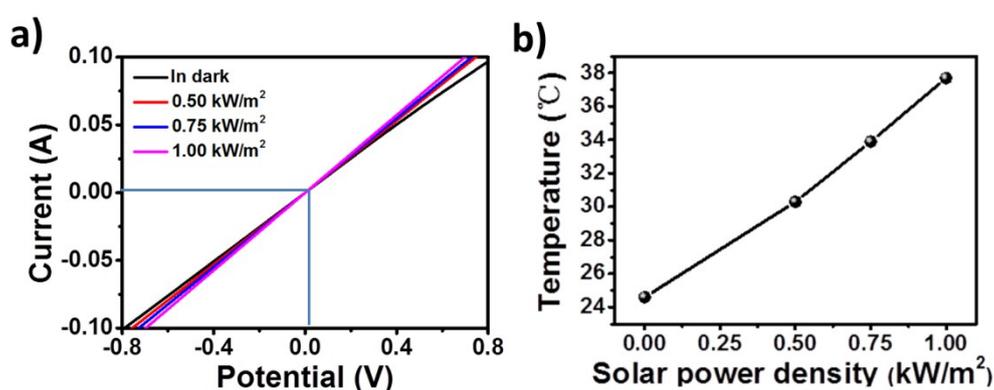
**Figure S5.** Photo-sensitive properties of bare graphene electrode and its derived supercapacitor. (a-c) CV curves (a), GCD curves (b) and Nyquist plots (c) of the supercapacitor based on bare graphene electrodes under illumination of simulated sunlight with different power intensities, respectively. (d) I-V curves of bare graphene electrode under illumination of simulated sunlight with different intensities. (e) The dependence of electrical resistance of bare graphene electrode on intensities of simulated sunlight. (f) The dependence of temperature of bare graphene electrode on intensities of simulated sunlight.



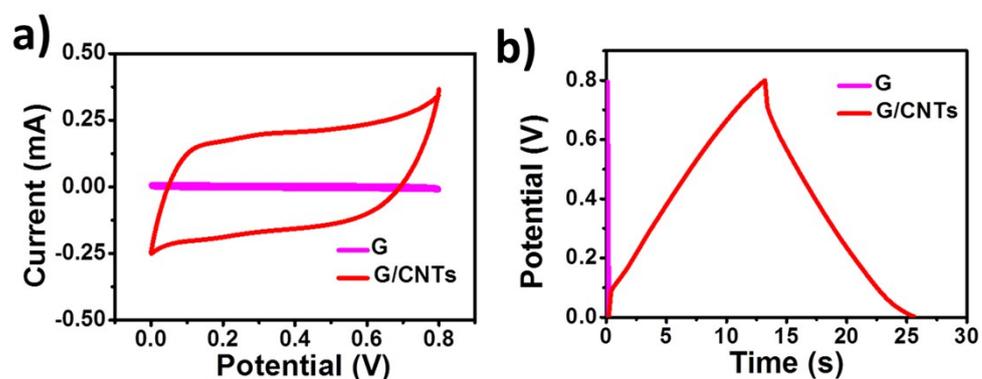
**Figure S6.** Photo-sensitive properties of supercapacitor based on bare CNTs film electrodes. (a-c) CV curves (a), GCD curves (b) and Nyquist plots (c) of the supercapacitor under illumination of simulated sunlight with different power intensities, respectively.



**Figure S7.** The equivalent circuit (simulated by Z-view) of the supercapacitor with photo-induced enhancement effect.  $R_S$ ,  $R_P$  and CPE represent equivalent series resistance, polarization resistance and constant phase element.

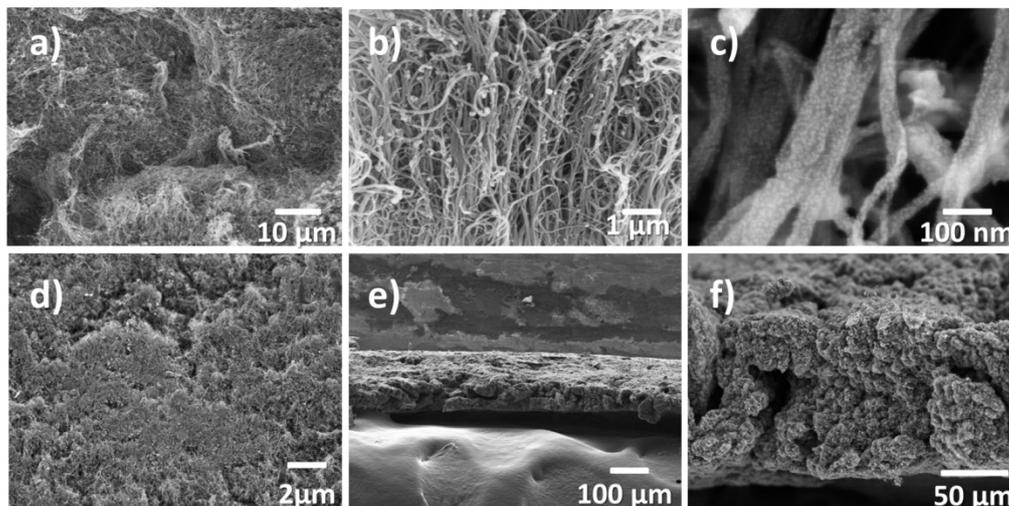


**Figure S8.** (a) I-V curves of G/CNTs electrode under illumination of simulated sunlight with different power intensities. (b) The dependence of temperature of G/CNTs electrode on intensities of simulated sunlight.

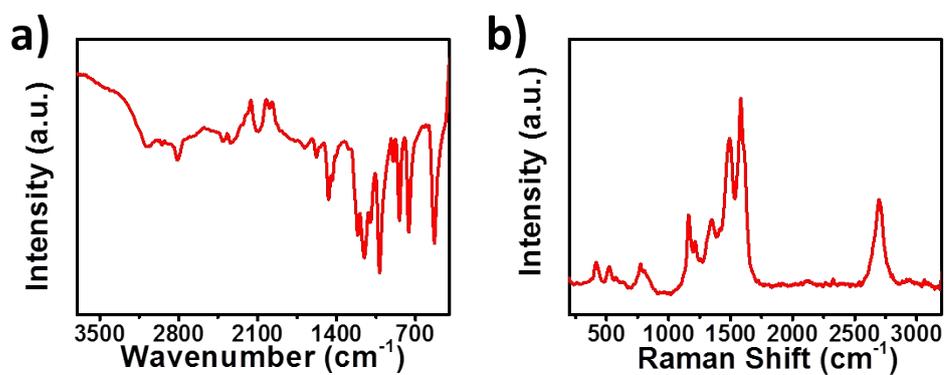


**Figure S9.** CV curves (a) at a scanning speed of 0.01 V s<sup>-1</sup> and GCD curves (b) under charge/discharge current of 1 mA of supercapacitors based on bare graphene (G) and

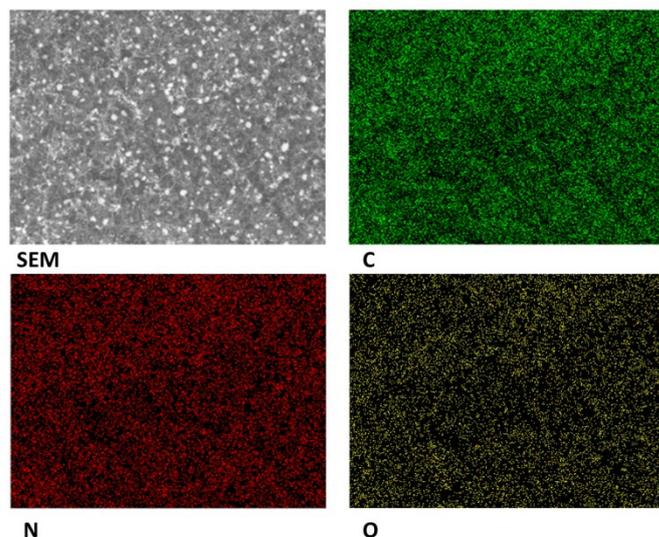
G/CNTs electrodes, respectively.



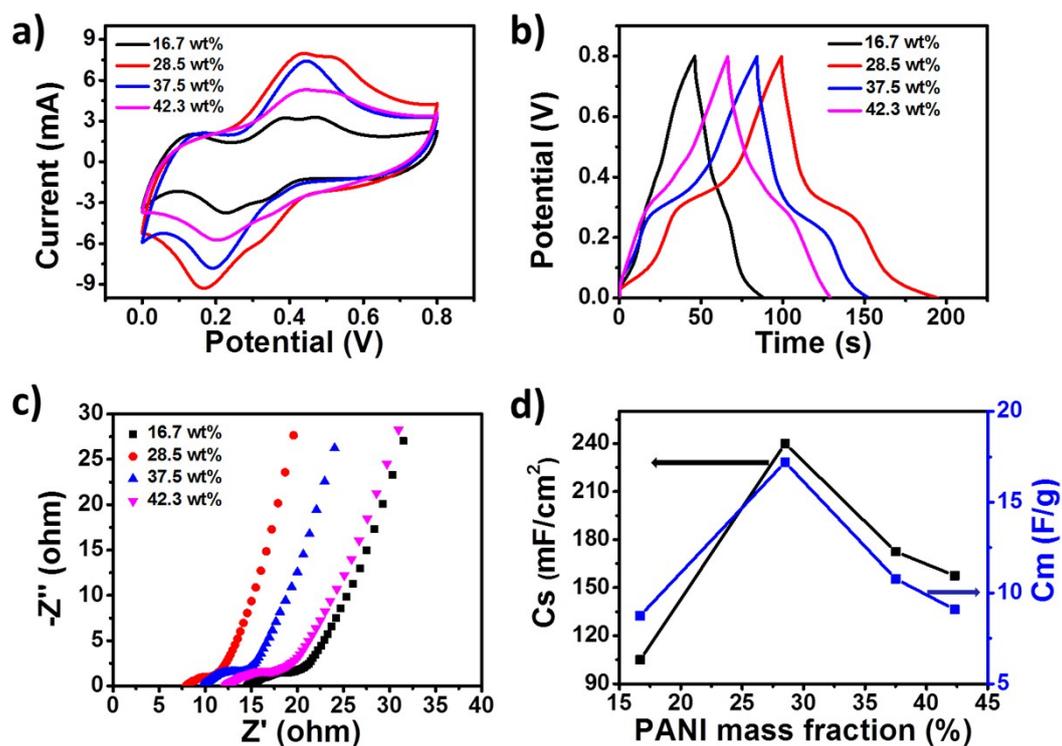
**Figure S10.** (a-c) SEM images of as-prepared G/CNTs/PANI under different magnifications. (d) SEM image of the pressed G/CNTs/PANI film with compact structure. (e, f) SEM images of the pressed G/CNTs/PANI film from side view.



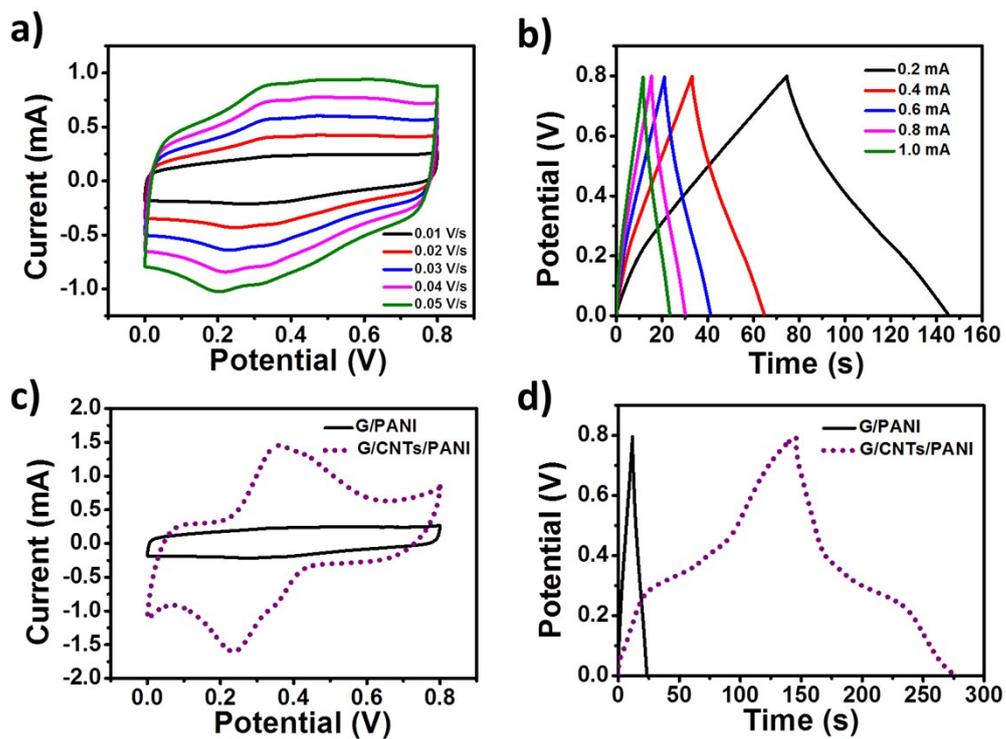
**Figure S11.** Infrared spectrum (a) and Raman spectrum (b) of G/CNTs/PANI composite.



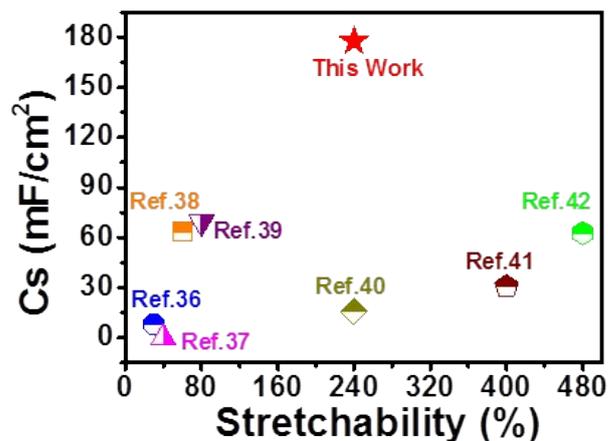
**Figure S12.** EDS mapping of carbon, nitrogen and oxygen elements in G/CNTs/PANI composite.



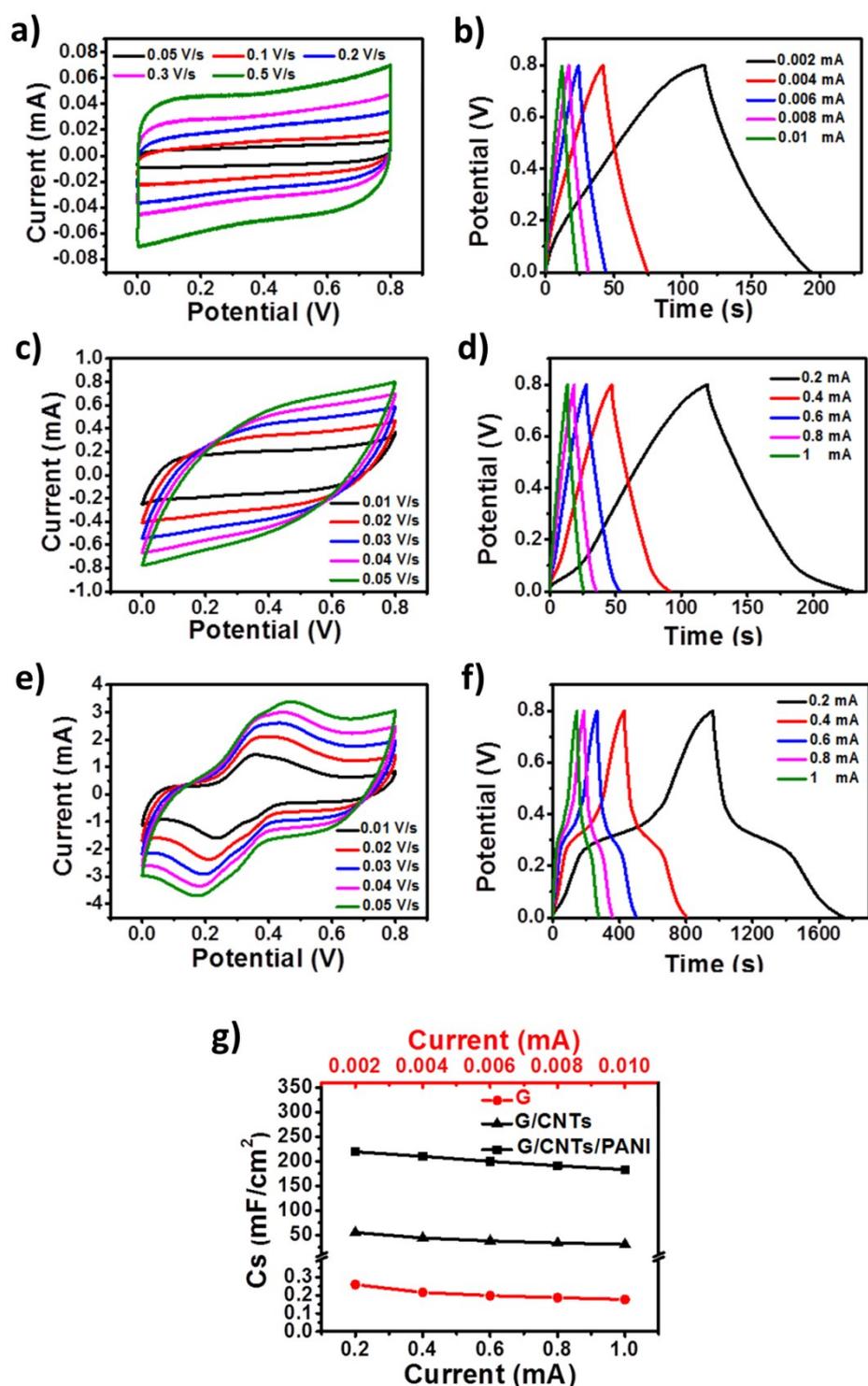
**Figure S13.** (a-c) CV, GCD and EIS curve of supercapacitors based on G/CNTs/PANI with different mass loading of PANI, respectively. (d) Dependence of specific capacitance of supercapacitors on the different mass loading of PANI in G/CNTs/PANI.



**Figure S14.** (a) CV curves of the supercapacitors based on G/PANI at different scan rates. (b) GCD curves of the supercapacitors based on G/PANI under different charge/discharge current. CV curves (c) at a scan rate of  $0.01 \text{ V s}^{-1}$  and GCD curves (d) under charge/discharge current of  $1 \text{ mA}$  of supercapacitors based on G/PANI and G/CNTs/PANI, respectively.

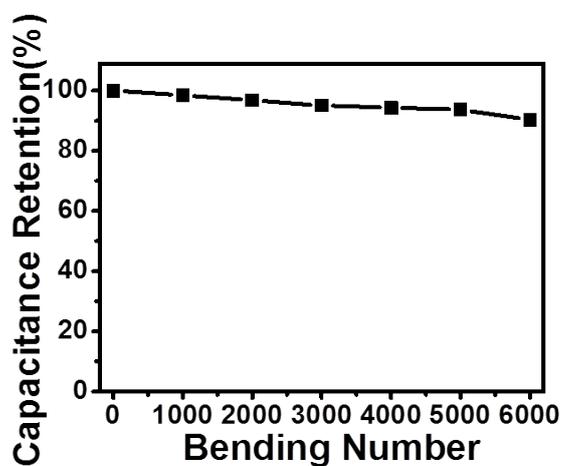


**Figure S15.** Specific capacitances versus stretchability of our supercapacitor compared with those of previously reported stretchable supercapacitors.

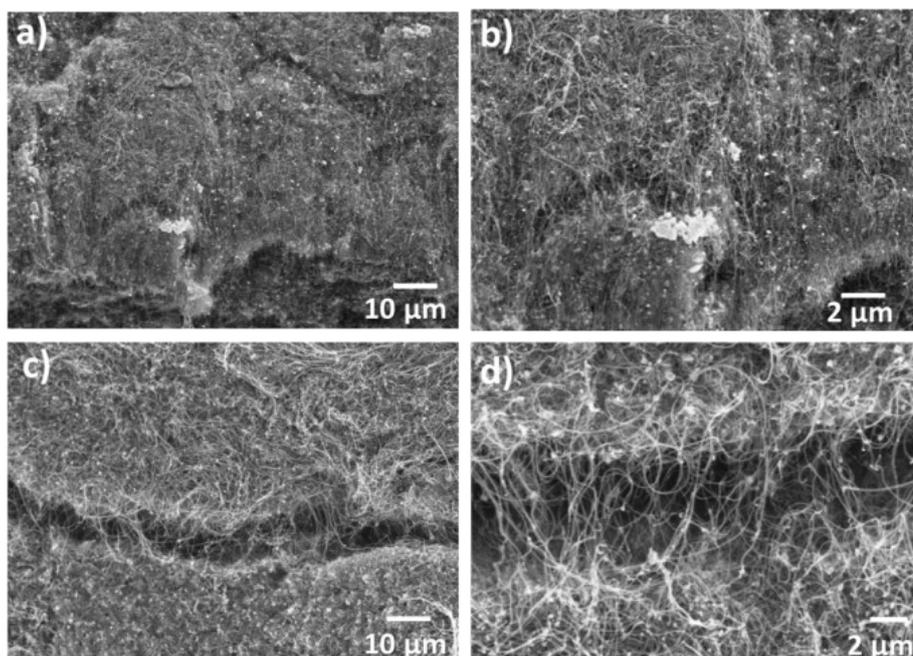


**Figure S16.** CV curves of the supercapacitors based on G (a), G/CNTs (c) and G/CNTs/PANI (e) electrodes at different scan rates, respectively. GCD curves of the supercapacitors based on G (b), G/CNTs (d) and G/CNTs/PANI (f) electrodes under different charge/discharge current. (g) Dependence of specific capacitance of supercapacitors based on G, G/CNTs and G/CNTs/PANI electrodes on the

charge/discharge current.



**Figure S17.** Capacitance retention of a supercapacitor during 6000 bending cycles.



**Figure S18.** (a-b) SEM images of G/CNTs hybrid material after being bent. (c-d) SEM images of G/CNTs hybrid material after being stretched. It can be seen that there were many CNTs well contacted with each other even in the crack area after bending or stretching.