Supporting Information

Designing free-standing 3D lamellar/pillared RGO/CNTs aerogels with ultra-high conductivity and compressive strength for elastic energy devices

Zilin Chen,[a] Yunlong Yang,[a] Tian Lv,[a] Yanan Liu,[a] Yunlong Qi,[a] Keyi Dong,[a] Shaokui Cao,[b] and Tao Chen*[a]

[a]Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China

[b]School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, 450001, China

*Corresponding mails: tchen@tongji.edu.cn

Experimental Section

1. Synthesis of RGO aerogel

The GO solution (5 mg mL^{-1}) was sonicated for 10 minutes before usage. graphene oxide (2 mL) and ascorbic acid (15 mg) were mixed in a glass bottle and kept in an oil bath at 95 ℃ for 1 hour. The glass bottle was placed in a refrigerator at -10 °C for 1 hour, and then transferred to an oil bath at 95 °C for further heating for 5 hours to obtain RGO gel. Then the RGO gel was dialyzed in water to remove soluble substances, and freeze-dried for 24 h to obtain RGO aerogel.

2. Synthesis of RGO/CNTs composite aerogel

The catalyst solution for growth of CNTs was a mixed aqueous solution containing ferric nitrate (50 mM), aluminum nitrate (50 mM) and PVA (3 mg mL^{-1}). First, the RGO aerogel was treated by nitrogen plasma for 5 minutes to improve its hydrophilicity, and the plasma-treated RGO aerogel was immersed in the above catalyst solution and vacuumed for 1 hour. The catalyst-loaded RGO aerogel was placed in a vacuum oven to dry overnight at room temperature. The catalyst-coated RGO aerogel was placed in a tube furnace, and heated from room temperature to 750 ^{o}C in 15 minutes with a mixed gas of argon (Ar, 400 sccm) and hydrogen (H_2, 30 sccm), and kept at 750 ^{o}C to grow CNTs with introduction of ethylene (C_2H_4, 90 sccm) for different time (5, 15 and 30 minutes). Finally, the hydrogen and ethylene were turned off, and the RGO/CNTs composite aerogel was obtained by naturally cooling to room temperature in an argon atmosphere.

3. Growth of MnO_2 on RGO/CNTs composite aerogel

The electrochemical deposition method was used to grow MnO_2 nanospheres in the RGO/CNTs composite aerogel. A RGO/CNTs composite aerogel, a saturated calomel electrode and a platinum sheet were used as the working electrode, the reference electrode and counter electrode, respectively. The electrolyte was a mixed aqueous solution containing $MnSO_4$ (0.05 M), CH_3COONa (0.05 M), and ethanol (10vol%). Electrochemical deposition was performed at constant current density of 5.0 mA cm^{-2} for 35 minutes. The as-prepared RGO/CNTs/MnO_2 composite aerogel was washed alternately with deionized water and ethanol three times, followed by drying in a

vacuum oven at 60 °C.

4. Fabrication of asymmetric supercapacitors

The PVA/LiCl gel solution was used as the polymer electrolyte, which was obtained by adding 1.0 g LiCl and 1.0 g PVA into 10 mL deionized water and stirring at 83 ^{o}C. PET (polyethylene terephthalate) film was used as substrate, and conductive ink (served as current collector for supercapacitors) was coated on PET film. The as-prepared RGO/CNTs and RGO/CNTs/MnO_2 were placed on PET films coated with conductive ink, respectively, and dried in an oven at 120 ^{o}C. All the electrodes were treated with nitrogen plasma for 5 minutes to improve their hydrophilicity, followed by solution-coating of PVA/LiCl gel electrolyte on the electrodes and vacuumed overnight to make the electrolyte completely penetrate into the electrode materials. Finally, the gel electrolyte-coated positive and negative electrodes were pressed together to obtain the asymmetric supercapacitor.

5. Synthesis of ZnO nanorods

The KOH solution (0.03 M) was added drop-by-drop to the $Zn(CH_3COO)_2$ solution (0.01 M), and heated at 60 °C for 2 hours to obtain the ZnO seeds solution. The RGO/CNTs was placed in the above solution and stirred at 60 °C for 4 hours to grow ZnO seeds. Then, the ZnO seeds-coated RGO/CNTs aerogels were immersed in a mixed solution of $Zn(NO_3)_2$ (0.1 M)/HMT (0.1 M) mixture solution in an autoclave, and heated at 85 °C for 7 hours to obtain the RGO/CNTs/ZnO.

6. Preparation of piezoelectric nanogenerator

The piezoelectric nanogenerator was prepared by placing RGO/CNTs/ZnO between two PET films coated with Al foils. Specially, a PDMS solution was prepared from a PDMS prepolymer and curing agent at a ratio of 10:1, then the PDMS solution was spin-coated on the RGO/CNTs/ZnO and cured in the oven at 80 °C for 1 h. Finally, the two current collectors are connected to the copper wire with silver paste to obtain the piezoelectric nanogenerator.

7. Finite element (FE) simulation of RGO aerogel and RGO/CNTs composite aerogel

ANSYS finite-element software was used to numerically simulate RGO aerogels

and RGO/CNTs composite aerogels. Specifically, the RGO layered structure and carbon nanotubes are simulated by SHELL188 and LINK180 units, respectively. The ratio between RGO and CNTs was 1:4 in approximate model, and a vertical axial force of 1 newton was applied to the aerogels. Based on this, the APDL command stream is compiled to complete the modeling, run the calculation and obtain the cloud diagram of the structural displacement and stress distribution.

8. Characterizations

Characterizations of the morphologies and structures of RGO, RGO/CNTs and MnO_2 were performed by high-resolution field-emission scanning electron microscopy (FESEM, Hitachi S-4800), high-resolution transmission electron microscopy (HRTEM, JEOL-2010), and X-ray diffraction spectroscopy (XRD, D8 Advance, Bruker) with Cu Kα radiation (V=30 kV, I=25 mA). Raman spectra were recorded on Raman spectrometer (Renishaw) equipped with a 514 nm laser. The current-voltage curves of aerogels were measured by a Keithley Model 2400 to test their electrical resistance. The sample size of RGO aerogel was 0.7 cm×0.06 cm, RGO/CNTs aerogel was 0.7 cm×0.02 cm. The mechanical properties of materials and devices were tested in a universal mechanical test machine (HY-0350, Shanghai Hengyi Co. Ltd). The electrochemical performance of devices was tested with an electrochemical workstation (CHI 760E, Chenhua, Shanghai).

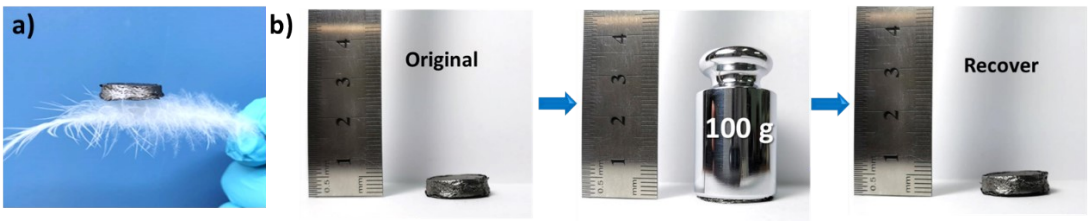

Fig. S1 The digital photographs showing the lightweight (a) and good mechanical property (b) of RGO aerogel.

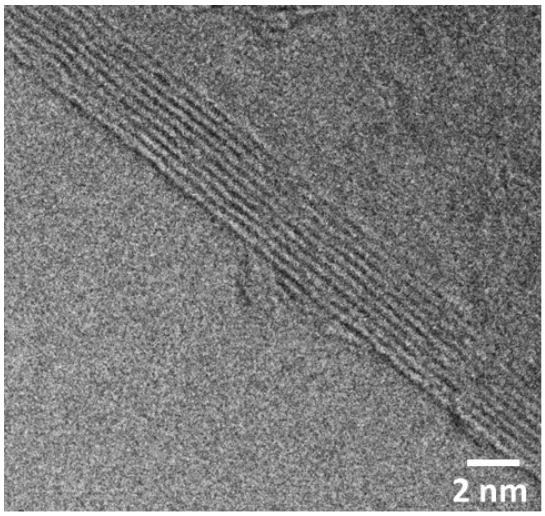

Fig. S2 TEM image of reduced graphene oxide.

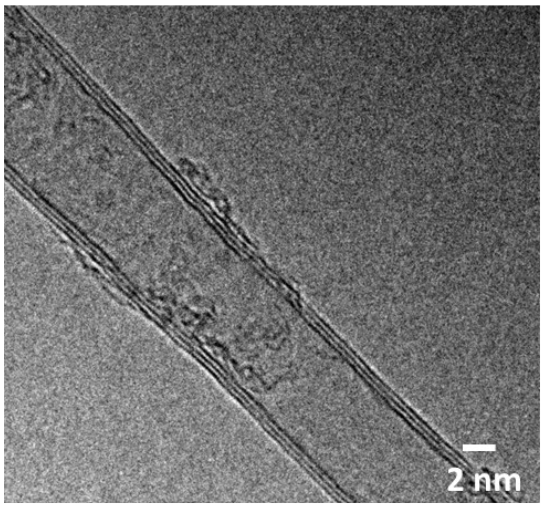

Fig. S3 TEM image of CNT.

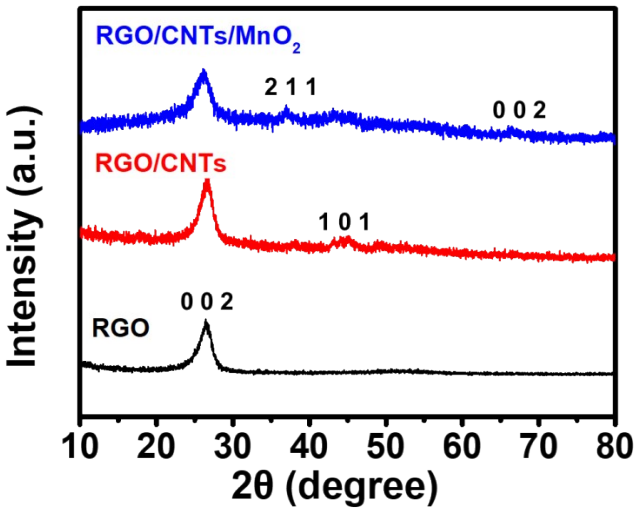

Fig. S4 XRD spectra of RGO, RGO/CNTs and RGO/CNTs/MnO_2 aerogels.

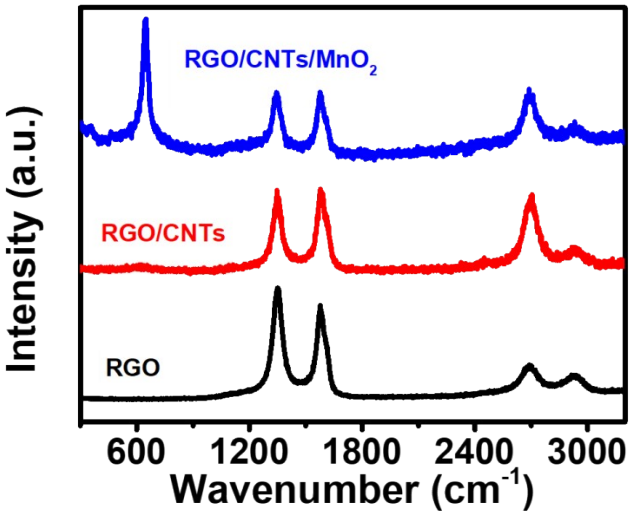

Fig. S5 Raman spectra of RGO, RGO/CNTs and RGO/CNTs/MnO_2 aerogels.

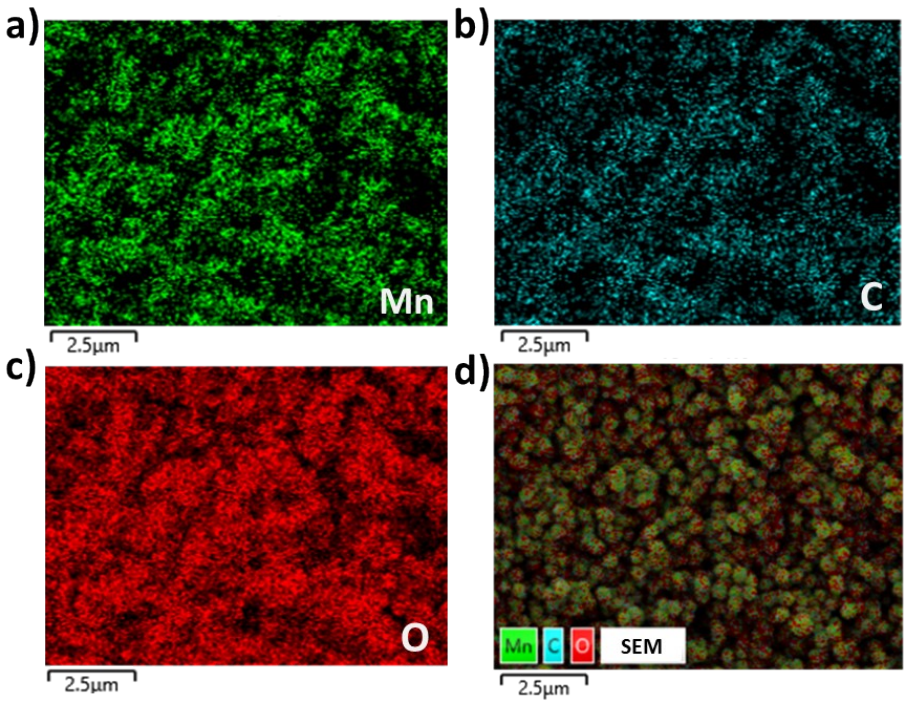

Fig. S6 EDS mapping of manganese (a), carbon (b) and oxygen (c) elements in RGO/CNTs/MnO_2 aerogel. (d) The three elements were overlay on the SEM image.

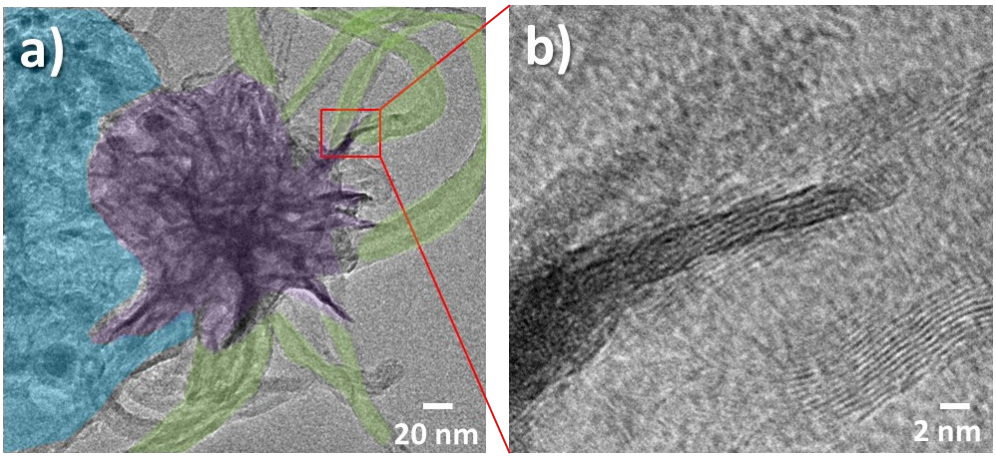

Fig. S7 (a) TEM image of RGO/CNTs/MnO_2 (The blue area represents RGO, the green represents carbon nanotubes, and the purple represents manganese dioxide). (b) TEM image of MnO_2 at high magnification.

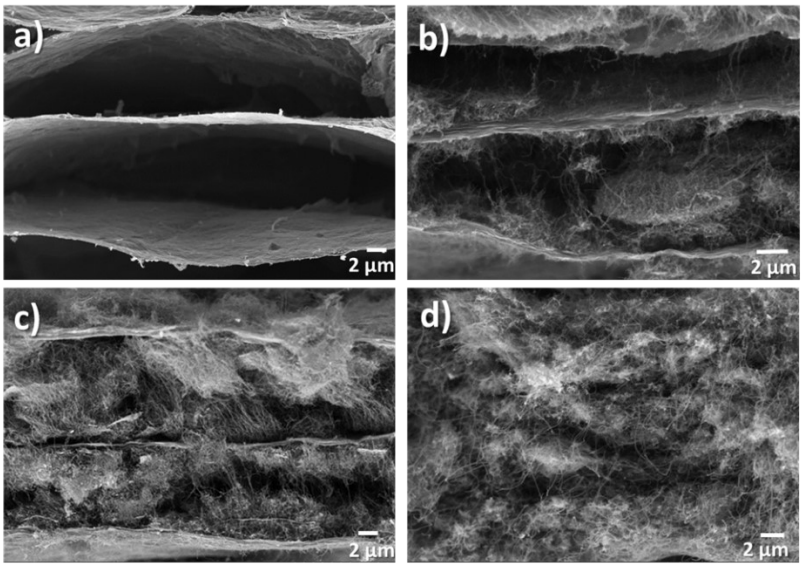

Fig. S8 (a) SEM image of RGO layers. (b-c) SEM images of RGO/CNTs aerogels with growing of CNTs for 5 mins (b), 15 mins (c) and 30 mins (d).

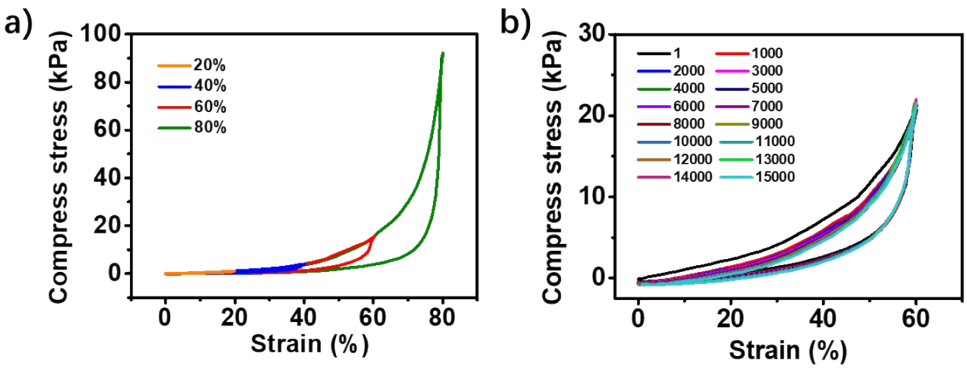

Fig. S9 Stress-strain curves RGO/CNT/MnO_2 aerogel under different compressive strains (a) and under different compressing cycles (b).

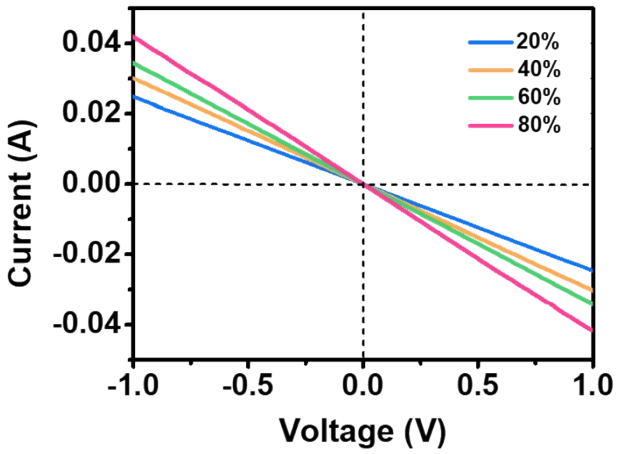

Fig. S10 I-V curves of RGO/CNTs under different compressive strains.

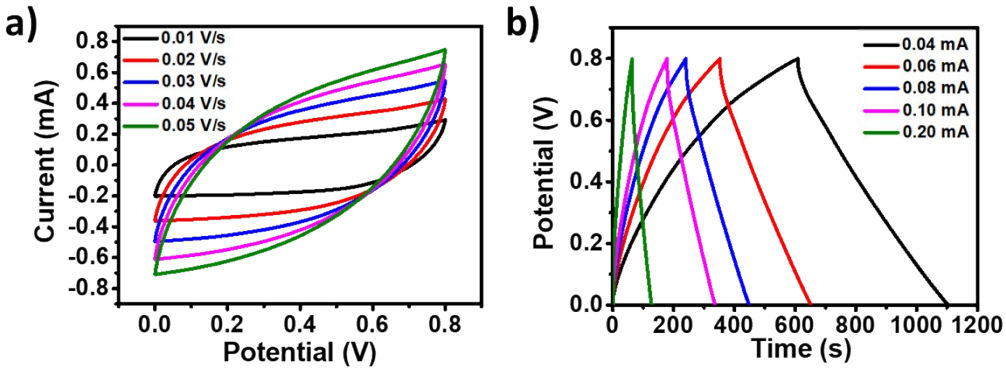

Fig. S11 CV curves at different scanning speeds (a) and GCD curves under different charge and discharge currents (b) of symmetric supercapacitor based on bare RGO aerogel electrodes.

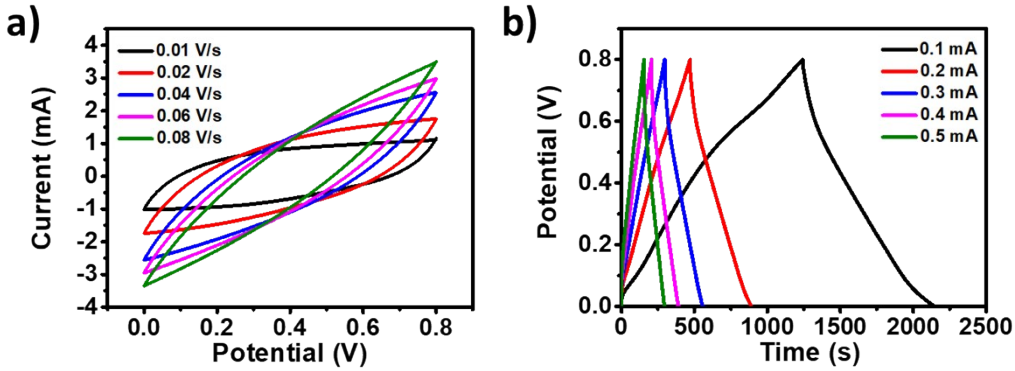

Fig. S12 CV curves at different scanning speeds (a) and GCD curves under different charge and discharge currents (b) of symmetric supercapacitor based on RGO/CNTs aerogel electrodes.

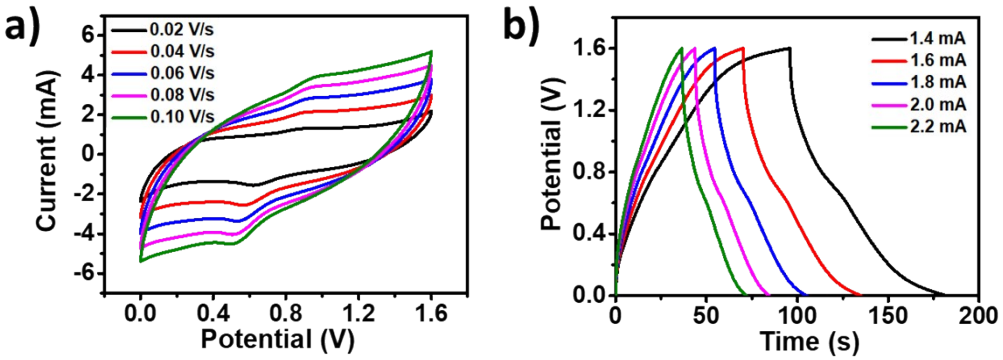

Fig. S13 CV curves at different scanning speeds (a) and GCD curves under different charge and discharge currents (b) of asymmetric supercapacitor based on RGO/CNTs/MnO_2 composite aerogel electrodes.

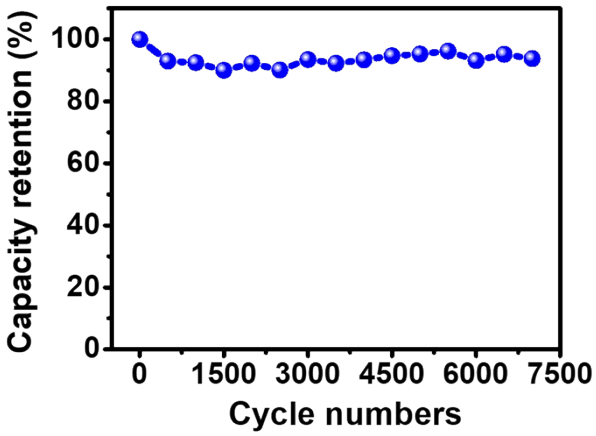

Fig. S14 Cyclic stability of an ASC based on RGO/CNTs/MnO_2 composite aerogel electrodes.

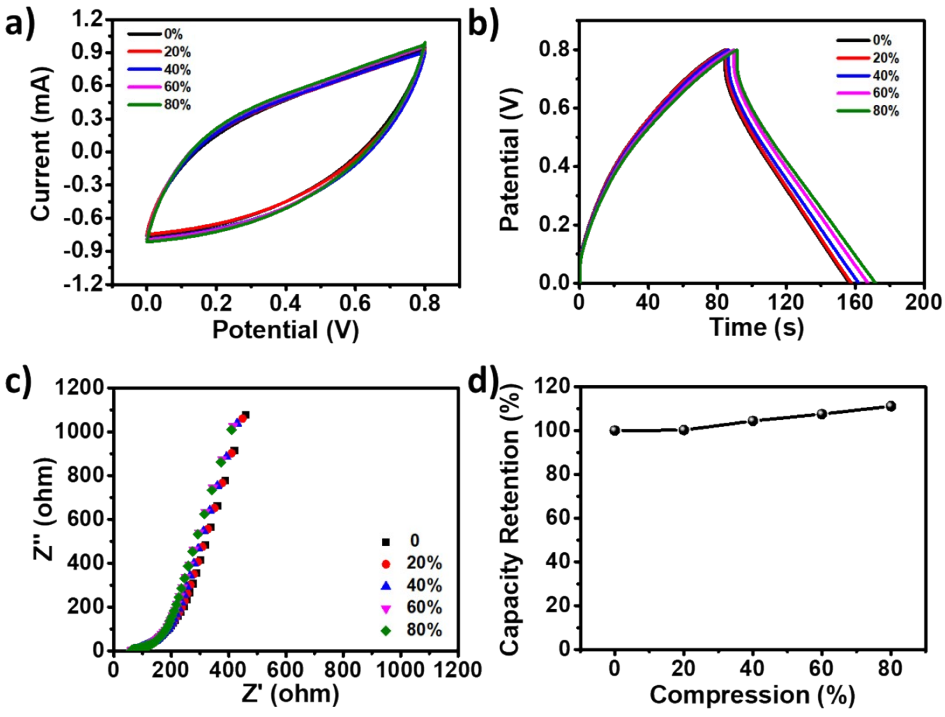

Fig. S15 CV curves (a), GCD curves (b) and EIS (c) of the supercapacitor based on RGO aerogel electrodes under different compressive strains. (d) The specific capacitance retention of the device under different compressive strains.

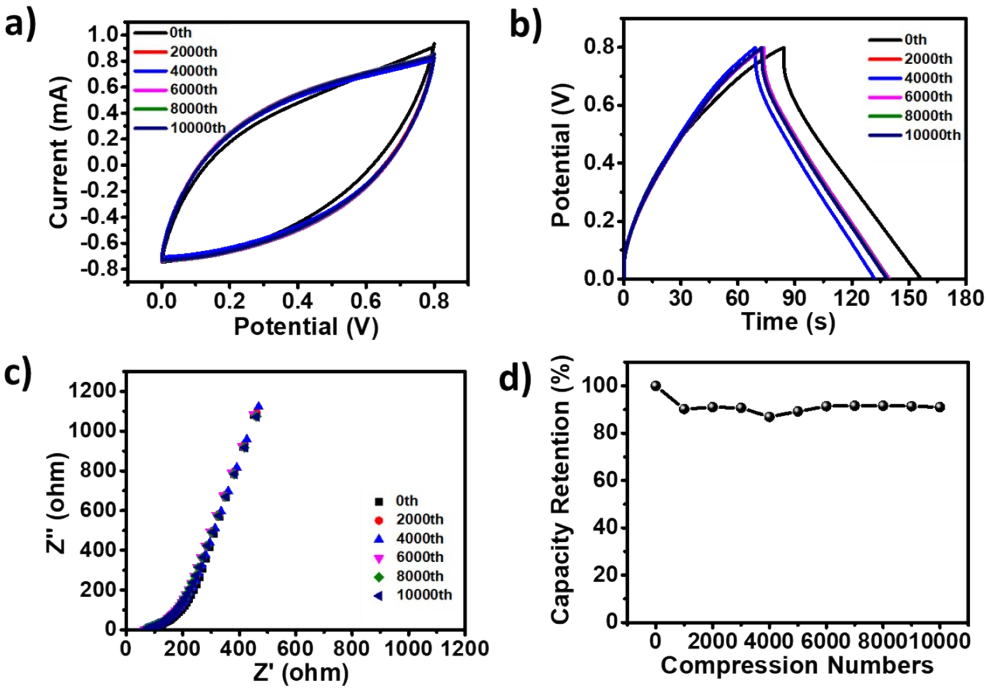

Fig. S16 CV curves (a), GCD curves (b) and EIS (c) of the supercapacitor based on RGO aerogel electrodes under different compressing cycles. (d) The specific capacitance retention of the device under different compressing cycles.

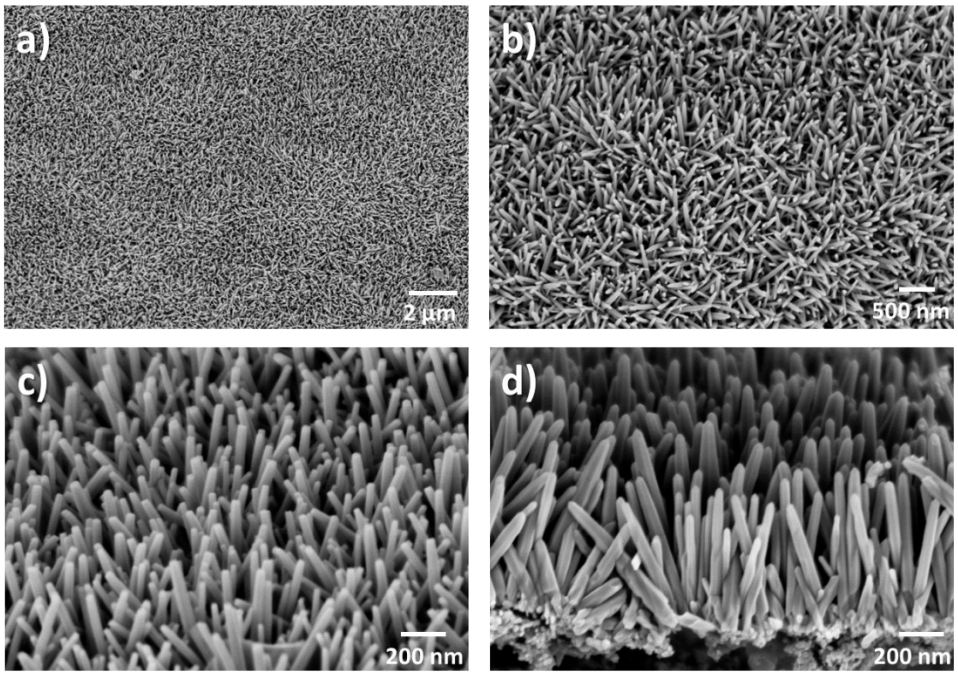

Fig. S17 SEM images of ZnO nanorods from the top view (a-c) and cross-section view (d).

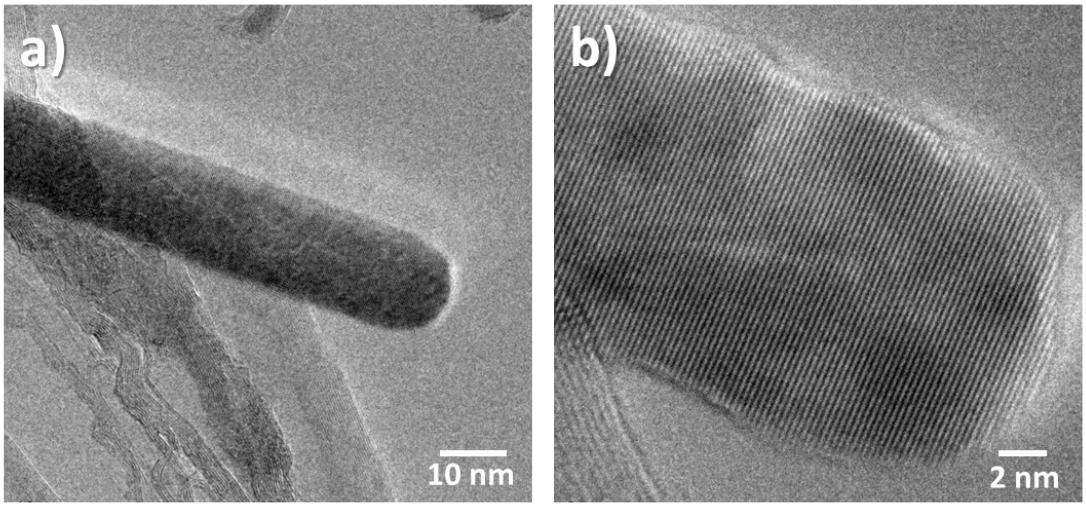

Fig. S18 TEM images of ZnO nanorod at low (a) and high (b) magnifications.

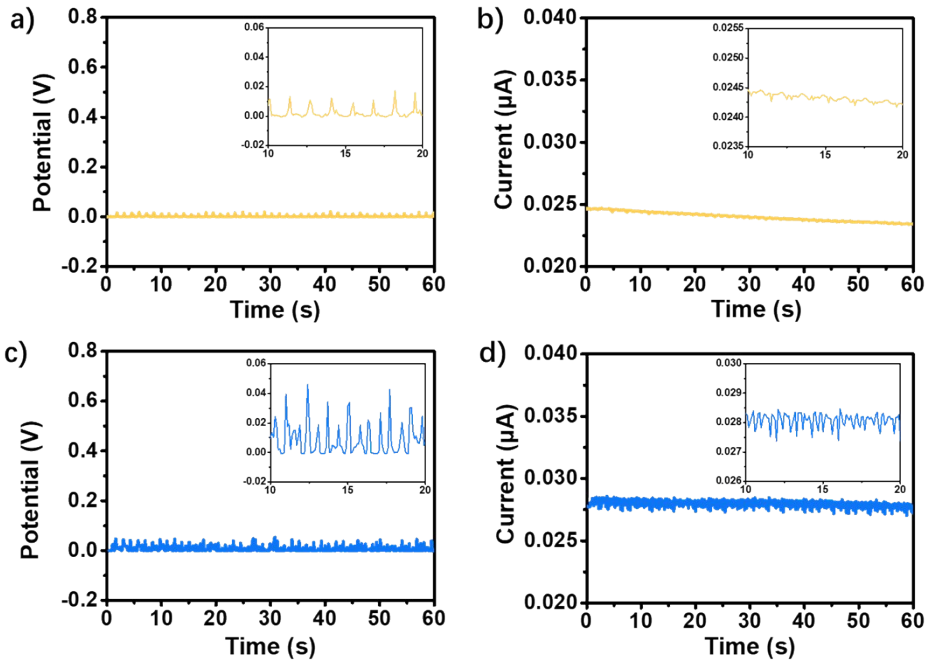

Fig. S19 Output voltage (a) and current (b) of RGO-based PENG. Output voltage (c) and current (d) of RGO/CNTs-based PENG.