CARBON NANOMATERIALS FOR A CLEAN ENERGY AND CHEMICAL PRODUCTION

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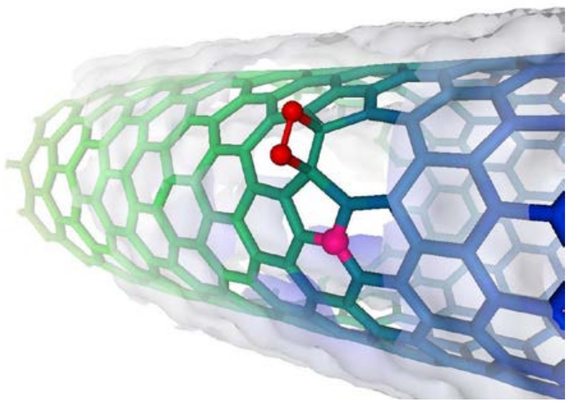

O_2 activation on N-doped carbon nanotubes for oxygen reduction reaction in PEM fuel cells

Nanocarbons offer many novel possibilities to develop advanced catalysts, catalytic electrodes and materials for clean energy. This contribution briefly introduces some aspects of the potentialities and open issues, in carbon nanomaterials for applications going from energy devices (to enable a larger use of renewable energy sources) to catalysis for cleaner processes and the use of alternative or renewable raw materials in chemical production. Nanocarbons can be considered a new class of materials for catalysis and clean energy, where their nano-engineering (from the control of nano-dimension to their doping/modification to insert specific surface reactive or functional groups) opens new possibilities to address the societal challenges for clean energy and chemical production

Nanomateriali di carbonio per la produzione di prodotti chimici ed energia pulita
I nanomateriali a base di carbone offrono molte possibilità per sviluppare nuovi catalizzatori avanzati, elettrodi catalitici e materiali per l'energia pulita. Questo contributo introduce brevemente alcuni aspetti delle potenzialità e dei problemi aperti in questi nanomateriali per applicazioni che vanno dai dispositivi per energia (per consentire un uso più ampio di fonti di energia rinnovabile) alla catalisi per processi più puliti e per l'utilizzo di materie prime alternative o rinnovabili. I nanomateriali a base di carbone possono essere considerati una nuova classe di materiali per la catalisi e l'energia pulita, dove la loro ingegnerizzazione a livello di nanoscala (dal controllo della nano-dimensione al loro doping/modifica per inserire specifici gruppi reattivi o funzionali sulla superficie) apre nuove possibilità per affrontare le sfide sociali per l'energia pulita e la produzione chimica sostenibile.

Introduction

Moving to a new and sustainable scenario for the low-carbon chemical and energy production[1,2] with minimized use of fossil fuels, requires a great effort to develop new materials and catalysts enabling this transition. Carbon nanomaterials, indicated also with the term nanocarbon to differentiate them from more conventional type of carbon materials such as active carbon, carbon paper/cloth, carbon glassy, etc., play a key role in this perspective[3,4,5]. They may be considered still one of the most successfully market examples of nanotechnologies. Carbon nanotubes (CNTs), for example, with their unique and extraordinary properties such as high electrical and thermal conductivities, very small diameters, large aspect ratios, outstanding mechanical properties and not least excellent price-performance ratio, make them suitable in many applications, from electronic to chemical/electrochemical devices.
Currently, the global CNTs market is growing at a Compound Annual Growth Rate (CAGR) of about 10%, reaching a global market of about $1.1 billion by 2016 (about 95% formed by multi-walled carbon nanotubes - MWCNTs)[6]. They are used in a wide range of industries including plastics and composites, electrical and electronics, and energy as well. However, there are today grounds for concern for the future of the market due to the dismissing of production from large producers such as Bayer, and reposition of the production in another large manufactures such as Nanocyl. These two are between the four major producers of CNTs (together with CNano Technology Ltd.

and Showa Denko K.K.), holding together the majority of the market share (66%). At the same time, large expectations are for "new" nanocarbon materials, particularly the graphene family. There is large market "excitement" on this topic, with companies on the market multiplying every year and about US$60 million of investment in private graphene companies over the years. Many academic initiatives, from the creation of various dedicated laboratories to large initiatives such as the EU flagship on graphene, are also pushing research in this area. A recent report by the IDTEchEx company[7] (specialized in market research and business intelligence on emerging technologies) on graphene market opportunities reported a US$20 million value in 2014 expected to grow to about US$390 million in 2024 at the material level. However, the report warns about serious market aspects actually inhibiting the realization of this market potential:

- graphene is still in search of its killer application that delivers a unique value proposition, e.g. the commercialization process remains a substitution game;
- graphene can target a broad spectrum of applications including energy storage, composites, functional inks, electronics, etc., but manufacturing techniques will be different for each sector, resulting in market fragmentation;
- there are technical hurdles in many possible applications preventing the full utilization of graphene potential; actual solutions are still largely not cost-competitive over alternatives (for example, the use of activated carbon in energy storage devices) or alternative less-costly materials are under development, for example for transparent conductive films.

These aspects indicate that the growing rate and market dynamics for graphene are probably overestimated and it is necessary to tune better R&D with respect to the critical hurdles of the market rather than only on scientific aspects. It is also evident how graphene is part of the general area of carbon nanomaterials and it is a reductive approach to focus only on graphene. This contribution aims to briefly introduce some aspects of the potentialities, but also still open issues, in carbon nanomaterials for applications going from energy devices (to enable a larger use of renewable energy sources) to catalysis for cleaner processes and the use of alternative or renewable raw materials in chemical production.

The evolving scenario for carbon nanomaterials

Carbon is used from decades as catalyst supports (mainly in the form of active carbons), to prepare electrodes and in many commercial energy devices (in batteries, for example). However, it may be also considered a new nanotech material, for the considerable recent advances in tailored synthesis, modification, characterization and nano-engineering[3-5,8,9,10,11,12,13,14,15,16,17,18]. Nanocarbons indicate here carbon materials having a tailored nanoscale dimension and functional properties critically depending on their nano-scale features and architecture[4]. With respect to conventional carbon materials, which include active carbons and related materials as well as the different types of carbon materials used currently in electrode applications (graphite, glassy carbon, carbon black, carbon cloths, etc.[19,20]), nanocarbons introduce new possibilities deriving from both their nanoarchitecture and the presence of active sites (or surface centers modifying the nature of supported metal particles) specifically related to their nano-dimension. We may distinguish three generations of materials in the development of nanocarbons (Fig. 1):

- the 1st generation, composed by the three basic type of nanocarbon materials (fullerene, graphene, and carbon nanotube - CNTs) and the various novel simple morphology carbon materials which may derive from them: carbon quantum dots, nanohorn, nanofiber, nanoribbon, nanocapsulate, nanocage and other nanomorphologies. These nanocarbons have a low dimensionality and morphology-defined properties;
- the 2nd generation of nanocarbon materials, deriving from the first generation, but in which the electronic structure is tailored by introducing heteroatoms (dopants) in order to tune their properties. A further level of control in the characteristics of these nanocarbons is introduced during the synthesis or by post-synthesis treatments;
- the 3rd generation of nanocarbon materials, where the development of hybrid and/or hierarchical systems (nano-engineering the architecture of the materials at the nano-scale level[21]) allows a further level of control. The concept of nano-architectured materials goes beyond the possibility of having a better mass transfer, which is the classical motivation to realize hierarchical structured catalysts.

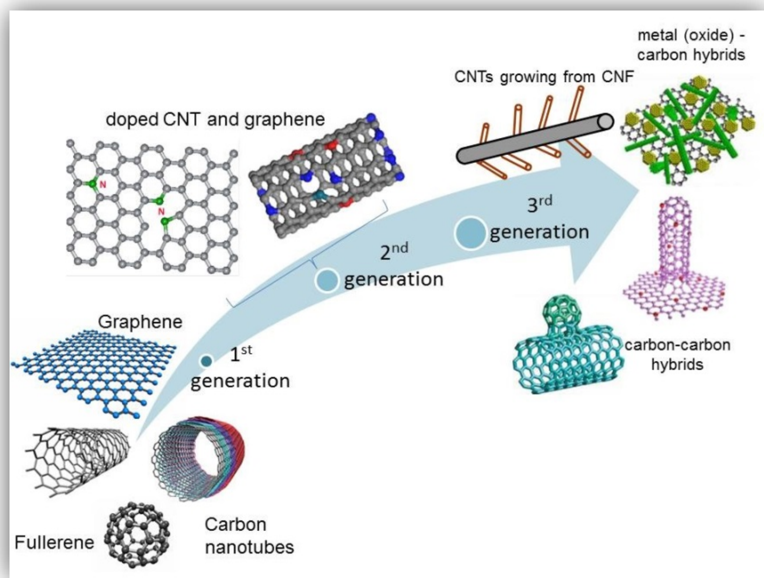

Fig. 1
Examples of nanocarbon three generation materials relevant for catalytic applications

Going from the first to third generation of materials, the possibilities offered to develop novel catalysts or materials for energy or chemical applications increases, but also decrease the level of understanding. For example, the doping with heteroatoms such as N or B introduces new reactive sites, but also changes hydrophilic/hydrophobic character, electronic conductivity and other properties important regarding reactivity and functional properties of these materials. In addition, many interfaces at nanoscale level are introduced in the more complexes 3rd generation materials, making difficult their full characterization. It may be also remarked that 1st generation materials are on the market, even if many problems in having reproducible materials still exist, but the availability of 2nd and especially 3rd generation materials is very limited out of laboratory scale.

Carbon nanomaterials and societal challenges
Nanocarbons possess many appealing requirements to develop novel or improved materials to address societal challenges such as i) cleaner and less energy/raw materials intensive processes, ii) enable a substantial reduction in greenhouse gas emissions by process industry and mobility, and iii) develop distributed technologies for using and particularly store solar energy. There are various distinct advantages in nanocarbons with respect to “conventional” carbon materials or other type of catalytic materials such as mixed oxides: i) the tailored pore structure, with large external surface and reduced micro-porosity, ii) the possibility to realize uniform characteristics at nanoscale level, iii) the possibility to realize synergetic effects and/or multiple functional properties by combining different types of nanocarbons, iv) the very effective electron and heat transport, v) the possibility to control electronic properties, from insulating to metallic properties through semi-conducting behavior, vi) the possibility to tailor surface properties and hydrophilic/hydrophobic behavior. The nanosize-related functional performances provide interesting opportunities in nanocarbons for the design of advanced catalytic materials, providing better mass and heat transfer and the possibility of synergistic interactions with other nanocarbons and/or metal particles or mixed oxides (realizing advanced hybrid materials[10]). Nanocarbons may be thus indicated as one of the best catalytic materials to realize the nano-engineering of the catalytic sites[3], the challenge to address the societal challenges previous discussed.
Also as advanced materials for clean energy applications, carbon nanomaterials offer many advantages. Between the key characteristics of nanocarbons for energy applications[5,8] may be cited: i) high “external” surface area and tuneable pore structure, ii) high electron, phonon and heat transport, iii) high accessibility by gaseous reactants and high mobility by ions, with a combination of mechanisms tuneable within a certain extend by controlling nanomorphology and properties of nanocarbons, iv) unconventional storage mechanisms.
Just to cite some less known aspects, zeolite-templated carbon (ZTC) can have uniformly ordered micropores as small as 1.2 nm and surface area up to over 4,000 m^2g^{-1} [22]. ZTC have a structure made up of buckybowl-like

nanographenes assembled into a three-dimensionally regular network[23]. By tailoring the pore alignment it is possible to obtain exceptional fast ion transport properties in these materials[24]. Due to this unique pore structure ZTCs possess high-performance as electric double layer capacitor and for H_2 storage. On the other hand, by using other silica templates (mesoporous materials and silica colloidal nanosphere) it is possible to obtain different ordered porous structures, with mono- or 3D-channel or pore structure and dimension of the channels or pre up to over 100 nm)[25]. These examples illustrate the unique variety of possible pore structure which can be obtained in nanocarbon materials, which do not find correspondence in other kind of nanomaterials.

However, this is still a limited control of the characteristics of nanocarbons, especially in less costly preparation methods such as by CVD (chemical vapor deposition), and of the interfaces between (nano)carbon materials and carbon-other materials (1D, 2D or 3D metal or metal oxides) in all hybrid nanocarbon systems. The interface is a critical aspect also in first generation nanocarbons, when it is necessary to utilize them in practical devices. For example, theoretical predictions yield an extremely high thermal conductivity for individual SWCNTs, e.g. k of about 6,600 $Wm^{-1}K^{-1}$, but the effective values in nanotube assemblies are lower by over one order of magnitude due to various reasons[26]: quenching of phonon modes in bundles reinforced by radial deformation of carbon nanotubes by van der Waals forces (phonon modes contribute to the heat flow), tube-tube interconnections and sheet imperfections like dangling fiber ends, loops and misalignment of nanotubes, impurities and structural irregularities in nanotubes inducing multiple elastic scattering of electrons. Nanotube junctions as well nanotubes quality have thus a greater impact on heat and electron transport and dissipation. Similar aspects are present in graphene-like materials.

There is a large recent effort to develop hybrid materials[27], for example for photoelectrochemical (PEC) devices, with nanocarbon layers or composites with nanocarbons to improve electron conductivity. However, performances are in the majority of the cases worse than expected for the lack of investigation of how quality of nanocarbons and the presence of multiple junctions affect the charge transport, heat transport and dissipation, phonon scattering, in relation to the use of these nanomaterials for developing solar cells and energy storage devices. This is an area which needs more attention in order to define the preferable design in the materials.

It may be useful to evidence with an example how the new possibilities offered from the development of new generation architectured nanocarbons can impact the performances, for example in a critical area for the development of energy storage materials such as that of Li-ion batteries. The small size and the specific morphology in nanocarbons provide new mechanisms for the storage of lithium ions, or Faradaic reaction for charge storage (pseudocapacity)[28]. Lithium can be stored in CNTs in different modes: (i) intercalation in the well graphitized part of multiwall CNTs, (ii) adsorption and accumulation on the outside of the surface, (iii) in the inner channel of the tubular structure in the form of either ions, atoms, or charged clusters in the case of opened CNTs, (iv) in the vacancy between normally entangled tubes and (v) in the form of intercalation and adsorption in/on the graphitic or amorphous carbon impurity in CNT materials (Fig. 2).

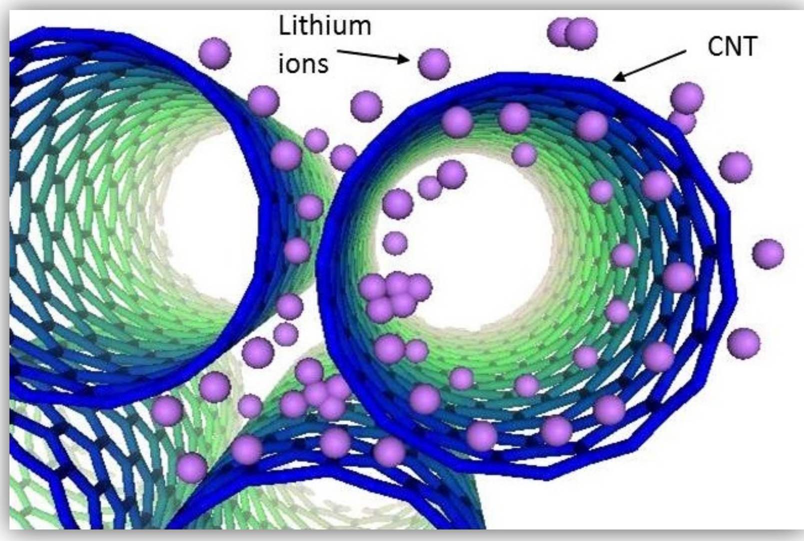

Fig. 2
Schematic view of various lithium storage positions in closed CNTs

It is possible to extend the Li storage capacity using novel concepts in hybrid nanocarbons, for example CNFs (carbon nanofibres) encapsulated within CNTs[29], or hybrid of nanocarbons with metals oxides (e.g. Ni, V, etc.) that react with lithium to boost the specific capacity with respect to that of conventional intercalation reactions. By realizing very dispersed and small nanoparticles of the metal oxides, it is possible to minimize the stresses related to the volume changes during the alloying/de-alloying processes with Li, which would cause critical mechanical damage to the electrode, resulting in a marked loss of capacity with time. By optimizing these factors in the design of nanocarbon hybrids it is possible to realize very high electrochemical performances in Li storage. These systems are indicated as lithium ion capacitors (LICs), e.g. an intermediate system between lithium ion batteries and supercapacitors to take advantages of both types of energy storage systems. Also in the use as supercapacitors carbon materials evidence that nanodimension brings new aspects that can be successfully used to develop high performance storage materials for energy applications.

Carbon nanomaterials as novel catalysts

As briefly mentioned before and discussed more in details in ref.[1,2,30,31], we are moving to a new scenario for chemical and energy production, which requires to develop conceptually new catalytic materials. Nanocarbons offer unique possibilities to tailor surface properties and nano-architecture, to create hybrid materials and to address the demanding requirements to develop novel catalytic materials and new devices[4,5]. There are many examples of chemical reactions where nanocarbons may play a key role to develop improved catalysts. Fischer-Tropsch to Olefin (FTO), particularly starting from CO_2 rather than from CO and based on the use of H_2 from renewable resources (rH_2)[1,32], is an active area of research to develop alternative processes to produce light olefins. The challenge is to maximize the selectivity (avoiding formation of methane and heavier products) and improve productivity. Catalysts based on doped iron nanoparticles supported over carbon nanofibres (CNF) give among the best results, with the behavior strongly depending on the ability of the CNF to stabilize specific shapes of iron nanoparticles, and at the same time avoid the presence of acid sites which can catalyze side reactions.

Nanocarbons play a critical role in design advanced photo- and electro-catalysts for producing rH_2 and for devices able to convert CO_2 to tailored chemicals (methanol, hydrocarbons, higher alcohols, etc.) using sunlight and water[33,34,35,36]. Nanocarbons play many roles: antenna centers to capture the light, systems for charge transport and separation, catalytic centers, etc.[4,5]. Nanocarbons are also critical in the design of advanced catalytic electrodes: examples include the electrocatalytic conversion of CO_2 to higher alcohols[34,37,38], advanced bio-electrodes, etc. Even in supported metal catalysts, the use of nanocarbons alternative to conventional carbon materials or traditional metal oxide supports may offer new opportunities. Very productive catalysts in direct H_2O_2 synthesis from H_2 and O_2 could be obtained by supporting Pd nanoparticles over N-doped carbon nanotubes[39,40], due to the stabilization of specific Pd shapes.

This is certainly not an exhaustive list of the possible areas where catalysts based on nanocarbons offer new possibilities, but the aim is to give just a glimpse of some of the possibilities in the new areas to move to sustainable energy and chemical processes. However, nanocarbons do not play only a role as support for metal or metal oxide nanoparticles, as outlined above, but may play an unique role as novel catalyst thanks to the defects and/or heteroatoms (due to pre- or post-functionalization) present in nanocarbons. Fig. 3 shows schematically the different types of catalytic active sites present in metal-free nanocarbon catalysts[4,41].

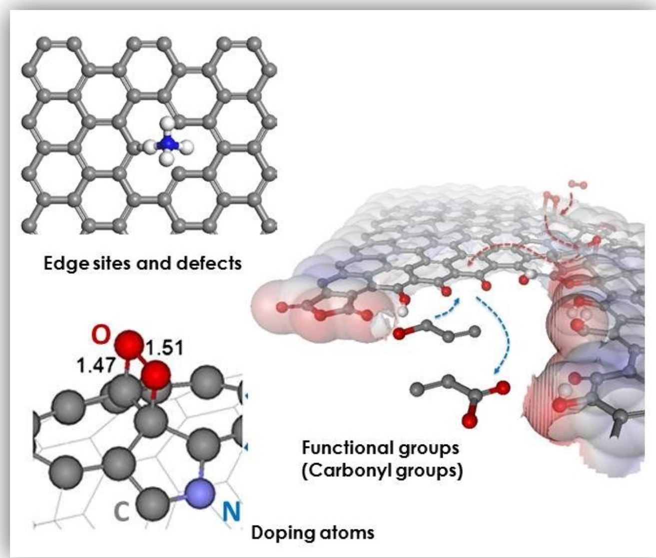

Fig. 3
Different types of catalytic active sites present in metal-free nanocarbon catalysts

As can be argued, these metal-free nanocarbon catalysts offer new unconventional possibilities as catalysts, starting from the known activity as alternative catalysts in oxygen reduction reaction (ORR) for PEM (proton exchange membrane) fuel cells going to a range of other new possibilities, like in hydrocarbon selective oxidation and (oxidative) dehydrogenation.

We may briefly distinguish three types of active centers present in nanocarbons (Fig. 3) and which may be involved in the reaction mechanism:

- functional groups, either with acid-base or redox character: they are active in various classes of reaction such as dehydrogenation, oxidation, hydrogenation, etc.;
- edge sites and defects: active for example in decomposition reactions;
- doped atoms: by influencing the properties on near-lying C atoms, they play a role in various reactions, from ORR to hydrochlorination, epoxidation, etc.

In some type of reactions, such as dehydrogenation and oxidative dehydrogenation, there are now extensive data, while for other type of reactions, from selective oxidation using multi-functional capabilities of nanocarbons to catalysis by edge and defects, research is just at the beginning, offering thus many different type of possibilities. Clearly the presence and amount of the active centers outlined above as well as the reactivity properties depend considerably from the type of nanocarbons, but intentionally we have avoided here to separate discussion per type of nanocarbons, or to focus on most popular topic such as graphene and related family of materials. In fact, it is necessary to have a common view on the characteristics of these materials and how they can be used for the development of novel catalysts or materials for energy. On the other hand, it is necessary starting to have a better comparative analysis between the different classes of carbon nanomaterials in terms of the different type of active sites, their stabilization and amount, as well as of other relevant properties which are needed to use them on larger scale in catalytic industrial applications. Fig. 4 reports a simplified comparison between CNT and graphene as catalysts (or photocatalysts) and some of the open questions to assess their advantages/limitations. As outlined, the nanomorphology influences the behavior, but it is still to clarify whether a CNT configuration (which formally is the rolling up of graphene sheets) or graphene itself are more suited for catalytic applications. It is also outlined that many open questions still exist to assess their advantages/limitations as catalysts and photocatalysts.

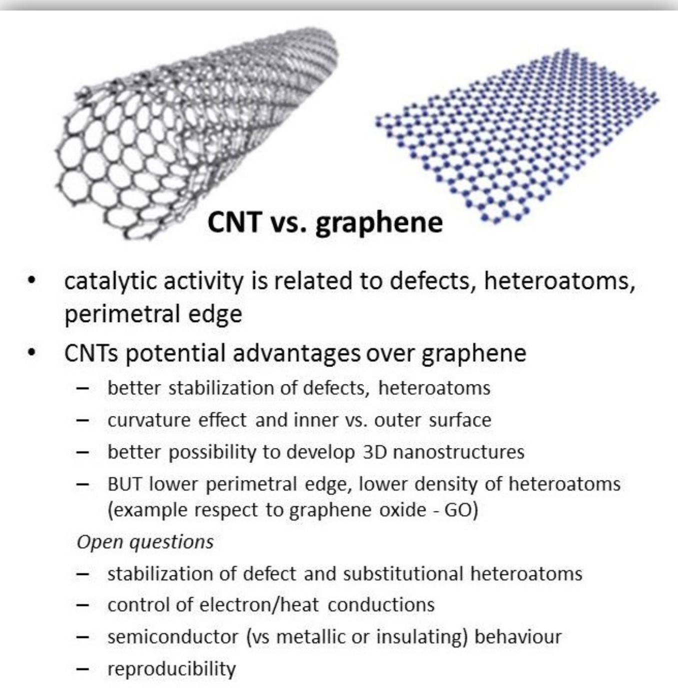

Fig. 4
Simplified comparison between CNT and graphene as catalysts and some of the open questions to assess their advantages/limitations as catalysts and photocatalysts

Enabling a larger use of carbon nanomaterials

The previous discussion remarked how the use of nanocarbons for preparing advanced (catalytic) materials will grow in the future to address the challenges for a sustainable and clean energy and chemical production, but there are some necessary conditions to enable this possibility:

- research in the use of nanocarbons materials, both as catalysts and advanced materials for energy, has to move to applications where there is the need of significant improvement in the performances for relatively large scale uses, which justify the investment necessary for its commercial introduction; research is often focused on the synthesis of nanocarbon rather than on the rational understanding of structure-reactivity or functional behavior;
- the peculiar properties of these materials, particularly in catalysis, have to be used with a more rational approach and to address novel pathways of reactions as well as the key challenges to move to a sustainable production (reduction of the number of steps in catalytic synthesis, costs of downstream processing and energy consumption, enable the use of alternative raw materials). Although researchers often claim these aspects, they are not often proven and limited effort in literature can be seen to discover game-changer applications of nanocarbon materials;
- the number of novel syntheses and type of nanocarbon materials has exponentially grown and more slowly also the understanding of their characteristics is increasing, including reactivity. It is necessary to turn approach, and develop a theory of catalysis by nanocarbon materials allowing to define which type of properties are specifically requested to improve the behavior in a specific catalytic reaction. Then synthetize the nanocarbon having these characteristics;
- reproducibility of the performances, especially at nanoscale level and in large-scale production, is still a critical element. Still many factors are uncontrolled.

Conclusions

Nanocarbons offer many novel possibilities to develop advanced catalysts, catalytic electrodes and materials for clean energy. This contribution has briefly introduced some aspects of the potentialities and open issues, in carbon nanomaterials for applications going from energy devices (to enable a larger use of renewable energy sources) to catalysis for cleaner processes and the use of alternative or renewable raw materials in chemical production. Nanocarbons can be considered a new class of catalytic materials, even if carbons (in the form mainly of active carbon materials) are already extensively applied as supports for catalysts. However, the control of nano-dimension and the improved understanding in tailoring the surface reactivity opens new possibilities for their nano-engineering and the development of novel catalytic materials. It is possible to have a true multifunctional behaviour, and especially tuneable within a relatively wide range by doping and controlling the nanostructure.

Carbon nanomaterials also play a critical role in the development of advanced energy storage devices. In Li-ion batteries, for example, the use of nanocarbons allow to introduce additional and/or alternative mechanisms of charge storage with respect to Li intercalation. In other type of batteries, not discussed here for conciseness (Li-S and Li-O_2, for example) the use of nanocarbon is essential to provide good conduction, high and stable performances. Supercapacitors and pseudo-capacitors are another example of how new 3rd generation nanocarbon materials with specific design are essential to enhance the performances. In the field of energy conversion (fuel and solar cells), there is also an urgent need to develop novel nanocarbon-based materials. The great potential of new materials/approaches such as carbon quantum dots and graphene quantum dot solar cells should be also remarked. In terms of application, nanocarbons for polymer solar cells appear as one of the main drivers for research in a short-medium term, while solar fuels cells, to develop PEC and artificial-leaf type devices, are a priority in a longer-term vision.

There are tools for nano-engineering of CNTs in terms of defects (type and concentration) and type/amount of heteroatoms. Both catalytic and functional properties of nanocarbons are greatly depending on these aspects, but a comprehensive understanding of the relationship is still far. Defects and heteroatoms play also an important role to stabilize/modify supported metal or metal oxide nanoparticles.

In conclusion, the understanding of nanocarbons, in terms of surface and nano-scale properties and their relationship between reactivity and functional properties, is significantly progressed in recent years, but still an intensive effort to exploit the great potentialities of these materials is required. However, it is necessary to move from first to third generation carbon materials and understand the many aspects related to this passage, including especially the issue of interfaces. As a final note it may be indicated that nanocarbons are more than just CNTs, fullerenes and graphene. The understanding of this concept, having various underlying implication, is the necessary step to move forward in enabling the potentialities of these materials.

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