Journal of Visualized Experiments

Precision Milling of Carbon Nanotube Forests using Low Pressure Scanning Electron Microscopy
--Manuscript Draft--

Manuscript Number:	JoVE55149R2
Full Title:	Precision Milling of Carbon Nanotube Forests using Low Pressure Scanning Electron Microscopy
Article Type:	Invited Methods Article - JoVE Produced Video
Keywords:	Carbon nanotube; scanning electron microscope; Nanofabrication; radiolysis; nanomaterial; milling
Manuscript Classifications:	92.23.4: chemistry (general); 92.23.5: materials (general); 92.27.3: carbon nanotubes (synthesis and properties); 93.35.17: electron microscopes; 93.37.48: manufacturing processes; 93.37.50: materials forming; 93.37.52: materials manufacturing; 93.37.82: tools
Corresponding Author:	Matthew Maschmann, Ph.D. University of Missouri Columbia Columbia, MO UNITED STATES
Corresponding Author Secondary Information:	
Corresponding Author E-Mail:	maschmannm@missouri.edu
Corresponding Author's Institution:	University of Missouri Columbia
Corresponding Author's Secondary Institution:	
First Author:	Josef Brown
First Author Secondary Information:	
Other Authors:	Josef Brown
	Benjamin Davis
Order of Authors Secondary Information:	
Abstract:	A nanoscale fabrication technique appropriate for milling carbon nanotube (CNT) forests is described. The technique utilizes an environmental scanning electron microscope (ESEM) operating with a low pressure water vapor ambient. In this technique, a portion of the electron beam interacts with the water vapor in the vicinity of the CNT sample, dissociating the water molecules into hydroxyl radicals and other species by radiolysis. The remainder of the electron beam interacts with the CNT forest sample, making it susceptible to oxidation from the chemical products of radiolysis. This technique may be used to trim a selected region of an individual CNT, or it may be used to remove hundreds of cubic microns of material by adjusting ESEM parameters. The machining resolution is similar to that of the imaging resolution of the ESEM itself. The technique produces only small quantities of carbon residue along the boundaries of the cutting zone, with minimal effect on the native structural morphology of the CNT forest.
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TITLE:

Precision Milling of Carbon Nanotube Forests using Low Pressure Scanning Electron Microscopy

AUTHORS:

Brown, Josef
Department of Mechanical & Aerospace Engineering
University of Missouri
Columbia, Missouri, USA
brownjosef@missouri.edu

Davis, Benjamin F.
Department of Mechanical & Aerospace Engineering
University of Missouri
Columbia, Missouri, USA
bfd895@mail.missouri.edu

Maschmann, Matthew R.
Department of Mechanical & Aerospace Engineering
University of Missouri
Columbia, Missouri, USA
maschmannm@missouri.edu

CORRESPONDING AUTHOR:

Matthew R. Maschmann
maschmannm@missouri.edu
573-882-2310

KEYWORDS:

Carbon nanotube, scanning electron microscope, nanofabrication, radiolysis, nanomaterial, milling

SHORT ABSTRACT:

Low pressure scanning electron microscopy in a water vapor ambient is used to machine nanoscale to microscale features in carbon nanotube forests.

LONG ABSTRACT:

A nanoscale fabrication technique appropriate for milling carbon nanotube (CNT) forests is described. The technique utilizes an environmental scanning electron microscope (ESEM) operating with a low pressure water vapor ambient. In this technique, a portion of the electron beam interacts with the water vapor in the vicinity of the CNT sample, dissociating the water molecules into hydroxyl radicals and other species by radiolysis. The remainder of the electron beam interacts with the CNT forest sample, making it susceptible to oxidation from the chemical products of radiolysis. This technique may be used to trim a selected region of an individual CNT, or it may be used to remove hundreds of cubic microns of material by adjusting

ESEM parameters. The machining resolution is similar to the imaging resolution of the ESEM itself. The technique produces only small quantities of carbon residue along the boundaries of the cutting zone, with minimal effect on the native structural morphology of the CNT forest.

INTRODUCTION:
Carbon nanotubes (CNTs) and graphene are carbon-based nanomaterials that have attracted significant attention because of their superior strength, durability, thermal, and electrical properties. Precision machining of carbon nanomaterials has become an emerging topic of research and offers the potential to engineer and manipulate these materials towards a variety of engineering applications. Machining CNTs and graphene requires nanoscale spatial precision to first locate a nanoscale area of interest and then to selectively remove only the material within the area of interest. As an example, consider the machining of vertically oriented CNT forests (also known as CNT arrays). The cross section of CNT forests may be precisely defined by lithographic patterning of catalyst films. The top surface of the vertically oriented forests, however, are frequently poorly ordered with non-uniform height. For surface-sensitive applications such as thermal interface materials, the irregular surface may impede optimal surface contact and reduce device performance. Precision trimming of the irregular surface to create a uniform flat surface could potentially offer better, more repeatable performance by maximizing the available contact area.

Precision machining techniques for nanomaterials frequently do not resemble conventional macroscale mechanical machining technologies such as drilling, milling, and polishing by means of hardened tooling. To date, techniques using energetic beams have been most successful at site-selective milling of carbon nanomaterials. These techniques include laser, electron beam, and focused ion beam (FIB) irradiation. Of these, laser machining techniques provide the most rapid material removal rate[1,2]; however, the spot size of laser systems is on the order of many microns and is too large to isolate nanometer-scale entities such as a single carbon nanotube segment within a densely populated forest. By contrast, electron and ion beam systems produce a beam that may be focused to a spot that is several nanometers or less in diameter.

FIB systems are specifically designed for nanoscale milling and deposition of materials. These systems utilize an energetic beam of gaseous metal ions (typically gallium) to sputter material from a selected area. FIB milling of CNTs is achievable, but often with unintended byproducts including gallium and carbon redeposition in surrounding regions of the forest[3,4]. When the technique is used for CNT forests, the redeposited material masks and/or alters the morphology of selected milling region, altering the native appearance and behavior of the CNT forest. The gallium may also implant within the CNT, providing electronic doping. Such consequences often make FIB-based milling prohibitive for CNT forests.

Transmission electron microscopes (TEMs) utilize a finely focused beam of electrons to probe the internal structure of materials. Acceleration voltages for TEM operation typically range from 80-300 kV. Because the knock-on energy of CNTs is 86.4 keV[5], the electron energy produced by TEM is sufficient to directly remove atoms from the CNT lattice and induce highly localized milling. The technique mills CNTs with potentially sub-nanometer precision[5-7]; however, the

process is very slow – often requiring minutes to mill a single CNT. Importantly, TEM-based milling approaches require CNTs to first be removed from a growth substrate and dispersed onto a TEM grid for processing. As a result, TEM-based methods are generally not compatible with CNT forest milling in which the CNTs must remain on a rigid substrate.

Milling of CNT forests by scanning electron microscopes (SEMs) has also received attention. In contrast to TEM-based techniques, SEM instruments are typically unable to accelerate electrons with sufficient energy to impart the knock-on energy required to directly remove carbon atoms. Rather, SEM-based techniques utilize an electron beam in the presence of a low-pressure gaseous oxidizer. The electron beam selectively damages the CNT lattice and may dissociate the gaseous ambient into more reactive species such as H_2O_2 and the hydroxyl radical. Water vapor and oxygen are the most commonly reported gases to achieve selective area etching. Because the SEM-based techniques rely on a multiple-step chemical process, numerous processing variables may influence the milling rate and precision of the process. It has been previously observed that increasing acceleration voltage and beam current directly increase the milling rate because of an increased energy flux, as expected[11]. The effect of chamber pressure is less obvious. A pressure that is too low suffers from a deficiency of the oxidizing agent, decreasing the milling rate. Further, an over-abundance of gaseous species scatters the electron beam and decreases the electron flux in the milling region, also decreasing the material removal rate.

To estimate the carbon removal rate, an approach similar to that used by Lassiter and Rack[12] was employed, whereby electrons interact with precursor molecules near the surface to generate reactive species that etch the substrate surface. From this model, the etch rate is estimated as

$$Etch\ Rate \approx \frac{N_A}{Z} x A_\sigma \Gamma_e$$

where N_A is the surface concentration of the etchant species, Z is the surface concentration of available reaction sites, *x* is a stoichiometry factor relating the volatile etching products generated relative to the reactants, A_σ represents the probability of generating the desired etching species from an electron-water vapor collision, and Γ_e is the electron flux at the surface. The factors of x and A_σ are assumed to be unity, while Z is assumed to be nearly constant and significantly larger than NA. Further details may be found in our previous work.[11]

In this article, a procedure is explored that uses low-pressure water vapor within a SEM to mill regions ranging from individual CNTs to large volume (tens of cubic micrometers) material removal. Here we demonstrate the technique used to mill CNT forests using an ESEM by the use of reduced area rectangles, horizontal line scans, and software-controlled rastering of the electron beam. Additional software and hardware are required for pattern generation, as outlined in the Materials Table. Emphasis is placed on removing relatively large (100's of cubic microns) material volume from a CNT forest, so the following processing conditions are relatively aggressive.

When handling the sample and the sample stub, it is important to wear disposable nitrile gloves. This will prevent oils from being transferred to the stub or sample and consequently deteriorating the effectiveness of the pumps.

PROTOCOL:

1. Preparation of CNT Forest Sample for Milling
1.1) CNT Synthesis
1.1.1)   Deposit 10 nm of aluminum oxide (alumina) on a thermally oxidized silicon wafer using atomic layer deposition[13] or other physical vapor deposition methods.

1.1.2) Deposit 1 nm of iron on the alumina support layer by sputtering[14] or other physical vapor deposition method.

1.1.3)   Synthesize CNTs using an established process, such as thermal chemical vapor deposition[15].

1.1.3.1) Heat a 20 mm diameter tube furnace to 750 °C in 400 standard cubic centimeters (sccm) of flowing helium and 100 sccm hydrogen. Introduce 100 sccm ethylene as a hydrocarbon feedstock gas for a growth rate of approximately 50 μm/min.

1.2) SEM Preparation
1.2.1)   Apply carbon tape to a standard 1/2" diameter SEM stub. If tilting the stage is required, overlap the region of the CNT forest sample to be milled over the edge of the stub. If software-controlled electron beam rastering will be used in the milling procedure, secure the CNT sample to an electron beam lithography mount in a similar manner.

1.2.2)   If milling the CNT cross section, secure the stub to a 45° stub holder with a set screw.

1.2.3)   Vent the ESEM by selecting the "Vent" icon from the ESEM control software.

1.2.4)   Open the ESEM stage door, and secure the stub to the SEM stage with a set screw.

1.2.5)   Close the SEM chamber and select "High Vacuum" in the ESEM control software.

1.2.6) While the ESEM chamber is pumping, select the electron beam parameters of 5 kV and spot size of 3.0 using the Beam Control tab within the control software.

1.2.7) Select the secondary electron detector by selecting Detectors | ETD(SE) in the ESEM control software.

1.2.8)   Select the "Beam On" icon in the control software. The beam can be activated only once the chamber vacuum is less than 10^{-4} Torr. Use manual SEM focus control knobs to focus the sample.

1.2.9)   Tilt the sample to 45° using manual tilt stage control knob or by inputting 45° in the "Tilt" field in the "Coordinates" tab of the ESEM software. Focus on the highest sample. Link the focal distance to the working distance by selecting Stage | Link Z to FWD in the ESEM software menu. Input 7 mm into the "Z" field in the "Coordinates" tab within the control software.

1.2.10) Adjust focus, stigmation, brightness and contrast using the manual control knobs to resolve a well-focused image.

1.3)   Beam Adjustment in High Vacuum Mode
1.3.1)   Locate a region for milling using navigation controls. Double click within the SEM image view or by manually turning the x and y control knobs of the SEM stage control to navigate.

1.3.2)   Navigate to an adjacent location approximately 100 µm away from the milling region.

1.3.3)   Consult Figure 1 to estimate the material removal rate of the CNT forest as a function of pressure, acceleration voltage, dwell time per pixel, and beam current.

1.3.4)   Adjust the acceleration voltage to 30 kV and spot size to 5.0 using the ESEM control software. Adjust image focus, brightness, and contrast using the ESEM control knobs. For nanometer-scale milling of individual or few CNTs, select 5 kV and spot size of 3.0.

1.3.5)   Select a 1 mm aperture by manual aperture adjustment. Adjust focus, stigmation, brightness, and contrast to obtain a well-resolved image, as previously detailed.

1.3.6)   Decrease magnification to < 1,000x.

1.4)   SEM Setup in Low Pressure Water Vapor
1.4.1)   Select a pressure of 11 Pa in the control software dropdown box.

1.4.2)   Select "Low Pressure" mode in the "Vacuum" settings in the ESEM software to introduce water vapor.

1.4.3)   Select "Beam On" in the control software upon pressure stabilization. Select a dwell time of <10 µs and a resolution of 1024 x 884 in the drop-down boxes of the control software.

1.4.4)   Adjust the image brightness, contrast, focus, and stigmation as previously detailed.

1.4.5)   Navigate to the desired milling region. Rotate the image orientation by selecting Scan | Scan Rotation in the control software, if required. Select a suitable rotation angle that aligns with the native vertical and horizontal scan orientation of the SEM.

1.4.6)   For milling feature sizes on the order of 1 µm, select a magnification of 40,000x. Select a magnification of 20,000x to mill features with dimensions up to 5 µm.

Pause the electron beam by selecting the ' " ' icon . An image of the CNT forest will be displayed and may be used for selecting reduced area milling regions while the beam is paused.

2. CNT Forest Milling
2.1)   Instructions for CNT forest milling using a rectangular selected area
2.1.1)   Choose the 'Reduced Area' tool in the control software, or select Scan-Reduced Area in the software menu. Extend a reduced area rectangle over the area to be milled.

2.1.2)   Adjust the image resolution to 2048 x 1768. Increase the dwell time to 2 ms. If 2 ms is not available, navigate to the Scan |Preferences and select the "Scanning" tab. Select an existing scan time and type "2.0 ms" into the "Dwell Time" field. Click "OK" to close the menu.

2.1.3)   Select the ' " ' icon in the control software to activate the electron beam.

2.1.4) Select the ' " ' icon so that the beam rasters over the selected area one time. Select the icon immediately after step 2.1.3. The scan duration depends on the size of the selected area, resolution and dwell time and may be approximated by multiplying the number of pixels within the scan area and the dwell time per pixel.

2.1.5)   Decrease magnification to < 1,000x once the beam has completed rastering the selected area. Revert to the parameters used in step 1.3, including High Vacuum. Select "Beam On" to engage the beam.

2.2) Instructions for CNT forest milling along a horizontal line
2.2.1)   Select the line scan feature by navigating to Scan | Line in the control software. The line width is determined by the size of the electron beam itself. Adjust the image resolution to 2048 x 1768 from the control software dropdown box. Increase the dwell time to 2 ms as detailed in step 2.1.2.

2.2.2)   Using the still image acquired before pausing the electron beam, place the line over the area to be milled.

2.2.3) Select the videoscope icon or navigate to the Scan menu and select "Videoscope." Using the videoscope tool provides feedback relative to when a line scan has fully completed.

2.2.4) Select the ' " ' icon to scan electron beam across the width of the line.

2.2.5) Select the ' " ' icon to blank the electron beam.

2.3) Instructions for CNT Forest milling using software-controlled electron beam rastering
2.3.1) Pattern Generation
2.3.1.1) Design a milling pattern of interest using a CAD software package such as AutoCAD.

2.3.1.2) Using "Nanometer Pattern Generation System" (NPGS) software, import the CAD pattern file.

2.3.1.3) Convert the shapes to solid features by selected "Filled Polygons" in the NPGS software.

2.3.1.4) Save the drawing as a '.dc2' file in a designated project folder of NPGS.

2.3.1.5) Using NPGS, navigate to the project folder containing the ".dc2" file. Right select the ".dc2" file and select "Run File Editor" to convert the drawing to NPGS code. Typical parameters used to pattern CNT forests at given conditions are as listed below:
Center-to-center distance = 5 nm
Line Spacing = 5 nm
Magnification = 10,000x
Desired Beam Current = 26
Line Dose = 100 nC/cm

2.3.2) Electron Beam Milling using NPGS Lithography Software
2.3.2.1) Select the "NPGS Mode" in NPGS software button to give control of the SEM to NPGS.

2.3.2.2) Highlight the pattern file and select "Process Run File" in NPGS to initiate milling.

2.3.2.3) Select "SEM Mode" in the NPGS software when patterning is finished. Select "High Vacuum" in the ESEM control software.

2.3.2.4) Select "Beam On" to inspect the milled region. Use conditions detailed in step 1.3.

3. Sample Removal
3.1) Vent the chamber by selecting "Vent" in the ESEM control software.

3.2) Open the ESEM door. Remove the stub by loosening the set screw.

3.3) Close the chamber door. Select "High Vacuum" in the control software.

REPRESENTATIVE RESULTS:
The ESEM technique was used to mill a CNT forest synthesized using thermal CVD[15,16]. Selected area removal of a few CNTs from within a forest is shown in Figure 2[11]. For this demonstration, parameters include 5 kV, spot size of 3, 11 Pa, 170,000x magnification, 2 ms dwell time, and an aperture of 30 μm.

To demonstrate a larger-scale area removal, the top surface of a CNT forest micropillar was selected for milling. SEM conditions are selected for rapid, large-area CNT forest removal. Namely, these conditions include a magnification of 20,000x, a pressure of 11 Pa, acceleration voltage of 30 kV, spot size of 5, dwell time of 2 ms, and a 1 mm aperture setting. A reduced

area box is chosen such that the irregular top surface to be removed is enclosed within the selected area. SEM micrographs of the CNT forest pillar are shown in Figure 3 before and after the selective area milling process. The red line in the figure represents the lower bound of the reduced area box used for milling.

Non-rectangular geometries achieved using software-controlled electron beam rastering and a relatively short 20 μm tall CNT forest. As shown in Figure 4, a 15 μm diameter circle was machined into a CNT forest. For this demonstration, the CNT forest was milled parallel to the CNT growth direction (normal to the substrate). Milling parameters used for this demonstration include a magnification of 10,000x, a pressure of 11 Pa, acceleration voltage of 30 kV, spot size of 5, dwell time of 2 ms, and 1 mm aperture setting. Figure 4 shows that the process milled the CNTs fully to the underlying silicon substrate.

Figure 1: Material Removal Rate Variation
Material removal rate (MRR) variation. SEM micrographs demonstrate the MRR in the transverse direction (a) by varying operating pressure from 133, 66, 33, 66, and 11 Pa (top to bottom) and (b) in the axial cutting direction by varying dwell time from 3, 2, 1, and 0.5 ms/pixel (left to right). The MRR is plotted as a function of incremental changes in pressure, acceleration voltage, beam current, and dwell time in the (c) transverse and (d) axial cutting directions. The MRR as a function of electron dose varies nearly linearly in both the (e) transverse and (f) axial milling orientation. This figure is reproduced with permission from reference[11].

Figure 2: Milling of Individual CNTs.
SEM micrograph showing individual CNTs from within a forest selected for local milling (a) before and (b) after milling. This figure is reproduced with permission from reference[11].

Figure 3: Milling of a CNT Forest.
A 10 μm wide CNT forest pillar (a) before and (b) after selective area milling using ESEM-based milling. Milling conditions include magnification of 20,000x, a pressure of 11 Pa, acceleration voltage of 30 kV, spot size of 5, dwell time of 2 ms per pixel, and 30 μm aperture. The red line in the figure represents the lower bound of the selective area rectangle used in the milling process.

Figure 4: Patterned Milling of CNT Forest.
Software-controlled electron beam rastering is used to define and mill a 15 μm diameter circle in a CNT forest. In this setup, the milling direction was parallel to the CNT growth direction from the top surface to the underlying substrate.

Figure 5: Deposited Carbon after Milling.
SEM micrographs showing the surface finish of ESEM milled CNT forests. (a) The top surface of a CNT forest shows the surface variation between the milled and as-synthesized regions. (b) Higher magnifications reveal that some amorphous carbon deposits are left behind during the cutting process.

DISCUSSION:

The protocol details best practices for milling relatively large (micron-scale) features in CNT forests. In general, the material removal rate may be reduced by reducing the acceleration voltage, spot size, and aperture diameter. To trim a specific CNT within a forest, recommended conditions include 5 kV, a spot size of 3, and an aperture that is 50 μm or less in diameter. Note that the milling technique using reduced area rectangles is detailed such that the electron beam rasters the enclosed region only one time. The reduced area may be scanned multiple times if additional cutting depth is desired; however, we illustrate a single scan for simplicity. We note that the extended electron beam dwell time, high current, and high acceleration voltage represent conditions that are frequently avoided for imaging of carbon-based materials; however, these aggressive parameters in a low-pressure water vapor ambient are critical for achieving large-scale milling. Further, we note that similar imaging conditions in the absence of low-pressure water vapor results in little CNT damage.

The ESEM-based milling method described in this work is a minimally disruptive machining method that preserves neighboring CNT forest structural morphology. The technique is amenable to removing nanoscale features such as segments of individual CNTs and also to removing regions spanning many microns. We demonstrate the technique using reduced area rectangles, lines, and arbitrary patterns using software-controlled electron beam rastering. While the technique is relatively clean compared to FIB-based milling, small amounts of carbon residue exists on milled surfaces. Current research is addressing avenues for reducing this residue. Additionally, the material removal rates shown in Figure 1 were obtained for a CNT forest with CNTs featuring an average outer and inner diameter of 10 and 7 nm, respectively. Material removal rates are expected to be a function of CNT density, CNT diameter, and CNT alignment. Figure 1 should be consulted as a guide, recognizing that the stated material removal rate is specific to this CNT forest morphology. While qualitative trends represented in the figure are expected to hold for all CNT forests, some experimentation may be required to find the optimal parameters for a different material system.

While the ESEM machining methodology is demonstrated using CNT forests, it is equally applicable for graphene and other carbon-based materials. The technique does not require delamination of the CNT forest for processing and does not introduce external heavy elements that may significantly alter the surrounding CNT forest morphology. The procedure may be used for inspecting CNT forest internal morphology, and perhaps for producing 3-D lattices structures for microscale prototyping which may be functionally coated (with alumina for enhanced stiffness[17,18], for example).

The technique is currently being utilized to examine the internal structural morphology of CNT forests. Because structural morphology is intimately linked with functional properties[16,19-22], characterization of CNT forest morphology in three dimensional space may provide additional insights into the governing structure-property relationships. With the ability to precisely mill into a forest and observe the internal nanotube interactions, CNT forest synthesis modeling and analytical models can be tuned and validated.

The emphasis of the ESEM milling technique to date has been directed towards rapid material removal with less focus on optimizing conditions for reducing the residual carbon residue. A future direction is to explore the mechanism of amorphous carbon deposition in the immediate vicinity of the cut surfaces when large volumes of materials are removed, as shown in Figure 5. With a broad parameter space available for exploration, including environmental gas composition, vapor pressure, acceleration voltage, probe current, and electron beam rastering conditions, enhanced surface cleanliness may be achieved.

DISCLOSURE:
The authors declare that they have no competing financial interests.

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Figure 1

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Figure 2

(a) 50 nm (b) 50 nm

Figure 3

Figure 4

5 μm
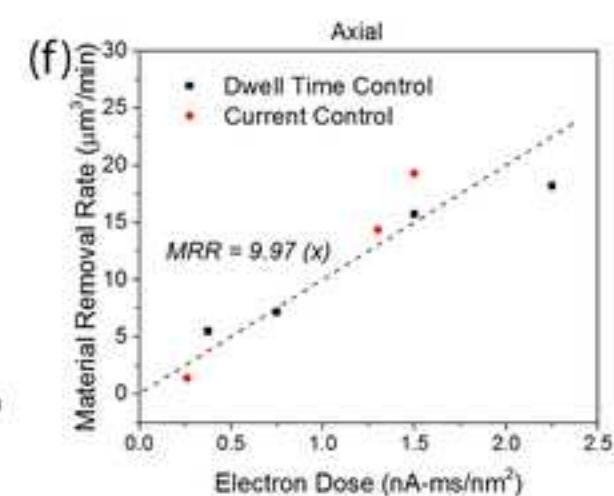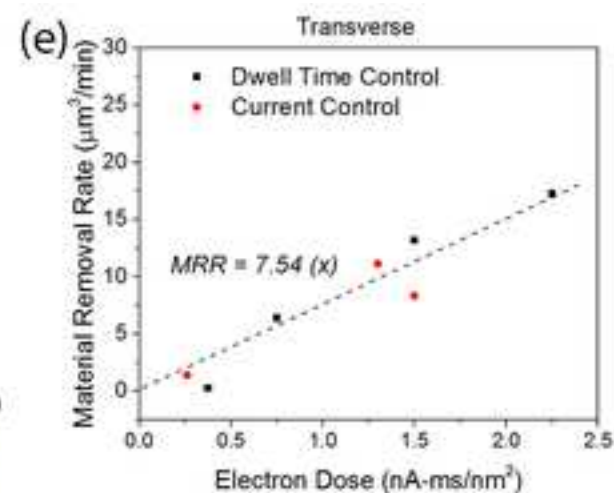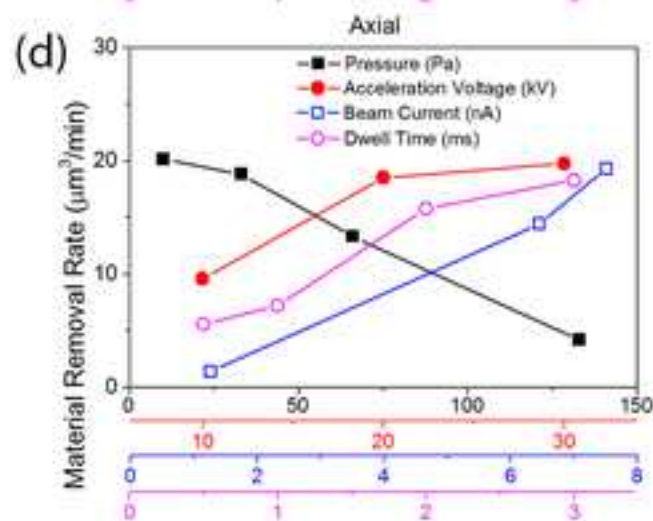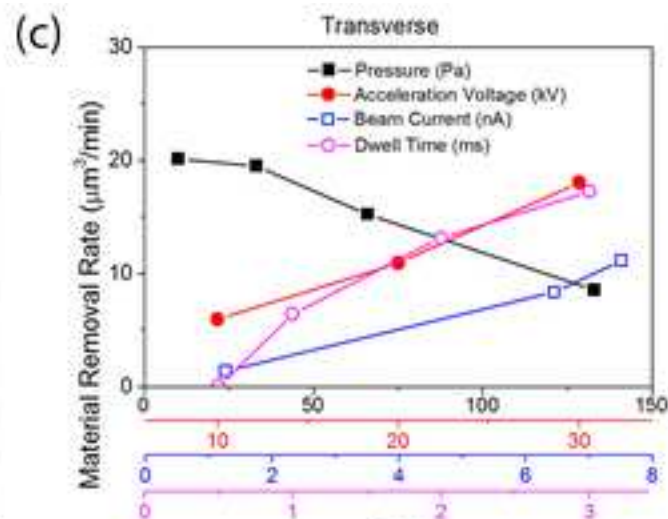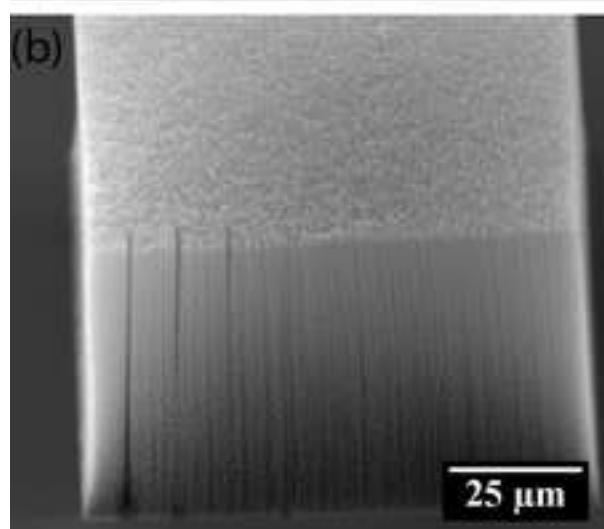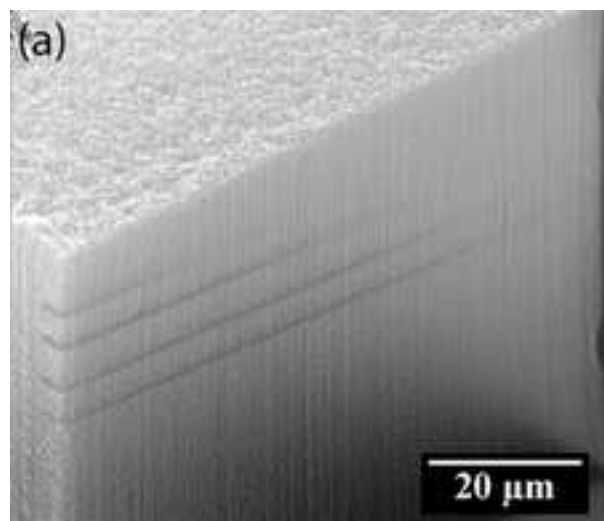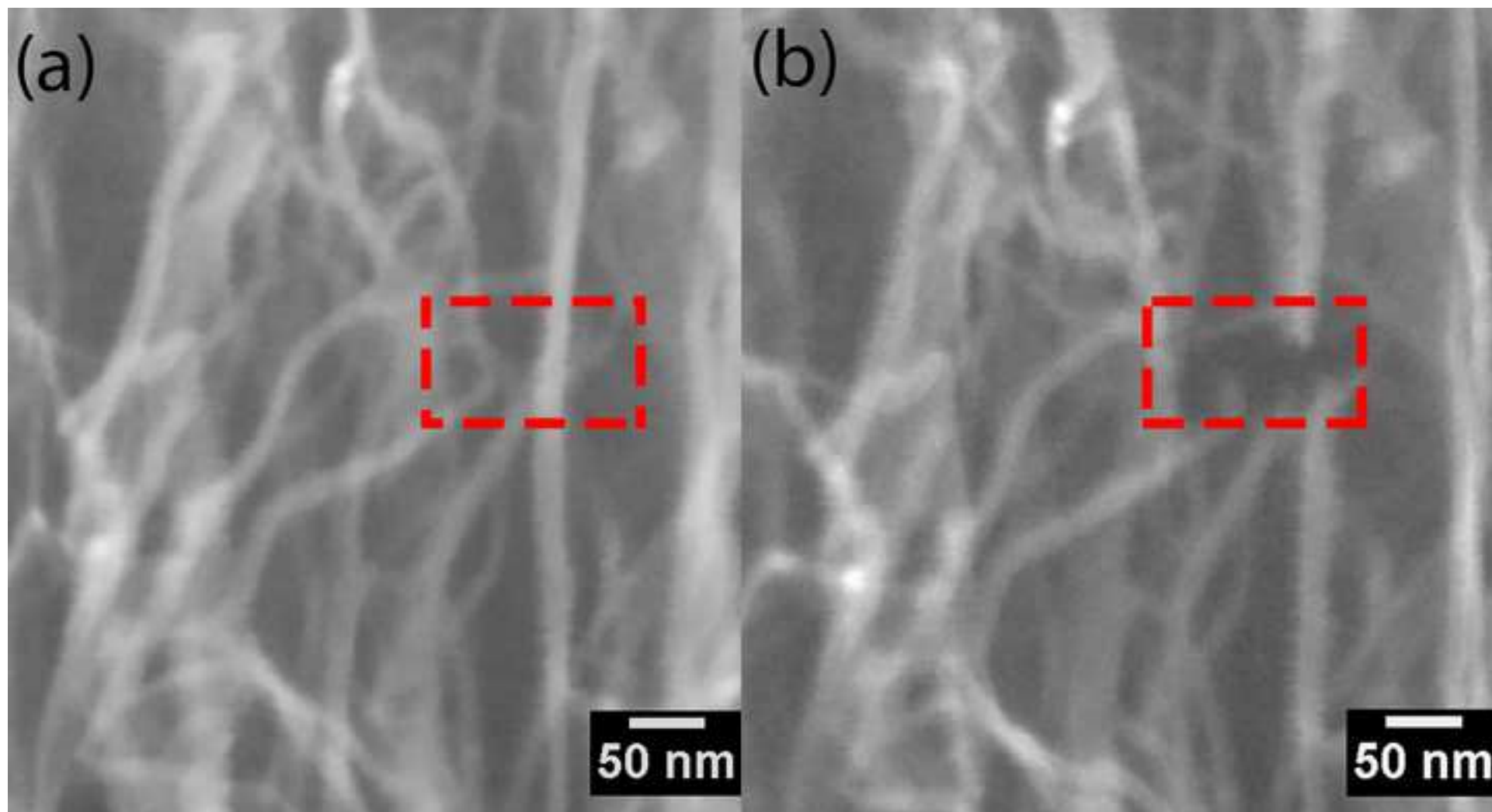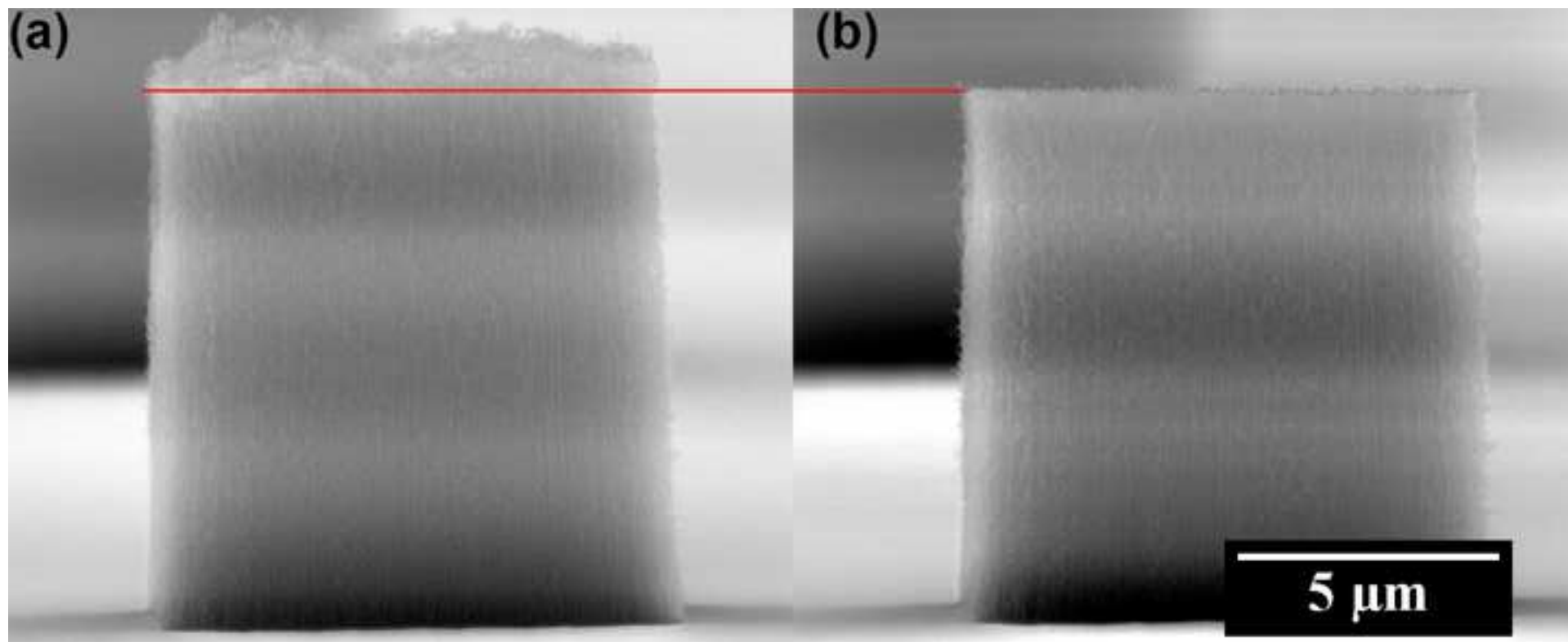
Figure 5
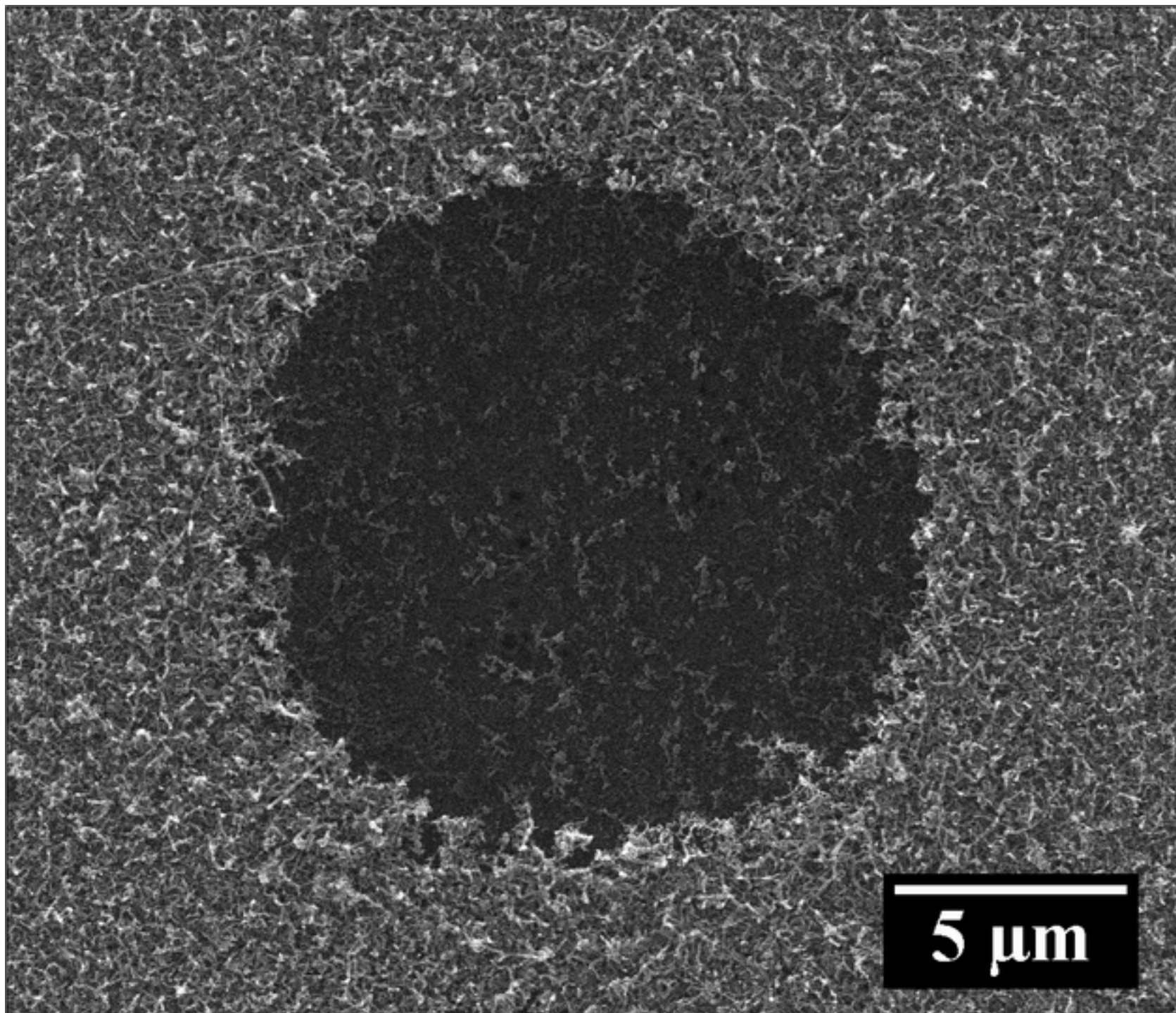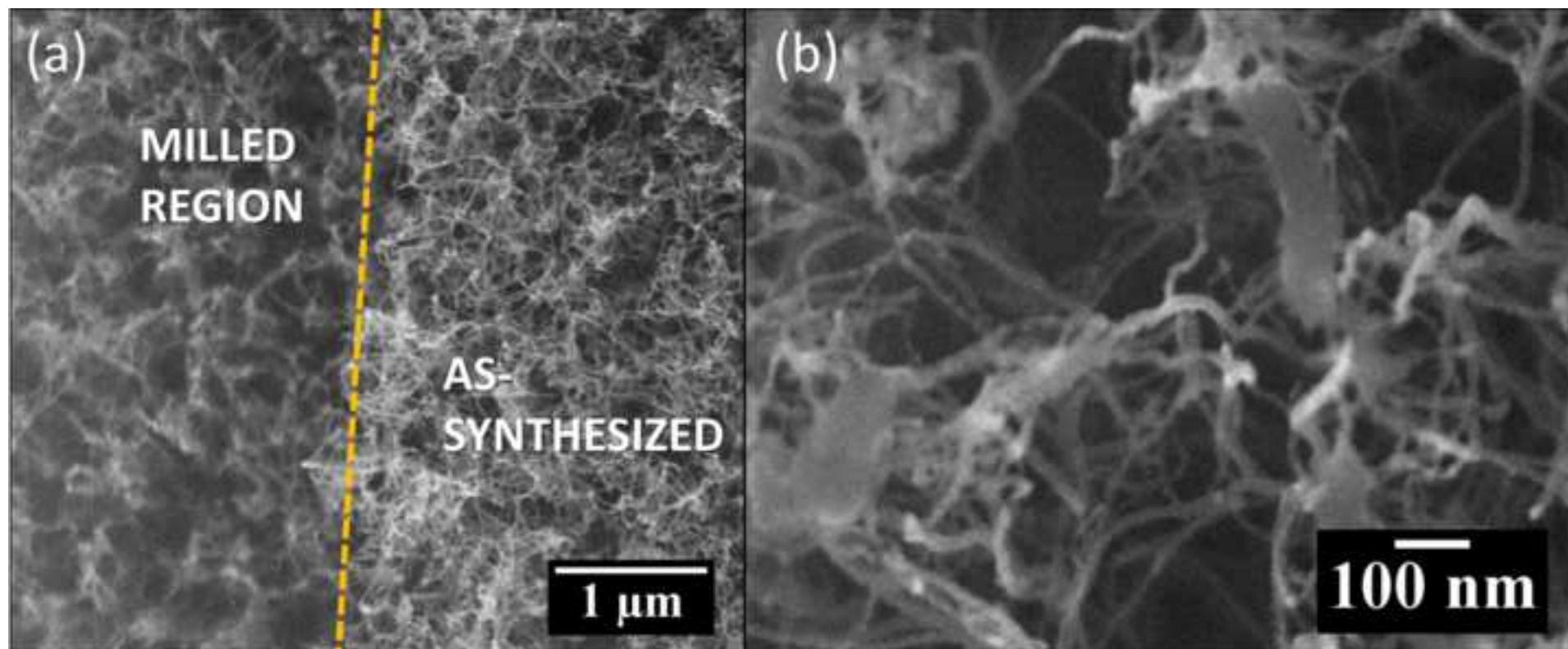
Name of Material/ Equipment	Company	Catalog Number	Comments/Description
100 mm diameter silicon wafer with 1 micron thermal oxide	University Wafer		Beginning substrate
Iron sputter target	Kurt J. Lesker	EJTFEXX351A2	Sputter target
Savannah 200	Cambridge		For atomic layer deposition of alumina
Quanta 600F Environmental SEM	FEI		Environmental scanning electron microscope used to support a low-pressure water vapor ambient environment for CNT forest milling
xT Microscope Control software	FEI	4.1.7	Control software used on Quanta 600F ESEM
Nanometer Pattern Generation System - Software	JC Nabity Lithography Systems	Version 9	Software used for electron-beam
Dedicated computer with PCI516 Lithography board			Equipment used for electron-beam lithography
DesignCAD software		V 21.2	Optional equipment used to generate patterns for electron-beam lithography
E-beam lithography mount	Ted Pella	16405	Electron beam lithography mount with a Faraday cup and gold nanoparticles on carbon tape
Picoammeter	Keithley	6485	Used with the Faraday cup to quantify beam current
12.7 mm diameter SEM stub	Ted Pella	16111	SEM stub

45 degree pin stub holder	Ted Pella	15329	Optional equipment used to mill the cross section of a CNT forest

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Author(s): Josef Brown, Benjamin Davis, Matthew Maschmann

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CORRESPONDING AUTHOR:

Name: MATTHEW R. MASCHMANN

Department: MECHANICAL AND AEROSPACE ENGINEERING

Institution: UNIVERSITY OF MISSOURI

Article Title: Precision Milling of Carbon Nanotube Forests using Low Pressure SEM

Signature: Matthew R Maschmann   Date: 6/20/2016

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Editorial comments:
The manuscript has been modified by the Science Editor to comply with the JoVE formatting standard. Please maintain the current formatting throughout the manuscript. The updated manuscript (555149_R1_070816.docx) is located in your Editorial Manager account. In the revised PDF submission, there is a hyperlink for downloading the .docx file. Please download the .docx file and use this updated version for any future revisions.

1. Formatting: Please number steps sequentially. For instance, there are two steps 2.1.4.

Completed

2. Grammar: Line 56 – "to selectively removing"

Corrected

3. Visualization: 1.3.3 should not be highlighted for filming as it cannot be visualized.

Figure 1 has been modified and updated.

4. Additional detail is required:
-1.3.3 – It is unclear how Figure 1 would help estimate these values.

Figure 1 has been modified and updated.

-1.3.8 – How is the milling location noted? Is it marked in the software?

This sentence was removed because it is unnecessary. The intent of the statement was to alert the user to recall where the location of interest was located within the field of view at lower magnification.

-1.4.5 – What determines the appropriate angle here?

This instruction has been modified with the following sentence: "Select a suitable rotation angle that aligns with the native vertical and horizontal scan orientation of the SEM."

-First 2.1.4 – When does rastering begin? How long is the beam on before pausing it?

Rastering begins in the prior step. The pause icon should be selected immediately after the previous step. This instruction has been modified.

-Second 2.1.4 – How long should the beam be on?

The scan duration depends on the size of the selected area, resolution and dwell time and may be approximated by multiplying the number of pixels within the scan area and the dwell time per pixel.

-2.3.2.4 – Which conditions? What step 2.1.4?

Step 1.3.6. This has been updated in the manuscript.

5. Please remove commercial branding: Line 113 – "FEI Quanta 600F" – Please indicate that other systems could be used.

Completed.

6. Discussion:
-Line 341 – Rates are not shown in Figure 1. Please clarify. Figure updated.
-Please discuss the critical steps of the protocol. Additional discussion added.

Reviewers' comments:
Reviewer #1:
Manuscript Summary:
This work demonstrates the milling of CNTs using precise oxidative processing. The pictures are sufficient to represent this technique, and the description seems accurate and thorough. I see no reason for this to not be accepted for whatever further steps are needed to process a video article.

Major Concerns:
N/A

Minor Concerns:
N/A

Additional Comments to Authors:
N/A

Reviewer #2:
Manuscript Summary:
In this work, the authors provide the protocols and examples for the CNTs milling methods using ESEM. The detailed processing conditions in ESEM were explained, as well as the synthesis of CNTs forests.

Major Concerns:
1. Although the authors explained the mechanism of CNTs milling process, the current manuscript is not enough to convey the central physics during those processes for the general readers who do not have experiences. More detailed descriptions about the underlying physics would be helpful for general readers.

Although the focus of this manuscript is procedural, we have added an equation to the manuscript to estimate the etch rate of CNTs based on the SEM parameters and the water vapor ambient. This equation relates observations to physical mechanisms, as detailed further in reference

2. As the authors mentioned, there have been several techniques to fabricate or manipulate CNT forests, such as TEM, FIB, and others. It is intuitive that ESEM is more effective and practical for large-scale applications. However, it would be important that ESEM milling process is able to control the precise parts or complex shapes. For the visualization of those points, the addition of samples which have more complex structures via the above CNT milling process would be needed.

The demonstration of a milled circle represents an arbitrary shape that may not be achieved with conventional x-y rastering of an electron beam. It is our intent to demonstrate that the technique may be utilized with electron-beam lithography software to enable arbitrary geometry control.

Minor Concerns:
1.1.1) and 1.1.2) This is the general procedure to synthesize vertically-aligned CNTs. In addition to ALD, it should be mentioned that other deposition methods, such as E-beam or thermal evaporation would be applicable.

The reviewer is correct in these statements. These steps have been modified to address this point.

1.3.3) Is there any quantified relation between the physical conditions of CNTs and the operating conditions of SEM? It would be needed to provide the regulation of the processing conditions.

Figure 1 has been modified to provide additional guidance relative to milling rates. Further, the addition of the etch rate equation on line 115 provides further guidance relative to the quantity of available reactions sites by CNT defects.

1.4.6) The relation between the milling feature size and a magnification might be described as some mathmatical formulas or fitting parameters. Or the authors can provide one table to describe the

correlation of feature sizes and magnifications.

The relationship between feature size and magnification is outside of our previous examinations and will depend intimately on all parameters discussed in the manuscript (acceleration voltage, spot size, ambient pressure, magnification, resolution, working height, etc.). While it is envisioned that minimum feature resolution is an important metric for specific applications, we feel that it is outside the scope of the current work.