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Supporting Information

Compressible and Conductive Carbon Aerogels from Waste Paper with Exceptional Performance for Oil/Water Separation

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Experimental Section

Materials: Office paper, newspaper and cardboard were randomly collected in daily life. SC, anhydrous ethanol, methylene blue, oil red O, dichloroethane, cyclohexane, *n*-hexane, tetrachloromethane and toluene were purchased from China National Medicines Co., Ltd., China. Other reagents used were all of analytical grade. Deionized water was used throughout the experiment. All chemicals were used as received without further purification.

Measurement of Oil Absorption Capacity: A piece of 3C aerogel was immersed in different oils at room temperature. The sample was taken out of the oils after 1 min, drained for several seconds and wiped with filter paper to remove excess oil. The oil absorption capacity Q of the sample was determined by weighing the sample before and after absorption and calculated according to the following equation:

$$Q = (m_t - m_i)/m_i \tag{1}$$

where m_t is the weight of the wet sample with absorbed oil (g) and m_i is the weight of the dry sample (g). Measurements of the weight of the samples were completed in ten seconds after taken out of the oils to avoid the influence of oil evaporation on accuracy of the results.

Porosity $\emptyset$ of the sample was calculated using the following equation:

$$\emptyset = \left(1 - \frac{\rho_0}{\rho}\right) \times 100\% \tag{2}$$

where ρ_0 is the bulk density of the 3C aerogel and ρ is the skeletal density of the 3C aerogel.

Gravity-Driven Oil/Water Separation: The Span 80 stabilized water-in-toluene emulsion was prepared by mechanically stirring the mixture of deionized water and toluene (1:99, v/v) at 1000 rpm for 20 min. The concentration of Span 80 in the emulsion is 1.0 mg mL^{-1}. The emulsion was stable over 24 h in room conditions without any demulsification or precipitation, and was freshly prepared before use. The droplet sizes are in the range of several hundreds of nanometers to 25 μm. The dyed emulsion was prepared according to the same procedure using the 100 ppm MB solution in water and the 100 ppm oil red O solution in toluene.

The 3C aerogel 16.0 mm in diameter and 17.0 mm in length was fitted into a glass tube with an inner diameter of 15.5 mm. When the water-in-toluene emulsion was filtrated through the aerogel, water and dyes were removed and the cleaned toluene, the filtrate, was collected in the vial below the glass tube. The water concentration in the filtrate was measured using a C20 Compact Karl Fischer Coulometer (Mettler Toledo, Switzerland). The concentration of MB and oil red O in the filtrate was recorded using a UV-Vis spectrophotometer (Specord 200, Analytik Jena AG) at their maximum absorbance wavelengths. The removal efficiency of water (RE_{water}) in the emulsion was calculated using the following equation:

$$RE_{\mathrm{water}} = (c_0 - c_{\mathrm{f}}) / c_0 \times 100 \tag{3}$$

where c_0 is the initial water concentration in the emulsion (ppm), c_{f} is the water concentration in the filtrates (ppm).

Characterization: The micrographs of the samples were taken using a field emission SEM (JSM- 6701F, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold (~7 nm). Digital micrographs of samples were taken using a Leica DM1000 microsystem (CMC GmbH, Germany). XRD patterns were obtained on X'pert PRO diffractometer with working conditions of Cu Kα, 30 mA and 40 kV (λ = 1.54060 Å). The scanning was made at room temperature between 10 ° and 90 ° in 2θ with a scanning speed of 0.02 ° per second. FTIR spectra of the samples were recorded on a Nicolet NEXUS FTIR spectrometer using potassium bromide pellets. XPS spectra were obtained using a VG ESCALAB 250 Xi spectrometer equipped with a monochromated Al Kα X-ray radiation source and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C 1s peak at 284.6 eV as the reference. TGA analysis was carried out using a STA 6000 (PerkinElmer Instrument Co., Ltd. USA) to investigate thermal stability of the samples over a temperature range of 25 to 1000 ℃ at a rate of 10 ℃ min^{-1} under N_2 atmosphere. The mechanical properties of samples were measured using a universal testing machine (CMT4304, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) equipped with a 50 N load cell at room temperature. The tests were performed with a gauge length of 20 mm and a loading speed of 10 mm min^{-1}. The electric resistance of the 3C aerogels was measured using a digital multimeter. Measurement of water contact angle was performed at 25 °C using 7 μL water droplets on a Contact Angle System OCA 20 (Dataphysics, Germany). For the contact angle measurement, the syringe was positioned in a way that the droplet of water could contact surface of the samples before leaving the needle. All the measurements were carried out in triple and the average values were presented.

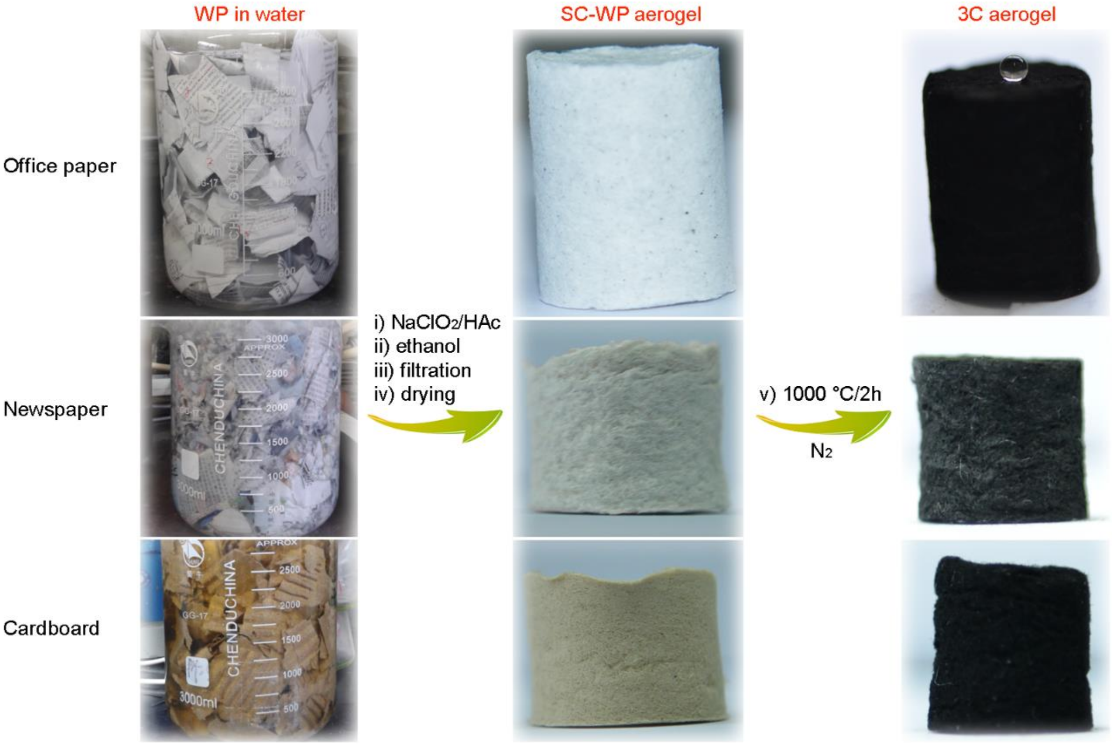

Fig. S1 Preparation of the 3C aerogels using different WP.

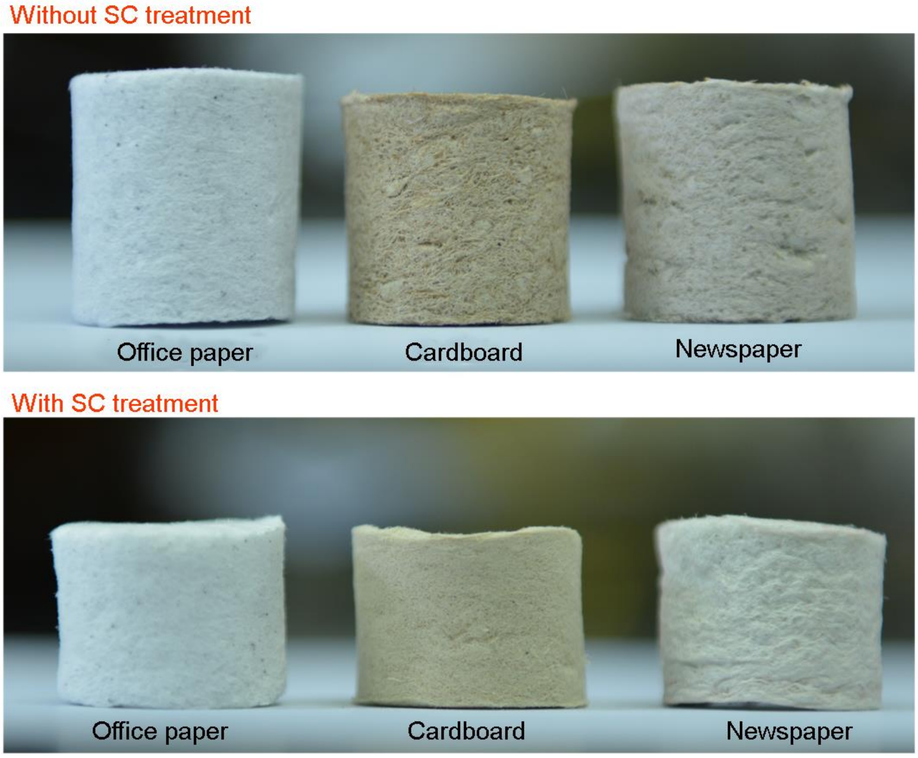

Fig. S2 Effect of SC treatment on macroscopic appearance of the aerogels prepared using different WP.

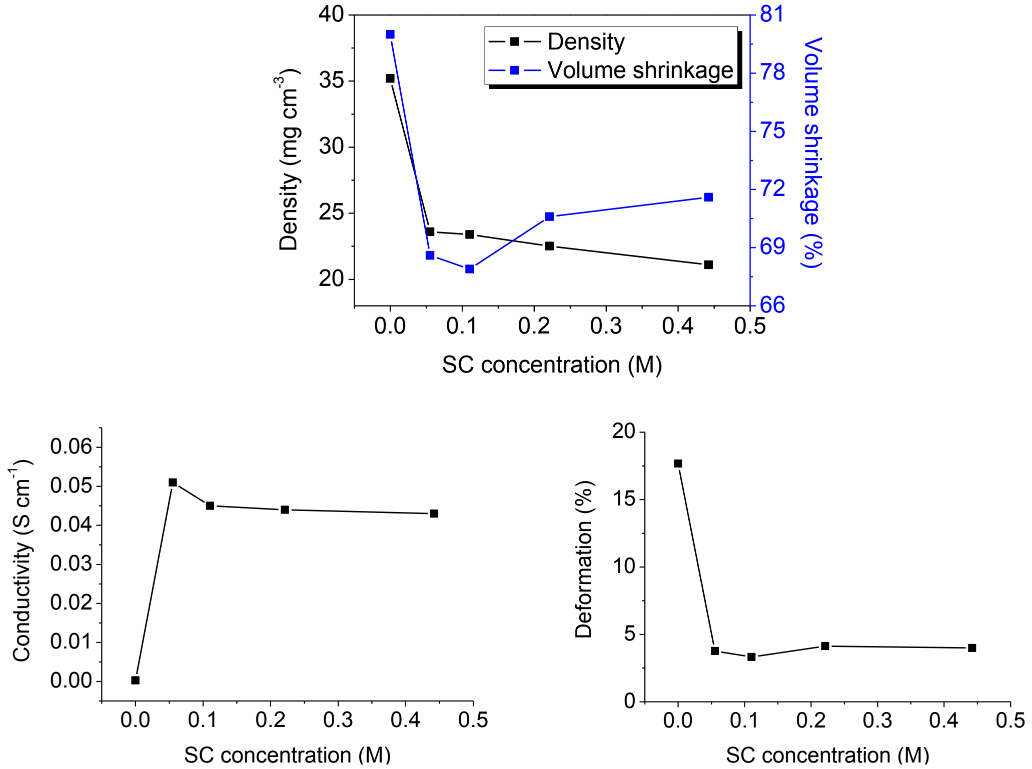

Fig. S3 Variation of (a) density and volume shrinkage, (b) electrical conductivity and (c) deformation in the first cycle of the compressive stress-strain test (50% strain) of the 3C aerogels with SC concentration. Carbonization was carried out at 1000 ℃ for 2 h.

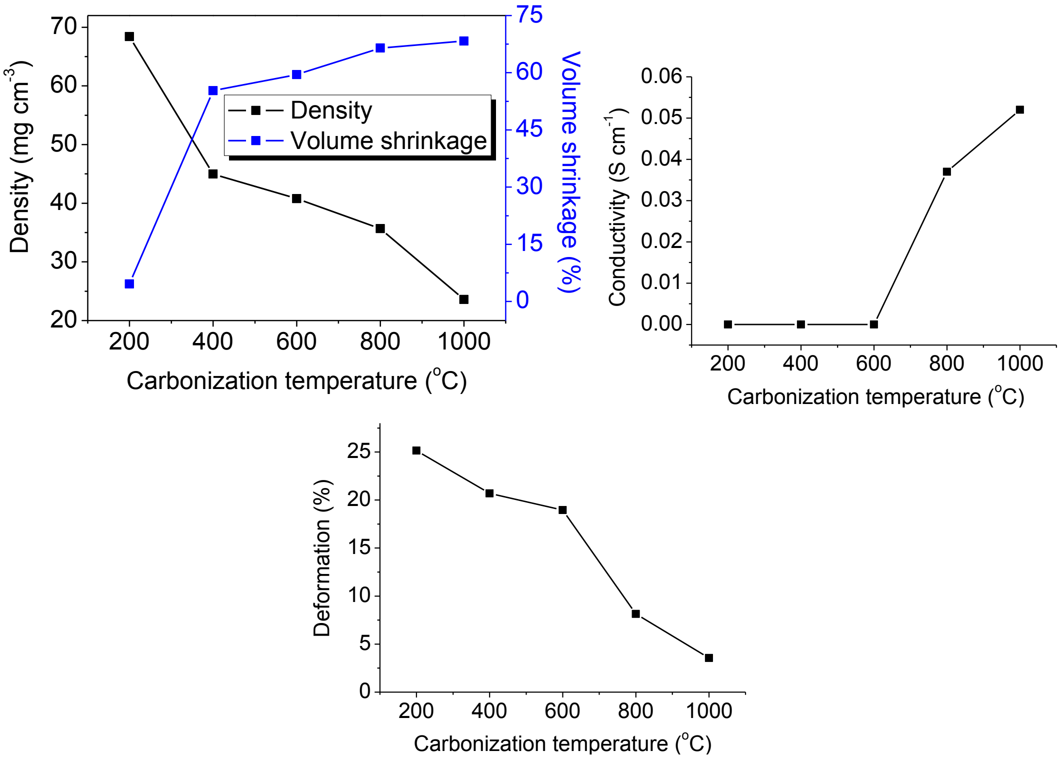

Fig. S4 Variation of (a) density and volume shrinkage, (b) electrical conductivity and (c) deformation in the first cycle of the compressive stress-strain test (50% strain) of the 3C aerogels with carbonization temperature (2 h). WP was treated with 55 mM SC.

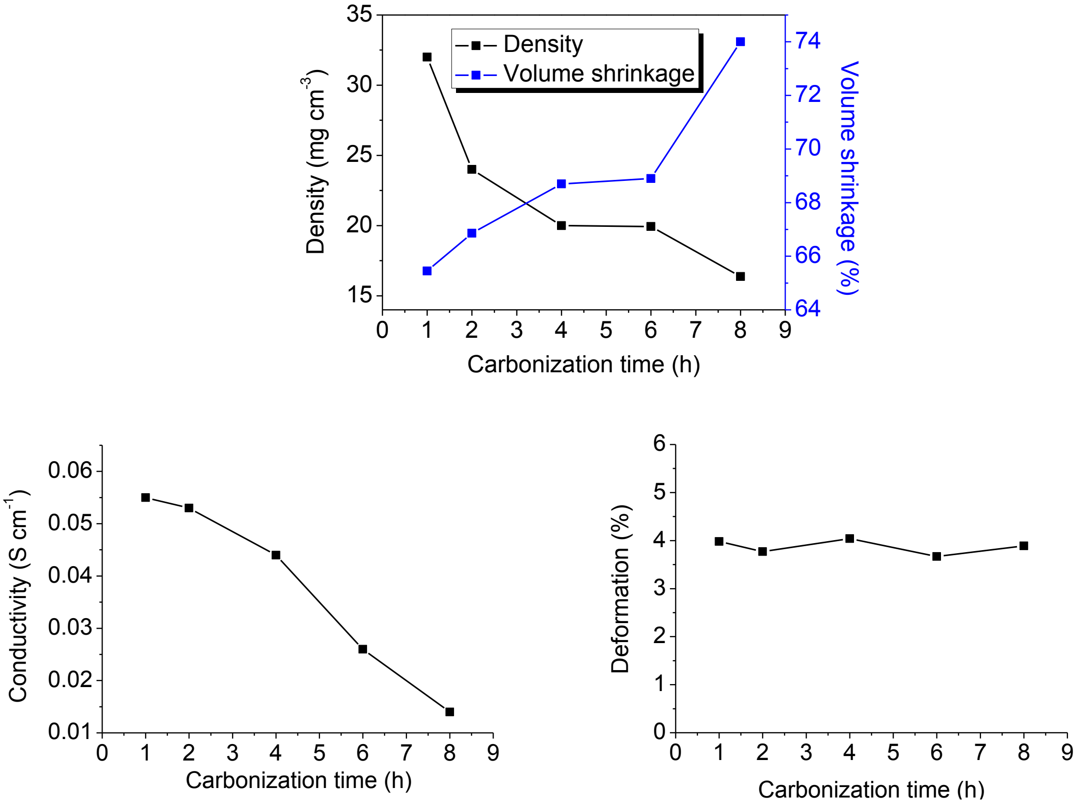

Fig. S5 Variation of (a) density and volume shrinkage, (b) electrical conductivity and (c) deformation in the first cycle of the compressive stress-strain test (50% strain) of the 3C aerogels with carbonization time (1000 ℃). WP was treated with 55 mM SC.

In order to fabricate 3C aerogels with excellent properties, the influences of the SC concentration, carbonization temperature and carbonization time on density, electrical conductivity and compressibility of the 3C aerogels from different WP were systematically investigated. Office paper was used as the representative WP, and the detailed data about newspaper and cardboard were partly shown.

The SC treatment could evidently reduce the density, and enhance the electrical conductivity and compressibility of the 3C aerogels (Fig. S3). After treated with the 55 mM SC solution, the density of the 3C aerogel decreased from 35 to 23.6 mg cm^{-3}, the electrical conductivity enhanced from 2.8×10^{-4} to 0.051 S cm^{-1}, and the deformation in the first cycle of the compressive stress-strain test at 50% strain reduced from 17.67% to 3.77%. This is because SC produced chlorine dioxide under acidic conditions, which decomposed lignin and impurities in WP, and broke a part of hydrogen bonding of cellulose.[1] The further increase in the SC concentration to 440 mM resulted in gradual decrease of the density to 21.1 mg cm^{-3}, but had no obvious influence on the electrical conductivity and compressibility.

The carbonization temperature also has great influences on the properties of the 3C aerogels (Fig. S4). The density of the SC-WP aerogel is 76.6 mg cm^{-3}. With increasing the carbonization temperature to 1000 ℃, the density of the 3C aerogel decreased to 23.6 mg cm^{-3} and the volume shrinkage increased to 68.3%. This means the weight of the resulting 3C aerogel is 9.77% of the SC-WP aerogel. Meanwhile, the aerogel became electrically conductive after carbonization at 800 ℃, and the increase in the temperature to 1000 ℃ could further enhance the electrical conductivity. Also, a higher temperature evidently improved compressibility of the 3C aerogel. For example, in the first cycle of the compressive stress-strain test at 50% strain, the deformation of the aerogel prepared at 400 ℃ is 25.15%, whereas that prepared at 1000 ℃ is only 3.77%. A longer carbonization time at 1000 ℃ could further decrease the density to 16.4 mg cm^{-3} but at a sacrifice of the electrical conductivity (Fig. S5). The increase of the carbonization time from 1 to 8 h has no influence on the compressibility.

Table S1. Electrical conductivity and deformation in the first cycle of the compressive stress-strain test (50% strain) of the 3C aerogels prepared using different WP (55 mM SC and 1000 ℃/2 h).

WP	Electrical conductivity (S cm^{-1})	Deformation (%)
Office paper	0.051	3.77
Newspaper	0.033	4.26
Cardboard	0.021	4.82

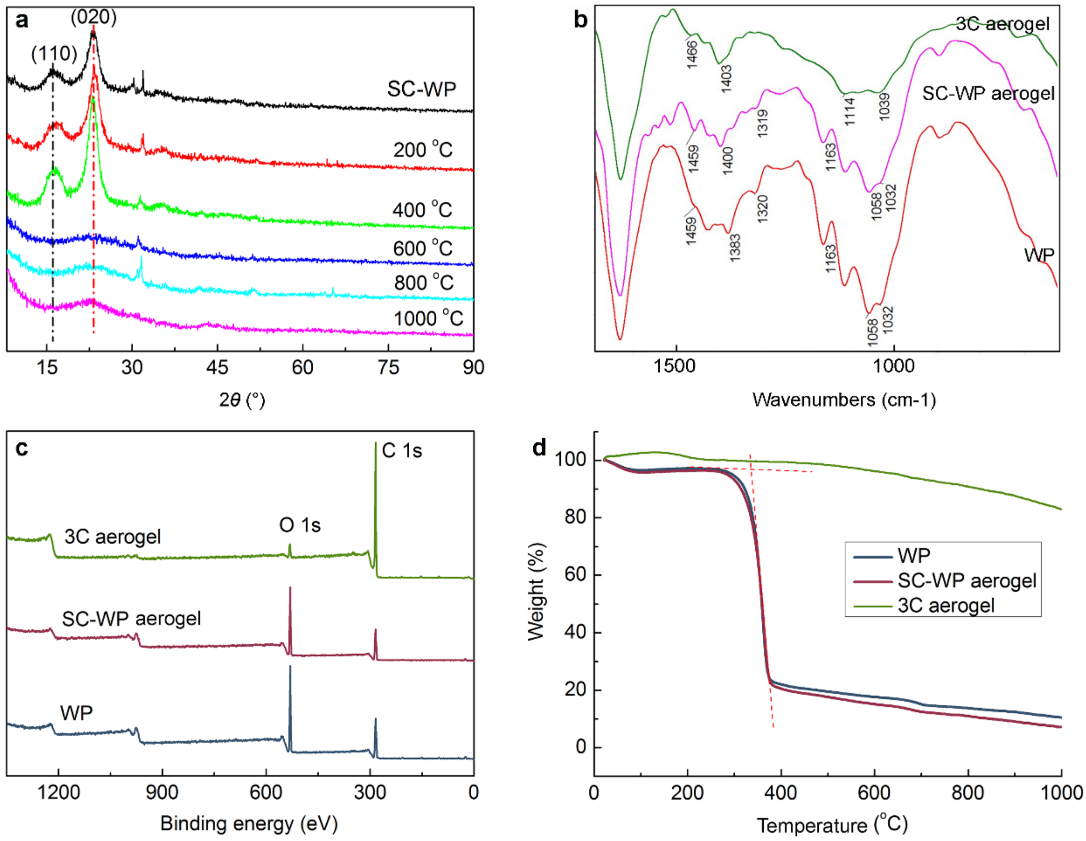

Fig. S6 (a) XRD patterns of SC-WP and the 3C aerogels prepared at different carbonization temperature, (b) FTIR spectra, (c) XPS spectra and (d) TGA curves in N_2 atmosphere of WP, the SC-WP aerogel and the 3C aerogel (55 mM SC and 1000 ℃/2 h).

Table S2. FTIR assignments of the main vibrations in the FTIR spectra of WP, the SC-WP aerogel and the 3C aerogel (55 mM SC and 1000 ℃/2 h).

WP	SC-WP aerogel	3C aerogel
1459 cm^{-1}, O-H in-plane deformation	no change	disappeared
1383 cm^{-1}, C-H bending	disappeared	disappeared
1320 cm^{-1}, CH_2 rocking	no change	disappeared
1163 cm^{-1}, Anti-symmetrical bridge C-O-C stretching	no change	disappeared
1058 cm^{-1}, C-O stretch	no change	disappeared
1032 cm^{-1}, C-O stretch	no change	disappeared

Table S3. Surface chemical composition of WP, the SC-WP aerogel and the 3C aerogel (55 mM SC and 1000 ℃/2 h).

Name	Atomic %		
	WP	SC-WP aerogel	3C aerogel
C 1s	60.7	60.63	98.77
N 1s	1.04	1.02	0
O 1s	38.26	38.35	1.23

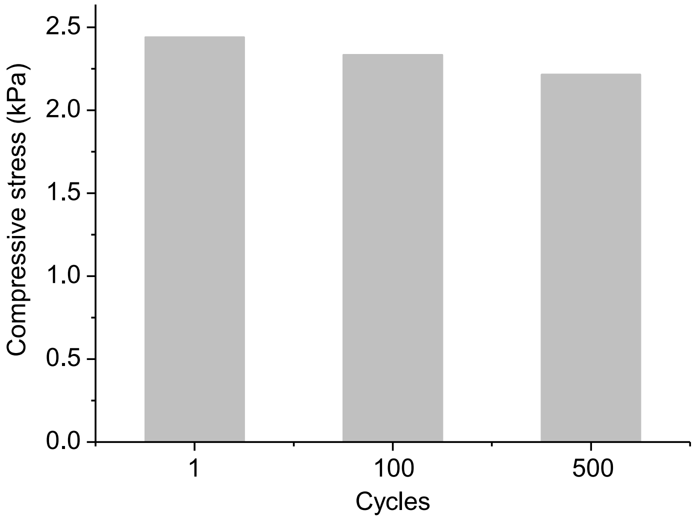

Fig. S7 Maximum compressive stress of the 3C aerogel at 50% strain after different cycles (55 mM SC and 1000 ℃/2 h).

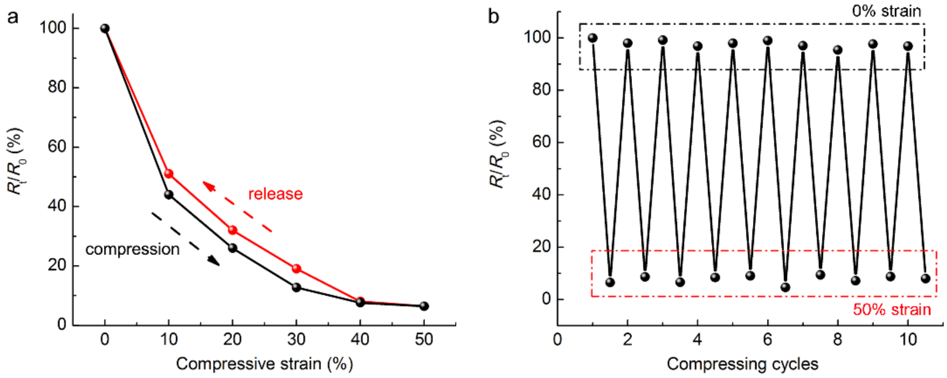

Fig. S8 Variation of R_t/R_0 of the 3C aerogel with (a) compressive strain in one cycle and (b) compressing cycles (50% strain) (55 mM SC and 1000 ℃/2 h).

The electrical conductivity of the 3C aerogel is controllable by the compressive strain (Fig. S8a). As can be seen, the electrical conductivity is highly dependent on the change in the compressive strain. The normalized electrical resistance (R_t/R_0) decreased quickly to 6.4% with the increase of the strain. The R_t/R_0 could almost change back to the initial state after release of the compressive stress. This is owing to the fact that the number of the contacting points among the microfibers is changing with the strain owing to reversible bending of the carbon microfibers in the compression-release process. Compared to most previously reported electrically conductive aerogels, the R_t/R_0 of the 3C aerogel is more sensitive to the strain. Furthermore, the response of R_t/R_0 to the strain of the 3C aerogel is stable in 10 cycles as demonstrated in Fig. S8b owing to its high compressibility.

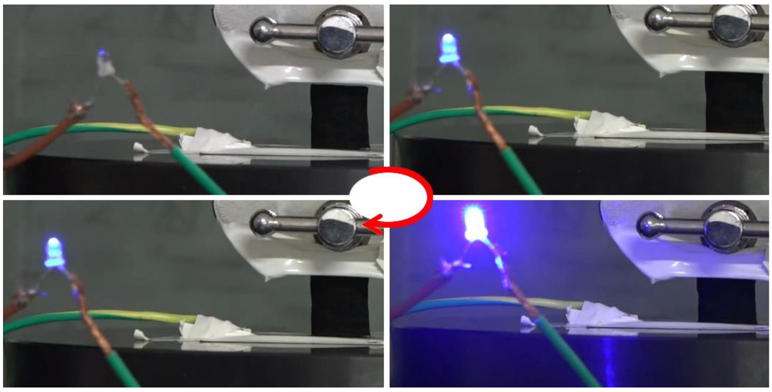

Fig. S9 Reversible and strain-controlled on-off of a light-emitting diode using the 3C aerogel (55 mM SC and 1000 ℃/2 h).

Movie S1. Strain-dependent brightness of the diode linked to a circuit using the 3C aerogel (55 mM SC and 1000 ℃/2 h).

Movie S2. Gravity-driven separation of the Span 80 stabilized water-in-toluene emulsion using the 3C aerogel (55 mM SC and 1000 ℃/2 h).

Movie S3. Gravity-driven separation of the Span 80 stabilized and dyed water-in-toluene emulsion using the 3C aerogel (55 mM SC and 1000 ℃/2 h).

References

[1] J. P. Zhang, L. Wu, Y. J. Zhang, A. Q. Wang *J. Mater. Chem. A* **2015**, 3, 18475-18482.