Viewpoint

Rediscovering Forgotten Members of the Graphene Family

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1. INTRODUCTION

Carbon materials with controlled nanostructure or, better, covalent two-dimensional systems are currently a scientific megatrend, but not new as such. Many applications ranging from conductance, sensing, selective sorption, over (electro) catalysis to stretchable electronics, energy conversion, and storage were recently presented and will constitute the core of future technology. It is also commonplace that all these applications can still be improved by the development of new carbon or carbon derived materials to be implemented at the industrial scale. The relatively recent exploration of graphene, as for instance explored also in the European Graphene Flagship, marked a turn-around in the societal perception of all of those technologies. However, delaminated graphene is not new as such, with the employed techniques by Hummers[1] or H. P. Boehm[2] as early as 1958 and 1962.

Being aware of old literature is very difficult and here not assumed. Science moved faster and faster over the last two decades. Indeed, by mid-2017 we already exceeded the 50 million scientific papers published, and more that 2.5 million papers are published each year.[3] This tendency leads to a quicker expansion of general knowledge but increases the risks of new scientists not reaching fundamental old papers at the same time. Interestingly, when reading closely the not so long bibliography of the 19th century with an open eye and in specific fields, one can find many publications giving first evidence for materials and technologies that were rediscovered much later. It is our discussion opener that a majority of the big success stories achieved in material sciences over the last decades turned out to be described by older science, while the topic was relegated to oblivion for reasons related to the structure of science. A very illustrative example in our own field is carbon nitride (C_3N_4), which was "re-discovered" at least two times. Liebig described its synthesis in 1834 by thermolysis of dithiocyan $(SCN)_2$,[4] a brilliant, but now forgotten synthesis. Linus Pauling kept its heptazine structure at his "new ideas blackboard" for a long time in the 1940s,[5] while the current wave of C_3N_4 research started in the mid 1980s with a theoretical paper that a hypothetic cubic carbon nitride could exceed diamond in many properties, like, for example, hardness.[6] Carbon nitride was long known, but it was the new view on this old structure making it to the current research field.

With this paper, we want to point out the inverse process: if it is so easy to forget, can we rediscover the overseen jewels of the past, other worth-to-examine cases where the original literature is still largely ignored and that hold a great potential to develop new and more advanced materials? Indeed, this is the theme of our ERC Advanced Grant, and we discuss the first two cases near low dimensional covalent materials, namely, "paracyan" and "red carbon". We are confident that their rediscovery in a modern context already extends the synthetic and application perspectives of layered covalent materials beyond the precedent scope marked by graphene, heteroatom-doped carbons, and C_3N_4.

2. PARACYANOGEN, THE FORGOTTEN RELATIVE OF C_3N_4

a. Lost Knowledge

The story of dicyan (e.g., N≡C—C≡N, $(CN)_2$ also named cyanogen) and paracyan (i.e., the polycondensed structure of cyanogen) stands out in this regard. As early as 1782, HCN and HgCN were produced by Macquer and Scheede.[7] In 1811, Gay-Lussac produced dicyan, a colorless gas composed only of carbon and nitrogen, by heating up HgCN. Soon after, in 1816, he heated up silver cyanides and managed to synthesize a brown solid with the same composition as that of dicyan, i.e., paracyan or paracyanogen (pCN, a C_1N_1 polymer).[8] From a nowadays perspective, it is important to mention that these materials obviously can only contain C and N and must be fully conjugated. Its brown color points to a medium bandgap semiconductor. During the early and mid-17th century, many scientists studied pCN and produced it from a variety of cyanides including that of mercury, silver, and potassium cyanides. In 1874, Delbrück had written a review on what was already known about both dicyan and pCN.[9] In brief, pCN is a brown residual product obtained by decomposition of metal cyanides. In 1914, pCN was described as a brown-black, light solid, insoluble in water, alcohol, alkaline and ammoniac, not affected by nitric acid but decomposing with concentrated sulfuric acid. pCN is very stable and does not oxidize but disintegrates back to dicyan completely at 860 °C.[10]

In 1954, Bircumshaw obtained pCN as a brown residual by heating up oxamide in a sealed tube. The dark brown residue was light and porous and black when polymerization was completed and behaved similarly to pCN obtained through the

conventional metal cyanide syntheses. More interestingly, Bircumshaw claimed to have a polymer with 32−34% C and 32−44% N with a complete conjugated double-bond system with no free cyanide groups.[11] He proposed the structures found in Scheme 1 as the most probable candidates for pCN, being the more popular and central one, known as the ladder pCN structure.

Scheme 1. Structures for pCN Proposed by Bircumshaw in 1954[11]
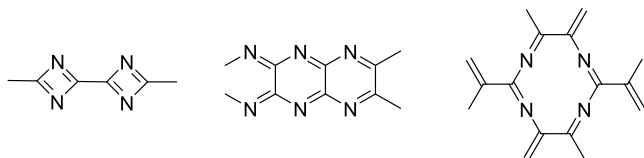
The tendency of pCN to form fibers was described by Bircumshaw in 1954 (see Figure 1A).[11] Later, from 1985 on, M. M. Labes and co-workers applied the knowledge on dicyan and paracyan to develop new materials. They reported the preparation of pCN fibers by electropolymerization of dicyan[12,13] as well as carbon fibers containing different amounts of nitrogen (starting by a C/N ratio of ca. 1:1 on) by pyrolysis of the pCN fibers at different temperatures (Figure 1B,C).[14,15] In 1986, they submitted a patent for the preparation of these materials and described that the pyrolysis product had an increasing C/N ratio with temperature that went from 1.5 at 400 °C to 9.3 at 900 °C.[16] Labes also highlighted the potential of pCN for material preparation at high temperatures since its thermal treatment leads to graphitic highly conducting materials (with even 3% N at 1800 °C).[17]

During the 1990s, some efforts were invested on photo-polymerizing dicyan into pCN.[18,19] However, the most important fact occurring in that decade was probably the suggestion of pCN as candidate to prepare C_3N_4 by Maya in

1993.[20] A bit afterward, in1996, Stevens and co-workers studied pCN, obtained from HgCN, as a possible g-C_3N_4 precursor using high temperatures and pressure.[21] Surprisingly, from that point on, the majority of the scientific efforts focused mostly on theoretical studies pointing out the super hardness of different C_1N_1 phases obtained at high pressures comprising only sp^3 carbons.[22−25]

Despite the interesting claims of Bircumshaw regarding a C:N sp^2 hybridized structure with a 1:1 stoichiometry, it is not until much later in 2009, when P. W. May et al. run detailed investigations about other possible crystal structures of CN, not comprising sp^3 carbons.[26] Besides the typical ladder structure (Scheme 2, structure A), they propose another two structures of two-dimensional sheets comprising electron delocalization and sp^2 hybridized carbons: one formed a continuous conjugated sheet (Scheme 2, structure B), and another one formed by six-membered rings (Scheme 2, structure C). They compared the stability of these new structures together with the classical ladder structure of pCN proposed by Bircumshaw in 1954 and concluded that the structure obtained strongly depends on the synthetic conditions, but at that low pressure, the thermodynamically preferred structure is conjugated with sp^2 carbon. However, little has been achieved thereafter.

b. What Comes Next in the pCN Story?

Looking back to structure A in Scheme 2 (the six-membered ring structure proposed by P.W. May), it is easy to see how nicely it aligns with other current materials, i.e., covalent triazine frameworks (CTFs)[27−32] and the more recently included hall-of-fame material C_2N.[33−36] For instance, CTF-0 produced by A. Thomas et al. in 2013 could be described as a "nitrogen unsaturated" version of pCN formed also by six-membered rings, but only containing three nitrogen atoms instead of six.[28] This comparison is by no means trivial, as of course dicyan is a much simpler compound, a gas that spontaneously polymerizes already at low temperatures. This
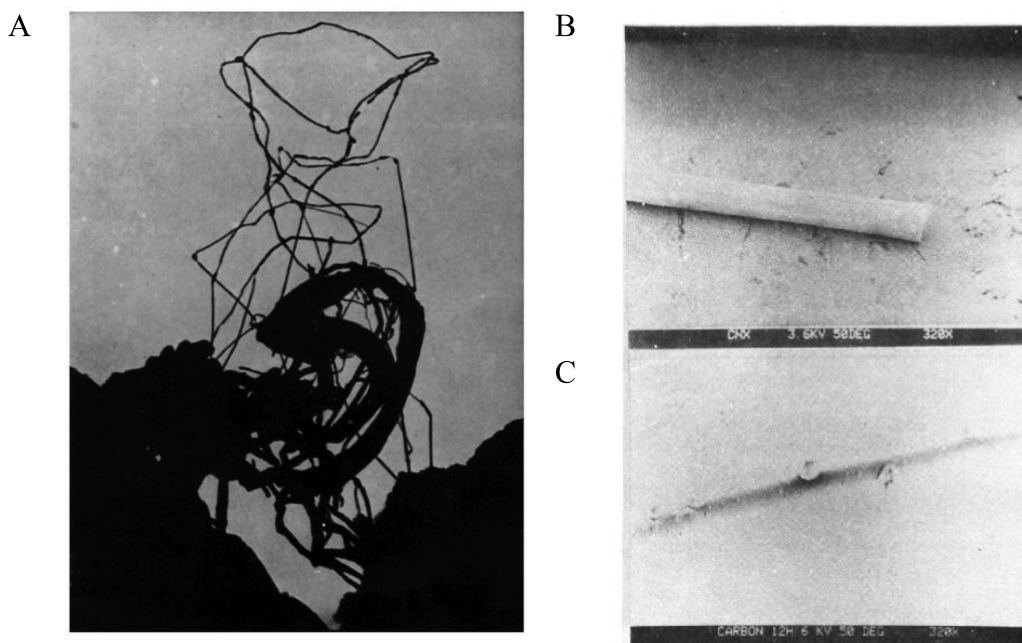
Figure 1. Ability of pCN to form fibers. (A) TEM image of the fibers. Reproduced with permission from ref 11. Copyright 1954 The Royal Society of Chemistry. (B) SEM image of a pCN fiber and (C) carbon derived fiber obtained by heat treatment of pCN. Reprinted from ref 14.

Scheme 2. pCN Structures Comprising sp² Hybridized Carbon As Proposed by P. W. May et al.,[26] Where Structure B Was Not Found to Our Knowledge[a]
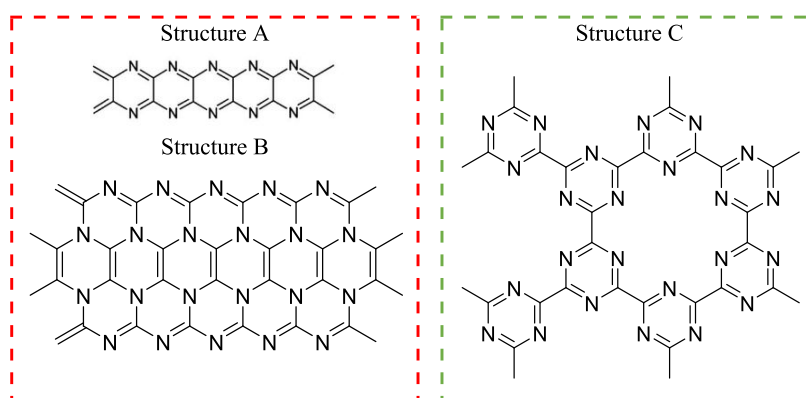
[a]Inside the green box, the most probable structure for pCN to our understanding is placed.

broadens the scope for pCN to new processes and potential applications, for example, low temperature CVD on sensitive substrates of polymerization or polymer-inspired structure control.

Dicyan, which is one of the most abundant carbon species in outer space[37,38] and treatable in a CVD machine or in an industrial environment, might be too toxic and very reactive for an unprepared environment. Here we point to the fact that Bircumshaw prepared pCN from oxamide (the addition product of dicyan and water, while at higher temperatures oxamide eliminates water to dicyan). Our own group uses biocompatible nucleobases as starting products (note that guanine or cytosine have in principle a "C_1N_1" composition),[39,40] and condensation reactions mostly process over a paracyan intermediate. Dicyan is then created just as a reactive intermediate, and those reactions are all rather "heat n' bake" processes.

Dicyan-type polymerizations are not restricted to the pure monomer but can include other polymerizeable nucleophiles, and there is a parathiocyanogen polymerization as well, which was achieved in the mid-20th century (i.e., S-doping). The resulting solid was, not surprisingly for a two-dimensional polymerization, not soluble in all common organic solvents but was also brick red in color. This means that we have to expect many complex codoped covalent semiconducting materials that can be accessed by rational design and selection of the precursors, using dicyan-like addition processes.[41−43]
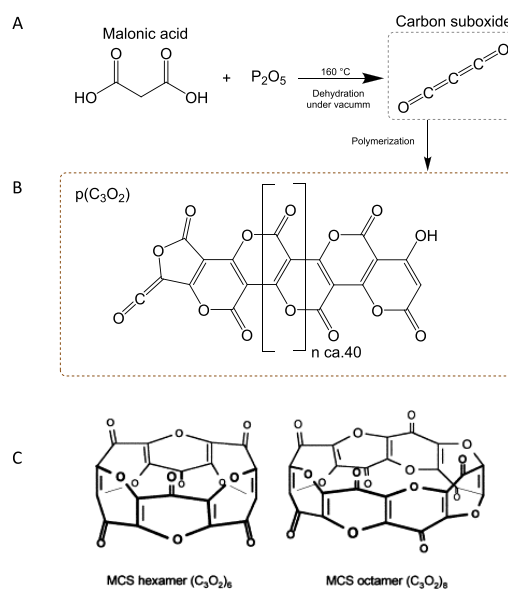
3. RED CARBON

If you ask new generation chemists about carbon−oxide compounds, they come up immediately with C=O and CO_2, and more trained people will add cyclohexaketone (C_6O_6), dioxane tetraketone (C_4O_6), and related compounds. As they contain no C—H bonds, the latter are already used as entry points for covalent, two-dimensional materials.[33,44] The other largely forgotten entry point is represented by carbon suboxide (C_3O_2) and its polymer derivatives. As a fact, there are many dehydration and dehydrohalogenation reactions resulting in this very interesting product under very mild conditions (ca. 150 °C).[45] C_3O_2 synthesis was first reported as early as in 1874 by Benjamin Collins Brodie Junior who obtained it electrochemically from C=O.[46] In 1891, M. Berthelot reported that heating pure carbon monoxide at about 550 °C created small amounts of carbon dioxide but no trace of carbon. Moreover,

he deduced that a carbon-rich oxide was created instead, the carbon "suboxide".[47] C_3O_2 is a rather simple to prepare and moderately stable gas that condenses at 6.8 °C, as reported by Diels et al. in 1906.[48] At smaller scale, it is commonly produced by dehydration of malonic acid using phosphorus pentoxide (Scheme 3A). However, about 100 years ago, C_3O_2 was an industrial product used for the sterilization of fruits and the treatment of furs, but these applications are forgotten.

Interestingly, carbon suboxide polymerizes spontaneously to a red, yellow, or black solid, i.e., a semiconductor or potentially a semimetal. This was described in 1938 by Klemenc.[49] Similarly to what happened with pCN, the work done on C_3O_2 was already extensively reviewed in the 1950s.[50,51] The product

Scheme 3. (A) Typical Reaction to Produce C_3O_2 from Malonic Acid. (B) Poly-C_3O_2 Structure According to P. Krieger-Beck et al.[a] (C) Oligocyclic-C_3O_2 Structures with the Common Formula $(C_3O_2)_n$ Described by F. Kerek et al.[b]

[a]Reprinted with permission from ref 53. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. [b]Reprinted with permission from ref 54. Copyright 2002 Elsevier.

of the condensation of C_3O_2(poly-C_3O_2) was already called "red carbon" and indeed was largely forgotten. Though its structure was postulated to be formed by graphitic-like layers composed of hexagonal aromatic structures with 10 Å diameter,[50,51] nowadays, a poly(α-pyronic) structure is the most accepted one (see Scheme 3B).[52,53] Moreover, it has been shown that carbon suboxide in an organism can quickly polymerize into macrocyclic carbonaceous structures with the common formula $(C_3O_2)_n$, mostly $(C_3O_2)_6$ and $(C_3O_2)_8$, and that those macrocyclic compounds are potent inhibitors of Na^+/K^+-ATP-ase (Scheme 3C).[54]

We analyzed the structure of the compounds and found that under slightly increased temperatures (above 100 °C, therefore, not in water) this structure was not stable, but eliminated first CO_2 and then $C=O$ to form rather pure carbon-rich species. Note that indeed structure B is an all-conjugated polyacetylene backbone only protected by simple CO_2 as edge functionalization. Thereby, eliminating CO_2 would indeed lead to multidimensional carbon polymerization, which must be topologically controlled. We also found additional old literature, which already probed that poly-C_3O_2 leads to carbon materials (80−90 wt % carbon, no hydrogen) after undergoing decarboxylation at extremely mild temperatures (below 200 °C).[55]

Besides the production of carbonaceous materials,[55,56] carbon suboxide has been also used in organic chemistry. For instance, in 1974, Ziegler and Kappe reviewed the different synthetic routes to prepare C_3O_2 and analyzed the different products obtained using carbon suboxide (i.e., heterocycles and mesoionic heterocycles containing oxygen, nitrogen and/ or sulfur, cycloadditions, photochemical or polymerization reactions, and others).[57] It is not the aim of this review to go into detail on the possibilities that C_3O_2 brings to the field of organic chemistry. However, it is important to point out that all the above-mentioned reactions were carried out at mild conditions (i.e., ca. RT) and the products (e.g., mainly heterocyclic ones) are a well-known tool for developing new advanced materials.

From this point, the real modern work is still to be done, but the promises of a process capable of generating from the gas-phase (C_3O_2) first a polymer layer (poly-C_3O_2 or other more advanced doped polymers) and then, by elimination at rather mild conditions, a conjugated carbon material (or carbonaceous material) is widespread. At this piont, we just want to use this case to illustrate how modern materials chemistry could profit from old literature, the main problem of which is to be "unreadable" as it is in pre-computer-era format and largely in other languages.

4. CONCLUDING REMARKS AND PERSPERCTIVE

This Viewpoint is admittedly unusual, and it is a proclamation of finding ways "not to forget" what we as a scientific community were already able to do. This is not an accusation but rather the intent is to highlight the fact that, with any change of "data storage" or "communication language", massive information is lost. We work heavily as a community to make raw data of scientific experiments accessible and transparent, but we forget to save the condensed old knowledge, which is a matter of advanced literacy!

We, however, also reported very practical details. A deeper understanding of the phenomena taking place during the polymerization of both dicyan and C_3O_2 will pave the way toward low temperature carbonaceous materials (i.e., being made below ∼200 °C), which carbonaceous materials being contrasted from organic polymers in being free of C−H bonds. Lowering the condensation temperature to the range of common polymer or organic chemistry will bring up a new way to make and understand covalent materials, plus processes of practical potential.

A library of condensation reactions toward covalent carbonaceous 2D materials can be envisioned, when handling of multidimensionality is approached and multifunctionality is mastered. It is indeed very difficult to delimit the impact that such a study could have for materials science and societal implications. We already know that highly porous versions of C_1N_1 extend the range of adsorption enthalpies and sorption selectivities of covalent materials for different gaseous and low molecular weight substrates,[39] and we can envision "sorption on demand" using such a library of condensation reactions will bring down to the temperatures of normal organic synthesis concepts other than those of carbonization. The ability to tailor chemical structure, porosity, and work functions will also have an impact on catalysis. The new materials not only can be designed to stabilize single metal atoms and metal clusters but also can be designed as stable covalent structures with enzyme-like catalytic activity. Moreover, we expect that activity to be applicable far from the comfort zone of biology. This could be a game changer for chemistry as such.

Especially under conditions where biology or metal organic chemistry are notoriously weak (e.g., reactions of biomass in superhot water, the presence of sulfur and CO in feed streams, or conversions in salt melts), we expect the resulting materials to enable new reaction schemes, understandable as organic versions of zeolites, but with adjustable solid state acid and base strength.

Applications of cheap and structure controlled organic semiconductors and semimetals in organic electronics, sensing, or as protection layers are obvious but are beyond our direct field of expertise.

These are indeed forgotten words, and discovering such "dinosaurs" by reading dust covered papers to fuel our fantasy is as old as ... a good book!

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Notes

The authors declare no competing financial interest.

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Nieves Lopez studied Chemical Engineering at the University of Murcia (Spain). Then she joined the Group of Bioinspired Materials at the Institute of Materials Sciences of Madrid to carry out her Ph.D. studies under the tuition of Francisco del Monte. After finishing her Ph.D. studies she joined the team of Prof. Markus Antonietti at the Colloid Chemistry Department of the Max Planck Institute of Colloids and Interfaces were she works now as Group Leader. Her current research interests are the preparation of carbons at low temperature and noble carbonaceous structured materials and their use as carbocatalyts.

Janina Kossmann studied business chemistry at the Heinrich-Heine-University in Düsseldorf. She wrote her bachelor thesis in the department of Organic Chemistry and Macromolecular Chemistry with Prof. Dr. Thomas J. J. Müller and finished her studies with a master thesis in cooperation with Evonik Ressource Effiency GmbH. In 2019 she joined the Colloid Chemistry Department of the Max-Planck Institute under Prof. Markus Antonietti in the group of Nieves Lopez-Salas where is now working on the synthesis, characterization and application of noble carbonaceous (C_1N_1) materials.

Markus Antonietti is the Director of the Max Planck Institute of Colloids and Interfaces and has worked in the field of functional materials for 30 years. His current scientific interests include green chemistry and material solutions for the energy change, porous materials, artificial photosynthesis, and carbocatalysis as well as the chemistry of cooking.

■ ACKNOWLEDGMENTS

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