

Into the carbon: A matter of core and shell in advanced electrocatalysis

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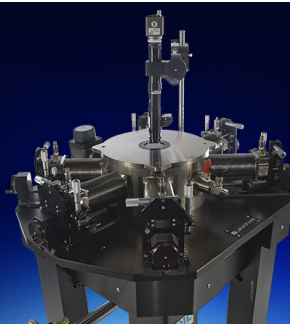
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ABSTRACT

Electrocatalysis, particularly related to fuel cell applications or other processes related to sustainability, has been steadily advanced by the design of new hierarchical materials involving two or more phases. One particularly appealing type of structure features metal species confined within carbon layers. These materials combine the benefits of the two components, which often work in synergy. However, given the intrinsic catalytic activity of carbon and the fact that the metal may be chemically inaccessible, in many cases, which of the two phases is the truly active site is not fully clear. Particularly for pure core-shell systems, where the metal is completely covered by carbon, the identification of the specific task of each component is not trivial. Many reported works on this type of bi-component catalyst are speculative in this regard. It is important for catalyst development that future studies on these systems will include a thorough cross-check of the reactivity aspects by means of combination of suitable techniques or experiments to unravel probable mechanisms and that assumptions are avoided.

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INTRODUCTION

The confinement of metal species within nanostructured matrices consisting of metal derivatives (oxides, halides, pure metals, carbides, etc.) is a powerful strategy for harnessing the buried metal with additional properties, exploitable in heterogeneous catalytic applications. In the first place, protection by an overlayer with precise architecture endows the catalytic metal with increased structural stability, avoiding, for instance, the notorious aggregation of the active metal species that compromises long-term operation. Embedded catalysts within inorganic channels or cavities (that function as supports) represent a big opportunity for advanced catalysis, not only because of the increased stability, but also because the extended surface contact between the metal and the support provides additional electronic properties that, in many cases, further promote the catalytic activity.¹ A peculiar kind of structure, where confinement is complete is the core-shell system, this structural configuration features the metal completely surrounded by an inorganic

matrix, maximizing the contact. A well-known class of core-shell catalysts is composed of two metals ($M@M'$), both active for a particular reaction and that synergistically drive the catalytic process with enhanced activity and better stability.² On the other hand, synthesis of noble metal core nanoparticles encapsulated into a shell of metal oxide is perhaps the most investigated type of materials, which can either capitalize on the intrinsic activity of the metal oxide to create synergistic effects³ or exploit the metal oxide as a mere structural support for steric and electrostatic protection of the active core metal.⁴ However, it is of paramount importance for catalytic purposes that the core metal is not fully isolated by the reaction environment as the reagents must find an accessible route to diffuse onto the core metal surface. This lays specific textural requirements of the shell, which has to retain appropriate porosity, such as mesoporosity, for allowing reagent passage.⁵ A common view, in most cases, when metals are confined into inorganic over-structures, is that the catalytic reaction occurs on the surface of the core metal (even though such metals may be considered as a co-catalyst for

photocatalytic processes). This paradigm ceases to exist when the metal coverage is made of carbon. Confinement of metal species within differently shaped and modified carbon shells has up to today been achieved via a variety of ingenious strategies resulting in the assembly of more and more sophisticated metal@carbon (M@C) systems. The main difference in having a carbon shell evolves from the highly facile electron mobility of nanostructured carbon phases and from their intrinsic activity in several catalytic reactions, particularly in electrocatalysis. In fact, it is well-recognized that nanocarbons such as graphene (G) and carbon nanotubes (CNTs) exhibit high conductivity arising from the polyconjugated sp^2 network,⁶ and such freely moving electrons can be used in reduction reaction. Moreover, the carbon surface can be modified by several routes, introducing *ad hoc* functional groups⁷ or doping non-metallic atoms,⁸ which markedly affect properties and reactivity. Carbocatalysis by nanocarbons has, therefore, become an important field of research on account of the cost-effectiveness of these materials.⁹ However, the inclusion of a metal inside the carbon nanostructure resulting in a core-shell or, more generally, in confined metal systems has the power to alter the properties of the carbon phase, imparting distinct catalytic behavior. It is not always so obvious to identify which of the two phases plays the actual catalytic role, and it is not to be ruled out that in various cases both the carbon and the metal are carrying out parallel catalytic steps. Therefore, understanding the metal confinement into nanocarbons will aid the development of these catalytic materials based on a rational design. In turn, this will allow the exploitation of the correct cooperativity in full for advanced sustainable catalysis, where the metal content can be suitably lowered to industrially appealing levels. As this perspective aims at highlighting the warnings related to one particular type of structure (core-shell), the discussion will only consider the most popular electrocatalytic reactions, in particular, those processes related to energy and fuel cells, where the bulk of work is existent, therefore, avoiding discussion on less explored reactions. In this perspective, the terms *core* and *shell* will be used in a more inclusive way, considering also systems where the metal is sitting deep in the confined areas of the carbon phase, even if not fully covered by carbon.

METAL@CARBON AND ELECTROCATALYSIS

Oxygen reduction reaction (ORR)

Historically, access to carbon-confined metals was achieved serendipitously: with the purpose of preparing specific nanocarbon morphologies, transition metals were used as catalysts in chemical vapor deposition (cvd) syntheses or even in pyrolysis methods to direct a controlled growth of the nanostructure.¹⁰ It was soon noted that acid leaching to yield the carbon pure material was almost never leading to the complete removal of the metal, and tunneling electronic microscopy (TEM) revealed that some of the metal catalysts remained incorporated into thick carbon layers, well-protected from the acidic environment. This finding, however, was not new. Carbon-coating of metal catalysts was already observed during reactions such as steam reforming, methanation reactions, water-gas shift reaction, and the deactivation of the catalyst was in fact ascribed to this coating process.¹¹ Structural isolation of the metal was initially associated with catalytic inactiveness, and researchers initially

regarded the endohedral metal as a spectator of the specific reaction. An important new insight into this conceptual pattern was provided by Deng *et al.*, who studied the electrocatalytic oxygen reduction reaction (ORR) by a nano-hybrid consisting of N-doped CNT-encapsulated Fe nanoparticles.¹² The catalytic activity of metal-free N-doped carbons in ORR has been thoroughly documented.¹³ The presence of a metal inside the N-doped carbon phase was tentatively recognized as an important factor for improving ORR activity, although the nature of the catalytic site remained uncertain.¹⁴ Previously, in another report, Pt@C core-shell catalysts were reported to be active and tolerant toward poisoning deriving from methanol oxidation reaction typically occurring in fuel cells. However, the authors discussed the reaction in terms of a diffusion of the small O_2 molecule through the micropores of the carbon shell, finally coming in contact with the Pt surface.¹⁵ Deng and co-workers, supported by density functional theory (DFT) calculations, proposed the hypothesis that the encapsulated Fe participated in the catalytic process *without directly* interacting with the O_2 molecules, but rather by electronically altering the outer wall of the CNTs. The Fe, located inside, was able to transfer charge to the carbon via a through-layer mechanism, decreasing the local work function of the N-CNTs and boosting chemical reactivity toward ORR. Moreover, the coverage with CNTs protected the Fe from detrimental oxidation, as observed by XAS studies, and from sulfur poisoning, which is notoriously deteriorating the performance of fuel cells based on Pt catalysts (Fig. 1).¹²

It was subsequently proved that this Fe@CNT hybrid was active in ORR as well as hydrogen evolution reaction (HER) even without recurring to N-doping, but rather modifying the outer surface of the CNTs through a covalent functionalization with organic groups bearing carboxylates.¹⁶ The non-innocent role of the hosted metal in ORR catalysis has been recently proved by our group, where Co@N-C (N-C = N-doped carbon shell) catalysts were prepared via pyrolysis of imidazole in the presence of Co salts, with final acid leaching. The resulting core-shell material, with the carbon surface free from Co species as confirmed by X-ray photoelectron spectroscopy (XPS), was notably active in the oxygen reduction through an almost selective 2-electron pathway, yielding H_2O_2 as the final product. The involvement of the metal in the catalysis was proved by a comparative study where other transition metals (Ni, Fe, Mn) are featured as the core. By changing the identity of the metal, the selectivity and activity were significantly altered, implying that the nature of the metal was critical and that it played a role in the catalytic reaction, presumably by distinctly fine-tuning the electronic properties of the outer carbon surface.¹⁷ Synthesis strategies have been developed to access materials where the metal could be confined within the layers of carbon nanostructures in a sandwich manner. For example, Fe_2O_3 nanoparticles were confined in small dosage to the shell of N-doped carbon hollow microspheres. The EDX scan profile confirmed the successful inside location of the metal oxide. The authors proposed that the macro-porosity of the carbon shells was the key to facilitate mass transfer, although the catalytic active sites were once again attributed to the carbon atoms adjacent to the N-doping atoms. DFT calculations supported the hypothesis that the Fe_2O_3 could be involved by facilitating the adsorption of O_2 onto the carbon (Fig. 2).¹⁸

It is interesting to note, however, that XPS analysis of the material could detect the peaks relative to the Fe nuclei. This is an

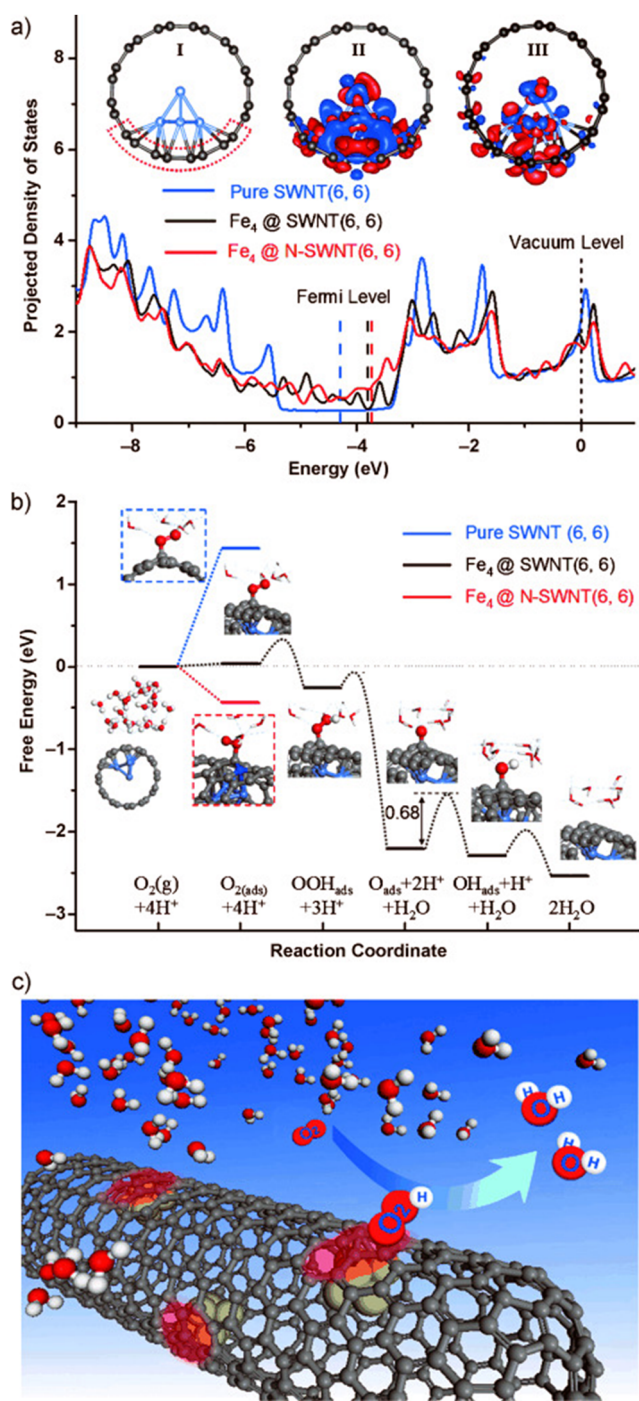


FIG. 1. (a) Projected DOS of the p orbitals of C atoms bonded to Fe₄ in Fe₄@SWNTs and Fe₄@N-SWNTs compared with that in pure SWNTs. Inset plots are for the optimized structures. (b) Free-energy diagram of ORR on Fe₄@SWNTs in water (black line) under experimental conditions [onset potential = 0.6 V vs normal hydrogen electrode (NHE), pH 0]. (c) A schematic representation of the ORR process at the surface of Fe₄@SWNTs. The gray is C, red is O, white is H, and yellow is Fe atom. Reprinted with permission from Deng *et al.*, *Angew. Chem., Int. Ed.* **52**(1), 371–375 (2013). Copyright 2013 Wiley and Sons.

important point, as XPS is a superficial technique, with relatively small penetrating ability, thus it is often used to confirm the absence of metal species from the carbonaceous surface. In this particular case, while contamination of the carbon outer surface cannot be totally ruled out, the fact that the carbon layer thickness was in the order of 12 nm (still in the range of typical XPS depth) could prevent confirmation using this type of spectroscopy. Nevertheless, in other cases, claimed deeply confined metal species could be detected via XPS, raising a warning that other characterization techniques ought to be applied to undoubtedly exclude the presence of metal on the surface of the carbon layer: this is essential to explain the catalytic mechanism, as even traces of metal in the form of single atoms can profoundly alter the catalytic behavior.¹⁹ For example, it has been very recently demonstrated that upon thermal treatment, Fe oxide nanoparticles confined within N,O-doped carbon nanospheres could migrate outwards, reaching the external area, and considerably changing the selectivity of ORR.²⁰ Hence, it is useful to support the occurred exclusive segregation by combination with other techniques, such as for instance chemisorption analysis. Recently, the incorporation of FeO_x nanoparticles into graphitic carbon shells was instrumental to extend the durability of the catalyst and its compatibility with acidic media for high-activity ORR catalysis. However, the authors attributed the catalytic activity to FeN_x species, formed during the pyrolysis treatment of the core-shell catalyst within mesoporous N-doped carbon matrices. Therefore, the migration of the metal species from the inner core to the outside is an element that must be carefully considered.²¹ Metal-nitrogen bonding can, however, also occur at the interface of the core and shell phases, as reported recently for Co@NCF (NCF = Nitrogen-doped carbon foam) catalysts for ORR, therefore, the structure of the carbon shell must be tuned in order to favor mass transfer rather than impeding.²² There are other valuable strategies to determine which between the metal core and the carbon shell is responsible for the observed catalysis. An interesting work was reported by Choi *et al.* on the selectivity of ORR toward H₂O₂ originating from the inclusion of Pt nanoparticles within an amorphous carbon shell. Typically, naked Pt nanoparticles supported on amorphous carbon are selective catalysts for the 4-electron reduction pathway to water.²³ However, Choi and co-workers noticed that by covering the NPs with layers of carbon through a CVD method, the selectivity was completely reversed in favor of a 2-electron pathway to H₂O₂. The reason for such a switch was attributed to the exclusive end-on adsorption configuration of the oxygen molecule, which is known to favor the reduction without cleaving of the O–O bond, in contrast with the side-on configuration. The exclusive end-on adsorption originated from the carbon layer that eliminated access sites to the Pt nanoparticles, preventing the more space-demanding side-on configuration. Interestingly, the authors investigated the true active site through poisoning experiments with CN[−] ions. CN[−] can poison selectively the Pt, while it has no effect on the carbon activity,²⁴ and the observed drop of ORR activity in the presence of cyanide ions substantially justified the identification of Pt as the dominant catalytically active site (Fig. 3).²⁵ This strategy represents a simple and powerful method for assessing catalytic behavior of core-shell systems without recurring to extensive characterization of the material.

Other than ORR, various other electrocatalytic reactions have been conducted. The envelopment of Ni₃S₂ nanoparticles into a

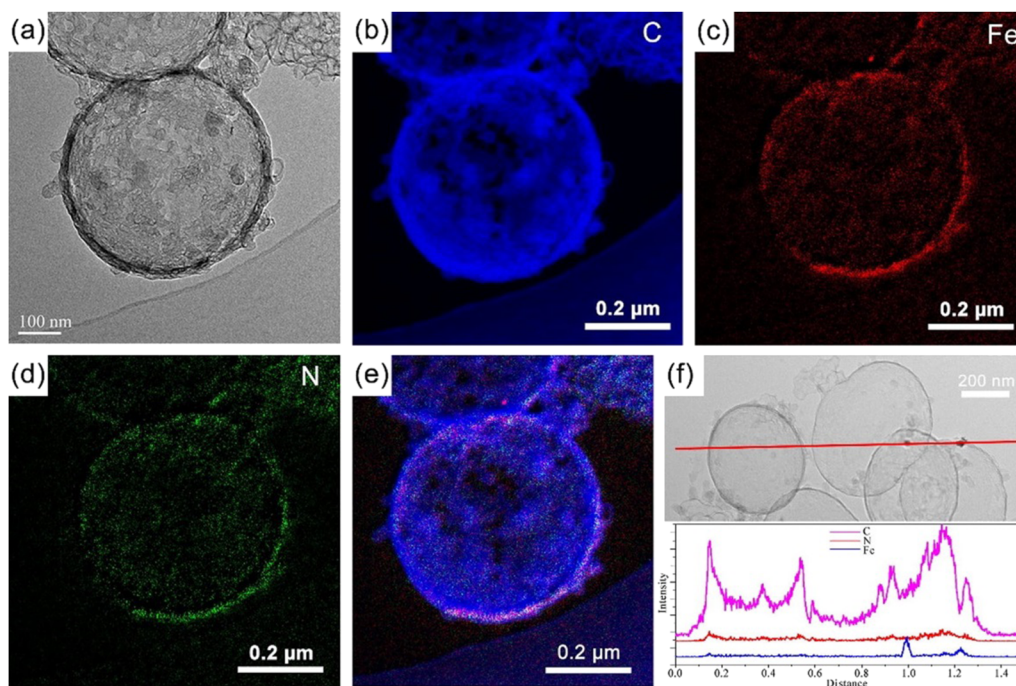


FIG. 2. Figure 3. (a) Typical TEM image and corresponding elemental mappings of (b) C, (c) Fe, and (d) N of the material. (e) Element distributions of C (blue), Fe (red), and N (green) on one hollow microsphere. (f) TEM image and EDX-line scanning profile of the obtained hollow spheres. Reprinted with permission from Xiao *et al.*, *Chem. Eng. Sci.* **207**, 235–246 (2019). Copyright 2019 Elsevier.

thin layer of onion-like graphene was exploited for the oxygen evolution reaction (OER), and it was found that an over-doping of the nanoparticles with segregated Fe was significantly enhancing the activity. In this case, XPS-responsive metals could be obviously justified by the thinness of the carbon layer (~ 2 nm), and the authors somehow assumed that the metal was accessible by the reagents and was the actual catalytic species, with the carbon layer improving also electrical accessibility, although no direct experimental proof of such accessibility was actually provided. To this end, the future investigations may recur on a post-synthesis acid leaching, evaluating the activity of the metal-free carbon component that would form if the metal is indeed removed from acidic treatment, meaning they are not chemically unavailable.²⁶ Hydrogen evolution reaction (HER) by $\text{FeS}_2@\text{C}$ was also reported, where the carbon layer role was discussed not only in terms of protection of the metal nanoparticles (being the active species), but also as a promoter of the catalytically active phase due to the interfacial interaction.²⁷

The accessibility of the core ruthenium nanoparticles encased within the graphene layer was for example robustly proven for another non-electrocatalytic reaction such as acetylene hydrochlorination. Based on catalytic tests with other reference materials, the authors concluded that the carbon shell (only about 5 nm) was permeable, and proved this aspect by analyzing the acetylene chemisorption. While only assumed by the authors, it was also sensible to suggest that such accessibility would quickly decrease with the increase in the number of graphene layers (Fig. 4).²⁸

Anodic reactions in fuel cells

Very recently, an extensive study was performed on the possibility of using Pd–Ni binary metallic nanoparticles shell-confined within carbon, prepared by a multi-step synthesis, for microfluidic direct ethylene glycol fuel cells. The resulting morphology showed Pd–Ni@CNT protruding from a N,S-doped cotton fiber with the bimetallic metal nanoparticles located at the tip of the tubes. The catalyst was active for the anodic ethylene glycol oxidation.²⁹ While well performed, this study still presents some unsolved matter: the authors relied on the metal as the active site, accounting on the $-\text{OH}$ adsorption (OH_{ads}), typically invoked in Pd and Pt-based alcohol electro-oxidation, which was facilitated by the inclusion of nickel. The metal was assumed to be chemically accessible by the ethylene glycol molecule through channels present in the porous carbon. Nevertheless, the same authors also indicated that the outer graphitic layer of the CNTs was catalytically activated by the endohedral metal via electron transfer through the layers. The question, therefore, remains unanswered on whether this catalyst features two distinct active sites, or if the metal is in contact with the electrolyte. Electrochemical surface area (ECSA) evaluation is hinting on the metal involvement, but it is not fully conclusive to use electrochemical data to speculate too much on subtle structural parameters such as chemical accessibility, and a physical characterization is required for strengthening the hypothesis. An interesting recent work aimed at unraveling the active site in OER/HER of a core-shell system featuring NiFe nanoparticles encased in Fe,N-co-doped

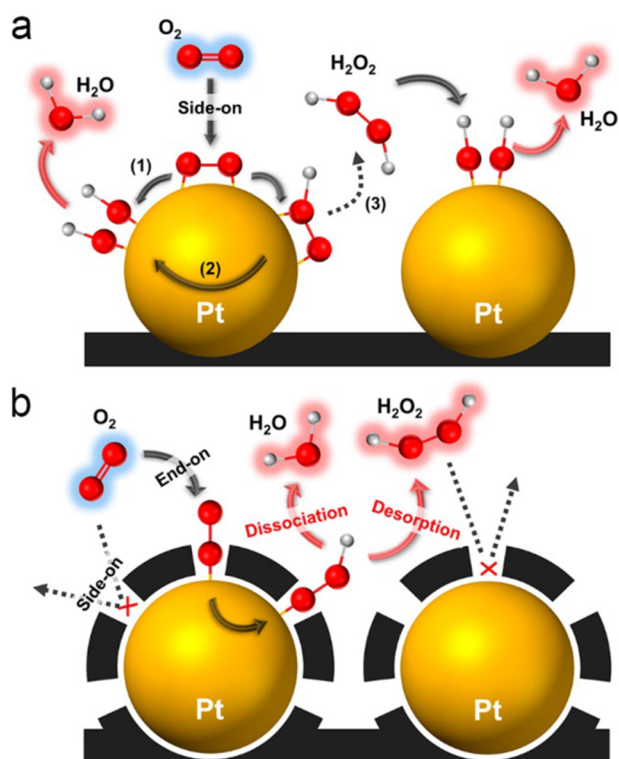


FIG. 3. Scheme of ORR pathways on the Pt Surface, showing the preferred side-on adsorption configuration of O₂ on naked Pt nanoparticles (a) and the favored end-on adsorption configuration when a carbon layer is laid (b). Reprinted with permission from Choi *et al.*, *J. Phys. Chem. C* **118**(51), 30063–30070 (2014). Copyright 2014 American Chemical Society.

carbon shells, trying to understand whether it was the NiFe NPs in the core or rather the metal on the surface of the carbon phase was responsible for the catalysis. The authors carried out a comparative work by removing either the surface metal dopant or by destroying the core-shell structure. They noted a synergy between the metal dopant and the inner NiFe NPs with the latter modifying the electronic structure of the shell by acting as an electron receptor.³⁰

A different case is when the metal is sandwiched between the two 2D layers, such as, for example, in the case of graphene. Pt nanosheets were intercalated between two few-layered G and used for the electrocatalytic glycerol oxidation. Several beneficial effects arise from this confinement, resulting in enhanced performance of the catalysts. While the catalytic active species was most obviously attributed to the Pt, the authors recognized the issue of mass diffusion of the reacting glycerol through the extended narrow gap between the graphene layers, and carried out experiments to mitigate such restrictions, such as the tuning of the final morphology, also providing a solid proof for the nature of the active species and the beneficial role of the G layers (Fig. 5).³¹

Yet, it must be, however, noticed that some theoretical and experimental studies on metals covered by graphene or parent structures (e.g., graphdiyne) unraveled that in the interface region between the graphene and the metal, charge transfer phenomena can take place, lowering the free energies of key intermediates. Hence, elusiveness of the active site persists.³² Regarding the mass diffusion problem, which hints on the importance of establishing the porosity of the carbon shell, one point of concern for future studies is considering the size of the reacting molecule as diffusion through the carbon is obviously more difficult for bulkier molecules. Model studies on smaller molecules can be employed as a tool for understanding the possible limitation to the core-shell catalyst, should the active site be truly the inner metal species.

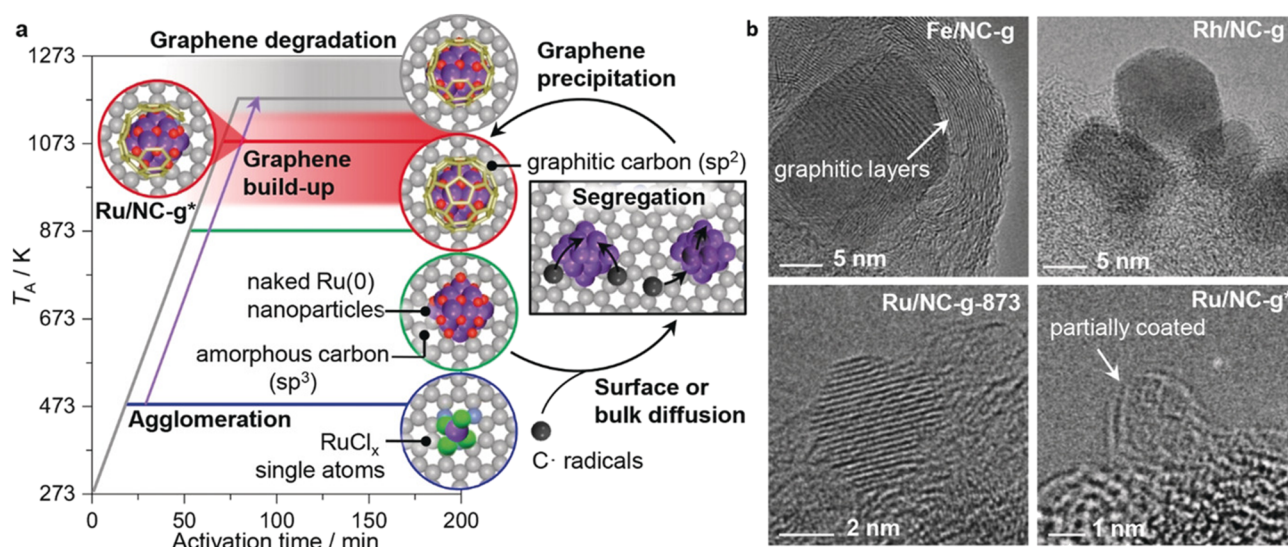


FIG. 4. Synthesis conditions and proposed mechanism for the formation of monolayer graphene-encapsulated Ru nanoparticles from RuCl_x single atoms (a) and HRTEM images (b). Reprinted with permission from Kaiser *et al.*, *Angew. Chem., Int. Ed.*, **58**(35), 12297–12304 (2019). Copyright 2019 Wiley and Sons.

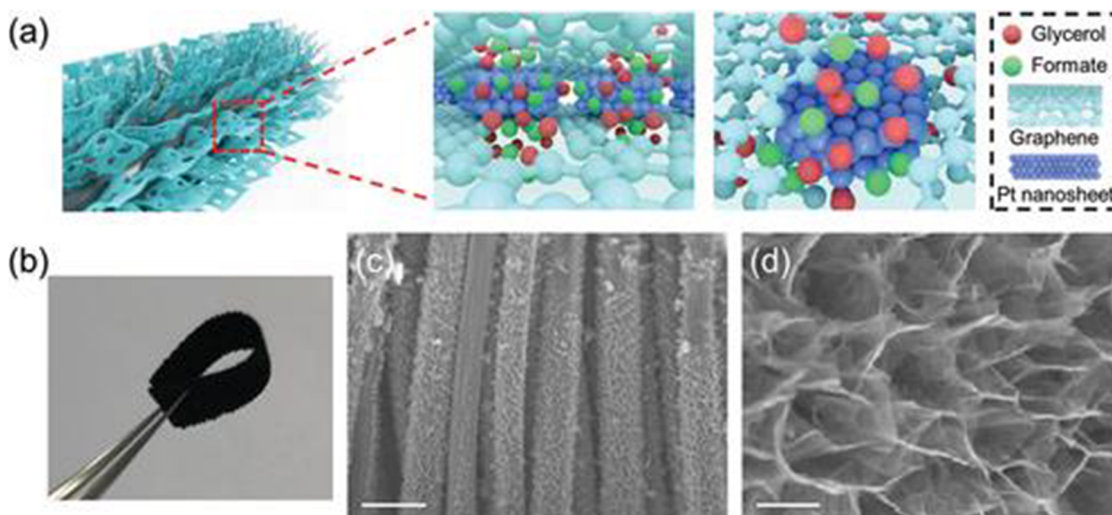


FIG. 5. The growth of Pt nanosheets within vertically grown graphene array. (a) Schematic of the interface-confined reaction in the 3D hierarchically porous catalyst; (b) digital photo of the as-prepared material; [(c) and (d)] SEM images at different magnifications. Scale bars: (c) 20 μm ; (d) 1 μm . Reprinted with permission from Chen *et al.*, *Adv. Mater.* 31(2), 1804763 (2019). Copyright 2019 Wiley and Sons.

Aspects of the structure/catalysis dependence

A sensible point when discussing carbon-confined metals arises when considering CNTs as the covering phase. Endohedral catalysis by metals within CNTs has been recognized in the first place for organic synthesis³³ and thermal reactions³⁴ where the *confinement effect* played an important role,³⁵ and where the reaction is assumed to proceed with the reagents diffusing within the CNTs and in contact with the confined metal. Hence, the CNTs was originally regarded as a nanoreactor. However, the diffusion of reagents is unlikely to take place if the tips of the CNTs are closed, particularly when the multi-wall CNTs (MWCNTs) are employed. Such tips may be opened by acidic oxidative treatments, but this step

may also cause the leaching of the metal from inside the CNTs. On the other hand, the metal can be introduced into the CNTs after the opening of the tips through a capillary action.³⁶ Still, given the availability of an exit point in the open-tip CNTs, the loss of endohedral metal can still occur under the catalytic conditions. Therefore, the rich organic synthesis with M@CNTs should be in each case very carefully evaluated.³⁷ The catalysis by M@CNTs was recently reviewed, and the types of catalysis were distinguished on the basis of whether the reagents were entering the carbon channels or were converted on the outer walls of the carbon surface (Fig. 6).³⁸

This consideration must be also extended to other M@C systems, where the metal is not fully enveloped, and the aspect needs

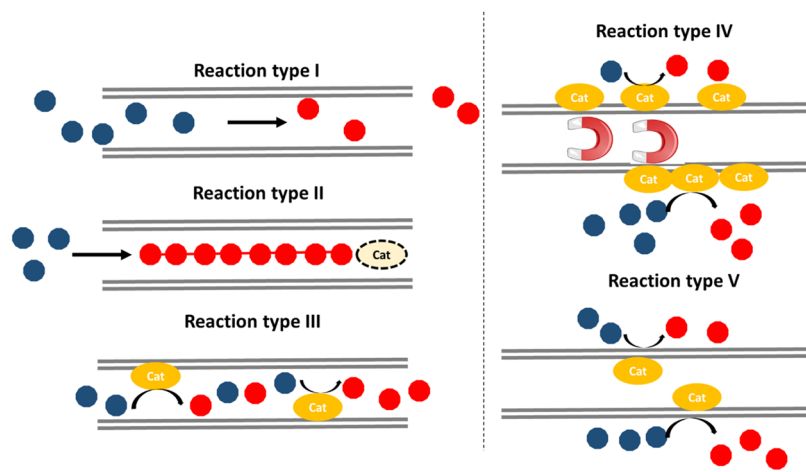


FIG. 6. Different types of reactions involving endohedral CNTs. The dotted line around the catalyst in reaction type II indicates that the reactions may occur with or without metal (indicated in the other reaction types as "cat"). Blue balls: reagents; red balls: final product.

to be clarified. In particular, electrocatalysis may be very sensitive to this issue because very often the electrolytes consist of acidic aqueous solution, which represents an ideal environment for metal dissolution, especially over long time operation.

An additional point is the wide concern over the mass transfer within CNT channels, which has been long under debate. For electrocatalysis, in particular, evaluation of the effective introduction of chemical species is made even more challenging by the effects of the electrical double layer.³⁹ An interesting study combined electrochemistry and the use of a quartz crystal microbalance (QCM) as a method for a more quantitative evaluation of the nanochannel mass transfer within CNTs. Prussian blue (PB) was introduced inside the CNTs (PB_{in}@CNTs), and used as a catalyst for the H₂O₂ reduction.⁴⁰ As the activity of PB is sensitive to the concentration of K⁺ ions from the electrolyte, the observed cyclic voltammograms (CVs) were put in relation to the effectiveness of the K⁺ diffusion in the nanochannels based on comparison with catalysts, where the PB was anchored on the outside of the CNTs (PB_{out}@CNTs), and therefore, in theory, more easily reachable by the K⁺ ions. It was, however, observed that at low scan rates, the catalytic current of H₂O₂ reduction of PB_{in}@CNTs and PB_{out}@CNTs was very similar, implying that the K⁺ diffusion was not largely affected, on such a time scale, by the restricted size of the channels. On the other hand, at higher scan rates, the differences in currents were very obvious, and therefore, the difficulty in diffusion was more obviously confirmed. We feel that this type of quantitative study should be encouraged.

CONCLUSIONS

The complexity of electrocatalytic processes by metal confined in carbon phases still gives rise to debates on the true mechanism and to what extent the metal is directly involved in the reaction. In contrast with thermal or organic reactions, the conductivity of graphitic carbon plays a more critical role in electrochemical processes. In this realm, the mobility of electrons is one of the dominant factors for the catalysis and, on this ground, the chemical unavailability of the confined phase combined with the excellent mobility of electrons on carbon surfaces has condemned the metal to be regarded mainly as a spectator, even in the more recent years.⁴¹ However, an increasing number of studies indicates that the encased metal may be non-innocent, triggering the catalysis through different mechanisms even when not directly in contact with the reagents. We feel that these types of materials used particularly for (but not limited to) electrocatalytic processes will have to be understood case by case in more depth, clarifying each phase task through combination of techniques and experiments. Characterization of the materials is highly important, and should be carried out thoroughly to avoid too many speculations and assumptions. Total confinement of the metal must be ascertained because even an extremely small percentage of metals in the form of single atoms or small clusters that remain on the external carbon surface can have an influence on the catalytic behavior of the material. Moreover, the porosity and permeability of the carbon shell, which in various cases is somehow assumed, should be unequivocally checked if the catalytic active species is suggested to be metal. To this end, chemisorption experiments are powerful tools. Finally, the synergy between the two components (metal and carbon) could

not only be derived from an electronic communication, but also the possibility of two separate active sites is not to be ruled out *a priori*.

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