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Grand challenges in carbon-based materials research

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CARBON IN ALL FLAVORS: CARBON MATERIALS CONSTITUTE THE MOST VERSATILE MATERIAL GROUP

Carbon materials constitute a large family of diverse structures and textures that underlie an increasing range of applications suggested by the impressive number of papers published on this topic. Several hundreds of thousands of publications have appeared since 1900, out of which, thousands were published in 2013 only (Web of Science™, 2014 Thomson Reuters, using as searching topics "carbon materials," "carbon chemistry," "carbon nanomaterials," "carbon nanotubes," and "graphene").

The popularity of carbon materials is due to a unique combination of physical and chemical properties such as high electrical conductivity, high surface area, good resistance to corrosion, high thermal stability, and high chemical stability in non-oxidizing environments and particular mechanical properties. Carbon materials are easy to process, provide a wide variety of structures and textures, have diverse surface chemical properties and are compatible with other materials, thus are ideal for composites as well (Inagaki et al., 2014).

This unique combination of properties is a consequence of the different hybridization of orbitals in C atoms and the possibility of combining with other heteroatoms. This makes possible to derive the different allotropes known to the moment and the large number of textures discovered up to now (Inagaki et al., 2014). The possibility of having different hybridization of the carbon atoms in the same material and other heteroatoms, forming multicomponent systems, led to the definition of "carbon alloys" (Yasuda et al., 2003). Carbon is an "old but new material" (Walker, 1990) with continuous discoveries that allows us to recognize the amazing and challenging research frontiers in carbon science.

An elegant way to introduce the huge synthetic possibilities of carbon materials is by classifying them into classic and new carbon forms (Inagaki and Radovic, 2002). Classic materials include activated carbons, graphite, and carbon black; new carbon forms contain carbons developed since 1960 such as carbon fibers, glassy carbons, diamond-like carbons, and recent low-dimensional carbons, e.g., fullerenes, carbon nanotubes, and graphene. The number of structures and textures that can be created by controlling the carbonization process are enormous, this leads to the discovery of numerous carbon nanoforms. Considering only sp^2 carbon nanoforms, more than 25 different forms have been identified. These can be found under different names in the literature that highlights the urgent need for a standardized nomenclature in the field (Suarez-Martínez et al., 2012).

THE NEXT DECADE: AN EXPANSION OF NOVEL CARBON FORMS

Carbon materials synthetic methods currently involve thermal treatments at moderate or high temperature for carbonization, gasification reactions, and eventually, graphitization for specific precursors (Inagaki et al., 2014). Hydrothermal synthesis practices, which can be generalized as solvothermal methods, are worth highlighting among the novel procedures with room for attractive development (Titirici, 2013). The use of templates has provoked an impressive increase of new carbon forms (Lee et al., 2006; Nishihara and Kyotani, 2012). Templates permit the design of very specific porous structure and texture, which can be obtained as the positive or negative replica of such template.

Various precursors can be used for the preparation of each carbon form; the only requirement for these precursors is to have high carbon content. Hydrocarbons, coal, biomass, and polymers are the best examples that can be transformed into desired or novel carbon materials. The use of carbon-containing residues or byproducts (like biomass) is a challenging aspect for preparing classic and new carbons in a sustainable manner.

Indeed, over the next years, the discovery of new carbon forms is meant to be in the frontline of carbon research exploiting the possibility of combining sp, sp^2, and sp^3 carbon atoms. I foresee a generation of new structures that can be added to the carbon phase diagram.

In addition, the combination of different existing nanostructures will boost this even further.

> Can we combine 0D, 1D, and 2D carbon nanostructures to build new 3D forms?
> Can we prepare carbon nanotube nets?
> Can nanowelding be controlled? (Terrones, 2003)
> Can we create new pore structures or as desired pore structures in new hierarchical materials?

I look forward to answering these questions over the next decade.

WE MUST DEEPEN OUR KNOWLEDGE ON CARBON MATERIALS

Surface chemistry plays a relevant role in the physical and chemical properties of carbon materials and is highly influenced by the presence of heteroatoms. Oxygen, nitrogen, phosphorus, boron, and sulfur may form different surface functionalities (Bandosz, 2009; Radovic, 2010). In addition to being naturally found on the carbon surface, their presence can be generated during the preparation phase or through material treatments. The occurrence of diverse surface functionalities over the carbon surface governs their reactivity, their chemical and physical stability, and their structure. Along with their porous structure, these properties dictate the potential use of carbon materials in adsorption, catalysis, energy storage, sensors, composites, biomedical applications, just to name a few. This is especially manifested in the case of the promising nanostructured carbon materials that were discovered in the last two decades, but it is also essential for classic materials like graphite, carbon blacks, and activated carbons.

One can easily identify two lines of research based on the critical contribution of surface chemistry: on one hand, we can find research trying to understand why small amounts of heteroatoms can induce such important changes in reactivity and structure; on the other hand, the community is trying to functionalize the carbon surface selectively, in order to get the best performance of the material.

Surface chemistry, together with structural issues, is essential to understand the reactivity of carbon materials: formation of functional groups and their mobility in the carbon structure must be thoroughly understood. Although some interesting contributions can be found recently (Radovic et al., 2011a,b; Vivo-Vilches et al., 2014), the complexity of carbon materials structure and texture, presence of heteroatoms and inorganic species leaves us with a plethora of unsolved issues.

The development and use of new *in situ* techniques as well as theoretical studies are mandatory to understand the creation, mobility, and reactivity of the different surface functionalities, unpaired electrons, for example. Functionalization of carbon materials is a very hot topic nowadays: it provides the possibility of tailoring surface chemistry on demand to adapt the material to a given application.

More work is necessary on theoretical studies, as well as on the development and use of more powerful techniques to get a better view of the structure, physical, and chemical properties.

Models proposed until now are far from the real material due to the structural and textural complexity of carbon-based materials. For example, the quantification of the pore size distribution (PSD) in porous carbons is still a matter of discussion. Nowadays, DFT methods applied to N_2 adsorption isotherms at 77 K are very much used to get the PSD and, in fact, they are used as routine characterization methodology. However, the pore models employed to get the theoretical isotherms to fit the experimental experiments are far away from the real structure. Slit-shaped pores are merely an approximate view of the pore structure in porous carbons, thus, more effort should be invested into research in this area.

CARBON MATERIALS UNDERLYING MATERIALS INNOVATION AND APPLICATION

Carbon materials form the basis of numerous applications in a wide variety of research and engineering areas. This causes publications on carbon-based materials to appear traditionally in various journals from both scientific and engineering domains.

Applications regarding environmental protection, energy storage and generation, semiconductors, transparent conducting materials, structural materials, biomaterials, chemical sensors, biosensors, catalysis, and photocatalysis, summarize most of the fields in which the presence of carbon materials play an essential role. Even though some of them are recent applications, we can already find interesting books that cover most of these topics (Burchell, 1999; Beguin and Frackowiak, 2010; Inagaki et al., 2014; Álvarez-Merino et al., 2014).

Certainly, new uses will appear considering the versatility of carbon materials. Instead of reviewing each application and challenges that should be explored, I will focus on a specific application area as an example that shows challenging issues that can be encountered and that are shared by most of the applications. I will refer to the use of carbon materials in energy storage and conversion systems.

There is plenty of room in the development of energy storage and conversion systems trying to get high energy and high power devices. In the electrochemical energy storage area, novel materials for capacitors are required that may fulfill the above key properties to be able to substitute the batteries but contributing with higher power. This means that new carbon materials and composites with adequate porosity, structure, and texture have still to be developed and have to be adapted to the specific electrolyte. Research to substitute Li by another more abundant element, like Na, is necessary in relation to batteries and metal–ion capacitors.

In electrochemical conversion systems, i.e., fuel cells, apart from developing new carbon-based catalysts supports, the synthesis of new non-precious metal containing catalysts is a critical objective. Interesting advances can already be found in the cathode of fuel cells, where heteroatom-doped carbon materials may have a key contribution (Trogadas et al., 2014). However, plenty of work is still necessary to unravel the role of the different functionalities and to selectively incorporate those more effective. In addition, the stability of the carbon material is essential and it must be related to the structure, porosity, and surface chemistry. Understanding the mechanisms of degradation of both the carbon material and the electrolyte is a very difficult and unsolved task.

In the case of fuel cells, the use of hydrogen makes necessary appropriate storage systems, what is another obstacle for the implementation of this technology. Either the use of different fuels (what makes necessary the selection of different catalysts or operation conditions) or new materials to store hydrogen are necessary. Carbon materials are one of the most promising for hydrogen storage (Lozano-Castelló et al., 2013); however, the low interaction energy with the hydrogen molecules makes necessary modification of the porosity and chemical composition, in order to increase this parameter to values that may permit to store enough amount of hydrogen at room temperature and moderate pressures (Lozano-Castelló et al., 2013). In this field, nanocarbons can be successful candidates provided that reproducible preparation methods can be developed and that the texture and structure can be controlled as desired.

Processing of carbon materials is another relevant topic from a technological point of view. This is especially important when trying to apply the new nanocarbons. In many cases, it is very difficult to handle the materials because of the nanometer scale size of the particles, what may require even special body protection. Thus, straightforward technologies that may conform the nanomaterials into different forms and shapes is essential. Technologies such as dip coating, spin coating, electrophoretic deposition, electrospinning, and electrospray can be helpful but they require the preparation of stable and appropriate inks and suspensions of the selected material.

Integration of carbon materials (especially nanocarbons) into other components to design functional or structural materials is a critical issue to transfer the fundamental knowledge into technological applications. For example, cylinders for high pressure hydrogen storage that can work up to 50 MPa are based on carbon composites since they have high specific mechanical properties. Functional materials constituted by a carbon material and another component such as a metal oxide or conductive polymer, are very much studied for energy storage. In this case, synthetic methods to achieve an adequate distribution of both components and improve synergies are still under development.

There are many challenging topics that assure a strong research in carbon-based materials in the future. The abovementioned grand challenges, the synthesis of new carbons with different structures and textures, the understanding and tailoring of surface chemistry are both extremely important and strongly connected to the development of new applications.

In summary, research on carbon-based materials is a very dynamic and growing area of study with nearly unlimited possibilities. We still have plentiful theoretical and applied issues to be understood regarding the structure, texture, and properties of carbon materials. The versatile chemistry of the carbon element makes that new carbon forms with new applications are being developed in spite of the fact that a wide knowledge base is already available. I am sure that this situation encourages the researchers to work on this amazing family of materials.

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