Review—Electrochemical Growth of Carbon Nanotubes and Graphene from Ambient Carbon Dioxide: Synergy with Conventional Gas-Phase Growth Mechanisms

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The rising levels of atmospheric CO2 threaten the promise of human sustainability on earth. Electrochemical conversion of CO2 into secondary chemicals and materials presents the most economically viable approach to solve this global challenge, and provides a method to utilize otherwise wasted CO2 as a chemical feedstock for the production of valuable products. Challenges by the processing cost versus value of converted materials, known routes for the production of hydrocarbons and alcohol products remain impractical. Electrochemical CO2 conversion into high-value carbon nanostructures presents a new area of research with the opportunity to build upon the last two decades of understanding of gas-phase synthesis processes for fullerenes, carbon nanotubes, and graphene. However, efforts so far to convert atmospheric carbon dioxide into functional carbon materials are limited by a systems-level approach that provides only coarse control over the types and quality of materials that can be synthesized. In this short review, we make a strong case for the synergy between the catalytic mechanisms that have been developed over past decades to understand carbon nanostructure growth and the emerging research area where electrochemical reduction of ambient CO2 can be used to produce carbon nanostructured materials. This presents a new opportunity for researchers to address one of the most pressing environmental issues for modern mankind with the synthesis of carbon materials that will shape our future.

The increased concentration of atmospheric carbon dioxide (CO2 atm), predominantly due to anthropogenic activities such as fossil fuel consumption, challenges the promise of long-term human sustainability on Earth. The rate of increase in anthropogenic CO2 emissions has more than doubled to over 2.5% from 2000–2014, compared to the previous 1.1% for the period from 1990–1999.1 If this rate of emissions remains constant over the next 40 years, the atmospheric concentration of CO2 will be over double pre-industrial levels. The impact of CO2 on global climate change has attracted the attention of researchers in efforts to develop technologies that can achieve a reduction in CO2 atm to a level of sustainability.2–5 Renewable energy sources is one specific approach, even though for established centralized power grids, such as that in the United States, only a low abundance of intermittent energy production can be managed. Additionally, limitations to widely proposed carbon storage techniques include the volume of available storage sites (depleted oil and natural gas reserves) and high probability of leaks.1

To address this, recent efforts have considered the capture of CO2 from release points, such as power plants, and conversion into chemicals including fornic acid, methanol, CO, and ethylene.6 In this technique, CO2 acts as the chemical feedstock for the manufacturing of useful chemicals and provides the potential for a viable secondary market for otherwise pollutant gases, which are normally expensive to sequester. However, these routes for CO2 conversion are bottlenecked by the cost of operation versus the perceived economic benefit to society, and these low-value materials produced at low efficiencies, often from expensive catalyst materials, undermine the rationale of this approach. These issues can be resolved with the development of techniques that capture and convert atmospheric CO2 into more valuable materials that can be developed into high-value products.

As CO2 is the most oxidized form of carbon, no natural chemical destruction mechanism exists for the decomposition of CO2. In contrast to the hydrogenation of CO2 into hydrocarbons and alcohols, liquid-phase electrochemical splitting of CO2 into its individual elemental constituents has been investigated beginning with aqueous electrolytes. However, low solubility of CO2 in aqueous solution and similar reaction potentials for water splitting were problematic. CO2 splitting in room temperature ionic liquids (RTILs) has been studied for their attractive electrochemical window and high solubility of CO2, but the high cost and toxicity of RTILs makes their commercial adoption impractical.7 In contrast to these methods, molten carbonates boast low cost and high ionic conductivity with a low vapor pressure, and have been proven as viable electrolytes for the capture and electrochemical splitting of CO2 dating back now seven decades.8 This method relies on the decomposition of dissolved CO2 between two biased electrodes, where elemental carbon is captured at the cathode, and the resulting structures of the deposited carbons are largely dependent on process parameters including electrolyte, current density, and electrode materials.9–10 The equations that govern this process are:

\[ \text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{C} + \text{O}_2 \]  
\[ \text{Li}_2\text{O} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 \]

The net equation from equations 1 and 2 is:

\[ \text{CO}_2 \rightarrow \text{C} + \text{O}_2 \]

This provides the electrochemical basis of both early and more recent studies using this technique.

Among naturally occurring elements, carbon is one of the most widely used in modern technological applications. Carbonaceous materials including activated carbons, graphite, carbon black, and biomass are used extensively in chemical production,97 electricity generation,10 fuel production,11 and in the construction of energy storage devices including lithium-ion batteries and supercapacitors.11,12 The last 25 years have been lauded as perhaps the most exciting for carbon researchers due to the emergence of nanostructured carbon materials with extraordinary mechanical, thermal, and electronic properties that cannot be replicated in other known materials. This era began with the discovery of C60 fullerene in 1985 and resulting Nobel Prize awarded to Curl, Kroto, and Smalley. Further, this was continued as the emergence of graphene led to the 2010 Nobel Prize awarded to...
Synergy Between CO₂ Conversion and CNT Synthesis

As schematically illustrated in Figure 2, electrochemical conversion of CO₂ into chemicals such as formic acid, hydrocarbons, carbon monoxide, and alcohols has been extensively studied and is an ongoing area of research. Briefly, the half reactions of conversion into these products rely on the hydrogenation of CO₂ at the surface of a catalyst under electrolytic conditions. Catalysts such as Hg, Pb, metal oxides, metal organic frameworks, and Sn have demonstrated the ability to produce formic acid with respectable faradaic efficiencies. While copper catalysts uniquely produce hydrocarbons and silver catalysts are state of the art for CO production. Whereas methanol is arguably the most desirable chemical produced through the hydrogenation of CO₂ due to its wide range of applications including direct use as fuel, its production is severely limited by the low faradaic efficiencies. The rationale for CO₂-derived production is also underpinned by an extremely low current cost of a few USD/gallon. As outlined by Jhung et al. on the electrochemical conversion of CO₂ to useful chemicals, the development of commercially viable catalysts are still lacking, and the reaction mechanisms for distinct catalysts remains elusive.

On the other hand, many of the same carbon-containing molecules produced through traditional CO₂ conversion are used as a carbon source to grow CNTs by gas phase methods including hydrocarbons, CO, and alcohols, as schematically illustrated in Figure 2. Of the methods utilized to convert these precursor gases into CNTs, including laser ablation, arc discharge, chemical vapor deposition (CVD),
and flame synthesis, CVD is by far the most widely used for its versatility and simplicity.\(^{25-27}\) Briefly, a hydrocarbon gas is passed over the surface of a catalytic nanoparticle (CNT) or surface (graphene) which promotes the dissociation of the gas and allows for diffusion of carbon intermediates into the metal. The particle/surface provides a nanoscale template for the precipitation of graphitic carbon, and hence the nucleation and growth of the CNT or graphene material.\(^{37}\) Nickel, iron, and cobalt are specifically three of the most common catalysts for CNT growth by CVD, though over two decades of research, many other elements and elemental alloy combinations have been proven suitable.\(^{54}\)

At the intersection of CO\(_2\) conversion and CNT growth lies the relatively unexplored field of electrolytic conversion of CO\(_2\) into CNTs, which utilizes the decomposition of CO\(_2\) between two electrodes, where elemental carbon is captured at the cathode and can be utilized to grow specific nanостructures depending on the surface of the cathode. We observe that the role of catalytic behavior is critical in both electrochemical conversion of CO\(_2\) and gas-phase growth of CNTs, and the only discussion so far on growth of CNTs from CO\(_2\) indicate that this process is also driven by catalytic processes.\(^{46,58}\) Notably, the electrodes are comprised of bulk conductive materials that contain the carbon synthesis community with the new challenges that arise for growth at a solid-liquid interface in an electrochemical system.

### Synthesis-Structure Relationship for CNT Growth

The structural characteristics of CNTs grown by CVD methods strongly depend on the experimental conditions under which they are prepared, including catalyst properties such as size,\(^{39,60}\) composition,\(^{31,34-36,41}\) reduction techniques,\(^{34,56}\) migration and particle ripening,\(^{32-40}\) and catalyst support layers;\(^{36,38}\) and global parameters such as time,\(^{33,38,41}\) temperature,\(^{34,54,56}\) and rate of carbon source.\(^{54}\) These are shown in Figure 3. Whereas many of the structural effects of these parameters are well understood in gas-phase CNT synthesis methods, they are virtually unexplored in the liquid-phase CO\(_2\) electrolysis for CNT growth. For example, a strong correlation between the size of the catalyst particles used in CVD and the diameter of the resulting CNTs is often observed and has been studied with \textit{in situ} TEM techniques.\(^{64-66}\) This understanding has been the basis of controlling the size distribution of the catalyst particles as the most standard way to tune the CNT diameter distribution, which is most commonly achieved by tuning the thickness of the deposited catalyst, the coarsening rate, or its evaporation during thermal treatment processes prior to growth.\(^{37}\) While we anticipate a similar trend to carry over into the liquid-phase growth process and likely be accelerated by the liquid phase medium, such effects remain fully unknown about this new system. Further, dynamic processes of catalysts have demonstrated that in two dimensions across the surface of the growth support, the high surface free energy of metal nanoparticles will instigate Ostwald ripening and catalyst coarsening.\(^{22-45}\) Similarly, in molten carbonate (melting point \(~750\)°C) electrochemical growth takes place at a similar temperature as gas phase processes, but mechanisms such as Ostwald ripening will now occur at the solid-liquid interface, instead of the solid-gas interface, yielding intriguing new roles for well-studied and characterized mechanisms.

Similar to catalyst size, catalyst composition is well known to dictate the carbon diffusion through the metal nanoparticle, and result in dictating the number of walls and diameter of resulting CNT structures. The ability of transition metals to bond with carbon atoms increases with the number of unfilled d-orbitals, and thus metals without d-vacancies in their electronic configuration display a negligible affinity for carbon. Metals with few d-vacancies such as Ni, Fe, and Co exhibit finite carbon solubility, which makes them ideal candidates for CNT catalysts.\(^{55}\) It is generally accepted that small diameter iron catalysts are the most ideally suited for growth of small diameter single-walled CNTs, due to their unique carbon diffusion properties.\(^{56}\) Once again, as the electrochemical processes often employed for carbon growth rely on (conductive) metal electrodes, often composed of Fe-rich steels, nickel, or other metals, this presents an opportunity to understand how metal nanoparticles can form at the solid-liquid interface and evolve over time to enable CNT growth. Similarly interesting is the reduction processes in electrochemical growth, since catalyst reduction with H\(_2\) in the gas phase prior to CNT or graphene growth is a critical step to achieve high quality materials. Until now, researchers employing electrochemical methods to grow a broad range of carbon nanomaterials have carried out no notable microscopic investigation of the substrate properties that can be correlated with nucleation and growth of the carbons and answer these questions for electrochemical growth processes. This is an exciting area to explore, and provides a direct connection between traditional gas-phase CNT growth and electrochemical growth techniques.

Whereas catalytic properties are some of the most influential parameters affecting CNT growth, global parameters such as time, temperature, carbon flux, and substrate choices can also have a large role in the structural properties of the CNTs produced. For example, carbon flux in traditional gas phase CNT growth processes is controlled by the partial pressure and flow rate of carbon precursors in the reaction system, whereas in liquid phase growth it is controlled by the current density, which dictates the rate of CO\(_2\) splitting between electrodes. The development of models, such as the Puretzky model,\(^{41}\) to study the relationship between carbon flux, diffusion and precipitation, and effects of catalyst poisoning under conditions of high carbon flux have led to a mechanistic understanding of the influence on gas-phase CNT growth, however this remains a new and interesting idea for electrochemical growth of CNTs. As carbon solubility is a function of temperature, gas phase processes are greatly influenced by the system temperature. For example, the solubility of carbon in iron at 700°C is \(~0.1\) at.%, whereas at 800°C it is \(~4\) at.%.\(^ {38}\) However in liquid phase CO\(_2\) reduction, as observed theoretically\(^ {64}\) and experimentally\(^ {66}\) in many studies of temperature effects in CO\(_2\) electrolysis, the deposition of C is favored below 950°C, above which CO is preferential. In this new CNT growth mechanism, the global parameter of temperature more closely likely influences the solubility of carbon into catalyst particles, but dictates the chemical species which is deposited at the cathode altogether. As time of growth increases in both CNT synthesis techniques, CNT yield increases. Some studies using electrochemical growth

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**Figure 3.** Schematic illustration of gas-phase CNT growth and liquid carbonate CNT growth with a table of parameters that influence CNT growth with correlation to each technique.
processes have speculated on the role of time on synthesis products, but careful time-dependent studies remain largely elusive in characterizing the electrode-catalyst-carbonate interface evolution and its impact on the growth. On a similar note, whereas many studies of gas phase CNT growths have focused on the effect of substrate and catalyst support materials, no work has looked at the effect of different substrates for liquid carbonate CO$_2$ electrolysis growth. In fact, the most traditionally utilized substrate for gas phase growth, silicon, corrodes in molten carbonate electrolytes and thus alternative substrates are necessary. The biggest qualification a substrate must demonstrate to be suitable for liquid-phase CNT growth are conductivity and chemical stability within the molten carbonate electrolyte.

**Types of Carbon Materials Produced from CO$_2$**

A brief timeline for the history of structures produced through CO$_2$ electrolysis is given in Figure 4, with corresponding SEM images in Figure 5. The first report of carbon deposition via CO$_2$ electrolysis in fused molten carbonates in 1966 resulted with a thin layer of structurally uncharacterized carbon deposited onto cathodes of gold, palladium, platinum, silver, and stainless steel. This carbon was likely structurally similar to the spherical carbon powders observed in 2003, and shown in Figure 5a, consisting of carbon particles $\sim$100 nm. However, 2001 marks the first observation of carbon deposits which structurally resemble the extraordinary nanocarbons grown from gas phase and studied today, with the observation of graphite (Figure 5b) and “nano ropes” (Figure 5c) of $\sim$50 nm by Kaplan et. al. The authors comment that the observed “nano ropes” observed are parallel carbon nanofibers bound together, though speculation of how the different carbon nanostructures are formed in electrolysis is not detailed in the report. In more recent years, the observation of higher quality carbon nanostructures has been studied, with the growth of few-layer graphene sheets (<5 layers) (Figure 5d) and carbon nanofibers with diameters >200 nm (Figure 5e) in 2015, and more recently carbon nanotubes with diameters >100 nm (Figure 5f) in 2016. These works begin to build upon mechanistic understandings gained from gas phase growth techniques, and start to bridge the gap between gas phase growth of carbon nanostructures and CO$_2$ electrolysis. The growth of CNTs and nanofibers has been carried out utilizing a corrosive Ni anode, and in this system it is presumed that the corrosion of the Ni is the basis for the catalyst. However, while these works demonstrate the promising intersection between traditional gas phase synthesis concepts and electrochemical growth techniques, further efforts to achieve the growth of high quality structures including small-diameter and single-walled CNTs, single layer graphene, and vertically aligned CNTs through the electrolysis of CO$_2$ will require future efforts that forge a distinct interface between these two growth processes.

**Forward Outlook and Open Questions**

Figure 6 illustrates the current state of carbon structures grown from CO$_2$, including large diameter multi-walled CNTs >100 nm in diameter, and few layer graphene sheets 1–5 layers thick. As modern society is tasked with the challenge of finding technologies for CO$_2$ sequestration to reduce the threat of global climate change, the most economically viable solution is the utilization of CO$_2$ as chemical feedstock for the production of high-value materials which can be utilized in a variety of modern consumer applications. We envision the ability to leverage the understanding from decades of CNT growth, applied to this system, in order to achieve carbon structures grown from CO$_2$ that have extremely high technological relevance, including single layer graphene, single-walled CNTs, and vertical CNT arrays. Achieving the electrolytic growth of these structures at the beginning of their widespread commercial adoption provides a route toward CO$_2$-negative manufacturing of applications that are based on these carbon nanomaterials. Such applications can include structural composites for clean energy applications such as wind turbines.
lightweight materials ideally suited for aircraft, spacecraft, and even sporting equipment, and energy storage applications including batteries and supercapacitors. As the market sizes for these nanostructured carbons grow in tandem with their increased commercial adoption, CO₂-negative manufacturing has the opportunity for a significantly positive environmental impact, achieving ~5% net annual United States carbon emissions reduction, which translates to ~1% globally, based on the current and projected state of the market for these materials. We estimate this based on the projected market sizes and average selling prices for carbon fiber ($7.51 Billion, $10/gram),\textsuperscript{70} CNTs ($8.1 Billion, $10/gram),\textsuperscript{71} carbon black ($28.05 Billion, $560/lb),\textsuperscript{72} graphene ($2.1 Billion, $2.50/gram),\textsuperscript{73} and activated carbon ($10.15 Billion, $350/ton),\textsuperscript{74} and use these figures to estimate a total mass of carbon that is manufactured into various applications. If we replace currently employed manufacturing techniques to utilize electrochemical conversion of CO₂ to produce these five key carbon structures using wasted CO₂ as the chemical feedstock, we can estimate the amount of CO₂ captured from the atmosphere for this manufacturing, and calculate an estimated net emissions reduction. This technique, which overcomes the limitations of other CO₂ capture and conversion approaches that produce low-value products, presents a new frontier for carbon researchers to apply a framework of understanding of synthesis methods and mechanisms to a process capable of generating functional carbon materials from a freely available global pollutant.

growth can be mapped onto this new system, where growth occurs at a solid-catalyst-liquid interface instead of a solid-catalyst-gas phase interface relevant to conventional synthesis processes. We emphasize the vision of leveraging the science underlying CNT and graphene growth mechanisms to produce high quality materials such as single-walled CNTs, vertically aligned CNTs, and single-layered graphene in bulk quantities and in an open system from CO₂. With promise for significant CO₂ emissions reduction with widespread CO₂ derived manufacturing, this technique provides an opportunity for researchers engaged in the synthesis and applications of carbon nanostructures to combat perhaps the most staggering challenge humanity has ever faced, and enlists new researchers to join efforts at the intersection of carbon nanoscience and environmental sustainability. The visionary long-term outcome stemming from embracing this approach is a set of technological all-carbon building blocks that shape our future, and a sustainability model for atmospheric carbon that shapes the future of our children, and their children.

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Conclusions
In conclusion, we provide a forward-looking review that highlights the exciting intersection between the electrochemical growth of carbon nanostructures from CO₂ that has been primarily carried out at systems-levels to adapt to environmental challenges, and the mechanistic nucleation and growth of carbon nanotubes and graphene that has been studied using primarily gas-phase systems over the past few decades. As electrochemical processes have been discussed with coarse control, current studies in this area do not characterize or assess the microscopic characteristics of growth, such as catalyst size, source, morphology, and composition. Alternatively, the growth of carbon nanostructures has primarily focused on mechanisms at the microscopic scale, with barriers of scaling these ideas to larger systems-level scales. In this manner, we highlight the synergy that exists in these two areas, with a powerful message that the key mechanistic observations of the past few decades for carbon nanostructure growth can be mapped onto this new system, where growth occurs at a solid-catalyst-liquid interface instead of a solid-catalyst-gas phase interface relevant to conventional synthesis processes. We emphasize the vision of leveraging the science underlying CNT and graphene growth mechanisms to produce high quality materials such as single-walled CNTs, vertically aligned CNTs, and single-layered graphene in bulk quantities and in an open system from CO₂. With promise for significant CO₂ emissions reduction with widespread CO₂ derived manufacturing, this technique provides an opportunity for researchers engaged in the synthesis and applications of carbon nanostructures to combat perhaps the most staggering challenge humanity has ever faced, and enlists new researchers to join efforts at the intersection of carbon nanoscience and environmental sustainability. The visionary long-term outcome stemming from embracing this approach is a set of technological all-carbon building blocks that shape our future, and a sustainability model for atmospheric carbon that shapes the future of our children, and their children.


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