Toward Small-Diameter Carbon Nanotubes Synthesized from Captured Carbon Dioxide: Critical Role of Catalyst Coarsening

Anna Douglas,†‡∥ Rachel Carter,‡ Mengya Li,‡ and Cary L. Pint*,†‡∥

*Interdisciplinary Materials Science Program and †Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States
‡Vanderbilt Institute of Nanoscale Science and Engineering, Nashville, Tennessee 37235, United States
∥SkyNano LLC, Oak Ridge, Tennessee 37830, United States

ABSTRACT: Small-diameter carbon nanotubes (CNTs) often require increased sophistication and control in synthesis processes, but exhibit improved physical properties and greater economic value over their larger-diameter counterparts. Here, we study mechanisms controlling the electrochemical synthesis of CNTs from the capture and conversion of ambient CO2 in molten salts and leverage this understanding to achieve the smallest-diameter CNTs ever reported in the literature from sustainable electrochemical synthesis routes, including some few-walled CNTs. Here, Fe catalyst layers are deposited at different thicknesses onto stainless steel to produce cathodes, and atomic layer deposition of Al2O3 is performed on Ni to produce a corrosion-resistant anode. Our findings indicate a correlation between the CNT diameter and Fe metal layer thickness following electrochemical catalyst reduction at the cathode-molten salt interface. Further, catalyst coarsening during long duration synthesis experiments leads to a 2× increase in average diameters from 3 to 60 min durations, with CNTs produced after 3 min exhibiting a tight diameter distribution centered near ~10 nm. Energy consumption analysis for the conversion of CO2 into CNTs demonstrates energy input costs much lower than the value of CNTs—a concept that strictly requires and motivates small-diameter CNTs—and is more favorable compared to other costly CO2 conversion techniques that produce lower-value materials and products.

KEYWORDS: carbon nanotubes, CNTs, electrochemistry, catalyst, coarsening, CO2, carbon dioxide

INTRODUCTION

Because of their impressive mechanical, electronic, and thermal properties, carbon nanotubes (CNTs) have been at the forefront of research and technological development for nearly two decades.1−9 These extraordinary physical properties are attributed to their atomic structure and size, motivating a significant body of work focused on understanding the mechanisms of CNT growth that govern their resulting structure.5,10−20 The structure and diameter of a nanotube significantly influences its mechanical and electronic properties11 and thus can impact its performance in a variety of applications.9,21,22 Furthermore, small-diameter CNTs including few-walled (ca. 3−10 walls), double-walled, and single-walled CNTs (SWCNTs) have higher economic value because of their enhanced physical properties, broader appeal toward applications, and greater difficulty in synthesis compared to their larger-diameter counterparts possessing greater wall numbers.23−25

Decades of gas-phase CNT growth research, most recently leveraging state-of-the-art in situ transmission electron microscopy (TEM) techniques, have determined a strong correlation between the size of the catalyst particles and the diameter of the resulting CNTs.26−28 This understanding has enabled diameter distribution control, which can be most easily realized by tuning the thickness of the deposited catalyst layer to control dewetted particle sizes.29 Furthermore, the catalyst size5,13,30,31 and dynamic evolution of size due to catalyst coarsening,11 catalyst diffusion,2 and mechanically driven collective growth termination22−24 enable a collective understanding of growth and termination during gas-phase processes. This challenge of maintaining small-diameter catalysts during growth duration has motivated growth processes such as water-assisted and short-duration “supergrowth,” which has been shown to overcome these deactivation mechanisms.1,35

From a general perspective, gas-phase CNT growth occurs as a carbon-containing precursor gas passes over the surface of a catalytic nanoparticle, decomposes on the particle surface, and precipitates from the particle as graphitic carbon.30 By contrast, the electrochemical reduction of CO2 to produce CNTs has only recently been reported and discussed and utilizes electrochemistry between two biased electrodes to dissociate a carbonate species and deposit elemental carbon onto a surface. In this process, catalyst evolution and carbon deposition from CO2 feedstock are decoupled because of the
addition of electrochemical controls that determine global synthesis parameters, such as carbon flux, independently from the activity on the catalyst surface. Whereas the origin of this technique to sequester CO	extsubscript{2} and produce amorphous carbon deposits dates back to the early 1960s,	extsuperscript{37} the growth of CNTs requires the additional control of the deposited carbon to sites where CNTs can be synthesized—a concept that has only recently been demonstrated.	extsuperscript{38–45} Early observations of hollow carbon fiber materials with diameters >100 nm relied on the in situ deposition of primarily nickel catalysts from corroded metal anodes onto the cathode,	extsuperscript{38–40} which favored this architecture over spherical carbon particles,	extsuperscript{47–49} flakes,	extsuperscript{37,48} or other carbon structures previously reported. However, the stochastic nature by which such in situ catalyst is formed, among other limitations, results in CNT materials possessing larger diameters (>100 nm) and lower quality than CNTs produced by other scalable methods, such as fluidized bed chemical vapor deposition (CVD). Recently, our work has demonstrated that by passivating the anode from corrosion, thereby eliminating the detrimental in situ catalyst formation, we can isolate control of catalysts sourced from the cathode, yielding CNTs with diameters near ~30 nm (vs >100 nm otherwise) and of moderate quality comparable to gas-phase processes.	extsuperscript{4} This also enables isolation of the catalyst formation and synthesis steps to a single electrode, as opposed to two electrodes during in situ catalyst formation. This gives promise toward routes intersecting state-of-the-art methods for diameter and chirality control, such as with high melting point metal catalysts, while retaining the cost-effective and scalable versatility and sustainability that builds from this electrochemical technique.

In this spirit, the aim of this study is to elucidate mechanisms that control electrochemical CNT growth in the context of the catalyst-support layer architecture that has been effective for the high yield growth of CNTs using gas-phase approaches. To accomplish this, we study Fe metal catalyst deposited at different thicknesses (0.5–5 nm) onto a passive stainless steel cathode, which is paired with a passive oxygen-evolving Ni anode to achieve electrochemical CNT growth originating from the cathode. Upon heating, we demonstrate dewetting of the Fe catalyst and electrochemical reduction that leads to CNT growth correlated with the catalyst particle diameter. However, time-dependent studies of CNT diameters elucidate rapid Ostwald ripening that limits diameter control over long growth durations and give promise to higher yield. Nonetheless, our results at short-growth durations indicate some double-walled CNTs among a population of small-diameter CNTs. This work provides a blueprint toward achieving high valued SWCNTs using this electrochemical approach, and synchs the challenges that remain pertinent for diameter control in gas-phase CNT growth with those in this electrochemical technique.

■ EXPERIMENTAL SECTION

Electrode Preparation. An Al	extsubscript{2}O	extsubscript{3}-coated Ni wire (Fisher Scientific, 99%, 1 mm diameter) anode was used in all electrolys experiments. The Ni wire was coated with 500 cycles (~50 nm) of Al	extsubscript{2}O	extsubscript{3} by a GEMStar Arradance atomic layer deposition tool. The thickness of this coating was determined through ellipsometry analysis of Al	extsubscript{2}O	extsubscript{3} coatings on silicon wafers with a J. A. Woollam spectrometer. To accomplish this, we utilized sequential 28 ms pulses of C	extsubscript{6}H	extsubscript{12}Al	extsubscript{2} (TMA) and H	extsubscript{2}O with a residence time of 1 s. The inert nature of this electrode is demonstrated by its ability to be reused for multiple experiments. The cathodes used in these experiments were 316 stainless steel (Trinity Brand Industries) sheets with thin layers of Fe deposited via e-beam evaporation using an Angstrom ebeam and a sputter tool.

Electrolysis. Experiments were carried out in an alumina crucible (AdValue Tech, 50 mL) containing 40 g lithium carbonate (Fisher Scientific, 99%) electrolyte, which was held at 750 °C (mp 723 °C) in a cylindrical ceramic heater (Thermcraft) using a bench top temperature controller (OEM Heaters). Electrodes were immersed into the electrolyte, and a constant current was applied across the electrodes. The current density is normalized to the approximate exposed surface area of the cathode. All electrolysis experiments in this study were carried out for 1 h, unless otherwise noted in the text. We observe no degradation of the lithium carbonate electrolyte and reused the same batch for five consecutive experiments before discarding. During the electrolysis, carbon accumulates at the cathode, which is removed from the electrolyte and cooled after electrolysis. The carbon product was removed from the electrodes by bath sonication in water (1 h) and purified from carbonates via washing in 2 M HCl, and the solvent was exchanged to water through centrifugation. The carbon was dried at 60 °C overnight.

Material Characterization. The carbon nanostructures were analyzed with a Zeiss MERLIN scanning electron microscope and an FEI Osiris transmission electron microscope at a beam voltage of 200 kV, with corresponding elemental mapping by energy dispersive X-ray spectrometry (EDS) technique to determine the catalyst composition. Diameter distributions were assessed by taking measurements of >100 CNTs from multiple scanning electron microscopy (SEM) images at multiple different spots. In the case of the 3 nm growth samples, diameter distributions were assessed by a combination of SEM and TEM imaging, to account for the population of CNTs that are too small to measure from SEM techniques. Cathode surfaces were characterized through TEM EDS. Raman spectroscopy was used to determine CNT crystallinity on a Renishaw inVia microscope with a 532 nm laser excitation, 10 s exposure time, and 10% laser power. All samples were purified through suspension in sodium dodecylbenzene sulfonate (Fisher Scientific) and centrifugation for 15 min at 2000 rpm for Raman characterization.

■ RESULTS AND DISCUSSION

The electrochemical reduction of CO	extsubscript{2} to CNTs via molten salt electrolysis has been previously described	extsuperscript{42} and relies on the splitting of the molten Li	extsubscript{2}CO	extsubscript{3} (mp 723 °C) electrolyte into C, which collects at the cathode, O	extsubscript{2} collected at the anode, and Li	extsubscript{2}O in the electrolyte. Li	extsubscript{2}O regenerates the Li	extsubscript{2}CO	extsubscript{3} electrolyte through a chemical reaction with ambient CO	extsubscript{2}. This takes place under a constant current of 100 mA/cm	extsuperscript{2} applied between a conductive stainless steel-based cathode and an inert Al	extsubscript{2}O	extsubscript{3}-coated Ni wire anode, which we have demonstrated as an ideal reusable oxygen evolution anode that enables the metal at the cathode—electrolyte interface to moderate the catalyst activity.	extsuperscript{41} However, despite the expectation that some of the conventional ideas guiding CNT growth carry over to this two-electrode growth system,	extsuperscript{42} no studies have been conducted that can enable the comparison or contrast between gas-phase and electrochemical growth processes. Therefore, in this study, we leverage the capability to isolate the catalytic activity to a single electrode and study electrochemical CNT growth from Fe catalyst layers deposited via e-beam evaporation with thickness ranging from 0.5 to 5 nm onto stainless steel surfaces. We chose stainless steel as the support for catalysts because of its high conductivity, low surface energy surface oxide that allows Fe dewetting, and inert chemical nature in molten carbonates. This approach enables the tuning of the catalyst size with the thickness of the deposited Fe, as schematically illustrated in Figure 1a,b. Figure 1c shows a catalyst-coated stainless steel cathode before electrochemical carbon deposition, with Figure 1d showing a CNT-coated cathode after 60
min of electrochemical growth. This duration of growth yields ∼50 mg of carbon deposited across an electrode with a total area of 2.5 cm², achieved under a constant current of 100 mA/cm² (∼90% Coulombic efficiency). Notably, this yield is higher than conventional CVD growth processes, where unlike electrochemical growth, the reaction rate is limited by the decomposition of hydrocarbons on the surface of the catalyst. Importantly, the precise nature of the ultrathin Fe coatings used for catalysts enables our study to focus on understanding of parameters that control and limit growth in this system in accordance with the conventional CNT synthesis. Control experiments conducted with no Fe catalyst demonstrate no CNT growth, making the observed CNT growth correlated with the Fe catalyst deposited.

Electrochemical CNT growth was studied for different catalyst thicknesses ranging from 0.5 to 5 nm Fe, with representative SEM images shown in Figure 2a–d and corresponding diameter distributions measured from the image analysis using multiple SEM images from multiple spots on the sample. The diameter distributions follow lognormal distributions (fits overlaid) with a diameter distribution shifting with the total thickness of the Fe catalyst. We observe a general trend of thinner catalyst layers yielding CNTs with smaller and tighter diameter distributions, with 0.5 nm Fe leading to CNTs ranging from ∼10 to 38 nm with a median diameter centered around ∼23 nm. Catalyst layers of 5 nm result in the widest and largest diameter distribution ranging from ∼19 to 62 nm with a median diameter centered around ∼33 nm. Normalized lognormal fits of the raw distribution data are overlaid and shown in Figure 2f, demonstrating the trend of increasing CNT diameter from increased Fe thickness, which is further shown in Figure 2g, with the median CNT diameter as a function of the Fe thickness plotted with a linear fit. Notably, all of the CNTs studied formed matlike morphologies rather than the dense self-assembled morphology that forms in CVD growth with this catalyst composition. As we expect that the percentage of active catalyst is high based on our measured yield, we speculate that hydrodynamic forces at the liquid–solid interface may play a role in modulating the resulting CNT morphology and preventing self-alignment.
Raman spectroscopy was used to characterize the multiwalled CNT (MWCNT) products, which exhibit the characteristic graphitized carbon G peak \( \sim 1580 \text{ cm}^{-1} \), indicative of in-plane sp\(^2\)-hybridized carbons, and a D mode \( \sim 1350 \text{ cm}^{-1} \), which corresponds to out-of-plane defective sp\(^3\)-hybridized carbons. Figure 3a shows the representative spectra for CNTs grown from all catalyst thickness conditions, and a higher D/G peak intensity ratio is observed for CNTs grown from thicker Fe catalyst layers. This observation indicates a greater concentration of sp\(^3\) carbon materials in the samples produced from thicker Fe catalyst layers. Figure 3b demonstrates the trend between the D/G intensity ratios \( I_D/I_G \) as a function of the Fe thickness, and we observe a trend where thicker Fe layers yield CNTs with a larger defect concentration, which is generally consistent with the presence of larger-diameter CNTs.

As Raman spectroscopy and SEM image analysis give statistical assessments of the CNTs grown, we performed high-resolution TEM (HR-TEM) imaging of representative CNTs synthesized from both extreme cases of 0.5 nm (Figure 3c) and 5 nm (Figure 3d) Fe thicknesses to give insight into the crystallinity and wall quality of the synthesized CNT materials. Consistent with our observations from Raman spectroscopy, we observe a high degree of crystalline carbon compared to other reports on electrochemically synthesized carbon. However, compared to other CNTs produced via CVD using similar catalyst layers, our CNTs exhibit localized crystallinity with a higher defect content than these materials that is common for larger-diameter CNT materials. We also observe sizes consistent with diameter distributions taken from SEM images, where smaller-diameter CNTs are observed in the case of 0.5 nm Fe films compared to larger-diameter CNTs grown from the 5 nm Fe films. However, we notably observe that there are on average slightly more walls in the smaller-diameter CNTs, which is opposite to that expected for CNTs where a constant carbon flux and growth rate is achieved. Because our electrochemical process produces a constant carbon flux per electrode area, we speculate this to be related to the following two points: (1) smaller-diameter catalyst, owing to their depressed melting point,\(^{50}\) will support increased carbon diffusion through the catalyst nanoparticle leading to different rates of carbon precipitation\(^{32}\) and (2) a CNT growing into a liquid medium will be required to displace the surrounding liquid, causing a drag force during growth that will be independent of the rate at which carbon diffuses to the growing CNT. Collectively, these two points can imply that smaller CNTs may exhibit a greater number of walls, even though the average number of walls between the CNTs grown from 0.5 and 5 nm is only different by approximately two walls. Our imaging also confirms the absence of amorphous carbon on the CNT wall, which we expect is due to the liquid—solid interface formed by the carbonate with the CNT during growth. This is different from CVD growth where hydrocarbons diffuse through the grown CNT materials before reaching the catalyst, often leading to amorphous carbon build-up on the walls.

So far, we have demonstrated a strong correlation between the predeposited catalyst film thickness and CNT diameter, emphasizing that the particle size and CNT diameter are correlated in this electrochemical process. However, with only 0.5 nm thickness of the Fe catalyst, the CNTs produced in our system have median diameters of \( \sim 23 \text{ nm} \), which is much larger than that observed in gas-phase growth processes that produce single or two—three walled CNTs from catalysts prepared with this thickness. Because emerging concepts for gas-phase CNT growth have demonstrated the importance of understanding the dynamic nature of the catalyst size through catalyst reduction to growth and termination,\(^{19,20}\) we performed experiments to study the evolution of the cathode surfaces in the environment where CNT growth takes place using SEM elemental mapping. We compared the as-deposited Fe thin films on stainless steel surfaces before and after prenucleation heat treatment to 750 °C in Li\(_2\)CO\(_3\) for 15 min (Figure 4a–d).
As shown in Figure 4a, the 5 nm Fe film appears uniformly distributed on the stainless steel surface until heated in the electrolyte, where the film forms larger particles, shown in Figure 4b. However, the 0.5 nm Fe film shows the formation of smaller well-distributed particles (Figure 4c,d). Whereas this imaging isolates the catalyst formation prior to CNT nucleation and growth, we further performed postmortem scanning transmission electron microscopy (STEM) EDS imaging on the CNTs to correlate the final products and the chemical identity of the catalyst particles that remain embedded inside the CNT tips (see the Supporting Information Figure S1) to confirm our prior observations. We know that only those elements that participate catalytically in CNT growth will be embedded in the CNTs following growth, and this serves to confirm the inert nature of our passivated anode. The compiled STEM EDS map is shown in Figure 4e, where we observe Fe as the only element that remains embedded inside a CNT tip grown from the 0.5 nm Fe catalyst layer. Figure 4f reports the first 10 s of a typical potential response from the galvanostatic electrolysis conditions applied to these Fe-based catalyst layers. We observe two distinct plateaus, including the first at around 1.2 V for 6 s and then a higher potential plateau at around 2.0 V, which extends for the duration of the hour-long electrolysis. We attribute the low-voltage initial plateau to the reduction of the Fe catalyst, which oxidizes during air exposure following deposition. As it is known that metallic Fe is necessary to precipitate CNTs,51 we emphasize this as a key step to achieve deposition. As it is known that metallic Fe is necessary to precipitate CNTs, we emphasize this as a key step to achieve deposition. As it is known that metallic Fe is necessary to precipitate CNTs, we emphasize this as a key step to achieve deposition. As it is known that metallic Fe is necessary to precipitate CNTs, we emphasize this as a key step to achieve deposition.

To better understand the effect of dynamic processes occurring between the first few seconds where catalyst reduction occurs and the conclusion of a 60 min duration synthesis experiment, we performed time-stop experiments for the cases of 0.5 and 5 nm Fe thicknesses for 3, 10, and 30 min growth times and compared the CNTs produced under these conditions to those grown for 1 h. The CNT diameter distributions and overlaid lognormal fits as representative SEM images of each time growth and thickness are shown in Figure 5. We observe at both thicknesses that smaller-diameter CNTs with a tighter size distribution are correlated with shorter growth times, with sizes ranging from ~8 to 22 nm for 0.5 nm Fe (Figure 5a) and ~3–37 nm for 5 nm Fe (Figure 5f) for 3 min growth conditions. These diameter distributions become wider with median sizes increasing under conditions of longer growth times. Representative Raman spectra for each growth condition is shown in the Supporting Information Figure S2 and demonstrates the characteristic peaks for graphitized carbon.

The median sizes for each condition are plotted in Figure 5i as a function of growth time for both thicknesses, with linear fits overlaid. In each case, we see a positive correlation between the growth time and the median CNT diameter, with larger diameters observed at each growth time for the 5 nm Fe grown CNTs compared to those grown from 0.5 nm Fe. To study the crystallinity and number of walls for the CNTs, we performed HR-TEM imaging for CNTs grown for 3 min and show representative TEM images across the spectrum of measured diameters as insets alongside the lognormal fits for 0.5 nm Fe (Figure 5j) and 5 nm Fe (Figure 5k) thicknesses. Notably, while the TEM imaging is generally consistent with the trends observed with SEM imaging, this technique is ideally suited to carry out assessment of the averages and the extremes. For example, TEM imaging reveals some small CNTs such as the double-walled CNTs grown from 5 nm Fe catalyst for 3 min, which is shown as an inset in Figure 5k—representing the smallest diameter CNT ever grown from CO₂. Whereas these small-diameter CNTs are a minority component of the CNTs grown, their presence indicates that the nucleation of such small-diameter CNTs can exist in this electrochemical approach, and we speculate that such species are rapidly overshadowed by the CNTs that nucleate and grow as the Fe catalyst undergoes catalyst coarsening.

Reflecting on the results of our studies in comparison to CVD techniques using similar catalyst materials, we attribute the larger diameter of CNTs we observe during electrochemical growth to Ostwald ripening-induced catalyst morphology evolution prior to CNT nucleation. This observation provides us with exceptional insight into how SWCNT growth can be achieved based on lessons learned over the past few decades in CVD growth. Whereas high-yield SWCNT growth is now readily achieved in CVD techniques, the enabling factor to achieve this was the incorporation of oxygen-containing additives into the gas mixture, including water vapor, ethanol, or oxygen.52,53 However, research studies later demonstrated the role of these additives to slow Ostwald ripening of catalyst particles, which was the mechanistic advance to achieving high density growth of SWCNTs.52,53 For electrochemical growth, this generates an intriguing question about the type of additives which can be introduced in a molten carbonate that could draw parallels to this important step in CVD. Additionally, another key feature to achieving controlled SWCNT growth has been linked to the fast reduction of the catalyst layer to produce the smallest possible catalyst particles. Whereas this is difficult to carry out in CVD without using highly reactive and toxic gas additives, such as hydrazine,54 the electrochemical growth of CNTs offers new electrochemical parameters that can be controlled to achieve this, noting that the catalyst reduction...
itself is an electrochemical process. Therefore, by understanding this Ostwald ripening mechanism by which the CNTs produced in our electrochemical method have larger diameters than CNTs grown through CVD, we can envision a path drawing on parallels and lessons learned from three decades of advances in gas-phase CNT growth to achieve SWCNT growth using electrochemistry in the future.

Finally, it is noteworthy to discuss overall the process energy and byproduct considerations for the electrochemical growth of CNTs from atmospheric carbon dioxide as compared to conventional synthesis routes. Conventional routes have been studied widely, but are limited to the thermal, instead of electrochemical decomposition of carbon-containing precursors (hydrocarbons).55,56 This requires a large energy footprint and is inefficient because energy is distributed into a cracking pattern from the hydrocarbon precursor to produce numerous carbon-containing byproducts, including methane, volatile organic compounds, and polycyclic aromatic hydrocarbons—most of which are not consumed in the reaction.57−60 Because catalytic activity in the conventional approach is associated with only a few active (minority) hydrocarbon species, the majority of these secondary products are process emissions, raising significant environmental and public health concerns when scaling-up CNT manufacturing technologies. By simple system level designs, such as the use of ZrO2 instead of Al2O3 thermal insulation materials, these costs can be lowered to below $5/kgCNT. In parallel, better control of underlying mechanisms in this system can enable the extremely valuable forms of CNTs such as single and double-walled CNTs. With a wave of research today centered on multistep CO2 conversion processes bottlenecked by low efficiencies due to energy coupled into a spread of chemical products, none of which are more valuable than the nominal cost of energy to produce them, our work demonstrates an alternate path to the quality and diameter of CNT materials that can overcome this limitation. Given the extraordinary properties, we anticipate this route to be the basis to produce all carbon nanostructures that can enable the batteries, composites, transparent films, fabrics, and coatings of tomorrow based on tapping into this abundant source of this CO2 feedstock in our air today.

**CONCLUSIONS**

In summary, we demonstrate that the electrochemical growth of CNTs from CO2 can be achieved from the Fe catalyst, with diameters controlled by the catalyst particle distribution and...
coarsening during the duration of growth. Our results demonstrate the ability to tune median CNT diameters from ∼33 to ∼23 nm by varying the catalyst thickness from 5 to 0.5 nm Fe. Raman spectroscopy and TEM characterization reveal a high level of crystallinity and lower concentration of defects for CNTs grown from thinner catalyst layers. SEM EDS measurements confirm the formation of catalyst particles on the surface of the stainless steel cathodes during pregrowth thermal treatment, which are responsible for MWCNT nucleation and growth, confirmed through postmortem STEM EDS imaging. Galvanostatic electrolysis indicates the electrochemical reduction of Fe catalyst particles, followed by carbon deposition to produce CNTs. Experiments studying the time evolution of CNT diameters highlight the rapid increase of the CNT diameter over growth duration, indicating strong coarsening or Ostwald ripening effects during growth. HR-TEM imaging reveals a high degree of crystallinity for the CNTs grown under short time conditions and a minority population of extremely small-diameter CNTs. Energy calculations for our process further paints a picture that distinguishes our efforts from other CO2 conversion processes, where the economic value of the CNT output is much greater than the energy consumption of the process. This is a picture unique to CNTs with small diameters ranging from MWCNTs to SWCNTs with diameters less than 20–30 nm and cannot be matched by routes to convert CO2 into methanol, ceramics, carbon fibers, or large-diameter CNTs (>100 nm) because of the low value of these materials in current markets. This work presents fundamental insights into the challenge of coarsening-induced diameter control to transition to SWCNT growth, giving promise to a powerful technique to convert a gas-phase environmental hazard into some of the most technologically valuable materials in the world.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b02834.

SEM images of Fe catalyst at CNT tips, Raman spectra of CNTs grown at short times, and energy analysis for the electrochemical CNT growth process.

**AUTHOR INFORMATION**

*Corresponding Author*
*E-mail: cary.l.pint@vanderbilt.edu.*

**ORCID**
Cary L. Pint: 0000-0003-4700-0852

**Notes**
The authors declare the following competing financial interest(s): C.L.P. and A.D. are joint founders of a company, Skynano LLC, which has financial interest in the approaches described in this manuscript.

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