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MATERIALS FOR A LOW CARBON FUTURE

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[T]his refined, minute, and quick-witted chemistry was "invented" two or three billion years ago by our silent sisters, the plants, which do not experiment, and do not discuss, and whose temperature is identical to that of the environment in which they live.

Primo Levi "Carbon" in *The Periodic Table*¹

5.1 Introduction

The world has changed since Primo Levi famously wrote his essay on the life of an atom of carbon, first published in 1975. Then, he could claim that "every element says something to someone", but that carbon was unique in that it says "everything to everyone",² and, therefore, lacks the specificity of other elements. Now, this otherwise mundane element has become highly specific in common usage, synonymous with climate change, in a way that is hard to imagine being the case for any other atom.

It is instructive, however, to recognise that the significance of the concept of the carbon cycle has led to a similar recognition of the need for material sustainability in the use of other elements. The nitrogen cycle relies on atmospheric nitrogen being fixed by plants. In the last century, it has been disrupted to the extent that now, half of the food grown on Earth relies on the synthesis of ammonia from nitrogen. While nitrogen is abundant enough in the atmosphere that this seems unproblematic, the overuse of nitrogen in farming has become an issue of real concern; less well known is that the chemical synthesis of ammonia accounts for two per cent of global energy use. Moreover, other fertilisers, such as those based on phosphorus, come from sources that are not inherently so sustainable.

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1 Primo Levi "Carbon" in *The Periodic Table* (Raymond Rosenthal (translator), Schocken Books, New York, 1984) 224 at 227.

2 Id, at 225.

It has gradually, therefore, become a central theme of modern materials science to consider our work as being about the smart use of natural resources, which might mean replacing the use of scarce elements with earth-abundant ones, or considering the whole life cycle of a material, from synthesis to disposal, as part of the research and development process. These considerations are particularly important in the context of negative emissions technologies, as we shall see, as the question arises: what should be done with the carbon, after it is captured?

The reduction of carbon emissions must be the central goal for efforts to avoid the worst scenarios of climate change. Much of what can and will be done comes down to behavioural change; it is also true, however, that materials science has a role to play in making some of the required economic and behavioural adjustments easier. In this chapter, as we discuss several current and emerging technologies, we wish to present these simply as options that materials science is able to place on the table, rather than as magic solutions that will permit society to continue with business as usual. All of the technologies on offer have a cost; so too, however, does all the carbon-costly technology that is in current usage.

In this chapter, we first address the reduction of emissions through provision of carbon-free energy, in the form of photovoltaic (PV) cells, a relatively mature materials science technology, but with further optimisation and development still to be expected. Secondly, we address the reduction of emissions that is possible through materials-based energy conservation. Here, energy may be saved through the use of advanced materials in energy hungry technologies, such as computing, where energy is both lost through the generation of heat, and then doubly wasted as it is used to keep computer servers from overheating as a consequence of this waste heat. Thirdly, we will look at the issue of carbon capture and storage. Here, the spotlight is on a range of porous materials that show promise in negative emissions technologies; notably, these extend beyond simple capture and storage, to the potential for productive repurposing of atmospheric carbon. As Levi said: "The number of atoms is so great that one could always be found whose story coincides with any capriciously invented story".³ Our role as materials scientists and nanotechnologists is merely to support the more useful pathways; to find ways of saying yes, to each carbon atom: take this pathway, here, this one.

5.2 Clean energy generation via solar PV cells

Solar PV cells unlock access to an energy source that is essentially unlimited on the scale of our needs; the amount of solar energy that reaches the surface of the Earth in one hour is equivalent to global energy used in an entire year. Even when considering that solar PV panels could only cover a small fraction of the surface of the Earth, the scale of available solar energy is immense. Accessing this energy through PV cells has been, and will increasingly be, a significant contribution of materials science towards a low emissions economy.

The total installed PV capacity now exceeds 400 gigawatts and produces roughly two per cent of global electricity. Until very recently, the growth in PV capacity for over 20 years has been

³ Id, at 232.

approximately exponential – doubling approximately every two years (Kabir et al, 2018).⁴ Behind this growing capacity is an exponentially decaying price; costing USD 76 per watt in 1977 (that is, USD 760,000 for a large 10 kilowatts home installation), silicon PV cells now cost a few dollars per watt.

First observed by Becquerel in 1839, the PV effect is the light-induced generation of an electrical voltage across the bandgap of a semiconductor. This bandgap describes a gap of energies that electrons cannot exist in the material, meaning electrons store electric potential when they are excited to the higher energy band. By attaching electrical contacts to this semiconductor layer, a current flows, thereby generating electrical power from the incident (solar) light (Figure 1).

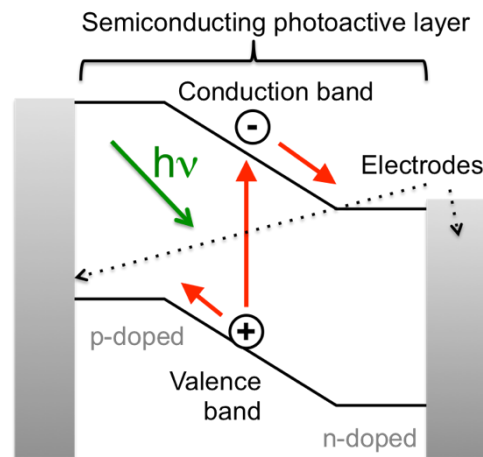


Figure 1: schematic illustration of a PV cell comprised of a semiconductor photoactive layer sandwiched between electrodes, where energy is the vertical axis.

5.2.1 Materials-driven growth of the PV industry

More than a century after this discovery, the first practical PV modules were manufactured by Bell Labs during the boom of the microelectronics industry in the 1950s. The pivotal role that materials science played in transforming that rudimentary device into the type of technology that can be installed on rooftops today is illustrated by the growth in materials diversity on which the silicon PV industry is built. Figure 2 shows the increasing utilisation of elements in silicon microelectronics industry over time. Whereas semiconducting silicon is the main constituent associated with solar PV panels, other elements and alloys are essential to optimising the PV function. For example, dopants are used to tune the energy levels inside the silicon layer and guide electrical current in the right direction. Additives are used to engineer the growth of large, pure crystals, with minimal defects at grain boundaries. Electrical contacts and interlayers are selected to extract current with minimal

⁴ See also International Energy Agency *Photovoltaic Power Systems Programme IEA-PVPS Annual Report 2017* (2018) at 21.

resistance, and with minimal shading of the active layer. Each of these material processing steps must be implemented with precision and at scale.

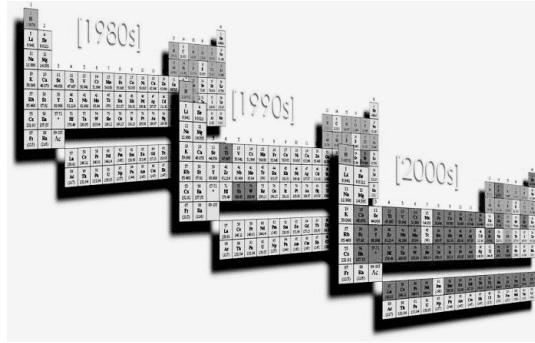


Figure 2: increasing utilisation of elements in the silicon microelectronics industry over time. Source: reproduced with permission from IBM Corporation.

The technical success of silicon PVs is tracked via their increasing power conversion efficiency over time (Figure 3). The efficiency of single junction polycrystalline silicon PV cells (comprising a single semiconductor layer) has approached saturation for the past two decades at around 26 per cent power conversion efficiency. This efficiency is approaching the thermodynamic limit of 31 per cent, the so-called Shockley-Queisser limit, which considers intrinsic losses through heat and transparency when a semiconductor is matched to the solar spectrum (Shockley and Queisser, 1961). The materials science and engineering of silicon PV cells was arguably near complete by the 1990s, and the 2000-fold surge in installed PV capacity since 1995 has been underpinned by falling prices as the scale of global PV manufacture has increased (Powell, Winkler, Goodrich and Buonassisi, 2013).

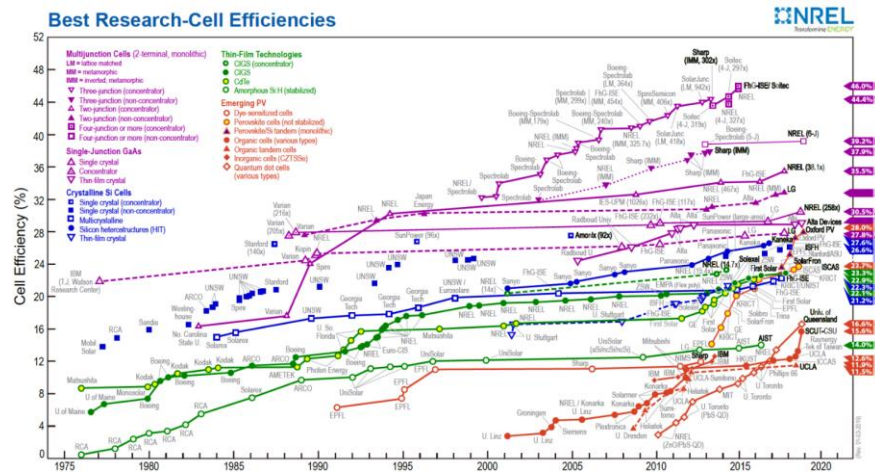


Figure 3: record-certified research PV cell efficiencies for different classes of PV cells over time. Source: reproduced with permission from the National Renewable Energy Laboratory of the United States of America.

Figure 3 also illustrates the remarkable rise of other classes of PV materials in recent years, including organic PVs (Brabec et al, 2010) and metal halide perovskites (MHP) (Stranks and Snaith, 2015). These emerging classes of PV materials offer numerous advantages over incumbent silicon technologies, and their development is even more dependent on materials discovery, design and development.

One important feature of both organic and MHP-based PVs is that they can be processed from solution at low temperature – the key benefit being that PV cells can then be printed roll-to-roll on lightweight, flexible substrates. In the future, when the optimum composition of these PV cells is settled and material production scaled up from current research levels to PV manufacturing levels, simple roll-to-roll production processes could substantially reduce the costs of PV technologies. Below, we describe some of the materials science that is rapidly boosting the efficiency of organic and perovskite PVs towards the Shockley-Queisser limit, and we highlight prospects for innovative materials that could circumvent this limit.

5.2.2 Printable organic PV cells

Organic PVs comprise organic molecules or polymers as semiconductors, rather than crystalline materials (Brabec et al, 2010). The optical and semiconducting properties of these materials are endowed by a so-called pi-conjugated structure – a pattern of alternating single- and double-chemical bonds. This pi-conjugated structure also governs the optical and electronic properties of natural organic compounds like those required for photosynthesis and vision.

In spite of possessing the requisite semiconducting properties to make PV cells, the function of organic PV cells is rather different to established inorganic silicon PV cells. One of the most consequential differences between organic and inorganic semiconductors is that the Coulomb attraction between photogenerated charge pairs is readily screened in inorganic semiconductors like silicon, allowing facile charge separation and photocurrent generation. On the other hand, light absorption in organic semiconductors leads to the formation of electrostatically bound charge pairs. This effect, along with the intrinsic disorder found in organic semiconductor films, means that organic semiconductors retain a strong molecular character that contrasts with the electronic band structure of their inorganic counterparts.

Overcoming the strong barrier towards charge separation in organic PV cells requires a mixture of at least two different materials in the active layer, as shown in Figure 4 (Yu et al, 1995). By matching materials with electronic energy levels to drive electrons into one phase and positively charged holes into the other, the Coulomb binding energy can be overcome to efficiently generate photocurrent. Understanding this key charge separation process has been a research priority in recent years in order to guide the design of better materials.

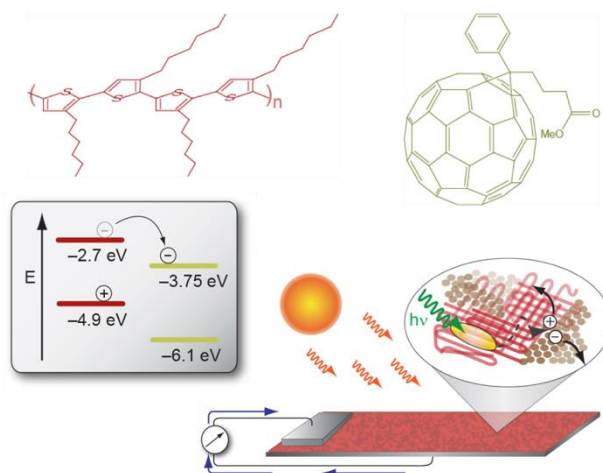


Figure 4: typical organic polymer (left) and fullerene (right) components of an organic PV cell, whereby the energy level offset drives interfacial charge separation in a nanostructured blend of the two.

The power conversion efficiency of organic PV cells has recently surged to over 15 per cent as a result of a global push to develop new active-layer materials. Until recently, soluble carbon fullerene derivatives (Figure 4) were the best performing electron acceptor materials in organic PVs.⁵ In spite of their weak optical absorption, carbon fullerenes perform well in organic PVs due to their excellent three-dimensional electron mobilities, and their ability to blend well with donor materials. Materials discovery and design focused largely on electron donor materials, and synthetic organic chemistry opens enormous possibilities of chemical structures with different optical absorption spectra, electronic conductivity, solubility, degree of structural order, mixing behaviour and stability – all critical parameters for organic PV cells. Understanding how to collectively optimize these parameters – even knowing what the optimum parameters are – has challenged the research community to work across research disciplines.

Understanding and controlling the nanostructured morphology of organic PV cells has been an important sub-discipline in the development of organic PV cells (Zhao, Wang and Zhan, 2018). The nanostructured donor-acceptor blend portrayed in Figure 4 is required to ensure that excitations created by light absorption are always close enough to reach a junction, while also ensuring that there is enough material in total to absorb all of the incident light. However, this morphology introduces a trade-off: if phase-separation is too fine-grained, charges do not flow freely and may recombine rather than being extracted from the active layer. On the other hand, too coarse phase separation reduces the probability that excitations will reach a charge-separating junction. The situation becomes more complex when considering that molecularly intermixed phases can also exist, and that molecular orientation can also be important. These factors have motivated significant research efforts to measure

⁵ Christoph J Brabec et al "Polymer–Fullerene Bulk-Heterojunction Solar Cells" (2010) 22(34) *Advanced Materials* 3839 at 3841.

the morphology of organic PV cells over different critical lengthscales, and also to control the resulting morphology. Some of the tools that materials scientists have developed to control morphology include adding different solubilising groups, employing solvent additives and using thermal annealing steps (Zhao, Wang and Zhan, 2018). The hundreds of publications that focus on a single material system alone is testament to the vast parameter space that materials scientists have explored (Dang, Hirsch and Wantz, 2011).

The field of organic PV cells has been buoyed by the recent emergence of non-fullerene electron acceptors, which now outperform fullerenes in record efficiency organic PV cells (Lin and Zhan, 2014). These new classes of molecular acceptors combine excellent electron mobility with strong optical absorption, and chemically tuneable energy levels. By tuning these parameters, materials scientists are discovering how to enhance the voltage, current and, ultimately, efficiency of this new sub-class of organic PV cells, stimulating rapid efficiency gains.

5.2.3 MHP PV cells

The search for solution-processable semiconductors with high PV power conversion efficiencies was considerably boosted with the discovery of MHP PV cells in 2012 (Lee et al, 2012; Stranks and Snaith, 2015). The active layer materials comprise metal halide (for instance, lead iodide) complexes and cations (for instance, methylammonium) that form a perovskite crystal structure (Figure 5) when deposited from solution, and they can now produce power conversion efficiencies over 23 per cent.

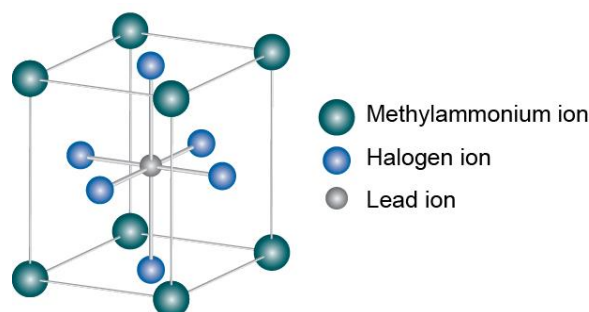


Figure 5: structure of the OMHP (CH_3NH_3) PbI_3 used in efficient PV devices.

Many of the same tools used to study organic PV cells have been applied to MHP PV cells in order to understand what makes them so efficient (Stranks and Snaith, 2015). They are a direct bandgap semiconductor, which means that only a thin layer is required to absorb all light. The bandgap of the most commonly used MHP materials is well matched to the solar spectrum, and is readily tuned by substituting the ions (for instance, using different halide ions, or mixtures thereof). Photoexcitation directly generates free charges, thus circumventing the charge separation problem that dominates organic PV cells, and the need for nanostructured junctions. Charges are long-lived and highly mobile, meaning that photocurrent is easily extracted before recombination occurs. The mobility of ions within MHP materials also appears to engender self-healing properties, meaning that defects are less detrimental to device function.

Aside from exploring the fascinating photophysical properties of MHP materials, significant research effort is now directed at understanding their stability (Niu, Guo and Wang, 2015). MHP-based PV cells generally suffer significantly poorer stability than organic PV devices, and early research efforts were plagued by hysteresis effects. As well as chemical degradation in the presence of moisture and oxygen, MHPs exhibit structural phase changes on account of the rotational freedom of methyl ammonium cations and migration of halide anions. The solution to this problem again appears to come from materials science, in the use of alloys of numerous anions and cations.

5.2.4 New paradigms for efficient PV cells

The Shockley-Queisser limit of around 30 per cent power conversion efficiency applies to single junction PV cells made from all classes of materials; photon energy absorbed above the bandgap is wasted as heat, and photons with lower energy than the bandgap are not absorbed at all (Shockley and Queisser, 1961). A frontier of PV materials research is in the development of materials that could circumvent this limit via two main approaches. One is to convert high energy photons into multiple lower energy excitations (Smith and Michl, 2010). In some organic materials with a particular electronic structure and packing arrangement, a photoexcitation can undergo a fission process that leaves a pair of excitations, each with half the original energy, on neighbouring molecules. When properly integrated into a PV cell, this means that high energy photons could produce twice the photocurrent that they otherwise would. The second approach to photon management is in "upconverting" multiple low energy photons into a photon with sufficiently high energy to be absorbed across the bandgap (Singh-Rachford and Castellano, 2010). Again, this idea does not violate conservation of energy because the energies of multiple photons are added together to give fewer higher energy photons. One implementation of this is through molecules whose photoexcited states can collide and react to produce higher energy excited states that emit higher energy photons. Materials scientists are developing design rules for both fission and upconversion, and creating materials with finely tuned energy levels, light absorption and emission spectra, and reaction kinetics.

In summary, solar PVs are already beginning to significantly impact global electricity production, and their importance as a carbon neutral energy supply will only continue to grow. Behind the evolution towards more efficient and lower cost solar PVs is a significant materials science effort, first in the development of industry standard silicon cells, and now in the rapid growth of a materially diverse set of next generation cells, including organic and MHP cells.

5.3 Energy conservation in computing and devices

One of the challenges in the public communication of the climate change crisis has been the essential invisibility of the key problem: human senses are not well-equipped to directly detect the relevant changes in atmospheric carbon. However, fossil fuels themselves are real and tangible, and the unpleasant emissions from a car exhaust are sufficient explanation of the basic problem for many people. Yet, the transition away from fossil fuel-based transport is one of the hardest forms of behavioural change that is needed: how much harder must the problem be, then, when the energy cost of a technology remains largely invisible?

This is the essential issue that underlies the importance of energy *conservation* in computing. The average consumer is aware of the energy that their mobile phone uses directly, of course, as their

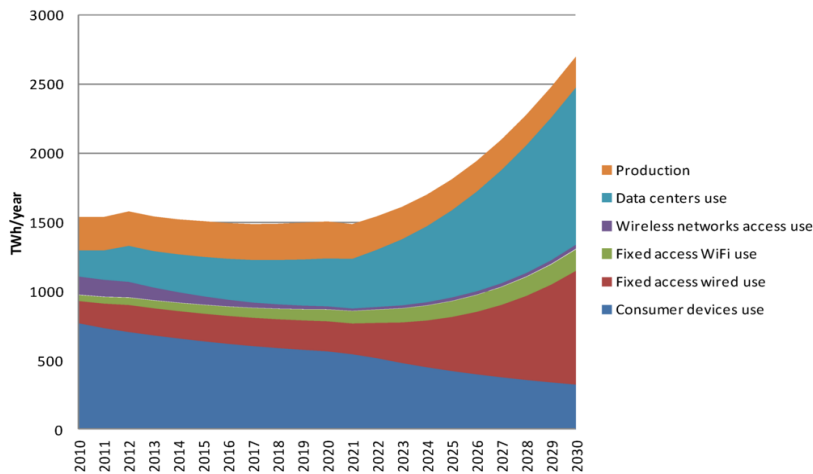
battery threatens to give out; very few have ever given any thought to the energy consumed by data servers on the other side of the world when they google the words "climate change". Nor when they use Facebook to organise an event to highlight climate change issues, nor when they store the photos from that event in the "cloud". Simply put: the cloud costs carbon.

Data centres use, as of 2018, around 200 terawatts (TWh) per year (Jones, 2018). The demand for data centre services is, of course, driven by the explosion of internet services, which are growing exponentially. This is, in some sense, the new Moore's Law, but one that is not so clearly bounded by an identifiable physical limit.

The carbon emissions from data centres alone sit at around 0.3 per cent of overall carbon emissions, but if the Information and Communications Technologies (ICT) ecosystem as a whole is taken into account (including personal digital devices), the value sits closer to two per cent. At this point, the carbon cost of computational technologies rivals that of air travel.

The comparison to the aviation industry is probably problematic enough to the average reader, but then again we have been told for a long time that aviation is an issue, and offsetting of carbon from flights is an idea that has had some, if limited, uptake from the public, with some associated behavioural change. A real concern around computing is that the invisibility of the carbon cost provides a real barrier to reduction through behavioural change, and some projections suggest that the ICT budget could grow to 20 per cent of global electricity use within not much more than a decade (Andrae and Edler, 2015). More optimistic projections reduce this to eight per cent, through enhanced energy efficiency of various parts of the system (Figure 6).

Best Case scenario CT electricity



(a)

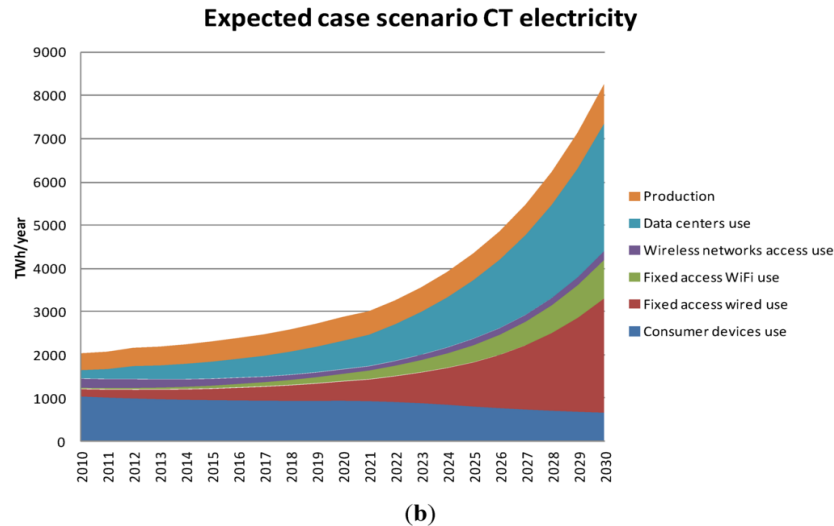


Figure 6: the expected growth in energy use by computing technology depends critically on technological advances to improve energy efficiency. Source: figure reproduced from Andrae and Edler, 2015 under a CCBY license.

5.3.1 Energy efficient computing paradigms

Novel materials that would enable computing paradigms that reduce energy usage, if realised in practical devices, include the following:

- *Superconductors.* Superconductors allow electrons to flow without the resistance that generates heat, a form of energy loss. This happens because electrons pair up – into so-called Cooper pairs – when a material becomes superconducting, at sufficiently low temperatures, and this pairing allows them to move without colliding within the superconductor. These collisions are what we normally refer to as resistance, which wastes energy (and produces heat). Superconducting computing components that are most promising include computer chips built from Josephson junctions, which consist of superconducting material separated by a very thin barrier that electrons can tunnel through. This creates the ability for current to be switched on and off, which is the basic ingredient necessary for information processing. However, all superconductors require very low temperatures, below a characteristic critical temperature for the material, in order to function, and there is an associated energy cost to cooling the material to such low temperatures.

- *Topological Insulators.* Topological insulators conduct electricity only along their surfaces and, therefore, a 2D topological insulator only conducts along its edges, and only in one direction, which eliminates resistance. The topological electronic state will not exist under all physical conditions; it can be switched on or off electrically, with a gate voltage, or even with the use of light.

- *Spintronic materials.* A spintronic material has an inherent magnetism due to the preferred orientation of the spin of some of its electrons. Instead of the electron charge needing to move through

the material to transfer information, the spin of the electron – its inherent magnetic dipole – can be used instead. This requires much lower energy input, as the spin can be transferred between electrons, much as a magnet can cause another magnet to rotate, without the electrons needing to move as far through the material. This relies on materials being found that have the necessary combination of semiconducting and magnetic properties; this can be achieved by using layers of semiconductors (for example, silicon) and magnetic metals (for example, iron), but also by designing new materials in which these properties co-exist (Granville et al, 2006). Spintronic materials also have some key advantages for memory storage – namely that the spin orientation is kept fixed when the computer is turned off, so no energy is needed to keep data in memory.

- *Neuromorphic computing.* A relatively new development, neuromorphic computing – or computers that "think like the brain" – use a range of different physical architectures of materials to process information. Instead of simple binary processing of zeroes and ones – whether by electron charge or spin – they process information in a more holistic way. The hardware varies, but requires a physical network consisting of many interacting parts – such as, for example, metal-based nanoparticles – which can be used to represent and optimize data. While this may not replace standard computational architectures for all problems, there are specific tasks – such as image recognition – that brains are more efficient at, as there is no efficient algebraic algorithm for finding the right answer. This is, of course, why images have long been used as CAPTCHA (Completely Automated Public Turing test to tell Computers and Humans Apart) to identify human users of computers.

- *Quantum computing.* A variety of material systems are being developed for use in quantum computing: the key difference is that instead of the bits – coded 0 or 1 – used in classical computing, they require qubits, that can be in states 0, 1, or a superposition, or combination of the two. The qubit (or quantum unit) can be based on some of the above material systems – for example, superconducting circuits consisting of Josephson junctions, or the spin state of an electron in a quantum dot (nanoparticle); so long as the coding is done by a particle that itself behaves quantum mechanically, it can in principle behave as a qubit. As in the case of neuromorphic computing, quantum computing has particular potential to reduce computational cost and associated energy requirements, when applied to problems that it is particularly well suited to solve. A relevant example is computational materials science itself: calculating the electronic structure of a material currently requires that the wave function that contains all information about the electrons be broken into many pieces to be processed independently, and then put back together again. A quantum computer would be able to create a representation of the wave function itself, and from this extract any necessary data much more directly.

Of the possibilities listed above, we will discuss in more detail here those that have the most direct impact on energy usage without the need for considerable cooling – namely those computing components based on spintronics, and topological devices. However, it is also worth noting that many of these technologies are not advancing in isolation from, or in competition with, the others: for example, the provision of superconducting circuits has significance as an enabling technology for some forms of quantum computing.

5.3.2 Spintronics

The field of spintronics has the potential to contribute to computing technologies in a variety of ways (Sinova and Žutić, 2012): from tunnelling magnetoresistance (TMR) and giant magnetoresistance (GMR) components for hard-drives, to magnetic random access memories (mRAM) and high density memory devices. The spin Hall effect, which makes the electrons in an electric current move in a way determined by their spin, has enabled the creation of spin field-effect transistors (FETs). Spintronics has also been integrated with silicon electronics, through the injection of electron spin into the traditionally used semiconductor: this has promise for the integration of spintronics with currently dominant technologies.

In Figure 7, the materials architectures underlying some of the simplest devices are presented.

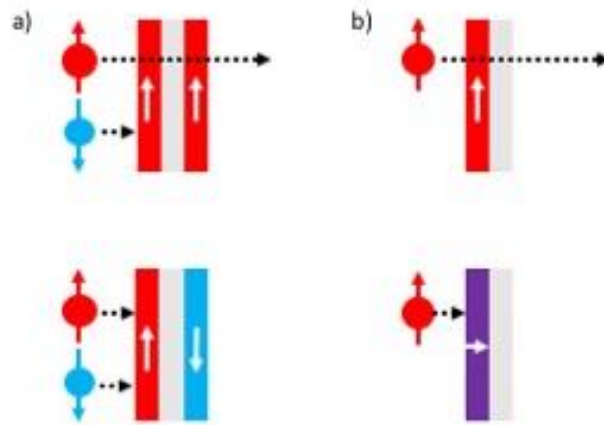


Figure 7: the alignment of electron spin within a device architecture has energetic consequences that allow for the processing, transmission and storage of information within computing hardware – (a) layers of ferromagnetic material, which can have a permanent magnetisation such as in a fridge magnet, can be placed either with their poles aligned (top) or in opposition (bottom); changing this alignment leads to a different flow of electrons of opposite spins; (b) Spin-orbit coupling, an effect that is important in heavy elements, makes it possible to align a single layer of material with the spin of electrons (top) or in a way that inhibits their flow (bottom).

Magnetoresistance – such as is created in the architectures shown in Figure 7, is what underlies the use of these materials in mRAM devices. The states are different when the magnetisation of the magnetic layers is changed; this provides a digital signal of "0" and "1" which is used to store information. The materials science challenge consists of finding materials that have a sufficiently high anisotropy, or resistance to switching orientation, so as to be stable under normal operating conditions – but not so high as to be difficult to switch at will.

5.3.3 Topological devices

Topological devices share considerable similarities with spintronics. The key difference is that the electrons are confined to the surface of a 3D material, or to the edge of a 2D material, as the

interior of the material remains insulating. This relies on a coupling of the electronic spin to the motion of the electron (spin-momentum locking), which means that these metallic surface states cannot be destroyed (unless, for example, a magnetic field is applied). Some of the excitement about the use of topological devices is due to the fact that materials with these properties have only been recently discovered: in 2007, for the 2D materials based on sandwiches of cadmium and mercury telluride (König et al, 2007); and in 2008, for 3D materials, in bismuth-antimony alloys (Hsieh et al, 2008). These materials are based on relatively heavy types of metals for the reason that these heavy atoms cause strong coupling of the spin of the electron to its momentum (spin-orbit coupling).

In summary, the discovery of new physics in new classes of materials has led to significant advances in computing technology over the last decades, beyond merely the increased computational power of an individual computer chip, to the development of smarter ways of computing, requiring new algorithmic paradigms which will be much more efficient for certain classes of computational problems. While these advances have been originally motivated by the concept of Moore's Law, that links increases in computational speed to reductions in chip size that are fundamentally limited by the number of atoms required to make the structures on a chip, it is increasingly recognised that computational efficiency is critical to reducing the carbon cost of our data hungry lives.

5.4 Negative emissions technologies: the role of materials science

There are two principal ways to reduce the levels of carbon dioxide in the atmosphere: lowering the release of new carbon dioxide; and capturing the gas that has been released historically. The latter process is termed the *negative emission* of carbon dioxide. It is much like a debt that needs to be repaid. We will discuss the need for negative emissions and the technologies that are available. The emphasis will be placed on the central role that fundamental research will play in developing sustainable porous materials for carbon dioxide capture.

Increasing levels of greenhouse gases in the atmosphere will result in a global temperature rise. The International Panel on Climate Change has projected the extent of this temperature rise based on various future greenhouse gas level. Even a temperature rise of 1.5 degrees Celsius above pre-industrial levels will require "rapid, far-reaching and unprecedented changes in all aspects of society".⁶

Mechanisms for pulling back on new carbon dioxide emissions are well established (Huisingh et al, 2015). Essentially, these hinge on reducing our combustion of coal, natural gas and petroleum. Reducing our reliance on these fossil fuels is likely to be a fairly gradual process, and the level of carbon dioxide in the atmosphere will continue to rise for the next several decades. This is because atmospheric carbon dioxide is long lived. It generally survives for around 50 years before it is consumed by photosynthesis, mixed into the ocean or destroyed by other processes. While cutting the emission of new carbon dioxide is essential, by itself it will not be sufficient to avoid dangerous temperature rises.

6 Intergovernmental Panel on Climate Change (IPCC) "Summary for Policymakers of IPCC Special Report on Global Warming of 1.5°C approved by governments" (press release, 8 October 2018) <<https://www.ipcc.ch>>.

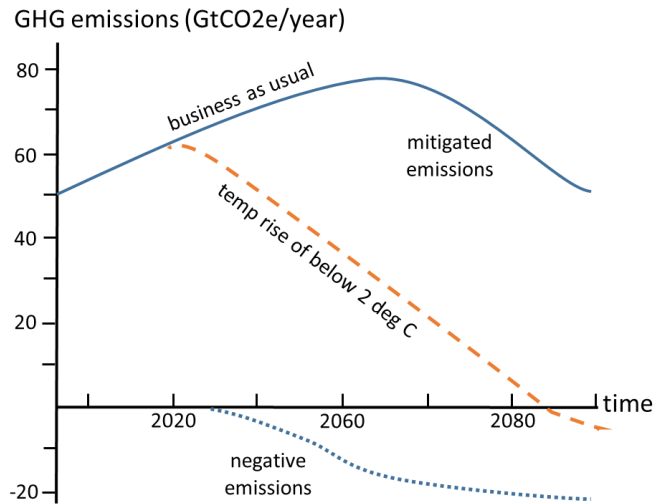


Figure 8: the central role of negative emissions in minimizing United Nations Environment Programme's projected temperature increases due to atmosphere greenhouse gases (GHGs). The y axis is in units of gigaton equivalents of carbon dioxide per year.

Negative emissions technologies must be deployed to augment the reduction of atmospheric carbon dioxide levels (Bui et al, 2018; Gasser et al, 2015). The Paris Agreement states that this should be carried out with haste: the large-scale capture of carbon dioxide should begin over the next decade.⁷ By 2050, an accumulated 40 billion tons of carbon dioxide will need to be extracted from the atmosphere. And to achieve net zero emissions, 20 billion tons will need to be captured annually.

These numbers are unfathomably vast. Do we have suitable technologies available to capture carbon dioxide on this scale? The simple answer is "No". Using current methods, we capture just 40 million tons of carbon dioxide per year. This needs to be scaled up a thousand-fold over the next decade. This will not be achievable simply by rolling out more of today's technology. We will need to develop new knowledge and processes, which in turn shall rest on advances made by fundamental research.

5.4.1 Strategies to capture carbon dioxide

Negative emissions technologies can be broken down into the following broad categories (Leung, Caramanna and Maroto-Valer, 2014; National Academies of Sciences, Engineering, and Medicine, 2018):

⁷ Paris Agreement 55 International Legal Materials 743 (adopted 12 December 2015, entered into force 4 November 2016), article 5. See Peter Christoff "The promissory note: COP 21 and the Paris Climate Agreement" (2016) 25(5) Environmental Politics 765.

- Blue carbon. Land use and management practices that increase the carbon stored in the open ocean or coastal ecosystems.
- Terrestrial carbon. Agricultural practices that enhance the storage of carbon dioxide in biological stocks such as woody biomass and soil, but is very land-intensive.
- Mineralization. Carbon dioxide is integrated into minerals, including mantle peridotite, basaltic lava, and to form limestone.
- Bioenergy with carbon capture and sequestration. Energy production in the form of electricity, liquid fuels and heat using plant biomass is combined with the capture of the emitted carbon dioxide (see next point), but is very land-intensive.
- Capture of carbon dioxide from point sources. Sequestration of carbon dioxide from streams where it is a significant component, such as flue gas, natural gas and geothermal vents.
- Capture of carbon dioxide directly from air.

The remainder of this discussion will focus on the latter two strategies for achieving negative emissions, with an emphasis on the role that fundamental research in materials science can play.

5.4.1.1 Point source carbon dioxide capture

A major benefit of point source carbon capture is that it allows for the interim use of fossil fuels while largely eliminating their emissions. This enables established industries to gradually transition to renewable energy sources while mitigating further adverse environmental impacts. The major users of this technology are coal- and gas-fired power plants, steel works, cement producers and natural gas providers, where it is often referred to as gas "sweetening".⁸ It is unsuitable for small-scale emissions involving liquid hydrocarbon fuels.

The conventional method for sequestering the carbon dioxide from point sources is to pass the gas streams through an aqueous solution of an amine such as ethanolamine. A chemical reaction takes place between the carbon dioxide and the amine. The reaction product remains in solution while the remaining components of the gas escape unimpeded. Upon saturation, the solution can no longer adsorb more carbon dioxide and it must be regenerated. This is an energy-intensive process since heating the solution, which is largely water, requires considerable thermal input. Moreover, the carbon dioxide is usually released into the atmosphere during this step. To achieve negative emissions, it should be captured and then stored or used (as discussed later). An additional drawback of amine solutions is their toxic and corrosive nature (Liang et al, 2015).

Solid adsorbents are alternatives to amine solutions. They operate by hosting the carbon dioxide in their networks of pores and channels (Oschatz and Antonietti, 2018). Since their interaction with the adsorbed carbon dioxide is relatively weak, they require minimal energy input in the regeneration step to drive the carbon dioxide out of their pores. Zeolites and activated carbons have traditionally

8 Mohammed Songolzadeh, Mansooreh Soleimani, Maryam T Ravanchi and Reza Songolzadeh "Carbon dioxide separation from flue gases: a technological review emphasizing reduction in greenhouse gas emissions" [2014] *The Scientific World Journal* 828131 at 25. See also Mohammed Songolzadeh, Maryam T Ravanchi and Mansooreh Soleimani "Carbon dioxide capture and storage: a general review on adsorbents" (2012) 6(10) *World Academy of Science, Engineering and Technology* 225.

dominated this area because they are inexpensive and available in bulk quantities. Membranes offer an alternative method of separating out the carbon dioxide while reducing the amount of material required to achieve an effective result. As outlined later, breakthroughs in materials science can underpin advances in this area to produce efficient and sustainable capture materials.

5.4.1.2 Direct air capture

Direct air capture is a process that sequesters carbon dioxide from ambient air and concentrates it in an adsorbent medium (Sanz-Perez et al, 2016). Once the adsorbent is saturated, the carbon dioxide is removed and the adsorbent recycled for a further round of capture (Figure 9). The concept of direct air capture was introduced in a formal way by Lackner in 1999 (Lackner, 2009). Initially deemed controversial, it is now seen as essential: negative emissions are baked into all climate change mitigation scenarios. Direct air capture is in an exciting phase from the viewpoint of materials science and technology. There are huge incentives, but large-scale operations are yet to be deployed.

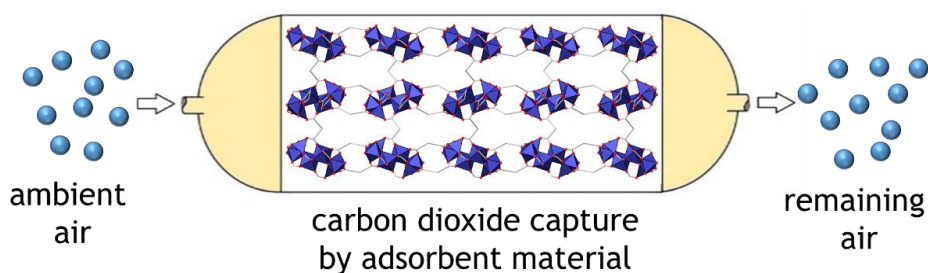


Figure 9: the direct capture of carbon dioxide by passing air through an adsorbent material that has a high affinity for carbon dioxide, but not the other components of air.

One of the biggest challenges that direct air capture faces is the low level of carbon dioxide in air. While it is too high for the global climate system, its concentration is 414 parts per million, which equates to 0.041 per cent. Just one out of every 2500 molecules in air is carbon dioxide, the remainder largely being nitrogen and oxygen. For direct air capture to be feasible, it, therefore, must be highly selective (Oschatz and Antonietti, 2018). The adsorbent must ignore the nitrogen and oxygen and bind only the carbon dioxide. Thankfully, this is feasible owing to the high reactivity and polarity of carbon dioxide relative to these other gases. It undergoes unique chemical reaction when bubbled through a solution containing an amine or other base. Or it can be more firmly caught in the pores of a solid adsorbent. The technical feasibility of scrubbing carbon dioxide from closed sources has been demonstrated in submarines and spaceships where it is employed to limit the build-up of carbon dioxide (Mattox, Knox and Bartot, 2013). As an interesting side-note, the rising levels of carbon dioxide onboard the crippled Apollo 13 spacecraft threatened the lives of the men on board until the lithium hydroxide filters designed for the command module could be adapted to the lunar module.

Commercially-available devices for the capture of carbon dioxide directly from air are emerging. Climeworks, a company based in Switzerland, offers a basic unit capable of capturing 135 kg of carbon dioxide per day (Bourzac, 2017). Multiple units can be run in parallel to eliminate five tons per day at an estimated cost of USD 600 per ton. Regeneration of the saturated adsorbent requires

temperatures of 100 degrees Celsius. This is a significant energy penalty and, naturally, the global analysis of the carbon-saving capabilities of these devices will be enhanced if they tap into renewable electricity sources. Renewable energy may also ameliorate concerns around devices that require the input air to be prepared or modified, for example by heating, cooling or pressurizing (all of which require energy).

5.4.2 The demand for new materials

The demand for technologies capable of capturing carbon dioxide from both point sources and directly from the atmosphere is compelling (Songolzadeh, Ravanchi and Soleimani, 2012). There is tremendous scope for fundamental research to identify and develop new ways of capturing carbon dioxide to discriminate it from other components in air in a sustainable way. Materials science will play a central role. Advances will come at the lab bench by designing, synthesizing and testing new porous materials. Ideally, these materials will be built up from earth-abundant and inexpensive precursors and they will be produced and recycled using energy-efficient protocols (Kumar et al, 2015).

Metal-organic frameworks (MOFs) feature prominently amongst the new generation of materials that will underpin advances in direct air capture (Furukawa, Cordova, O'Keefe and Yaghi, 2013). MOFs are crystalline porous materials that are built up using both metal and organic components. Unlike many other adsorbents, such as zeolites and silicas, the size, shape and chemical characteristics of their pores can be tuned by altering the building blocks. In this way, their affinity and selectivity for carbon dioxide can be optimized (Shalini et al, 2018; Sumida et al, 2012). A plethora of MOFs can be imagined, and the current challenge is translating structural blueprints into tangible materials. It is likely that fundamental research advances in this domain will produce adsorbents that meet the criteria for large-scale deployment at point sources or for atmospheric sequestration.

Looking ahead to the potential deployment of direct air capture, an ideal mass-produced device would be equivalent to a car in terms of weight and complexity and would capture one ton of carbon dioxide per day. Producing five million air capture units of this type could eliminate nearly two billion tons of carbon dioxide from the atmosphere per year. Given that more than 70 million cars are produced every year, deployment on this scale seems eminently achievable.

5.4.3 What to do with the captured carbon?

The negative emissions processes discussed thus far do not themselves convert the captured carbon dioxide into other compounds. Since carbon dioxide is a gas at room temperature, its direct release would see it enter the atmosphere and negate the negative emissions process. Storage of carbon dioxide in solid form, dry ice, is possible, but requires low temperatures (- 78 degrees Celsius), and, therefore, is not energy efficient. Moreover, to store 40 billion tons of carbon dioxide would require a storage reservoir equivalent to a mind-boggling 10 million Olympic-size swimming pools.

Using the captured carbon dioxide is difficult (Aresta, Dibenedetto and Angelini, 2014). Small quantities can be consumed in greenhouses, where it is converted to biomass by photosynthesis. It can be incorporated in polycarbonates, a family of tough polymers that are employed in the electronics

and construction industries. However, carbon dioxide used in these ways would rapidly saturate market demand.

The opportunity exists to initiate sequence of catch-convert-use (Figure 10). For example, if the captured carbon dioxide is converted to a liquid fuel such as methanol or gasoline, the fuels can then be used, releasing carbon dioxide which is subsequently captured to closed-cycle. This air-to-fuels cycle has numerous attractive features. Based in Squamish, British Columbia (Canada), Carbon Engineering captures carbon dioxide from air and, via calcium carbonate and calcium oxide intermediates, converts it to liquid fuels together with hydrogen from solar-powered water electrolysis (Keith, Holmes, Angelo and Heidel, 2018). Advances in fundamental research coupled with smart engineering are certain to further promote the efficiency of this process. Substantial recent investment in this firm by Chevron and BHP signals the perceived value of this approach.

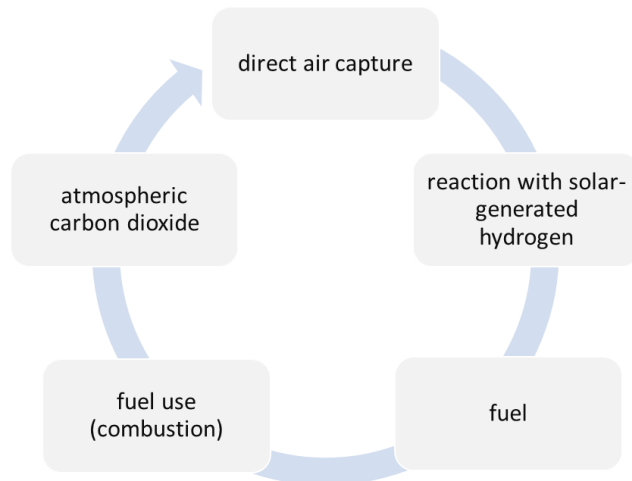


Figure 10: a closed loop involving direct air capture of carbon dioxide and its conversion to usable fuel.

In the context of research incentives, a broad group of benefactors is offering a USD 20 million prize, the so-called "Carbon XPRIZE", to the best new technology for converting carbon dioxide into valuable products and commodities. The finalists in this global competition present an insight into the activity and breadth of research in this domain, and include Breathe, an Indian enterprise that converts the carbon dioxide emitted from coal-fired power stations into methanol, and Carbon Cure, a Canadian company that converts carbon dioxide into advanced concrete products.

In addition to fuels, the conversion of the carbon dioxide to urea is another possibility. This occurs by the reaction with ammonia. Employing urea as a fertilizer results in its conversion back to carbon dioxide and ammonia, and capture of this carbon dioxide by direct air capture would close the cycle.

As an alternative to using the captured carbon dioxide, it can be permanently stored. One approach is to convert it to minerals such as calcium carbonate (limestone) or sequester it in peridotites. Alternatively, the carbon dioxide can be pumped into geological reservoirs that have been emptied, at least in part, by fossil fuel extraction. The injected carbon dioxide can lead to "enhanced oil

recovery", that is, recouping even more fossil fuels. This calls into question the sustainability of this solution. Nevertheless, it has been established that stable storage over long periods of time is possible while avoiding drawbacks such as the disturbance of underground sources of drinking water and the distances over which the carbon dioxide must be transported (Bui et al, 2018).

5.4.4 Pricing and timescales

A common refrain when discussing negative emission technologies is the question of how much it will cost to capture the carbon dioxide. The current benchmark for a process to be deemed economical is set at USD 100 per ton. Existing technologies for capturing flue gas meet this target and lie in the range of USD 30-100 per ton. The costs of direct air capture are highly debated, exacerbated by the absence of any commercial-scale deployments (Tollefson, 2018). The best guesses lie in the range of USD 60-1000 per ton, which is a wide range that will narrow as pilot-scale processes are initiated.

While the cost of carbon dioxide is a legitimate question, the current estimates do not include a price on carbon. They are simply generated using current taxation rates. However, it seems certain that governments will move to protocols whereby emitters shoulder their fair burden of costs, rather than externalizing them. This will raise the threshold for economical technologies, and allow those that draw on more expensive materials to become viable.

Significant costs are associated with new technologies such as fundamental research and prototyping, capital investment, energy for operating the process, including the need to regenerate the adsorbent, and maintenance. For point source capture, commercial enterprises will need to be convinced of the economic case of switching to new technologies so the overall profitability of their enterprises is not threatened. This economic case will be very sensitive to government policies. In the case of direct air capture, the lack of an established market may empower start-ups and newcomers with the commercial driver coming in the form of a high carbon price.

An interesting comparison can be made between the current state of carbon dioxide capture and the sequestration of sulfur dioxide and nitrogen oxides from the smokestacks of coal-fired power plants, which was implemented in the United States of America around 30 years ago. It has been noted that a timeframe of around 20 years was typically required to deliver a new process from the concept stage to commercial reality. Despite the clear environmental benefits, many processes were not commercially viable until a series of legislative measures were made (Joskow, Schmalensee and Bailey, 1998).

This is a common theme in the discussion of technological solutions to climate change. The science has been, and is still being, done, and the technologies are both available and continually improving. But implementation matters, and international experience to date has only reiterated the importance of the interplay between research advances, technological progress and the political measures needed to affect structural change. As Primo Levi suggested, the many possible pathways

for an atom of carbon have always existed – we just need to change our own behaviour to catch up with the plants, and their use of "refined, minute, and quick-witted"⁹ chemistry.

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