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A Personal Declaration on the Working Philosophy of my department

After being a sufficiently successful scientist for so many years and facing the last 15 years of the very active part of my business life, I decided to devote these remaining years to some real problems of humankind, at least those we can solve with a creative materials solution.

Clean water, energy, CO₂ remediation and carbon cycle, or just a sustainable supply of society with chemicals and materials: The possibilities seemed to be endless to commit yourself. However, after some years of working, I found out that all those problems are at least interconnected and only apparently diverse: Having the correct framing or view on the problem, all these issues compose a very cohesive topic: a chemistry for at least the next 20 years in constructive dialogue with Nature. This sounds maybe too idealistic, but has a very realistic core and perspective, and being a positive idealist is a part of my nature.

The following topics will be discussed in detail, and the tight interdependencies which make the diverse projects a joint cohesive approach will be explained.

- 1) Artificial photosynthesis with cheap, sustainable materials
- 2) The biorefinery concept: solvothermal making fuels and value chemical from biomass waste
- 3) Green and biodegradable polymers
- 4) Hydrothermal carbonization: bringing fertility to the planet while lowering atmospheric CO₂ levels
- 5) New electrocatalysts: decentral processes for water cleaning and chemical production
- 6) Clean water and air: developing new sorbents for specific adsorption and removal
- 7) Sustainable Materials for energy conversion and storage
- 8) New structural and insulation materials based on wood waste

Young scientists in my department are always allowed to develop their profile also along own ideas and open opportunities, but of course being aligned with at least some targets and committed to the future accelerates synergies.

- 1) Artificial photosynthesis with cheap, sustainable materials

I think our 2009 paper (A metal-free polymeric photocatalyst for hydrogen production from water under visible light, X Wang, K Maeda, A Thomas, K Takanabe, G Xin, JM Carlsson, K Domen, M. Antonietti, Nature Materials 8 (1), 76-801) is meanwhile a classic, but the fact that ordinary polymeric carbon nitride, a polymer already Justus Liebig and Linus Pauling were fascinated about, is a semiconductor turning sun light into hydrogen and oxygen came to most of the people as a total surprise. Carbon nitride is in addition most sustainable: it can be made from simple urea by condensation for about 1 €/kg, is super-stable and essentially non-toxic. As current systems have reached (in our hands as a firsthand experience, but also in many other labs) and apparent quantum yield of AQY = 0.56 for the complete Photosynthesis cascade (the remainder also being imperfect process engineering, such as use and coupling in of light), the challenges have moved from light capture and charge dissociation towards active sites (indeed often solved) to the balance of process rates and system engineering.

The 56 % AQY are realized by a very fast hole acceptor, but the usually considered water oxidation is a complicated 4 electron process, admittedly very slow, and determines the overall performance. I regard meanwhile oxygen liberation as a “false positive” lead of Nature: oxygen does not bring any “value” for e.g. a company to run the technology, and other 1-electron hole acceptors enable much higher rates, but also a product value at the same time. Instead of only ONE product, i.e. hydrogen, mankind could use two or three, thus leveraging the practical application of such systems. We are currently working on a number of those options, with good interim results.

- Creating higher value products which can partly not been made otherwise. Hantzsch –Ester synthesis, cycloadditions, photoketalisation, thiamide synthesis, photohalogenation are just a few of the options currently published by the scientists of my group, and essentially all of these reactions expand the toolbox of organic chemistry while running all operation in a most green and sustainable fashion. This is indeed an unexpected harvest obtain from the wish to mimic photosynthesis with most simple systems!

Another exciting option comes from the cooperation with the Gilmore/Seeberger group who are currently reinventing flow chemistry to drive light reactions with highest performance. The combination of those machines with our target-reaction designed, selective, heterogeneous catalysts has indeed high immediate potential-

- 2) The biorefinery concept: solvothermal generation of fuels and value chemical from biomass waste

An obvious approach to lower CO₂- footprint and to increase the sustainability of compounds is the biorefinery, i.e. the conversion of plant products (and side-products) in a completed usage cascade to generate value chemicals. Fermentation of bioethanol or lactic acid are along those lines, but as typical 1.Generation Biorefinery products they are at the borderline of being not sustainable when doing a fair ecobalance. Even highly optimized bioethanol production recovers only 45 % of the original energy stored in the primary sugar, and as all those sugars to be fermented are edible, we run into the so called food-fuel competition.

On the contrary to those approaches, my group is doing biorefining under solvothermal conditions, e.g. in superhot water under pressure, and typical reactions turn then very fast and very efficient. Recent cases include a 3 min synthesis of lactic acid by a highly efficient splitting of C6-sugars or a close-to-100 % energy yield conversion of carbohydrates into a liquid combustion fuel in two steps under flow conditions with an overall reaction time of 40 min. Such processes of course bear the chance to alter the whole combustion fuel scenario, as liquid fuels can then be generated decentrally in a highly energy efficient fashion, beating all current solutions by at least a factor of 2.5. A key enabler in these processes and the source of our originality is the creation of catalysts and catalyst supports being stable against biomass functionality and especially water under those conditions, and classical catalysts indeed disintegrate in superhot water with the same speed as the biomass.

Another focus molecule is lignin, which is currently produced as a side stream of paper and cellulose productions in amounts of ca 60 Gt/year, and there would be much more available if isolation would meet a market. We developed a number of disintegration processes to access plasticizers, antioxidants, or surfactants on the base of this chemical, but a key target was found to be the oligophenolic products for sustainable gluing purposes. Such products could potentially replace

bisphenol-A, alkylphthalates and methylparabenes from consumer products, while being less toxic and endocrine disruptive. This is also the base of the remix wood project discussed below.

3) Green and biodegradable polymers

Very close to this subject, but coming with a different background of expertise is our work on biodegradable polymers. Mass polymers are made in largest amounts (ca 250 Mt/year) so that their generation from regrowing, carbon neutral resources would be a worthy endeavor. However, the biggest problem of consumer plastics is not in the materials as such, but human misbehavior. The great pacific garbage patch, but also microplastic in our sweet-water lakes seriously harm the aquatic fauna and are simply a shame to look at. As I am less positive about correcting human behavior, this means that disintegration in misuse must be a built-in property of modern green polymers. Especially when reading chapters 1 and 2 above, the chances are about endless. Polyfurane esters or polylactid acid are known technological solutions, but biorefinery approaches can improve such polymers and especially make them cheaper than the petrochemical alternatives (while not believing in human behavior, I believe in the power of better economy...). Beside polyesters, sugar chemistry is the choice of nature for packaging, and here, the options for polymer chemistry have been explored for a long time (e.g. cellophane), but were “forgotten” due to petrochemical “mainstreaming” and lobbying. One can envision poly-(carbohydrate esters) and similar chimera materials, where the esters take care of degradation, while the carbohydrates provide secondary interactions and stability by mesophase formation.

Another option is to bring in inherent photochemical sensitivity into the polymers, and if it is by an added photocatalyst, as discussed above.

4) Hydrothermal carbonization: bringing fertility to the planet while lowering atmospheric CO₂ levels

Currently, the world crude oil production amounts to about 4 Billion tons or 4 km³ / year. (Official Energy Statistics of the US Government, <http://www.eia.doe.gov/ipm/supply.html>). Assuming a price of 70 \$/barrel, this corresponds to a value of 1.76 Trillion US-\$. As essentially all oil ends up –sooner or later- as CO₂ in the earth system, the opposite side of this economy is the generation of an excess 12.5 Billion tons CO₂/year, with the known implications on the world climate. The overall CO₂ offset is even larger (we also burn coal and make for instance steel and cementum), and 9 Gt/year carbon equivalents is a fair estimate. The conventional discussion to handle this problem is to replace a minor part of the fuel and/or energy production by biomass schemes. We sign that point, as discussed above, but it is in this context to be stated that biological fuel production schemes however can only lower the further increase of CO₂, but cannot compensate for the already and still emitted CO₂ from fossil resources.

Concerning the climate change and the role of CO₂ within, it would therefore be highly desirable not only to slow down further CO₂ emission, but even to invert the current development by sequestering the atmospheric CO₂ of former years of industrialization. The biggest carbon converter with the highest efficiency to bind CO₂ from the atmosphere is certainly biomass. A rough estimate of terrestrial biomass growth amounts to 118×10^9 tons/year, when calculated as dry matter, i.e. more than enough to balance anthropogenic CO₂ emissions. Biomass however is just a short term, temporary carbon sink, as microbial decomposition exactly liberates the amount of CO₂ formerly bound in the plant material. Nevertheless, as biomass contains about 0.4 mass equivalents of carbon,

removal of 8.5 % of the freshly produced biomass from the active geosystem would indeed compensate for the complete CO₂ liberation from oil, all numbers calculated per year. To make biomass as a carbon sink “effective”, the carbon in the biomass has to be fixed by “low-tech” operations, and coal formation is certainly one of the natural sinks being active in the past on the largest scale.

Natural coalification of biomass takes place on the timescale of some hundred (peat) to hundred million (black coal) years. Due to its slowness, it is usually not considered in renewable energy exploitation schemes or as an active sink in CO₂ cycles. Nevertheless, it is obvious that carbon fixation into coal is a lasting effort, as brown or black coal (contrary to peat) are obviously practically not biodegradable. Sufficient chemical “condensation” is mandatory for the purpose of carbon fixation. Hydrothermal carbonization (HTC) is an especially promising process for this carbon sequestration process. First experiments were carried out by Bergius and Specht, who described already in 1913 the hydrothermal transformation of cellulose into coal like materials at temperatures between 150 ° and 350 °C. We work now for some years on this simple process, found a variety of components to accelerate coalification, generated exciting and also useful nanostructures, but also analyzed if the presence of ternary components in complex biomass (such as orange peels or oak leaves) seriously alters the decompositions schemes. Unexpectedly, rather an improvement of properties of the carbonaceous structures for certain applications was found, e.g. smaller structural size, higher hydrophilicity of the surfaces and higher water capillarity.

The described accelerations of HTC for coalification by a factor of 10⁶ – 10⁹ under rather soft conditions down to the hours scale however make hydrothermal carbonization (HTC) to a considerable, technically attractive alternative also for sequestration of carbon from biomass on larger and ultra-large scales. Besides that, HTC has a number of other practical advantages. HTC inherently requires wet starting products or biomass, as effective dehydration only occurs in the presence of water, plus, the final carbon can be easily filtered off the reaction solution. That way, complicated drying schemes and costly isolation procedures can conceptually be avoided. In addition, most of original carbon stays bound to the final structure. Carbon structures produced with that route – either for deposit or materials use- are therefore carbon negative and most CO₂-efficient.

For a negative atmospheric CO₂ – balance, the generated carbonaceous materials have to be deposited on the large scale. The most attractive application with a high secondary value is the use as a water- and ion-binding component to improve soil quality. “Black or carbonaceous soil” is presumably the largest active carbon sink of the earth system, and soil researchers already proposed “terra preta”, i.e. artificial coal enriched soil, as a potential carbon sink of global dimensions, improving at the same time soil quality and plant growth. Spending just 10% of our expenses for oil for the global CO₂ sequestration would compensate for carbon fixation costs of 44 \$/ ton, a target, which can to our opinion be quite easily met (HTC is essentially just heating an aqueous dispersion, where even the energy is generated by the process itself) and does not consider the added value for the geosystem or agriculture.

For the final material use, e.g. as a fertilizing soil additive, the carbonaceous material not only has to have a distinct chemical structure (the molecular level) but also a specific structural texture, i.e. nanoarchitecture and surface chemistry. For soil- or sorption use–beside being free of toxic or cancerogenic compounds- the carbonaceous product has to be water-wettable and highly porous.

This is an attractive task for hydrothermal carbon chemistry, involving a mind-set where carbonization is nothing but a polycondensation procedure (the “chimie douce” of carbon), which is still full of novel possibilities and tasks.

Most of the academic problems in this process have been indeed solved, and it is now a matter of technology transfer and creating appropriate outside business models.

5) New electrocatalysts: decentral, small scale processes for water cleaning and chemical production

Throughout our work with hydrothermal carbonization and carbon synthesis in general, we quickly developed chemical tools to change local aromatization schemes and heteroatom functionalization/doping. For electrocatalysis, the systems of course have to be electronically conductive, but some systems allow to move the point of beginning electronic conductivity rather low in temperature schemes (for thermal carbon condensation, 700 °C is low.)

These carbons are - even without metals- effective electrocatalysts for a variety of reactions, well known the case of the oxygen reduction reaction. The real good thing is that they are cheap, non-toxic, extremely stable, and can be put into the hand of any citizen for chemical generation. Although oxygen evolution from water is nice and a schoolbook electrochemistry reaction, it does not come with any added value, as oxygen from the atmosphere is otherwise free. This is why we focus on novel, more beneficial oxidation reactions, such as urea oxidation (disinfection..), biomass and carbon oxidation (drug removal, waste water treatment), H₂O₂ synthesis (disinfection, cleaning agent), and some other stronger oxidants with an even larger application range.

The sustainable aspect is that such electrochemical devices can be incorporated in any water tubing, washing machine, or similar household technical devices, and that consumer chemicals can be made by the consumers on demand without even seeing them.

6) Clean water and air: developing new sorbents for specific adsorption and removal

Beyond, but also in support of electrochemistry, also sorption can help to refine water and air quality. Activated carbons are well known, the chemical content of tea filter cartouches, but the classical versions are not powerful and especially non-selective enough.

This of course is something a materials chemist can change: understanding the physical chemistry of adsorption and understanding for instance multifunctionality and multipodal binding, we can plan to make an ion exchange filter with leaves the good and healthy ions in water, but takes lead, mercury, arsine, or cadmium with the strongest possible force. In gas separation, we are still not able to have an adsorbent which binds CO₂ from air, as the required selectivity of 1500 of CO₂/N₂ is present in Rubisco, but in no men-made materials. The number of such chemically specific sorption cases in demand is apparently endless and just depends on your imagination, and each realization of those separations is a massive step forward. Imagine if we could simply separate helium from methane (two essentially inert gases): the helium demand problem of humankind would be solved.

This is why developing specific sorption materials based on carbon and carbon nitrides, and pore design based on pore size and the inner “functional decoration” is the central tool. An interesting possible extension we only conceptualize about is the combination of liquid absorption and solid adsorption, which could lead in good cases in a combination of the favourable figures of merit.

7) Sustainable Materials for energy conversion and storage

The energy landscape is one of those technical issues which changed the most since I have started to study sciences. Due to the arrival of wind and solar energy, we meanwhile give away excess energy for free, and energy storage has turned to a main issue to drive the field forward, say for the electrification of cars.

The main problem of current electricity carriers is indeed economy and sustainability: the ability to store 1 kWh of electric energy in a lithium ion battery is about 500 €/kWh, with about 1000 – 3000 loading cycles. This makes the storage of 1 kWh 4 times more expensive than its generation. In addition, ecobalancing the production of a battery is not very favourable, and some serious studies say that an electric car has to be run for 8 years until the original CO₂ footprint of fabricating the battery is compensated. CO₂-free energy for loading assumed. This makes the forced electrification of private transport a big dogmatic charade, and more sustainable energy storage materials are eagerly needed.

This problem is broadly discussed in the scientific public, and moving from lithium to sodium and magnesium is a possible step in the right direction. Our own expertise of course goes in a different direction and employs sustainable carbons and polymers as energy storage media. On the anode side, it is my opinion that for batteries, pure metal or metal-carbon framework electrodes will quickly take over (the nanocarbon framework to drive rate performance and to avoid dendrite formation), while on the cathode side, surface ion adsorption on carbon and polymer frameworks might complement the classical (very limited) inclusion processes. Literature shows that lignin is such a redox active ion adsorption material, which of course adds sustainability. Flow batteries go into the same direction: they have not necessarily a higher charge density, but can store every electron in a cheaper polymer with less “engineering infrastructure”, i.e. they lower price and improve applicability.

A very exciting topic for us are supercapacitors, where energy is stored both in the compression of the electric double layer as well as in Faradayic surface reactions. This principle promises very low prices, cheap organic surface reactions, but also relates on the ability to make carbon frameworks with controlled porosity and surface functionality, which is described above for the other purposes. Especially ionic liquids have a high operation voltage and interesting secondary possibilities, and some first of our lab supercapacitor experiments favorably compete with the Li ion battery technology.

8) New structural and insulation materials based on wood waste

It was already mentioned that lignocellulosic biomass represents a major feedstock of chemicals on this planet, much bigger than the whole crude oil industry, with 1 Gt/a of sugar cane leftovers (“bagasse”) created only in Brazil in an industrially useful fashion. It was also already discussed that we produce 150 Mt/a of cellulose fibers from wood in paper factories, with at least 60 GT/a of lignin being essentially only burned as it has no other use. All that of course composes the feedstock of a future biorefinery, but some more clever coworkers of mine put themselves the question of this cannot be used as a material as such. There are of course a number of waste paper or wastewood products, but plywood or fiber boards are not really made from low quality cellulose or lignin.

This is how we came up with the idea of remixed wood, where the involved persons currently start to create a company before the science behind is to be published. The story is however very nice and should be told nevertheless.

Let us assume by concept that we could separate any lignocellulosic biomass into its three major components cellulose fibers, hemicelluloses, and lignin. This is of course done – more or less- in any paper factory. The novel idea is that you now remix/reconstitute the original wood structure, however under control of porosity and thereby density, pore structure as such and potentially fibril orientation. YOU would end with wood-a-like materials, however with a much broader property range, covering from ironwood (i.e. very dense, very hard wood types) to cork (= very porous, insulating wood foam) a possible and previously impossible species. Chemically, such a wood would be indistinguishable from wood, and it would be a carbon-negative, atmospheric CO₂ – binding product. As we would add other, not woody but sustainable products such as silica and clay on top, the typical technical problems coming with wood, such as water-uptake and swelling, biofouling, and of course combustibility could be solved, i.e. remix wood is not only wood, but a technologically improved version addressing the weaknesses of the natural product, while keeping (hopefully) most of its strengths.

In the lab, were realized larger parts of this concept and already created very hard material species the hardness of which is clearly beyond ordinary wooden plates usually used for furniture and architecture, but also very porous species with low combustibility, but hydrophobicity and very low heat permeation coefficients. The rest is now in the hands of the young entrepreneurs to explore market perspectives in a variety of application ranges.

Guestbook

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