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Multifunctional, Ultra-Flyweight, Synergistically Assembled Carbon Aerogels

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Since the first report of aerogels by Kistler in 1930s,^[1] several ultralight cellular materials such as silica aerogels.^[2] metallic foams,^[3] CNT aerogels,^[4] and polymer foams^[5] have been prepared to exploit their wide applications, covering from thermal insulation to oil or heavy metal-absorption, energy storage, catalyst supports, and supercapacitors.^[6-11] Following the accessibility of ultralow density below 10 mg cm⁻³, the next dream target is to achieve ultra-flyweight aerogels (UFAs) with a density (ρ) less than 1 mg cm⁻³, which is even smaller than that of air at ambient conditions (1.2 mg cm⁻³). Recently, periodic microlattice-constructed Ni foams^[3] with ρ of 0.9 mg cm⁻³ were made by electroless plating and subsequently etching away the polymer template; microtubes-interconneted aerographite^[12] with ρ as low as 0.18 mg cm⁻³ was gained by ZnO templatebased CVD approach. The template-directed synthesis strategy could bring the merits of ordered and hierarchical structures, yet in the same breath limits the scalability of resulting aerogels because of the hard accessibility of well-organized, largesize template itself. A template-free strategy (i.e., a hydrogel or sol-gel method) is desirable for scalable manufacture, but the densities of corresponding aerogels are relatively high ($\rho \ge$ 1 mg cm⁻³)^[2,13,14] because of the lack of control over the fine structures. Accordingly, to produce UFAs in large-scale with advanced structural design is still a big challenge unresolved.

Given their marvelous mechanical strength, low density, fine elasticity, good electrical conductivity, and extremely high aspect ratio,^[15–17] CNTs and graphene are theoretically considered as the best candidates to make ultralight yet elastic and conductive aerogels. In fact, aerogels composed of either CNTs or graphene have demonstrated multi-functionality indeed,^[4,6,8–10],] whereas the recorded lowest ρ is 2 mg cm⁻³, far from the ultra-flyweight target. Graphene coating on CNT aerogels could bring superelasticity and complete fatigue resistance under large cyclic strains,^[18] whereas the corresponding ρ increased from 8.8 to 14.0 mg cm⁻³.

Here, we fabricated all carbon UFAs ($\rho \ge 0.16 \text{ mg cm}^{-3}$) by freeze-drying aqueous solutions of CNTs and giant graphene oxide (GGO) sheets (Figure S1),^[19] followed by chemical reduction of GGO into graphene with hydrazine vapor (the detailed protocol is described in Methods and Supporting Information).

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The macroscopic-assembled, all carbon aerogels offer the integrated properties of extremely low density, temperature-invariant super recyclable compressibility, and elasticity-responsive conductivity, originating from the synergistic effect between elastic CNT ribs and giant graphene cell walls. The hydrophobic aerogels have a porosity of ~99.9%, possessing ultrahigh oil-absorption capacity, 215-913 times of their own weights dependent on the oil density. Such capacities are generally 2–4-fold higher than the reported highest values,^[20] and one to two orders of magnitude higher than those of commercial oilabsorbents.

Our UFAs are directly made by cryodesiccation from the aqueous, fluid solutions of CNTs and GGO (the frozen system can reversibly become fluid when being warmed), rather than from hydrogels generally needed in previous methods.^[2,6] So we can coin our protocol as "sol-cryo". Because of the simplicity of assembly process in our template-free "sol-cryo" methodology and the large-scale availability of GGO and CNTs, the integrated all carbon aerogels with desired densities and shapes such as rods, cylinders, papers and cubes were readily accessible (Figure 1a, and Figure S2). More significantly, UFAs can be easily manufactured in a large-scale (Figure 1b and 1c and Figure S2e). For example, a UFA cylinder up to 1000 cm³ was made with a mold of 1 L plate (Figure 1c). SEM images show the UFA exhibits an interconnected, porous three-dimensional (3D) framework of randomly oriented, crinkly sheets with continuous macropores ranged from hundreds of nanometers to tens of micrometers (Figure 1d, Figure S3, S4), similar to those of previous neat graphene aerogels.^[14] Zooming in on a single sheet reveals entangled, spaghetti-like CNT network covered on the graphene cell wall (Figure 1e). Detailed observations proclaim multiform interconnections of sheets: overlapping (Figure 1f), twisting (Figure 1g), and enwrapping (Figure 1h) (the corresponding cartoons of CNT-coated graphene building block and its interconnections are shown in Figure 1i-l). TEM images further indicate that CNTs with lengths of several hundreds of nanometres to tens of micrometers (Figure S5) are tightly adhered to the graphene substrates (Figure 1m), which is quite different from the case of CVD-grown CNT aerogels that required ultralong nanotubes.^[8,9,20] High-resolution transmission electron microscopy (HRTEM) analysis revealed single layer graphene (~0.3 nm of thickness) and its curled edge (inset of Figure 1m and Figure S6). At the selected naked graphene region, we detected a set of hexagonal diffraction spots in selected area electron diffractions (SAED), which is the typical pattern of monolayer graphene (inset of Figure 1n).^[21,22] The SAED on a UFA foam presents cyclic patterns due to the covering of CNTs. Multi-sets of hexagonal spots also appear in the diffraction patterns, which could originate from the rotatedstacking structures of monolayer graphene sheets (Figure S7).

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Figure 1. Macroscopic and Microscopic structures of UFAs. (a) Digital photograph of UFAs with diverse shapes. (b) A 100 cm³ UFA cylinder standing on a flower like dog's tail (*Setaira viridis* (*L.*) *Beauv*). (c) A ~1000 cm³ UFA cylinder (21 cm in diameter and 3 cm in thickness). (d-e) Microscopically porous architecture of a UFA at different magnifications, showing CNT-coated graphene cell walls. (f-h) SEM images of different interconnections for CNTs-coated graphene (graphene@CNTs) cell walls: overlapping (f), twisting (g), and wrapping (h). (i) Cartoon of a flattened CNT-coated graphene cell wall. (j-l) Cartoon models corresponding to the three interconnection styles shown in (f-g) respectively. The gray lamellar, orange wires and brown wires represent the graphene sheet, CNTs coated on the top and CNTs coated on the back of the graphene sheet, respectively. (m,n) TEM images of CNT-coated graphene cell walls, the HRTEM image of a cell wall edge (inset in (m), scale bar is 2 nm) and the SAED patterns (inset in (n)) taken at the labeled area. (o) Schematic illustration of idealized building cells of our UFA made by synergistic assembly of graphene and CNTs. (p) SEM image and photograph (inset in (p)) of the lightest neat graphene aerogel ($\rho = 0.16$ mg cm⁻³, i.e., 1.38 mg in 8.6 cm³).

On the basis of these observations, a structural model for the UFAs is proposed (Figure 1o). It is further abstracted as a geometric model (Figure S8) to calculate approximately the lowest density (ρ_{cal}) of UFAs, $\rho_{cal} = 1/(657.5wf)$ (where w denotes the average lateral width of graphene, f is the weight fraction of graphene in the aerogel). In our typical case ($w = 18.5 \ \mu m, f = 0.6$), ρ_{cal} is 0.137 mg cm⁻³. The experimental value is 0.45 mg cm⁻³ (Figure S2f, S2g and Movie S1), close to the calculated lowest density. For foams made from neat graphene, we achieved 0.16 mg cm⁻³ (Figure 1p, Figure S9 and Movie S2), the lowest density of ultralight materials ever reported. Lighter aerogels could be fabricated using larger graphene sheets (e.g., the ultimate aerogel is constructed with only one macroscopic graphene sheet).

Compression experiments on the UFAs showed a nearly complete recovery after 50–82% compression. As shown in Movie S3, our UFAs undergo a transverse contraction when compressed in one direction and behave a negative Poisson's ratio,^[23] which has also been observed in honeycomb and CNT aerogel materials.^[24] The stress-strain (σ - ε) curves show two distinct stages during the loading process (Figure 2a, Figure S10). The linear-elastic regime at ε < 29% with an elastic modulus just over 4 KPa records the elastic bending of cell wall, and the non-linear regime at 29% < ε < 50% has an increased slope with a modulus of 22 KPa, where the deformation is still recoverable because of the elastic buckling of the cell walls (Figure 2a). Such behaviors are similar to those of foam-like CNT films.^[4,8] The σ - ε curve of the 1000th cycle is identical to that of the first cycle, with the exception that the compressive stress at $\varepsilon = 50\%$ decreases slightly to 88% of the original value (Figure 2b). After the fatigue test of 1000 cycles, the UFA still kept its original thickness, macroscopic shape (inset of Figure 2b) and porous 3D microscopic structure, and the interaction between the cell walls remained intact (Figure 2e). The CNTs were also tightly covered on the graphene sheets (Figure 2f), similar to the case of as-prepared UFAs (Figure 1e). These measurements





Figure 2. Viscoelastic properties of our UFA. (a) Stress-strain (σ - ε) curves of multicycle compressions on a UFA (ρ = 5.6 mg cm⁻³, f = 0.5), exhibiting recoverable deformation. Inset, Photographs of the UFA under a compressing and releasing cycle. During the compression, the top head was shuttling between a set fixed distance (strain) at a speed of 2 mm/min (b) Stress-strain curves of several selected cycles on a UFA (r = 1 mg cm⁻³, f = 0.5) during repeated compression (the 1st, 10th, and 1000th cycle). Inset, Photographs of the UFA under fatigue test for 1000 cycles. The compression and release speed is 600 mm/min. (c) Temperature dependence of the storage modulus (cyan), loss modulus (black) and damping ratio (blue) of the UFA (ρ = 7.6 mg cm⁻³, f = 0.5). (d) Typical mechanical measurements under tensile loading of UFA (ρ = 1.5 mg cm⁻³, f = 0.5). The strain rate is 5% min⁻¹. (e-f) SEM images of the UFA (ρ = 1 mg cm⁻³, f = 0.5) after 1000 cycles of compression-release process at different magnifications.

demonstrate the super-elasticity of the macroscopic-assembled all carbon aerogels. Furthermore, as shown in Figure 2c, the elastic properties of the UFAs such as storage modulus, loss modulus and damping ratio measured by dynamic thermomechanical analysis (DMA) are nearly constant over a wide temperature range from -190 to 300 °C limited by our DMA instrument. In fact, the UFAs annealed at 900 °C for 5 h under N2 are still intact in shape, and are of excellent elasticity (Figure S11). Such a temperature-invariant elasticity would be quite useful in extreme temperature conditions. Additionally, the UFA exhibits a typical plastic deformation at room temperature under tensile strength. In the elastic region, the aerogel has a typical Young's modulus of 329 KPa at small deformation (<0.5%). Importantly, the UFA is of high toughness with fracture elongation as high as 16.5%, and its fracture strength is measured to be 10.9 KPa (Figure 2d), promising the practical application of the all carbon aerogels.



To probe the mechanism of the elasticity, we utilized SEM to in situ observe the microscopic structural evolution of the UFAs during the compression-release period (Figure 3 and Figure S12). For clear seeing, we cut a UFA to make a sharp edge (Figure 3a). Upon loading, the edge is bent to a large degree even folded without breakage (Figure 3b), and recovers to its original shape once the loading is released (Figure 3c). Such a 3D structural integrity under large deformations for our UFAs is mainly attributed to the isotropic assembly of graphene and CNTs, which could avoid the sliding and splitting of graphene sheets along a certain direction.^[20] Zooming in the edge tip, we see the clear-cut profile of one graphene sheet coated with CNTs (G@CNTs) (Figure 3d). It can be contorted to 180° and bent to ~60° simultaneously without breaking graphene flake and stripping CNTs from the substrate (Figure 3e), and regains original form upon the removal of compressive load (Figure 3f). We also observed multicycle compression-release process of a single sheet at the waist of the aerogel (Figure S13). The in situ observations on a single sheet indicate that the elasticity of our UFAs originates from the deformation of the cell walls rather than the sliding between them.

We contribute the good elasticity of our UFAs to the synergistic effect between graphene cell walls and CNT ribs. Giant graphene flakes build a framework with macro-pores, making the aerogel ultralight; the coating of CNTs reinforces the relatively flexible graphene substrate and endows their intrinsic elasticity^[25] to the co-organized aerogel (a model is shown in Figure 3g). This synergistic effect is demonstrated by series of compression tests on the UFAs with various *fs* (Figure 3h and Figure S14-18). Neat graphene sheets prepared

with this protocol could form ultra-flyweight porous foam (f =1, $\rho = 0.16 \text{ mg cm}^{-3}$) with similar architectures to UFAs indeed (Figure S19). However, the foam shows weak elasticity, and can not resume its original shape after the compression test, owing to the flexibility of giant graphene sheets (Figure S20). Similar phenomenon was also reported by Li and co-workers.^[26] Strikingly, adding a small amount of CNTs is enough to gain good elasticity (e.g., f = 0.95), and the resultant aerogel can completely recover after compression as $\varepsilon \leq 63\%$, despite only part of graphene sheets are coated with CNTs (Figure S15). Upon increasing the CNT fractions, the compressibility of aerogels increases remarkably, and achieves the maximum ($\varepsilon = 82\%$) at f = 0.5, and then decreases gradually to $\varepsilon = 53\%$ at f = 0.1 where bulky CNTs aggregates appear (Figure S20). Similar to the neat graphene foams, pure CNT foams (f = 0) display little elasticity, due to the strong aggregation of CNTs into giant bundles (Figure S21, S22) that results in inefficient load transfer between ligaments.

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Figure 3. In situ SEM observations of UFAs under cycled compression. (a-c) The compression and release process of the UFA ($\rho = 2 \text{ mg cm}^{-3}$, f = 0.5). a, Before deformation. (b) Under deformation. (c) Full recovery after removal of load. (d-f) The recoverable deformation process of one single graphene@CNTs cell wall at the taper tip (indicated by the arrow in (a)). (d) Original shape. (e) Under deformation. (f) Full recovery after removal of load. The blue cycle indicates the frame of reference for SEM observations. (g) The schematic model of a single graphene@CNTs cell wall in the process of compressing and releasing shows the elastic mechanism of our UFAs: the deformation of cell walls rather than the sliding between them. (h) The recoverable compressive strain (ε) of the UFA ($\rho = 1.5 \text{ mg cm}^{-3}$) as a function of graphene weight fraction (f) in the UFA.

The synergistic effect is strongly affected by the Van der Waals attraction between graphene and CNTs. The foams of CNTs-coated GGO exhibit weak elasticity (Figure S23), while the super-elasticity appears immediately after treated with hydrazine vapor. Thus, the chemical reduction of GGO is crucial for achieving fine elasticity, since reduced graphene has stronger π - π interaction between the two building blocks due to the restoring of conjugated carbon net (spectra of X-ray photoelectron spectroscopy (XPS) shown in Figure S24). The even and tight covering of CNTs favors the load transfer from graphene to elastic CNTs, resulting in super-elasticity for the whole aerogels.

The chemical reduction yet brings the elasticity-dependent electrical conductivity of UFAs (Movie S4). A LED lamp can be illumined under 6V circuit when connected with a UFA bulk, and its brightness fluctuates upon compressing and releasing the aerogel (Figure 4a and Movie S5). This phenomenon promises the application of UFAs as pressure-responsive sensors.^[4] The UFAs can also be applied to prepare conductive composites with ultralow content of fillers. The composites of UFA (ρ = 1.4 mg cm⁻³, f = 0.5) filled with liquids such as CCl₄ and solids such as 1-hexadecanol have a filler fraction of only 0.1 vol.%, equal to the calculated geometric percolation threshold for randomly oriented oblate ellipsoids with an aspect ratio of 1000,^[27] while they show an electrical conductivity of ~ 0.6 S m⁻¹. This value is five orders of magnitude higher than the reported conductivity for CNT-based composites at 0.1 vol.% (~10⁻⁶ S m⁻¹),^[28] and also much higher than that of graphene-based composites at 1 vol.% (~0.1 S m⁻¹).^[22] The filler content can be further

decreased with the lower density of UFAs as host framework. Significantly, our composites can still be connected in a circuit to illumine LED lamp (Figure 4b and Movie S6), indicating the fine conductivity of the whole composites. Such a method of filling guest compounds into the host of UFAs opens a versatile avenue to highly conductive composites with extremely low filler fraction.

The robust UFA (ρ 0.75 mg cm⁻³) is of highly hydrophobic (the contact angle is ~132.9°, has a surface area of ~272 m² g⁻¹ with an average pore size of 123 nm (Figure S25), possessing super-high absorption capacities and ultrafast absorption rate for organic solvents and oils. As shown in Figure 4c, 1.1 g toluene (stained with Sudan Black B) on water is absorbed completely by a 3.2 mg UFA within 5 s, indicating an average absorption rate of 68.8 g per gram of UFA per second (g $g^{-1} s^{-1}$) that is much faster than the previous graphene (~0.57 g g $^{-1}$ s $^{-1}$). $^{[29]}$ Figure 4d and Table S1 show the absorption capacities (Q, the ratio of the final weight after full absorption to the initial weight of UFA) of the UFA to various solvents and oils, achieving 215–743 g g^{-1} dependent on the liquid density. The Q to crude oil is as high as 290 g g^{-1} . This is to say, less than 3.5 kg UFA can absorb 1 ton petroleum, promising great potential in the applications of oil spill and pollution treatments. For the identical organic liquids, the Q of our UFAs is 2-4 times higher than the highest values of previous foams including CNTs^[10,20] and graphene aerogels.^[29] Notably, these Qs obtained at air condition can be even further enhanced by absorption in vacuum to avoid air blocking in the pores. We tested the absorption of CCl₄ under vacuum, and the Q records 913 g g^{-1} (22.9% improvement compared with Q in







Figure 4. Elasticity-responsive conductivity and the oil absorption properties of the UFA ($\rho = 1.4 \text{ mg cm}^{-3}$, f = 0.5). (a) A circuit constructed with the UFA as lightweight conductive bulk. The brightness fluctuates upon compressing and releasing UFA. (b) The circuit constructed with the UFA ($\rho = 1.4 \text{ mg cm}^{-3}$, f = 0.5) as ultralight conductive bulk filled with n-hexane. The brightness fluctuates upon compressing and releasing UFA. (c) Absorption process of toluene (stained with Sudan Black B) on water by the UFA within 5 s. (d) Absorption capacities (Q) of the UFA measured for a range of oils and organic solvents in terms of their densities (ρ). The numbers (1-10) represent n-hexane, ethanol, crude oil, toluene, motor oil, vegetable oil, 1,4-dioxane, ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate), chloroform, and phenixin, respectively. (e) The diagram of absorption capacities of various absorbents for pump oil. The numbers represent the UFA in this study (1), CNT sponge (2, ref. [20]), graphene sponge (3, ref. [28]), expanded graphite (4), polyurethane sponge (5), paper towel (6), a commercial oil absorbent material (7), and activated carbon (8). Inset: A UFA ($\rho = 4.0 \text{ mg cm}^{-3}$, f = 0.5) repetitively absorbed n-hexane and released its vapor under heat treatment (85 °C) for 10 cycles. Triangles: the restored weight of UFA after removing the n-hexane, squares: the weight gain after absorption of n-hexane during different cycles.

air), corresponding to 1.46 ton CCl_4 per cubic meter UFA. This capacity is approaching the ultimate value of a single-graphene bucket (1.59 ton m⁻³). As control experiments, we also tested Qs of common absorption materials to pump oil, including expanded graphite, polyurethane aerogel, paper towel, commercial oil absorbent material, and activated carbon (Figure 4e and Table S2). The Q of our UFA (320 g g⁻¹) is one to two orders of magnitude higher than those of the commercial materials

 $(Q \le 47 \text{ g g}^{-1})$. Due to the fine elasticity and excellent thermal stability of our UFAs, the absorbed liquids can be readily released by mechanical extrusion or heating, or can be completely burned off from the aerogels in air without destroying the porous structures (Figure S26, Movie S7). The regenerated aerogels still keep their original shape and ultrahigh absorption capability after more than 10 cycles (inset of Figure 4e), making the UFAs ideal candidates for practical applications in



Table 1. Thermal properties of neat paraffin and paraffin-filled UFA (ρ = 1.4 mg cm^{-3}, f = 0.5).

Sample	Melting			Solidifying		
	T _{t,m} [°C] ^{a)}	T _m [°C] ^{a)}	ΔH_m [J/g] ^{a)}	T _{t,f} [°C] ^{b)}	T _f [°C] ^{b)}	ΔH_{f} [J/g] ^{b)}
Paraffin	36.45	58.23	172.2	28.12	43.57	148.9
paraffin-filled UFA	36.09	56.06	185.6	29.59	46.63	191.7

^{a)}The codes "T_{t,m}", "T_m", " Δ H_m" represent solid–solid phase transition temperature, melting temperature, and melting latent heat in the melting process, respectively. ^{b)} The codes "T_{t,f}", "T_f", " Δ H_f" denote solid–solid phase transition temperature, freezing temperature, and freezing latent heat in the solidifying process, respectively.

the absorption-removal of organics, particularly in the environmental protection and pollution control.

In addition, solids can also be absorbed into the UFAs by melting infiltration to prepare phase-change energy storage materials. High phase-change enthalpy (Δ H) is vital for a good phase-change materials (PCMs). We found that the melting latent heat (Δ H_m) and freezing latent heat (Δ H_f) for the paraffin-filled UFAs are 7.8% and 28.7% higher than those of neat paraffin (Figure S27, S28 and Table 1), likely due to the interaction between paraffin and hydrophobic surfaces of graphene and CNTs. Such an enhancing effect was rarely found in previous reports^[30] where the Δ H of composite is generally lower than that of neat PCM.

In summary, we have developed a template-free, synergistic assembly strategy for the scalable fabrication of macroscopic, multiform (1D, 2D, and 3D), ultralight aerogels with controlled densities. The all-carbon aerogels with a monolith 3D framework were constructed with cell walls of giant graphene sheets and CNTs ribs. The ideal combination of the giant size of constituent graphene sheets and the cooperative effect between graphene and CNTs offers the as-prepared aerogels integrated properties, such as outstanding temperature-invariant elasticity, ultralow density, excellent thermal stability, extremely high absorption capacities for organic liquids and PCMs, and good electrical conductivity. These desirable multifunctional attributes would enable many UFA applications, including elastic and flexible conductors, high-performance conductive polymer composites, organic absorbents, environmental remediation materials, phase-change energy storage, sensors, supercapacitors, and catalyst beds.

Experimental Section

Preparation of UFAs via the "sol-cryo" method: Typically, to a 100 mL beaker containing GGO aqueous dispersion (1.0 mg mL⁻¹, 28 mL), CNTs aqueous dispersion (1.0 mg mL⁻¹, 28 mL) was added. The mixture was stirred with a magnetic bar for 1.5 h, and then poured into the desired mold followed by freeze-drying for 2 days. The as-prepared GGO/CNTs foam (~57 mg) was chemically reduced by hydrazine vapor at 90 °C for 24 h, followed by vacuum-drying at 160 °C for 24 h, affording 42.6 mg of UFA (ρ = 0.75 mg cm⁻³, f = 0.5). The density was calculated by the weight of solid content without including the weight of entrapped air divided by the volume of aerogel (the density measured in vacuum is identical

to that in air, Figure S29).^[3] We have obtained the UFAs with densities ranged from ~0.16 to 22.4 mg cm⁻³ by adjusting the concentration of aqueous solutions. We believe that lighter and heavier carbon aerogels can be accessed by this protocol.

Supporting Information

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

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- [1] S. S. Kistler, Nature 1931, 127, 741.
- [2] T. M. Tillotson, L. W. Hrubesh, J. Non-Cryst. Solids 1992, 145, 44.
- [3] T. A. Schaedler, A. J. Jacobsen, A. Torrents, A. E. Sorensen, J. Lian, J. R. Greer, L. Valdevit, W. B. Carter, *Science* 2011, 334, 962.
- [4] J. H. Zou, J. H. Liu, A. S. Karakoti, A. Kumar, D. Joung, Q. Li, S. I. Khondaker, S. Seal, L. Zhai, ACS Nano 2010, 4, 7293.
- [5] L. J. Gibson, M. F. Ashby, Cellular Solids: Structure and Properties, Cambridge Univ. Press, Cambridge, 1997.
- [6] Y. Zhao, C. G. Hu, Y. Hu, H. H. Cheng, G. Q. Shi, L. T. Qu, Angew. Chem. Int. Ed. 2012, 51, 11174.
- [7] Z. P. Chen, W. C. Ren, L. B. Gao, B. L. Liu, S. F. Pei, H. M. Cheng, *Nat. Mater.* 2011, 10, 424.
- [8] A. Cao, P. L. Dickrell, W. G. Sawyer, M. N. Ghasemi-Nejhad, P. M. Ajayan, *Science* **2005**, *310*, 1307.
- [9] M. Xu, D. N. Fubata, T. Yamada, M. Yumura, K. Hata, Science 2010, 330, 1364.
- [10] 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.
- [11] Y. X. Xu, K. X. Sheng, C. Li, G. Q. Shi, ACS Nano 2010, 4, 4324.
- [12] M. Mecklenburg, A. Schuchardt, Y. K. Mishra, S. Kaps, R. Adelung, A. Lotnyk, L. Kienle, K. Schult, Adv. Mater. 2012, 24, 3486.
- [13] Z. Xu, Y. Zhang, P. G. Li, C. Gao, ACS Nano **2012**, *6*, 7103.
- [14] M. A. Worsley, P. J. Pauzauskie, T. Y. Olson, J. Biener, J. H. Satcher Jr., T. F. Baumann, J. Am. Chem. Soc. 2010, 132, 14067.
- [15] D. Qian, G. J. Wagner, W. K. Liu, M. F. Yu, R. S. Ruoff, Appl. Mech. Rev. 2002, 55, 495.
- [16] C. Lee, X. D. Wei, J. W. Kysar, J. Hone, Science 2008, 321, 385.
- [17] Z. Xu, C. Gao, Nat. Commun. 2011, 2, 571.
- [18] K. H. Kim, Y. Oh, M. F. Islam, Nat. Nanotechnol. 2012, 7, 562.
- [19] Z. Xu, H. Y. Sun, X. L. Zhao, C. Gao, Adv. Mater. 2013, 25, 188.

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- [20] 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.
- [21] K. Kim, Z. Lee, B. D. Malone, K. T. Chan, B. Alemán, W. Regan, W. Gannett, M. F. Crommie, M. L. Cohen, A. Zettl, *Phys. Rev. B* 2011, *83*, 245433.
- [22] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* 2006, 442, 282.
- [23] R. Lakes, Science 1987, 235, 1038.
- [24] Y. J. Ma, X. F. Yao, Q. S. Zheng, Y. J. Yin, D. J. Jiang, G. H. Xu, F. Wei, Q. Zhang, Appl. Phys. Lett. 2010, 97, 061909.
- [25] M. R. Falvo, G. J. Clary, R. M. Taylor, V Chi, F. P. Brooks, S. Washburn, R. Superfine, *Nature* **1997**, *389*, 582.
- [26] L. Qiu, J. Z. Liu, S. L. Y. Chang, Y. Z. Wu, D. Li, Nat. Commun. 2012, 3, 1241.
- [27] E. J. Garboczi, K. A. Snyder, J. F. Douglas, M. F. Thorpe, *Phys. Rev. E* 1995, *52*, 819.
- [28] Z. Ounaies, C. Park, K. E. Wise, E. J. Siochi, J. S. Harrison, Compos. Sci. Technol. 2003, 63, 1637.
- [29] 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.
- [30] A. Sari, A. Karaipekli, Appl. Therm. Eng. 2007, 27, 1271.