

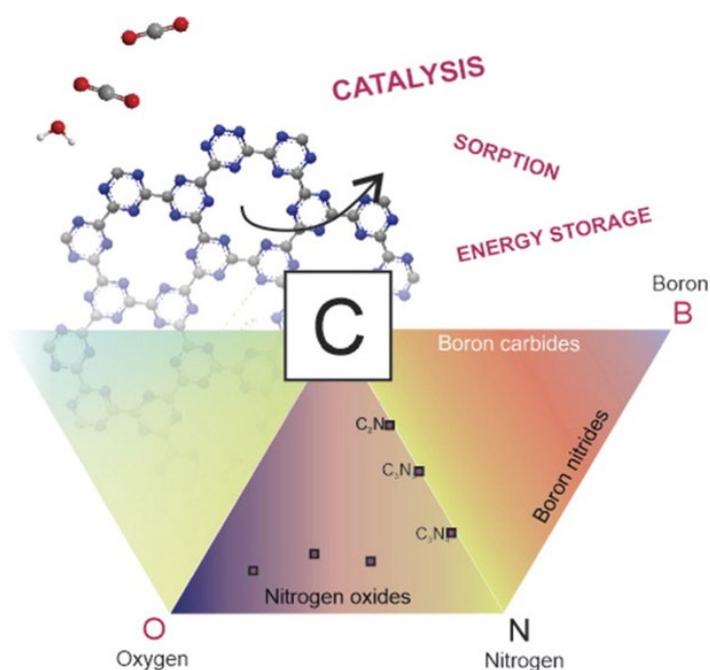


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## Carbonaceous Materials : The beauty of simplicity

Nieves Lopez Salas, Markus Antonietti



**Materials chemistry**, as well as chemistry as such, should be redesigned: from glassware to preparing materials minimizing wastes and side products. Carbon based chemistry is among the most versatile ones when discussing materials sciences. Re-designing carbon chemistry and, at the same time, outperform other materials in any of the many challenging technologies is not easy. Herein, we give our critical opinion on the different strategies new generation scientist should go through to achieve such a goal.

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# Carbonaceous Materials: The beauty of simplicity

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## Abstract

The current mandates of a sustainable society and circular economy lead to the request that materials chemistry, but also chemistry as such, has to become significantly redesigned. Changes include commonplaces as the glassware we use, the minimization of wastes and side products or replacement strategies in the materials choice, among others. In this context, “carbons” are very versatile and already have found their place in a myriad of applications for a “carbon-neutral” society. They already take key enabling positions for sensors and biomaterials preparation, as energy conversion and storage electrode, or as effluent remediation sorbents. Herein, we describe how carbon chemistry can be again re-designed to outperform benchmark materials in a number of fields, especially in energy storage, (electro)catalysis, as sorbent, but also in a new chemistry of the confined state.

**Keywords:** Designer materials, noble carbons, nanoarchitecture

## 1. Introduction

Science has turned in the last 50 years from a more national to a global community operation. The numbers of involved scientists is exploding, and the race for the best ideas is now more competitive than ever. Together with digital data tools and exchange, this has led to an acceleration of innovation and a previously non-imaginable competence to find solutions for pressing problems. Material chemists for instance are in a constant run to prepare new and always more advanced materials in order to satisfy the demands of a “fully connected”, energy and resource consuming society. Over the last decades, many innovations illustrate that boost, as for example, fullerenes, graphenes, MXenes, metal organic frameworks (MOFs) and covalent organic frameworks (COFs), photo- and electrochemistry or flow processes, among many others.

From materials science point of view, we are now facing a further superlative of this process: the world is fronting that acceleration and classical materials growth is not infinite and successively encounters physical and political restrictions. For example, climate change implies that our society should slowly leave fossil fuels or resources and technologies that are not circular and sustainable. As a direct consequence, power production and storage, as well as energy vectors like hydrogen are now key areas, and thus, research on materials for energy storage and production is among the most funded ones.

A second example that maybe is less public in EU, but is currently at the core of Japan interests is the “rare element strategy”. Many technological innovations crucially depend on the availability of minor amounts of rare chemical elements. A recent report by the Ministry of Economy, Trade and Industry (METI) from Japan gives an updated list of such elements and states where they are needed and how they are politically monopolized (a process which can harm local technological development).<sup>1</sup> In our approach to handle this problem, we feel deeply rooted to an opinion article of Nakamura and Sato published in 2011.<sup>2</sup> They described how materials chemistry can potentially outmaneuver such political-economic operations exemplifying that with cases, as for instance, how nitrogen-doped carbons can replace platinum in fuel cells or how the simple croconic acid is a high performance organic ferroelectric.<sup>3</sup> In this line, lithium and cobalt might one day be not so crucial for electric energy storage anymore, and speculations on scarcity might become vain.

We will argue in this article that in all these new mandates for material science, modern versions of “activated carbons” might still be winning horses. We phrase our considerations for the preparation of new functionalized carbon based materials as their synthesis should now be green, the sources to prepare the materials should be renewable and resulting materials should outperform benchmark standards, including noble metals.

## 2. General rules for carbonaceous materials preparation

Porous charcoal seems to be a Japanese invention. Potentially used for thousands of years for drinking water purification, the most refined artisan charcoal available to our hands now is Binchō-tan (備長炭), the white charcoal from the Edo period. We (as westerners) can only speculate why the knowledge on porous materials was so refined in Japan, but a nearby explanation lies in the *Godai*, the five-element theory of the world (Figure 1). Extending the western four element theory, the *Godai* has “void” as the fifth element at the top. Interestingly, modern chemistry just discovered the importance of no matter near the presence of matter (i.e. pores).<sup>4, 5</sup>

Porous activated carbons are currently widely used worldwide. Commercial active carbon materials are currently prepared through two-step processes. First, a suitable biomass source is submitted to carbonization and then to chemical or physical activation to generate a pore network. However, over the last decades, researchers have used also more rational recipes to optimize carbon materials at pore network level. Among the different techniques used, using surfactants self-assembly to introduce porosity in polymeric precursors (first reported by Dai group<sup>6</sup> and Zhao group<sup>7</sup>) or the use of already assembled advanced materials as casting molds (like for example zeolites, as first reported by Tomita<sup>8</sup>) stand out as the most extensively used ones to control porosity. More recently, the use of already assembled advanced porous materials like, for example, metal organic frameworks<sup>9, 10</sup> or covalent organic frameworks<sup>11, 12</sup> as precursors for advanced carbons has also become a trend. However, one should keep in mind that all these synthetic efforts are justified under the premise that the performance of the final material in a given application is worth the chemical and energetic effort to produce it.

In this context, the boundaries of the physico-chemical properties of carbonaceous materials are indeed getting broader every year and have long left the classical “physical” range; in other words, they are linked to their chemical composition and not only to their pore network. For instance, it is well known that introducing heteroatoms in a carbon network not only changes the overall conductive behavior but also the material position of the valence and conductive bands and their work function. Thus, the oxidative/reductive, acid/base behavior and chemical

resistance of carbonaceous materials can be modified by adding, for example, nitrogen, boron, sulfur or phosphorus to the precursor and hitherto to the final network. Extreme examples are that of carbon nitrides or boron carbon nitrides (where carbon is only one minor component) which can exhibit different work functions depending on the element composition and structure, and valence bands as low as +2.98V (vs. SHE) were reported.<sup>13</sup> For comparison, ordinary coal, diamond or graphene have an electrochemical electron potential of ca. 0 V while platinum and gold have standard potentials of +1.2V and +1.4V, respectively. This makes of carbonaceous materials real candidates to replace noble scarce metals by doped carbons.<sup>2</sup>

This new era of carbon-based materials must comprise specific compositions and pore networks able to synergistically facilitate the interaction (or even couple) of different substances to the carbon (i.e. solvents, electrolytes, substrates, adsorbates). However, to produce such materials, to our opinion, a series of rules is to be memorized in order to maximize the viability and potential value of the new carbonaceous material:

(1) Minimizing wastes and chemicals used. These two points do not only relate to environmental sustainability but are also a matter of industrial feasibility. Large wastes translate into disposal issues and ultimately into larger costs of the final products which will hinder the large-scale production and commercialization of the material.

(2) Process simplification: large scale applicability of carbon materials will rely on how simple is to adapt a “lab-scale” process to a useful production scale. Thus, the number of steps should be minimized.

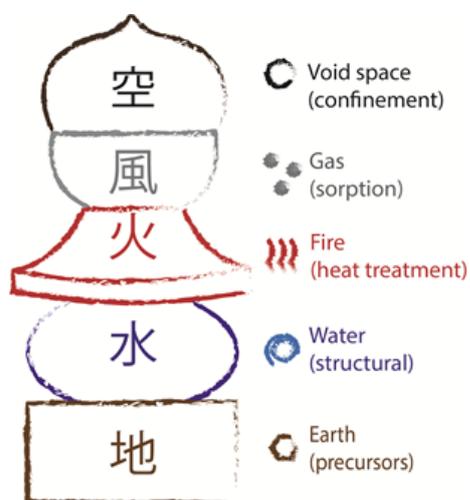
(3) Energy consumption should be minimized. Though it is intimately related to the previous two rules, generating such advanced materials at milder conditions should be a process goal for researchers on its own.

In a nutshell, all the previous statements can be summarize as “keep it simple” since not always the objective can justify the means. But maybe it is even the simplicity which is the real beauty, and all that is only the “*wabi sabi*” of materials creation.<sup>14</sup>

## 3. In the seek for a simple strategy

The use of assembled “nanoparts” towards larger organized nanostructures was named by Aono as nanoarchitectonics.<sup>15, 16</sup> As mentioned above, the concept of nanoarchitectonics has been extensively used in advanced carbonaceous materials preparation: from soft templates to introduce porosity to using small molecules to assemble large structures that were then subjected to carbonization. Herein, we want to put special emphasis on an extreme simplification of nanoarchitectonics in the context of heteroatom/functionalized carbonaceous materials synthesis. This simplify route consist on taking molecules as precursors, i.e. as “nanoparts”.

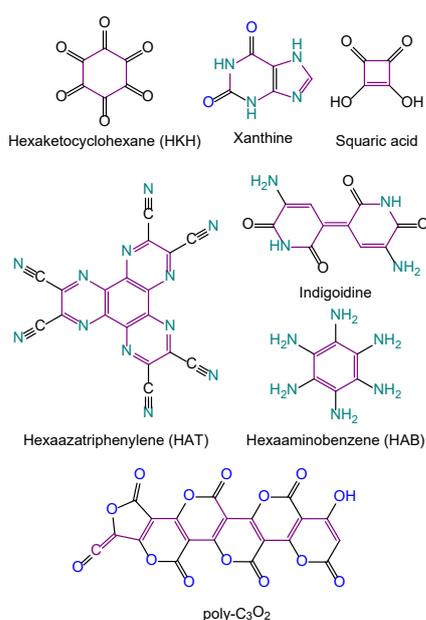
This approach has been used for many years in “on-surface” syntheses (e.g. chemical or physical vapor deposition) and, more recently in cycloaromatization routes to prepare graphene and graphene nanoribbons using, for example, oligoynes, coronenes or polydiacetylenes.<sup>17, 18</sup> However, physical and chemical vapor deposition of carbon materials are energy consuming and/or need of gas phase precursors and



cycloaromatization routes rely on large amounts of organic solvents and/or start from sophisticated precursors. Thus, we will not discuss these techniques in this review since they do not satisfy the above-mentioned criteria for “simplicity”.

Well chosen molecular precursors allow simple encoding of information or element connectivity in a very precise manner, as long as this sequence is not rearranged throughout heat treatment. To choose properly a molecular precursors, different aspects should be considered besides the pre-coded compositional information. First, the low volatility of the precursor throughout condensation can enable large carbon yields. This can be addressed either by molecules with strong intermolecular interactions (e.g. supramolecular structures, multiple H-bonding) or by organic precursors with very low vapor pressure, e.g. ionic liquids (ILS) and deep eutectics. Secondly, the elimination schemes throughout condensation, as in polymer science, should yield thermodynamically stable leaving molecules, such as water, CO and CO<sub>2</sub> (similar to those of typical polymerizations), H<sub>2</sub>S or NH<sub>3</sub> (specific of carbon condensation). And third, the avoidance of very stable “disturbing bonds”, such as aromatic C-H or C-Cl bonds will facilitate condensation towards carbonaceous like structures. Figure 2 shows some of these molecules, partly already from the beginning without any C-H bond, partly with hydrogen only in clear eliminating positions, which are ready for lower temperature condensation towards C-H free sp<sup>2</sup>-conjugated structures. Interestingly, many biomass derived molecules (e.g. carbohydrates, polyketides, or xanthenes) already follow to a large extend these principles, and this is why the manufacture of designer activated carbons is a traditional art.

Carbons derived from task specific ILs are an outstanding example of molecular nanoparts that satisfy many of the above mentioned criteria and, from which no extra solvent or large amounts of energy are needed to produce carbonaceous materials.<sup>19, 20</sup> The preparation of carbon materials from ILs was reviewed by Xie and Zhang et al.<sup>21, 22</sup> Carbon yields when using ILs are improved by (i) selection of ILs containing condensable groups (e.g. cyano groups) that upon heating would



**Figure 2.** Selection of molecular precursors with encoded information.

form stable polymer intermediates preventing formation of volatiles, and (ii) the usage of protic ionic liquids and salts.<sup>23</sup> In order to avoid using expensive ILs (as the cyano/nitrile containing ones are claimed to be), confinement in different structured solids<sup>20, 24-26</sup> and the pre-preparation of poly-ionic liquids was also used.<sup>27, 28</sup> Polymer ionic liquids also allow coating and pre-shaping and the consecutive conversion into carbon while keeping the shape and architecture (i.e. membranes or fibers).<sup>29, 30</sup>

A simpler one-step strategy to generate a low vapor pressure liquid from molecular precursors is using salt melts as solvents and templating agents.<sup>31, 32</sup> Salt melts are mixes of inorganic metallic salts (e.g. NaCl and ZnCl<sub>2</sub>) that melt at relatively low temperature upon heat treatment (e.g. the melting point of a NaCl/ZnCl<sub>2</sub> mix with 0.68:0.32 molar ratio is 260°C<sup>32</sup>) and can be then used to dissolve rather polar organic molecules. The condensation of the precursor promotes the formation of colloidal intermediate structures similar to those obtained in polymerization routes at mild conditions (e.g. resorcinol-formaldehyde like polycondensations). After the synthesis, the salt melts can be washed away from the final product by using water and reused in further synthesis loops, i.e. the solvent is save and sustainable. Besides the already well documented ability to induce large pore volumes in the final carbonaceous materials, these ionic mixtures interact strongly with the molecular precursors and prevent their sublimation. This open the doors for exploring many molecules as carbon precursors that otherwise could not be used. Herein, it is important to highlight that no emphasis was made in describing other well-known templating techniques (e.g. nanohard templating or soft templating) since they have been extensively reviewed elsewhere and they do not follow the above listed rules.

#### 4. Noble carbons

In order to remove connectivity degrees of freedom out of carbonization process and to end up with more homogeneous materials, one can choose an already thermodynamically very stable precursor from which only more stable covalent structures tend to form to satisfy 1<sup>st</sup> law of thermodynamics. As regular structures are usually also more stable than disordered ones, the second cannot form. The exerted control is thereby by knowledge of reaction thermodynamics. As a result, noble carbons are produced. When the starting material contain also large amounts of heteroatoms, only specific mutual motifs prefer to form.<sup>33</sup> Many ILs can be regarded as very stable (i.e. their electrochemical stability window is usually larger than 4 V) and thus, many of the above mentioned carbonaceous materials derived from ILs are de facto noble carbons. This was impressively shown by Yuan who applied a welding torch under oxygen at 1000 °C on a high surface area noble carbon derived from ionic liquids and poly ionic liquids and essentially got no change (Figure 3).<sup>34</sup>



**Figure 3.** Photographs of noble carbon foams resisting a welding flame at 1000 °C. Reproduced with permission from reference<sup>34</sup>

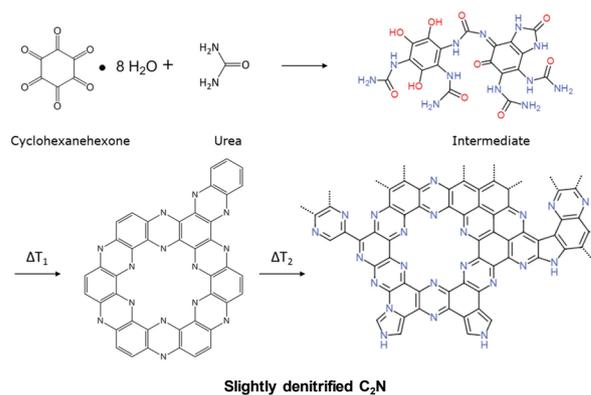
In 2009, Dai group reported that nitrogen doped carbon nanotube arrays exhibited high electrocatalytic activity as catalyst for the oxygen reduction reaction (ORR) pointing at the modification of the chemical nature of the incorporated nitrogen directly affecting the mechanism through which the ORR takes place (i.e. 2- or 4 electron path).<sup>35</sup> Later in 2012, Fellinger et al. reported the preparation of highly selective electrocatalysts from N-butyl-3-methylpyridinium dicyanamide being selective towards the much more valuable  $\text{H}_2\text{O}_2$ , showing that IL derived materials are indeed a new type of carbonaceous materials for “new” chemistry (i.e. very specific functionalities of the material were able to extend ORR).<sup>36</sup>

### 5. Exploring the CN family

The possibility of using molecules as carbon precursors as described above (Figure 2) also opens the path to explore high heteroatom content covalent structures. In the family of carbon nitrides,  $\text{C}_3\text{N}_4$  is without any doubt the most prominent and covered member and illustrates the executed principles very well.  $\text{C}_3\text{N}_4$  can be seen as a graphene structure where every second carbon is replaced by a nitrogen, and this is a heritage on the monomers chosen and the condensation scheme applied, e.g. starting from melamine. The fame of  $\text{C}_3\text{N}_4$  derives from its chemical stability and photoactivity.

However, there are many more of these CN structures possible, and these less explored family member materials such as  $\text{C}_3\text{N}_7$ ,  $\text{C}_3\text{N}_6$ ,  $\text{C}_3\text{N}_5$ ,  $\text{C}_3\text{N}_3$ ,  $\text{C}_3\text{N}_2$ ,  $\text{C}_2\text{N}$ ,  $\text{C}_3\text{N}$  or  $\text{C}_4\text{N}$  are attracting more and more interests as covalent, 2d-designer materials.<sup>37-42</sup> As nitrogen usually comes with three covalent linkages (except when charged), higher amounts of structural nitrogen automatically leads to structures comprising N-lined, electron rich pores (e.g. a line-up of six regular nitrogen atoms, a “N6-cavity” in  $\text{C}_2\text{N}$ ,  $\text{C}_1\text{N}_1$  or porous  $\text{C}_3\text{N}$  or the much larger line up of eighteen nitrogen atoms in  $\text{C}_3\text{N}_5$ ). Such pores nicely underline the *Godai*-principle and make the voids a relevant part of the structure. These pores are able to chelate metallic single atoms, adsorb strongly molecules with electron acceptor groups (i.e.  $\text{CO}_2$  or  $\text{H}_2\text{O}$ ) or act as good catalysts and electrocatalysts, per se. When choosing the molecular precursor properly, such structures can be produced by direct condensation in the presence of salt melts. Fechler et al. reported the preparation of  $\text{C}_2\text{N}$  structures from mixes of cyclohexanehexone and urea in the presence of salt melts (Figure 4).<sup>43</sup> In this synthesis, urea was also used as a part of the eutectic liquid mixture that act as a solvent. More recently, Tian et al. explored the substitution of cyclohexanehexone by the inexpensive, sustainable gallic acid. As a result, oxygen doped  $\text{C}_2\text{N}$  and  $\text{C}_3\text{N}$  like structures were obtained using the salt melt synthetic approach.<sup>44, 45</sup> The introduction of oxygen heteroatoms in the  $\text{C}_2\text{N}$  structures tuned their hydrophilicity enhancing their water uptake. On the other hand, when oxygen was introduced in  $\text{C}_3\text{N}$ , different guest molecules including aspirin could not crystallize due to surface interactions and confinement effects. More interestingly, when using gallic acid and thiourea as precursors,  $\text{C}_2(\text{N}_x\text{O}_y\text{S}_z)_1$  structures were obtained that exhibited record capacitance values when used as supercapacitors electrodes.<sup>46</sup>

Here it is worth mentioning that the high regularity of such structures without outer control is puzzling for someone who is used to characterize activated carbons (in which connectivity motifs are nearly completely disordered). This high structural



**Figure 4.**  $\text{C}_2\text{N}$  synthesis from molecular precursors in the presence of salt melts. Reproduced with permission from reference <sup>43</sup>.

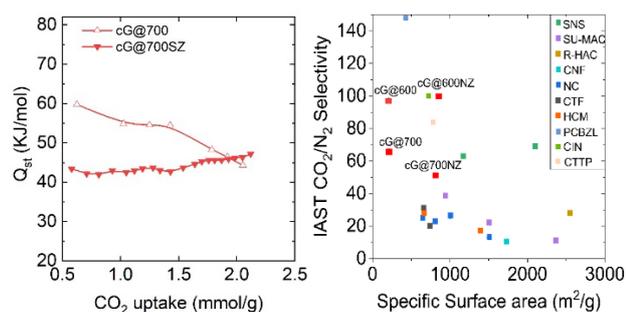
homogeneity was recently reasoned within the concept of noble carbons.<sup>33</sup>

### 6. Nucleobases and xanthenes.

Nucleobases also have to be very thermodynamically stable since they are the chosen molecules to store genetic information in single chemical functionalities. Yang et al. prepared in 2011 advanced nitrogen doped carbonaceous materials using nucleobases as additives to different ILs and carbonizing at  $1000^\circ\text{C}$ .<sup>47</sup> The results showed that the mixtures were able to retain up to 12 wt% of nitrogen at that temperature which is very remarkable for such high carbonization temperatures and points at the large stability of the prepared materials. Inspired by various reports using nucleobases as nitrogen doped carbonaceous precursors,<sup>48, 49</sup> and the concept of noble carbons, we started recently exploring the covalent materials obtained by using xanthenes as “nanoparts” for direct condensation (e.g., guanine and uric acid, among others). These are thereby a group of molecules along the selection rules described above. For example, guanine ( $\text{C}_5\text{H}_5\text{N}_5\text{O}$ ) is a xanthine comprising superbase like moieties (i.e. similar to those present in 1,8-diazabicycloundec-7-ene) as well as a  $\text{C}=\text{O}$  and an amino group that foster H-bond formation which prevents its sublimation.

As already observed by Yang et al.,<sup>47</sup> the nitrogen content of the samples obtained using guanine as carbonaceous precursor is very large. For instance, the final materials keep the original C/N ratio of guanine (i.e. 1) up to  $700^\circ\text{C}$ . The analysis of  $\text{CO}_2$  adsorption showed that the materials were able to adsorb very strongly  $\text{CO}_2$  (heat of adsorption of ca. 59 kJ/mol) and on top very selectively (IAST  $\text{CO}_2/\text{N}_2$  selectivity of up to 91).<sup>50</sup> Even more interestingly, when the same precursor was submitted to heat treatment in the presence of salt melts, the materials exhibited much larger surface area but composition, selectivity and affinity towards  $\text{CO}_2$  was kept, further pointing to the validity of the stability arguments based on precursor thermodynamics (Figure 5).<sup>51</sup>

Uric acid as carbonaceous precursor was condensed at different temperatures ranging from  $500^\circ\text{C}$  to  $900^\circ\text{C}$  in salt melts.<sup>52</sup> With increasing temperature, the atomic C/N ratio decreased (from 1.1 to 5.9) and the total pore volume increased from virtually 0 to  $3.7 \text{ cm}^3/\text{g}$ . The sample prepared at  $800^\circ\text{C}$  turned out to be structurally and functionally self-optimized: it



**Figure 5.** (Left)  $CO_2$  heat of adsorption against  $CO_2$  uptake of samples derived from guanine at  $700^\circ C$  and (right) a plot showing the  $CO_2/N_2$  IAST selectivity of guanine condensates compared within the state of the art of carbon based materials. Reproduced with permission from reference <sup>50</sup>.

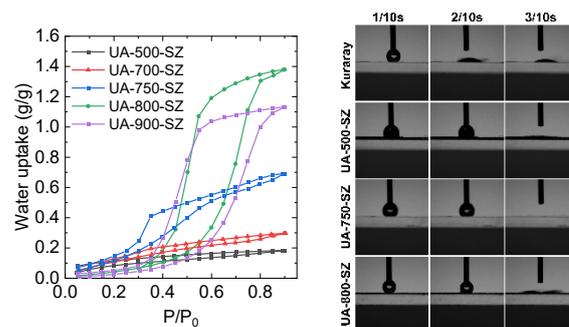
exhibited ultralarge and fast water uptake of up to ca.  $1.4 g_{H_2O}/g_C$  (Figure 6). These values are among the larger values reported for porous materials and similar to those

obtained by highly ordered metal organic frameworks, however at a much higher chemical stability. These results make of the materials promising candidates for their application in adsorption chillers, the long looked for, energy saving alternative for air conditioning.<sup>52</sup>

We also used caffeine ( $C_8H_{10}N_4O_2$ ) as a carbon precursor in the presence of salt melts. Caffeine perfectly exemplify the advantages of using salt melts as solvents and porogens. For instance, caffeine sublimates at relatively low temperature (ca.  $180^\circ C$ ) but, using a  $NaCl-ZnCl_2$  salt melt, caffeine derived noble carbonaceous materials were obtained in a 30% yield when treating the sample at  $800^\circ C$ . The caffeine derived carbons had a C/N ratio of 4 and  $1496 m^2/g$  and were used as electrode for Li-ion capacitors.<sup>53</sup> To be processed in the form of electrodes, the powdered materials were ball milled in stainless steel jars with the rest of the electrode additives. The materials resistance upon oxidation was compared to that of a commercial carbon and a N-doped carbon. While caffeine derived materials were able to stand harsh ball milling conditions without significant oxidation, the commercial not noble carbons were both oxidized and their iron content significantly increased after the treatment. These results point again to the formation of very stable CN structures by simple selection of their molecular precursor.

## 7. New materials, new habits

In the seek to prepare new and more advance carbonaceous materials, an important point to consider is if we go to new chemical properties and performances is: are the processes which were good enough for the old still suitable? In fact, it already turned out many times that this is faulty. For instance, composition analysis by elemental analysis or infrared usually gave wrong compositions and wrong spectra, until we found out by vacuum analysis that absorbed  $CO_2$ , water, and even nitrogen is a part of the 1 bar structure. This is then confirmed by thermogravimetric measurements which gives well defined gas desorption steps of up to 20 % of the weight, partly well above  $100^\circ C$ . It essentially means that the voids become so attractive for matter that gases become a part of the ambient equilibrium structure.<sup>51, 52</sup> The clean system only exists on paper, but is hard to keep clean. Thus, though the characterization techniques to



**Figure 6.** (Left) Isotherms showing record values of water adsorbed in carbonaceous materials derived from uric acid. (Right) Photographs showing the very fast adsorption of water in uric acid derived materials compared to Kuraray carbon. Reproduced with permission from reference <sup>52</sup>.

analyze the new materials must be the same but, special care must be taken in considering adventitious molecules as part of the materials. For example, PHIs are clearly porous and allow a cross-flow of water but the pores are not accessible even to Ar gas sorption, the standard process to characterize very small pores.<sup>54, 55</sup> But, what is the physical chemistry of such water, if it does not boil, and what is its viscosity, what are its electrochemical properties?

A look to nature permeation machinery, i.e. water porines, shows that we are allowed to expect a very unusual but useful bouquet of responses.<sup>56</sup> Similar results are found in confined water in carbon nanotubes,<sup>57</sup> boron nitride tubes<sup>58</sup> and other structured materials.<sup>59</sup> But, are there even smaller voids in such materials only seen in a lower average density but not accessible by molecules at all? Systematic variation of condensation conditions indicated the presence of such “cryptopores” in samples derived from xanthines.<sup>51, 52</sup> and it is a half-open question how the modification of matter with vacuum modifies the polarity and dielectric properties.

## 8. Conclusion and outlook

In search for materials serving the new energy cycles and considering the rare element strategy, porous carbons, or better porous covalent carbon based materials, have turned out to be a very promising choice. This is because carbon is conductive, can be easily changed by doping with other lightweight elements and surface terminating functionalities, and is either a semiconductor or a semimetal with collective electron properties. In addition, there is enough carbon on this planet, even from functional re-growing precursors as biomass. Most importantly, it can be made porous as only little amount of materials can do, and this allows to blend in the *Godai*-element of “void”, i.e. the local absence of matter, a blending which controls practically all materials properties as blending two materials does. This combination was shown to allow a variation of materials space well beyond the limits of classical expectations, i.e. such materials can be (electro)catalyst as such, can be more noble than platinum (and even  $IrO_2$ ), can polarize water and other organic molecules with binding strengths much higher than even metals, and many more.

Another important Japanese concept we wanted to underline is the beauty of simplicity, or the *wabi-sabi* of materials chemistry. In their search for new materials, researchers should always try to keep their synthetic approaches as much as possible simple, as not always the efforts justify the

outcome. The learning of fundamental details about a material can request and permits complexity, but a valuable and also beautiful synthesis is mostly simple. These views are not exclusive for carbon-based materials, but maybe valued in a broader context and we hope they inspire other scientists.

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### References

- 1 in *Book Japan's new international resource strategy to secure rare metals*, ed., ed. by Editor, Ministry of Economy, Trade and Industry City, **2020**, Chap. Chapter.
- 2 E. Nakamura, K. Sato, *Nat Mater* **2011**, *10*, 158-61 10.1038/nmat2969.
- 3 S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai, Y. Tokura, *Nature* **2010**, *463*, 789-92 10.1038/nature08731.
- 4 J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, T. W. Ebbesen, *Angew Chem Int Ed Engl* **2012**, *51*, 1592-6 10.1002/anie.201107033.
- 5 T. Schwartz, J. A. Hutchison, C. Genet, T. W. Ebbesen, *Phys Rev Lett* **2011**, *106*, 196405 10.1103/PhysRevLett.106.196405.
- 6 C. Liang, K. Hong, G. A. Guiochon, J. W. Mays, S. Dai, *Angewandte Chemie International Edition* **2004**, *43*, 5785-5789 <https://doi.org/10.1002/anie.200461051>.
- 7 Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu, D. Zhao, *Angewandte Chemie International Edition* **2005**, *44*, 7053-7059 <https://doi.org/10.1002/anie.200501561>.
- 8 T. Kyotani, T. Nagai, S. Inoue, A. Tomita, *Chemistry of Materials* **1997**, *9*, 609-615 10.1021/cm960430h.
- 9 C. Wang, J. Kim, J. Tang, M. Kim, H. Lim, V. Malgras, J. You, Q. Xu, J. Li, Y. Yamauchi, *Chem* **2020**, *6*, 19-40 <https://doi.org/10.1016/j.chempr.2019.09.005>.
- 10 W. Chaikittisilp, K. Ariga, Y. Yamauchi, *Journal of Materials Chemistry A* **2013**, *1*, 14-19 10.1039/C2TA00278G.
- 11 C. Guo, J. Xu, L.-P. Lv, S. Chen, W. Sun, Y. Wang, *New Journal of Chemistry* **2021**, *45*, 8683-8692 10.1039/D1NJ00610J.
- 12 X. Chen, Y. Xu, F.-H. Du, Y. Wang, *Small Methods* **2019**, *3*, 1900338 <https://doi.org/10.1002/smtd.201900338>.
- 13 P. Giusto, D. Cruz, T. Heil, N. Tarakina, M. Patrini, M. Antonietti, *Adv Sci (Weinh)* **2021**, e2101602 10.1002/advs.202101602.
- 14 A. Juniper, *Wabi sabi : the Japanese art of impermanence*. Editor, First edition. Boston : Tuttle Pub., 2003., **2003**.
- 15 K. Ariga, Q. Ji, J. P. Hill, Y. Bando, M. Aono, *NPG Asia Materials* **2012**, *4*, e17-e17 10.1038/am.2012.30.
- 16 M. Aono, K. Ariga, *Advanced Materials* **2016**, *28*, 989-992 <https://doi.org/10.1002/adma.201502868>.
- 17 A. Jolly, D. Miao, M. Daigle, J.-F. Morin, *Angewandte Chemie International Edition* **2020**, *59*, 4624-4633 <https://doi.org/10.1002/anie.201906379>.
- 18 S. Rondeau-Gagné, J.-F. Morin, *Chemical Society Reviews* **2014**, *43*, 85-98 10.1039/C3CS60210A.
- 19 J. S. Lee, X. Wang, H. Luo, S. Dai, *Advanced Materials* **2010**, *22*, 1004-1007 <https://doi.org/10.1002/adma.200903403>.
- 20 J. P. Paraknowitsch, J. Zhang, D. Su, A. Thomas, M. Antonietti, *Advanced Materials* **2010**, *22*, 87-92 <https://doi.org/10.1002/adma.200900965>.
- 21 Z.-L. Xie, D. S. Su, *European Journal of Inorganic Chemistry* **2015**, *2015*, 1137-1147 <https://doi.org/10.1002/ejic.201402607>.
- 22 S. Zhang, K. Dokko, M. Watanabe, *Materials Horizons* **2015**, *2*, 168-197 10.1039/C4MH00141A.
- 23 S. Zhang, M. S. Miran, A. Ikoma, K. Dokko, M. Watanabe, *Journal of the American Chemical Society* **2014**, *136*, 1690-1693 10.1021/ja411981c.
- 24 Z. Li, G. Li, L. Jiang, J. Li, G. Sun, C. Xia, F. Li, *Angewandte Chemie International Edition* **2015**, *54*, 1494-1498 <https://doi.org/10.1002/anie.201409579>.
- 25 B. Qiu, C. Pan, W. Qian, Y. Peng, L. Qiu, F. Yan, *Journal of Materials Chemistry A* **2013**, *1*, 10.1039/c3ta10774d.
- 26 Y. Ding, X. Sun, L. Zhang, S. Mao, Z. Xie, Z.-W. Liu, D. S. Su, *Angewandte Chemie International Edition* **2015**, *54*, 231-235 <https://doi.org/10.1002/anie.201408201>.
- 27 J. Yuan, C. Giordano, M. Antonietti, *Chemistry of Materials* **2010**, *22*, 5003-5012 10.1021/cm1012729.

- 28 J. Yuan, H. Schlaad, C. Giordano, M. Antonietti, *European Polymer Journal* **2011**, *47*, 772-781  
10.1016/j.eurpolymj.2010.09.030.
- 29 J. Yuan, A. G. Márquez, J. Reinacher, C. Giordano, J. Janek, M. Antonietti, *Polymer Chemistry* **2011**, *2*, 1654-1657  
10.1039/C1PY00196E.
- 30 H. Wang, S. Min, C. Ma, Z. Liu, W. Zhang, Q. Wang, D. Li, Y. Li, S. Turner, Y. Han, H. Zhu, E. Abou-Hamad, M. N. Hedhili, J. Pan, W. Yu, K. W. Huang, L. J. Li, J. Yuan, M. Antonietti, T. Wu, *Nat Commun* **2017**, *8*, 13592  
10.1038/ncomms13592.
- 31 X. Liu, N. Fechner, M. Antonietti, *Chem Soc Rev* **2013**, *42*, 8237-65 10.1039/c3cs60159e.
- 32 N. Díez, A. B. Fuertes, M. Sevilla, *Energy Storage Materials* **2021**, *38*, 50-69  
<https://doi.org/10.1016/j.ensm.2021.02.048>.
- 33 M. Antonietti, M. Oschatz, *Advanced Materials* **2018**, *30*, 10.1002/adma.201706836.
- 34 Y. Men, M. Siebenbürger, X. Qiu, M. Antonietti, J. Yuan, *Journal of Materials Chemistry A* **2013**, *1*, 10.1039/c3ta12302b.
- 35 K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* **2009**, *323*, 760 10.1126/science.1168049.
- 36 T. P. Fellingner, F. Hasche, P. Strasser, M. Antonietti, *J Am Chem Soc* **2012**, *134*, 4072-5  
10.1021/ja300038p.
- 37 K. Sakaushi, M. Antonietti, *Bulletin of the Chemical Society of Japan* **2015**, *88*, 386-398  
10.1246/bcsj.20140317.
- 38 I. Y. Kim, S. Kim, S. Premkumar, J.-H. Yang, S. Umaphathy, A. Vinu, *Small* **2020**, *16*, 1903572  
<https://doi.org/10.1002/smll.201903572>.
- 39 I. Y. Kim, S. Kim, X. Jin, S. Premkumar, G. Chandra, N. S. Lee, G. P. Mane, S. J. Hwang, S. Umaphathy, A. Vinu, *Angew Chem Int Ed Engl* **2018**, *57*, 17135-17140  
10.1002/anie.201811061.
- 40 G. P. Mane, S. N. Talapaneni, K. S. Lakhi, H. Ilbeygi, U. Ravon, K. Al-Bahily, T. Mori, D.-H. Park, A. Vinu, *Angewandte Chemie International Edition* **2017**, *56*, 8481-8485  
<https://doi.org/10.1002/anie.201702386>.
- 41 S. N. Talapaneni, G. Singh, I. Y. Kim, K. AlBahily, A. H. Al-Muhtaseb, A. S. Karakoti, E. Tavakkoli, A. Vinu, *Adv Mater* **2020**, *32*, e1904635 10.1002/adma.201904635.
- 42 S. Kim, M. Hankel, W. Cha, G. Singh, J. M. Lee, I. Y. Kim, A. Vinu, *Nano Energy* **2020**, *72*, 104702  
<https://doi.org/10.1016/j.nanoen.2020.104702>.
- 43 N. Fechner, N. P. Zussblatt, R. Rothe, R. Schlögl, M.-G. Willinger, B. F. Chmelka, M. Antonietti, *Advanced Materials* **2016**, *28*, 1287-1294 10.1002/adma.201501503.
- 44 Z. Tian, N. Fechner, M. Oschatz, T. Heil, J. Schmidt, S. Yuan, M. Antonietti, *Journal of Materials Chemistry A* **2018**, *6*, 19013-19019 10.1039/C8TA03213K.
- 45 Z. Tian, T. Heil, J. Schmidt, S. Cao, M. Antonietti, *ACS Applied Materials & Interfaces* **2020**, *12*, 13127-13133  
10.1021/acsami.9b20478.
- 46 Z. Tian, F. Lai, T. Heil, S. Cao, M. Antonietti, *Science China Materials* **2020**, *63*, 748-757 10.1007/s40843-019-1254-9.
- 47 W. Yang, T.-P. Fellingner, M. Antonietti, *Journal of the American Chemical Society* **2011**, *133*, 206-209  
10.1021/ja108039j.
- 48 J. Maruyama, I. Abe, *Chem Commun (Camb)* **2007**, 2879-81 10.1039/b703723f.
- 49 J. Maruyama, N. Fukui, M. Kawaguchi, I. Abe, *Journal of Power Sources* **2009**, *194*, 655-661  
10.1016/j.jpowsour.2009.06.048.
- 50 J. Kossmann, D. Piankova, N. V. Tarakina, J. Heske, T. D. Kühne, J. Schmidt, M. Antonietti, N. López-Salas, *Carbon* **2021**, *172*, 497-505  
<https://doi.org/10.1016/j.carbon.2020.10.047>.
- 51 J. Kossmann, T. Heil, M. Antonietti, N. Lopez-Salas, *ChemSusChem* **2020**, 10.1002/cssc.202002274.
- 52 J. Kossmann, R. Rothe, T. Heil, M. Antonietti, N. López-Salas, *Journal of Colloid and Interface Science* **2021**, *602*, 880-888 <https://doi.org/10.1016/j.jcis.2021.06.012>.
- 53 I. K. Ilic, E. Lepre, N. López-Salas, *ACS Applied Materials & Interfaces* **2021**, *13*, 29612-29618  
10.1021/acsami.1c06013.
- 54 D. Dontsova, C. Fettkenhauer, V. Papaefthimiou, J. Schmidt, M. Antonietti, *Chemistry of Materials* **2016**, *28*, 772-778 10.1021/acs.chemmater.5b03722.
- 55 K. Xiao, P. Giusto, L. Wen, L. Jiang, M. Antonietti, *Angew Chem Int Ed Engl* **2018**, *57*, 10123-10126  
10.1002/anie.201804299.
- 56 P. Agre, *Angew Chem Int Ed Engl* **2004**, *43*, 4278-90 10.1002/anie.200460804.

57 J. Köfinger, G. Hummer, C. Dellago, *Physical Chemistry Chemical Physics* **2011**, *13*, 15403-15417  
10.1039/C1CP21086F.

58 C. Y. Won, N. R. Aluru, *Journal of the American Chemical Society* **2007**, *129*, 2748-2749 10.1021/ja0687318.

59 I. Kocsis, Z. Sun, Y. M. Legrand, M. Barboiu, *npj Clean Water* **2018**, *1*, 10.1038/s41545-018-0013-y.