

# Carbon Fiber Aerogel Made from Raw Cotton: A Novel, Efficient and Recyclable Sorbent for Oils and Organic Solvents

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In order to solve the environmental and ecological problems in the earth arising from the increasing pollution from the crude oil, petroleum products and toxic organic solvents, it is urgent to develop an economic and feasible strategy.<sup>[1–4]</sup> Although many conventional methods such as combustion, the use of oil booms or oil skimmer vessels,<sup>[2]</sup> and sorbents such as expanded perlite,<sup>[5]</sup> zeolites<sup>[6]</sup> and activated carbon,<sup>[7]</sup> have been developed to solve the aforementioned problems, they either show poor efficiency or may introduce other types of contamination during the cleanup procedure.<sup>[2,5–11]</sup>

Carbon-based three-dimensional (3D) networks with outstanding properties, such as low density, high electrical conductivity, high porosity, large specific surface area and chemical inertness, have been extensively investigated and shown much potential in catalyst supports, supercapacitors, gas sensors and so on.<sup>[12–15]</sup> In particular, their low density, high porosity and hydrophobic properties make them attractive candidates for the removal of pollutants and the separation of oil and water. Generally, there are three types of carbon-based 3D frameworks, including organic aerogels pyrolyzed in an inert atmosphere,<sup>[16,17]</sup> sponges of carbon nanotubes (CNTs) or their derivatives fabricated by chemical vapor deposition (CVD),<sup>[18,19]</sup> and graphene-based aerogels from self-gelation.<sup>[4,20,21]</sup> However, the organic aerogels are fragile and dense in weight, and thus are not effective in oil absorption.<sup>[16,17]</sup> In addition, the preparation of CNT-based sponges needs expensive precursors and complex equipment that hamper their massive production for practical applications.<sup>[18,19]</sup> Graphene-based aerogels could be used for sorption

of various oils and organic solvents that was demonstrated by our group,<sup>[4]</sup> presenting a high sorption capacity and outstanding recyclability. However, the use of large amount of chemicals and generation of acidic waste during the preparation of GO seriously restrict their industrialization, which pushes us to explore a facile, economical and environmentally friendly strategy to massive production of carbon-based aerogels.

Due to their low cost, rich source, nontoxicity to humans, etc., materials from the nature are receiving increasing attention.<sup>[12,22,23]</sup> Cellulose is one of the most abundant, sustainable and environmentally friendly materials in nature. Recently, the production of carbon nanofiber aerogels from bacterial cellulose, an artificially synthetic cellulose, has been achieved and the resultant materials presented good performance in sorption of oils and organic solvents.<sup>[12]</sup> However, the production process is complicated and expensive, thus restricting their industrial applications. Raw cotton, a typical natural material, is cheap and sustainable and contains 90–95% cellulose,<sup>[24,25]</sup> making it a promising raw material for fabrication of carbon-based aerogels. Although raw cotton fibers have been used for sorption of dyes,<sup>[26,27]</sup> heavy metals<sup>[28]</sup> and heavy oil,<sup>[29,30]</sup> their poor buoyancy characteristics, low oil-sorption capacity, unsatisfactory hydrophobicity and recyclability, etc. hamper their application in removal and separation of pollutants from water. Herein, lightweight, hydrophobic and porous aerogels made from twisted carbon fibers (TCF) are produced via a facile route by using cotton fibers as raw materials. Importantly, the TCF aerogel can absorb a wide range of organic solvents and oils with a maximum sorption capacity up to 192 times the weight of the pristine TCF aerogel. Moreover, the TCF aerogel also exhibits the excellent recyclability, and maintains a high sorption capacity even after five cycles through distillation, burning or squeezing. We believe that such natural cotton-derived novel carbon aerogel with good performance will have great potential for industrial applications and environmental protection.

A few pieces of purified raw cotton with cylindrical shape (see the experimental section for details) were pyrolyzed at 800 °C for 2 h at a low pressure (~0.5 mbar) under argon atmosphere to generate black and lightweight TCF aerogels. After pyrolysis, the diameter of the cylindrical cotton decreased from 3 cm to 1.5 cm (insets in **Figure 1a** and **1b**, respectively) and the height decreased from 1.5 cm to 0.9 cm. The volume of the TCF aerogel is thus only ~15% of that of the raw cotton. The TCF aerogel has a low density of ~12 mg cm<sup>-3</sup> measured by Archimedes' principle. Scanning electron microscopy (SEM)

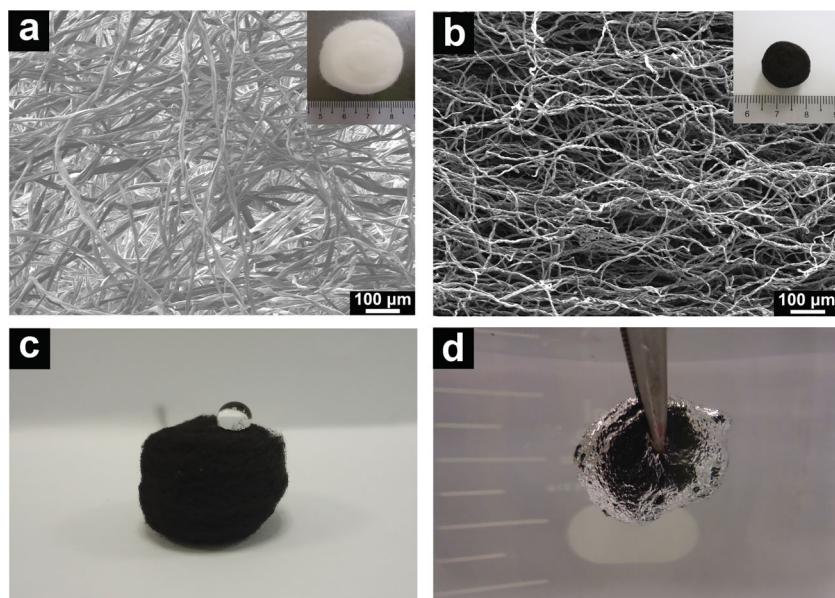
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**Figure 1.** a) SEM image of the cellulose fibers in raw cotton. Inset: photograph of a piece of raw cotton. b) SEM image of the carbon fibers in TCF aerogel. Inset: photograph of a piece of TCF aerogel. c) Photograph of a water droplet supported on a TCF aerogel. d) Mirror-reflection can be observed when a TCF aerogel was immersed into water, which is convincing evidence for the hydrophobicity of the TCF aerogel.

image shows that the raw cottons are porous and interconnected 3D networks (Figure 1a). The fibers are very long and most of them are up to a few centimeters or longer (Figure 1a). High-magnification SEM images indicate that the fibers with a diameter of 15–20 μm in raw cotton are slightly twisted with a pitch length of 50–200 μm (Figure S1a and S1c in the Supporting Information). In contrast, the fibers in the TCF aerogel showed a smaller diameter of 5–10 μm and a further twisted morphology with a pitch length in the range of 10–20 μm (Figure S1b and S1d in Supporting Information).

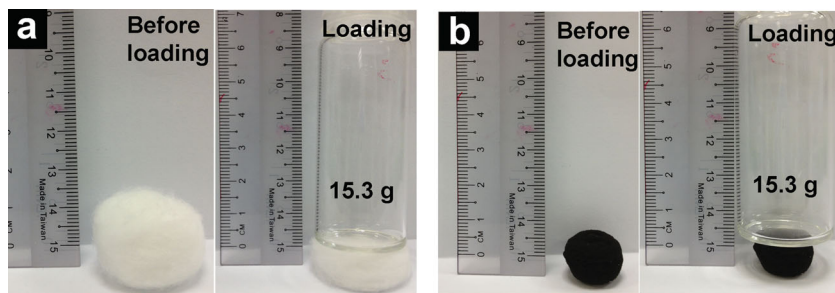
While the raw cotton can absorb water effectively (Figure S2 in Supporting Information) due to its hydrophilicity, the TCF aerogel is hydrophobic and can support a spherical water droplet on its surface (Figure 1c). To further confirm the hydrophobicity of the TCF aerogel, it was held by a pair of tweezers and immersed into water. A uniform mirror-reflection was observed on the surface of the aerogel (Figure 1d), arising from the formation of an interface between the entrapped air in the

3D aerogel and the surrounding water.<sup>[31]</sup> The different wettability between the cotton and TCF aerogel can be justified by Fourier transform infrared spectroscopy (FTIR) analysis. The FTIR spectrum of raw cotton shows several peaks of hydrophilic functional groups, such as C=O, C-O, and -OH (Figure S3a in the Supporting Information). In contrast, after pyrolysis, the resultant TCF aerogel showed no functional groups, leading to its hydrophobicity (Figure S3b in the Supporting Information).

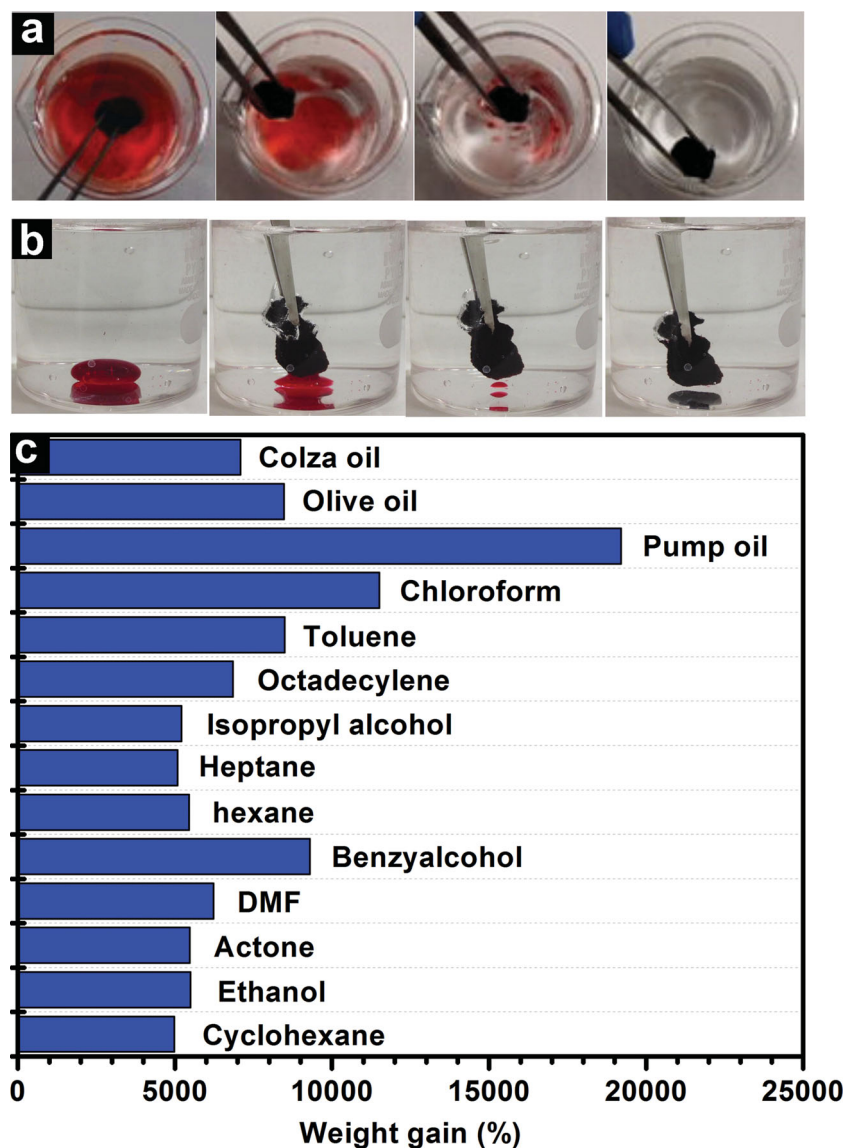
Moreover, the TCF aerogel also exhibited good mechanical property which is beneficial to practical applications. As shown in Figure 2a and 2b, a glass bottle with weight of 15.3 g was placed on top of the raw cotton and the TCF aerogel, respectively. It can be clearly seen that the raw cotton deformed by ~60% in height, while the TCF aerogel only deformed by ~18% (Figure 2b). Additionally, the aerogel showed excellent fire resistance (Figure S4 in the Supporting Information) when it was exposed to flame.

The 3D porous structure, good mechanical property and surface hydrophobicity of the TCF aerogel make it an ideal candidate for the removal of pollutants such as oils and organic solvents. The strong sorption capability of TCF aerogel was demonstrated in Figure 3a, 3b, Movie S1 and Movie S2 in the Supporting Information. When the TCF aerogel was brought into contact with a heptane layer (stained with Sudan red 5B) on a water surface, it absorbed the heptane completely and rapidly (Figure 3a and Movie S1 in the Supporting Information). Because of its low density and hydrophobicity, the TCF aerogel floated on the water surface after sorption of the heptane, indicating its potential use for the facile removal of oil spillage and chemical leakage and the ease for recycling. In addition, the TCF aerogel can also be used to quickly absorb chloroform, which was stained with Sudan red 5B at the bottom of water (Figure 3b, Movie S2 in the Supporting Information).

In order to study the sorption capacity quantitatively, the weight gain, wt%, is defined as the weight of absorbed substance per unit weight of the dried TCF aerogel. Various kinds of organic liquids were studied, such as the commercial petroleum products (e.g. pump oil), fats (e.g. olive oil, colza oil) and ketones with different carbon chain lengths, which are dominant components of crude oil. These materials are common pollutants in our daily life as well as from industry. In addition, the sorption of organic solvents, such as toluene, ethanol and acetone, was also tested. The TCF aerogel showed a very high sorption capacity for all of the aforementioned organic liquids. In general, TCF aerogel can uptake these liquids at 50 to 192 times its own weight (Figure 3c).



**Figure 2.** a) Photographs of a piece of raw cotton (left) before and (right) after a glass bottle with weight of 15.3 g was placed on its top. b) Photographs of a piece of TCF aerogel (left) before and (right) after a glass bottle with weight of 15.3 g was placed on its top.



**Figure 3.** Sorption of organic liquids by TCF aerogel. a) Photographs showing the sorption process of heptane by using a TCF aerogel taken at intervals of 10 s. Heptane stained with Sudan red 5B floating on water was completely absorbed within 40 s. b) Photographs showing the sorption process of chloroform by using a TCF aerogel. Chloroform stained with Sudan red 5B at the bottom of water was completely absorbed within 5 s. c) Sorption efficiency of the TCF aerogel for various organic liquids. Weight gain here is defined as the weight ratio of the absorbate to the dried TCF aerogel.

Importantly, the obtained TCF aerogel has showed much higher sorption capacity than many previously reported sorbents (Table 1),<sup>[6,8,10,12,18,31–44]</sup> such as wool-based non-woven (9–15 times),<sup>[6]</sup> polymers (5–25 times),<sup>[10]</sup> nanowire membrane (4–20 times),<sup>[32]</sup> magnetic exfoliated graphite (30–50 times),<sup>[35]</sup> spongy graphene (20–86 times)<sup>[4]</sup> and CNT sponge doped with boron (25–125 times).<sup>[43]</sup> Although the sorption capacity of TCF aerogel is still lower than that of nitrogen-doped graphene foam,<sup>[41]</sup> ultra-flyweight aerogels<sup>[44]</sup> and CNF aerogel,<sup>[12]</sup> the production method for TCF aerogel is simplest and its precursor material, i.e. raw cotton, is the cheapest among all these sorbents. Therefore, our TCF

aerogel is a cost-effective and promising sorbent for the removal of pollutants.

The recyclability of sorbents and the recoverability of pollutants are key criteria for the oil/chemical cleanup, because most pollutants are either useful and precious raw materials or toxic, e.g. crude oil and toluene. There are three common methods for recycling. For example, for those flammable and useless pollutants, combustion is a good choice. Distillation is suitable for removal of valuable pollutants or those with low boiling points. On the other hand, for precious or nonflammable pollutants with high boiling points, squeezing is an attractive alternative method. The recycling process of TCF aerogel is illustrated in Figure 4. For example, ethanol sorbed by TCF aerogel can be removed by combustion, after which the aerogel remained its shape, size, and inherent 3D porous structure (Figure 4a). In contrast, octadecene with a high boiling point of 314 °C can be recovered by squeezing the aerogel (Figure 4b).

Furthermore, repeated recycle tests were performed for TCF aerogel through distillation (Figure 4c), combustion (Figure 4d) and squeezing (Figure 4e). To demonstrate the cyclic distillation test, heptane with a boiling point of 98.5 °C was sorbed by the TCF aerogel. After that the material was heated to 95 °C to release the vapor of heptane (note that the temperature chose for evaporation should be around the boiling point of the absorbate). This sorption-evaporation process was repeated for 5 times. As shown in Figure 4c, less than 1 wt% of residual heptane remained in the TCF aerogel after each cycle, and no obvious change of sorption capacity was observed after 5 cycles, indicating a stable sorption and recycling performance of the TCF aerogel. In addition, no structural damage was observed to the TCF fibers after the test (Figure S5 in the Supporting Information). In the case of recycle through combustion, ethanol was used as the absorbate. After 5 cycles of sorption-combustion process, the sorption capacity of the aerogel dropped by 3.7% compared to the capacity in the first cycle (Figure 4d), most likely due to the deposition of residues on the surface of fibers after combustion of ethanol (Figure S6 in the Supporting Information). It is worth noting that the 3D fibrous networks of the TCF aerogel and the twisted structure of the fibers remained after the repeated sorption-combustion cycles (Figure S6 in the Supporting Information). Lastly, as for the cyclic sorption-squeezing test, particularly for those pollutants with higher boiling point or being nonflammable, octadecene with a high boiling point of 314 °C was used as an example. In the first cycle, 656 mg of octadecene could be



**Table 1.** Comparison of various sorbent materials.

Sorbent materials	Absorbed substances	Sorption capacity (g g <sup>-1</sup> )	Cost	Ref.
Wool-based nonwoven	diesel, crude oil, SN 150	9–15	low	[6]
Vegetable fiber	crude oil	1–100	low	[8]
Polymers	oils and organic solvents	5–25	medium	[10]
Nanowire membrane	oils and some organic solvents	4–20	low	[32]
Exfoliated graphite	heavy oil	60–90	low	[33]
Activated carbons	benzene, toluene	<1	low	[34]
Carbon nanotube sponges	oils and organic solvents	80–180	high	[18]
Magnetic exfoliated graphite	oils	30–50	high	[35]
Graphene/a-FeOOH composite	cyclohexane, toluene, vegetable oil, etc.	10–30	high	[36]
Graphene/CNT foam	compressor oil, organic solvents	80–140	high	[37]
Graphene-based sponges	oils and organic solvents	60–160	high	[31]
Carbonaceous nanofiber aerogel	oils and organic solvents	40–115	high	[38]
Graphene sponge	oils and organic solvents	60–160	high	[39]
Reduced graphite oxide foam	cyclohexane, chlorobenzene, toluene, petroleum, motor oil	5–40	high	[40]
Nitrogen doped graphene foam	oils and organic solvents	200–600	high	[41]
Marshmallow-like gels	oils and organic solvents	6–15	high	[42]
CNT sponge doped with boron	oils and organic solvents	25–125	high	[43]
UFAs	oils and organic solvents	215–913	high	[44]
CNF aerogels	oils and organic solvents	106–312	low	[12]
TCF aerogel	oils and organic solvents	50–192	quite low	present work

sorbed by the TCF aerogel, but the remnant mass became up to 270 mg after squeezing because of incomplete compression of the TCF aerogel. It is noteworthy that the strain caused by squeezing should not exceed 80% in order to sustain the good sorption capability of the TCF aerogel. Otherwise, the long twisted carbon fibers could be broken into many short fibers (Figure S7 in the Supporting Information). From the second cycle onwards, the performance of the TCF aerogel became stable, i.e. the weight gain remained constant (Figure 4e). This is because the porous structure of the aerogel and the twisted fibers remained unchanged during the whole process (Figure S8 in the Supporting Information). Therefore, benefiting from its good thermal stability and excellent mechanical properties, any of the three common methods mentioned above, i.e., distillation, combustion and squeezing, or a combination of them can be applied for recycling TCF aerogels dependent on the type of pollutants.

In conclusion, TCF aerogels with hydrophobicity, high sorption capacity, and good recyclability have been prepared by a facile method using an economic, environmentally friendly raw material, i.e., raw cotton. The TCF aerogel possesses the high sorption capacity of 50–190 times its own weight. Because of its good thermal stability and mechanical properties, the distillation, combustion and squeezing processes can be used for the recycling of the TCF aerogel. Most importantly, the natural source and simple preparation method make the TCF aerogel cost-effective for possible industrial application. Therefore, the

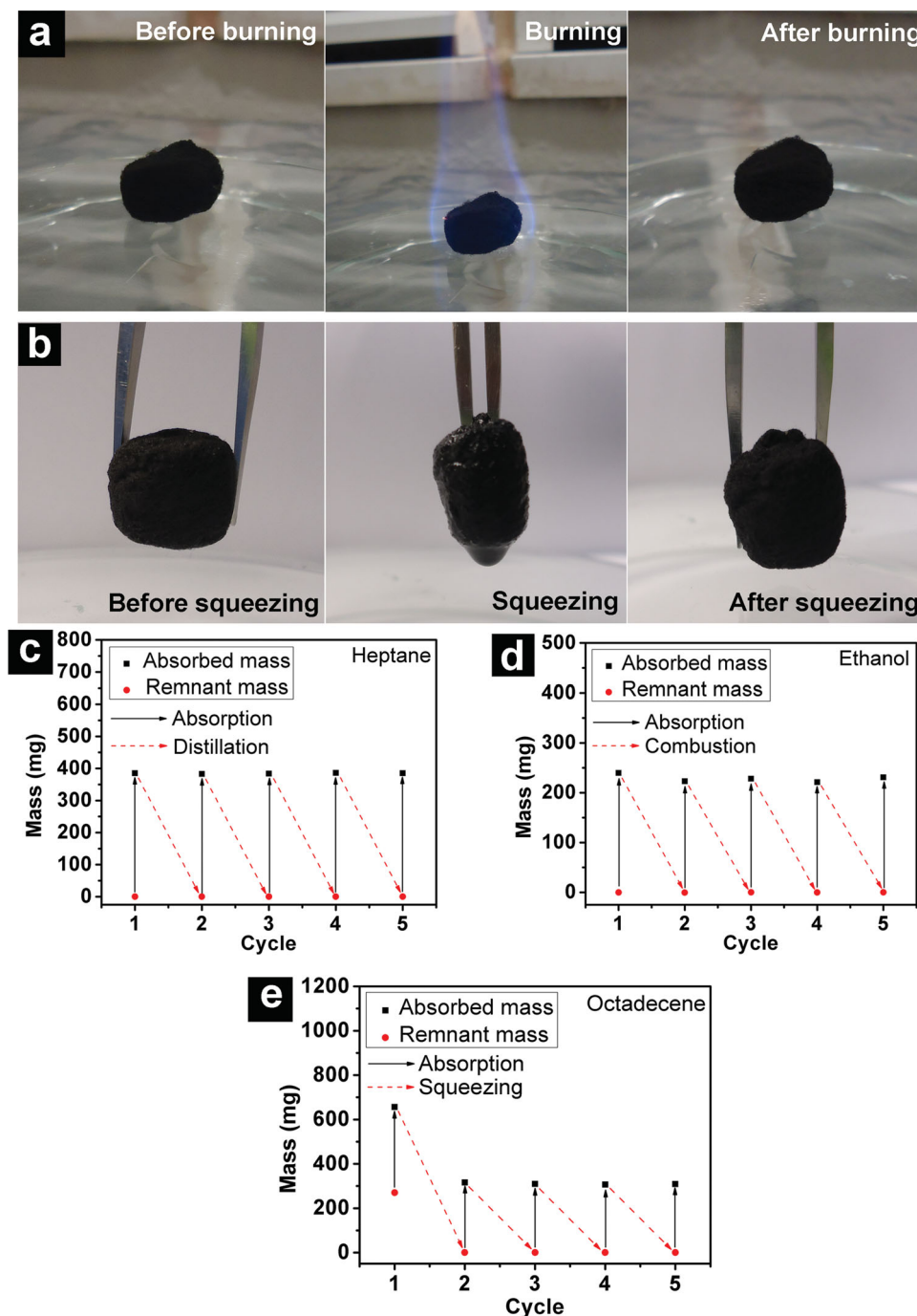
TCF aerogel is highly promising as an economic, efficient, and safe sorbent for environmental and ocean protection. Furthermore, it is also anticipated that TCF aerogel can be used as 3D electrode material for energy storage devices, such as supercapacitors and lithium-ion batteries, as well as a building block for functional composite materials.

## Experimental Section

**Preparation of twisted carbon fibers (TCF) aerogels:** Cylindrical shaped pieces of raw cotton were rinsed several times by deionized water, and then dried in vacuum at 60 °C for 12 h. After that, the dried cotton was transferred to a tubular furnace for pyrolysis. In order to remove the air trapped in the cotton completely, we first evacuated the furnace, and then introduced argon gas, followed by evacuating the furnace again. After that, the furnace was heated up to 800 °C at a heating rate of 5 °C min<sup>-1</sup> and held at 800 °C for 2 h in argon atmosphere at a low pressure of ~0.5 mbar. Finally, the furnace was cooled down to room temperature naturally to obtain the low-density TCF aerogels.

**Characterization of raw cotton and TCF aerogel:** All samples were characterized by a field emission scanning electron microscope (FESEM, JEOL, JSM-7600F) and Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Instruments Spectra, GX FTIR spectrometer).

**Sorption of oils and organic solvents:** In a typical sorption test, a TCF aerogel was placed in contact with an organic liquid until the aerogel was completely filled with the organic liquid, and then taken out for weight measurement. In order to avoid evaporation of the absorbed organic liquid, especially for those with low boiling points, the weight measurement should be done quickly. The weight of a piece of TCF



**Figure 4.** a) Photographs showing the process of recycling TCF aerogel via combustion. b) Photographs showing the process of recycling TCF aerogel via squeezing. (c-e) Recyclability study of TCF aerogel. (c) Distillation was applied to recycle the TCF aerogel for sorption of heptane, (d) combustion was applied to recycle the TCF aerogel for sorption of ethanol and (e) squeezing was used to recycle the TCF aerogel for sorption of octadecene.

aerogel before and after sorption was recorded for calculating the weight gain.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] M. Toyoda, M. Inagaki, *Spill Sci. Technol. Bull.* **2007**, *8*, 467.
- [2] H. M. Choi, R. M. Cloud, *Environ. Sci. Technol.* **1992**, *26*, 772.
- [3] T. Dalton, D. Jin, *Mar. Pollut. Bull.* **2010**, *60*, 1939.
- [4] H. C. Bi, X. Xie, K. B. Yin, Y. L. Zhou, S. Wan, L. B. He, F. Xu, F. Banhart, L. T. Sun, R. S. Ruoff, *Adv. Funct. Mater.* **2012**, *22*, 4421.
- [5] D. Bastani, A. A. Safekordi, A. Alihosseini, V. Taghikhani, *Sep. Purif. Technol.* **2006**, *52*, 295.
- [6] M. M. Radetić, D. M. Jocić, P. M. Jovančić, Z. L. Petrović, H. F. Thomas, *Environ. Sci. Technol.* **2003**, *37*, 1008.
- [7] A. Bayat, S. F. Aghamiri, A. Moheb, G. R. Vakili-Nezhaad, *Chem. Eng. Technol.* **2005**, *28*, 1525.
- [8] T. R. Annunciado, T. H. D. Sydenstricker, S. C. Amico, *Mar. Pollut. Bull.* **2005**, *50*, 1340.
- [9] A. M. Atta, R. A. M. El-Ghazawy, R. K. Farag, A.-A. A. Abdel-Azim, *React. Funct. Polym.* **2006**, *66*, 931.
- [10] A. Li, H. S. Sun, D. Z. Tan, W. J. Fan, S. H. Wen, X. J. Qing, G. X. Li, S. Y. Li, W. Q. Deng, *Energy Environ. Sci.* **2011**, *4*, 2062.
- [11] R. K. Farag, S. M. El-Saeed, *J. Appl. Polym. Sci.* **2008**, *109*, 3704.
- [12] Z. Y. Wu, C. Li, H. W. Liang, J. F. Chen, S. H. Yu, *Angew. Chem. Int. Ed.* **2013**, *52*, 2925.
- [13] N. Hüsing, U. Schubert, *Angew. Chem. Int. Ed.* **1998**, *110*, 22.
- [14] A. M. ElKhatat, S. A. Al-Muhtaseb, *Adv. Mater.* **2011**, *23*, 2887.
- [15] A. C. Pierre, G. M. Pajonk, *Chem. Rev.* **2002**, *102*, 4243.
- [16] D. C. Wu, R. W. Fu, S. T. Zhang, M. S. Dresselhaus, G. Dresselhaus, *Carbon* **2004**, *42*, 2033.
- [17] R. W. Fu, B. Zheng, J. Liu, M. S. Dresselhaus, G. Dresselhaus, J. H. Satcher, T. E. Baumann, *Adv. Funct. Mater.* **2003**, *13*, 558.
- [18] X. C. Gui, J. Q. Wei, K. L. Wang, A. Y. Cao, H. W. Zhu, Y. Jia, Q. K. Shu, D. H. Wu, *Adv. Mater.* **2010**, *22*, 617.
- [19] M. K. Shi, J. Oh, M. Lima, M. E. Kozlov, S. J. Kim, R. H. Baughman, *Adv. Mater.* **2010**, *22*, 2663.
- [20] Y. X. Xu, K. X. Sheng, C. Li, G. Q. Shi, *ACS Nano* **2010**, *4*, 4324.
- [21] H. C. Bi, K. B. Yin, X. Xie, Y. L. Zhou, N. Wan, F. Xu, F. Banhart, L. T. Sun, R. S. Ruoff, *Adv. Mater.* **2012**, *24*, 5124.
- [22] B. Hu, K. Wang, L. Wu, S. H. Yu, M. Antonietti, M. M. Titirici, *Adv. Mater.* **2010**, *22*, 813.
- [23] H. R. Yang, H. J. Zhu, M. M. R. M. Hendrix, N. J. H. G. M. Lousberg, G. de With, A. C. C. Esteves, J. H. Xin, *Adv. Mater.* **2013**, *25*, 1150.
- [24] L. Segal, P. J. Wakelyn, in *High technology fibers, Part A*, Vol. 3 (Ed.: M. Lewin, J. Preston), Marcel Dekker, Inc, New York **1985**, pp. 809.
- [25] O. Carmody, R. Frost, Y. F. Xi, S. Kokot, *Surf. Sci.* **2007**, *601*, 2066.
- [26] M. Jabli, M. H. V. Baouab, M. S. Roudesli, A. Bartegi, *J. Eng. Fabrics* **2011**, *6*, (11).
- [27] C. Kaewprasit, E. Hequet, N. Abidi, J. P. Gourlot, *J. Cotton Sci.* **1998**, *2*, 164.
- [28] A. M. A. Nada, N. A. El-Wakil, M. L. Hassan, A. M. Adel, *J. Appl. Polym. Sci.* **2006**, *101*, 4124.
- [29] M. Hussein, A. A. Amer, I. I. Sawsan, *J. Petrol. Technol. Alternative Fuels* **2011**, *2*, 132.
- [30] M. O. Adebajo, R. L. Frost, J. T. Klopogge, O. Carmody, *J. Porous Mater.* **2003**, *10*, 159.
- [31] D. D. Nguyen, N. H. Tai, S. B. Lee, W. S. Kuo, *Energy Environ. Sci.* **2012**, *5*, 7908.
- [32] J. Yuan, X. Liu, O. Akbulut, J. Hu, S. L. Suib, J. Kong, F. Stellacci, *Nat. Nanotechnol.* **2008**, *3*, 332.
- [33] M. Toyoda, M. Inagaki, *Carbon* **2000**, *38*, 199.
- [34] M. A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, *Carbon* **2005**, *43*, 1758.
- [35] G. Wang, Q. Sun, Y. Zhang, J. Fan, L. Ma, *Desalination* **2010**, *263*, 183.
- [36] H. P. Cong, X. C. Ren, P. Wang, S. H. Yu, *ACS Nano* **2012**, *6*, 2693.
- [37] X. C. Dong, J. Chen, Y. W. Ma, J. Wang, M. B. Chan-Park, X. M. Liu, L. H. Wang, W. Huang, P. Chen, *Chem. Commun.* **2012**, *48*, 10660.
- [38] H. W. Liang, Q. F. Guan, L. F. Chen, Z. Zhu, W. J. Zhang, S. H. Yu, *Angew. Chem. Int. Ed.* **2012**, *51*, 5101.
- [39] J. Zhao, W. Ren, H. M. Cheng, *J. Mater. Chem.* **2012**, *22*, 20197.
- [40] Z. Niu, J. Chen, H. H. Hng, J. Ma, X. Chen, *Adv. Mater.* **2012**, *24*, 4144.
- [41] Y. Zhao, C. Hu, Y. Hu, H. Cheng, G. Shi, L. Qu, *Angew. Chem. Int. Ed.* **2012**, *51*, 11371.
- [42] G. Hayase, K. Kanamori, M. Fukuchi, H. Kaji, K. Nakanishi, *Angew. Chem. Int. Ed.* **2013**, *52*, 1986.
- [43] D. P. Hashim, N. T. Narayanan, J. M. Romo-Herrera, D. A. Cullen, M. G. Hahm, P. Lezzi, J. R. Suttle, D. Kelkhoff, E. Muñoz-Sandoval, S. Ganguli, A. K. Roy, D. J. Smith, R. Vajtai, B. G. Sumpter, V. Meunier, H. Terrones, M. Terrones, P. M. Ajayan, *Sci. Rep.* **2012**, *2*, 363.
- [44] H. Y. Sun, Z. Xu, C. Gao, *Adv. Mater.* **2013**, *25*, 2554.