Functional materials impact every area of our lives, from electronic and computing devices to transportation and health. Here we examine the relationship between synthetic discoveries and the scientific breakthroughs that they have enabled. By tracing the development of some important examples, we explore how and why the materials were initially synthesized and how their utility was subsequently recognized. Three common pathways to materials breakthroughs are identified. In a small number of cases, such as the aluminosilicate zeolite catalyst ZSM-5, an important advance is made by using design principles based on earlier work. There are also rare cases of breakthroughs that are serendipitous, such as the buckyball and Teflon. Most commonly, however, the breakthrough repurposes a compound that is already known and was often made out of curiosity or for a different application. Typically, the synthetic discovery precedes the discovery of functionality by many decades; key examples include conducting polymers, topological insulators and electrodes for lithium-ion batteries.

Our examples include unsung heroes such as the aluminosilicate zeolite catalysts, which play crucial roles in the chemical and petrochemical industries, among others, but have never attracted major recognition in terms of awards such as Nobel prizes. By contrast, high-profile discoveries such as the high-temperature cuprate superconductors and the buckyball, $C_{60}$, have been honoured with Nobel prizes but have not yet had the technological impact that was initially anticipated. This is not very surprising, because important scientific discoveries do not necessarily lead directly to commercial applications. Nevertheless, in their different ways, all of these different types of breakthrough have a major influence on science and the scientific community. Figure 1 illustrates some diverse examples of chemical compounds, both molecular and extended solids, that have had a technological impact following their original synthesis in the laboratory. Each of these cases will be discussed in more detail below.

We have identified three common pathways to technological breakthroughs based on the synthesis of novel compositions of matter. At one end of the spectrum there are materials that were made as a consequence of design principles established from earlier successes and a well-defined material need. A substantial fraction of materials discovery is conducted in this way, following the mandates of funding bodies that prescribe specific missions and goals. However, we find that very few major breakthroughs are made in this manner, although incremental advances can lead to important practical applications. At the other end of the spectrum are compounds that were discovered serendipitously by scientists who were looking for something entirely different, but who had the vision to realize the implications of their unexpected findings. In between, there are compounds that have sat on the shelf for many years until their functionality and commercial potential were finally recognized. We discuss examples of each pathway, and the timelines of some important cases are illustrated in Fig. 2. We also explore developments in data mining and artificial intelligence (AI) for the enabling of materials discovery and discuss whether high-throughput computational approaches, coupled with high-throughput synthesis and AI methods, will eventually replace the role of chemical intuition and exploratory synthesis.

Materials discoveries using design principles

In practice, novel and exciting compositions of matter are rarely found by using design principles developed earlier, although large numbers of incremental advances—some very important—have been made in this way. Aluminosilicate zeolites provide some interesting examples, including the eye-catching case of zeolite ZSM-5, an entirely new polymorph of $\text{Al}_2\text{Si}_x\text{O}_{2x+2}$ ($A$ is typically a univalent metal cation or a proton). ZSM-5 was synthesized using an amine-template methodology that was widely adopted in the zeolite community. By using a rather large quaternary amine cation—tetrapropylammonium—a group at Mobil made not only a new zeolite architecture (Fig. 1a), but a material with a much higher Si/Al ratio than typical zeolites. This higher Si/Al ratio led to enhanced thermal and chemical stability, as a consequence of which ZSM-5 has found widespread commercial use as an acid catalyst for high-temperature processes such as xylene isomerization and hydrocarbon cracking. Another landmark discovery in the porous materials area was the synthesis of the first nanoporous polymorphs of $\text{AlPO}_4$, which exploited the known relationship between the structures of $\text{SiO}_2$ and berlinite ($\text{AlPO}_4$), while again adopting the amine-template strategy. This templating strategy is still used today to create zeolitic architectures and chemistries, such as the germanosilicate ITQ-56. In a closely related, game-changing discovery,
serendipitous by its discoverer, Roy Plunkett. A group of chemists and chemical engineers at the DuPont Company were working on chlorofluorocarbon refrigerant gases in the 1930s. These gases were mostly based on single-carbon-atom molecules, but Plunkett was working on more complex two-carbon-atom molecules derived from tetrafluoroethylene (TFE). He prepared a large amount of TFE and stored it in a metal gas cylinder to be converted at a later date to a chlorofluorocarbon. Months later, when Plunkett needed some TFE for the synthesis of these gases, there was no gas pressure in the cylinder, yet it did not lose any weight. To see what had happened, he and his co-worker cut the cylinder open and discovered that the inside contained a white, waxy solid that was insoluble in all common solvents and inert to most chemicals. Plunkett concluded that the gas had polymerized completely on the metal surface of the cylinder. Although there are refrigerants based on chlorotrifluoroethylene, there appear to be no commercial refrigerants based on TFE.

The discovery of the buckyball, C_{60}, followed a series of earlier ideas and observations that, with the knowledge of hindsight, might have led to its characterization before the famous 1985 experiment that resulted in the 1996 Nobel Prize in Chemistry for Curl, Kroto and Smalley. For example, the concept of hollow carbon molecules had been suggested by David Jones (a.k.a. Daedalus) in the New Scientist in 1966 and there were theoretical studies that predicted a stable, aromatic cage of 60 carbon atoms in 1970. In addition, work by Kaldor and his colleagues at Exxon in 1984 on the carbon soots that build up on hydrocarbon cracking catalysts revealed a large number of clusters with even numbers of carbon atoms between approximately C_{40} and C_{100} (ref. 16). C_{60} did not attract attention as being special, although its mass spectrometry signature was ~20% stronger than the neighbouring clusters. The pre-eminence of C_{60} among the many clusters that had been observed by Kaldor was first recognized by Curl, Kroto, Smalley and their co-workers in a search for medium-sized carbon molecules that might be found in interstellar space.

The experimental conditions in their graphite vaporization chamber, before detection by mass spectrometry, enabled them to obtain a more quantitative distribution of carbon clusters in which C_{60} (and to a lesser extent C_{70}) was dominant. The subsequent development of a synthesis that yielded a bulk solid product enabled a wide range of exciting developments, such as the preparation of superconducting fullerides. Even more importantly, the discovery of C_{60} arguably led to the nanotechnology revolution and the discoveries of other nanoscale carbons, particularly carbon nanotubes and graphene. In an interesting recent twist to this story, it has now been confirmed spectroscopically that C_{60} is actually present in space, where it contributes to the fine structure of the diffuse interstellar bands.
Perspective Nature Synthesis

The majority of breakthroughs in materials science involve the application of compounds that were already known and had either been initially synthesized out of curiosity or were repurposed for a new application. Here we discuss some important examples, both inorganic and organic, with their timelines (Fig. 2).

Delayed impact of known compounds

The breakthroughs in materials science involve the application of compounds that were already known and had either been initially synthesized out of curiosity or were repurposed for a new application. Here we discuss some important examples, both inorganic and organic, with their timelines (Fig. 2).

Polyacetylene. Although it was initially observed as a highly cross-linked black powder called cuprene by Berthelot in 1866, polyacetylene (CH) was first synthesized by a known polymer synthetic method by Natta in the 1950s. He obtained a pure, linear crystalline polymer that resulted in an unusual organic photovoltaic. However, C60 is only sparingly soluble in organic solvents, so a solution to this problem was found with the discovery of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, Fig. 1b), a derivative that is more soluble.

Its doping into MEH-PPV produced a much higher photovoltaic efficiency and the discovery of the bulk heterojunction phenomenon that is ubiquitous in organic photovoltaics. Conducting polymers continue to find applications in diverse areas, most recently in thermoelectrics and wearables.

(1860 1880 1900 1920 1940 1960 1980 2000 2020)

Fig. 2 | Timelines for some important functional materials with delayed impact. The left-hand extreme of each line (in brown) shows the year of the original synthesis, and the year in which the discovery of functionality was published is shown by a green bulb. The references for the original synthesis and discovery of materials functionality are provided in the Supplementary Information. For the cases that resulted in a Nobel Prize, the year of the prize is indicated by a red laurel. Ongoing work following the key discovery is shown by blue dots. Such ongoing work is often incremental, but in some cases it results in significant optimizations and commercial applications.
coordinated with iodides. Nevertheless, the field of hybrid halide perovskites is still thriving 44 years after the initial discovery of (MA)PbI₃, and many more exciting developments are anticipated.

Topological quantum materials. Materials have long been understood on the basis of the symmetries they display. Transitions between different material phases—a paramagnet to a ferromagnet, or a metal to a superconductor as examples—are understood in terms of certain symmetries being broken. For example, the continuous symmetry of spins in the paramagnetic state, associated with their being able to point in any direction of the crystal, is broken when the crystal becomes ferromagnetic upon cooling and the spins are obliged to take in specific (lower symmetry) arrangements. The 2016 Nobel Prize in Physics, awarded to Thouless, Haldane and Kosterlitz, recognized that—beyond symmetry, topology can play a role in our understanding of materials and their properties. Several features of materials, for example, the manner in which electronic energy bands cross one another or the manner in which collections of spins assemble into complex textures, can be associated with topological indices. In topological quantum materials, the indices calculated on the inside of the crystal may not correspond with the indices calculated for a vacuum. This sudden change of the topological index at the interface between the crystal and the vacuum can give rise to surface states associated with the crystal being ‘cut’, by analogy with the need to cut a doughnut (topological index: genus = 1 for the single hole) to transform it into a doughball (genus = 0 for the absence of a hole).

The prediction of the existence of materials with so-called Z₂ topological order led to the realization that certain valence-precise semiconductors with high-atomic-number elements (a prerequisite for strong spin–orbit coupling) could display the characteristics of a topological insulator, with a bulk semiconducting gap, but with spin-polarized conducting states at the surface. Some obvious materials choices, with the added benefit of being layered and cleaving readily (important for surface science studies), are the Bi₂Te₃ chalcogenides, such as Bi₂Te₃ (Fig. 1d). The structure of Bi₂Te₃, today a well-known thermoelectric material, has been known since 1939, and the existence of Bi₂Te₃ compounds with the ratio 2:3 since at least 1905. An examination of the band structure of these compounds confirmed the existence of the requisite surface states in insulating Bi₂Te₃, establishing it to be a topological insulator.

Following hot on the heels of topological insulators came the prediction and realization of Weyl semimetals. Crystals that host Weyl fermions are characterized by arcs connecting Weyl points on the Fermi surface. Weyl fermions have long been known as massless quasiparticles that could arise from solutions to the relativistic Dirac equation, but their experimental realization has been elusive. The compound TaAs, which crystallizes in the I₄/̅md space group and lacks inversion symmetry, was structurally characterized in 1963. An examination of its electronic structure indeed suggested the features expected for a Weyl semimetal, and this has since been experimentally verified.

Lithium cobalt oxide. Lithium cobalt oxide, Li₃Co₂O₂, was first prepared in the 1950s at the Westinghouse Research Laboratories in Pittsburg PA at a time when there was general interest in layered structures of the transition metals of general formula LiₓMₓ₋ₓO₂, M = Mn, Ni, Cu. The primary focus of the Li₃Co₂O₂ study, aside from establishing the composition range and crystal structure, was to understand the role played by changing the ratios of Co²⁺ and Co³⁺ in determining the magnetic properties. It was found that the structure was cubic in the range 0 < x < 0.2, like CoO₂, but rhombohedral and layered at x = 0.5, that is, LiCoO₂ (Fig. 1e). More than 20 years later and shortly after the first demonstration of using a reversible lithium insertion compound, Li[TiS₂, as the cathode in a rechargeable battery, Goodenough and colleagues (at Oxford) selected LiCoO₂ as the cathode for their oxide-based lithium-ion battery (LIB). The choice of oxides was made on the basis that the oxide would give a higher cell voltage and better stability, and the composition of their cathode was initially believed to range reversibly between x = 0.067 and 1.0 in LiₓCoO₂ within a single non-stoichiometric phase. This classical material, and its derivative discussed below, subsequently became the cathode of choice for future LIBs.

One of the attractions of LiₓCoO₂ is that the lithium and cobalt cations are ordered within alternating layers of the crystal structure, (Fig. 1e), which facilitates relatively short Co–Co distances that enable good electronic conductivity, an important requirement for battery electrodes. In fact, it has been shown that LiₓCoO₂ becomes metallic on charging. It also has a high operating voltage of ~4 V owing to the highly oxidizing nature of Co⁴⁺. In addition, because the as-synthesized cathode contains lithium, it can be paired with a graphite anode rather than a lithium metal one. Nevertheless, Li₃CoO₂ is not as reversible as the 1980 paper had believed, because oxygen gas is evolved when the cathode is repeatedly charged beyond ~Li₁.₃CoO₂ due to the overlap between the Co⁴⁺ d levels and the top of the O²⁻ 2p band. This reduces its practical capacity to ~140 mA h g⁻¹. In addition, because cobalt is relatively expensive and its availability from mines in the Democratic Republic of the Congo has been hampered by geopolitical issues, alternative LiₓMO₂ (M = 3d transition metal) phases with the same crystal structure as Li₃CoO₂ have been intensively studied over the past two decades. However, no other single element can approach the performance of cobalt in LiₓCoO₂, so most of the recent focus has been on the complex system LiₓNi₁₋ₓ₋ₓMnₓCoₓO₂ (known as NMC), especially on compositions that are low in cobalt. The optimal composition is a balance between five factors: chemical stability, structural stability, electrical conductivity, elemental abundance and environmental friendliness, as discussed in a recent review by Manthiram. The general trend is to reduce the cobalt content of the cathode while increasing the nickel content, thereby lowering the cost while increasing the capacity towards 300 mA h g⁻¹ (ref. 43).

In addition to the extensive work on the layered transition metal oxides, substantial progress is also being made on other classes of cathodes for LIBs, especially those based on spinels and polyanion oxides such as LiₓFePO₄ (ref. 45). By contrast, there has been relatively little progress in the area of alternatives to the widely used graphite anodes. Recently, however, TiNbO₇ (Fig. 1f) has emerged as a new anode for fast-charging LIBs. This interesting material presents another striking example of repurposing a compound that has been known for many decades. In this instance, TiNbO₇ was first identified at the Batelle Research Institute in the early 1950s for possible applications in the nuclear industry, and the TiO₂–Nb₂O₅ phase diagram was reported shortly afterwards. However, the use of TiNbO₇ as an anode in LIBs was not recognized until almost 60 years later.

The role of high-throughput synthesis, data and AI

The history of high-throughput or combinatorial synthesis in materials science began in the 1990s, with efforts at companies such as Symyx in California and HTE in Germany, as well as in academia. There were some early publications in the area, but there has not been a great deal of visible impact in terms of new materials. One notable exception is the discovery of metal–organic frameworks (MOFs), which were optimized for CO₂ capture by working within a well-defined family of candidates in 9,600 organic frameworks (MOFs), which were optimized for CO₂ capture by working within a well-defined family of candidates in 9,600 microreactions. More recently the area has been re-energized by its integration with exciting developments in computational materials science, as discussed below.

It is interesting to consider the increasing dual role that AI and machine learning (ML), combined with data mining, play in materials discovery. First are the contributions to materials synthesis.
In the world of organic chemistry, the combination of tractable (and transferable) valence rules associated with carbon and the lighter main group elements, coupled with the ability to carry out systematic and stepwise bond breaking and making, has allowed much of organic synthesis to be formalized. Since the 1960s, this has led to the development of computer-aided synthesis including, increasingly, the use of AI and ML methods.

Extended inorganic compounds, in contrast, are based on the entirety of the periodic table and usually form thermodynamic products, rather than kinetic products. Consequently, predictive, controllable synthesis has evolved more slowly. Recently, the use of AI and ML methods based on full text learning of the literature has identified synthetic conditions, usually for known materials, with the potential to extend to unknown materials. An unusual approach called the ‘Dark Reaction Project’, based on learning from successes (as is typically embodied in the laboratory notebooks) to arrive at the conditions that would be most likely to yield synthesis products, albeit within a restricted chemical parameter space. The most common use of prediction employs high-throughput quantum-mechanical calculations of formation energies to predict potentially stable compounds that have not been reported previously. Such studies do not usually prescribe a synthesis procedure. One of the challenges of these approaches relates to dealing with metastability, and the fact that many materials require kinetic trapping. Nevertheless, advances in the computational understanding of the pathways to metastable materials are indeed being made. In terms of thermodynamic products, an early attempt predicted stable four-element alloys. More recently, computation energetics have been employed in conjunction with ML methods, as exemplified by the prediction of unreported ternary oxides with the general composition \( A_B_2O \) (ref. 7). An increasingly popular approach is to focus on specific structural classes of materials, such as the Heusler compounds, that are known to display a rich range of properties, to learn from known compounds so as to extrapolate to the as yet unknown. We see great potential in such approaches, particularly when combined with high-throughput synthesis using mobile robots.

These computational approaches to new materials require large and searchable databases of known compounds. The databases have, in turn, been populated through data mining in chemical parameter space by generations of researchers. The origins of structural databases can be traced to the work of Bernal and Kennard, and the founding of the Cambridge Crystallography Data Centre, which inspired the Inorganic Crystal Structure Database (ICSD). There is also a dedicated database of experimental MOF structures. When the structures and compositions of such databases are fed into a high-throughput computational framework to obtain electronic structures and materials properties, ensuing databases, exemplified by the Materials Project, have become essential components in aiding the screening of materials for interesting functional properties.

Outlook

Over the past 150 years, synthetic chemists have built a repository of compositions and crystal structures that now run into the hundreds of thousands. Materials scientists have access to this vast body of information and can explore it in the search for novel functionalities. At the same time, computational tools enable us to interrogate these compounds automatically and to predict their properties. It is reasonable to ask whether we already have enough compositions and structures. Is there a need to synthesize more? We would argue, on the contrary, that it remains essential to continue adding to this chemical repository to give ever more options to those who will search for the next generation of functional materials. There is typically a lag of many decades between the initial synthetic discovery and the subsequent applications. We offer the following general conclusions:

- Many of the most important materials advances involve compounds that were originally synthesized out of curiosity or for entirely different applications. It is important that chemists should continue to contribute to the chemical repository for the benefit of future generations of materials scientists.
- Digital resources that are readily searchable, such as the Inorganic Crystal Structure and the Cambridge Crystallography Data Centre databases, will continue to play key roles, both for experimental and computational materials scientists who are seeking new functionalities.
- Data-driven materials discovery using AI/ML techniques will make increasingly important contributions, but their success will be enhanced by expanding the current databases with new compositions of matter and crystal structures.
- Funding agencies need to recognize that curiosity-driven synthetic chemistry will be essential for the discovery of next-generation functional materials.

Finally, it is interesting to explore whether we can already see the beginnings of new materials applications among the novel compounds that have been reported more recently, or among compounds that have been known for many years but are currently attracting a lot of renewed attention. We do not have a crystal ball, but we do see exciting potential in several areas. In the field of quantum materials, the recently discovered Kagome structure, \( CsV_2Sb_6 \) (ref. 1), is already showing exciting promise as a Z_2 topological metal with a superconducting ground state. In the area of halide perovskite photovoltaics, the compound \( (NH_4)Bi_2I_9 \), which was proposed recently as a materials candidate for lead-free photovoltaics, is reported to have outstanding potential for highly sensitive X-ray detection. Furthermore, in terms of well-established materials seeing a new lease of life, we note that the NaSICON materials, which were first reported in 1968, are now receiving a lot of attention in relation to the development of solid-state sodium ion batteries.
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