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Graphene-based nanomaterials in innovative electrochemistry

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RESEARCH HIGHLIGHTS

- Graphene and its derivatives play an important role in today's electrochemical based technologies as outlined in this article
- Examples are given for energy driven applications and electrocatalytic processes with the aim to replace Pt/C bench mark electrode
- The high performance of graphene-based electrodes in biosensing and biomedical driven applications is presented

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Introduction

Electrochemical science has become a discipline of wide scientific and technological interest due to the important role in present-day technologies. Batteries, fuel cells, supercapacitors, electrochromic devices, gas separation membranes, and sensors are some examples of applications of electrode materials. The success in electrochemical technology is largely due to the continued design and development of novel material electrodes that meet the needs of modern society. Emerging two-dimensional nanomaterials, including next to graphene, h-BN, MoS₂, NbSe₂, TiS₂, TaS₂, WS₂, WSe₂, TaSe₂, etc., metal-organic frameworks (MOFs) and many more, are at the forefront of interest because of their superior potential for electrochemically driven applications in many different fields [1-4]. The success of graphene-based electrode materials, such as chemical vapor deposition produced graphene as well as chemically derived graphene derivatives, in numerous electrochemical based technologies (**Figure 1**) is due to a number of factors, which are key to most of the applications [4-7].

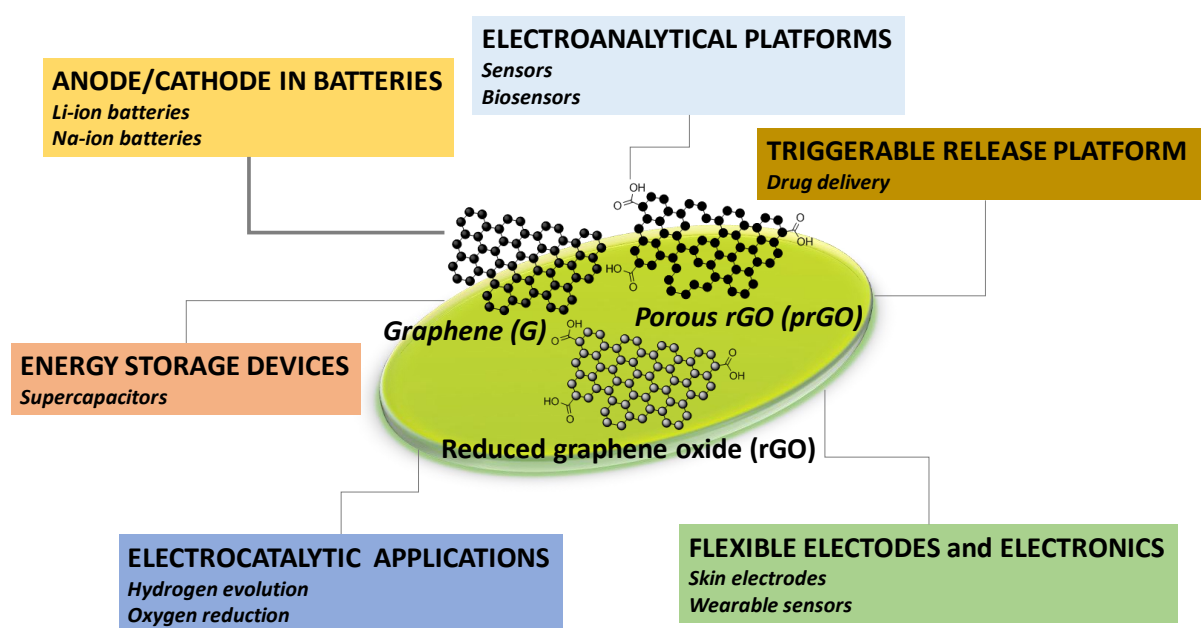


Figure 1: Graphene interfaces for innovative electrochemical based applications.

Indeed, graphene exhibits a large surface area, which can be further tuned through the generation of porous structured graphene and incorporation of dopants. Additionally, graphene as a highly conjugated network (π -conjugation) bears hydrophobic properties providing an ideal platform for immobilizing organic and inorganic molecules in an easy manner. Graphene exhibits also high conductivity and mediates electron transfer mostly at its edge planes [8]. Those properties have made graphene of potential interest for electrochemical and biosensing oriented applications. To evaluate graphene's performance as an electrode

material, the heterogeneous electron transfer (ET) rate between graphene and a redox mediator has to be determined and compared with its naturally occurring counterpart 3-D graphite.[9,10] The literature offers some contrasting views on the reactivity of mono and multilayered graphene. Accelerated kinetics data are reported on mechanically exfoliated monolayer graphene compared to bilayer graphene and graphite.[11,12] Guell et al. observed increased ET kinetics with increasing number of CVD stacked graphene flakes (from 1 to 7) using a ferrocene derivative as a mediator. However, no increased ET was observed at the edges or steps in comparison to the basal plane.[13] To shed more light into the electrochemistry of graphene, Velicky et al. determined the electron transfer rates of three redox mediators on mechanically exfoliated graphene layers (1-100) supported on insulating Si/SiO₂ substrates. A large variation in kinetics is observed across the basal plane of the same flake, indicating that local surface conditions affect the electron transfer kinetics. While the growing number of commercial sources of graphene represents certainly an important step towards the commercialization of graphene-based materials in the near future, for a large number of electrochemical applications, it is not graphene but chemically derived reduced graphene oxide (rGO) which is used. In contrast to pristine graphene, rGO contains lattice defects and residual oxygen-containing groups. While these defects impact on the electrical readout, they are actually beneficial to achieve fast heterogeneous electron transfer. Additionally, the presence of oxygen-containing groups offers plenty of opportunities for covalent immobilization of surface ligands to target specific sensing or drug delivery applications [8,14]. The promising electrochemical characteristics such as large potential window, fast electron transfer kinetics and increased capacitance of rGO based materials together with their low cost of production make them ideal materials for electrochemical-driven applications [14,15].

This article is not aiming to discuss in details all the different recent examples of rGO based electrochemical applications ranging from energy to electroanalytical and biosensing driven applications. It should be seen as a general review to a broad audience interested in graphene based electrochemistry and its different aspects. The review will thus highlight some important works with details to be found in the respective articles. It will also address certain aspects to further enhance the use of graphene nanomaterials in innovative electrochemical designs.

Recent examples from the literature

1. Energy driven applications: Energy storage and energy conversion

The development of novel materials for energy storage is of great importance to fulfill the increasing demand of energy. Lithium ion batteries are highly promising devices for powering portable electronics and also electrical vehicles. Currently, the use of graphite anodes with a theoretical capacity of 372 mAh g^{-1} has become insufficient to satisfy the increasing energy and power densities demand, making the search for efficient and stable anode materials possessing high lithium capacity of high importance. Mullins and co-workers developed a composite of N-doped rGO and nanocrystalline tin sulfides and tested it as anode in lithium batteries [16]. When cycling at a specific rate of 0.2 A g^{-1} , a Coulombic capacity of 562 mAh g^{-1} was retained after the 200th cycle, which is believed to be due to the presence of conductive rGO cushioning the stress associated with the expansion of lithiation of Sn. Lin et al. reported a composite lithium metal anode composed of 7 wt.% layered rGO with nanoscale gaps that can host metal lithium. The composite exhibited low dimensional variations (20%) during cycling, good mechanical flexibility next to retaining up to 3.390 mA g^{-1} of capacity in a carbonate electrolyte [17]. Graphene encapsulated Si microparticles were proposed by Li as anode in lithium ion batteries, where the graphene cage acts as a flexible and mechanically strong buffer during deep galvanostatic cycling, allowing the microparticles to expand and fracture within the cage while retaining electrical connectivity on both the particle and electrode levels.

Among the new battery chemistries being developed, sodium-ion batteries are considered to be the most promising ones due to similar intercalation chemistry to Li-ion ones and natural abundance of sodium resources. Anodes of rGO, with uniformly anchored Fe_2O_3 single crystallites with a particle size of $\approx 300 \text{ nm}$ displayed a reversible capacity of 610 mAh g^{-1} at 50 mA g^{-1} , high coulombic efficiency (71% for the first cycle) and a good cyclability with 82% capacity retention after 100 cycles, suggesting a potential feasibility for sodium-ion battery [18]. The Na^+ intercalation/de-intercalation properties of mesoporous WO_{3-x} encapsulated in N-doped macroporous graphene, formed by heat treatment of a co-assembly of amine-functionalized mesoporous silica/metal oxide and GO with subsequent silica removal, were recently demonstrated by Kim et al. [19].

To tackle the challenge in the preparation of high-capacity electrode materials with good structural stability and flexibility, Mo et al. proposed a 3D interconnected porous nitrogen-doped graphene foam (NGF) with encapsulated Ge quantum dots@nitrogen-doped graphene (Ge-QD@NG), exhibiting high specific capacity of 1.220 mAh g^{-1} and long cycling capability [20]. It is well recognized that the ever-growing demands in future flexible electronics such as

wearable devices, portable implants, biomedical products, have aroused a worldwide research interest in the development of electrodes that maintain their conductivities under repeated stretching deformation. A solid-state electrochemical capacitor was recently developed using wavy rGO displaying a specific capacitance of 67.25 mF cm^{-2} at a current density of 1 mA cm^{-2} , and excellent stability [21].

Next to batteries, supercapacitors (SC) are the key devices for energy storage due to their high specific capacitance, high power density, ultrafast charging/discharging rate, extremely low internal discharge, long cycle life (300.000 cycles) and low cost [22,23]. We reported recently on an all solid-state SC using N-doped porous rGO with a specific capacity of 230 F g^{-1} at 1 A g^{-1} current density and good capacitance retention up to 88% even after 10.000 galvanostic charge/discharge cycles recorded at 5 A g^{-1} (**Figure 2A**) [23]. While symmetric SC have many reported outstanding properties, asymmetric designs using graphene-based materials as negative electrode materials allowed widening the negative working potential range. A high performance asymmetric SC using MnCo_2O_4 nanofibers as anode and N-doped rGO aerogels as cathode was proposed [24]. The MnCo_2O_4 nanofibers store negative charges such as solvated OH^- , while the N-doped rGO aerogel stores positive charges, providing an operating potential of 1.8 V with energy and power densities of 54 Wh kg^{-1} and 9851 W kg^{-1} , respectively and 85.2 % capacity retention over 3.000 cycles. The charge storage mechanism of the spinel-type oxide materials remains however unclear, even though synchrotron-based X-ray absorption spectroscopy (XAS) was used to determine the oxidation states of Co and Mn at the MnCo_2O_4 electrode after being electrochemically tested.

Last but not least, microbial fuel cells are perceived as a promising renewable power source harvesting electricity from organic matter by microorganisms. Their practical application is still greatly impeded by their lower power density compared to conventional fuel cells, mainly due to the sluggish extracellular electron transfer and low bacteria loading. 3D hierarchically structured porous MWCNTs/rGO nanohybrids were found to be useful anode materials for the growth of rich bacterial biofilms, displaying a power density of 789 mW m^{-2} in *Shewanella putrefaciens* CN32 microbial fuel cells (**Figure 2B**), being 6-fold higher than that of conventional carbon cloth [25].

2. Catalytic driven reaction

Metal nanoparticle-rGO composites have been largely investigated as advanced electrode materials due to their interesting electrocatalytic features. Introduction of rGO to the catalytic system enhances the catalytic activity not only due to its large surface area, high conductivity and excellent electrochemical properties, but also as rGO stabilizes efficiently the catalytic nanostructures from aggregation. Such nanocomposites have found widespread applications for green and renewable sources of energy, including electrochemical water splitting reaction, putting oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) at the forefront of interest. Similarly, the oxygen reduction reaction (ORR) is important to renewable energy technologies, including fuel cells and metal-air batteries. Platinum based catalysts have long been used for ORR and HER, and carbon supported platinum (Pt/C) is still one of the bench mark catalysts [26]. Indeed, based on its adsorption energetics of the H atom, platinum is the optimal material for fuel cell electrocatalysis. The high cost of platinum and low catalytic efficiency due to CO poisoning along with thermal instability remain nevertheless the major limiting factors for enhancing the energy-conversion efficiency in fuel cells and other energy driven devices. Non-Pt group electrocatalysts and even metal-free catalysts have shown their efficiency towards the different electrocatalytic processes [3]. For example, CoMn oxide nanoparticles (Co:Mn ratio of 2:1) supported over N-doped porous reduced graphene displayed ORR activity under basic conditions comparable to that of commercial Pt/C catalyst (**Figure 2C**), where the high activity was attributed to the cooperative effect arising from the metal entities and the defects in N-doped porous rGO [27]. PdAg particles embedded on ZrO₂/porous carbon/rGO nanocomposites resulted in electrodes with excellent activity for the dehydrogenation of formic acid with 100% hydrogen selectivity [28]. Zheng et al. demonstrated that g-C₃N₄@N-doped reduced graphene oxide was a highly efficient metal-free HER catalyst [29]. Tri-doped rGO (nitrogen, phosphorus, fluorine), obtained by thermal activation of a mixture of polyaniline-coated GO and ammonium hexafluorophosphate, was found to exhibit excellent electrocatalytic activities for ORR, OER and HER and could be used as an OER-HER bifunctional catalyst for oxygen and hydrogen gas production in an electrochemical water-splitting unit, which was powered by an integrated Zn-air battery based on an air electrode made from the same electrocatalyst for ORR (**Figure 2D**) [30].

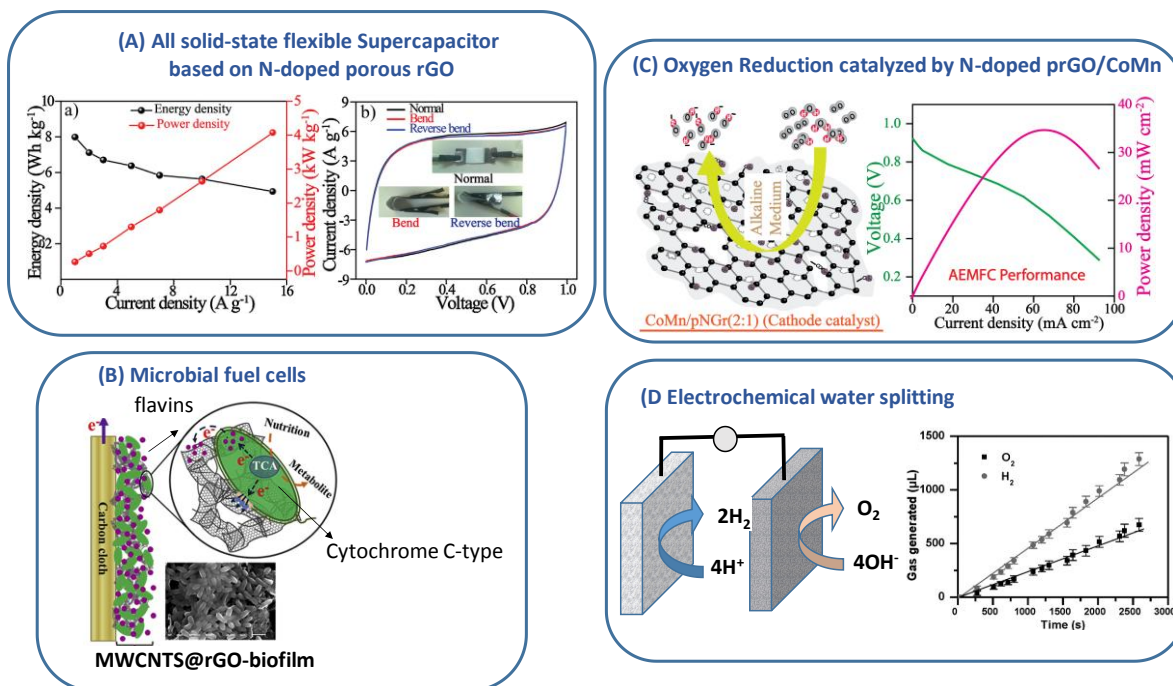


Figure 2: Selected examples for energy and electrocatalytic driven applications: (A) Electrochemical testing of an all solid-state supercapacitor device fabricated with N-doped porous rGO: (a) Plots of the energy density and power density as a function of charge-discharge current density and (b) demonstration of flexibility of the device with different bending states (reprint with permission from Ref.[31]); (B) Mechanism of anodic biofilm on enhanced bioelectrocatalysis; (C) (left) ORR using CoMn/N-doped prGO (2:1) as cathode catalyst, (right) power density of a primary Zn-air battery using this cathode catalyst [27]; (D) (left) Schematic of electrochemical water splitting, (right) O_2 and H_2 production volume as a function of water splitting time (reprint permission from Ref.[30]).

3. Sensing and biomedical applications

The attractive properties of rGO based nanomaterials have paved more recently the way for the fabrication of a wide range of electrochemical based biosensors with improved analytical performance [32-34]. The underlying principle of an electrochemical sensor is to convert a biological binding event into a measurable electrical signal. This approach is represented by electron transfer between the rGO coated interfaces and an electroactive species, which can be either the molecule to be analyzed or a species, whose electrochemical signal correlates with the presence of the target analyte. Aspects governing electron transfer on graphene coated electrodes become of importance to obtain large output signals, allowing to reach low detection limits needed when analyzing clinical samples. Impressive electrocatalytic performance was obtained on multi-layered graphene flakes coated Si wafers in response to biomolecules such as dopamine and ascorbic acid due to the large area of edge planes that are available on such an interface to allow rapid heterogeneous electron transfer [35]. The other advantages of rGO in the electroanalytical context is the high surface area of rGO supporting

the integration of a high density of analyte specific ligand. Nickel [36] and copper oxide [37] supported on rGO or ammonia-doped porous rGO allowed non-enzymatic glucose sensing due to the electro-catalytic properties of the nanostructures for glucose under alkaline conditions with a 0.25 μM detection limit in the case of using N-doped prGO/CuO modified electrodes (**Figure 3A**) [37]. In a similar manner, non-enzymatic sensing of hydrogen peroxide can be achieved using Pt NPs modified rGO-chitosan-ferrocene carboxylic acid structures,[38] hollow TiO_2 -rGO microspheres encapsulating hemoglobin,[39] or Au@Prussian blue core-shell structures embedded onto rGO,[40] with detection limits in the nanomolar range.

Real-time quantitative monitoring of biomarkers, a specific class of biological substances whose expression in serum and saliva correlates with a certain illness, has become essential for early detection of the disease, directing personalized treatments and analysis of treatment efficacy. An immunosensing platform for the electrochemical detection of oral cancer, based on anti-IL8/Au NPs-rGO coating, was recently proposed [41]. Porous rGO electrodes modified with anti-gliadin antibodies using 1-pyrenecarboxylic acid as linker molecule to porous reduced graphene oxide (prGO) allowed for sensitive sensing of gliadin in food samples (**Figure 3B**) [42]. We have also demonstrated that an rGO modified electrode can analyze the level of folic acid protein in human serum with a picomolar detection limit,[43] while molybdenum disulfide-rGO hybrid electrode allowed the direct detection of folic acid in human serum with a limit of detection 10 nM [44]. rGO and/or porous rGO modified electrodes are also highly adapted as general platforms for the efficient on-demand delivery of a variety of drugs using electrochemical triggered approach (**Figure 3C**), as shown for the controlled delivery of a therapeutic protein such as insulin,[45] an anticancer drug like doxorubicin,[46] ondansetron, an antagonist to prevent nausea and vomiting caused by chemotherapy,[47] as well antibiotics such as ampicillin [47]. Porous rGO (prGO) has, in addition, found its interest for the analysis of protein aggregation in pharmaceutical formulations (**Figure 3D**) [48].

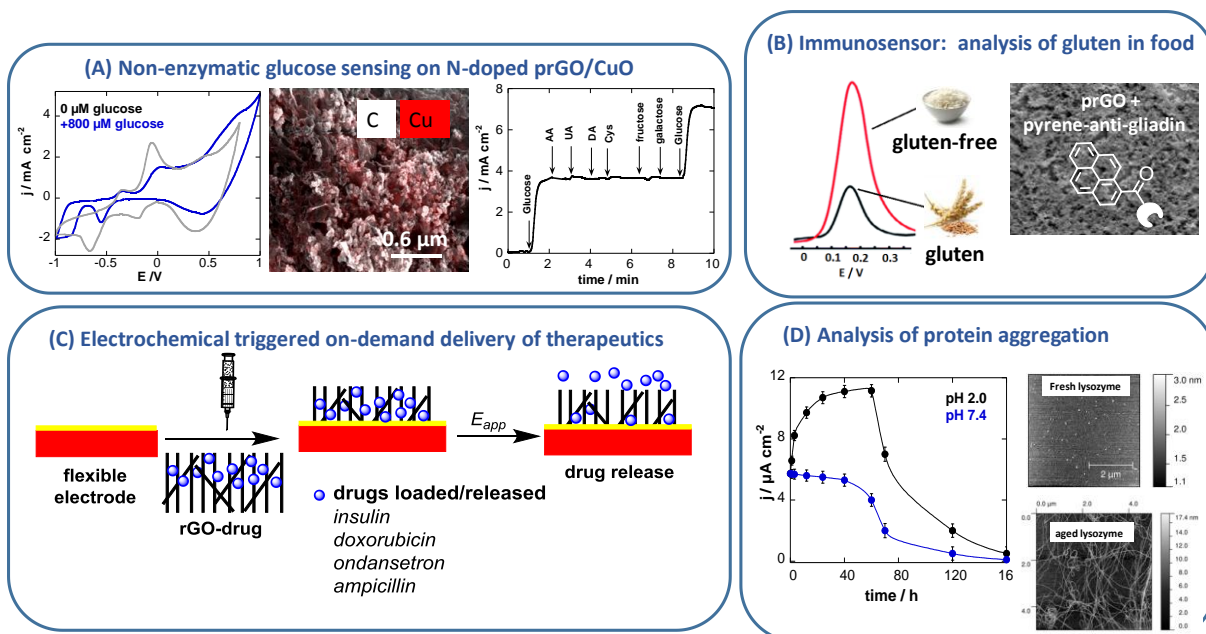


Figure 3: Selected examples of the use of rGO and prGO modified electrodes for biomedical applications: (A) Non-enzymatic glucose sensing: (left) CV of N-doped prGO/CuO electrode in the absence and presence of glucose (800 μM) in 0.1 M NaOH, (middle) EDX analysis of N-doped prGO/CuO electrodes, (right) Amperometric response to 1 mM glucose and 10 mM interfering species such as ascorbic acid (AA), uric acid (UA), dopamine (DA), cysteine (Cys), fructose, galactose in 0.1 M NaOH [37]; (B) (left) Differential pulse voltammograms of anti-gliadin modified prGO electrodes in the absence and presence of gliadin using $\text{Fe}(\text{CN})_6^{3-}$ (5 mM)/PBS (0.1 M) as a redox couple, (right) SEM image of prGO based immunosensor [42]; (C) Schematic illustration of formation of drug loaded graphene based electrodes and electrochemically triggered on demand release; (D) (left) Change in oxidation current density of a lysozyme solution (700 μM) submitted to forced degradation at pH 2 and pH 7.7, (right) AFM image of a fresh lysozyme solution and an aged one [48].

4. Opinion for potential users of graphene in electrochemical methods

The rich electrochemistry of graphene is due to its intrinsic favorable properties to molecules of aromatic structure, where π - π stacking interactions can result in enhanced and better defined electrochemical signals [35], and the ease by which catalytic sites in form of nanoparticles and others can be irreversibly anchored onto graphene-based materials. While there has been tremendous progress in the development of graphene based materials, there is still room for further research on the determination of underlying reasons for the activity of graphene, such as the insight which established that ORR catalysis on N-doped graphene stems from the electron-deficient carbon neighboring pyridine nitrogen. In the case of electrochemical sensors, even though a large amount of graphene based sensors are reported in the literature exhibiting good sensing characteristics, the performance in real biological samples, where next to a variety of other proteins high salt concentrations are present, is often

not considered and information is largely lacking. These are only one of the different challenges to overcome, in order to bring some of the current sensors into real biomedical applications. The realization of graphene-based, next-generation electrochemical guided applications, depends in addition essentially on a reproducible, large-scale production of graphene. The large scale production of monolayer graphene films by of chemical vapor deposition (CVD) in uniform and homogenous manner remains a key challenge. The limited mechanical properties and stability of CVD graphene in solution are one of the most significant obstacles for its use in graphene-based flexible devices. The mass production of high-quality GO and rGO, achieved by chemical oxidation/reduction and exfoliation of low-cost graphite, is on the other hand a promising way to connect to real-world applications and commercialized products. Much effort has thus been more lately devoted into assembling well dispersed multifunctional chemically reduced graphene oxide nanosheetes onto and into ordered macrostructures without loss of their electrochemical properties and keeping mechanical strength and conductivity. Such flexible light-weight and functional materials are of interest for classical energy driven applications (fuel cells, Li-ion batteries, supercapacitors) as well as wearable energy systems and sensors.

CONCLUSION AND OUTLOOK

The above examples are not an exhaustive list of applications where graphene based materials have resulted in innovative electrochemical applications. It is rather a collection of relevant examples from the literature from different research teams with different perspectives and should serve as triggering further interest in graphene-based electrochemistry. They were chosen as they underline important advancements where graphene was the core of the improvement. It is with no doubt, that this field is currently advancing mainly by developing and finding the miracle material. Basic electrochemical concepts remain mainly untouched, but are essential in understanding mechanistic aspects and potential limitations/advantages of different graphene nanostructures. With the rapid progress that has been made in the last two years on the synthetic aspects of graphene related materials together with advances in *in situ* spectroscopic methods and powerful theoretical modeling, it is certain that the next five years will be fruitful for advancing graphene-based electrochemical technological inventions. One of the limitations of graphene-based materials remains certainly the variation of the chemical composition and metal contamination, depending on the origin of the graphite precursor and oxidation process conditions. Although for certain applications, this would not affect much their performance, for catalytic and electrocatalytic applications, the nature and concentration

of metal contaminant can have a huge impact on the performance and reproducibility of the electrode material.

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