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Chalcogenides and Carbon Nanostructures: Great Applications for PEM Fuel Cells

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Abstract

Nanostructured metal chalcogenides (NMCs) and carbon nanostructures (CNS) are attracting significant attention due to their features such as high stability in an acidic environment, especially if they have a significant oxygen reduction activity and remarkable superconducting properties. The broad range of CNS exhibits novel physicochemical properties, and thus it is triggering intense research about carbon nanoscience with numerous applications. In this context, new synthesis routes are designed under moderate conditions, which are definitely needed in order to simplify the process, reduce costs, and allow the production of NMCs at lower temperatures and CNS whose size and shape can be controlled. Some related studies about Pt based on sulfides and selenides, transition metal chalcogenides (TMCs), and carbon nanostructures (nanotubes and graphene) are revealed here; however, they show promise for fuel cells that these NMCs, CNS, or even NMC-CNS materials have been applied for other energy devices. Until now, a good response for cathodic reactions is employing TMCs based on tungsten and CNS without metal. According to experimental results and in terms of catalytic activity, durability, and chemical/electrochemical stability, much more research is required to produce commercially valid non-noble catalysts, electrocatalysts, or supports; however, one approach on this field is metal-free CNS.

Keywords: chalcogenides, nanostructures, carbon, catalyst, solar, fuel cells, oxygen reduction, transition metals, electrocatalyst

1. Design considerations for electrocatalysts

Several advantages on the design of proton exchange membrane (PEM) fuel cells are the cost-effective and innovative synthesis methods, which are necessary for new catalyst discovery

and catalyst performance optimization. In addition, the carbon support functionality should be emphasized in terms of the active surface increase, the coordination effect of catalyst and support, and the distribution of active catalytic sites.

The main focus is the oxygen reduction reaction (ORR); this electrochemical reaction plays an important role in the operation of fuel cells. Nevertheless, due to its complexity, we are far to reach a full comprehension about the mechanisms involved in these systems. The development and study of novel materials that have useful electrocatalytic properties to carry out the reactions involved in these electrochemical devices is needed.

Platinum is considered in such a traditional catalyst for reactions involved in PEM fuel cells. However, their high costs keep us researching on new approaches to reduce the platinum load on the electrocatalytic material, and, therefore, Pt loading catalyst is still the main issue. Some methodologies for the preparation of disperse transition of metal nanoparticles and carbon nanostructures (CNS) have been developed and are described here.

Catalysis with transition metal sulfides (TMS) also play a crucial role in petroleum industry, owing to their exceptional resistance to poisons. TMS are unique catalysts for the removal of heteroatoms (S, N, O) in the presence of a large amount of hydrogen [1]. In particular, they are the optimal materials to carry out the numerous reactions [2–5]. Through effective synthesis procedures, new non-noble catalysts have been discovered. TMS synthesized by carbonyl route using sulfides and selenides are promising. Besides platinum and noble metal nanoparticles and its alloys, other kinds of materials have shown important electrocatalytic activity in PEM fuel cells. Alonso-Vante and coworkers have proposed semiconducting TMS (sulfides and selenides) as efficient catalysts for cathode fuel cell reactions with significant oxygen reduction activity and high stability in acidic environment. A strategy to synthetize these materials in nanodivided way, is using carbonyl-based molecular clusters as precursors [6]; this route of synthesis offers the possibility to produce well-shaped nanoparticles with right stoichiometries. Ruthenium carbonyl ($Ru_3(CO)_{12}$) is extensively employed as feedstock to obtain diverse types of compounds and metallic clusters for new electrocatalysts; the main objective in the catalyst design is to replace and overcome the platinum properties [6–10].

However, platinum metal and its alloys with other transition metals are important catalysts for low-temperature fuel cells. The catalysts are typically developed in a form of nanoparticles for a better dispersion and/or minimum loading of platinum. Since they have the best activities and chemical stability, the problem is the high costs of Pt loadings in operating cathodes. ORR has been examined in the presence of Pt and Pt alloy nanoparticles on carbon-supported, CoN_4 catalysts, Chevrel-type chalcogenide materials, and Ru_xSe_y clusters [7, 11]. The ability to fabricate new model systems in which one can control the number of particles, size, and shape would be of tremendous fundamental importance in catalysis and electrocatalysis, as well as in other technologically important areas that use nanoparticles.

On the other hand, chalcogenides are synthesized under mild conditions in the nano-length scale by simple and fast methods. In the final form of the catalyst, chalcogenide atoms interact with surface metal atoms in a chemical way to avoid poisoning. Evident effects were observed in the presence of organic molecules as CH_3OH or $HCOOH$. Synthesized catalysts have been compared with commercial Pt/C [7, 11]. Further, the ORR kinetics was not perturbed, assessing this phenomenon wherein the sulfur atoms and organic molecules showed a little effect against the molecular oxygen adsorption. Some results demonstrated that the fuel crossover is no longer a major concern; however, the nature of the active sites on the chalcogenides and more investigations on dispersion and synthesis methods will follow for the development of very small and low-cost fuel cells, such as microsystems [12]. Therefore, results suggest the development of novel systems that is not size restricted, and its operation is mainly based on the selectivity and nature of its electrodes.

1.1. Sulfides and selenides: catalysts based on chalcogenides

The challenges of scale-up and commercialization of fuel cells depend on the optimal choice of fuel as well as on the development of cost-effective catalysts. One approach for the ORR is the use of transition metal chalcogenides (TMCs) or dichalcogenides (TMDs), which also have the great advantage of being selective in the presence of methanol. However, the target is to develop materials based essentially on non-noble metals and reduction of the Pt loading [5, 13]. These results promise new opportunities to design cathodic catalysts.

On the other hand, $W_6S_8(PEt_3)_6$ was reported as the first soluble model clusters of the molybdenum Chevrel phases and their (unknown) tungsten analogs [14]. However, according to the literature reviewed, until 2003 tungsten, Chevrel phases had not been reported, despite many years of effort. As reported in many studies, chalcogenides are markedly less sensitive than platinum catalysts to methanol. In accordance with this idea, we endeavored to explore the nature of chalcogenides based on sulfur and thiosalts. These results described a significant tolerance toward some carbonaceous species like monoxide and methanol. Likewise, we called "the decorative nanoexfoliation of platinum model" to explain the effect of sulfur species on the surface of platinum, and further studies demonstrated how the WS_2 planes are highly exfoliated around platinum nanoparticle to avoid the poisoning (see **Figure 1**).

This idea is to design selective catalysts with high activity for PEM fuel cells based on sulfur. We reported novel platinum chalcogenides as cathodic catalysts from platinum with tungsten and molybdenum thiosalts, as well as platinum and sulfide in acid media, and in other studies, we also analyzed the promising results for anodic electrode [15, 16]. In addition, we have studied the interaction with the supported TMS on Vulcan carbon. **Figure 1(a)** and **(b)** shows HRTEM images of the unsupported $Pt_xW_yS_z$. In concordance, **Figure 1(c)** shows a significant effect of the chalcogenide on the platinum surface and the catalytic activity is better in comparison with the commercial platinum at 20 wt.% metal loading [16].

Carbon-supported PtW nanoparticles are usually prepared by impregnation or chemical co-reduction of chloroplatinic acid and ammonium tungstate. However, these methods are not suitable for preparing carbon-supported PtW nanoparticles with well-controlled particle size
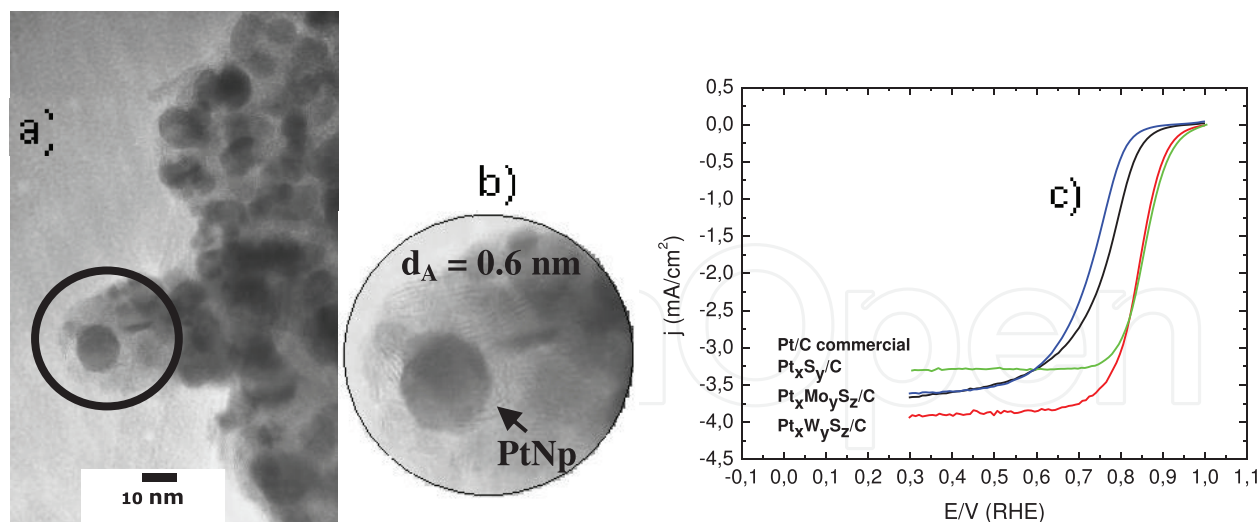
Figure 1. (a) HRTEM image of the unsupported catalyst $Pt_xW_yS_z$, (b) HRTEM image at high magnification of one platinum nanoparticle decorated by WS_2 nanostructures, and (c) current-potential curves for oxygen reduction for $Pt_xMo_yS_z/C$, $Pt_xW_yS_z/C$, Pt/C commercial, and Pt_xS_y/C. All samples were immobilized on a glassy carbon RDE, and the measurements were carried out in O_2-saturated 0.5 M H_2SO_4 solution at 5 mV s^{-1} at 1600 rpm rotation speed and 25°C. The current densities were normalized to the geometric surface area.

and homogeneous composition [17]. In **Figure 1(c)**, we report the ORR polarization curves for three synthesized catalysts and compared it to commercial Pt/C Vulcan at 20 wt.% of metal load. As shown, in all samples, the current density values are higher than the Pt/C. Furthermore, it was noticeable that cathodic current due to the reduction of O_2 commences at much more positive potential for PtWS/C catalyst than the synthesized samples and similar than commercial sample but increases upon further cathodic scan, and overall it shows a significant enhancement versus the Pt/C.

TMCs are a group of materials that show activity toward ORR. It is worthwhile to mention that TMS are the optimal catalysts to carry out the numerous reactions of hydrogenation and hydrogenolysis on different processes for the refining industry. We have reported catalytic materials sulfided by DMDS, and their activities are similar than H_2S. It is an advantage, in order to determine the effect of sulfur on trimetallic catalysts and explore other sulfiding agents. This experimental procedure is also on research by our group [18].

Ruthenium (Ru)-based chalcogenide catalysts synthesized by Alonso-Vante et al. [8, 10, 11] have been among the most promising, due to their high activity and stability toward the ORR in acidic media [19]. Particularly, RuS_2 also has been extensively employed as catalyst for hydrodesulfurization (HDS) reactions. It has been shown that semiconducting transition metal sulfides, such as PdS, PtS, Rh_2S_3, Ir_2S_3, and RuS_2, have higher catalytic activity than the metallic sulfides [20]. However, the electronic environments of the surface of Ru atoms are also compared to the electronic environments and reactivities of metal centers found in d^6 transition metal complexes that incorporate thiophenic ligands [20, 21].

Cluster compounds of the Chevrel type (MosXs) contain molybdenum octahedral and form metals with the Fermi level clearly below the energy gap. It clearly shows the molybdenum cluster octahedron (accommodating 20 electrons) surrounded by a cube of chalcogen

atoms. It is also possible to distinguish the crystal channels between the clusters into which guest atoms can be inserted.

Alonso-Vante and Tributsch were the first that communicated that semiconducting ruthenium-molybdenum chalcogenides having the general formula $Mo_xRu_yXO_2$ (with X = chalcogen: essentially, one of the elements O, S, Se, and Te) and forming Chevrel phases exhibit good catalytic activity for ORR in acidic solutions and catalyze the four-electron reduction to H_2O over the H_2O_2 route [22]. It was soon found that the catalytic activity is not restricted to Chevrel phases, but other varieties of such chalcogenides are active as well. Many other studies go on; using similar compounds are synthesized in different ways, and this is the purpose of this contribution, in order to enhance the catalytic activity, selectivity, and stability; thus, new modifications on active phases and carbon supports have been explored.

1.2. Carbon nanostructures

1.2.1. Carbon nanotubes and graphene

The morphology, structure, and composition of the support material significantly affect the catalytic activity of the fuel cell catalyst [23]. Carbon is most often used as catalyst support in cathodes because it is inexpensive; it can be prepared in a pure form as high-surface area powders, and it is electrically conductive. However, the atomic arrangement of carbon atoms on the network is the key to determine well-defined properties and therefore specific applications. In order to improve the electrocatalytic efficiency, various carbon support materials such as carbon nanotubes and graphene have been applied recently by our group. Some requirements for these supports are electrical conductivity, good metal-carbon interaction, high surface area, and high inertness in harsh chemical and electrochemical conditions.

Since Iijima's landmark paper in 1991 [24], carbon nanotubes (CNTs) have been studied by many researchers all over the world. Their large length (up to several microns) and small diameter (a few nanometers) give them a large aspect ratio. CNTs are mainly produced by three techniques: arc discharge, laser ablation, and chemical vapor deposition. Research has been targeted toward finding more cost-efficient ways to produce these structures.

According to theoretical models, all of these structures may appear due to non-hexagonal carbon rings that are incorporated in the hexagonal network of the graphene sheet. In particular, coiled carbon nanotubes were first predicted to exist in the early 1990s by Ihara [25] and Dunlap [26], but they were experimentally observed until 1994 by Zhang [27]. On a microscale, periodic incorporation of pentagon and heptagon pairs into the predominantly hexagonal carbon framework in order to create positively and negatively curved surfaces, respectively, can generate a carbon nanotube with regular coiled structure [28].

A large variety of tubule morphologies as straight, coiled, waved, branched, beaded, and regularly bent have been synthesized and observed; however, there are no studies about the growth time which affects CNT morphology. Herein, the growth time promotes the arrangement by hexagonal lattices to produce different shapes [26]. Hence, to prepare high-quality metal catalyst supports, it is necessary to deposit dispersed metal particles onto nanotubes, ideally particles that have diameters within the nanometric range. It is worthwhile to mention

that a combination of catalytic metals, chiefly transition metals such as iron, cobalt, or nickel, leads to the growth of extremely forms of CNTs such as helically wound graphite spirals. Under catalytic conditions, a wide variety of carbon nanotubes, which may not be linear but resemble spaghetti piles, are possible and may not be recognized as carbon.

Recently, aligned and coiled multiwalled carbon nanotubes were successfully obtained inside of quartz tubing by our group using the modified spray pyrolysis method. In **Figure 2**, two types of morphology of multiwalled carbon nanotubes (MWCNTs) are shown. In concordance to these results, variable control is essential to produce CNTs [25, 29].

On the other hand, preparative methods of synthesis of CNS such as graphene are also currently a heavily researched and important issue. The search for a methodology that can reproducibly generate high-quality monolayer graphene sheets with large surface areas and large production volumes is greatly sought after. A popular aqueous-based synthetic route for the production of graphene utilizes GO. It is produced via graphite oxide by various different routes. Hummer's method, for example, involves soaking graphite in a solution of sulfuric acid and potassium permanganate to produce graphite oxide. In this method, we have done some modifications on the variables of synthesis. Our focus to take advantage of the TMD catalytic activity is on the development of different pathways of synthesis to accelerate the electron transport. Therefore, carbon support is another factor that affects the catalysis. Some studies have Wilkinson reported the effect of carbon support on catalytic activity and found the relation between the kinetic and the specific surface areas, pore size distribution, and the N or O content of the carbon support [7].

Here, it is worth to mention that various syntheses and preparations of catalyst routes have been reviewed, with emphasis on the problems and prospects associated with the different methods. However, we reported a simpler synthesis method to prepare Pt-WS$_2$ nanoparticles supported on Vulcan carbon [30] and later on MWCNT synthesized by modified spray pyrolysis. These results were used to compare the catalytic electroactivity toward the ORR in acid media, in order to carry out studies about the influence of the exfoliated sulfides on Pt nanoparticles to modify its catalytic properties and to enhance the activity of pure Pt. In **Figure 3**, the result of chalcogenides versus Pt on carbon supports is shown. It is clear to
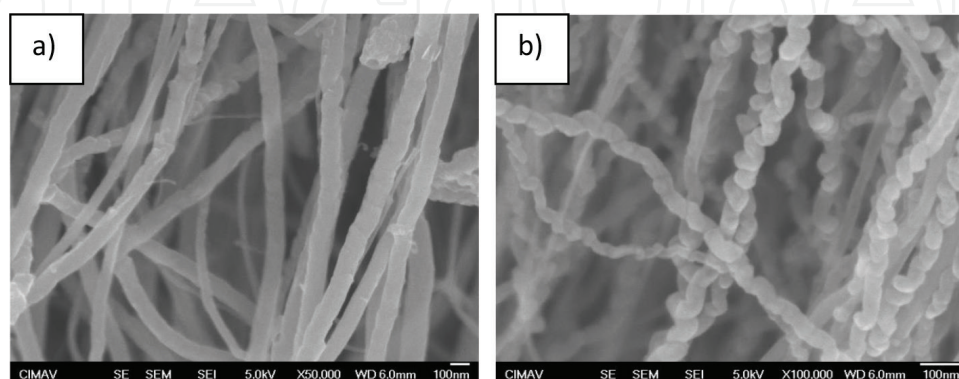

Figure 2. (a) TEM image of straight MWCNT and (b) TEM image of coiled MWCNT synthesized by modified spray pyrolysis method.
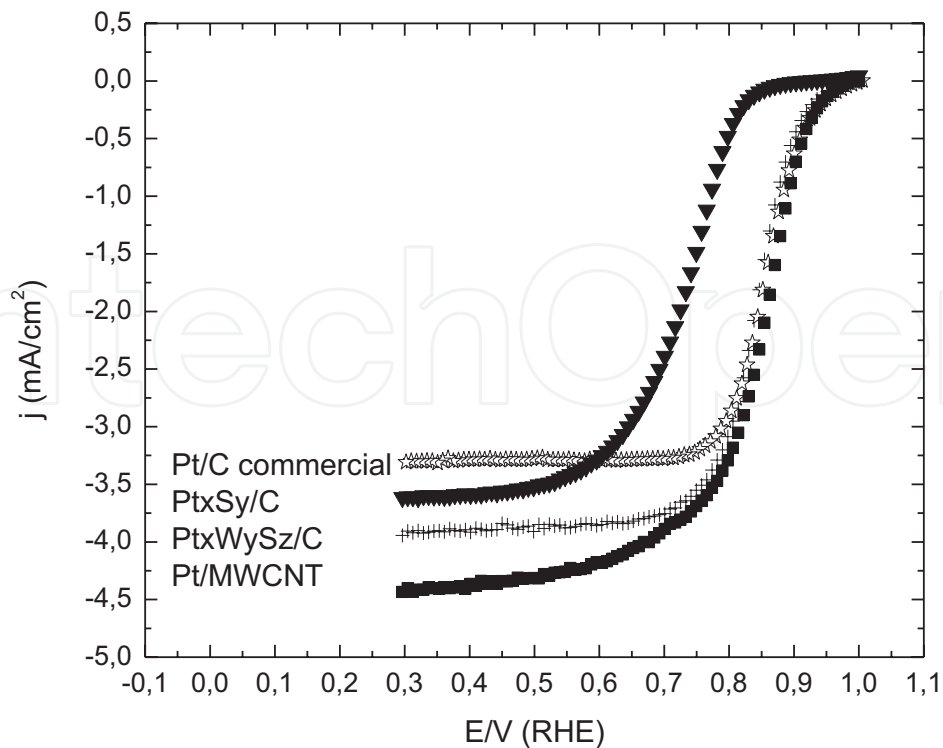
Figure 3. ORR polarization curves in oxygen-saturated 0.5 M H_2SO_4 as a function of potential for different platinum electrocatalysts. Pt/C commercial and electrocatalysts synthesized from sulfur (PtxSy/C), tungsten thiosalt, and Pt/ MWCNT. All samples have 20 wt.% of active phase. Measurements were carried out in O_2-saturated 0.5 M H_2SO_4 solution at 5 mV s^{-1} at 1600 rpm rotation speed and 25°C.

observe the effect of the arrangement of carbon atoms on the kinetic response to increase the current density. The overview of several studies has also suggested that a strong coupling (synergistic effect) interaction between catalysts and substrates is a promising approach for promoting electrocatalytic performance [7, 11, 15, 30].

It should be noted that the constituent atoms of graphite, fullerenes, and graphene share the same basic structural arrangement in what structure begins with six carbon atoms which are tightly bound together (chemically, with a separation of approx. 0.142 nm) in the shape of a regular hexagonal lattice. Moreover, at the next level of organization, graphene is widely considered as the "mother of all graphitic forms." In this sense, compared to black carbon, CNTs show much higher catalyst loading efficiency, electrical conductivity, better durability, and lower impurities. However, due to their high aspect ratio and strong π-π interactions, the dispersion and difficulty to achieve uniform deposition of metal nanoparticles are some challenges in this field. In contrast, the graphene displays better electrical, mechanical, and physical properties and much larger surface area than MWCNTs, which are highly desirable for the catalyst support [31].

1.2.2. Nanostructured hybrids

In PEM fuel cells, platinum-based electrocatalysts are still widely utilized as anode and cathode electrocatalysis. However, carbon nanostructures (nanotubes and graphene), supported on Fe

or Co nanoparticles, show promise for fuel cells, and these nanostructured metal chalcogenides (NMCs), CNS, or even NMC-CNS could also be applied for other energy devices. Some recent reports about utilized GNSs and nitrogen-doped GNS as catalyst supports for Pt nanoparticles toward the ORR, where the constructed fuel cells exhibited the power densities of 440 and 390 Mw cm^{-2} for nitrogen-doped GNS-Pt and GNS-Pt, respectively. It is clear that the nitrogen-doped device exhibited an enhanced performance, with improvements attributed to the process of nitrogen doping which created pyrrolic nitrogen defects that acted as anchoring sites for the deposition of Pt nanoparticles and is also likely due to increased electrical conductivity and/or improved carbon-catalyst binding. On the other hand, Pt nanoparticles deposited on graphene submicroparticles (GSP) in addition to carbon black and CNT via reduction method. Results demonstrated that the Pt/GSP was two to three times more durable than the CNT and carbon black alternatives [30].

The main issues about graphene-based materials are focused on structural characteristics, interaction between nanoparticles or functional groups, and their electrochemical performance as catalysts, and a wide variety of graphene-based hybrid nanocomposites are grouped into the next categories: doped/modified graphene, noble metal/graphene hybrids, and graphene/nonmetal composites.

Figure 4 shows catalyst prepared from nitrogen-doped graphene-carbon nanotube hybrids (NGSHs) and their electrochemical behavior toward ORR for graphene-SWCNT hybrids (GSHs), NGSHs, and Pt/C supported on GC electrodes [32]. Those edge planes of GNS also provide defects for the uniform dispersion of Pt nanoparticles, subsequently increasing catalytic activity by increasing the surface area of an electrode as well. However, nitrogen dopants increase the number of defects on the CNT surface, subsequently improving the distribution of a catalyst. Since nitrogen is introduced into the growth process of GNS-CNT hybrid nanostructure, these substituted nitrogen sites prevent the Pt nanoparticles from aggregation [33].

The fast development of nanocarbon materials like graphene enables them to play an increasingly important role in the improvement of non-precious metal-based catalyst (NPMC) performance. ORR activity of Co_9S_8-N-C catalysts, for instance, was much higher than that of the state-of-the-art Pt/C 0.1 M NaOH solution. Dai et al. synthesized a Co_xS-reduced graphene oxide (RGO) hybrid material by a mild solution-phase reaction followed by a solid-state annealing step. Strong electrochemical coupling of the RGO support with the Co_xS nanoparticles and the desirable morphology, size, and phase of the Co_xS nanoparticles mediated by the RGO template rendered the hybrid with a high ORR catalytic performance in acid media [5, 33]. **Figure 5** shows an illustration of carbon nanostructures and nanoparticles, synthesis, and functionalization methods commonly used by our group.

1.3. Synthesis methods of carbon nanostructures and nanoparticles

Nowadays, the nanoscience has reached the status of a leading science with basics and applied implications in all physics, life, earth sciences, as well as in engineering and materials sciences. **Figure 6** shows the schematic illustration of the focus on research from the synthesis methods of carbon support materials, such as carbon nanotubes and graphene, and metallic nanoparticles that also can be obtained by different methodologies, until the surface modification of these nanomaterials. It could be on TMS or non-noble metals as the active phase of the catalysts for PEM fuel cells.
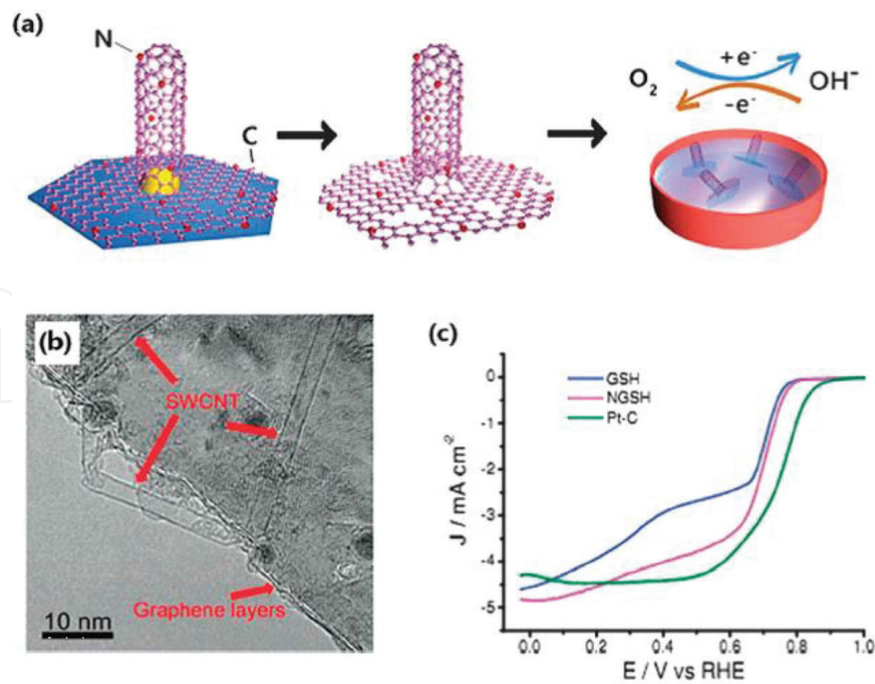
Figure 4. (a) Schematic illustration of the preparation of the nitrogen-doped graphene-carbon nanotube hybrids (NGSHs). (b) TEM image of the NGSHs. (c) ORR polarization for graphene-SWCNT hybrids (GSHs), NGSHs, and Pt/C supported on GC electrodes at a rotating rate of 1225 rpm.
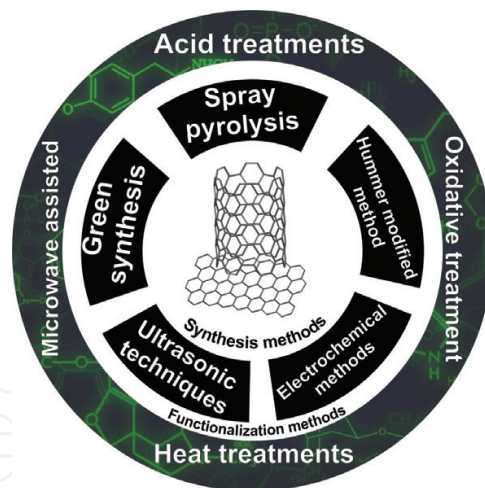

Figure 5. Schematic illustration of carbon nanostructures and nanoparticles, synthesis, and functionalization methods reported by our group. Potential applications could be reached with these preparation routes in terms of catalytic activity, time, and cost-effectiveness.

In this regard, our strategy is to generate nanomaterials that could be fabricated by simple methods with the purpose of controlling and understanding at nanoscale the properties of the catalysts based on NMCS and CNS through the atomic behavior at specific conditions, in order to enhance the catalytic activity. This concept focuses on the design and the creation of novel morphology and structure to probe, tune, and optimize the properties to develop functional materials for multiple applications. Nevertheless, significant electrochemical effects
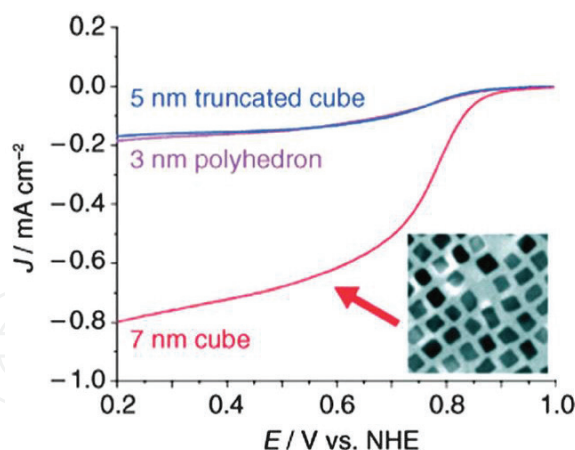
Figure 6. ORR polarization curves in oxygen-saturated 0.5 M H_2SO_4 as a function of potential for different Pt catalysts at the rotation speed of 1600 rpm. (Reprinted with permission from Royal Society of Chemistry. Lic. No. 4171470897994).

have been observed in different samples of platinum. Morphology and structure dependence can be shown in **Figure 6**. It displays the ORR polarization curves in oxygen-saturated 0.5 M H_2SO_4 as a function of potential for different geometries of Pt at the rotation speed of 1600 rpm. The response of the kinetic behavior on the atomic structure is clear to observe [5].

On the other hand, it is worth to mention some synthesis methods that are well known and developed by our group. **Table 1** shows some catalysts based on TMC and their method to obtain materials with high catalytic activity on specific reactions [34]. However, a recent development in the field of organometallic chemistry has been the use of organometallic complexes for the high-yield catalytic synthesis of CNT [35–37].

Table 1 An overview of synthesis reports using platinum, sulfur, or selenium.

Some results reported about the ORR activity of the thiospinel compounds were directly related to the type of metal utilized, with an order of Co > Ni > Fe. Moreover, decreased performance was also observed when sulfur was partially replaced with O, Se, or Te. **Table 1** shows an overview of catalyst synthesized for PEM fuel cells. The main methods that we have used to obtain catalysts are spray pyrolysis and Hummer's method, electrochemical methods, ultrasonic techniques, and green synthesis.

First, the experimental procedure of modified spray pyrolysis is simple and is one of the most commonly used; this methodology represents advantages among others due to its characteristics of using non-sophisticated equipments as well as easiness of scalability. To start, an aqueous solution containing the metal precursor is nebulized into a carrier inert gas that is passed through a furnace. Second, the nebulized precursor solution deposits onto Vycor tube as a substrate, where it reacts and forms the final product. To form nanoparticles, the aerosol is pyrolyzed under inert atmosphere and a set temperature [17, 29].

Recently, we are also producing graphene for PEM fuel cells and other specific applications. In accordance with Hummer's method, we modify some steps in the original method. However, it is worth to mention about a specific application, for instance, about the storage energy, the combination of carbon nanostructures as support, and the functionalization with a pseudocapacitive

Catalyst	Synthesis method conditions	Reference
NEBH$_2$S NEB DMDS NEBDMS	Two aqueous solutions were prepared (A and B). Solution A consisted of ammonium heptamolybdate and ammonium metatungstate dissolved in water at 363 K under stirring. The pH of this solution was maintained at about 9.8 by adding NH$_4$OH. Solution B consisted of nickel nitrate dissolved in water at 363 K while stirring; solution B was slowly added to solution A at 363 K; a precipitate was formed; and then the solid was filtered, washed with hot water, and dried at 393 K. The molar ratio Mo:W:Ni of precipitate was 1:1:2 and was represented as NH$_4$-Ni-Mo$_{0.5}$W$_{0.5}$-O. Sulfidation was carried out in a tubular furnace at 673 K for 2 h using H$_2$S, DMDS, or DMS (10 vol. % in hydrogen).	Gochi Y et al., 2005 [2]
Pt$_x$S$_y$/C	First, the synthesis of catalytic precursor is from molecular sulfur, and ammonium hexachloroplatinate ((NH$_4$)$_2$PtCl$_6$, Alfa Aesar) was reacted under a constant agitation for 12 h at room temperature. The solution was mixed with carbon Vulcan (E-TEK) and stirred continuously for 24 h at room temperature. The precipitates were filtered, washed with distilled water, and dried for 12 h at room temperature on a drier. Finally, the precursor was treated thermally at 350°C under (75% v/v) N$_2$/H^2 atmosphere for 2 h.	Gochi-Ponce Y et al., 2006 [15]
Pt$_x$Mo$_y$S$_z$/C, Pt$_x$W$_y$S$_z$/C, or MWCNT	Tungsten or molybdenum thiosalts, as appropriate, and ammonium hexachloroplatinate were reacted under constant agitation for 12 h at room temperature. The solution was mixed with the carbon support and is stirred for 24 h at room temperature. The precipitates were filtered, washed with distilled water, and dried for 12 h at room temperature. The supported precursor was treated at 400°C under N$_2$/H$_2$ atmosphere for 2 h.	Gochi-Ponce Y et al. 2006 [16]
Pt/ MWCNT-Fe PtFe/ MWCNT Pt/MWCNT	The coordination complex salt of Pt was synthesized by Burst-Schiffrin method. Ammonium hexachloroplatinate was dissolved into 10 ml triply distilled water. This solution was added to 15 ml of a TOAB in 2-propanol solution at room temperature (25°C). The Pt precursor was filtered under vacuum, washed with deionized water, and dried at 70°C for 8 h. MWCNTs (raw, treated, or cleaned and synthesized by spray pyrolysis) are added to 2-propanol and dispersed in an ultrasonic bath for 1 h. The Pt precursor dissolved in 5 ml 2-propanol solution was added to the MWCNT-Fe suspension and stirred for 1 hr. Finally, 10 mL aqueous solution of NaBH$_4$ in excess, 1:10 was added by drip during 5 min to the suspension, which was stirred at room temperature for 12 h to reduce Pt^{4+} to Pt^0. The obtained mixture was then filtered and washed with acetone and water, to be finally dried at 70°C for 4 h.	Rodriguez JR et al. 2014 [35]
Pt-Ni/ MWCNT	MWCNTs were synthesized in a spray pyrolysis. For the MWCNT-Ni, it was necessary to use a thin film (manganese oxide) as substrate previously deposited in the inner walls of the Vycor tubing. The temperatures of MWCNT synthesis were 900 and 800°C for ferrocene and nickelocene, respectively. After the process, once the substrate was completely cold, the MWCNTs were removed (scratched) from the Vycor tubing.	Valenzuela-Muñiz AM et al. 2013 [36]
Ru$_x$Se$_y$	Carbon-supported Ru$_x$Se$_y$ (20 wt.%) nanoclusters were prepared in aqueous media using RuCl$_3$_xH$_2$O and SeO$_2$. Typically, 0.124 g carbon (Vulcan XC-72) was dispersed in 100 mL of water under nitrogen under vigorous stirring. The resulting suspension was heated to 80°C, mixed at this temperature for 30 min to remove oxygen in water, and then cooled down to room temperature. Subsequently, 4 mmol RuCl$_3$_xH$_2$O and 1 mmol SeO$_2$ were added to the above suspension and then mixed for another 1 h. Thereafter, 100 mL of a mixture solution containing 0.1 M NaBH$_4$ and 0.2 M NaOH was added dropwise (1.25 mL min^{-1}) to the suspension to reduce the metal ions. The suspension was kept for further reaction for another 10 min and then heated to 80°C for 10 min. The final black powder was collected on the Millipore filter membrane washed with water and dried under vacuum at room temperature.	Saul Gago A et al., 2012 [12]

Table 1. An overview of synthesis reports using platinum, sulfur, or selenium.

material which generates a synergistic effect in capacitance, thus, in the energy density with an excellent electrochemical performance throughout the system. The main determining factor on this material is the surface area of each electrode that makes up the supercapacitor. Through the synthesis methods of carbon nanostructured materials such as graphene and nanotubes, the size and morphology of the compounds are tunable. This approach favors some specific properties for applications on fuel cell systems such as high surface area, stability, electroconductivity and catalytic activity.

1.3.1. Galvanic displacement

Some progress has been made in catalytic materials and supports preparation techniques, although none of these catalysts has reached the level of a Pt- or Ru-based catalyst in terms of catalytic activity, durability, and chemical/electrochemical stability. In order to make non-noble catalysts commercially feasible, cost-effective, and innovative, synthesis methods are needed for new catalyst discovery and catalyst performance optimization. The use of electrochemical methods, such as galvanic displacement and ultrasonic techniques, for instance, was chosen to describe here.

Figure 7 shows the preparation of core-shell nanoparticle catalysts. We also report here the electrochemical response obtained by PtPd/MWCNT. The parameters investigated were Pt concentration and sonication by a simple and fast galvanic displacement (GD) method, finding that both play a key role in the physicochemical features and, thereby, modifying the performance of the catalysts toward the oxygen reduction reaction (ORR) activity and according to results highly dispersed $Pt_{10}Pd_{90}$/MWCNT was produced [13, 36, 38].

1.3.2. Ultrasonic-assisted strategy

In addition, it is of great significance to explore different methods to obtain efficient catalysts for the PEM fuel cells. Ultrasonic-assisted strategy is known as a unique synthesis method in materials chemistry. Sonochemical reaction techniques have been introduced in the 1980s by Suslick's group. However, most of the literature works on electrocatalysis published until 2010 are cited by Eunjik Lee (2016) [39]. A number of alloy and core-shell NPs are well discussed. During the past years, a number of new alloy and core-shell NPs based on Pt and Pd have been synthesized by sonochemistry and studied for their electrocatalytic properties [40]. Therefore, in light of the importance of finding more dependable catalysts in the present status of FC researches. Some works cited here are the syntheses of Pt-Pd/MWCNT for enhanced ORR of Pt/MWCNT and PtNi/MWCNT catalysts with high electroactivity, and further ultrasound treatment is used because carbon nanotubes are uniform in size and well dispersed by this via [32]. We also reported about Pt/CNT/TiO$_2$ catalyst, and here we note the effect of the amount of MWCNT with the current density. In addition, the CO tolerance performance increases in the next sequence of Pt/CNT < Pt/TiO$_2$ < Pt/CNT/TiO$_2$ [41].

1.3.3. Green chemistry

According to the principle of green chemistry, the feed stock of any industrial process must be renewable rather than depleting a natural resource. Moreover, the process must be designed to achieve maximum incorporation of the constituent atoms (of the feed stock) in to the final product [39].
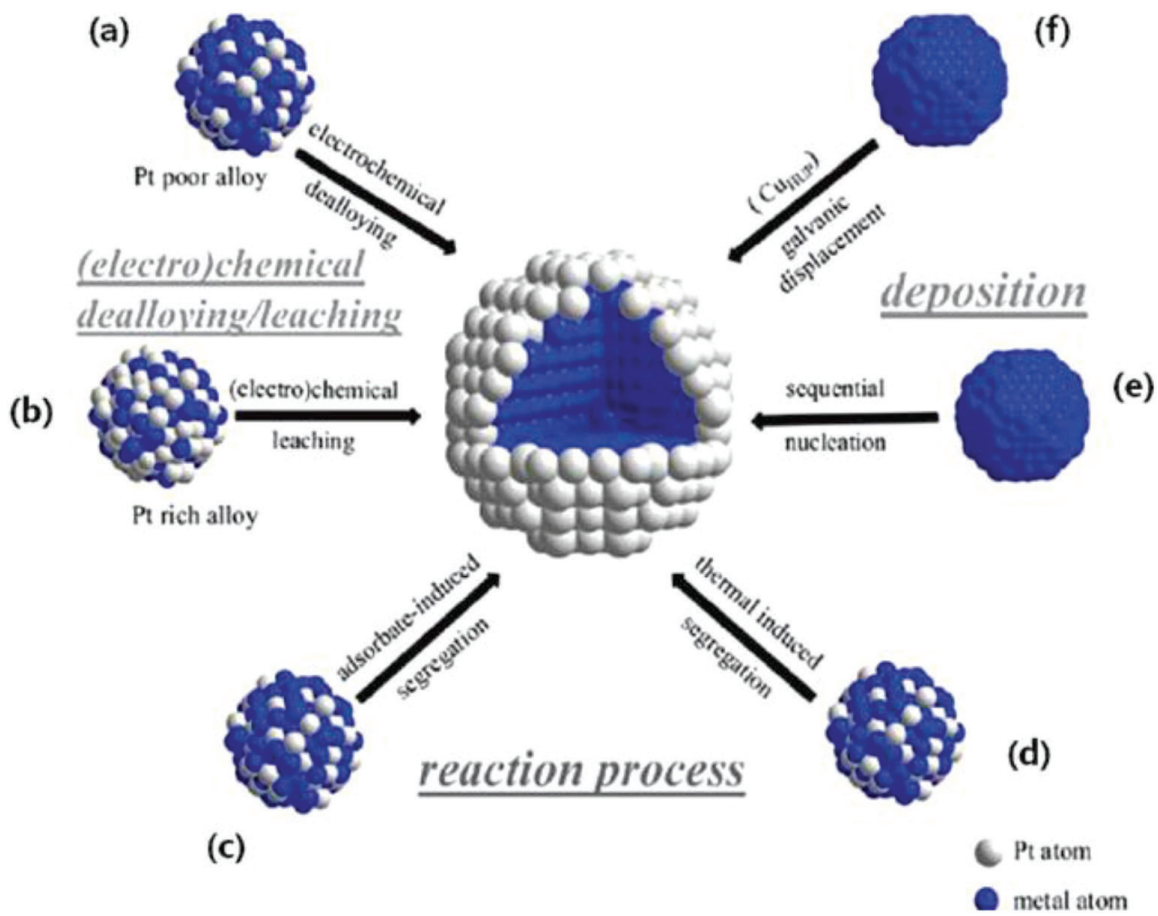
Figure 7. Illustration of basic synthesis approaches for the preparation of core-shell nanoparticle catalysts. Electrochemical (acid) dealloying/leaching results in (a) dealloyed Pt bimetallic core-shell nanoparticles, and (b) Pt-skeleton core– shell nanoparticles, respectively. Reaction process routes generate segregated Pt skin core-shell nanoparticles induced by either (c) strong binding to adsorbates or (d) thermal annealing. The preparation of (e) heterogeneous colloidal core-shell nanoparticles and (f) Pt monolayer core-shell nanoparticles is via heterogeneous nucleation and UPD followed by galvanic displacement, respectively. (Reprinted with permission from Royal Society of Chemistry. Lic. No. 4171470897994).

A great advantage is the use of aqueous solutions instead of any surfactants, additive reagent, or posttreatment in the nanoparticles and CNS synthesis. The preparation of sulfide chalcogenides as reference Pt_xS_y, $Pt_xW_yS_z$, and $Pt_xMo_yS_z$ catalysts were carried out only with water and at room temperature [19, 20] as well as other synthesis methods to produce CNS such as graphene or MWCNTs and nanoparticles, recently cupper nanoparticles, for instance [42].

1.4. Surface modification methods

The functionalization of carbon materials is essential processes for the utilization of these materials. Functional groups or molecules can be directly attached on the periphery of the surfaces of the carbons through various treatments with acids, etc. A large number of oxygen functional groups are created during the activation process by saturation of dangling bonds with oxygen. This creates a rich surface chemistry which is used for selective adsorption. In addition, it determines the ion exchange properties that are relevant for catalyst loading with active components. In **Figure 8**, an illustration of multiple routes of the chemistry of carbon nanotubes in biomedical applications is shown [43, 44]. Although the applications of
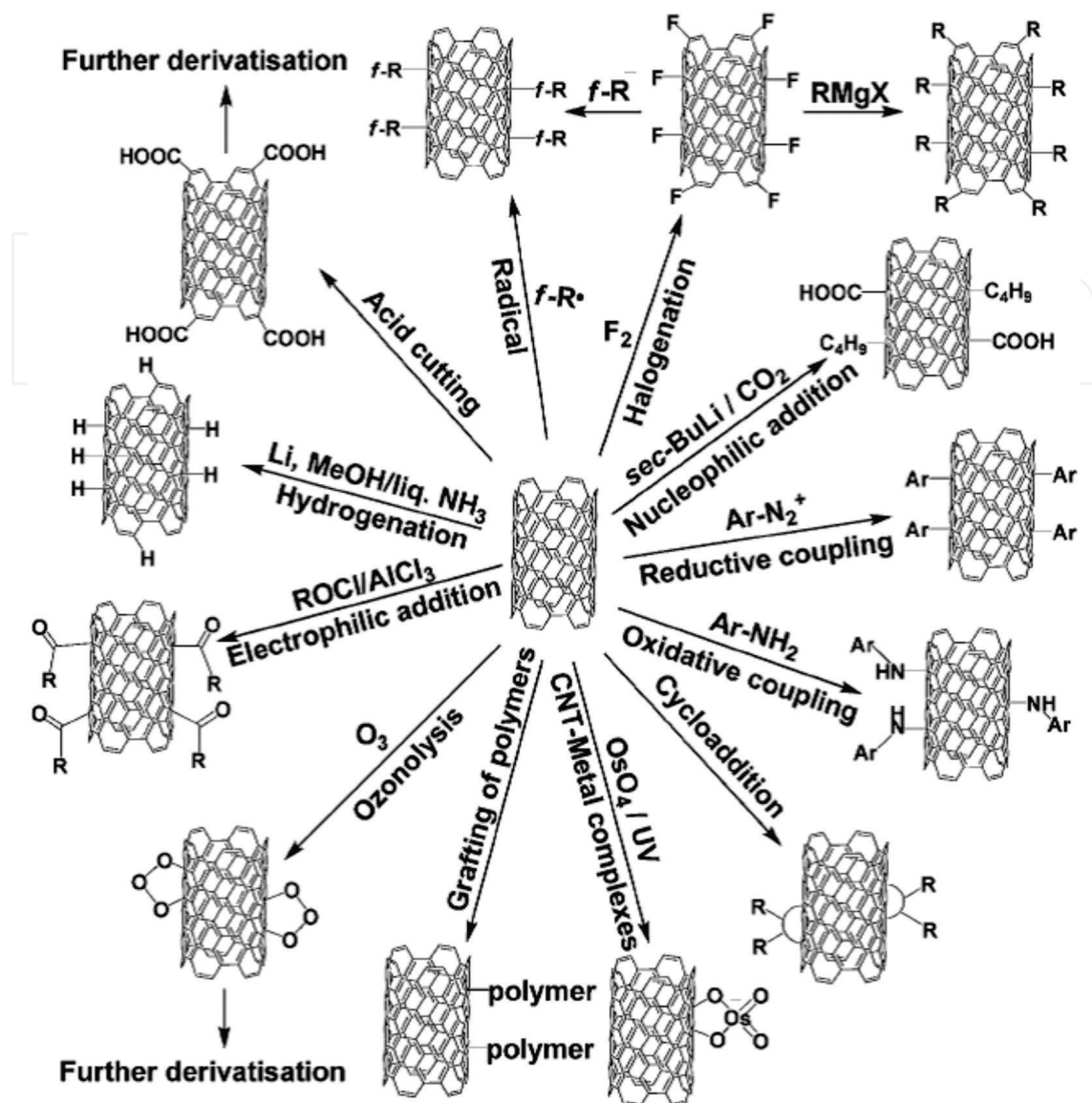
Figure 8. Illustration of the chemistry of carbon nanotubes in biomedical applications. Reprinted with permission from (Royal Society of Chemistry. Lic. No. 4171820715591).

functionalized carbon nanotubes are numerous, the modification surface of the individual carbon nanotubes by decorating the surface with OH, COOH, NH_2, F, or other groups promotes dispersion in a wide variety of solvents and polymers enabling the use of nanotubes in many more applications and different fields of studio. The image above details only one specific application enabled the functionalized carbon nanotubes.

Another example of the modification of carbon nanostructures for different applications is on the design of ultrasensitive biosensors with advantages in the detection of organic molecule. The preparation of the CNT-graphene hybrid, with regard to the complex molecules and nanoparticles that can be anchored to the surface of these nanostructured materials after the oxidation. These results are a significant contribution to the properties that have the nanomaterials mentioned here. Recently, carbon-supported highly dispersed Ru_xSe_y chalcogenide
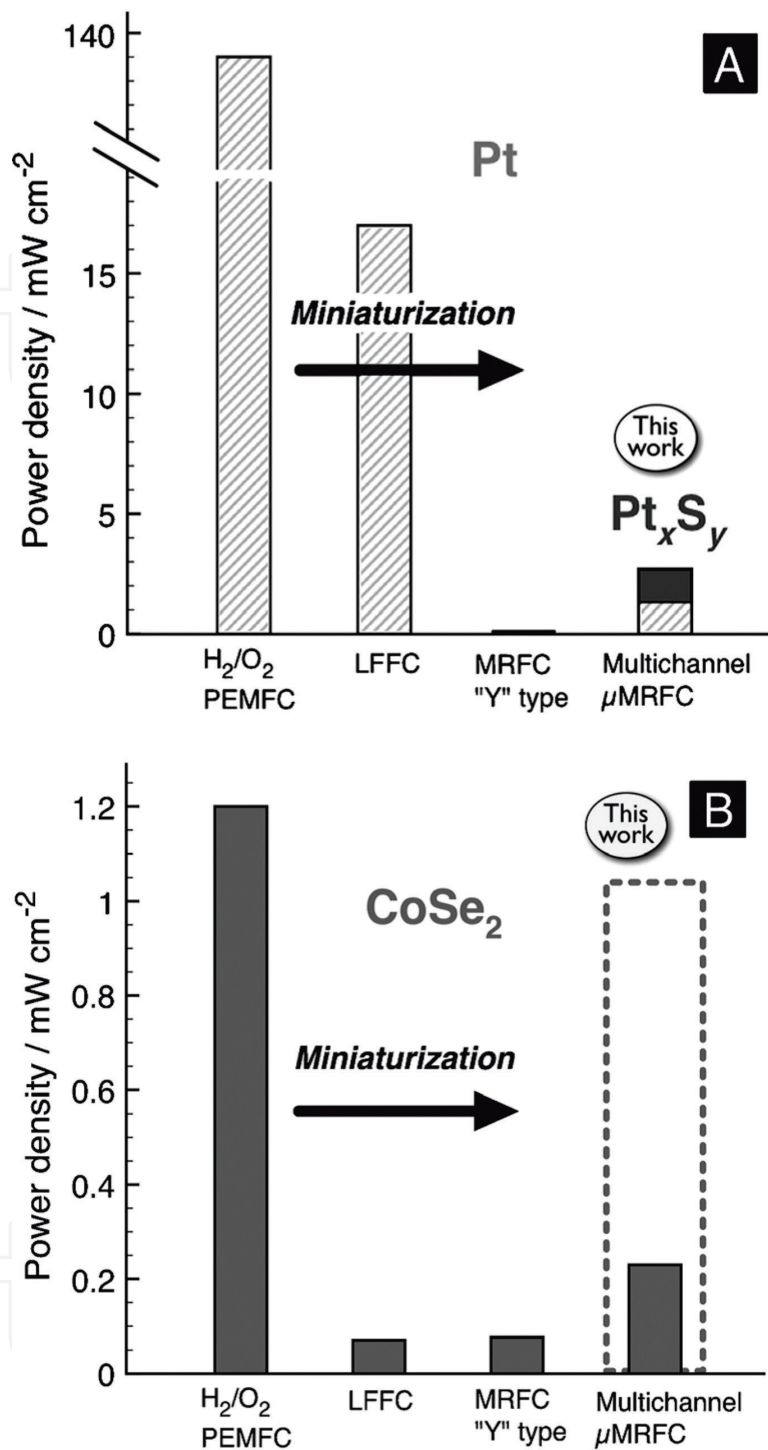
Figure 9. Maximum power density achieved with (A) Pt-based and (B) CoSe$_2$ cathodes of a H$_2$/O$_2$ PEM fuel cell, an LFFC, a Y-type MRFC, and a multichannel mMRFC (this work). The dashed bar in (B) corresponds to the use of 10 mgcm^{-2} Pd at the anode, 10 m HCOOH, and pure O$_2$. Preparation of MEAs for the H$_2$/O$_2$ systems was done under the same conditions as those used for Pt and CoSe$_2$ systems. (Reprinted with permission from John Wiley and Sons. Lic. No. 4166570806290).

nanoparticles (1.7 nm) were synthesized; here, Ru and Se precursors in a simple microwave-assisted polyol process. In other studies, Ir$_{85}$Se$_{15}$/C was synthesized with an average particle size less than 2 nm by the same method [13].
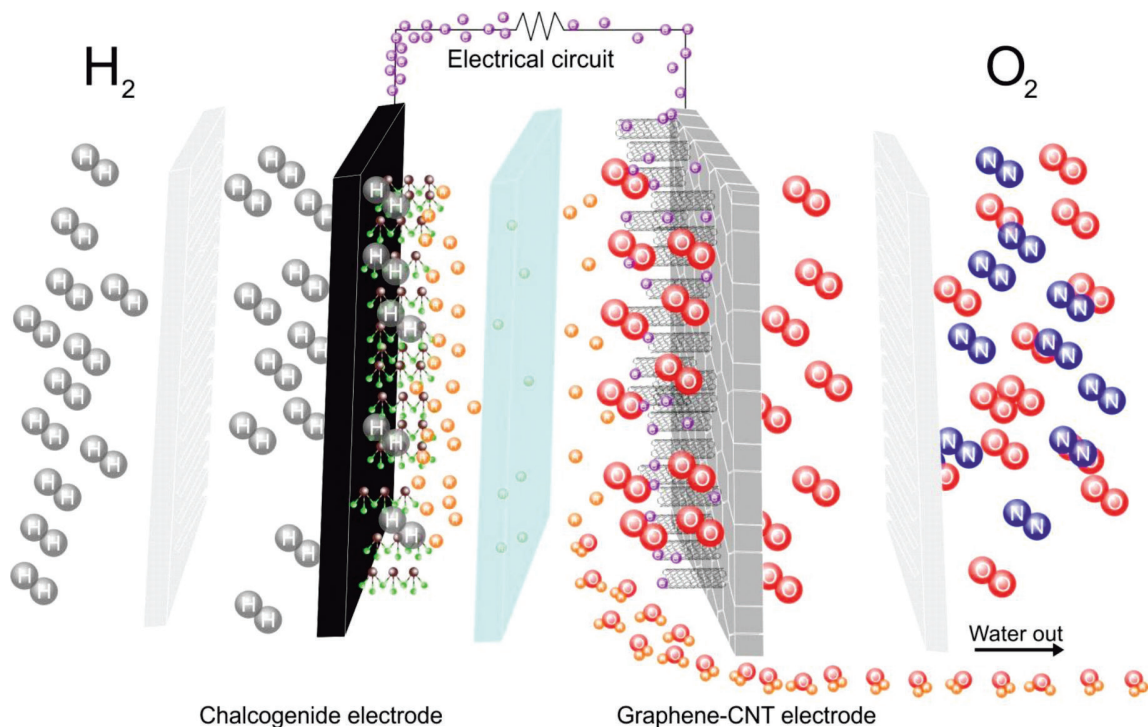
Figure 10. Schematic illustration of a PEM fuel cell and the use of chalcogenides and carbon nanostructures as anodic and cathodic electrodes.

Different routes of modification of CNS have been used by our group. Some synthesis and modification methods by microwave-assisted are used, the oxidizing agents are acids or even, hydrogen peroxide. On the other hand, the heat treatment is also a key factor of the nanostructures obtained [2, 15, 16, 44–46]. Traditionally, acids have been widely used for attaching to CNT. However, the microwave-assisted polyol is a versatile method for synthesis, dispersion, and surface modification of chalcogenides and CNS. Other important aspects of CNT and graphene are on chemistry, the level of purity and functionalization degree of the starting materials. Actually, our interests are on this direction, and the focus is the search of new catalysts for PEM fuel cell based on chalcogenides and CNS synthesized by rapid and efficient methods.

1.5. Applications for PEM fuel cell systems

To date, microscale system research has focused mostly on miniaturization of functional components, for instance, specialized devices such as clinical and diagnostic test, microanalytical systems for field tests, and various portable devices. Thus, here we mention about chalcogenide such as Ru_xSe_y, $CoSe_2$, Pt_xSe_y, and Pt_xS_y that have showed a remarkable selectivity toward the oxygen reduction reaction (ORR) for membraneless microlaminar-flow fuel cell. **Figure 9** shows a significant comparison between Pt, Pt_xS_y, and $CoSe_2$. The maximum power density for fuel cells are achieved with (A) Pt-based and (B) $CoSe_2$ cathodes of a H_2/O_2 for the PEM fuel cell, an LFFC, a Y-type MRFC, and a multichannel mMRFC [12].

This work is inspired by the excellent electrocatalytic activity of chalcogenides and carbon nanostructures which open the door for the development of a novel type of micro- or even

nano-fuel cell. **Figure 10** displays a schematic illustration of an application for a PEM fuel cell. Some basic concepts about advantages and disadvantages of these devices were reported by Taner [47, 48]. It is a challenge to develop an active cathode catalyst for the ORR that is tolerant at the same time. One strategy proposed is the use of chalcogenides as anodic catalyst and CNS as cathodic catalyst. On the one hand, this type of chalcogenides can be used as anode, because are tolerant to CO molecules and by other sides of carbon nanostructures can be placed as cathode because of the atomic arrangement of the carbons can behaviors as metal and also can be modified on the surface, it means, doped or well-functionalized to support non-platinum metals, N_2, B, P, S, etc. Either as cathode or anode, chalcogenides based on sulfur are promising. The target is to generate a maximum power density, and the key is on the methods of synthesis such as here we described. Moreover, many other studies about these materials are furthered from here. Nevertheless, in addition we report on micro-fabricated membraneless fuel cells with Pt_xS_y- and $CoSe_2$-tolerant cathodes and show how such materials can be used for developing smaller, simpler, and cheaper for PEM fuel cells.

Acknowledgements

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