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Mini-Review on Graphene Quantum Dots as an electro-catalyst in fuel cell Bita Roshanravan*a; Habibollah Younesi^a

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ABSTRACT

Due to a significant increase in the demand for usable power, research focused on energy-material relations has garnered considerable attention. Fuel cells, characterized by their high efficiency, high energy density, quiet operation, and environmental friendliness, are regarded as a promising future power source that provides clean power at the point of use. The incorporation of functionalized graphene quantum dots (GQDs) has been shown to enhance catalytic activity and stability, making them attractive materials for various device applications, particularly in fuel cells. This review presents an overview of different synthesis methods for GQDs and discusses the utilization of GQD-doped composites with optimized content and enhanced electro conductivity as electrocatalysts in fuel cells.

Keywords: Fuel cell, Graphene Quantum Dot, Electro catalyst, conductivity

1. Introduction

In the past decades, research on new environmentally friendly energy sources and their practical applications has drawn a growing amount of interest due to technological advancement, the rapid expansion of energy consumption in people's lives, and the depletion of fossil fuel supply [1-3]. Among the proposed clean energy sources, an innovative technology based on the utilization of fuel cells (FCs) has been demonstrated to be a crucial conduit for converting processes to electricity generation and thus for tackling energy and environmental issues. In addition, they are small, discreet, and have much lower EIs than other conventional devices or technologies during their operational phase [4]. FCs have additional benefits. For instance, they can be used for applications ranging from a few watts to several gigawatts [5]. A fuel cell is a device that produces electricity by chemical reactions at its two electrodes, a positive electrode (a cathode) where a reduction reaction (or gain of electrons) happens, and a negative electrode (an anode) where electrons are lost (or oxidation reaction) [6].

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Thus, electrons move from the negative terminal to the positive one, generating an electric current that flows from the Cathode to the Anode of the fuel cell. This is a Reaction of Oxidation and Reduction (ORR) [7]. Additionally, it has an electrolyte solution or a selectively permeable membrane that allows only suitable ions to travel between the cathode and anode chambers. FCs are superior to conventional technologies due to their unique properties, which include energy savings, great thermodynamic efficiency, and power generation. [8-14]. The classification of fuel cells is based on the utilization of electrolytes and fuel, as shown in Table 1. [15, 16]. Despite the fact that FCs are considered to be more environmentally friendly than conventional energy conversion systems, there are still noticeable operational and environmental drawbacks between FC varieties. The life cycle assessment (LCA) of FCs is similar to that of conventional power sources, owing to the environmental impact statement (EIs) associated with fuel sourcing and material acquisition, whether for precious metals used in low-temperature FCs or thermally and chemically stable materials used in medium- and high-temperature FCs [17].

The slow oxygen reduction reaction (ORR) on the cathode side of fuel cells is the present barrier in the

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technology behind fuel cells. The development of novel electro catalysts for fuel cells, one of the most recent energy resources, in order to reduce the needed overvoltage is an essential feature in the electrocatalysis sector. To date, the chosen electrocatalysts are Pt and platinum group metals (PGM), which pose a substantial obstacle to the commercialization of fuel cells due to their scarcity and high cost. The discovery of low-cost alternative catalysts with excellent activity and endurance in the ORR, including metal-free heteroatom doped carbon materials, has received considerable attention, [18-20] such as zero-dimensional graphene quantum dots (GQDs) have attracted great interest also are expected to be one of the most promising alternatives to Pt-based catalysts due to their low-cost, high electro catalytic activity, selectivity, and stability [20-25].

2. Synthesis of GQD

Most of the synthesis techniques for graphene quantum dots (GQDs) can be categorized into two main approaches: top-down and bottom-up methods. In the top-down strategy, GQDs are derived from larger carbon-based materials such as graphene, fullerenes, and carbon nanotubes by means of physical or chemical cutting processes. On the other hand, the bottom-up approach involves controlled chemical reactions using molecular precursors to gradually build GQDs [26].

2.1. Top – Down approaches

2.1.1. Hydro and solvo-thermal methods

For the preparation of graphene quantum dots (GQDs), hydrothermal and solvothermal approaches are commonly employed as simple and rapid methods. These methods involve the cutting of carbon materials into GQDs under high temperature and high-pressure conditions. Prior to the reactions, the carbon compounds typically undergo intense oxidation treatments [28, 29].

Pan et al. were the first to attempt the synthesis of GQDs with sizes ranging from 5 to 13 nm using oxidized graphene sheets as the raw material through the **Table 1** Evel cell types and their features

hydrothermal technique at 200°C [30]. It was reported that the oxidized graphene sheets (GSs) contained oxygen-enriched functional groups such as ketone, carboxyl, hydroxyl, and ether groups, which enhanced the quantum yield. Through hydrothermal de-oxidation, the oxygen atoms from the epoxy groups were removed, resulting in the formation of GQDs with an average diameter of 9.6 nm.

The size of GQDs can be easily controlled using the solvothermal technique with various organic solvents, including dimethyl sulfoxide (DMSO), dimethylformamide (DMF), or benzene. The final size and morphology of the resulting GODs can be directly influenced by the physicochemical properties of the solvent. For example, sonicating graphene oxide (GO) in DMF solvent can produce green-emitting fluorescent GQDs by breaking down the graphene oxide [31]. The photoluminescence characteristics of the GODs can be adjusted by combining methanol and methylene chloride as the solvents and using water as the mobile phase during an 8-hour process [32].

2.1.2. Ultrasound Techniques

Ultrasonic is a simpler approach to shearing the carbon layer materials into GQDs by low and high creation of alternating pressure waves in liquid [26]. In a typical technique, the sonication of the mixture has occurred to form GQDs for 12h after GSs oxidation in a high concentration of sulfuric or nitric acids [24]. By this typical approach, a 3-5 nm diameter size of GQDs monodisperse was created. In a recent study, a straightforward ultrasonic technique with chemical activation utilizing KOH for GQDs synthesis was described by sonicating few-layer graphene sheets and activated graphene directly [27]. After numerous purifications, GQDs were synthesized as 3-5 nm average diameter with bluish fluorescence.

2.1.3. Lithography Process

Large graphene flakes obtained through microchemical cleavage of graphite crystals were employed using the

| Table 1. Fuel cell types and then features | | | | |
|--|----------------|--------------------|-------------------------------------|-------------------|
| Туре | Temperature °C | Fuel | Electrolyte Mobile | Ion |
| PEM: polymer electrolyte membrane | 70–110 | H_2 | Sulfonated polymers | $(H_2O)_nH^+$ |
| | | CH ₃ OH | (Nafion®) | |
| AFC: alkali fuel cell | 100-250 | H_2 | Aqueous KOH | OH- |
| PAFC: phosphoric acid fuel cell | 150-250 | H_2 | H_3PO_4 | H^+ |
| MCFC: molten carbonate fuel cell | 500-700 | Hydrocarbons | (Na,K) ₂ CO ₃ | CO3 ²⁻ |
| | | CO | | |
| SOFC: solid oxide fuel cell | 700-1000 | Hydrocarbons | $(Zr,Y)O_2-\delta$ | O ²⁻ |
| | | CO | | |

standard "scotch-tape" exfoliation process in a topdown manner [37]. These graphene flakes were then transferred onto a SiO2/silicon wafer with a thickness of 300 nm. Electron-beam lithography was utilized to fabricate graphene quantum dots (GQDs) from the graphene flakes. Several research groups have successfully achieved the generation of 30-50 nm GQDs using this method [38]. It is important to note that there is a minimum size limitation imposed by the resolution of the lithography device.

However, isolating and characterizing graphene flakes can present challenges. Firstly, optical microscopy is employed to identify single-layer graphene flakes, and secondly, Raman spectroscopy is the primary method for analyzing such flakes. The quality of the obtained GQDs is significantly influenced by various factors, including the thickness of the SiO2 layer, surface cleanliness, and the procedures involved in dividing the graphite chemical bonds [39].

2.1.4. Exfoliation by "Nanotomy" Technique

Mohanty et al. report that graphite dissection is the first step of a two-phase fragmentation procedure [28]. Following a diamond-induced "nanotomy" procedure, the graphite bonds were chemically exfoliated using super acids. The graphene nanostructures that were produced displayed geometries of nano squares, nano triangles, and nanorectangles with diameters ranging from 10 to 50 nanometers and having smooth edges and zig-zag patterns. The use of a high-speed self-regulating nanotoning system makes it possible to generate GQDs on a wide scale; nevertheless, the sizes of the GQDs produced by this method are larger than those acquired from chemically and electrochemically produced ones.

2.1.5. Chemical Exfoliation

In this method, artificial graphite was synthesized through the thermal treatment of hexa-perihexabenzocoronene at 1200°C. The resulting graphite was then subjected to exfoliation using the Hummers method [41]. The obtained graphene oxide was subsequently refluxed with poly (ethylene glycol) (Mw 1500) for two days, followed by reduction with hydrazine. The resulting graphene quantum dots (GQDs) exhibited a disk-like shape with a diameter of 60 nm and an average thickness of 2-3 nm, which is equivalent to three to four layers of graphene.

Recently, this method has been further improved by introducing a single-step, wet-chemical procedure for GQDs preparation [42]. This modified approach also led to the production of micro-sized carbon fibers with a reinforced surface. The carbon fibers were treated at different temperatures for 24 hours in concentrated H_2SO_4 and HNO_3 , resulting in GQDs with adjustable diameters: 1-4 nm at 80°C, 4-8 nm at 100°C, and 7-11 nm at 120°C. Moreover, this method has been successfully employed using CX-72 carbon black as the starting material to synthesize GQDs with sizes ranging from 15 to 18 nm [43].

2.1.6. Microwave-Assisted Exfoliation

Microwave methods have gained popularity in the production of nanomaterials due to their numerous advantages, including rapid and high-yield synthesis of both organic and inorganic compounds [44]. Li et al. conducted a study on the synthesis of green-yellow luminescent graphene quantum dots (GQDs) using microwave-assisted chemical reduction. In this method, graphene oxide (GO) nanosheets were treated with strong acids (HNO₃ and H₂SO₄) for a duration of 3 hours [24]. Subsequently, the GO nanosheets underwent further reduction using NaBH₄, resulting in a transformation of the luminescence from green-yellow to blue. Notably, despite the change in luminescence color and an increase in intensity, the size and shape of the GQDs remained unchanged.

2.1.7. Graphene Sheet Scissoring Using an Electrochemical Technique

This method was considered a reliable strategy for making fluorescent C-points [29, 30], regarded as a potential technique for the manufacturing of GODs. Here, a huge graphene layer that was electrochemically cleaved was treated with oxygen plasma to increase its water solubility [31]. The graphene sheets (GSs) were produced by oxidizing reduced graphene oxide (rGO) with KMnO₄ and reducing it with aqueous N_2H_4 [32]. Then, they were subjected to a 3 V potential, which caused electrolyte ions to permeate the graphene layers and induce the oxidation of C-C bonds inside the graphene structure. For cyclic voltammetry, an external voltage (swept between 0.3 and 0.3 V) was supplied to a graphene film (working electrode) immersed in 0.1 M phosphate buffer solution (PBS). The resultant GQDs were collected using a membrane bag after filtering and dialysis. This technique yields monodisperse GQDs with a narrow size range (between 3-5 nm in diameter and 1-2 nm in thickness) (about three layers of graphene). Electrochemical oxidation causes sheet fragmentation into GQDs at the faults induced by GSs' chemical and physical treatment.

2.2. Bottom-Up Approaches

2.2.1. Pyrolysis of Precursors

Pyrolysis is the process of breaking down organic molecules into their component parts at very high temperatures. This process takes place in the absence of oxygen and creates irreversible chemical and physical compositional changes. By changing the carbonization conditions and spreading the pyrolyzed products in alkaline media, pyrolysis of a precursor such as citric acid can produce GQDs with a diameter of 15 nm (0.5-2.0 nm) [33]. Prolonged heating of the precursor can cause complete carbonization, resulting in GO nanostructures just 100 nm in width (1 nm thickness). Tang et al. pyrolyzed glucose using a combination of hydrothermal and microwave techniques (595 W for 5 minutes) to produce GODs with a diameter ranging from 2.9 to 3.9 nm [34]. By varying the microwave reaction period (1-9 minutes), the size of GQDs may be adjusted between 1.65 and 21 nanometers. The ratio of carbon, hydrogen, and oxygen content was generally 1:2:1 for the carbohydrate precursors; however, hydrogen and oxygen predominated in the form of carbonyl, hydroxyl, and carboxyl groups since these functional groups often dehydrate through а hydrothermal process.

2.2.2. Step-by-Step Organic Synthesis

Due to the rigid backbones of polycyclic aromatic hydrocarbon molecules, high-quality, (PAH) homogeneous, and well-ordered GQDs can be produced by incorporating PAHs into this method. However, due to their aggregated state caused by insufficient lateral aliphatic side-chains and the edges of aromatic molecules interacting, the creation of large GQDs with acceptable solvability is extremely challenging [35-37]. Covalent bonding decorates the edges of graphene moieties with 2,4,6-triakyl phenyl groups and reduces the surface contacts between graphene layers [38]. This leads to the formation of three-dimensional cages around the graphene moieties, which increases the distance between each layer and improves the solubility of bigger GQDs that contain the following conjugated carbon atoms: 168 (C168, 2), 132 (C132, 1), and 170. (C170, 3). Recently, electron-removal or electrondonating groups have been applied to the surface of GQDs to modulate their redox potential and bandgap [37]. This method has the ability to synthesize a range of functional GQDs and exemplifies the typical benefit of wet-chemistry approaches in the synthesis of wellordered graphene nanostructures. However, it remains difficult to synthesize, purify, and characterize bigger GQDs using these techniques [39].

2.2.3. Decomposition of Fullerene

As a carbon supply, fullerene C60 was employed to construct homogeneous GQDs on a Ru (0001) substrate [40]. The latter catalyzed the disassembly of the C60 cage, and the resulting fragments were then reconstituted into clusters. When C60 samples were washed at 500–550 K, thermal hopping and dissociation initiated by adatom-vacancy processes were seen on the terrace using scanning tunneling microscopy. At 650 K, the C60 molecules fully disintegrated into carbon clusters. Clusters generated from C60, with a diffusion coefficient of 10^{-15} – 10^{-16} cm² s⁻¹, consist of a sequence of atomically uniform GQDs, which are difficult to get when derived from other predecessors, such as C₂H₄. When C60 was annealed for 2 minutes at 725 K, various GQD forms began to develop (e.g., triangular, parallelogram-shaped, and trapezoid-shaped). A further increase in annealing temperature to 825 K for 2 minutes resulted in the formation of hexagonal GQDs of 5-10 nm in size.

In addition, Chen et al. found that KOH oxidizes and activates graphene-oxide-like quantum dots (GOLQDs) [41]. A modified version of the Hummers process was used to synthesize GOLQD on a wide scale, with a yield of about 25% wt. from oxidizing C60 molecules. The GOLQDs were very water-soluble and contained carbon rings in addition to the hexagonal structures. After drying, the average height of the substrates was around 1.2 nm, and the diameter distribution ranged from 0.6 to 2.2 nm [42].

3. GQD as an Electro-Catalyst Material

Nanoparticles have evolved into stable heterogeneous catalysts and substrate frameworks with a great deal of surface area, which enhance compounds for a longer duration than conventional materials. In addition, the activity of Nano catalysts can be tailored by modifying their size, shape, composition, and surface morphology. Carbon, graphite, graphene, inorganic nanotubes, carbon nanotubes, aluminum, silver, cobalt, copper, zinc oxide, silicon dioxide, iron oxide, cerium oxide, titanium dioxide, quantum dots, and clays have demonstrated promising results in previous studies involving various catalytic reactions, making them a potential candidate for industrial applications in the scientific community [43, 44]. GQDS as a catalyst have a variety of applications, such as electrocatalysts.

GQDs have various disadvantages, such as being difficult to assemble into a film and having low conductivity, etc. It may be possible to overcome some of the obstacles and improve their overall performance by forming GQD composites or doping them with other materials. This might then lead to the development of a wide variety of innovative applications. Polymer materials [45, 46] and nano-materials [47-52] may be combined with GQDs to create composites. More active sites meant a faster charge transfer rate in the GQD/PPy composite film because of the film's porosity features.

Future potential for composites of GQDs and organic materials is without question immense. It is interesting to note that Zor et al.[53] developed a brand-new multifunctional composite made up of magnetic silica beads, GQD, and molecularly imprinted polypyrrole. The optical and magnetic characteristics of the composite were improved. As a result of its improved qualities, the GQD composite might be used in a wide variety of contexts. In recent years, there has been an increasing interest in producing innovative GQD composites. The nanofiber combination of GQDs and polyaniline was created by the lab of Mondal's [54] for use as a supercapacitor electrode material. The composite material increased the 1 Ag-1 current density and cycle stability. Chen et al.[55] assembled 0D GQDs and 3D graphene (3DG) using a novel, non-toxic electrochemical technique. The high surface area and active sites of the GQDs-3DG composite material were employed to develop a supercapacitor with improved performance. External quantum efficiency (EQE) of 57681% (at -1 V bias) at wavelength 340 nm was demonstrated by Dhar and colleagues [56] for a combination of ZnO and GQDs, which they showed can improve the performance of UV photodetectors. The performance of the composite material consisting of ZnO nanorods/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and GQDs was significantly superior to that of GQD-modified ZnO nanorods and pure ZnO nanorods. Other ZnO shapes, such as leaf-shaped ZnO (L-ZnO) [57], were also employed to produce composites with GQDs. In the same manner, nanocomposites composed of TiO₂ and GQDs were produced by Bu [58]. Due to the increased energy barrier between NGQDs and B-TiO₂, the nanocomposites utilized as photocatalysts demonstrated extraordinarily high photocatalytic activity, resulting in enhanced light absorption and higher electron density. Ji et al. [59] constructed a lithium-ion battery by combining MnV12 with GQDs in a composite material. The performance of the lithium-ion battery can be optimized by using bar-shaped composites, which can enhance the interfacial contact area, improve charging and discharging behavior, and therefore optimize the battery's overall performance. Another interesting experiment [60] was conducted by assembling Mn₃O₄ and GQDs into nanocomposites. These nanocomposites can vary the energy level of the materials without the need for doping with heteroatoms or regulating the size and shape of GQDs. In many catalytic applications, composite materials containing GQDs are preferred because of their high surface area to volume ratio. Catalyst composites of GQDs and Au nanoparticles were synthesized by Wu et al.[61]. A wide variety of

inorganic materials, such as SnO₂[62], ZnS [63], MoS2 [64], ferroelectric liquid crystal [65], ceria [66], Zn [67], and Fe₂O₃ [68] have been employed to create composites with GQDs. Copper GQD composites exhibit superior electrocatalytic activity compared to platinum-GQD due to the increased oxygen affinity of copper [69]. In fuel cells, the replacement of N atoms with GQDs has the potential to modify the electronic structure and provide an increase in the number of active sites for the oxygen reduction reaction (ORR) [70-72]. GQDs (N-GQDs) N-doped with oxygen-rich functionalities have been synthesized by Qu et al., and these N-GQDs have been shown to have enhanced electrocatalytic reactivity toward ORR [73]. Another paper demonstrated the effect of N-GQD size on ORR, revealing that increasing NGQD size results in an increase in current density [74]. N-GQDs were electrochemically produced, and their size-dependent ORR electrocatalytic activity was assessed [75]. N-GQD-based hybrid electrocatalysts have also been created recently to take advantage of the promising features of N-GQDs for ORR [72, 76]. Particularly, the integration of N-GQDs on various carbon supports has garnered considerable interest for the fabrication of alternative, highly efficient electro catalysts for oxygen reduction reaction (ORR) [72, 77]. Materials made of heteroatom-doped nanocarbon, such as carbon nanotubes, graphene, and porous carbon, display excellent stability and electro catalytic performance for the oxygen reduction reaction (ORR) [78, 79]. Hydrothermally attached boron- and nitrogen-doped GQDs on graphene platelets have been shown to be an effective electrocatalyst for oxygen reduction reaction (ORR) [76]. Boron-nitrogen-doped GQDs have the maximum activity for performing ORR in contrast to other materials as a result of the synergistic effect that boron and nitrogen have on one another [80].

Similarly, a novel class of GQD-coated graphene nanoribbons with enhanced electro catalytic activity in alkaline media was created using a one-step reduction procedure [23]. The electro catalytic activity for the oxygen reduction reaction was studied by Fan et al., who found that the presence of multiple types of N-C or C-S-C bonding in metal-free N,S-GQDs considerably increased this activity (ORR) [81].

Using a simple self-assembly technique, N-GQDs/graphene nanocomposites have been synthesized and employed as an effective electro catalyst for oxygen reduction reaction (ORR) [82]. NGQDs-graphene demonstrated exceptional electro catalytic activity and long-term stability. Two-dimensional (2D) metal chalcogenides, particularly molybdenum disulfide (MoS₂), have been shown to be prospective candidates

for ORR because to their unique features, such as strong electrical conductivity and vast surface area [83, 84]. N-GQDs hybrid played a good role in ORR, especially that made by using pyridine as a nitrogen precursor. N-GQDs have their uses in electro-catalytic activity [85].

In brief, GQD composites and N,S-GQDs are endowed with unique structural features and are promising candidates for metal-free electrocatalysts and improve the performances of devices. Novel functionalities of GQDs can be developed using composites and doping, which would open up new applications for GQDs.

4. Future prospects

Among the suggested clean energy sources, an innovative technology based on the use of microbial fuel cells (MFCs) has been proved as a critical pathway for bioconversion processes towards electricity generation, then for addressing energy and environmental problems. Three special features, including energy saving, less sludge production, and less energy production, make MFCs outstanding compared with the existing technologies [8-14]. Among these cells, the proton exchange membrane fuel cell (PEMFC) is one of the most promising technologies for transportation. The most significant part of MFCs is the proton exchange membrane (also termed the polymer electrolyte membrane (PEM)) with high protonic conductivity, low electronic conductivity, Fuel gas or liquid impermeability, Good mechanical strength in both dry and hydrated conditions, and High oxidative and hydrolytic stability in the environment of fuel cells, responsible for the proton transfer from the anode to the cathode and therefore the complete fuel cell's performance. The PEMFC, which is composed of a perfluorinated polymer membrane, Nafion, exhibits high proton conductivity at a certain range of temperature and humidity, but they still have some barriers, such as high fuel permeability and high cost [11-14]. However, developments of cost-effective materials and advanced membranes have been successful for reducing this limitation [86].

Studies have been focused on alternative solutions, including the fabrication of nanocomposite membranes by incorporating different nanofillers [87-89]. Zerodimensional (0D) materials such as silica nanoparticles [90-92], ceramic oxides nanoparticles [93, 94], etc [89, 95, 96] and one-dimensional (1D) nanomaterials such as carbon nanotube [97, 98], titania [99, 100], titanate [101] nanotube have been incorporated into the polymer matrix as versatile nanofillers. These nanocomposite membranes exhibited great enhancement in performance, endowing strong competitiveness in fuel cell application. 2D single-layer nanostructure called graphene with sp2-hybridized conjugated carbons [102, 103] can be investigated due to the exotic electrical, mechanical, and thermal properties [103-105] as well as its high surface area, chemical stability, and low fabrication costs [106, 107]. Zarrin et al. fabricated a nanocomposite membrane filled with functionalized graphene oxide (GO), and both proton conductivity and single-cell performance were significantly enhanced [108].

High proton conductivity, low water permeability, and good thermal and mechanical stability are some properties of the recent developed fuel cell materials and membranes [109].

The conversion of 2D graphene into 0D graphene quantum dots (GQDs) can be targeted by many studies in future years. The newly synthesized membrane can show greater thermal stability due to the formation of three-dimensional network structures in the presence of Functionalized Quantum Dots (FQDs) [110].

4. Conclusions

Recent advancements in sustainable and renewable energy sources have led to the emergence of fuel cells as a promising technology. Graphene quantum dots (GQDs), as innovative nanostructured materials, can be synthesized using diverse methods, resulting in active units with adjustable electronic and optical properties. These GQDs show great potential in a wide range of energy and environmental applications. Fuel cells offer numerous possibilities for electricity generation, but they are subject to limitations associated with the cost of catalysts and electrodes. Therefore, subsequent developments have focused on the exploration of new materials, hybrids, and composites aimed at addressing the limitations of conventional fuel cell components.

Nomenclature

| GQDs | Graphene quantum dots |
|--------|----------------------------------|
| FC | Fuel cell |
| ORR | Oxygen reduction reaction |
| PEM | Polymer electrolyte membrane |
| AFC | Alkali fuel cell |
| PAFC | Phosphoric acid fuel cell |
| MCFC | Molten carbonate fuel cell |
| SOFC | Solid oxide fuel cell |
| PGM | Platinum group metals |
| GSs | Graphene sheets |
| DMSO | Dimethyl sulfoxide |
| DMF | Dimethylformamide |
| KOH | Potassium hydroxide |
| rGO | reduced Graphene oxide |
| PBS | Phosphate buffer solution |
| PAH | Polycyclic aromatic hydrocarbon |
| GOLODs | Graphene-oxide-like quantum dots |

| PPy | Polypyrrole |
|--------------------|---|
| 3DG | 3D graphene |
| PEDOT:PSS | Poly(3,4-ethylenedioxythiophene) |
| | polystyrene sulfonate |
| L-ZnO | Leaf-shaped ZnO |
| B-TiO ₂ | Titanium dioxide (B) |
| 2D | Two-dimensional |
| MFCs | Microbial fuel cells |
| PEMMFCs | Proton exchange membrane microbial fuel |
| | cells |
| 0D | Zero-dimensional |
| 1D | One-dimensional |
| GO | Graphene oxide |
| FQDs | Functionalized Quantum Dots |
| LCA | life cycle assessment |
| EIs | Environmental impact statement |
| | |

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References

[1] M. Armand, J.-M. Tarascon, Building better batteries, nature. 451 (2008) 652.

[2] T.R. Cook, D.K. Dogutan, S.Y. Reece, Y. Surendranath, T.S. Teets, D.G. Nocera, Solar energy supply and storage for the legacy and nonlegacy worlds, Chem. Rev. 110 (2010) 6474-6502.

[3] J. Potočnik, Renewable energy sources and the realities of setting an energy agenda, Sci. 315 (2007) 810-811.

[4] M.A. Abdelkareem, A. Allagui, E.T. Sayed, M.E.H. Assad, Z. Said, K. Elsaid, Comparative analysis of liquid versus vapor-feed passive direct methanol fuel cells, Renew. Energ. 131 (2019) 563-584.

[5] Y. Wang, K.S. Chen, J. Mishler, S.C. Cho, X.C. Adroher, A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research, Appl. energy. 88 (2011) 981-1007.

[6] X. Huang, Z. Zhang, J. Jiang, Fuel cell technology for distributed generation: an overview, in: 2006 IEEE International Symposium on Industrial Electronics, IEEE. 2 (2006), 1613-1618.

[7] K. Liu, Y. Song, S. Chen, Oxygen reduction catalyzed by nanocomposites based on graphene quantum dots-supported copper nanoparticles, Int. J. Hydrog. Energy. 41 (2016) 1559-1567.

[8] A. ElMekawy, H.M. Hegab, K. Vanbroekhoven, D. Pant, Techno-productive potential of photosynthetic microbial fuel cells through different configurations, Renew. Sust. Energ. Rev. 39 (2014) 617-627.

[9] R. Kumar, L. Singh, A. Zularisam, Exoelectrogens: recent advances in molecular drivers involved in extracellular electron transfer and strategies used to improve it for microbial fuel cell applications, Renew. Sust. Energ. Rev. 56 (2016) 1322-1336.

[10] E.G.F. Mercuri, A.Y.J. Kumata, E.B. Amaral, J.R.S. Vitule, Energy by Microbial Fuel Cells: Scientometric global synthesis and challenges, Renew. Sust. Energ. Rev. 65 (2016) 832-840.

[11] Z. Chai, C. Wang, H. Zhang, C.M. Doherty, B.P. Ladewig, A.J. Hill, H. Wang, Nafion–carbon nanocomposite membranes prepared using hydrothermal carbonization for proton-exchange-membrane fuel cells, Adv. Funct. Mater. 20 (2010) 4394-4399.

[12] S. Mohanapriya, S. Bhat, A. Sahu, A. Manokaran, R. Vijayakumar, S. Pitchumani, P. Sridhar, A. Shukla, Sodiumalginate-based proton-exchange membranes as electrolytes for DMFCs, Energy Environ. Sci. 3 (2010) 1746-1756.

[13] V. Neburchilov, J. Martin, H. Wang, J. Zhang, A review of polymer electrolyte membranes for direct methanol fuel cells, J. Power Sources. 169 (2007) 221-238.

[14] R. Wang, X. Wu, X. Yan, G. He, Z. Hu, Proton conductivity enhancement of SPEEK membrane through n-BuOH assisted self-organization, J. Membr. Sci. 479 (2015) 46-54.

[15] L. Mond, C. Langer, V. A new form of gas battery, Proc.R. Soc. 46 (1890) 296-304.

[16] P. Sector, Fuel cell today industry review 2011, Platin. Met. Rev. 55 (2011) 268-270.

[17] M.A. Abdelkareem, K. Elsaid, T. Wilberforce, M. Kamil, E.T. Sayed, A. Olabi, Environmental aspects of fuel cells: A review, Sci. Total Environ. 752 (2021) 141803.

[18] K. Chizari, A. Deneuve, O. Ersen, I. Florea, Y. Liu, D. Edouard, I. Janowska, D. Begin, C. Pham-Huu, Nitrogendoped carbon nanotubes as a highly active metal-free catalyst for selective oxidation, ChemSusChem. 5 (2012) 102-108.

[19] X.-K. Kong, C.-L. Chen, Q.-W. Chen, Doped graphene for metal-free catalysis, Chem. Soc. Rev. 43 (2014) 2841-2857.

[20] W.A. Saidi, Oxygen reduction electrocatalysis using Ndoped graphene quantum-dots, J. Phys. Chem. Lett. 4 (2013) 4160-4165.

[21] M. Favaro, L. Ferrighi, G. Fazio, L. Colazzo, C. Di Valentin, C. Durante, F. Sedona, A. Gennaro, S. Agnoli, G. Granozzi, Single and multiple doping in graphene quantum dots: unraveling the origin of selectivity in the oxygen reduction reaction, ACS Catal. 5 (2014) 129-144.

[22] J.Y. Cheon, J.H. Kim, J.H. Kim, K.C. Goddeti, J.Y. Park, S.H. Joo, Intrinsic relationship between enhanced oxygen reduction reaction activity and nanoscale work function of doped carbons, J. Am. Chem. Soc. 136 (2014) 8875-8878.

[23] H. Jin, H. Huang, Y. He, X. Feng, S. Wang, L. Dai, J. Wang, Graphene quantum dots supported by graphene

nanoribbons with ultrahigh electrocatalytic performance for oxygen reduction, J. Am. Chem. Soc. 137 (2015) 7588-7591.

[24] L.L. Li, J. Ji, R. Fei, C.Z. Wang, Q. Lu, J.R. Zhang, L.P. Jiang, J.J. Zhu, A facile microwave avenue to electrochemiluminescent two-color graphene quantum dots, Adv. Funct. Mater. 22 (2012) 2971-2979.

[25] Y. Liu, P. Wu, Graphene quantum dot hybrids as efficient metal-free electrocatalyst for the oxygen reduction reaction, ACS Appl Mater Interfaces. 5 (2013) 3362-3369.

[26] S. Zhuo, M. Shao, S.-T. Lee, Upconversion and downconversion fluorescent graphene quantum dots: ultrasonic preparation and photocatalysis, ACS nano. 6 (2012) 1059-1064.

[27] M. Hassan, K.R. Reddy, E. Haque, S.N. Faisal, S. Ghasemi, A.I. Minett, V.G. Gomes, Hierarchical assembly of graphene/polyaniline nanostructures to synthesize free-standing supercapacitor electrode, Compos. Sci. Technol. 98 (2014) 1-8.

[28] N. Mohanty, D. Moore, Z. Xu, T. Sreeprasad, A. Nagaraja, A.A. Rodriguez, V. Berry, Nanotomy-based production of transferable and dispersible graphene nanostructures of controlled shape and size, Nat. Commun. 3 (2012) 844.

[29] L. Zheng, Y. Chi, Y. Dong, J. Lin, B. Wang, Electrochemiluminescence of water-soluble carbon nanocrystals released electrochemically from graphite, J. Am. Chem. Soc. 131 (2009) 4564-4565.

[30] J. Zhou, C. Booker, R. Li, X. Zhou, T.-K. Sham, X. Sun, Z. Ding, An electrochemical avenue to blue luminescent nanocrystals from multiwalled carbon nanotubes (MWCNTs), J. Am. Chem. Soc. 129 (2007) 744-745.

[31] H. Li, X. He, Y. Liu, H. Huang, S. Lian, S.-T. Lee, Z. Kang, One-step ultrasonic synthesis of water-soluble carbon nanoparticles with excellent photoluminescent properties, Carbon. 49 (2011) 605-609.

[32] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets, J. Am. Chem. Soc. 130 (2008) 5856-5857.

[33] Y. Dong, J. Shao, C. Chen, H. Li, R. Wang, Y. Chi, X. Lin, G. Chen, Blue luminescent graphene quantum dots and graphene oxide prepared by tuning the carbonization degree of citric acid, Carbon. 50 (2012) 4738-4743.

[34] L. Tang, R. Ji, X. Cao, J. Lin, H. Jiang, X. Li, K.S. Teng, C.M. Luk, S. Zeng, J. Hao, Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots, ACS nano. 6 (2012) 5102-5110.

[35] J. Sakamoto, J. van Heijst, O. Lukin, A.D. Schlüter, Twodimensional polymers: just a dream of synthetic chemists?, Angew. Chem. Int. Ed. 48 (2009) 1030-1069. [36] C.D. Simpson, J.D. Brand, A.J. Berresheim, L. Przybilla, H.J. Räder, K. Müllen, Synthesis of a giant 222 carbon graphite sheet, Chem. Eur. J. 8 (2002) 1424-1429.

[37] X. Yan, B. Li, X. Cui, Q. Wei, K. Tajima, L.-s. Li, Independent tuning of the band gap and redox potential of graphene quantum dots, J. Phys. Chem. Lett. 2 (2011) 1119-1124.

[38] X. Yan, L.-s. Li, Solution-chemistry approach to graphene nanostructures, J. Mater. Chem. 21 (2011) 3295-3300.

[39] Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou, L. Qu, An electrochemical avenue to green-luminescent graphene quantum dots as potential electron-acceptors for photovoltaics, Adv Mater. 23 (2011) 776-780.

[40] J. Lu, P.S.E. Yeo, C.K. Gan, P. Wu, K.P. Loh, Transforming C 60 molecules into graphene quantum dots, Nat. Nanotechnol. 6 (2011) 247.

[41] G. Chen, Z. Zhuo, K. Ni, N.Y. Kim, Y. Zhao, Z. Chen, B. Xiang, L. Yang, Q. Zhang, Z. Lee, Rupturing C60 Molecules into Graphene-Oxide-like Quantum Dots: Structure, Photoluminescence, and Catalytic Application, Small. 11 (2015) 5296-5304.

[42] E. Haque, J. Kim, V. Malgras, K.R. Reddy, A.C. Ward, J. You, Y. Bando, M.S.A. Hossain, Y. Yamauchi, Recent advances in graphene quantum dots: synthesis, properties, and applications, Small Methods. 2 (2018) 1800050.

[43] Z.A.C. Ramli, N. Shaari, T.S.T. Saharuddin, Progress and major BARRIERS of nanocatalyst development in direct methanol fuel cell: A review, Int. J. Hydrog. Energy. 47 (2022) 22114-22146.

[44] S.N. Shreyanka, J. Theerthagiri, S.J. Lee, Y. Yu, M.Y. Choi, Multiscale design of 3D metal–organic frameworks (M– BTC, M: Cu, Co, Ni) via PLAL enabling bifunctional electrocatalysts for robust overall water splitting, Chem. Eng. J. 446 (2022) 137045.

[45] H.C. Lim, S.H. Min, E. Lee, J. Jang, S.H. Kim, J.-I. Hong, Self-assembled poly (3, 4-ethylene dioxythiophene): poly (styrenesulfonate)/graphene quantum dot organogels for efficient charge transport in photovoltaic devices, ACS Appl Mater Interfaces. 7 (2015) 11069-11073.

[46] C. Luk, L. Tang, W. Zhang, S. Yu, K. Teng, S. Lau, An efficient and stable fluorescent graphene quantum dot–agar composite as a converting material in white light emitting diodes, J. Mater. Chem. 22 (2012) 22378-22381.

[47] D.K. Chan, P.L. Cheung, C.Y. Jimmy, A visible-lightdriven composite photocatalyst of TiO2 nanotube arrays and graphene quantum dots, Beilstein J. Nanotechnol. 5 (2014) 689-695.

[48] X. Chu, P. Dai, Y. Dong, W. Sun, L. Bai, W. Zhang, The acetic acid gas sensing properties of graphene quantum dots (GQDs)–ZnO nanocomposites prepared by hydrothermal method, J. Mater. Sci. Mater. Electron. 28 (2017) 19164-19173.

[49] J. Liu, L. Qin, S.-Z. Kang, G. Li, X. Li, Gold nanoparticles/glycine derivatives/graphene quantum dots composite with tunable fluorescence and surface enhanced Raman scattering signals for cellular imaging, Mater. Des. 123 (2017) 32-38.

[50] L.M. Long, N.N. Dinh, T.Q. Trung, Synthesis and characterization of polymeric graphene quantum dots based nanocomposites for humidity sensing, J. Nanomater. 2016 (2016).

[51] X. Wu, Y. Zhang, T. Han, H. Wu, S. Guo, J. Zhang, Composite of graphene quantum dots and Fe 3 O 4 nanoparticles: peroxidase activity and application in phenolic compound removal, RSC Adv. 4 (2014) 3299-3305.

[52] X. Zhou, X. Gao, F. Song, C. Wang, F. Chu, S. Wu, A sensing approach for dopamine determination by boronic acid-functionalized molecularly imprinted graphene quantum dots composite, Appl. Surf. Sci. 423 (2017) 810-816.

[53] E. Zor, E. Morales-Narváez, A. Zamora-Gálvez, H. Bingol, M. Ersoz, A. Merkoçi, Graphene quantum dots-based photoluminescent sensor: a multifunctional composite for pesticide detection, ACS Appl Mater Interfaces. 7 (2015) 20272-20279.

[54] S. Mondal, U. Rana, S. Malik, Graphene quantum dotdoped polyaniline nanofiber as high performance supercapacitor electrode materials, Chem comm. 51 (2015) 12365-12368.

[55] Q. Chen, Y. Hu, C. Hu, H. Cheng, Z. Zhang, H. Shao, L. Qu, Graphene quantum dots-three-dimensional graphene composites for high-performance supercapacitors, Phys. Chem. Chem. Phys. 16 (2014) 19307-19313.

[56] S. Dhar, T. Majumder, S.P. Mondal, Phenomenal improvement of external quantum efficiency, detectivity and responsivity of nitrogen doped graphene quantum dot decorated zinc oxide nanorod/polymer schottky junction UV detector, Mater. Res. Bull. 95 (2017) 198-203.

[57] A. Cai, X. Wang, Y. Qi, Z. Ma, Hierarchical ZnO/S, N: GQD composites: Biotemplated synthesis and enhanced visible-light-driven photocatalytic activity, Appl. Surf. Sci. 391 (2017) 484-490.

[58] X. Bu, S. Yang, Y. Bu, P. He, Y. Yang, G. Wang, H. Li, P. Wang, X. Wang, G. Ding, Highly Active Black TiO2/Ndoped Graphene Quantum Dots Nanocomposites For Sunlight Driven Photocatalytic Sewage Treatment, ChemistrySelect. 3 (2018) 201-206.

[59] Y. Ji, J. Hu, J. Biskupek, U. Kaiser, Y.F. Song, C. Streb, Polyoxometalate-Based Bottom-Up Fabrication of Graphene Quantum Dot/Manganese Vanadate Composites as Lithium Ion Battery Anodes, Chem. Eur. J. 23 (2017) 16637-16643.

[60] C. Lan, J. Zhao, L. Zhang, C. Wen, Y. Huang, S. Zhao, Self-assembled nanoporous graphene quantum dot-Mn 3 O 4 nanocomposites for surface-enhanced Raman scattering based identification of cancer cells, RSC Adv. 7 (2017) 18658-18667. [61] X. Wu, S. Guo, J. Zhang, Selective oxidation of veratryl alcohol with composites of Au nanoparticles and graphene quantum dots as catalysts, Chem comm. 51 (2015) 6318-6321.

[62] X. Chu, J. Wang, J. Zhang, Y. Dong, W. Sun, W. Zhang, L. Bai, Preparation and gas-sensing properties of SnO 2/graphene quantum dots composites via solvothermal method, J. Mater. Sci. 52 (2017) 9441-9451.

[63] Z. Zhang, C. Fang, X. Bing, Y. Lei, Graphene quantum dots-ZnS nanocomposites with improved photoelectric performances, Mater. 11 (2018) 512.

[64] J. Guo, H. Zhu, Y. Sun, L. Tang, X. Zhang, Doping MoS2 with graphene quantum dots: structural and electrical engineering towards enhanced electrochemical hydrogen evolution, Electrochim. Acta. 211 (2016) 603-610.

[65] V. Kumar, A. Kumar, A.M. Biradar, G. Reddy, D. Sachdev, R. Pasricha, Enhancement of electro-optical response of ferroelectric liquid crystal: the role of graphene quantum dots, Liq. Cryst. 41 (2014) 1719-1725.

[66] P.R. Kharangarh, S. Umapathy, G. Singh, Synthesis and luminescence of ceria decorated graphene quantum dots (GQDs): Evolution of band gap, Integr. Ferroelectr. 184 (2017) 114-123.

[67] Z. Protich, P. Wong, K. Santhanam, Composite of Zinc Using Graphene Quantum Dot Bath: A Prospective Material For Energy Storage, ACS Sustain. Chem. Eng. 4 (2016) 6177-6185.

[68] T. Hu, X. Chu, F. Gao, Y. Dong, W. Sun, L. Bai, Trimethylamine sensing properties of graphene quantum Dots/ α -Fe2O3 composites, J. Solid State Chem. 237 (2016) 284-291.

[69] H. Liu, Q. Zhao, J. Liu, X. Ma, Y. Rao, X. Shao, Z. Li, W. Wu, H. Ning, M. Wu, Synergistically enhanced activity of nitrogen-doped carbon dots/graphene composites for oxygen reduction reaction, Appl. Surf. Sci. 423 (2017) 909-916.

[70] S. Kundu, R.M. Yadav, T. Narayanan, M.V. Shelke, R. Vajtai, P.M. Ajayan, V.K. Pillai, Synthesis of N, F and S codoped graphene quantum dots, Nanoscale. 7 (2015) 11515-11519.

[71] L. Tang, R. Ji, X. Li, K.S. Teng, S.P. Lau, Energy-level structure of nitrogen-doped graphene quantum dots, J. Mater. Chem. C. 1 (2013) 4908-4915.

[72] X. Zhou, Z. Tian, J. Li, H. Ruan, Y. Ma, Z. Yang, Y. Qu, Synergistically enhanced activity of graphene quantum dot/multi-walled carbon nanotube composites as metal-free catalysts for oxygen reduction reaction, Nanoscale. 6 (2014) 2603-2607.

[73] Y. Li, Y. Zhao, H. Cheng, Y. Hu, G. Shi, L. Dai, L. Qu, Nitrogen-doped graphene quantum dots with oxygen-rich functional groups, J. Am. Chem. Soc. 134 (2011) 15-18.

[74] Q. Li, S. Zhang, L. Dai, L.-s. Li, Nitrogen-doped colloidal graphene quantum dots and their size-dependent

electrocatalytic activity for the oxygen reduction reaction, J. Am. Chem. Soc. 134 (2012) 18932-18935.

[75] D.B. Shinde, V.M. Vishal, S. Kurungot, V.K. Pillai, Electrochemical preparation of nitrogen-doped graphene quantum dots and their size-dependent electrocatalytic activity for oxygen reduction, Bull. Mater. Sci. 38 (2015) 435-442.

[76] H. Fei, R. Ye, G. Ye, Y. Gong, Z. Peng, X. Fan, E.L. Samuel, P.M. Ajayan, J.M. Tour, Boron-and nitrogen-doped graphene quantum dots/graphene hybrid nanoplatelets as efficient electrocatalysts for oxygen reduction, ACS nano. 8 (2014) 10837-10843.

[77] X. Wu, F. Tong, X. Yong, J. Zhou, L. Zhang, H. Jia, P. Wei, Effect of NaX zeolite-modified graphite felts on hexavalent chromium removal in biocathode microbial fuel cells, J. Hazard. Mater. 308 (2016) 303-311.

[78] C. Tang, Q. Zhang, Nanocarbon for oxygen reduction electrocatalysis: dopants, edges, and defects, Adv Mater. 29 (2017) 1604103.

[79] J. Zhang, L. Dai, Heteroatom-doped graphitic carbon catalysts for efficient electrocatalysis of oxygen reduction reaction, ACS Catal. 5 (2015) 7244-7253.

[80] M. Kaur, M. Kaur, V.K. Sharma, Nitrogen-doped graphene and graphene quantum dots: A review onsynthesis and applications in energy, sensors and environment, Adv. Colloid Interface Sci. 259 (2018) 44-64.

[81] T. Fan, G. Zhang, L. Jian, I. Murtaza, H. Meng, Y. Liu, Y. Min, Facile synthesis of defect-rich nitrogen and sulfur Codoped graphene quantum dots as metal-free electrocatalyst for the oxygen reduction reaction, J. Alloys Compd. 792 (2019) 844-850.

[82] M. Fan, C. Zhu, J. Yang, D. Sun, Facile self-assembly Ndoped graphene quantum dots/graphene for oxygen reduction reaction, Electrochim. Acta. 216 (2016) 102-109.

[83] J. Kibsgaard, Z. Chen, B.N. Reinecke, T.F. Jaramillo, Engineering the surface structure of MoS 2 to preferentially expose active edge sites for electrocatalysis, Nat. Mater. 11 (2012) 963.

[84] T. Wang, D. Gao, J. Zhuo, Z. Zhu, P. Papakonstantinou, Y. Li, M. Li, Size-Dependent Enhancement of Electrocatalytic Oxygen-Reduction and Hydrogen-Evolution Performance of MoS2 Particles, Chem. Eur. J. 19 (2013) 11939-11948.

[85] L. Sun, Y. Luo, M. Li, G. Hu, Y. Xu, T. Tang, J. Wen, X. Li, L. Wang, Role of Pyridinic-N for Nitrogen-doped graphene quantum dots in oxygen reaction reduction, J. Colloid Interface Sci. 508 (2017) 154-158.

[86] J.K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J.R. Kitchin, T. Bligaard, H. Jonsson, Origin of the overpotential for oxygen reduction at a fuel-cell cathode, J. Phys. Chem. B. 108 (2004) 17886-17892.

[87] A.M. Herring, Inorganic–polymer composite membranes for proton exchange membrane fuel cells, J. macromol. sci., Polym. rev. 46 (2006) 245-296.

[88] M. Maréchal, F. Niepceron, G. Gebel, H. Mendil-Jakani, H. Galiano, Inside the structure of a nanocomposite electrolyte membrane: how hybrid particles get along with the polymer matrix, Nanoscale. 7 (2015) 3077-3087.

[89] A.K. Mishra, S. Bose, T. Kuila, N.H. Kim, J.H. Lee, Silicate-based polymer-nanocomposite membranes for polymer electrolyte membrane fuel cells, Prog. Polym. Sci. 37 (2012) 842-869.

[90] P. Antonucci, A. Arico, P. Creti, E. Ramunni, V. Antonucci, Investigation of a direct methanol fuel cell based on a composite Nafion®-silica electrolyte for high temperature operation, Solid State Ion. 125 (1999) 431-437.

[91] E.-B. Cho, D.X. Luu, D. Kim, Enhanced transport performance of sulfonated mesoporous benzene-silica incorporated poly (ether ether ketone) composite membranes for fuel cell application, J. Membr. Sci. 351 (2010) 58-64.

[92] Y.-H. Su, Y.-L. Liu, Y.-M. Sun, J.-Y. Lai, D.-M. Wang, Y. Gao, B. Liu, M.D. Guiver, Proton exchange membranes modified with sulfonated silica nanoparticles for direct methanol fuel cells, J. Membr. Sci. 296 (2007) 21-28.

[93] D. Jung, S. Cho, D. Peck, D. Shin, J. Kim, Performance evaluation of a Nafion/silicon oxide hybrid membrane for direct methanol fuel cell, J. Power Sources. 106 (2002) 173-177.

[94] R. Nagarale, G. Gohil, V.K. Shahi, R. Rangarajan, Organic– inorganic hybrid membrane: thermally stable cation-exchange membrane prepared by the sol– gel method, Macromol. 37 (2004) 10023-10030.

[95] B.P. Tripathi, V.K. Shahi, Organic–inorganic nanocomposite polymer electrolyte membranes for fuel cell applications, Prog. Polym. Sci. 36 (2011) 945-979.

[96] F. Xu, S. Mu, Nanoceramic oxide hybrid electrolyte membranes for proton exchange membrane fuel cells, J. Nanosci. Nanotechnol. 14 (2014) 1169-1180.

[97] S. Gahlot, V. Kulshrestha, Dramatic improvement in water retention and proton conductivity in electrically aligned functionalized CNT/SPEEK nanohybrid PEM, ACS Appl Mater Interfaces. 7 (2014) 264-272.

[98] Y.-L. Liu, Y.-H. Su, C.-M. Chang, D.-M. Wang, J.-Y. Lai, Preparation and applications of Nafion-functionalized multiwalled carbon nanotubes for proton exchange membrane fuel cells, J. Mater. Chem. 20 (2010) 4409-4416.

[99] Y. Jun, H. Zarrin, M. Fowler, Z. Chen, Functionalized titania nanotube composite membranes for high temperature proton exchange membrane fuel cells, Int. J. Hydrog. 36 (2011) 6073-6081.

[100] B. Matos, E. Santiago, J. Rey, A. Ferlauto, E. Traversa, M. Linardi, F. Fonseca, Nafion-based composite electrolytes for proton exchange membrane fuel cells operating above 120

C with titania nanoparticles and nanotubes as fillers, J. Power Sources. 196 (2011) 1061-1068.

[101] B.R. Matos, E.I. Santiago, F.C. Fonseca, M. Linardi, V. Lavayen, R.G. Lacerda, L.O. Ladeira, A.S. Ferlauto, Nafiontitanate nanotube composite membranes for PEMFC operating at high temperature, J. Electrochem. Soc. 154 (2007) B1358-B1361.

[102] K.S. Novoselov, A.K. Geim, S. Morozov, D. Jiang, M. Katsnelson, I. Grigorieva, S. Dubonos, Firsov, AA, Twodimensional gas of massless Dirac fermions in graphene, nature. 438 (2005) 197.

[103] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and graphene oxide: synthesis, properties, and applications, Adv Mater. 22 (2010) 3906-3924.

[104] Y. Huang, J. Liang, Y. Chen, An overview of the applications of graphene-based materials in supercapacitors, Small. 8 (2012) 1805-1834.

[105] Y. Zhang, D. Li, X. Tan, B. Zhang, X. Ruan, H. Liu, C. Pan, L. Liao, T. Zhai, Y. Bando, High quality graphene sheets from graphene oxide by hot-pressing, Carbon. 54 (2013) 143-148.

[106] H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, Flexible graphene–polyaniline composite paper for high-performance supercapacitor, Energy Environ. Sci. 6 (2013) 1185-1191.

[107] A.K. Geim, Graphene: status and prospects, sci. 324 (2009) 1530-1534.

[108] H. Zarrin, D. Higgins, Y. Jun, Z. Chen, M. Fowler, Functionalized graphene oxide nanocomposite membrane for low humidity and high temperature proton exchange membrane fuel cells, J. Phys. Chem. C. 115 (2011) 20774-20781.

[109] D. Carter, M. Ryan, J. Wing, The fuel cell industry review 2013, Fuel Cell, 21 (2012).

[110] R.S. Malik, U. Soni, S.S. Chauhan, P. Verma, V. Choudhary, Development of functionalized quantum dot modified poly (vinyl alcohol) membranes for fuel cell applications, RSC Adv. 6 (2016) 47536-47544.