

Carbon Welding by Ultrafast Joule Heating

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Supporting Information

ABSTRACT: Carbon nanomaterials exhibit outstanding electrical and mechanical properties, but these superior properties are often compromised as nanomaterials are assembled into bulk structures. This issue of scaling limits the use of carbon nanostructures and can be attributed to poor physical contacts between nanostructures. To address this challenge, we propose a novel technique to build a 3D interconnected carbon matrix by forming covalent bonds between carbon nanostructures. High temperature Joule heating was applied to bring the carbon nanofiber (CNF) film to temperatures greater than 2500 K at a heating rate of 200 K/min to fuse together adjacent carbon nanofibers with graphitic carbon bonds, forming a 3D continuous carbon network. The bulk electrical conductivity of the carbon matrix increased four orders of magnitude to 380 S/cm with a sheet resistance of 1.75 Ω /sq. The high temperature Joule heating



not only enables fast graphitization of carbon materials at high temperature, but also provides a new strategy to build covalently bonded graphitic carbon networks from amorphous carbon source. Because of the high electrical conductivity, good mechanical structures, and anticorrosion properties, the 3D interconnected carbon membrane shows promising applications in energy storage and electrocatalysis fields.

KEYWORDS: Junction resistance, ultrafast graphitization, high temperature, 3D carbon matrix, battery current collectors

arbon-based nanomaterials such as carbon nanofiber (CNF), carbon nanotube (CNT), and graphene are featured with lightweight, flexible, anticorrosion, highly conductive, and high surface area, and are important materials as conductive host for electrocatalysis and electrochemical energy storage applications.^{1–6} For example, lightweight and highly conductive carbon membrane can replace conventional copper and nickel current collectors for improved energy density and long-term usage.⁶⁻⁹ However, attempts to mechanically join and create bulk structures from individual carbon nanomaterials often result in the loss of key perform-ance metrics.^{2,10–18} For example, single-walled CNTs are known to exhibit electrical conductivity above 10 000 S/cm, but the reported conductivity of assembled CNT membranes is two orders of magnitude less, approximately 100 S/cm. $^{19-21}$ This decrease can be attributed to the poor physical contacts between nanotubes that lack effective bonding to maintain the intrinsic, nanoscale properties. It is reasonable to believe that by addressing the poor contacts between carbon nanomaterials, the bulk performance of 3D carbon structures could be improved significantly and could open up new areas of large scale development of high performing, bulk carbon based materials from nanostructures.

In the literature, there are many techniques reported to mechanically or chemically fuse carbon nanomaterials.^{12,14–16,22–26} Materials can be uniformly deposited along

junctions to form a continuously interconnected structure using chemical vapor deposition (CVD) of amorphous carbon,²⁷ SiC,²³ or atomic layer deposition (ALD) of Al_2O_3 .²⁸ For example, Z. Lin et al. report an increase in the compressive strength of CNT sponges with an amorphous carbon coating by three orders to 72 MPa.¹² To form a covalent chemical bond at junctions between carbon nanostructures, boron doping has been reported to form elbow junctions with B–C bonds.¹⁶ Although extensive studies have been conducted, none of the reported methods offers a cost-effective and scalable approach to fundamentally improve the contacts between carbon nanostructures for macroscale designs.

To address this challenge, we propose a simple, repeatable method to build a 3D interconnected carbon network by forming covalent bonds between carbon nanostructures. Although such 3D covalently bonded carbon structures have been predicted by theoretical simulations,²⁹ no experimental work has been achieved. Here we report a 3D covalently interconnected carbon network by applying Joule heating to polyacrylonitrile (PAN) based carbon nanofibers at a high temperature (>2500 K) and an ultrafast rate (~200 K/min).

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Figure 1. Schematic of the welding process of CNFs and selected characterization results. (a) Schematic of the carbon welding process of CNFs triggered by Joule heating. (b) Raman spectra for pristine CNF and Joule heated CNF. The change in ratio between I_D/I_G and an increase in peak sharpness is indicative of the high crystallinity and graphitization of welded CNFs. (c, d) SEM images of the pristine CNF and welded CNF.

The ultrafast heating produces a high-temperature environment that enables further carbonization of the nanofibers and induces welding between adjacent nanofibers with graphitic carbon bonds, which form a 3D continuous carbon network. The bulk electrical conductivity of the carbon matrix increased four orders of magnitude to 380 S/cm with a sheet resistance of 1.75 Ω /sq compared to the pristine CNF membrane (0.0133 S/cm and 18400 Ω/sq). The high temperature Joule heating not only enables fast graphitization of carbon materials at high temperature, but also provides a new strategy to build covalently bonded graphitic carbon networks from amorphous carbon source. Because of the high electrical conductivity, good mechanical structures, and anticorrosion properties, this 3D interconnected carbon membrane can be potentially used in a range of applications such as electrochemical energy storage and electrocatalysis.

Figure 1, panel a shows an electric current being applied to the pristine intertwined CNFs to induce an ultrafast heating rate and result in (a) highly crystallized CNFs as well as (b) covalently welded CNFs at their junctions. Both the temperature and the heating rate of the Joule heating technique were controlled by the electrical field with a millisecond time resolution. The high crystallinity of CNFs after high-temperature Joule heating was revealed in the Raman spectra as shown in Figure 1, panel b. The pristine CNFs show broad Raman peaks, and the interested Raman region $(800-1700 \text{ cm}^{-1})$ can be deconvoluted into four peaks (Supporting Information, Figure S2), similar to the literature reported.³⁰ For welded CNF, only D-band and G-band are present and clear, while the other bands are suppressed. Raman peaks at 1350 cm⁻¹ are indicative of the disorder (D) band and structural defects in the CNF matrix. The graphitic (G) band at 1580 cm⁻¹ identifies first-order scattering in sp² carbon domains of the E_{2g} mode.³¹ After Joule heating to 2800 K in 10 min, the D-band peak was almost completely suppressed for the welded CNFs, and the intensity of all other peaks in the Raman spectra became much sharper in comparison to the spectra of CNFs precarbonized at 873 K. The intensity ratio between D-peak and G-peak (I_D/I_G)

decreases from 1.14 for pristine CNFs to 0.035 for welded CNFs. This is the lowest value reported in the literature for carbonized CNFs characterized by Raman spectroscopy.^{32–35} In addition, the graphitization process takes ~10 min by Joule heating but would take days by furnace heating, which further illustrates the high efficiency of the Joule heating method.³⁴

The welding of CNFs at junctions was shown by scanning electron microscopy (SEM) images in Figure 1, panels c and d. For pristine CNFs, the individual fiber has a smooth surface and is semitransparent due to its amorphous structure. Overlapping nanofibers in the pristine CNF matrix are in physical contact with their neighbors, but van der Waals interactions are weak. After Joule heating, the smooth fibers become rough, and the physical contacts were welded at junction points, which formed an integral fiber network (Figure 1d). By Joule heating, the amorphous intertwined CNFs become highly graphitic CNFs with fibers welded at junction points. Such highly graphitized and covalently interbonded structure effectively reduces contact resistance and facilitates fast electron transfer. Therefore, drastically increased conductivity after Joule heating can be expected and was measured. Furthermore, the mechanical properties of welded CNFs are also improved due to the covalent welding at fiber junctions, which locked the fibers from easy sliding.

CNF films were obtained by electrical spinning of PAN in dimethylformamide (8 wt %) followed by thermal stabilization at 260 °C and carbonization at 600 °C (Figure S1). PANderived CNFs were chosen because of the simple molecular structure, easiness to form nanofibers by electrospinning, and also the resultant high quality CNFs.¹⁰ The Joule heating process was controlled by an electric field to the set temperatures with at a controllable rate. Joule heating is a controllable method through adjusting input electrical current, as reported in literature of Joule heating applied to other carbon materials.³⁶ In our experiments, rotational drum was used to collect the electro-spun PAN fibers to ensure samples uniformity in thickness and density for Joule heating. In addition, all the samples are controllably heated to above 2500



Figure 2. Joule heating process of CNF. (a) Schematic to show the Joule heating experiment and setup of the temperature measurements. (b) Real image of the Joule heated CNF at high power, and inset is the film after Joule heating. (c) The calculated resistance (R = V/A) versus power plot during the Joule heating process with the measured voltage as a function of input current, inset. (d) The emitted spectra at high temperatures fitted to gray body radiation for temperature measurements at different powers. (e) Temperature versus power curve for a typical CNF sample. (f, g) Plots of the I_D/I_G ratio and Raman profiles during the graphitization process for CNF during Joule heating.

K for welding and graphitization, which ensures the output quality of welded-CNF. The Joule heating setup is displayed in Figure 2, panel a. The CNF samples were connected to copper electrodes by silver paste and suspended on a glass substrate to avoid the thermal damage during the Joule heating process. The CNF films were heated to a high temperature in an argon protected atmosphere.

Figure 2, panel b demonstrates a large CNF film (20 mm × 3 mm × 30 μ m in length, width, and thickness) loaded at 15 W, with a temperature of around 2000 K. The gradual lighting process of CNF films at different input powers can be found in Figure S3 of the Supporting Information. The optically emissive behavior indicates that high temperatures are reached in the CNF films. The Joule heating process was also carried out on CNF film (4 mm × 2 mm × 30 μ m in length, width, and thickness) with the driving current increasing from 0.1 mA to 1 A (Figure 2c). In comparison to the linear current–voltage (*I*–*V*) profile of a pure resistor, the measured resistivity of the CNF film shows a continuously decreasing profile for four orders of magnitude during the Joule heating process.

The temperature of lighted CNF can be calculated by fitting the emitted light spectra to the gray body radiation equation.^{37–40} The light spectrum was collected by an optical fiber (diameter 400 μ m, ocean optics) from 350–950 nm, and then the spectra were fitted to a gray body radiation curve to calculate the film temperature as shown in Figure 2, panel d. With an increase in input power, the intensity of emitted light gets higher and brighter in emission. We fitted the spectra profiles of the gray body radiation equation (eq 1), which obtained the temperature as a fitting parameter:^{6,36,41}

$$B_{\lambda}(\lambda, T) = \gamma \varepsilon \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda k_{\rm B}T} - 1}$$
(1)

where ε is the gray emissivity (~0.8 for carbon materials),⁴² $k_{\rm B}$ is the Boltzmann constant, *h* is the Planck constant, *c* is the speed of light, λ is the wavelength, and the constant γ is introduced for fitting. The temperature versus power relation in Figure 2, panel e illustrates a sublinear relation due to the decrease of heating efficiency at high temperatures: more heat is dissipated by radiation, convection, and conduction. This repeatable temperature –power relation can be used to precisely control the temperature of the Joule heating technique for future CNF experiments. The whole heating process takes about 10 min, with an average heating rate of 200 K/min.

Figure 2, panels f and g demonstrate the evolution of Raman spectra at different temperatures to reveal the bonding structure evolution during the Joule heating process. With increasing input power, there is a clear tendency for the D-band peak to become suppressed, while the G-band and 2D peaks become sharper. Figure 2, panel f summarizes the I_D/I_G relation at different temperatures and shows a drastic decrease from 1600 to 2400 K, which corresponds to the carbonization and graphitization of CNFs that occur above 1600 K. After Joule heating to 2800 K, the lowest I_D/I_G ratio of 0.035 was obtained, which indicates that the majority of carbon bonds in CNFs are sp² bonds graphitic carbon (graphene structure) after Joule heating.

The highly graphitic structure of the CNF network after Joule heating was confirmed by high-resolution transmission electron microscopy (HR-TEM). Before Joule heating (Figure



Figure 3. Morphological characterization of the welded CNF structure. High-resolution TEM images of (a) Joule-heated CNF and (b) the junction between Joule-heated CNFs. (c-f) SEM images showing the morphological evolution of CNFs by Joule heating at (d) 1500 K, (e) 1800 K, and (f) 2300 K.

S4), the main structure of the CNF is dominated by amorphous carbon, and few graphitic carbon layers can be observed by TEM. By applying the Joule heating treatment, the CNF film formed a highly crystallized carbon structure with graphitic carbon layers in the longitudinal direction as indicated by the arrow in Figure 3, panel a. During the high temperature Joule heating process, hydrogen and nitrogen are removed from the PAN-derived carbon structure, which facilitated the crosslinking into a crystallized graphitic structure. To verify the graphitic structure for welded CNF, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analysis were measured and shown in the Supporting Information (Figures S9 and S10). From the XPS result, the pristine CNF membrane shows a higher oxygen and nitrogen content (C, 82.71%; O, 11.67%; N, 5.62%) than those in welded CNF film (C, 97.08%; O, 2.55%; N, 0.37%). The eliminating of O and N from amorphous CNF purifies the structure so that graphitic C-C bonds can be formed at high temperature. In the XRD analysis, the pristine CNF shows a broad peak in the range of 20-30°, which indicates a low degree of graphitic carbon contained, while the welded CNF shows a sharp peak at 26.5°, which corresponds to the (002) for the graphitic layer structure. The sharp peak of welded CNF indicates increased crystallinity in welded CNF after high temperature Joule heating, which is consistent with Raman, HRTEM, and XPS results. Figure 3, panel b shows TEM images of the junctions between welded carbon nanofibers after the Joule heating process. Highly crystallized carbon layers are clearly observed at the junction point that bridges the neighboring CNFs. As far as we know, this is the first report of welding behavior for PANderived carbon materials.^{33–35,43}

To understand the welding behavior in the context of the Joule heating treatment, we controlled the temperature induced by Joule heating to observe the morphological evolution of CNFs as shown in Figure 3, panels c–f. The pristine CNF film displays smooth, intertwined fibers with a diameter around 200 nm and semitransparent optical properties due to their amorphous structures. After Joule heating to 1500 K, fibers start to stick together both in parallel, therefore forming a "Y"

shape, as well as in crossover, forming a "+" shape. Clear boundaries between these fibers were still present at 1500 K, which indicate incomplete welding between the carbon nanofibers. At 1800 K, the fiber surface becomes rough, and the nanofibers start to merge and weld together, which result in ambiguous boundaries between fibers. At 2300 K, the fiber junctions are completely welded together without distinct boundaries (welded structures also in Figure S8). It is interesting to note that high temperature Joule heating enables not only welding of adjacent crossover fibers, but also welding of parallel fibers, which results in a broad range of fiber diameters. The micromorphology of CNFs at different temperatures during the Joule heating process confirms the fusion of CNFs between 1500 and 2300 K. Within this temperature range, amorphous CNFs underwent carbonization and graphitization processes such that defects atoms were removed and C-C bonds were formed at the nanofiber junctions. Further high-temperature treatment above 2400 K anneals the fibers and fuses the nanofiber junctions into a highly crystalline, graphitic carbon matrix.

From the above experiments, it can be concluded that fast heating to high temperature played a key role in the formation of welded graphitic carbon structures by inducing fast graphitization process during which the fiber junctions were welded and annealed to graphitic structures. Another important condition for the welding of fiber junctions lies in the starting materials of amorphous CNFs whose structure can be tuned at high temperatures. To study the Joule heating effect on different carbon structures, CNT was selected due to its highly crystallized carbon structure, which is used to compare with the amorphous carbon of CNF. A thin CNT film was prepared and tested under similar conditions as the amorphous CNF samples. After Joule heating, no fusion was observed between the CNT fibers, and the Raman spectra of the CNT film exhibited more D-band defects as seen in Figure S11. The defects can be attributed to the decomposition of the solvent and surfactant that were used to synthesize the CNT inks and create thin films. The lack of fusion between CNT fibers is due to the high crystallinity of the as-prepared carbon nanotube



Figure 4. Molecular dynamic simulation of carbon welding at fiber junction. (a) Schematic of the crystalline (c-Carbon) and amorphous (a-Carbon) carbon fibers before and after the high temperature Joule heating technique. (b, c) SEM elemental mapping of nitrogen for pristine CNF and welded CNF. (d) Evolution of the amorphous carbon structure at fiber crossover region in LAMMPS. The equilibrium structure started from room temperature (300 K) and was heated to 3000 K. After the removal of nitrogen and hydrogen atoms, highly crystalline and graphitic structure was formed. Cyan, carbon. Pink, nitrogen. White, hydrogen.

structures. As schematically shown in Figure 4, panel a, even though high temperatures can be generated at the junction between carbon nanotubes (c-Carbon), the highly crystalline carbon structure cannot weld together without first deforming the stable C-C bonds and CNT structure that are already present.44 For amorphous carbon fibers (a-Carbon), Joule heating enables the defects of nitrogen and hydrogen in the amorphous structure to activate at a high temperature. With the removal of H and N, Bergman cyclization between adjacent CNFs takes place and new bonds are formed to weld the amorphous nanofibers together. Nitrogen elemental mapping of the CNF films before and after Joule heating is given in Figure 4, panels b and c. A large amount of nitrogen can be detected on the pristine CNF surface, and only a small amount of nitrogen can be observed on the welded CNF films, especially at the junctions between nanofibers. The elimination of nitrogen is an indication of the improved graphitization of carbon at high temperatures during the Joule heating method.

To study the welding behavior of PAN-derived carbon on an atomic scale, molecular dynamic (MD) simulations were performed using a large-scale atomic/molecular massively parallel simulator (LAMMPS)⁴⁵ and REAXFF potential^{46,4} (Figure 4d,e; Figure S15). Because of the higher resistance at the contact point between CNFs, a higher temperature environment at the junction is expected and helps initiate the welding and ordering of the amorphous carbon matrix. On the atomic level, we envision that Joule heating could greatly accelerate the purification and ordering of CNFs, particularly at the high temperature junctions between nanofibers. During Joule heating, the collisions between electrons that produce a current and the atoms in the nanofibers cause excessive vibrations of the amorphous carbon layers. Figure 4, panel d shows the equilibrated CNFs at 300 K where the in-plane two directions are subjected to periodic boundary conditions, and the out-of-plane direction is subjected to a reflected wall to simulate the excessive vibration of the atoms. The equilibrium structure at 300 K was heated to 3000 K, and a certain degree of nucleation of carbon chains is observed. After the nitrogen molecules were cyclically removed from the system and the simulation kept running, carbon atoms began to nucleate. After we continued to remove hydrogen molecules from the system, eventually, carbon atoms nucleated into the graphitic structure.

A detailed simulation can be found in the Supporting Information. Since the temperature of the Joule heating technique is highly dependent on the resistance of the CNF matrix, the welding of amorphous nanofibers benefits from the larger contact resistance at junction points, and graphitic structure can be expected after defects removal at high temperature.

Both the high graphitization and junction welding of welded CNF film can benefit the electron transport in bulk scale CNF structures and result in significantly improved conductivities. The electrical conductivity for the CNF film increased by a factor of 30 000 from 13.3 mS/cm to 381 S/cm, and a sheet resistance of 1.75 Ω/sq (Figure 5a). This calculation is determined without subtracting the porosity of the CNF film with a density of around $0.2 \sim 0.3 \text{ g/cm}^3$. As far as we know, this is the highest conductivity and lowest sheet resistance reported for CNF films in the literature,^{10,33} which confirms the superior performance of a bulk, 3D interconnected carbon matrix with welded junctions. To understand the role of junction welding in the enhancement of electrical properties, we measured the conductivity of a single fiber by a shadow-mask technique (Figure 5b). A single fiber was sonicated from CNF film and transferred to a silicon wafer. The 100 nm Au electrodes were deposited through a shadow mask to either end of the fiber (Figure 5b inset). The low temperature carbonized single fiber CNF (s-CNF) shows a conductivity of 4.67 S/cm, which is in accordance with literature studies.⁴⁸ After high temperature Joule heating, the conductivity of the single fiber (j-CNF) increases ~180-times to 822 S/cm by two-probe measurement. The electrical conductivity of a pristine CNF film, a welded CNF film, a single CNF fiber, and a single CNF fiber after Joule heating are presented in Figure 5, panel c. After Joule heating, both the film as well as single fiber conductivity increased substantially but by different magnitudes. The change in conductivity of the CNF film is a factor of 30 000-times, while the single nanofiber only increased by a factor of 180. We speculate that the welding of nanofiber junctions in CNF film is also critically important to the enhancement of conductivity of welded CNF film.

Besides the tremendous enhancement in conductivity, the mechanical properties of welded CNF film also improved because of the welded junctions, which is critical for its



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Figure 5. Electrical conductivity of the welded CNF (w-CNFs) structure. (a) Conductivity measurement results for the CNF film before and after the high temperature Joule heating process. (b) Conductivity measurement results for a single fiber (s-CNF) before and after Joule heating (j-CNF). (c) The conductivity of pristine CNF film (CNFs), welded CNF film (w-CNFs), a single fiber CNF (s-CNF), and a Joule heated single fiber CNF (j-CNF). (d) Schematic diagram to show the change in structure of separate and welded fibers after polymer resin infiltration. (e) Conductivity measurement results of pristine CNFs, welded CNFs, and welded CNFs after polymer infiltration (w-CNFs-epoxy). (f) Chart comparing the conductivity of CNF films, CNT films, and their composites.

application as battery current collector. Figure S14 demonstrates the strain-stress curves of pristine, welded, and polymer infiltrated CNFs films, respectively. The pristine CNF membranes (CNFs) have poor mechanical properties due to their porous structure and lacking of effective bonding between adjacent fibers to prevent fibers sliding during stress loading, which results in very low stress and several stepwise stress loading profiles. After high temperature Joule heating, nanofibers in the welded CNF films (w-CNFs) become highly crystalline and fuse together to form stiffer, interlocked carbon structure. The fused junctions in welded CNF matrix can prevent cross-slip between fibers and result in approximately 10-times higher tensile strength (from 0.31 to 3.86 MPa) and toughness (from 1.265 kJ/m³ to 20.65 kJ/m³). The mechanical property of welded CNF film can be further enhanced by infiltration polymer. As shown in schematic Figure 5, panel d, the nanofibers of a pristine CNF film will experience a large contact resistance when infiltrated by polymer layers.^{11,18} In comparison, the welded CNF film forms an interconnected structure with well-bonded junctions, and the outer polymer coating will not affect the electron transport inside the interconnected matrix. We therefore infiltrated epoxy resin into the open structure of a welded CNF matrix to create a composite material with improved mechanical properties as well as excellent bulk electrical conductivity. After polymer resin infiltration, the tensile strength and toughness were further enhanced to 10.6 MPa and 501.1 kJ/m³. Notably, as shown in Figure 5, panel e, the conductivity of welded CNF

after epoxy resin infiltration remained relatively constant due to the 3D interconnected continuous conductive pathways.

We summarized the electrical conductivity of CNF films and compared these values to typical fiber networks and fiberpolymer composites in Figure 5, panel f.^{10,11,21,35,49-53} The conductivity of the CNF film increases with an increase in the graphitization temperature. According to the literature, the CNF films carbonized at 600 °C have a conductivity of 19 mS/ cm, while films carbonized at 2800 °C exhibit ~20 S/cm. CNT films/papers synthesized by a filtration method have higher conductivities of 50 S/cm, while the welded CNF film exhibits the highest conductivity (\sim 380 S/cm) with an ultralight density $(0.2-0.3 \text{ g/cm}^3)$. It is expected that a higher conductivity can be obtained if the CNF film is more densely packed before it is Joule heated. In the meantime, our CNF-polymer composite exhibits a higher conductivity (340 S/cm) over most of the CNT-enhanced polymer composites reported in the literature, which proves that this material and the Joule heating technique could lead to further promising developments in the field of highly conductive polymer composite design.

The desirable properties for current collectors are lightweight, highly conductive, and anticorrosion for increased energy density and long-term usage. We have demonstrated the welded CNF membrane used as current collector by constructing a cathode electrode for Li-ion battery (Supporting Information, Figure S16). Different from conventional current collectors in 2D geometry where the active materials are coated on the current collector, our w-CNF membrane is a 3D porous structure where the cathode material LiFePO₄ (LFP) can be

infiltrated inside of the film, which forms a 3D w-CNF-LFP composite. Owing to the 3D interconnected carbon structure in w-CNF, the conductivity of w-CNF-LFP cathode materials is not heavily affected by the infiltrated LFP, and the sheet resistance is still as low as 2.35 Ω /sq. Such a composite structure also greatly reduces the electron conductive distance for LFP during electrochemical reactions. To summarize, the w-CNF film is super lightweight with a density of 0.2-0.3 g/cm₃; the welded fiber structure forms continuous conductive pathways with a high conductivity of 380 S/cm and low sheet resistance of 2 Ω/sq ; its porous structure also enables infiltration of active materials inside and therefore reduces the electron conductive distances during electrochemical reactions; and it also has good anticorrosion properties coming from the highly crystallized carbon structure. Therefore, w-CNF film shows great promise as current collectors for energy storage applications.

Conclusion. We present high temperature Joule heating method to achieve covalent welding of adjacent fibers in a 3D carbon nanofiber matrix to address scaling issues for carbon nanomaterials. The CNF film was heated to high temperatures (>2500 K) at an ultrafast rate $(\sim 200 \text{ K/min})$, thereby significantly improving the bulk electrical and mechanical properties. The bulk electrical conductivity of the carbon structure increased four orders of magnitude to ~380 S/cm with a sheet resistance of 1.75 Ω /sq. This work demonstrates that high temperature Joule heating method can enable fast graphitization of carbon materials at a high temperature and also provides a new strategy to build a covalently interconnected carbon network from amorphous carbon. We anticipate that this method can be extended to other carbon materials such as graphene and carbon nanotubes by proper surface modification, such as using polymer to produce graphitic carbon coating on those graphene and carbon nanotube networks, to form covalently interconnected carbon structures via high temperature Joule heating method.

Experimental Section. *CNF Preparation.* PAN was purchased from Sigma-Aldrich and dissolved in dimethylformamide (DMF) to form a 8 wt % solution and stirred at 60 °C for 12 h. The resulting transparent solution was electrospun at a voltage of 10 kV, a spinning distance of 15 cm, and a feeding rate of 1 mL/hour. The electrospun nanofibers were collected by a rotation drum at a speed of 80 rpm. The PAN nanofibers were then stabilized at 260 °C for 2 h in air and carbonized at 600 °C in an argon protected atmosphere.

Joule Heating Process. Joule heating was performed in an argon-filled glovebox. The CNF film was connected to copper tape electrodes by silver paste. A Keithley 2400 source meter was used as an input power source for current below 1 A or power below 20 W. A higher power transformer (Volteq HY6020EX) was used for current up to 20 A. The emitted light was collected by an optical fiber (400 μ m diameter) and connected to a spectrometer (Ocean Optics). The measurement system was calibrated by a National Institute of Standards and Technology (NIST)-traceable light source.

Characterizations. The morphology of the CNF samples was observed by a Hitachi SU-70 FEG-SEM at 10 kV and JEOL 2100 LaB6 TEM. Raman characterization was done with a Horiba Jobin-Yvon with the laser wavelength at 532 nm and the integration time of 4 s repeated for four times. The mechanical strain–stress curves were measured by dynamic mechanical analysis (DMA Q800) with TA Instruments.

Conductivity Measurement. The conductivity of the CNF films and single fibers was measured by a four-point probe. For the single fiber conductivity, a single carbon nanofiber was sonicated from the CNF film and transferred to a silicon wafer. A shadow mask was used to deposit Au electrodes, and then the single fiber was prepared by electrical Joule heating and the conductivity was measured by the two electrodes method with a bias voltage of 10 mV.

ASSOCIATED CONTENT

Supporting Information

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Experimental details and proofs; simulation description (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Carbon Welding by Ultrafast Joule Heating

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Pristine carbon nanofibers

Figure S1 shows pictures and scanning electron microscopy (SEM) images of the carbon nanofibers (CNF) pre-carbonized at 873 K showing randomly intertwined fibers with a diameter of 200 -300 nm.



Figure S1. (a)-(b) Images of pristine CNF in a flat and bent state. (c)-(e) SEM images of the pristine CNF at different magnifications.

We have deconvoluted the Raman peaks of pristine CNF as shown below (Fig. S2). It can be seen that the Raman peaks of region (800-1700 cm⁻¹) can be deconvoluted into 4 peaks: TPA (transpolyacetylene) band, D band, A band and G band. The deconvoluted G peak for pristine CNF is at 1590 cm⁻¹, while the G peak for welded CNF is at 1585 cm⁻¹. This red shift of G peak can be attributed to the increased graphitic degree in welded CNF. The A band is commonly observed in disordered carbon, and therefore is attributed to the point defects. For welded CNF, only D band and G band is present and clear, while the A band is suppressed. The deconvoluted Raman peaks again indicate the increased graphitic crystallinity in welded CNF as compared with pristine CNF.



Figure S2. Deconvoluted Raman peaks of pristine CNF.

Joule heating process

Figure S3 shows the high temperature light emitting effect induced by Joule heating at different powers. Figure S3a to S2d are images of the CNF film under Joule heating from 0 W to 1 W, 2 W and 3 W, with increasing brightness with increasing input power. Figure S3e to S2h show the light intensity change at 550 nm with 100 milliseconds exposure time at different temperatures.



Figure S3. (a)-(d) *In-situ* images and (e)-(f) thermal microscope images for the lighting process induced by Joule heating at different powers and temperatures.

Microstructures of pristine and Joule heated CNF

Figure S4 shows a high-resolution transmission electron microscopy (HRTEM) image of the pristine CNF with an amorphous carbon structure. No crystalline graphitic layer were observed in CNF matrix before Joule heating.



Figure S4. HRTEM image of the pristine CNF film.

After Joule heating at 2800 K, a crystalline, graphitic carbon structure was observed in Fig. S5.



Figure S5. HRTEM observation of the CNF after Joule heating.

Figure S6 and S7 show the HRTEM images of the CNF film before and after Joule heating. The pristine CNF shows overlapping between two fibers at a junction point while for the Joule heated CNF film, clear graphitic carbon layers continuously connect two nanofibers.



Figure S6. HRTEM observation of pristine CNFs at a fiber junction. The white arrows indicate the fiber directions.



Figure S7. HRTEM observation of a Joule heated CNF at a fused fiber junction. The white arrows indicate the previous fiber directions. A continuous weld or fusion between two fibers is observed.

Figure S8 shows SEM images of the welded CNF at different magnifications.



Figure S8. (a)-(d) SEM images of the welded CNF.

Composition analysis

Figure S9 shows the composition change of CNFs film before and after the high temperature Joule heating. The N and O defects drastically decreased after Joule heating.



Figure S9. XPS analysis of the CNF film before and after the high temperature Joule heating.

The XRD of pristine CNF and welded CNF were measured and shown below (Fig. S10). The pristine CNF shows a broad peak in the range of 20-30 degree. In contrast, the welded CNF shows a very sharp peak at 26.5 degree, corresponding to the (002) peak. The sharp peak of welded CNF indicate increased crystallinity in welded CNF after high temperature Joule heating.



Figure S10. X-ray diffraction pattern of pristine CNF and welded CNF.

CNT after Joule heating

Figure S11 shows the Raman spectra and conductivity measurements of the CNT film before and after the Joule heating technique. After Joule heating, the Raman D peak of the CNT film increased substantially, which means more defects are generated during the Joule heating process. This is in contrary to the Raman D band peak evolution of the CNF film after Joule heating. As a result, the conductivity of the CNT film decreased after Joule heating.



Figure S11. Raman spectra and conductivity measurements of the CNT film before and after Joule heating process.

Conductivity measurement

The CNF film electrical conductivity was measured at different powers as shown in Figure S12a. The resistivity was measured with a 10 mV bias voltage and then the current. Figure S12b and S12c shows the cross-section SEM images of pristine and welded CNF films used for the conductivity calculations. The films are thinner after Joule heating.



Figure S12. CNF film conductivity measurement results. (a) Voltage-current profiles of the CNF film after different Joule heating conditions (driving currents). (b) and (c) Cross-section SEM images of pristine and welded CNF films.

For single fiber conductivity measurements, the CNF film was first sonicated and then single fiber was transferred to the silicon wafer. A micrometer feature size shadow mask was used to measure the conductivity of this single fiber as shown in Figure S13a and S13b. The conductivity of a single fiber first went up and then decreased at excessively high current values. The maximum increase was around 180 times. The highest conductivity was calculated to be 822 S/cm.



Figure S13. Single fiber conductivity measurement. (a) and (b) Au electrodes on a single carbon nanofiber made by a micrometer sized shadow mask. (c) Single fiber voltage-current profiles under a bias field of 10 mV.

Polymer infiltration

Figure S14a shows strain-stress curves of pristine, welded, and polymer infiltrated CNFs films. Figure S14b and S14c show the cross sectional SEM images of the pristine and welded CNF films after polymer infiltration.



Figure S14. (a) The strain-stress curves for pristine CNFs, welded CNFs (w-CNFs) and welded CNFs after polymer infiltration (w-CNFs-epoxy). (b) and (c) Cross-sectional SEM images of the pristine and welded CNF after polymer infiltration.

Simulation details

We are effectively simulating the region that is at the intersection of two fibers, as shown in Figure S15(a). We first construct an initial structure, in which 6 parallel PAN chains on top (representative of the surface area of Fiber 1) are in perpendicular to another 6 parallel PAN chains on the bottom (representative of the surface area of Fiber 2), as shown in Figure S15(b). We used the large-scale atomic/molecular massively parallel simulator (LAMMPS) and REAXFF potential to perform molecular dynamics simulations. The time step is set to 0.25 fs. The simulation is performed on a canonical ensemble (NVT), controlled by a Nosé-Hoover thermostat. We first put the structure of Figure S15(b) into a relatively larger simulation box. The in-plane two directions are subjected to periodic boundary condition while the one out-of-plane direction is subjected to a reflected wall, as a way to introduce the excessive vibration of the atoms. We then equilibrate this structure at 300 K while gradually shrinking the simulation box size to 3.8 nm by 3.8nm by 0.68 nm within 50000 time steps. We make the out-of-plane simulation box size small so that the effect from the reflect wall at

the box boundary could be maximized on the entire structure, when considering that the electrons are passing through the simulation box from out-of-plane direction. The equilibrated structure is shown in Figure S15(c) and (d). The system has a density of 2.1 g/cm3, which is relevant to the experimental carbonization conditions. After the equilibrated structure is obtained, we use this structure for the input coordinates for subsequent simulations. Due to the limitation of time scale at any MD simulation, we are not able to match our simulation to the experimental heating rate. Instead, this structure is directly subject to a canonical ensemble (NVT) at 3000 K, controlled by a Nosé-Hoover thermostat, for 800000 time steps. Then we have obtained the structure as shown in Figure 4(b) in main text. After that, we manually delete the isolated nitrogen molecules/atoms and rerun the simulation. We repeated this process until all nitrogen molecules/atoms are removed. Then we use the same protocol on the subsequent removing the isolated hydrogen molecules/atoms.



Figure S15. Simulation strategy. (a) Schematic of simulated region: the contact area of two adjacent fibers. (b)

The initial structure of CNFs and (c) top view and (d) side view of equilibrium CNFs structure at 3000 K.

Battery current collector demonstration



Figure S16. Demonstration of welded-CNF membrane applied as a battery current collector. (a) Photo images of cathode slurry casted on w-CNF film 0 and 2 minutes. (b) Sheet resistance of w-CNF, w-CNF loaded with LFP and a commercial LFP cathode material. (c)-(d) SEM images of LFP cathode infiltrated into w-CNF as a battery current collector. (e)-(f) SEM images of higher loading of LFP on w-CNF membrane.

As shown in Fig. S16a, the as-casted cathode slurry sits on w-CNF membrane with a good wetting angle of $\sim 30^{\circ}$, and quickly infiltrate into w-CNF membrane within 2 minutes with the assistant of vacuum, indicating that the porous structure of w-CNF membrane is suitable as a 3D current collector to incorporate micro- and nano-powders like LFP. Due to the unique

3D interconnected carbon structure with a continuous electron conductive pathway, the sheet resistance of w-CNF loaded with LFP cathode materials is still as low as 2.35 Ω /sq (Fig. R6b). In comparison, the commercial LFP cathode sheet (MTI) has a sheet resistance of 310 Ω /sq measured from in-plane LFP side, addressing the advantages of 3D current collector. The microstructures of the w-CNF-LFP composite are shown in Fig. S16c-d. The cross-section view shows the infiltration of LFP cathode material into w-CNF film. This is clearly displayed in Fig. S16d, that LFP powders are embedded into the 3D conductive w-CNFs scaffold. Such a w-CNF-LFP composite greatly reduces the conductive distance and therefore the resistance during electrochemical reactions. For higher mass loading, the SEM images are shown in Fig. S16e-f. From the cross-section view, the LFP electrode has a thickness of 45 µm while the w-CNF film is 15 µm, resulting in a mass loading of 4.8 mg/cm².