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5 Ultrafine Silver Nanoparticles for Seeded Lithium Deposition toward Stable Lithium 6 Metal Anode 7

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- 16 nearing, Li dendri
- 18 Abstract

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19 To exploit the high energy density of the lithium (Li) metal battery, it is imperative to address 20 the dendrite growth and interface instability of the anode. Three-dimensional (3D) hosts for Li 21 metal are expected to suppress the growth of Li dendrites. Heterogeneous seeds are effective 22 in guiding Li deposition and realizing spatial control over Li nucleation. Herein, we show that 23 ultrafine silver (Ag) nanoparticles, which are synthesized via a novel rapid Joule heating 24 method, can serve as nanoseeds to direct the deposition of Li within the 3D host materials, 25 resolving the problems of the Li metal anode. By optimizing the Joule heating method, 26 ultrafine Ag nanoparticles (~40 nm) are homogenously anchored on carbon nanofibers. The 27 Ag nanoseeds effectively reduce the nucleation overpotential of Li and guide the Li 28 deposition in the 3D carbon matrix uniformly, free from the dendrites. A stable and reversible Li metal anode is achieved in virtue of the Ag nanoseeds in the 3D substrate, showing a low 29 30 overpotential (~0.025 V) for a long cycle life. The ultrafine nanoseeds achieved by rapid 31 Joule heating render uniform deposition of Li metal anode in 3D hosts, promising a safe and 32 long-life Li metal battery for high-energy applications.

1 Electrochemical energy storage systems with high energy densities are crucial for portable 2 electronics, electric vehicles, and grid-scale energy storage. Among many candidates, lithium 3 metal batteries, which combine a Li metal anode and high-energy cathodes such as sulfur and oxygen, possess high theoretical energy densities and low cost, and are considered as the 4 next-generation energy storage systems.^[1] Li metal is attractive as an anode because of its 5 extremely high specific capacity (theoretically 3860 mA h g⁻¹) and low electrochemical 6 potential (-3.04 V vs standard hydrogen electrode), which promise a high energy density in 7 Li metal batteries.^[2] Currently, the practical utilization of Li metal anodes is hindered by 8 9 several problems, including the formation of dendritic Li metal during deposition, instability 10 of the Li metal interface, and huge volume change effect. The uncontrollable and dendrite-11 forming growth of Li metal could lead to low reversibility, short cycle life, potential internal 12 short-circuit, and safety hazards, which have greatly impeded the application of Li metal anodes.^[3] 13

14 For decades, tremendous efforts have been made to improve the electrochemical performance and cycling life of the Li metal anodes. Studies have shown that the deposition behavior and 15 16 interface stability of Li metal anodes can be greatly reinforced by modifying the electrolyte and additives,^[4] engineering protective interface layers,^[5] and constructing 3D host structures 17 for Li metal.^[6] Among various approaches, the Li host structures have attracted considerable 18 19 interest because they are effective in regulating Li deposition, suppressing the growth of Li 20 dendrites, reducing the local current density, and homogenizing the Li-ion flux. Moreover, nanotechnology can introduce great opportunities to further develop innovative host structures 21 to solve the intrinsic problems of Li nucleation and Li interfacial issues.^[7] However, Li 22 deposition in 3D host materials (typically C or Cu) is hampered by a poor affinity of Cu and C 23 for Li metal.^[8] Li shows poor wettability on C and Cu substrates; nucleation overpotentials 24 25 occur during Li nucleation on C and Cu, indicating the unfavorable Li deposition on these substrates. Recently, Cui et al. pioneered selective Li deposition through heterogeneous 26

seeded growth.^[9] Using nanomaterials that have zero overpotential of Li nucleation (such as
 gold nanoparticles) as seeds, Li will selectively nucleate on the seeds and can be spatially
 controlled on anode substrates.^[9-10]

4 Heterogeneous seeded Li nucleation opens a new approach to directing Li deposition in 3D 5 host structures. Heterogeneous nanoseeds dispersed on the skeleton of 3D substrates are 6 expected to guide Li deposition into the 3D substrates and thus constrain the growth of Li 7 dendrites. To this end, the nanoseeds should also be homogeneously and strongly anchored on 8 the 3D host materials for reversible Li plating/stripping. Herein, we show silver (Ag) 9 nanoparticles (AgNPs) anchored on carbon nanofibers (CNFs) can spatially direct the deposition of Li metal, forming a dendrite-free Li metal anode. Ag has an appreciable 10 solubility in Li according to the Li-Ag phase diagram,^[11] thus favoring Li electrodeposition 11 on Ag with zero overpotential. As depicted in Figure 1a, via a novel Joule heating method,^[12] 12 13 ultrafine AgNPs can be synthesized homogeneously on CNFs. The ultrahigh temperature 14 during Joule heating enables strong binding between the AgNPs and the carbon substrate. Guided by the uniform Ag nanoseeds, Li is preferentially plated on the CNFs and 15 16 accommodated in the 3D substrate free from dendritic morphology. Without the seeding with 17 AgNPs, however, Li deposition on the CNF substrate is unregulated and could form Li rods 18 vertically grown from the substrate, irrespective of the 3D structure of the host (as illustrated 19 in Figure 1b). The Li anode using the AgNP-modified 3D substrate exhibits a low nucleation 20 overpotential (~0.025 V), smooth deposition morphology, and excellent plating/stripping 21 stability over 500 h.



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Figure 1. (a) Schematic illustration of the strategy to deposit Li metal uniformly on 3D host materials via nanoseeds. Li deposition and growth are seeded by AgNPs, which are homogeneously anchored on the CNF substrate via Joule heating. Li metal is thus directed into the 3D substrate forming an even Li anode. (b) Schematic of Li deposition on bare CNF substrate without AgNPs, on which a non-uniform Li anode is plated.

7 To obtain ultrafine Ag nanoparticles with strong binding on CNFs, Joule heating was applied 8 for rapid high-temperature treatment. As illustrated in Figure 2a, the CNFs were soaked with 9 silver acetate (AgAc) and rapidly heated via an electric thermal shock using a homemade 10 Joule heating setup (Figure S1). CNFs were prepared by electrospinning (see the inset of 11 Figure 2a for the scanning electron microscopy (SEM) image of CNFs) and served as the 12 electric conductor for AgAc. During the rapid Joule heating, the temperature was drastically elevated to ~1600 K within 20 ms (Figure 2b). A bright light was emitted from the AgAc-13 14 CNF samples at high temperature (see inset in Figure 2b) due to gray-body radiation. The light spectrum was in-situ recorded to determine the temperature according to gray-body 15 radiation equations.^[12-13] The temperature of the AgAc-CNF during thermal shock was 16 17 calculated from the emitted light spectra based on the gray-body model.^[13a, 14] As shown in Figure 2b, the thermal shock proceeded at temperatures up to 1700 K and held briefly for 0.1 18 s before rapid quenching. The heating/cooling temperature ramp rate was roughly 7×10^4 K s⁻ 19

1 ¹, several orders of magnitude higher than that in a traditional furnace (normally less than 100) K min⁻¹).^[15] Ultrafast thermal decomposition of AgAc at the high temperature produces Ag 2 nanoparticles on CNFs.^[16] The high temperature and ultrafast ramp rate cause instantaneous 3 decomposition of AgAc to form metallic Ag on CNFs while preserving the nanostructure. 4 5 During heating above the melting point of Ag (962 K) for only 0.1 s, the molten Ag selfassembled to nanoparticles guided by the defects on CNFs.^[17] Before the Ag nanoparticles 6 7 could further agglomerate and grow into large particles, the temperature was decreased 8 abruptly to below the melting point of Ag. Hence, ultrafine Ag nanoparticles were obtained 9 because of the rapid Joule heating and quenching process. The rapid thermal shock also 10 preserves the graphitic structure of the CNFs. As shown in the Raman spectra of CNFs 11 (Figure S2), the D and G bands of CNFs are scarcely changed after the thermal shock, 12 indicating that the rapid Joule heating method averts side reaction of the CNFs despite the 13 high temperature.

14 The SEM image (Figure 2c) exhibits homogeneous Ag nanoparticles (AgNPs) of ~40 nm in 15 diameter on CNFs. The content of Ag on CNFs is approximately 6 atom% according to the 16 energy-dispersive spectrum (Figure S3). The homogenous distribution of Ag nanoparticles is 17 attributed to the ultrafast Joule heating and is critical for a uniform Li deposition on the 18 nanoseeds, which will be discussed below. In comparison, if heated in a conventional furnace. 19 the low temperature ramp rate leads to diffusion and aggregation of Ag, forming large Ag 20 particles with a broad size range (see SEM image in Figure S4). Moreover, synthesized at the 21 high temperature (~1600 K) during Joule heating, the AgNPs are firmly anchored on the CNF 22 substrate, which is evidenced by the high-resolution transmission electron microscopy (TEM) 23 image (Figure 2d). The high temperature realized by the thermal shock guarantees strong 24 bonding between the carbon substrate and the nanoparticles. The defects on the surface of CNFs induced energy barriers that constrain the migration of AgNPs.^[17a] The solid bonding of 25 AgNPs on CNFs ensures the reliable seeded Li nucleation and growth in repeated cycles. 26



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Figure 2. (a) Schematic of Joule heating method for Ag nanoparticles on CNFs (the inset image shows the morphology of CNFs prepared by electrospinning). (b) Temporal evolution of the temperature during Joule heating (inset: digital photo of the CNFs emitting light at 1400–1700 K). (c) SEM image of AgNPs dispersed on CNFs synthesized via Joule heating for 0.5 s. (d) High-resolution TEM image of an Ag nanoparticle anchored on the CNFs.

7 To best exploit the seeded growth of Li anode on AgNPs, particle size and distribution of 8 AgNPs were optimized by tuning the Joule heating time. As nanoparticles are liable to diffuse 9 and accumulate into large particles at high temperature, it is critical to realize rapid pyrolysis 10 via a thermal pulse for preserving the nanostructures. Figure 3a-d show the morphologies of 11 the AgNPs on CNFs synthesized via Joule heating for 0.05, 0.1, 0.5, and 4 s, respectively. 12 Homogeneous and ultrafine AgNPs are obtained after rapid Joule heating for 0.05–0.5 s. The 13 particle sizes are plotted in Figure 3e as a function of the thermal shock time. The particle size 14 is found to be reduced through short thermal shock time. By rapid Joule heating (0.05-0.5 s),

1 ultrafine AgNPs are obtained with homogeneous particle size and an average size of 29-57 2 nm. The AgNPs synthesized by 4 s thermal shock exhibit a broader size distribution and a much larger particle diameter (~280 nm) than those synthesized via rapid Joule heating. If 3 4 synthesized via conventional calcination in a furnace, Ag particles grow to even larger and 5 more discrete particles (~850 nm in average, Figure S4), with little binding with the CNFs. 6 Ultrafast thermal shock generally yields smaller nanoparticles; however, thermal shock that 7 was too short would not sufficiently decompose the precursor to obtain AgNPs (see Figure S5 8 for the AgNPs synthesized via 5-ms Joule heating with residual AgAc precursor).

The initial Li metal deposition onto different substrates at 0.2 mA cm⁻² was characterized in 9 10 Figure 3f to reveal the effect of the Ag nanoseeds on Li nucleation. The deposition of Li metal 11 onto bare CNFs has an obvious nucleation overpotential (a voltage dip at the very first nucleation), which is approximately 15 mV at 0.2 mA cm⁻². As studied by Cui and co-12 workers,^[9] host materials (such as carbon) that have no solubility in Li metal have nucleation 13 14 overpotentials during Li nucleation, whereas host materials that have certain solubility in Li (such as Au, Ag, etc.) favor Li deposition without a nucleation overpotential. For the CNFs 15 16 decorated or coated by AgNP heterogeneous nanoseeds, Li is selectively nucleated on AgNPs 17 with a negligible nucleation overpotential. The nucleation overpotential, as well as the seeded 18 growth of Li, is closely related to the particle size and homogeneity of AgNPs on CNFs. 19 Prepared by the rapid Joule heating (0.05-0.5 s thermal shock), AgNPs of ~40 nm in size are 20 well distributed on the substrate and can guide nucleation of Li on AgNPs with zero nucleation overpotential at 0.2 mA cm⁻² (Figure 3f). For the CNF mat with scattered Ag 21 22 particles (denoted as Ag-CNFs), which were prepared by 4 s thermal shock or conventional 23 pyrolysis in a furnace, minor nucleation overpotential is still observed, indicating that Li 24 metal is still able to deposit on the bare CNFs. Therefore, the optimal Ag nanoparticles with 25 homogeneous dispersion on CNFs and uniform particle size (~40 nm via 0.1 s thermal shock, denoted as AgNP/CNFs) are used as the nanoseeds for further Li electrodeposition study. 26



Figure 3. SEM images of AgNPs on CNFs synthesized via Joule heating for (a) 0.05 s, (b)
0.1 s, (c) 0.5 s, and (d) 4 s. (e) Size of Ag nanoparticles prepared by Joule heating for different
thermal shock time and by conventional calcination in a furnace. (f) Voltage profiles during
initial Li deposition at 0.2 mA cm⁻² onto various substrates: bare CNFs, AgNP/CNFs via
Joule heating (0.1 s or 4 s), and Ag-CNFs synthesized via conventional furnace heating (at
900 °C for 4 h).

1 Seeded growth of Li metal on the uniformly distributed AgNPs can form a well-regulated Li 2 anode in the 3D CNF substrate. As shown in the schematic (Figure 4a), starting from 3 AgNP/CNFs with a particle size of ~40 nm (Figure 4b) as nucleation sites, Li is selectively 4 nucleated on the AgNPs due to the zero nucleation overpotential. Li first allovs with AgNPs 5 and is then plated as metallic Li on AgNPs (Figure 4c). Because the AgNPs are uniformly 6 anchored on CNFs, Li metal deposition is directed onto CNFs, forming a smooth Li coating layer on the CNF substrate after plating 1 mA h cm⁻² of Li (Figure 4d). During ensuing Li 7 8 deposition, growth of Li from AgNP/CNFs gradually fills in the voids between the CNFs and 9 forms an even Li metal anode without dendrites (Figure S6). After Li stripping, AgNPs 10 remain fixed on CNFs with a layer of solid electrolyte interface (SEI) film due to their strong 11 binding interaction (Figure 4e), which can repeatedly guide the seeded nucleation of the Li 12 anode.

13 For comparison, Li deposition behaviors on bare CNFs and CNFs with scattered Ag particles 14 (Ag-CNFs, synthesized by conventional pyrolysis in a furnace) were also investigated. The bare CNF 3D host without AgNP nanoseeds (Figure 4f) cannot constrain a smooth Li metal 15 16 anode because Li deposition is not guided onto the carbon skeleton. Because carbon has no Li metal wettability or affinity,^[8] Li is not inclined to nucleate on CNFs but instead forms non-17 18 uniform Li that agglomerates and grows vertically outside of the CNFs (Figure 4g). The 19 uncontrolled Li growth without spatial confinement would deteriorate the cycling stability of Li metal anode and cause dendrite problems.^[7a, 18] The seeded Li growth by AgNPs is 20 21 effective only if the nanoseeds are uniformly anchored on the 3D host materials. Using the 22 Ag-CNFs synthesized by conventional pyrolysis as the substrate (Figure 4h), although partial Li metal growth is seeded by the randomly dispersed Ag particles, the majority of Li metal is 23 not uniformly hosted by the 3D substrate but forms mossy Li (Figure 4i). This explains the 24 25 slight nucleation overpotential of Li on Ag-CNFs in Figure 3f. These results highlight the

- 1 importance of utilizing uniform nanoseeds on 3D host materials for Li metal anode, which has
- 2 been demonstrated by the AgNPs via the rapid Joule heating.





Figure 4. (a) Schematics of Li nucleation and growth seeded by Ag nanoparticles on CNFs.
SEM images of (b) pristine AgNP/CNFs without Li deposition, (c) initial Li nucleation on
AgNP/CNFs, (d) 1 mA h cm⁻² of Li deposited on CNFs guided by AgNPs, and (e)
AgNP/CNFs after the first plating/stripping cycle. SEM images of control samples: (f) bare
CNFs without Ag nanoseeds, (g) Li deposited on bare CNFs, (h) Ag-CNFs synthesized via
conventional furnace heating, and (i) Li deposited on Ag-CNFs.

10 The Li deposition behavior has a significant effect on its electrochemical performance. Using 11 the bare CNFs as a 3D substrate without seeding, the self-nucleation of Li forms Li pillars and 12 dendrites, which could produce dead Li (electrically disconnected from the current collector) 13 and be adverse to the cycle performance of the Li anode. This is evidenced by cycling Li metal anode with the bare CNF substrate at 0.5 mA cm⁻² (Figure 5a). After cycling for shortly 14 15 100 h, the overpotential is increased due to the decomposition of the electrolyte, and erratic voltage behavior is observed, indicating the formation of fractal Li dendrites on the bare 16 CNFs.^[3] A similar phenomenon is found using the large Ag particles that are not solidly 17 anchored on the CNF substrate. Taking the Ag-CNFs synthesized in the furnace as an 18

example, Li nucleation can be seeded by the Ag particles but is not uniformly deposited within the 3D host structure and still forms mossy Li (Figure 4i), because the seeds are not homogeneously fixed on the substrate. After cycling for 100 h (~25 cycles), the formation of mossy Li increases the growth of SEI films and leads to the increased plating/stripping polarization (Figure S7).

6 In contrast, using the rapid Joule heating, uniform and ultrafine Ag nanoparticles are solidly fixed on the CNF substrate. As the nucleation and growth of Li metal are seeded by the Ag 7 8 nanoparticles on CNFs, Li metal can be deposited into the 3D host material uniformly and 9 reversibly. The cycling performance of Li metal anodes using the AgNP/CNFs host materials (Ag particles size of \sim 40 nm) is shown in Figure 5b, which were cycled at 0.5 mA cm⁻² for 1 10 mA h cm⁻² (additional 1 mA h cm⁻² of Li was deposited as the anode during the initial plating). 11 The Li metal anode with the AgNP/CNFs substrate shows an exceptional cycling stability at 12 0.5 mA cm⁻² for 500 h without short-circuiting due to the seeded Li growth on AgNPs. The Li 13 anode with Ag nanoseeds exhibits a high Coulombic efficiency, which is stabilized to ~98% 14 after cycling (Figure S8), compared with that of the Li anode on bare CNFs (~96%). Stable 15 cycling performance is also obtained at 1 mA cm⁻² for 2 mA h cm⁻² (Figure S9). The thickness 16 of the AgNP/CNF substrate has a great influence on the available areal capacity of the Li 17 metal anode. By rationally increase the thickness and porosity of the 3D substrate, the 18 19 capacity and stability of the Li anode can be further improved for practical applications. The 20 discharge/charge voltage profiles of Li anode on AgNP/CNFs are shown in Figure 5c in 21 comparison with the bare CNF substrate. On the bare CNFs, plating or stripping of Li is 22 accompanied with an obvious initial nucleation overpotential due to the unfavorable Li nucleation on carbon. The Li anode seeded by AgNP/CNFs shows a low overpotential (~25 23 mV) with negligible nucleation overpotential at 0.5 mA cm⁻², indicating the controlled Li 24 deposition into the 3D substrate with ultrafine AgNPs. The polarization of the cell with Ag 25

- 1 nanoseeds is smaller than that without AgNPs, especially during the initial Li plating, which
- 2 is attributed to the uniform deposition of Li enable by the Ag nanoseeds on the substrate.



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Figure 5. Cycling performance of Li anode plating/stripping at 0.5 mA cm⁻² for 1 mA h cm⁻²
on (a) bare CNFs and (b) AgNP/CNFs (via rapid Joule heating for 0.1 s). (c) Discharge/charge
voltage profiles of Li metal anode on bare CNFs and AgNP/CNFs at 0.5 mA cm⁻² for the first
3 cycles. (d) Nyquist plots of Li metal anode before and after cycling.

1 The uniform Li anode on AgNP/CNFs also renders the SEI film on the anode stable during 2 cycling. The electrochemical impedance spectra (EIS, Figure 5d) of the Li anode with AgNP/CNF substrate show that the charge-transfer resistance (R_{ct}) at the Li–AgNP/CNF 3 interface (77 Ω) is much smaller than that with bare CNFs (145 Ω , see EIS of Li anode on 4 5 bare CNFs in Figure S10). R_{ct} of the Li–AgNP/CNF anode is not significantly increased after 6 Li deposition (98 Ω) and dissolution (113 Ω) compared to the fresh cell (77 Ω). The charge-7 transfer impedance remains stable (~134 Ω) for the following 200 cycles. The stable interface 8 originates from the heterogeneous seeded nucleation of Li on AgNPs and reversible 9 dissolution, which also contributes to the exceptional cycling performance. 10 In summary, we have demonstrated ultrafine AgNPs anchored on CNFs for seeded nucleation 11 and growth of Li metal. The AgNPs obtained by rapid Joule heating yield ubiquitous and 12 uniform nanoseeds on 3D host materials, on which Li metal are guided to form smooth Li 13 metal anode without dendrite problems. The rapid Joule heating is advantageous in terms of fast and facile fabrication, particle size optimization, and strong binding between the 14 15 nanoparticles and the 3D substrate. The 3D Li host substrate modified by the ultrafine 16 nanoseeds can effectively regulate the Li deposition behavior and inhibit the Li dendrites. Our 17 results show that Li nucleation and growth seeded by AgNPs on CNFs realize smooth Li 18 anode coated on the CNFs without dendrites. The resultant Li anode exhibits low voltage 19 overpotential and an exceptional cycling stability without short-circuiting problems. 20 Rationally designed 3D architecture with the ultrafine nanoseeds by rapid Joule heating 21 provides a promising approach to a dendrite-free Li metal anode for safe and long-life Li 22 metal batteries. The novel rapid Joule heating method is also expected to create more 23 possibilities in nanofabrication for advanced energy-storage materials.

1 **Experimental Section**

2 Synthesis. CNFs were prepared by electrospinning and carbonization. Polyacrylonitrile was 3 dissolved in dimethylformamide with a concentration of 8 wt% and was used as the precursor 4 for electrospinning. For electrospinning, a high voltage of 10 kV was applied between a 5 needle and an aluminum foil on a rotation drum (distance: 15 cm). The polyacrylonitrile solution was electrospun at a rate of 1 mL h⁻¹. The as-spun nanofiber mat was collected and 6 7 calcined at 260 °C for 5 h in air and then at 800 °C for 2 h in argon flow to obtain CNFs. The 8 CNF mat was soaked with silver acetate (AgAc) solution (0.05 mol L^{-1}) by vacuum 9 infiltration, followed by drying at 60 °C.

10 The AgAc-CNFs were treated by electric Joule heating to form Ag nanoparticles on the CNFs. 11 To perform Joule heating, the AgAc-CNF mat was attached to copper electrodes with silver 12 paste and suspended above a glass pedestal (Figure S1). The total resistance of the AgAc-13 CNF mat and silver paste was typically 800–1000 Ω . The AgAc-CNF mat with the pedestal was placed in an argon-filled glovebox and electrically connected to external power source 14 15 (Keithley 2400 Source Meter). A current pulse of ~1 A was applied through the AgAc-CNF 16 mat, which created a Joule thermal shock for a very short time (0.005–4 s). The emitted light 17 during Joule heating was in situ collected by an in-house built spectrometer system, which 18 employs a 0.5 m spectrometer (Sp-500i) with 1200 grooves/mm gratings. The dispersed light 19 through the gratings was collected by a photomultiplier tube array (H-7260, 32-channel) to 20 integrate the full spectrum. By fitting the full spectrum, the fitted temperature throughout the 21 time span was obtained. Note that the spectrometer cannot properly analyze temperature 22 below 1000 K.

Characterizations. The morphology and particle size of AgNP/CNFs were observed by SEM
(Hitachi SU-70) and TEM (JEOL 2100 FEG). Elemental analysis was conducted on an
energy-dispersive X-ray spectroscopy system with SEM. Raman spectra were collected on
Horiba Jobin-Yvon with a laser wavelength of 532 nm.

1 *Electrochemistry.* Coin cells were employed to test Li plating/stripping performance. The 2 Celgard separator and an ether-based electrolyte (1 M bis(trifluoromethane)sulfonimide 3 lithium salt dissolved in 1,3-dioxolane/1,2-dimethoxyethane, 1:1 by volume) were used to 4 assemble the cells. A Li foil was used as the counter/reference electrode in a cell and the 5 AgNP/CNF film (or other control samples) was used as the working electrode. 6 Electrochemical impedance spectra of the cells were tested on a Biologic VMP3 multichannel 7 electrochemical system. Galvanostatic Li plating/stripping was conducted on a LAND battery 8 system.

9 Supporting Information

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

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Ultrafine silver nanoparticles (AgNP) are synthesized and anchored on carbon nanofibers
 via a rapid Joule heating method for seeded Li deposition. Directed by the AgNP seeds, a
 smooth Li anode can be well regulated in the carbon substrate without dendrites. The Li
 anode with AgNP nanoseeds exhibits low overpotential, excellent cycling stability, and a long
 cycle life.

6
7 Keywords: Electrochemical energy storage, Li metal anode, Ag nanoparticles, ultrafast Joule
8 heating, Li dendrites
9

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Ultrafine Silver Nanoparticles for Seeded Lithium Deposition toward Stable Lithium Metal Anode

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- 15 ToC figure
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- 3 Supporting Information
- 4 5

6 Ultrafine Silver Nanoparticles for Seeded Lithium Deposition toward Stable Lithium

7 Metal Anode

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- 13



2

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- 3 Figure S1. Digital image of the setup for Joule heating. The sample was connected to copper
- 4 electrodes and heated by a current pulse in an argon-filled glove box.
- 5



Figure S2. Raman spectra of CNFs before and after rapid Joule heating. The Raman
characteristics of CNFs changed very little after the Joule heating, indicating the graphitic
structure of CNFs is maintained after the rapid thermal shock despite the high temperature.



1

2 Figure S3. EDX of AgNPs on CNFs synthesized via Joule heating. The content of Ag is

- 3 approximately 6 atom% according to the spectrum.
- 4



Figure S4. SEM image of Ag particles on CNFs synthesized by heating at 900 °C for 4 h. Ag
particles are scattered on CNFs. The Ag particles have a particle size of approximately 800
nm and are not fixed on the CNFs.



1

Figure S5. SEM image of AgNPs on CNFs synthesized via 5-ms Joule heating. The
AgCH₃COO precursor was not completely decomposed.

4



Figure S6. SEM image of 2 mA h cm⁻² of Li deposited on AgNP/CNFs. Uniform Li
deposition and growth seeded by AgNPs forms an even Li anode surface without dendrites.



1

Figure S7. Cycling performance of Li anode plating/stripping on Ag-CNFs synthesized via
conventional pyrolysis in a furnace. Non-uniform deposition of Li metal on the Ag-CNFs
leads to increased polarization and poor cycling stability.



Figure S8. Coulombic efficiencies of Li plating/stripping on CNF substrate with Ag
nanoseeds (AgNP/CNFs) and without Ag (bare CNFs). In each cycle, Li was plated at 0.5 mA
cm⁻² for 2 h and charged to 1.5 V at 0.5 mA cm⁻².



2 Figure S9. Cycling performance of Li anode plating/stripping on AgNP/CNFs at 1 mA cm⁻²





Figure S10. EIS of Li anode with bare CNF substrate before cycling and after 20 cycles.