Iron catalyzed growth of crystalline multi-walled carbon nanotubes from ambient carbon dioxide mediated by molten carbonates

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ABSTRACT

Until now, research efforts focused on electrochemical conversion of carbon dioxide into stable carbon-based materials have been limited by poor understanding of catalytic effects occurring at surfaces. Here, we demonstrate the capability to simultaneously use atomic layer deposition (ALD), electrode composition control, and current density as a means to direct the formation of iron-based catalysts and grow highly crystalline multi-walled carbon nanotubes at high yields (99%) and with controlled average diameters of 27.5 nm from ambient carbon dioxide captured and dissolved in molten carbonate electrolytes. ALD of passive alumina coatings on a Ni anode prevents electrode corrosion processes and adverse deposition of Ni on the cathode that results in increased CNT diameters, lower CNT quality, and non-CNT products. On the cathode side where CNT growth occurs, our results elucidate the fine balance of iron catalyst accessibility from the cathode interior and the surface chemical properties in order to achieve high yield and high quality CNT growth. Our work provides an intersection between decades of research understanding on catalytic gas-phase growth of CNT materials and the ability to leverage these ideas to sustainably capture ambient carbon dioxide and produce functional CNT materials.

1. Introduction

The concentration of carbon dioxide in the atmosphere, $\text{CO}_{2\text{atm}}$, now sits at around 405 parts per million, the highest concentration in history [1, 2]. Due to the relationship between CO_2 and global climate change, capture and storage or conversion of carbon dioxide has attracted the attention of researchers in the effort to achieve a reduction in $\text{CO}_{2\text{atm}}$ [3-6]. Sequestration technologies to store CO_2 underground are often bottlenecked by the limitations of available reserves (depleted oil and natural gas reserves) and the probability of gas leaks [1]. Similarly, injection of CO_2 gas into basaltic rock is promising, but limited by the long mineralization time (> 3 years) and energy intensive injection [7]. At present, technologies studied for transforming CO_2 include: chemical, photochemical, and biological transformation of CO_2 into hydrocarbons and alcohols (including methanol and ethanol) [8, 9]. Promising as a drop-in replacement fuel for gasoline, many researchers have concentrated their efforts on the chemical transformation of CO_2 into methanol [10-13], but these low-value hydrocarbons and methanol produced at low system efficiencies undermine the rationale of this approach. The challenge remains for efficient conversion of CO_2 into high-value secondary products.

The electrolytic conversion of CO_2 into nanostructured carbons has been investigated beginning with aqueous electrolytes [14]. However, the low solubility of CO_2 in aqueous solution and the similar reaction potential of water decomposition made the reaction impractical. Reduction of CO_2 was more recently investigated in room temperature ionic liquids (RTILs) due to their attractive electrochemical window and high solubility of CO_2 , however the high cost and toxicity of RTILs inhibits their

adoption in commercial applications [15]. Carbonate melts offer a low cost and high ionic conductivity with a low vapor pressure, and have been demonstrated to be a viable electrolyte for the reduction of CO₂. The deposition of carbon onto gold wire electrodes in molten eutectic carbonate electrolytes was first reported in the mid 1960s [16]. Building from early experiments, nanostructured carbon films deposited from low temperature eutectic electrolytes have more recently been investigated using inexpensive working electrodes such as aluminum, Ni, and steel [17-21], even though control of carbon products remains a challenge. Energy storage applications such as supercapacitors have utilized high surface area carbon deposited from these low temperature eutectic electrolytes [8]. In the case of pure carbonate electrolytes, recent advances have observed the formation of CO in Li₂CO₃ at elevated temperatures (> 850 °C) [22], and ultrathin graphite sheets onto steel electrodes in calcium electrolytes [23, 24].

Owing to their extraordinary mechanical, electrical, and thermal properties, growth of carbon nanotubes (CNTs) has been at the forefront of research for nearly two decades [25-27]. In past years, comprehensive models of CNT growth have been developed to account for the various factors that impact gas phase surface supported growth, such as precursor chemistry [28], catalyst composition and oxidation state [29-31], catalyst size [32], catalyst support properties [33-35], temperature [36-38], and dynamic processes during growth such as Ostwald ripening, metal catalyst diffusion into the support layer, and mechanochemical termination processes [39-42]. Generally, it is accepted that iron catalyst nanoparticles are the most ideally suited for CNT growth, and typical processes achieving high density CNT growth in compact arrays utilize an iron

catalyst layer supported by alumina. In contrast, growth of carbon nanostructures from electrochemical techniques remains a new idea, and recent studies leading to the first observation of carbon nanofibers [43] or large-diameter CNTs (> 100 nm) [44] have been carried out using a corrosive Ni anode and steel cathode. The first report of carbon nanofibers grown from this process utilized a mixture of carbonates and soluble metal oxides between inexpensive steel cathodes and either Ni or Ir anodes, and found there to be a positive effect from Ni and Zn to grow fibers [43]. In this system, it is presumed that corrosion of the Ni is the basis for the metal catalyst, and no apparent route exists to control the formation of a surface-bound catalyst for CNT growth [43, 44]. Whereas these works have studied the interplay between cathode surfaces and electrodeposited catalysts (in the case of Zn coated cathodes and corroded Ni catalysts), currently no studies have been carried out to correlate catalytic activity in the presence of carbonates to the *inherent* catalytic properties of the electrode materials themselves. This is especially important since decades of gas phase carbon nanotube growth research has led to unequivocal correlation between catalyst composition, size, and the resulting CNTs that are grown [38, 45].

While previous works have observed the catalytic activity of *in-situ* deposited catalysts to grow fibers and large diameter CNTs, here, we provide the first study on electrode processes in electrochemical growth of carbon nanostructures, building on observations of traditional gas-phase CNT growth processes, which typically use only one active substrate. To control and understand growth, we utilize ALD, cathodes with different surface coatings and Fe metal composition, and varying anode-cathode current density. Our results indicate the ability to use these concepts to direct the formation of

iron-based catalyst nanoparticles to grow high yield (99%) and highly crystalline multi-walled carbon nanotubes with average outer diameter of ~ 27 nm from ambient carbon dioxide captured from the atmosphere.

2. Experimental

2.1 Electrode Preparation: Three different anodes were used in electrolysis experiments. Anodes included untreated Ni wire (Fisher Scientific, 99%, 1 mm diameter), thermally oxidized Ni wire (1 hr at 450 °C in air), and Ni wire coated with 500 cycles (~ 50 nm) of Al_2O_3 by a Gemstar Arradiance atomic layer deposition (ALD). The thickness of this coating was determined through ellipsometry analysis of Al_2O_3 coatings on silicon wafers with a J.A. Woollam spectrometer. To accomplish this, we utilized sequential 28 ms pulses of $\text{C}_6\text{H}_{18}\text{Al}_2$ and H_2O with a residence time of 1 second. The cathodes used in these experiments were three different steels: 16 gauge galvanized steel wire (Home Depot), 216 stainless steel shim (Trinity Brand Industries), and 1010 steel shim (McMaster-Carr). The surface properties of each steel, characterized by SEM EDS imaging are described in the Supplementary Information Fig. S1.

2.2 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). 5 cm^2 electrodes (coiled wires or square shims) were immersed into the electrolyte and a constant current was applied across the electrodes. All electrolysis experiments in this study were carried out for 1 hr. 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 electrolyte and cooled after electrolysis. Carbon product was removed from the electrodes by bath sonication in water (1 hr), and purified from carbonates *via* washing in 2 M HCl, and solvent exchanged to water through centrifugation. The carbon was dried at 60 °C overnight.

2.3 Material Characterization: The carbon nanostructures were analyzed with a Zeiss Merlin scanning electron microscopy (SEM) and an FEI Osiris transmission electron microscope (TEM) at a beam voltage of 200 kV with corresponding elemental mapping by energy dispersive x-ray (EDS) technique to determine catalyst composition. The yield of carbon nanotubes in the overall electrolysis product was estimated from SEM images of raw material. The crystallinity of the carbon nanostructures was determined by Raman spectroscopy on a Renishaw inVia microscope with a 532 nm⁻¹ laser excitation, 10 seconds exposure time, and 10% laser power.

3. Results and Discussion

The general process of carbon nanotube growth relies on the decomposition of a carbon containing precursor most commonly on the surface of a metal catalyst. Only recently has the growth of carbon nanotubes been demonstrated through liquid phase electrolysis of CO₂, and parameters commonly related to traditional CNT growth, such as catalyst composition, carbon flux, and catalyst size, remains elusive without a clear understanding of how these components originate or evolve. Therefore, the focus of the present study is to elucidate and control these parameters to control CNT growth to achieve high yield and high quality CNT materials from carbon dioxide. The molten carbonate electrolysis technique used to convert CO₂ into nanostructured carbon is

illustrated in Fig. 1. Lithium carbonate was chosen as the electrolyte because of the lower standard reduction potential of C compared to the alkali metal, causing C to deposit onto the cathode rather than Li [21]. Briefly, a constant current is applied across a carbon collecting cathode (steel) and an oxygen-generating anode (Ni). This splits molten Li_2CO_3 into C, which collects at the cathode, O_2 collected at the anode, and Li_2O . The remaining Li_2O reacts with ambient CO_2 to regenerate Li_2CO_3 electrolyte. The equations are:

The net equation from equations (1) and (2) is:

This four-electron process converts CO_2 to carbon at a theoretical rate of 84 grams C/kilowatt-hour at 100% faradaic efficiency and a potential of 1.33 V. Previous works have justified the argument of CO_2 capture by molten carbonate electrolytes, and work by Ren *et al.* demonstrated an ^{13}C isotope experiment to track CO_2 uptake and transformation into carbon nanofibers and large diameter nanotubes [46]. To assess the effect of the electrode on the CNT growth process, three different cathodes and anodes are studied and schematically represented in Fig. 1. The three anodes studied

Fig. 1. (a) Schematic illustration of electrolysis set-up including the different cathodes and anodes utilized in this study, and SEM images of carbon nanotube products grown on (b) ZnO coated (galvanized) steel and (c) uncoated (1010) steel electrodes.

include untreated Ni wire, semi-passive thermally oxidized NiO, and fully passivated Al_2O_3 coated Ni wire. The three cathodes studied include galvanized steel, (ZnO-coated, Fe > 95%), stainless steel (Cr_2O_3 coating, 72% Fe), and 1010 steel (99% Fe). Without detailed understanding of the catalytic process, these three electrodes can be coupled with Ni-based anodes to produce a variety of carbon nanostructures including carbon fibers or nanofibers, petaled graphite materials, and carbon nanotubes. However, the lack of

understanding of how the anode or cathode impacts the formation of each of these products limits a controlled route to design the system to optimize tailored growth of one species. In this manner, our efforts herein are focused on tailoring these electrode materials to achieve high yield growth of highly crystalline CNTs (Fig. 1b,c).

Whereas no previous experimental efforts have been made to address the catalyst species in molten carbonate electrolysis, it has been hypothesized that Ni corrosion into the electrolyte leads to plating onto the cathode and is responsible for the nucleation of carbon nanofibers (or carbon nanostructures) on the surface [43]. In order to understand the source of the catalyst for CNT growth, we carried out studies aimed to fully deactivate corrosion on the Ni anode in our system by forming passive, uniform coatings of alumina using atomic layer deposition. Whereas previous work demonstrated the inert nature of Ir anodes in molten carbonate electrolytes [43], we focused on studying the tunable surface properties of Ni anodes, in an effort to utilize inexpensive electrode materials. Three cases were compared – untreated Ni wire, thermally oxidized Ni wire, and Ni wire coated with ~ 50 nm of alumina using ALD. In each case, a current density during electrolysis of 100 mA/cm^2 was used and the cathode material was galvanized steel. As shown in Fig. 2, the carbon products obtained by varying the anode are significantly different implying the importance of the anode in steering the catalytic properties. In the case of an untreated Ni wire anode material, the growth results primarily in carbon fibers with some small minority species of large-diameter CNTs. When the Ni wire is thermally oxidized to produce a rough oxide layer coating that exceeds the thickness of the native oxide, the carbon product in an identical process is steered toward the formation of hollow-center CNTs with large diameters ($\sim 100+$ nm)

and wavy surfaces that are indicative of a high sp^3 (defect) content. Finally, when ALD is utilized to produce a moderately thick (50 nm) and dense barrier layer on the Ni anode surface, straight CNTs with smaller diameters are observed. To understand these differences, we carried out post-mortem STEM EDS imaging of the CNT materials to correlate the synthesis product and the chemical identity of the catalyst particles that remain embedded in the product. Despite trace metals present in galvanized steel, post-mortem SEM EDS imaging reveals the catalytic behavior of metals, as only those metals that participate catalytically will be embedded in the CNTs. In both cases of the Ni wire and thermally oxidized Ni wire anodes, we consistently observed the presence of Ni-rich bimetallic Ni-Fe catalyst particles at the exterior edges of grown carbon nanostructures. However, in the case of the ALD coated Ni anode, we observe no signature of Ni in the catalyst particles (which reveals that Ni is sourced from the anode in the previous experiments), and observe only Fe-based catalyst materials positioned at the ends of the MWCNTs. We note that while previous reports have observed fibers grown with dissolved iron oxide salts in carbonate electrolyte, this is the first report to utilize *inherent* catalytic properties of the steel substrate and elucidate Fe as the only catalyst, through SEM EDS imaging. Individual elemental EDS maps for the bimetallic catalysts and corresponding high angular dark field electron images are shown in Supplementary Information Fig. S3.

Fig. 2. Schematic illustrations of the three anodes and their corrosive nature in electrolyte, SEM images of the carbons grown from each anode, and STEM EDS analysis of the catalysts left inside CNTs for (a-c) bare Ni anodes, (d-f) thermally passivated Ni anodes, and (g-i) ALD alumina passivated Ni anodes.

As herein we show the anode can be deactivated from taking part in the catalytic process, this allows the CNT growth process to be directly controlled by the composition and properties of the cathode material. In this spirit, we therefore performed a series of experiments using galvanized steel (ZnO coating, >95% Fe), stainless steel (Cr₂O₃ coating, 72% Fe), and 1010 steel (99% Fe) cathodes. We subjected these electrodes to either high current density (100 mA/cm²) or low current density (25 mA/cm²) and compared the carbon structures produced. As the carbon flux is a parameter commonly associated with gas-phase catalytic CNT growth, the analogous parameter of our system to changing carbon flux is the current density since this controls the rate at which CO₂ is

split between electrodes. In these three different cathodes, the source of catalytic metal (bulk Fe) will have different accessibility based on the surface coating of the steel that dictates whether it is galvanized, stainless, or 1010.

Shown in Fig. 3 are representative SEM images of the carbon products grown on each steel cathode. In all cases, if CNTs are observed, SEM images of these are shown with relative yields overlaid. In all cases carbon is deposited, but here we define relative yield as the concentration of CNTs relative to non-CNT carbon products. These yields were estimated based on SEM analysis of multiple images. Images of carbon nanostructures produced other than CNTs are shown in the Supplementary Information Fig. S5. In the case of galvanized steel, we observe under low current densities (Fig. 3a) the formation of 30% CNTs among amorphous carbon, whereas high current densities (Fig. 3b) drive the growth of 99% yield MWCNTs. We attribute this high yield growth to the combined ability to activate the catalyst from beneath the ZnO layer with high current densities, but also sustain catalytic CNT growth in conditions of higher carbon flux. At low current densities, we speculate that a combination of amorphous carbon overcoating of catalytic Fe metal combined with low accessibility of the Fe from the interior of the steel inhibit high yield CNT growth. At higher current densities, faster carbon deposition kinetics and greater Fe migration through the ZnO coating, driven by the increased electric field, to the electrode surface lead to high yield MWCNT growth. This effect was experimentally observed with SEM EDS imaging of the substrate surface before growth, after ten minutes of heating in the carbonate electrolyte, after five minutes of applied current, and after a full hour-long electrolysis. Supplementary Information Fig. S3 and S4 show that as a bare electrode, the galvanized steel is primarily zinc and

oxygen, and as the electrolysis proceeds, the concentration of zinc decreases while the concentration of iron increases. This relationship between current density and metal migration to the surface of the catalyst is schematically represented in Fig. 3g.

Fig. 3. (a-f) SEM images of the carbons grown on the three different untreated steel cathodes, at (a, c, e) 25 mA/cm² and (b, d, f) 100 mA/cm², and (g) schematic illustration of the mechanism of sourcing Fe from within the steel.

On the other hand in the case of the stainless steel cathode (Fig. 3c,d) we observe the formation of amorphous carbon at all current densities, with no CNTs observed. In this case, we conclude the Cr₂O₃ layer actively prevents the migration of Fe to the surface of the electrode and drives the formation of amorphous carbon, schematically represented in

Fig. 3g. This result also implies that amorphous carbon deposition using galvanized steel electrodes is a result of increased accessibility of catalytic metal as opposed to the adverse effect of slow carbon deposition on the surface. Finally, we studied carbon products grown on 1010 steel (Fig. 3e,f). We observe no CNTs grown at low current densities on 1010 steel, whereas high current densities drives the formation of MWCNTs as the majority product (90% yield). This trend, consistent with the case of galvanized steel, is attributed to the current-induced Fe diffusion through a native oxide layer to the electrode-electrolyte interface. Whereas previous reports have correlated positive catalytic activity to the zinc coating at the surface of the cathode, in our studies we believe this coating to be inert due to the observance of CNTs grown on 1010 steel, which has no zinc coating. Rather, we attribute the porous oxide coatings on both the galvanized and 1010 steel to aid in the diffusion of Fe to the surface for catalytic activity. We note that in the cases of galvanized steel and 1010 steel where CNTs are observed, some CNTs appear to be partially filled with catalyst metal. Here, as the CNTs are grown *via* tip-growth as supported by TEM imaging, metal filling will be a result of favorable energetics on the CNT interior in agreement with the capillary effect. We also note that during electrolysis experiments, the conductive nature of CNTs enables electrical connectivity between catalyst situated on growing CNTs and the cathode where the Fe metal catalyst is sourced from.

Our results indicate that crystalline MWCNTs are best achieved through growth on the galvanized steel cathodes at high current densities, utilizing Fe catalyst particles accessible from the interior reservoir of iron within the steel. From TEM analysis of MWCNTs grown under these conditions (Fig. 4a-e), we observe highly crystalline,

straight graphitic walls. This crystalline nature is further confirmed through Raman Spectroscopy (Fig. 4f), where we observe a sharp G mode $\sim 1580\text{ cm}^{-1}$, 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. The average ratio of D to G peak intensities across a map of 50 scans is 0.89, consistent with that of graphitic MWCNT spectra. ImageJ image analysis software was used to assess the size distribution of MWCNTs evident in the multiple TEM images to obtain a log-normal distribution of MWCNTs with outer diameter sizes between 15 and 50 nm and an average diameter centered near $\sim 27.5\text{ nm}$ (Fig. 4g). While CVD commonly grows single-walled and double-walled CNTs with smaller diameters than observed in this study, this is likely due to dewetting energetics of catalyst nanoparticles at a gas-solid interface. In our study, the catalyst particle dewetting occurs at a solid-liquid interface which controls particle size prior to CNT nucleation. Notably, we observe a log-normal diameter distribution of CNT diameters grown in our process that is similar to the CNT diameter distribution shape in gas phase CVD growth where it is well accepted that CNT diameter is correlated to the catalyst nanoparticle size [47]. This range of CNT diameters is consistent with those produced in many gas phase processes, but represents a significant decrease from existing prior work on CO_2 -derived CNTs, where the products exist as large diameter materials with diameters 150+ nm, and generally mixed with other non-CNT products.

Fig. 4. (a-e) TEM images of highly crystalline MWCNT grown on untreated galvanized steel cathode with inert Al₂O₃ coated Ni anode at 100 mA/cm² including both (b) high resolution image of wall crystallinity, and (c-e) a representative selection of CNT products (f) representative Raman spectra, and (g) size distribution assessed through ImageJ using multiple images acquired through TEM.

4. Conclusion

In this study we demonstrate the synergy between traditional gas phase CNT growth mechanisms and electrolytic growth of CNTs by leveraging an electrode design

strategy to understand and direct the catalytic process toward iron-catalyzed growth. We show the ability to capture CO₂ and electrochemically convert this into highly crystalline MWCNTs with an average diameter of 27.5 nm and a high degree of crystallinity by leveraging iron based CNT catalysts for the first time. This builds on using ALD to produce a passive alumina coating on the Ni anode surface to inhibit mass transfer and isolate Fe as a primary catalyst species at the cathode where CNTs are grown, and engineer the surface properties of the Fe-containing cathode to optimize the accessibility of internally-contained catalyst material. Whereas previous works have studied the interplay between cathode surface properties and in-situ deposited catalytic particles [43], herein we present the first study of catalysts inherent to the cathode materials, which can either be activated or deactivated, based on the engineered surface properties of the anode. SEM, TEM, and Raman spectroscopic imaging reveals the ability to produce highly crystalline CNT materials with high yield of 99% relative to other carbon products, and touting a CNT diameter distribution that intersects products formed in state-of-the-art traditional gas phase CNT processes. As decades of gas-phase CNT research has lead to the understanding that catalyst size and support layer dictate CNT growth, future works to modulate catalyst size to achieve smaller diameter CNTs and study the influence of catalyst support are of interest. More significantly, this work provides the first intersection between concepts present among the vast community of researchers studying gas phase CNT growth and the concepts and mechanisms behind the electrolytic growth of CNTs from ambient carbon dioxide.

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Figure 1

Figure 2

Figure 3

Figure 4