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Chapter 8

Nanocarbons

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Graphite and diamond have been used since prehistory, long before they were recognized as two *allotropes* of elemental carbon [1 pp. 39–61]. From *allos*, ‘other’ + *tropos* ‘manner’, ‘way’ or ‘mode’, allotropy refers to the ability of an element to form different simple bodies made up of the same atoms bounded together in various specific ways. Of all elements, carbon is the champion of allotropy. At the threshold of bulk matter, the nanometer scale,¹ carbon affords many more allotropes than its two worldly macroscopic forms graphite and diamond. The recent avatars of good old carbon have so unexpected behaviors that they figure out as star materials worthy of heavy Research and Development investments. Since 2000 they have generated great expectations in all technological sectors. As a few of them enter in industrial production, they are exemplars of the economy of promises attached to new materials.

1. A Zoo of Exotic Structures

The spherical structure of fullerene² came to be known in the 1980s as the “third carbon allotrope” [2,3]. “Buckyballs” generated renewed interest in two other carbon allotropes, nanotubes and graphene, that had been repeatedly observed and described long before they were ‘discovered’ in the 1990s and 2000s, respectively.

Fullerenes, nanotubes and graphene are the most iconic carbon nanomaterials, because of their typical ‘low-dimensional’ geometries. However, they came along with a whole menagerie of other exotic nanocarbons, characterized by electron microscopy, diffraction, mass or X-ray spectroscopy. To mention only a few: nanocones, fullerene pipes, nanohorns, nanofoam, nanotori, nanoscrolls, nano-onions, nanobuds, nanoribbons, and even nanobamboos (Figure 1). This large family thrives on carbon’s ability to form a wide variety of two-dimensional sheet structures that can loop back on themselves, bend, fold or twist in many different ways, each one affording specific properties. The number of different nanocarbons can reasonably be considered indefinite. Assuming that low-dimensions underpin at least partially higher-ones, such unlimited form-generative potential bears something of a world-forming character.

¹ One billionth of a meter.

² Named after the visionary architect Buckminster Fuller, famous for his geodesic domes.

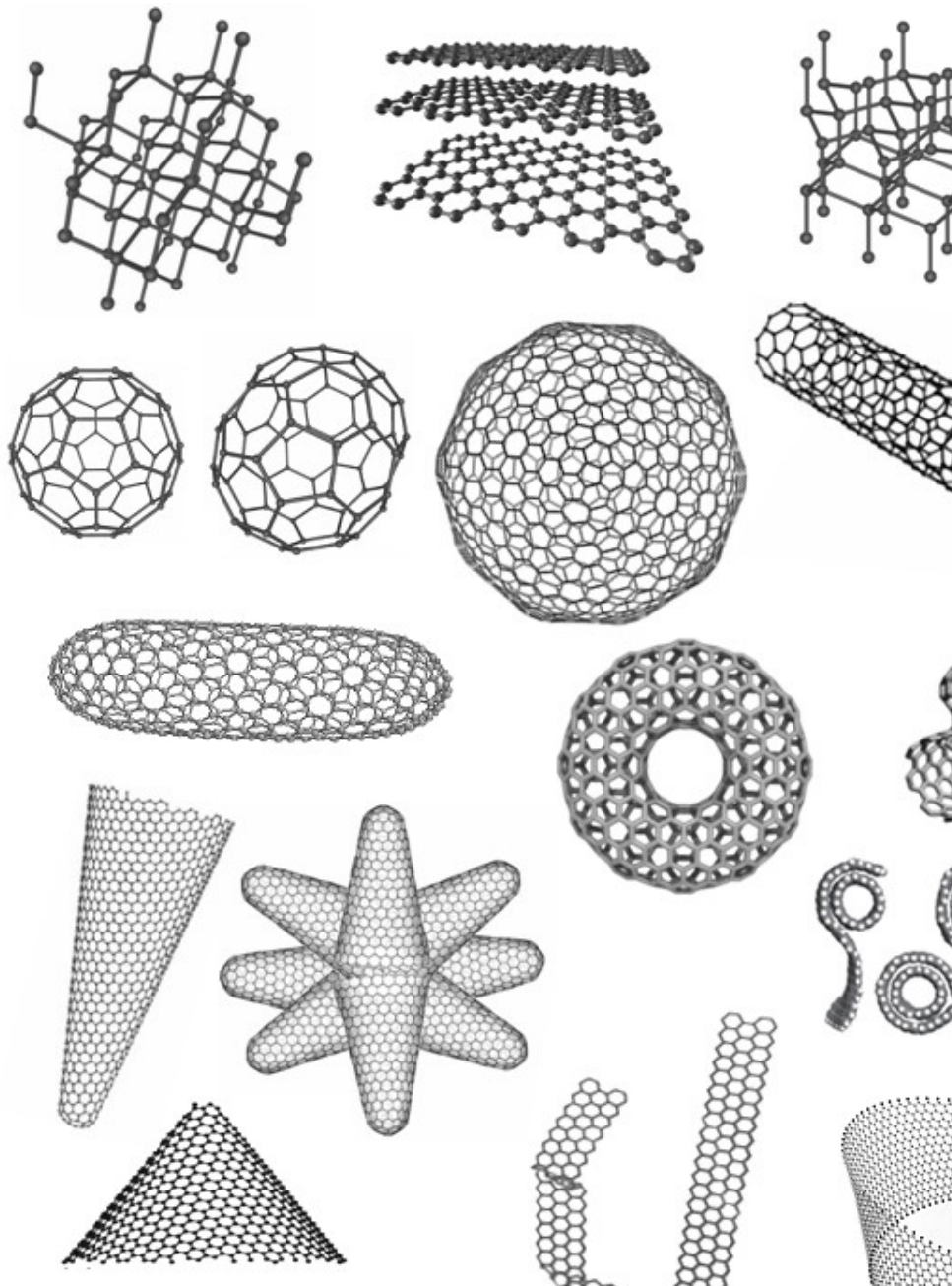


Figure 1. A collection of carbon allotropes. From top left: diamond, graphite, lonsdaleite (hexagonal diamond), amorphous carbon, fullerenes C_{60} , C_{70} , C_{960} , single and multi-walled carbon nanotubes, nanosausage, nanotori, nanobuds, nanohorns, nanoscrolls, carbon onion, nanocone, nanoribbon, Möbius carbon ribbon, nanofoam, carbon bamboos, fullerene pipes. Bottom: graphene, the mother structure of all hexagonal nanocarbons. Picture by the author (objects not on scale).

2. Welcome to the Nanoworld

At the nanometer scale, carbon seems to open up a parallel world, the ‘nanoworld.’ Invisible to the naked eye, the nanoworld is nevertheless amply visible in popular media and science policy as it is saturated by promises. Nanocarbons are showcased as a cornucopia of futuristic products: ultra-fast computers, ultra-thin sensors, touch-screens, pollutant-capture devices, targeted drug delivery carriers, not to mention a space elevator with a giant cable made of braided carbon nanotubes! [4] As Richard Smalley, the co-discoverer of fullerenes, once declared, “These nanotubes are so beautiful that they must be useful for something.”

The variety of potential nanocarbons depends not only on structural configurations (electron orbitals) but also on the process of synthesis (combustion, carbonization, graphitization, laser ablation, catalytic growth ...).

Nanocarbons have changed the perspective on the old and familiar element carbon. The hero of the thermo-industrial revolution was still soaked in black with soot. The heroes of the nanoworld are pure surfaces, light, immaculate, geometric, with elegant structures not dissimilar to those generated in origami-kirigami games. How could a material so common, used and overused by heavy industries, reveal such surprises? Nanocarbons have given new life and visibility to carbon chemistry. It is neither entirely organic nor inorganic chemistry, as nanocarbons are neither organic molecules nor crystalline solids. These new kind of objects—carbon nanomaterials—have interconnected and reorganized entire research fields, henceforth labelled ‘nano’(-science, -technology, -engineering ...). Like a phoenix, carbon was born again from its own ashes, embarking on new technological adventures.

The lifestory of nanocarbons could be told from different perspectives, depending on the people and contexts the biographer focuses on. Smalley’s story of the discovery of fullerenes for example, is very different from the one told by his co-discoverer Harold Kroto. The latter tells a story of dreamy and disinterested science, which begins by deciphering the sky, when the former insists on real-world problems and technological applications [5]. Carbon binds these stories together and could afford many others.

Another striking feature of the large family of nanocarbons is that there is no competition between them on the market. Rather they support each other: fullerenes helped to make nanotubes visible, which prompted a new interest in graphite, that led to the graphene. “The only character of true genius in the story is carbon,” Smalley noted [3].

Without entering into the priority disputes raised by the discovery of carbon nanotubes [6], I will focus on “the true genius” itself. And I will follow the life trajectory of carbon nanotubes (CNTs) as exemplars of the large family of nanocarbons.

3. Mechanical Champions

In a sense, CNTs are the descendants of carbon fibers manufactured for making composite materials for the past 50 years. Carbon fibers extended the market of plastics. Dubbed “the new steel”, carbon fibers have a high elastic modulus and low density and rigidity that offers mechanical performance five or six times higher than aluminum or titanium alloys when used as reinforcing structure in composite materials. The processes for synthesizing CNTs are inherited from those of carbon fibers, such as electric arc furnaces, oxyacetylene torches, and chemical vapor deposition techniques. The most used technique consists of cracking a molecular carbon-containing precursor (a plastic or a raw material like benzene) at the surface of small metallic catalytic nanoparticles: the molecule breaks down and releases carbon, which reorganizes itself to form a small cap (half a fullerene) in which carbon atoms bind together in hexagons and pentagons; the small cap grows gradually as carbon is incorporated and forms a nanotube. Depending on the synthesis conditions, the tubes can be single- or multi-walled, or a mixture of both. Carbon fibers are ultimately multi-wall CNTs.

It took years to uncover this type of growth. However, scientists were actually *rediscovering* a phenomenon that had long been observed in blast furnaces: the unexpected — and at that time undesirable — occurrence of “carbon filaments” so hard that they could crack bricks. These “filamentous carbons” were, in fact, most likely multi-wall CNTs. And CNTs were also required in the formation process of carbon fibers, as the central structure around which the fiber thickens, as highlighted by the Japanese material scientist Morinobu Endo.

As early as in the 1970s, Endo unveiled the “central hollow tube” hidden in the core of his vapor-grown carbon fibers. But he was not interested in the tube itself. He viewed it as a

key for the mechanical robustness of the fiber, its strongest part which “never breaks when the fiber breaks” Endo viewed it as a structure crucial for the mechanical robustness of the fiber, its strongest part which “never breaks when the fiber breaks” [7]. The high mechanical performances of CNTs originate in the strength of the carbon–carbon bond in hexagonal planes, which only high temperatures can break. Very few materials have equivalent mechanical robustness combined with such flexibility. With Young modulus up to 1 teraPascal, a nanotube can be bent without breaking, and returned to its original state. Added to this is their extreme lightness: not only is carbon a light element, but they are hollow materials! Combining robustness, flexibility and lightness — everything that engineers dream of — CNTs have been touted as revolutionary materials.

However, these mechanical marvels are nothing new given their ascendancy with carbon fibers. Endo, for instance, was already mass-producing these hollow microtubules for electric batteries when he learnt — much to his stupefaction — that the same material have been ‘discovered’ by another Japanese scientist working at NEC Corporation, Sumio Iijima [8].

4. A Rising Star in Electronics

August 2019: A team from MIT assembled and operated a microprocessor made up of 14,000 carbon nanotube field-effect transistors (CNFET) using standard industrial methods [9]. How could CNTs become a star electronic material?

Twenty years ago, field-effect transistor based on a single nanotube was an unrealistic project: to isolate a nanotube, to place it on electrodes and measure its electric transport properties required an army of students. They would spend days and nights depositing a drop of CNT solution on a substrate and scanning the surface in the hope of finding a few carbon nanotubes well positioned on the top of two electrodes. However, these experiments confirmed the predictions based on calculus that there would be two types of carbon nanotubes: metallic and semiconductor. Graphite (at least very pure graphite) can be modeled as a stacking of hexagonal carbon monolayers, a pile of graphene sheets. Before graphene became a star material in the 2000s, the term “graphene” (coined after *graphite* + *benzene*) was used to refer to a single layer of graphite. This 2D structure was viewed as a laboratory curiosity. Graphene was promoted as a material in the 2000s when Andrej Geim and Konstantin Novoselov crafted a tiny device showcasing its extreme electronic tunability [10]. In turn, the nanotube has been modeled as a cut-out of a single graphene sheet rolled on itself.

CNTs have a diameter between 0.4 to 100 nanometers for lengths that can go up to tens of centimeters. Like all “nano”-materials, their size matters, not for itself, but for the properties it brings out:

First, CNTs are both nano-objects and potentially macro-objects, and can be engineered at both scales. This is also true for an individual graphene sheet: sub-nano in thickness, it can be very large in the two dimensions.

Second, the length-to-diameter ratio, which can be as high as several millions-to-one and has no known theoretical limit, makes CNT properties extremely anisotropic, i.e. direction-dependent and tunable. As a result, this “one-dimensional conductor” affords “ballistic conduction”³ and is highly versatile: a tiny alteration of the tube structure completely changes its electronic characteristics.

Third, depending on their winding angle, diameter and length, the number of possible nanotube structures is theoretically indefinite.

³ In the inner vacuum space of the tube, electron transport shows negligible resistivity due to scattering and simply follows Newton’s second law of motion.

Finally, because of the perfectly calculable matching between the rolling-up structure and the electronic properties of CNTs, between “fold and function”, their potential for electronics appeared straightforward. CNTs were a serious candidate to move beyond silicon and continue the exponential growth in the miniaturization of electronic chips according to Moore’s law.

5. From Laboratory to Industry

However, the difficulties in the synthetic process of CNTs moderated the enthusiasm. Not that they are difficult to make since carbon spontaneously assembles into fullerenes and nanotubes wherever it condenses. It has this “genius wired within it” as Smalley remarked in his Nobel Lecture. But CNTs are difficult to make in a predictable way that would deliver exclusively the specific tubes with the desired properties described by the theory. A “genius” is always somewhat whimsical!

Today, despite routine industrial processes, it is still a challenge to determine which synthesis conditions allow obtaining a tube of interest with the desired diameter, length and chirality. Even with more delicate techniques such as laser ablation or vaporization, their synthesis remains empirical and highly dependent on the environment, especially the catalyst. Some processes produce statistically more metallic CNTs, others more semiconductors. All of them yield mixtures of various purities, chiralities, diameters and lengths of CNTs, often agglomerated or bundled together like overcooked spaghetti (Figure 2). Up to now, the level of industrial mastery of the material’s intrinsic properties remains largely below that which has been achieved with silicon for decades.

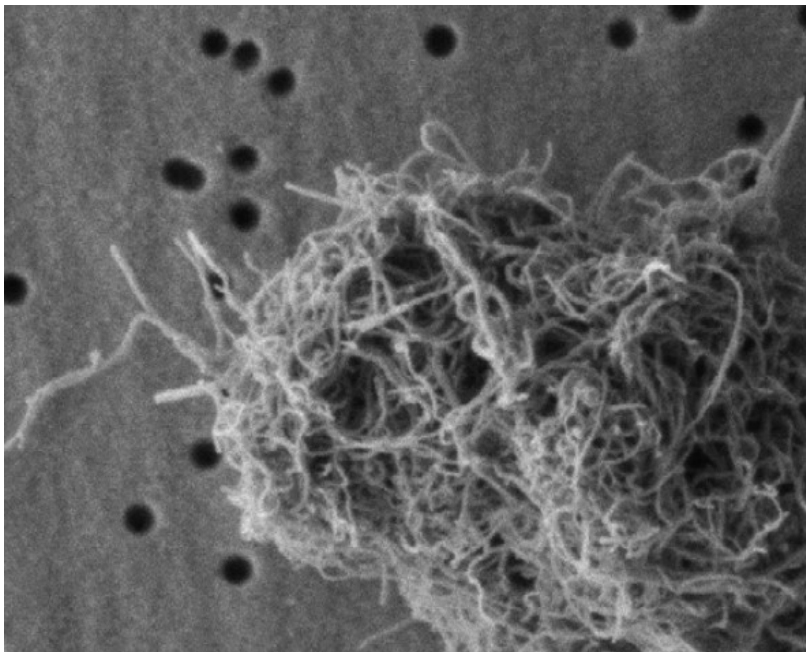


Figure 4. Bundled nanotubes. Transmission electron microscopy [11].
Source: <http://www.inrs.fr/media.html?refINRS=ND%202286>.

Industrial CNTs are rather used in common, incremental applications where mixtures of various purities can be used either to reinforce structures or as electric conductors. When immersed in the transparent film of solar panels, they can promote and preserve its transmittance. However, these mechanical and electrical applications are not exactly

disruptive, they do not call for new technological concepts. In both cases, engineers use the morphology of the material and its ability to integrate with other well-controlled compounds. It just improves the existing technology.

Eventually, to enhance the yield of nanotubes with desired properties, one had to give up the idea of rational design and instead to improve post-synthesis sorting. Indeed, each of the processes mentioned above delivers a variety of objects. At our scale, they look alike, but at the atomic level they are all different. Current solutions involve an entire toolbox of physical and chemical cues that play on their selective affinities in order to sort them out.

In short, it took about 20 years of research to learn how to work with this material: how to handle it, how to deal with its environment and how this environment acts in return on its properties, and finally, how to mass-produce components made of a large number of CNTs. It is after all a relatively short period of time compared to that required for the development of electronic silicon materials (it took no less than 40 years to master the synthesis of very large ultra-pure silicon crystals).

However, faster mastery doesn't mean equal mastery. Even with the improvements in the industrial production of carbon nanotubes, these materials are not about to overthrow silicon. They are rather meant to complement it.

A. A Disruptive Innovation: Optoelectronics

The highest promises of CNTs rest on their special and unique performances in optoelectronics. Semiconductor CNTs interact strongly with light. They absorb light of certain colors, in specific wavelengths such as near infrared, which is of particular interest for medical imaging (living tissues are relatively transparent in the near infrared) or, again, for photovoltaic energy.

CNTs can also emit light in specific ways that depend on their geometry. In this respect, these materials are paradigmatic of nanoscience in the sense that their properties and performances depend on their interaction with the environment as much as on their chemical composition. Depending on which atoms are (intentionally or not) attached to the surface of the object, its behavior will differ. If we do not take care, it will interact randomly with the environment and this interaction will modify its properties. Smalley's team learned how to take care of these tiny objects, for example, by encapsulating them into a small protection bubble, a micelle, which isolates them from the rest of the world, so that they agree to show their optical properties. These studies demonstrated that their optical behaviors are far more diverse than those predicted by theory because of coupling effects with their milieu [12].

The promising optoelectronics applications of CNTs are the so-called "hybrid" photonics, that is, integration of CNTs *on silicon*. As for graphene, which has been touted so much over this last decade as the future material for the post-silicon age, it has no band gap and is thus not a semiconductor; it is therefore not further destined to replace silicon, but rather to complement it with high-frequency applications. Noticeably, nanotube-chip designers [9] never compared the performance of the carbon chips against equivalent silicon chips, which benefits from more than 50 years of research and development fuelled by huge commercial returns. They rather insist that carbon chips can be built using existing technology and integrate with the mainstream of silicon. For not only is it difficult to radically change a technology that has taken so long to develop, it is also crucial for a new technology to connect with the old and integrate a diverse ecology of materials. The realization of all-carbon computers would require an alternative industrial ecosystem [13].

Finally, nanocarbons are less to be seen as competitors — between themselves as well as between them and silicon — than as mediators or go-betweens. They pave the way to an entire class of low-dimensional materials other than carbon: in the one-dimension, to

nanowires, and other nanotubes, such as manganese vanadium oxide nanotubes; in 2D, to giant flat molecules: boron nitride (graphyne), silicene, borophene, germanene, phosphorene, etc. Nanocarbons make the nanoworld proliferate because the material ways of being they have initiated are to some extent transferable to other elements. Even silicon can form nanotubes!

7. Health Promises and Risks

Because carbon is the main element of biological life, fullerenes and carbon nanotubes have first been naturally considered biocompatible. Moreover, due to carbon's genius of association, nanocarbons can be quite easily functionalized. They are grafted with other compounds at their surface such as therapeutic agents, pH-sensitive molecules, DNA or peptide. They accordingly qualify as good candidates for drug, gene or protein delivery in the cell. Targeted drug delivery has become a popular concept in nanomedicine and is undoubtedly the most successful and uncontroversial application of nanotechnology. Being extremely stable physically and chemically, CNTs are not easily biodegradable.⁴ This is seen as an asset for traveling unscathed a path strewn with pitfalls through the bloodstream and various intercellular milieus. Their mechanisms of internalization in the cell vary according to geometry, size, charge density and functionalizing agents. CNTs can cross membranes by passive diffusion, acting as nano-needles, or by energy-dependent mechanisms involving membrane deformation processes: the cell membrane can then form vesicles, small bubbles which encapsulate the nanotubes and travel inside the cell before releasing them with their therapeutic agents.

In addition, thanks to their capacity of light-absorption in the near-infrared, they can be used to damage diseased cells by heating. This photothermal therapy can be combined with their use as imagery agents, providing precise probes to enlighten specific zones of the body's inner space (theragnostics, i.e. therapy + dia/prognostics). Their potential in nanomedicine derives once again from their conjunction of original properties and their ability to infiltrate various milieus (here living tissues).

However, the same wonder virtues, in particular their capacity to cross biological barriers, raise serious toxicological concerns. In particular, some studies have shown structural and toxicological similarities between CNTs and asbestos fibers [14]. Yet, in order to study their toxicity it is not enough to consider the chemical nature of the material (carbon, biocompatible). Nanotubes and nanomaterials in general induced a paradigm shift in toxicology: from the dogma 'the dose makes the poison' to a much more complex view of sources of toxicity that raise endless controversies. Because of their size first nanotubes have been proved cytotoxic by some studies, while others have concluded to a high pulmonary toxicity independent of length [15, 16]. But also: the type of exposure (ingestion, inhalation, epidermal contact), the detail of the crystalline structure, the geometrical shape, their relations between them (their agglomeration behavior, for example), with the co-agents (e.g. the catalysts required for the synthesis of CNTs sometimes remain as residues in the final product) and with the environment, and the way this relation can be tuned by proper functionalization. For instance, nanotubes tend to agglomerate in aqueous environment but can be rendered soluble by coating them with micelles. Each variation of these factors completely changes their toxicological effect. It is thus not the *substance* of the object (its intrinsic properties) that matters but its *reliance*. It is the coupling of certain specific features

⁴ Except for some bacteria and fungi. However, some studies show that they are some mechanisms of CNT clearance by macrophages in the rat lung (but not yet, so far, in the liver). The CNTs are chemically modified and cleaved, and then metabolized into innocuous carbohydrates.

of the object with some of its milieu of operation that redefines the nano-object as an object of reliance, and, I would say, as an object of care.

As a result, there is no simple answer to the question of toxicity. Nanotoxicological studies look on a case-by-case basis at each type of nanomaterial in its specific milieu of operation and use. In some cases, however, good cooperative relationships have been established between nanocarbons and living cells, for instance, in restoring damaged nervous tissues, which is of interest for spinal chord or brain regeneration after injury [17]. The nanotubes play two roles here, the first relates to their morphology, the other to their electronic properties. On the one hand, it turns out that they constitute a favorable substrate for the growth of neurons in vitro. They “feel good” on contact with the nanotubes and reweave their damaged fibrous network along them. On the other hand, the electronic properties of nanotubes help distant neurons to reconnect with each other and recover electrical function even when the biological nerve itself is still damaged — another illustration of their reliance. These two mutually supportive processes are strongly dependant on the type of nanotube (single or multi-walled, metallic or semiconductor, etc.). As a result, the potential developments of carbon nanostructures for neurobiology are now rapidly expanding from molecular imaging to neuro-regenerative scaffolds and graphene-based neural interfaces.

However, in vivo uses of nanocarbons require special safety measures and clinical trials. They have to be highly purified, strictly characterized and standardized. Yet, toxicological studies of CNTs often remain controversial because CNTs interact with the biological milieu, which is never fully controllable. Therefore, despite great advances nanocarbons are still essentially promising materials.

To be sure, many of their potential applications are likely to remain speculative, doomed to feed the kitsch retro-futurism of tomorrow. But these wonder materials and their ways of being “materials” are no less intriguing. For it is also and perhaps foremost the different kinds of carbons’ worldliness at this scale that justifies the phrase “nanoworld”, as a world of endless production of allotropes.

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