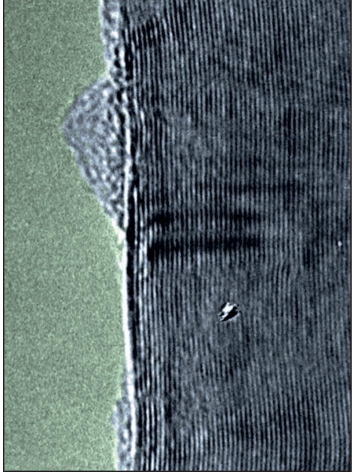

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The path of CO_2 and CH_4 conversion to environmentally friendly materials

By **Eva Karatairi**
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Carbon and carbon-based materials, from charcoal and diamonds, to graphene, carbon fibers, and nanotubes are fundamental to society for their ubiquity, versatility, and functionality and have sparked scientific innovations and an industrial revolution. Today, in its gaseous CO_2 form (carbon dioxide), carbon is inextricably linked to one of the biggest environmental issues of all times—the rise of global temperature. Conversion of CO_2 to high-value carbonaceous products is a story about new emerging technologies and huge scientific challenges. If addressed successfully, CO_2 conversion will help mitigate climate change while at the same time stimulating economic growth and transforming the structural materials market.

CO_2 conversion can create a USD$1 trillion market opportunity by 2030, consuming ~10% of CO_2 emissions, according to estimations of the Global CO_2 Initiative (GCI), an organization created with the goal to lead the development and commercialization of products based on recycled CO_2. Producing materials with a moderate to high market value from an abundant source, while reducing CO_2 emissions, can be achieved, but at a financial and environmental cost. Moreover, thermodynamics does not favor CO_2 conversion, which requires driving a reaction up a steep energy hill.

Daniel Matuszak, who manages the carbon utilization program at the Office of Fossil Energy in the US Department of Energy, explained how converting CO_2 gas to a solid carbon material is an energy-intensive process. Yet, Matuszak said that, "Since trees have found a way to convert carbonaceous gas to organized solids at a very low efficiency, I see no reason why science cannot find another solution. It remains to prove how."

Trees use solar energy to drive conversion of CO_2 to lignin and cellulose at rather modest efficiency. For chemical processes that focus on turning CO_2 into solids, polymers, or fuels with a high efficiency, one of the challenges is to minimize the energy inputs required, while maximizing selectivity, yield, and throughput in thermochemical and electrochemical reactions that have been the subject of decades of research. In contrast, the quest to transform CO_2 into useful solid materials such as carbon fiber or carbon black is an uncharted area.

Being one of the few groups to address the challenge of CO_2 conversion into a useful material has its advantages. "At the moment, some target materials are rather expensive. In addition to a very good payout for creating a lower-cost process, the impact of a breakthrough can be really big," said Issam Dairanieh, CEO of CO_2 Sciences, a company at the frontiers of CO_2 conversion that has emerged as the nonprofit arm of GCI. It also offers a supporting platform that could help developing conversion technologies make the next step in and out of the lab and prepare for the market.

CO_2 Sciences is developing an understanding of technical challenges and market trends, supported by life-cycle analysis and techno-economic assessment tools. They have identified an opportunity in carbon fiber, an expensive material, costing approximately USD$100/kg. "Despite the high cost, the market is growing at a rate of 12%–13% a year. Can you imagine how big the growth can be if a new technology brings down the cost of the production to $10/kg?" said Dairanieh.

Lack of funding is a problem that holds back not only those entering the developing research landscape, but also teams that are making progress. "At the beginning, it is of course difficult to prove that it makes sense to spend time and money on a project," said Dairanieh. "Further down the road, when one has to take a reaction that was performed in a beaker and make it happen on a larger scale in a pilot trial, the risk goes down, but the amount of money you need to spend goes up," he added. Dairanieh hopes that creating some awareness will drive capital into CO_2 conversion technologies. Identifying which technologies will deliver valuable materials with the right structure and dimensions is an even bigger challenge.

In 2015, Stuart Licht, professor of chemistry at George Washington University, published work on transforming CO_2 gas directly to carbon nanofibers (CNFs) and carbon nanotubes (CNTs). The high yield and low electrolysis voltage synthesis is based on electrolytic splitting of CO_2 dissolved in a 750°C molten lithium carbonate electrolyte, producing O_2 at the nickel anode and CNFs or CNTs at the steel cathode. Starting with the natural carbon isotope mix (primarily $^{12}CO_2$), the process results in the more expensive product, CNTs, while equivalent synthetic conditions with heavier $^{13}CO_2$ favor CNFs. The synthesis allows morphology control at the liquid/solid interface that is not available through conventional chemical vapor deposition and has low energy demands. Licht's work has opened new directions that deserve to be explored further and still needs to address concerns such as whether it is energy efficient and cost-effective.

Direct conversion of CO_2 is the most obvious approach to economically beneficial products, but an alternative is to practice CO_2 avoidance. The roundabout in incorporating carbon to high-value materials is using methane (CH_4), the main compo-

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nent of natural gas, as a carbon feedstock. In this case, CH_4 is decomposed directly to solid carbon and hydrogen (H_2), which is itself a CO_2-free energy source.

Representatives from the academic, industrial, and public sectors agree that turning carbon into high value, carbonaceous material, while at the same time valorizing a significant portion of the energy content of the natural gas in the form of hydrogen, is the basic motivation for those who work in the field. While making meaningful carbon materials in itself is challenging, making meaningful materials that will meet large market needs is an even bigger task. According to the US Energy Information Administration, in 2016, the United States used approximately 30 quads (~30 exajoules) of natural gas. Generation of H_2 from natural gas with the energy content of 1 quad would be accompanied by the production of approximately 22 million metric tons of carbon. This would be a cube with a side a little larger than two soccer fields. To deal with such quantities, utilization by the steel and potentially concrete industries is necessary, because these utilize carbon feedstocks on an order of magnitude larger than specialty chemicals, such as polymers.

Monolith Materials' pilot plant in Redwood City, Calif. Credit: Monolith Materials, Inc.

Jonah Erlebacher, professor and chair of the Department of Materials Science and Engineering at Johns Hopkins University, added another perspective on why one must think in terms of industries, such as building materials: "To mitigate CO_2 emissions, you have to do it at a scale that is huge. I could turn the carbon into graphene, but I suspect even a few tons of material would saturate the market."

Very few reactions are known to break the C–H bond in CH_4 without producing CO_2 as a byproduct, and Erlebacher serendipitously discovered a new one—a process based on the reduction of nickel(II) chloride ($NiCl_2$) by CH_4. By reversing the reaction, $NiCl_2$ is regenerated. What are left behind are solid byproducts, among which are pure nanostructured carbon, and H_2 gas.

"The thermochemistry suggested it should work, and indeed when we tried it in the lab, it worked like a charm. Essentially, we run an energetically unfavorable reaction at a high temperature where it is entropically favorable, and then we run the reverse reaction at a reduced temperature in an energetically favorable case, which does not regenerate CH_4. But what was completely jaw dropping was the moment I realized I couldn't find any reference of this kind of reaction in the literature," said Erlebacher. He is now exploring ways to capitalize on this success by taking the next step toward commercialization of the patent they have been issued and is working with industrial partners to scale up the process.

Scaling up a technology that uses CH_4 to deliver carbonaceous materials has been successful only in a few cases. Closer to commercialization is Monolith, a company that runs a pilot scale facility in California that produces carbon black. An electric plasma arc process is used to break CH_4 into carbon and H_2 with zero CO_2 emissions. No catalyst is involved in the process, but instead, the temperature generated by the arc drives the decomposition of CH_4.

Monolith has just ordered their equipment for a commercial scale facility in the town of Hallam, Neb., which will direct the final product into the rubber and plastic market, while the H_2 will be sold separately to a Neb. Public Power District electricity facility, which operates in this same town. There, H_2 will be used to fuel a boiler, which will replace a coal-fired boiler. "The local environment will see a million ton per year reduction of CO_2 emissions, due to the conversion of the fuel from coal to hydrogen," according to John Reese, vice president of sales and marketing of the company.

"Making the electric arc and cracking the methane is fairly easy, in comparison to other issues that had to be solved during the pilot phase, like developing the equipment that would keep the process running for an extended period of time and also controlling the process in order to expand the range of carbon products we could make," said Reese. "The electricity used exceeds the amount that can be produced using our hydrogen. However, the environmental impact reflects this delta. The change outlined above from a coal fired boiler to a hydrogen fired boiler results in net positive environmental impact," he added. Major tire companies have seen and evaluated Monolith's products, and the company is sampling other market niches as well.

Ingesting CH_4 into the manufacturing process of a carbon-based material is a process used by companies such as Merck and Nanocomp. Nanocomp, in particular, has developed Miralon—extremely long CNTs (1–10 mm) that form bundles and are lighter than carbon fiber. One of their potential applications is as a carbon fiber replacement in composites for lightweight vehicles. "Where we can make a difference is that we could save as much as 10% of the current fuel consumption in the US alone just by attacking the transportation market and replacing steel and aluminium," said John Gargasz, president of Nanocomp.

In the newly shaped landscape of CO_2 and CH_4 conversion, the approaches that are currently being researched face big challenges and exciting opportunities. Which one(s) will manage to sequester CO_2 or avoid its production, and provide high-value carbon materials, while at the same time achieving cost-effective scale up of the process? "This is a very big problem, and I believe at the end, there is no one-answer-fits-all solution," said Dairanieh. It seems, however, that joint efforts in the field will certainly accelerate the road to success. □