
Defect Engineering in Reduced Graphene Oxide toward Advanced Energy Conversion

Guilherme Luís Cordeiro

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.77386>

Abstract

Defect engineering in reduced graphene oxide (rGO) for a smart design of fuel-cell supports has become an effective approach to improve the restricted two-dimensional (2D) mass and charge transfer and to boost the alcohol oxidation reaction. The present mini-review describes recent trends across prominent characteristics of tailored reduced graphene oxides, which include but are not restricted to, engineered three-dimensional (3D) nanostructures for better mass transport, tuned electron/hole conduction for easier electrical transport, and hybridized surfaces for high electrocatalytic activity. Special focus fixes upon the experimental progress on defect engineering, from three-dimensional structure assembly to surface metal complexation and heteroatom doping to size-controlled defect formation. Given their crucial impact on reduced graphene oxide properties, controlled methods for synthesis, and processing offer considerable promise toward next-generation carbon nanomaterials for electrocatalysis.

Keywords: defect engineering, reduced graphene oxide (rGO), electrocatalysis, fuel cells

1. Introduction

In response to an increasingly carbon-constrained world, the adoption of policies aimed at developing new technologies has emerged in the face of cleaner energy production. In this context, direct alcohol fuel cells (DAFCs) have been recognized as promising systems to provide continuous and low-carbon power supply. Basically, a DAFC operates by electrochemically oxidizing an alcohol, such as methanol or ethanol, at the anode, to produce protons (H^+ ions), and electrons. Protons are transferred to the cathode through the proton exchange

membrane and react with OH^- ions, which are generated from the electrochemical reduction of oxygen, at the cathode, to produce water, heat, and electricity [1–4].

In spite of the attractiveness of these non-stop and low-carbon energy generation systems, important commercialization issues still need to be addressed. The kinetics of the alcohol oxidation reaction largely determines the overall efficiency of the fuel cell. In order to boost conversion efficiencies, highly active catalysts are required because of the low operating temperatures (60–120°C). Therefore, far, it is undisputed that platinum (Pt) provides the best correlation between energy adsorption and exchange current density [5]. With studies demonstrating the high instability of Pt catalysts [6–9] and the overall performance dependence on large Pt loadings [10–12], it has become imperative to design improved, durable, and highly efficient electrocatalysts.

Various attempts, such as the dispersion of Pt on high area conductive supports [13–19] and its combination with another metal [20–23] have been addressed for improving Pt utilization in fuel-cell reactions. Regarding the former approach, it is well-known that a suitable fuel-cell support provides a high surface-to-volume ratio of metal particles, which, in turn, maximizes the available area for electrochemical reactions [24]. In comparison to state-of-the-art C black, reduced graphene oxide (rGO) sheets have been demonstrated as an advanced electrocatalyst support for DAFCs due to the unique characteristics of the two-dimensional (2D) structure [24, 25]. The high theoretical surface area ($2.630 \text{ m}^2\cdot\text{g}^{-1}$ for a single layer) and ultra-large surface-to-volume ratio, when combined with the fast heterogeneous electron transfer (HET) rate, high specific capacitance ($550 \text{ F}\cdot\text{g}^{-1}$), and intrinsic redox activity, make rGO an ideal platform for homogeneous dispersion of Pt nanoparticles and faster charge and mass transport properties [26–28].

In spite of the appealing properties noted above, restacking of the sheets due to the strong van der Waals interaction greatly reduces the accessible Pt surface area, resulting in low catalyst utilization, and transport pathway for reaction species. Material processing techniques, broadly defined as the approaches for tailoring physicochemical properties, have been extensively applied to control the interactions between rGO sheets and make them aggregation-resistant in both wet and solid state [29]. In this context, some solutions have been paving the way for further research and development on the assembly of two- or three-dimensional (3D) structures with desirable microstructural features for electrocatalysis. Positive progresses, such as the development of intercalation composites [30–34] and the usage of geometrical modification strategies [35–37], have greatly improved the utilization of supported Pt catalysts by increasing the density of exposed active sites.

Besides tailoring the physicochemical properties of the 2D structure, further advantageous characteristics for energy-conversion applications may be achieved by tuning the bandgap relative to the Dirac point in the C–C double bond network. Through electronic modulation of the support, high catalyst activity may be achieved by tuning the interaction between support and catalyst surfaces. In this sense, geometrically modified and/or heteroatom-doped rGO sheets, that is, can facilitate the property control of the Pt-support electronic effects. By enriching catalyst electronic structure due to catalyst/support synergism, novel characteristics, such as smaller catalyst particle size, increased catalyst particle dispersion, increased catalyst durability and stability, can effectively improve catalyst utilization [38–43].

Since the above observations reinforce the potential of intentional rGO modification as a strategy for boosting the 2D mass and charge transfer, defect engineering in rGO, which refers to the introduction of controlled defects in the material structure, is focused on this mini-review. Although this chapter makes no attempt to be exhaustive, the present contribution describes new breakthroughs on defect engineering in rGO that have recently been published since 2017, including recent advances and trends on state-of-the-art synthesis and utilization of engineered rGO sheets as fuel-cell support materials for the methanol and ethanol oxidation reactions. Future perspectives for further development are also proposed.

2. Overview of defect engineering in rGO for energy conversion

Defect engineering in 2D semiconductor technology refers to the introduction of controlled defects at the atomic level, such as heteroatoms and size-controlled vacancies, for the modification of the two-dimensional structure and properties. In spite of these, other two strategies, a 3D structure assembly approach and a surface metal complexation methodology, have been included as part of a broadened view of defect engineering in reduced graphene oxide, as summarized in **Figure 1**. To produce tailor-made support materials with desirable characteristics for fuel-cell catalysis, the usage and/or combination of defect-induced procedures is proposed toward the development of the next-generation rGO support materials.

In the first subsection of this mini-review, recent progresses on the synthesis and electrocatalysis of 3D engineered rGO-based platinum catalysts toward methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR) are discussed. Then, advances in heteroatom doping for designing highly conductive three-dimensional rGO-based platinum catalysts and the impacts on electrocatalysis are presented. In the last subsection, research directions on surface metal complexation and size-controlled defect formation through metal-organic frameworks (MOFs) are proposed as future perspectives of further development.

2.1. Current trends in 3D structure assembly for enhanced mass transfer

Crumpling the sheets into porous frameworks has been highlighted as an attractive methodology for enabling the interaction among nanoparticles and reactants. Kwok et al. [44] produced a high-quality platinum-decorated rGO aerogel with the aid of a solvothermal method. Their observations indicated that the rGO aerogel porous framework can be optimized by simply changing the GO concentration input for the gelation process. Tests on the supported ultra-fine platinum nanoparticles (sizes ranging from 1.5 to 3 nm) showed that the electrochemically active surface area (ECSA) increased by about 8.92 times in comparison to a benchmark Pt/C catalyst, resulting in a 358% increment in specific power for a methanol-fed fuel cell.

In order to enhance catalyst utilization, Radhakrishnan et al. [45] fabricated a three-dimensional assembly of platinum nanostructures with dominant (100) plane on rGO by a co-electrodeposition method. They found that the morphology, active site, and the electrochemical activity of the catalyst were highly dependent on the number of electrochemical cycling used for the deposition. Their nanocomposite showed a high mass activity toward MOR, which



Figure 1. General schematic roadmap of defect engineering strategies in reduced graphene oxide support materials for achieving advanced energy conversion.

was attributed to the strong metal-support interactions. At the atomic level, the single-step approach for growing morphology-controlled nanostructures incurred in geometric and an electronic changes of platinum surface for enhanced mass/charge transfer.

Abundant mass transfer channels were recently introduced by a geometric change of rGO surface, as reported by Qiu et al. [46]. Following the development of a sacrificial template method, platinum nanoparticles on 3D reduced graphene oxide hollow nanospheres were synthesized. The enhanced activity for the methanol oxidation reaction was provided by the three-dimensional microporous structure, which facilitated the exposure of the active sites thereby promoting the ion and mass transfer processes. In addition, the improved activity of the electrocatalyst was ascribed to the electronic effects of platinum when alloyed with transition metals (iron, cobalt, nickel) for achieving low platinum loading in fuel cells.

Further research and development on material processing approaches may be illustrated by the recent work of Wang et al. [47]. In their contribution, intercalation was extended to a polyaniline (PANI) functionalization method. Deposited PANI effectively prevented rGO sheets from restacking during the preparation of the electrodes while a three-dimensional structure could

also be produced during the process. Synergistic effect of the porous framework was associated to faster mass and electron transfer, resulting in superior methanol electrooxidation. The advantage of the novel synthesis procedure is that the conductivity of rGO could be preserved with the increase in porosity due to the conductive polymeric network created by intercalated PANI. In related work in terms of covalent functionalization, Pinithchaisakula et al. [34] also demonstrated that polydopamine PDA-functionalized reduced graphene oxide improved the MOR activity. Very recently, Waenkaew et al. [48] also pointed the effect of PDA on the electrocatalytic activity of Pt on rGO toward the oxidation of both methanol and ethanol.

As briefly pointed out, a three-dimensional hierarchical porous structure enables rGO sheets to efficiently improve the MOR activity due to the facilitated mass transfer arising from the 3D morphology. Revisited works indicate the superior advantage of an architected reduced graphene oxide structure over conventional carbon black support materials. In light of recent developments [44, 47], further porous electrode optimization is highly recommended for maintaining the electrical conductivity of the rGO with the increase in porosity and decrease in density. By combining the heteroatom doping strategy, that is, to boost electrode conductivity, the porous materials will pave a way for fuel-cell development in the future.

2.2. Current trends in heteroatom doping for improved charge transfer

Efficiency increase in fuel cells has put forward a new prospect for the rational design of heteroatom-doped carbon nanomaterials for advanced energy conversion. This, together with the high-cost and scarcity of platinum has driven an intensive research effort for the development of metal-free cathode catalysts. Indeed, heteroatom-doped reduced graphene oxide has led to a huge amount of literature on metal-free catalysts for oxygen electrocatalysis [49, 50]. Nevertheless, doped carbon nanomaterials could largely impact anode technology, guiding advances on supported catalysts with low platinum content.

Since current graphene derivatives suffer from low intrinsic conduction as fuel-cell catalyst supports and current carriers, heteroatom doping, the process in which some carbon atoms are replaced by heteroatoms, could have a positive impact on the development of highly conductive support materials. By considering the most recent works on this hot topic, current trends indicate that heteroatom doping is capable of simultaneously providing proper nanoparticle dispersion and size-controlled active sites, and along with tuning catalyst d-band for achieving superior catalyst electrochemical activity [51–53].

Among various heteroatom doping strategies, the incorporation of nitrogen (N) has been the most studied because quaternary N atoms (substitutional N-doping), as depicted in **Figure 2**, can introduce high positive charge distribution in the nearby C atoms due to the high electron-withdrawing ability of N [50]. Furthermore, substitutional defects in the two-dimensional network can act as electron donors, providing n-type conductivity [54]. As a consequence, the former feature could lead to defective sites for efficient attachment of catalyst nanoparticles, whereas the latter could enhance an electron transport from support to the attached platinum nanoparticles, thereby increasing catalyst tolerance to poisoning.

Further development on the heteroatom doping approach may be followed with the work of Kanninen et al. [51]. In their methodology, reduced graphene oxide was co-doped with nitrogen

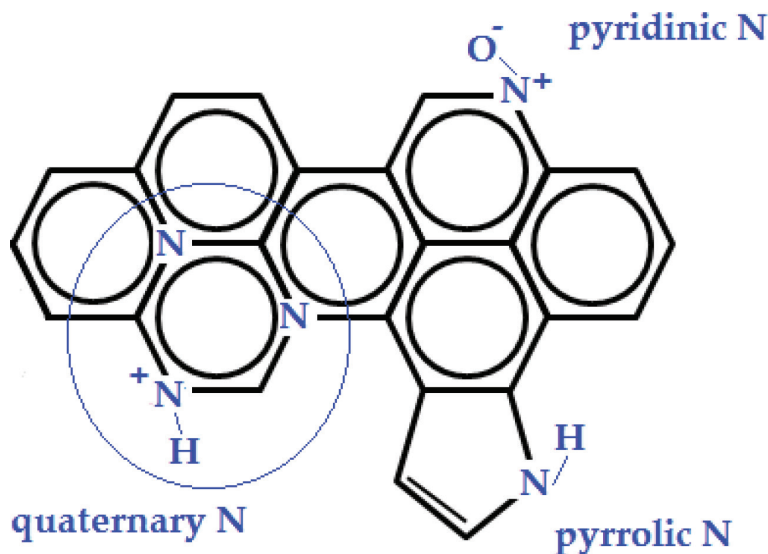


Figure 2. Schematic diagram of nitrogen dopant configuration in the 2D carbon-carbon network.

and sulphur atoms by a thiol-ene click chemistry approach. Co-doping changed platinum-support interaction, leading to a clear improvement on catalyst activity toward EOR in comparison to platinum supported on an undoped rGO. In addition, the induced defect sites generated from the co-doping strategy promoted the stabilization of the supported nanoparticles, resulting in enhanced catalyst durability. The latter was confirmed after a potential cycling test, revealing a minor loss in ECSA. After 500 potential cycles, the order of ECSA decrease was: Pt/C ($-12.3 \text{ m}^2\cdot\text{g}^{-1}$) > Pt/rGO ($-3.8 \text{ m}^2\cdot\text{g}^{-1}$) > Pt/rGO/ double-walled carbon nanotube (DWCNT) ($-2.7 \text{ m}^2\cdot\text{g}^{-1}$) > Pt/NS-rGO-DWCNT ($-2.0 \text{ m}^2\cdot\text{g}^{-1}$). Moreover, mixing double-walled carbon nanotubes (DWCNT) could prevent the restacking of the rGO sheets, leading to faster mass transfer.

Rethinasabapathy et al. [52] strategically tuned the MOR activity of supported platinum nanoparticles by designing an interconnected porous N-doped rGO through a hydrothermal method with urea as N source. They found that the incorporation of nitrogen atoms broke the 2D lattice symmetry, creating induced-defect sites for an efficient attachment of metal nanoparticles. Electrochemical characterization revealed a significant higher catalytic activity toward MOR in comparison to a nitrogen-free rGO support, which was attributed to the smaller particle size, narrower size distribution, and better dispersion of nanoparticles. The synergetic effect of N doping also contributed to an improvement of electronic conductivity, facilitating charge transfer from platinum-support interface to the strongly adsorbed MOR intermediates.

Inspired by the advantage of a three-dimensional assembly-assisted method, Zhao et al. [53] prepared a three-dimensional N-doped rGO through a feasible and simple one-pot hydrothermal process. By using melamine-cyanurate as both N source and pore forming agent, they reported the formation of an interconnected micrometer-scaled porous structure that could

Catalyst	Synthesis conditions	Reaction	Performance parameter		Refs.
			ECSA (m ² ·g ⁻¹)	I' (mA·mg ⁻¹)	
Recent electrode materials tailored by the 3D structure assembly approach					
Pt/GO	Pt-precursor in 2 mg·mL ⁻¹ GO autoclaved @ 180°C/12 h	MOR	188 (~9× more than Pt/C)	–	[44]
rGO-PtI	Thermal exfoliation of GO @ 180°C/3 h	MOR	>6 K (~3× more than Pt/C)	~2.5 K (~2.5× more than Pt/C)	[45]
Pt/3D-GNs (PANI)	Pt-precursor and Ani in 2 mg·mL ⁻¹ GO autoclaved @ 180°C/24 h	MOR	48 (~2.4× more than Pt/C)	~550 (~3.5× more than Pt/C)	[47]
Recent electrode materials tailored by the heteroatom doping approach					
Pt/NS-rGO/DWCNT	NS-functionalized GO by a thiol-ene click reaction @ 70°C/12 h	EOR	Stability test: 500 potential cycles. ECSA loss: Pt/C (–12.3 m ² ·g ⁻¹) and Pt/NS-rGO-DWCNT (–2.0 m ² ·g ⁻¹).		[51]
PtRuFe/NG	GO/urea (1:300 m/m) autoclaved @ 180°C/12 h	MOR	96 (~2× more than PtRuFe/rGO)	–	[52]
Pt/NGA	Melamine in 2 mg·mL ⁻¹ GO autoclaved @ 180°C/6 h followed by annealing @ 1000°C/1 h under Ar	MOR	60.6 (1.16× more than Pt/C)	~20 (~3× more than Pt/C)	[53]

*Current value obtained after chronoamperometry.

Table 1. Overview of the performance of some highly active electrode materials for alcohol electrocatalysis.

expose abundantly accessible catalyst sites, which led to an ECSA increased by 1.16 times in comparison to a benchmark Pt/C catalyst. As a result, platinum on rGO could enhance the MOR activity by approximately three times when compared to platinum on carbon black. Their recent results also revealed the advantage of N-doping, proper control of the platinum-support electronic effects, increasing catalyst particle dispersion, and decreasing catalyst particle size and holding a high prospect for application as an anode catalyst toward MOR.

Briefly, current methodologies for synthesizing defect-induced 3D C nanosheets were aimed on the design of high-performance rGO fuel-cell support materials and current carriers. Also, noteworthy is the influence of the electronic interaction between support and catalyst in electrocatalysis. Based on these, non-metal heteroatom doping in architected or expanded stacks of reduced graphene oxide is proposed herein as an alternative for maintaining the electrical conductivity of the porous electrode. In addition, future trends toward superior electrocatalysis should extend the modulation of the electronic properties of both support and supported catalysts to incorporation of different non-metal heteroatoms, such as boron (B), fluorine (F), and sulphur (S), into the carbon–carbon 2D network. In **Table 1**, a summary of the performance of some highly active electrode materials is presented.

2.3. Future perspectives in defect engineering for superior electrocatalysis

Immense research work has been done in the field of materials science toward the study of MOFs for highly efficient oxygen electrocatalysis [55]. Basically, MOFs are a class of composite materials with a unique and highly ordered nanoporous (pore sizes smaller than 100 nm) structure, which are designed from a self-assembly of inorganic metals and organic linkers through co-ordination bonds. From an electrochemical aspect, co-ordinated metals could contribute to an electronic effect as a consequence of the changes in platinum electronic structure, directly influencing catalyst activity. Thanks to abundant dual-metal active sites, superior electrocatalysts with ultra-low platinum content could be developed for alcohol electrocatalysis further improving specific activity beyond the conventional platinum alloy approach.

Moreover, surface modification of rGO-supported platinum could lead to improved three-dimensional nano- (or micro-) structures, resulting in synergistic effects for achieving faster mass and charge transport properties. In this context, proper synthetic procedures based on the controlled carbonization of the organic linkers (primarily containing heteroatoms) might serve as novel rational design strategies for the development of highly porous heteroatom-doped supported catalysts. Also, noteworthy is that such a synthetic method, especially for large-scale production, should meet the requirements for commercialization, which include low cost, environmental sustainability and high reproducibility.

Last but not least, another contribution of the metal-organic framework process could be the *in situ* generation of metal oxide nanoparticles and their concomitant dispersion on rGO upon carbonization of the metal-organic complex. Thus, the deposited metal oxide nanoparticles could act as seeds for vacancy generation by etching the carbon-carbon network along the rGO-metal oxide interface. Size-controlled vacancies in the matrix of reduced graphene oxide are not only predicted to break the two-dimensional lattice symmetry, thereby tuning conduction mechanisms, but also act as trapping sites for heteroatom doping [56]. Therefore, in addition, heteroatom-doped porous and open structures on the basal planes together with the metal oxide nanoparticles might serve as novel active sites with high bifunctional activity. Precisely, a bifunctional effect has been associated to the presence of sites that aid in the dissociation of water to form surface hydroxides, which can readily oxidize strongly adsorbed reaction intermediates. Indeed, development of heteroatom-doped size-controlled vacancies could positively contribute toward the improvement of platinum activity in alcohol oxidation reactions.

3. Conclusions

As summarized in this mini-review, an ideal fuel-cell electrode should be porous, and possess high conductivity, accessible electrochemical surface sites, and improved charge and mass transfer pathways. Defect engineering, which involves manipulating the type, concentration, or spatial distribution of heteroatoms and size-controlled vacancies within a solid, along with materials processing approaches, such as three-dimensional structure assembly and surface metal complexation methodologies, has demonstrated its potential to tackle the challenges triggered by energy conversion concerns in direct alcohol fuel cells. With continuous progress on the knowledge

gained from the engineered nanosheets, a transition from bench-scale nanotechnology to pilot plant manufactures and, eventually, commercial production is likely to be configured.

Acknowledgements

The author acknowledges the Brazilian National Council for Scientific and Technological Development (CNPq) for research funding.

Conflict of interest

The author declares no conflict of interest.

Abbreviations

B	boron
C	carbon
DAFC	direct alcohol fuel cell
DWCNT	double-walled carbon nanotube
ECSA	electrochemically active surface area
EOR	ethanol oxidation reaction
F	fluorine
H	hydrogen
HET	heterogeneous electron transfer
MOF	metal-organic framework
MOR	methanol oxidation reaction
N	nitrogen
O	oxygen
PANI	polyaniline
PDA	polydopamine
Pt	platinum
rGO	reduced graphene oxide
S	sulfur

Author details

Guilherme Luís Cordeiro

Address all correspondence to: gcordeiro@usp.br

Materials Science and Technology Center, Energy and Nuclear Research Institute (IPEN-CNEN/SP), São Paulo, Brazil

References

- [1] Kordesch KV, Simader GR. Environmental impact of fuel cell technology. *Chemical Reviews*. 1995;**95**:191-207. DOI: 10.1021/cr00033a007
- [2] Fuller TF, Perry ML. A historical perspective of fuel-cell technology in the 20th century. *Journal of the Electrochemical Society*. 2002;**149**:S59-S67. DOI: 10.1149/1.1488651
- [3] Sharaf OZ, Orhan MF. An overview of fuel cell technology: Fundamentals and applications. *Renewable and Sustainable Energy Reviews*. 2014;**32**:810-853. DOI: 10.1016/j.rser.2014.01.012
- [4] Wang Y, Chen KS, Mishler J, Cho SC, Adroher XC. A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. *Applied Energy*. 2011;**88**:981-1007. DOI: 10.1016/j.apenergy.2010.09.030
- [5] Holton OT, Stevenson JW. The role of platinum in proton exchange membrane fuel cells. *Platinum Metals Review*. 2013;**57**:259-271. DOI: 10.1595/147106713x671222
- [6] Shao-Horn Y, Sheng WC, Chen S, Ferreira PJ, Holby EF, Morgan. Instability of supported platinum nanoparticles in low-temperature fuel cells. *Topics in Catalysis*. 2007;**46**:285-305. DOI: 10.1007/s11244-007-9000-0
- [7] Galeano C, Meier JC, Peinecke V, Bongard H, Katsounaros I, Topalov AA, Lu A, Mayrhofer KJJ, Schüth F. Toward highly stable electrocatalysts via nanoparticle pore confinement. *Journal of the American Chemical Society*. 2012;**134**:20457-20465. DOI: 10.1021/ja308570c
- [8] Marcu A, Toth G, Kundu S, Colmenares LC, Behm RJ. Ex situ testing method to characterize cathode catalysts degradation under simulated start-up/shut-down conditions—A contribution to polymer electrolyte membrane fuel cell benchmarking. *Journal of Power Sources*. 2012;**215**:266-273. DOI: 10.1016/j.jpowsour.2012.05.010
- [9] Hashimasa Y, Numata T. Comparison of test results on load cycle durability of polymer electrolyte fuel cell cathode catalysts. *International Journal of Hydrogen Energy*. 2015;**40**:11543-11549. DOI: 10.1016/j.ijhydene.2015.04.031
- [10] Zhou W, Zhou Z, Song S, Li W, Sun G, Tsiakaras P, Xin Q. Pt based anode catalysts for direct ethanol fuel cells. *Applied Catalysis B: Environmental*. 2003;**46**:273-285. DOI: 10.1016/S0926-3373(03)00218-2

- [11] Rousseau S, Coutanceau C, Lamy C, Léger J-M. Direct ethanol fuel cell (DEFC): Electrical performances and reaction products distribution under operating conditions with different platinum-based anodes. *Journal of Power Sources*. 2006;**158**:18-24. DOI: 10.1016/j.jpowsour.2005.08.027
- [12] Glass DE, Olah GA, Prakash GKS. Effect of the thickness of the anode electrode catalyst layers on the performance in direct methanol fuel cells. *Journal of Power Sources*. 2017;**352**:165-173. DOI: 10.1016/j.jpowsour.2017.03.106
- [13] Wang Y, Zou S, Cai W. Recent advances on electro-oxidation of ethanol on Pt- and Pd-based catalysts: From reaction mechanisms to catalytic materials. *Catalysts*. 2015;**5**:1507-1534. DOI: 10.3390/catal5031507
- [14] Joo SH, Choi SJ, Oh I, Kwak J, Liu Z, Terasaki O, Ryoo R. Ordered nanoporous arrays of carbon supporting high dispersions of platinum nanoparticles. *Nature*. 2001;**412**:169-172. DOI: 10.1038/35084046
- [15] Yoshitake T, Shimakawa Y, Kuroshima S, Kimura H, Ichihashi T, Kubo Y, Kasuya D, Takahashi K, Kokai F, Yudasaka M, Iijima S. Preparation of fine platinum catalyst supported on single-wall carbon nanohorns for fuel cell application. *Physica B: Condensed Matter*. 2002;**323**:124-126. DOI: 10.1016/S0921-4526(02)00871-2
- [16] Hui CL, Li XG, Hsing I-M. Well-dispersed surfactant-stabilized Pt/C nanocatalysts for fuel cell application: Dispersion control and surfactant removal. *Electrochimica Acta*. 2005;**51**:711-719. DOI: 10.1016/j.electacta.2005.05.024
- [17] Li X, Hsing I-M. The effect of the Pt deposition method and the support on Pt dispersion on carbon nanotubes. *Electrochimica Acta*. 2006;**51**:5250-5258. DOI: 10.1016/j.electacta.2006.01.046
- [18] Kou R, Shao Y, Mei D, Nie Z, Wang D, Wang CM, Viswanathan VV, Park SK, Akasay IA, Lin Y, Wang Y, Liu J. Stabilization of electrocatalytic metal nanoparticles at metal-metal oxide-graphene triple junction points. *Journal of the American Chemical Society*. 2011;**133**:2541-2547. DOI: 10.1021/ja107719u
- [19] Xue T, Sun ZP, Wei L, Wang X, Lee J-M. One-step dual template synthesis of platinum on mesoporous carbon nanowires for electrocatalysts. *International Journal of Hydrogen Energy*. 2013;**38**:2754-2759. DOI: 10.1016/j.ijhydene.2012.12.034
- [20] Neto AO, Giz MJ, Perez J, Ticianelli EA, Gonzalez ER. The electro-oxidation of ethanol on Pt-Ru and Pt-Mo particles supported on high-surface-area carbon. *Journal of the Electrochemical Society*. 2002;**149**:A272-A279. DOI: 10.1149/1.1446080
- [21] Tayal J, Rawat B, Basu S. Bi-metallic and tri-metallic Pt-Sn/C, Pt-Ir-Sn/C catalysts for electro-oxidation of ethanol in direct ethanol fuel cell. *International Journal of Hydrogen Energy*. 2011;**36**:14884-14897. DOI: 10.1016/j.ijhydene.2011.03.035
- [22] da Silva SG, Silva JCM, Buzzo GS, de Souza RFB, Spinacé EV, Neto AO, Assumpção MHMT. Electrochemical and fuel cell evaluation of PtAu/C electrocatalysts for ethanol electro-oxidation in alkaline media. *International Journal of Hydrogen Energy*. 2014;**39**:10121-10127. DOI: 10.1016/j.ijhydene.2014.04.169

- [23] Pham VV, Ta V-T, Sunglae C. Synthesis of NiPt alloy nanoparticles by galvanic replacement method for direct ethanol fuel cell. *International Journal of Hydrogen Energy*. 2017;**42**:13192-13197. DOI: 10.1016/j.ijhydene.2017.01.236
- [24] Sharma S, Pollet BG. Support materials for PEMFC and DMFC electrocatalysts—A review. *Journal of Power Sources*. 2012;**208**:96-119. DOI: 10.1016/j.jpowsour.2012.02.011
- [25] Brownson DAC, Kampouris DK, Banks CE. An overview of graphene in energy production and storage applications. *Journal of Power Sources*. 2011;**196**:4873-4885. DOI: 10.1016/j.jpowsour.2011.02.022
- [26] Zhang B, Fan L, Zhong H, Liu Y, Chen S. Graphene nanoelectrodes: Fabrication and size-dependent electrochemistry. *Journal of the American Chemical Society*. 2013;**135**:10073-10080. DOI: 10.1021/ja402456b
- [27] Ambrosi A, Chua CK, Latiff NM, Loo AH, Wong CHA, Eng AYS, Binanni A, Pumera M. Graphene and its electrochemistry—An update. *Chemical Society Reviews*. 2016;**45**:2458-2493. DOI: 10.1039/C6CS00136j
- [28] Ambrosi A, Chua CK, Bonanni A, Pumera M. Electrochemistry of graphene and related materials. *Chemical Reviews*. 2014;**114**:7150-7188. DOI: 10.1021/cr500023c
- [29] Luo J, Kim J, Huang J. Material processing of chemically modified graphene: Some challenges and solutions. *Accounts of Chemical Research*. 2013;**46**:2225-2234. DOI: 10.1021/ar300180n
- [30] Marinkas A, Arena F, Mitzel J, Prinz GM, Heinzl A, Peinecke V, Natter H. Graphene as catalyst support: The influences of carbon additives and catalyst preparation methods on the performance of PEM fuel cells. *Carbon*. 2013;**58**:139-150. DOI: 10.1016/j.carbon.2013.02.043
- [31] Mu S, Chen X, Sun R, Liu X, Wu H, He D, Cheng K. Nano-size boron carbide intercalated graphene as high performance catalyst supports and electrodes for PEM fuel cells. *Carbon*. 2016;**103**:449-456. DOI: 10.1016/j.carbon.2016.03.044
- [32] Sanli LI, Bayram V, Yazar B, Ghobadi S, Gürsel SA. Development of graphene supported platinum nanoparticles for polymer electrolyte membrane fuel cells: Effect of support type and impregnation–reduction methods. *International Journal of Hydrogen Energy*. 2016;**41**:3414-3427. DOI: 10.1016/j.ijhydene.2016.08.210
- [33] Sanli LI, Bayram V, Yazar B, Ghobadi S, Gürsel SA. Engineered catalyst layer design with graphene-carbon black hybrid supports for enhanced platinum utilization in PEM fuel cell. *International Journal of Hydrogen Energy*. 2017;**42**:1085-1092. DOI: 10.1016/j.ijhydene.2016.08.210
- [34] Pinithchaisakula A, Themsirimongkon S, Promsawan N, Weankeaw P, Ounnunkad K, Saipanya S. An investigation of polydopamine-graphene oxide composite as a support for an anode fuel cell catalyst. *Electrocatalysis*. 2017;**8**:36-45. DOI: 10.1007/s12678-016-0338-6

- [35] Cheng K, He D, Peng T, Lv H, Pan M, Mu S. Porous graphene supported Pt catalysts for proton exchange membrane fuel cells. *Electrochimica Acta*. 2014;**132**:356-363. DOI: 10.1016/j.electacta.2014.03.181
- [36] Zhao D, Shi M-Q, Liu W-M, Chu Y-Q, Ma C-A. Special microwave-assisted one-pot synthesis of low loading Pt-Ru alloy nanoparticles on reduced graphene oxide for methanol oxidation. *IET Micro & Nano Letters*. 2014;**9**:50-54. DOI: 10.1049/mnl.2013.0525
- [37] Nardecchia S, Carriazo D, Ferrer ML, Gutiérrez MC, del Monte F. Three dimensional macroporous architectures and aerogels built of carbon nanotubes and/or graphene: Synthesis and applications. *Chemical Society Reviews*. 2013;**42**:794-830. DOI: 10.1039/C2CS35353A
- [38] Wei M, Qiao L, Zhang H, Karakalos S, Ma K, Fu Z, Swihart MT, Wu G. Engineering reduced graphene oxides with enhanced electrochemical properties through multiple-step reductions. *Electrochimica Acta*. 2017;**258**:735-743. DOI: 10.1016/j.electacta.2017.11.120
- [39] Soo LT, Loh KS, Mohamad AB, Daud WRW, Wong WY. An overview of the electrochemical performance of modified graphene used as an electrocatalyst and as a catalyst support in fuel cells. *Applied Catalysis A: General*. 2015;**497**:198-210. DOI: 10.1016/j.apcata.2015.03.008
- [40] Tao L, Dou S, Ma Z, Shen AS, Wang S. Simultaneous Pt deposition and nitrogen doping of graphene as efficient and durable electrocatalysts for methanol oxidation. *International Journal of Hydrogen Energy*. 2015;**40**:14371-14377. DOI: 10.1016/j.ijhydene.2015.02.104
- [41] Jafri RI, Rajalakshmi N, Dhathathreyan KS, Ramaprabhu S. Nitrogen doped graphene prepared by hydrothermal and thermal solid state methods as catalyst supports for fuel cell. *International Journal of Hydrogen Energy*. 2015;**40**:4347-4348. DOI: 10.1016/j.ijhydene.2015.02.008
- [42] Jiao Y, Zheng Y, Davey K, Qiao S. Activity origin and catalyst design principles for electrocatalytic hydrogen evolution on heteroatom-doped graphene. *Nature Energy*. 2016;**1**:1-9. DOI: 10.1038/nenergy.2016.130
- [43] Li Y, Li W, Ke T, Zhang P, Ren X, Deng L. Microwave assisted-synthesis of sulfur-doped graphene supported PdW nanoparticles as a high performance electrocatalyst for the oxygen reduction reaction. *Electrochemistry Communications*. 2016;**69**:68-71. DOI: 10.1016/j.elecom.2016.06.006
- [44] Kwok YH, Tsang ACH, Wang Y, Leung DYC. Ultra-fine Pt nanoparticles on graphene aerogel as a porous electrode with high stability for microfluidic methanol fuel cell. *Journal of Power Sources*. 2017;**349**:75-83. DOI: 10.1016/j.jpowsour.2017.03.030
- [45] Radhakrishnan T, Snadhyarani N. Three dimensional assembly of electrocatalytic platinum nanostructures on reduced graphene oxide—an electrochemical approach for high performance catalysts for methanol oxidation. *International Journal of Hydrogen Energy*. 2017;**42**:7014-7022. DOI: 10.1016/j.ijhydene.2016.12.132

- [46] Qiu X, Li T, Deng S, Cen K, Xu L, Tang Y. A general strategy for the synthesis of PtM (M=Fe, Co, Ni) decorated three-dimensional hollow graphene nanospheres for efficient methanol electrooxidation. *Chemistry*. 2018;**24**:1246-1252. DOI: 10.1002/chem.201704959
- [47] Wang Y, Li Z, Xu S, Xie Y, Lin S. Highly dispersive platinum nanoparticles supporting on polyaniline modified three dimensional graphene and catalyzing methanol oxidation. *Materials Research Bulletin*. 2018;**102**:172-179. DOI: 10.1016/j.materresbull.2018.02.028
- [48] Waenkaew P, Themsirimongkon S, Ounnunkad K, Promsawan N, Pinitchchaisakula A, Saipanya S. Successive electrodeposition of polydopamine and PtPd metal on a graphene oxide support for use as anode fuel cell catalysts. *Composite Interfaces*. 2018;**25**:317-333. DOI: 10.1080/09276440.2018.1436798
- [49] Hu C, Liu D, Xiao Y, Dai L. Functionalization of graphene materials by heteroatom-doping for energy conversion and storage. *Progress in Natural Science: Materials International*. DOI: 10.1016/j.pnsc.2018.02.001. (Forthcoming)
- [50] Fan M, Feng Z-Q, Zhu C, Chen X, Chen C, Yang J, Sun D. Recent progress in 2D or 3D N-doped graphene synthesis and the characterizations, properties, and modulations of N species. 2016;**51**:10323-10349. DOI: 10.1007/s10853-016-0250-8
- [51] Kanninen P, Luong ND, Sinh LH, Flórez-Montañó J, Jiang H, Pastor E, Seppälä J, Kallio T. Highly active platinum nanoparticles supported by nitrogen/sulfur functionalized graphene composite for ethanol electro-oxidation. *Electrochimica Acta*. 2017;**242**:315-326. DOI: 10.1016/j.electacta.2017.05.019
- [52] Rethinasabapathy M, Kang S-M, Haldorai Y, Jankiraman M, Jonna N, Choe SR, Huh YS, Natesan B. Ternary PtRuFe nanoparticles supported on N-doped graphene as an efficient bifunctional catalyst for methanol oxidation and oxygen reduction reactions. *International Journal of Hydrogen Energy*. 2017;**42**:30738-30749. DOI: 10.1016/j.ijhydene.2017.10.121
- [53] Zhao L, Sui X-L, Li J-Z, Zhang J-J, Zhang L-M, Huang G-S, Wang Z-B. Supramolecular assembly promoted synthesis of three-dimensional nitrogen doped graphene frameworks as efficient electrocatalyst for oxygen reduction reaction and methanol electrooxidation. *Applied Catalysis B: Environmental*. 2018;**231**:224-233. DOI: 10.1016/j.apcatb.2018.03.020
- [54] Rybin M, Pereyaslvtsev A, Vasilieva T, Myasnikov V, Sokolov I, Pavlova A, Obraztsova E, Khomich A, Ralchenko V, Obraztsova E. Efficient nitrogen doping of graphene by plasma treatment. *Carbon*. 2016;**96**:196-202. DOI: 10.1016/j.carbon.2015.09.056
- [55] He X, Yin F, Wang H, Chen B, Li G. Metal-organic frameworks for highly efficient oxygen electrocatalysis. *Chinese Journal of Catalysis*. 2018;**39**:207-227. DOI: 10.1016/S1872-2067(18)63017-7
- [56] Jiang D, Cooper VR, Dai S. Porous graphene as the ultimate membrane for gas separation. *Nano Letters*. 2009;**9**:4019-4024. DOI: 10.1021/nl9021946