Graphene-Based Electrocatalysts

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Abstract The utilization of electrochemical conversion and energy storage has become feasible in tackling the growing concerns related to energy and environment. One of the primary challenges in the practical application of these devices is the sluggishness of their reaction kinetics. There should be a heightened focus on examining electrocatalysts that exhibit superior efficiency and enhance kinetics rate. Graphene is one of the most extensively researched electrode materials for electrochemical applications among advanced nanomaterials. The incorporation of graphene with nanomaterials can make it easier to take advantage of the material's inherent features. Particularly, graphene and graphene derivatives have been utilized as templates for the synthesis of numerous noble-metal nanocomposites, which have demonstrated exceptional performance in electrocatalytic applications, such as the sensors, ORR, OER, HER, CO_2RR, SCs, and so on. In this chapter, we undertake an examination of the progress made in the development of graphene and its composites-based electrodes for the electrocatalytic field.

Keywords Electrocatalyst · Carbon-based materials · Graphene · Sensors · Biosensors

1 Introduction

The global community is confronted with a pressing concern known as the energy crisis, which has emerged as a significant challenge due to the exponential increase in energy use and the gradual exhaustion of traditional energy equipment [1, 2]. Electricity, which is the most extensively utilized energy source, is predominantly generated by the combustion of fossil fuels such as petroleum, coal, and natural gas.

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The combustion of fossil fuels results in the generation of substantial quantities of toxic gases, which contribute to the pollution of marine ecosystems and food webs, in addition to the emission of carbon dioxide that influences climate change [3]. Electrocatalyst active sites can be employed to mitigate excessive electrical energy consumption. This technology holds significant promise in addressing our impending energy demands and mitigating the challenges posed by climate change.

Electrocatalysts play a vital role in facilitating the efficient conversion between electrical and chemical energies, thereby enabling the implementation of water, carbon, and nitrogen cycles dependent on renewable energy sources. The desired electrocatalysts should exhibit exceptional performance in terms of activity, stability, and product selectivity, while simultaneously reducing or eliminating the reliance on precious metals [4]. At least three factors should be met at the same time by the catalytically active sites of desirable electrocatalysts. (I) It is imperative that the catalysts possess a substantial level of intrinsic activity. (ii) The catalysts must have a significant density on their surfaces. (iii) The catalysts should be readily accessible to molecules participating in the reaction. The advantages stem from the fact that electrocatalytic processes can be used to transform surplus and off-peak electricity into chemical bonds in molecules. This opens several potential commercial opportunities.

Some surface sites contribute to catalyst activity, known as catalytic active sites. Determining catalytic sites is of great significance in furthering our understanding of electrocatalytic reactions and promoting the advancement of improved electrocatalysts. The usual approach utilized for the identification of active sites in heterogeneous catalysts entails the production of catalysts with various sizes, employing the scanning transmission electron microscopy (STEM) analysis. There exists a clear correlation between the dimensions of catalyst particles and the number of corners and edges they possess, which subsequently impacts their catalytic activity [5]. Porous electrocatalysts are a significant category of materials that exhibit a variety of properties that enable efficient electrocatalysis. The presence of carbon-based materials (CBMs) can lead to the formation of electrocatalytic active sites, owing to their inherent properties. The objective is accomplished through the manipulation of the charge distribution and spin density of neighboring CBMs, as well as the optimization of their adsorption and desorption properties concerning essential intermediate species. The utilization of defect engineering can be employed as a strategy to activate the π electrons present in undoped CBMs, thus leading to the generation of active sites that facilitate electrocatalysis.

Recent studies have further confirmed the importance of dopant-induced and intrinsic defect sites in CBMs concerning their electrocatalytic activity. To date, a variety of SACs including, platinum (Pt), palladium (Pd), ruthenium (Ru), iridium (Ir), molybdenum (Mo), and iron (Fe), have been successfully prepared to facilitate a wide range of electrochemical reactions. The main cause of this phenomenon can be ascribed to the unique characteristic of metal atoms that exist in isolation at the atomic scale, frequently attached to supporting materials. Recently, single-atom catalysts (SACs)-based CBMs have emerged as highly promising materials for electrocatalysis in a diverse array of applications.

The establishment of effective coordination between metal atoms and support materials, such as CBMs, has the potential to generate electrocatalytically active sites exhibiting significant levels of activity. These catalysts' high electro-catalytic activity is often due to their strong metal-support interactions. These interactions change the local coordination environment, regulate metal atom-support material electronic transfer, and increase reaction intermediate chemisorption energies.

CBMs, like carbon quantum dots (CQDs), nanowires, nanotubes ((CNTs) (multi-wall carbon nanotubes (MWNTs)), single-wall carbon nanotubes (SWCNTs), fibers, and graphene, graphene oxide (GO) are predicted to play crucial roles in overcoming obstacles and making advances in catalysis process. The fundamental cause of this phenomenon can be attributed to their distinct composition and inherent characteristics, which include large specific surface area, electrochemical and chemical inertness, and good biocompatibility, on the other hand, straightforward synthesis procedures have boosted research in life science, energy, and environmental domains. Graphene, an up-and-coming star in the fields of material science and technology, is speculated to be capable of resolving a wide variety of critical problems. It has been demonstrated that graphene possesses a substantial variety of fascinating features, some examples of which are as follows: charge transport mobility (~10,000 $cm^2 V^{-1} s^{-1}$), excellent chemical stability (~1.0 TPa), and huge specific surface area. In addition, given its exceptional mechanical strength and flexibility, outstanding thermal and electrical conductivity (~5000 $Wm^{-1} K^{-1}$), optical transparency (~97%), and remarkable electronic characteristics [6].

The electrical characteristics of graphene exhibit variations based on the number of layers and the relative arrangement of atoms in neighboring layers, often known as stacking order. Double-layer graphene can have a stacking order of AA (atoms on top of each other) or AB (second layer atoms on top of first layer hexagon center). Several techniques have been devised for the synthesis of this promising graphene material, including the Hummers method, chemical vapor deposition (CVD), direct liquid exfoliation, and others [7, 8]. From the perspective of condensed matter physics, graphene is composed of carbon atoms bound together through sp_2 hybridization of their atomic orbitals, specifically s, px, and py orbitals. This hybridization results in the formation of three robust σ bonds between each carbon atom and its three neighboring atoms.

Graphene can be divided into two-dimensional (2D) and three-dimensional (3D) materials, with carbon atoms arranged in a honeycomb-like hexagonal lattice [6]. Specifically, the design of 3D graphene that is formed through the assembly of 2D has significant attention has been drawn to 3D graphene due to its unique features and ability to retain 2D graphene properties. Some notable characteristics of this 3D material include the ability to modify pore shapes, high mechanical strength, and exceptional electronic conductivity. Based on these fascinating characteristics, 3D graphene as a catalyst or electrocatalyst support has already met a number of the prerequisites for consideration as an advanced catalyst process, which contributes more to the improvement of catalytic performance. It should be noted that the 3D confinement of electrocatalytic components graphene stabilizes catalytic active sites. In addition to the described here, the use of 3D graphene offers catalysis benefits:

(i) 3D graphene modified with functional groups such as -NH$_2$, -COOH, and -OH directly contributes to catalysis. (ii) The utilization of defect-related or heteroatom-doped 3D graphene has demonstrated commendable efficacy in catalytic reactions, particularly in the domain of electrocatalysis. (iii) 3D graphene is widely recognized as a substrate that enhances catalytic functions, including metal oxides, phosphides, chalcogenides, and nitrides. (iv) The utilization of 3D graphene has been seen to serve as cocatalysts to enhance the efficiency of photocatalytic reactions. For modifying graphene's electronic/optical properties, heteroatom doping is a simple method for creating n-type, p-type, or hybrid graphene. Similar variations are also observed in other parameters, such as thermal conductivity and thermal expansion. The incorporation of foreign elements such as nitrogen (N), boron (B), and sulfur (S) into support materials has been shown to enhance their electrical properties and catalytic performance [9, 10]. Carbon materials have been widely utilized as support materials to stabilize single-metal catalytic sites, owing to their numerous significant advantages. Vital progress has been made in the past decade regarding the application of graphene-based electrocatalyst materials in various electrochemical reactions. These reactions include the solar cells (SCs), oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), carbon dioxide reduction reaction (CO$_2$RR), and oxygen evolution reaction (OER), supercapacitors, sensors, and biosensors (Fig. 1).

2 Application

2.1 Solar Cells

Fossil fuels possess the characteristic of being non-renewable resources, with their reserves undergoing depletion at a rate that surpasses the discovery or creation of new reserves. The advancement of clean and sustainable energy sources is crucial to address the continuously growing global energy needs resulting from rapid economic growth and the expanding world population. At present, there is a significant focus on the extensive investigation of emerging technologies for energy conversions, such as SCs and fuel cells, as well as energy storage, including super-capacitors. The performance of these devices is heavily influenced by the materials utilized. Several electrocatalysts exhibiting specific nanostructures and significant surface/interface areas have been successfully synthesized for utilization in energy-related devices. CBMs have been significant in driving industrial and technical progress since the onset of the previous century. In contrast to conventional energy materials, carbon nanostructures demonstrate distinctive features that are influenced by their size and surface characteristics. These qualities, which include morphological, electrical, optical, and mechanical attributes, contribute to the improved performance of energy conversion processes. In recent times, significant endeavors have been undertaken to explore
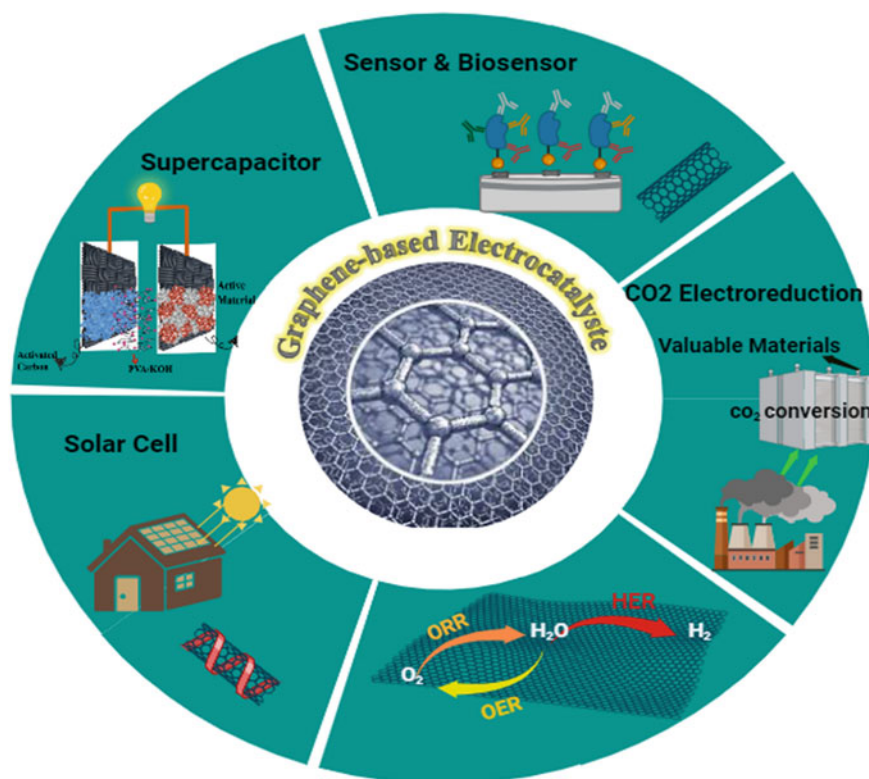
Fig. 1 Electrocatalysts application of graphene

the potential applications of graphene in energy-related devices and enhance their efficiency, processability, stability, and cost-effectiveness.

There is a projected demand for the global energy supply to undergo a twofold increase by the year 2050. In typical photovoltaic cells, inorganic semiconductors like amorphous silicon, gallium arsenide, and sulfide salts are commonly utilized to directly produce free electrons and holes from photon absorption. Although (semiconductor III–V) inorganic multijunction SCs have achieved over 40% power conversion efficiency (PCE) in the lab. Their widespread use is limited due to challenges in modifying their bandgap and high costs associated with elaborate fabrication processes at elevated temperatures and vacuum [11]. The cost of inorganic SCs remains prohibitively high in comparison to conventional grid electricity, hindering their competitiveness. Dye-sensitized solar cells (DSSCs) are a new subtype of photovoltaic cells that employ a sensitizer molecule, typically in the form of dye molecules, to convert sunlight into electrical energy. The most current reported peak PCE achieved for a DSSC stands at 12.3%. Even though DSSCs now exhibit lower efficiency compared to silicon SCs, their affordability and straightforward manufacturing process have rendered them highly appealing for "low-density" purposes,

such as rooftop solar collectors. As elucidated in this section, graphene has been employed in nearly all constituents of a DSSC. Given the inherent properties of great transparency and excellent conductivity exhibited by graphene, numerous research groups have utilized graphene as a transparent cathode in DSSCs.

Claudia et al. directed their attention on examining the technical viability of utilizing graphene synthesized through CVD as a potential substitute for tin oxides inside the photoanode component of DSSCs. This study represented the pioneering utilization of graphene as the photoanode transparent conductor in a tin oxide-free DSSC, where ZnO serves as the mesoporous semiconductor. The superior optical transparency exhibited by graphene led to the generation of higher open circuit voltage and short circuit current density compared to devices utilizing FTO [12].

The utilization of organic or polymer materials as alternative ways has garnered significant interest due to their advantageous characteristics such as cost-effectiveness, lightweight nature, flexibility, and capacity to be processed. Unlike inorganic SCs, conjugated polymers with graphene commonly form bound electron–hole pairs termed excitons during photon absorption at ambient temperature. Active layers in polymer solar cells (PSCs) are often a mixture of donor and acceptor materials that are sandwiched between a cathode and an anode [13].

Fei Pan et al. fabricated a solution-processable n-doped graphene cathode interfacial material (CIM) PDINO–G was formulated for organic solar cells (OSCs) through the incorporation of graphene into the conventional PDINO ((N, N-dimethyl-ammonium N-oxide) propyl perylene di imide) material. PDINO-G CIM with n-doping exhibited enhanced conductivity, decreased work function, diminished charge recombination, and augmented charge extraction rate. The impact of the charge injection material (CIM) on the photovoltaic efficiency of organic solar cells (OSCs) was investigated using a photovoltaic model system consisting of PTQ10 as the donor and IDIC-2F as the acceptor. The organic solar cells (OSCs) utilizing PTQ 10: IDIC-2F with PDINO-G CIM exhibited the highest power conversion efficiency (PCE) of 13.01%. This PCE was notably improved compared to the devices lacking graphene modification on the PDINO CIM, which achieved a PCE of 12.23% [14]. During illumination, photoinduced charge transfer between donor and acceptor generates electrons and holes, which travel to and are collected by the cathode and anode. To enhance the efficiency of charge collection by the electrodes, it is common practice in perovskite solar cells (PSCs) to incorporate an electron extraction layer between the cathode and the active layer, as well as a hole-extraction layer between the anode and the active layer. The most popular transparent electrode in PSCs, indium tin oxide (ITO), has several drawbacks including its high production cost and its fragility. Another disadvantage of using ITO electrodes is the limited amount of indium in nature. To investigate their involvement in PSCs, nitrogen and sulfur functionalized GQDs were produced using a hydrothermal technique. These GQDs were subsequently employed to modulate the interfacial characteristics of all-inorganic $CsPbIBr_2$ PSC. The highest possible efficiency of carbon-electrode-based the highest possible $CsPbIBr_2$ PSCs with excellent long-term stability is achieved through the interaction between GQDs and under-coordinated Pb^{2+} ions, based on Lewis's acid–base chemistry. This interaction effectively reduces the detrimental non-radiative

recombination, particularly for functionalized GQDs-tailored PSCs. As a result, the efficiency of these PSCs reaches 9.80% [15].

2.2 Cathodic Reaction: ORR, HER, ECR

The cathode catalyst, which is involved in the ORR and HER is a crucial component in both fuel cells and metal-air batteries, as it significantly influences their performance. Efficiency in transforming chemical energy into electrical energy is one of the performance characteristics of energy devices. The factors that are commonly considered in evaluating the performance of a system include energy efficiency, cycling life, kinetic reaction, and other relevant parameters. The effective conversion of molecular oxygen (O_2) to water (H_2O) plays a pivotal role in various energy systems, encompassing essential biological processes such as respiration and photosynthesis, as well as developing energy technologies. This section presents a short overview of the fundamental aspects of the ORR, encompassing mechanism and catalytic materials. The process of ORR can occur in two pathways. The first is a four-electron process where oxygen interacts directly with electrons and protons to produce water. The second is a less efficient two-step, two-electron approach that involves the formation of hydrogen peroxide ions as an intermediary. The ORR would exhibit a sluggish rate in the absence of a catalyst at the cathode [16].

Pt nanoparticles (NPs) have historically been recognized as the most effective catalyst for the ORR. However, electrodes based on Pt are prone to time-dependent drift and deactivation caused by carbon monoxide (CO). The exorbitant expense associated with Pt catalysts poses a significant barrier to the widespread adoption of fuel cells in commercial settings. Recently, there has been a significant surge in research endeavors aimed at mitigating or substituting Pt-based electrodes in ORR. To enhance the effectiveness and productivity of Pt catalysts, a commonly employed strategy involves the immobilization of Pt constituents onto a cost-effective and highly conductive substrate. CBMs, specifically graphene, are extensively employed as a carbon substrate for Pt catalysts due to their notable attributes of possessing a large surface area and being economically advantageous. The researchers from the Xin Tong group investigated three different categories of graphene materials, which were utilized as support materials for immobilizing Pt through a wet impregnation technique. The superior ORR performance found in this study can be due to the decreased size and minimized aggregation of Pt NPs that are immobilized on the graphene sheets. This process led to the fabrication of catalysts known as Pt/graphene catalysts.

The influence of the composition of supporting materials on catalytic performance was examined and elucidated through the utilization of DFT simulation. The surface characteristics of graphene materials have the potential to influence both the size and distribution of Pt on the surface, as well as alter the electrical structure of Pt [17]. Seonghee Kim's group investigated the utilization of a pyridinic-N doped few-layer

graphene material that encapsulates a cobalt catalyst (Co-N/C) as a promising electrocatalyst for rechargeable seawater batteries (SWBs), as shown in (Fig. 2). The presence of Cl^- ions on the metal surface has been observed to have a detrimental effect on the catalytic activity, resulting in a decrease in reaction kinetics. This is attributed to the interference caused by Cl^- ions in the cleavage of O–O bonds during the oxygen reduction reaction (ORR), thereby altering the reaction mechanism from a 4-electron process to a 2-electron process. This study represents the inaugural utilization of a meticulously designed interface dipole moment in cobalt-graphene heterojunctions to impede the ingress of negatively charged chloride ions through Coulombic repulsion. In the experimental investigation, it was shown that the catalytic activity of a certain configuration of N-doped graphene-encapsulated cobalt (Co 4 mmol-N/C) with several layers exhibited exceptional performance in both alkaline and seawater environments [18]. The performance of catalyst is typically influenced by ion transport. Therefore, an optimal catalyst for ORR in seawater should possess both corrosion resistance and high activity. This can be achieved by repelling chloride ions (Cl^-) and attracting hydrogen ions (H^+) to its surface. Furthermore, theory and experimental research have shown that heteroatom-doped graphene nanomaterials, like those doped with nitrogen, can change their electronic properties and chemical reactivity. Also, these nanomaterials that have been doped can have new functions. So, they are seen as a very hopeful group of electrocatalysts for ORR that don't use noble metals.

Joseph H. Dumont et al. have conducted a study whereby they have successfully synthesized catalysts composed of nitrogen-doped GO. These catalysts exhibit
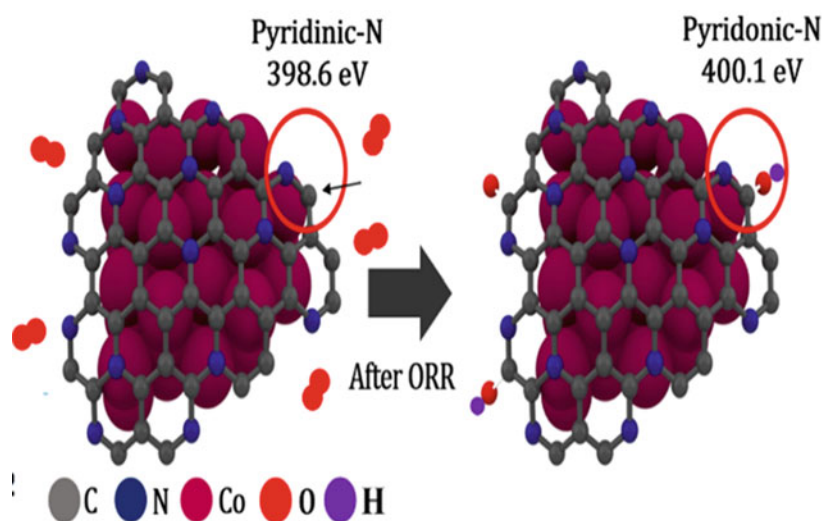

Fig. 2 Illustration of the conversion of pyridinic-N to pyrrolic-N in Co 4 mmol-N/C after cycling test. Adapted with permission [20], Copyright (2022), Elsevier

increased activity and four-electron selectivity for the ORR, achieved through the implementation of the simplest solvent and electrochemical treatments. The selection of solvents, guided by Hansen's solubility parameters, significantly influences the morphological characteristics of functionalized graphene materials. This influence is observed through two main mechanisms: (i) the creation of microporous voids in the graphitic sheets, resulting in the formation of edge defects, and (ii) the induction of a 3D structure within the graphitic sheets, which enhances the ORR. The experiment revealed a significant level of ORR activity in an alkaline electrolyte. The ORR activity commenced at an onset potential of around 1.1 V and reached a half-wave potential of 0.84 V compared to the reversible hydrogen electrode (RHE). In addition, the results of long-term stability potential cycling experiments demonstrated a little decrease in the half-wave potential (<3%) for both N_2- and O_2-saturated solutions. Moreover, the selectivity towards the four-electron reduction was enhanced after 10,000 cycles [19].

The HER is a notable electrocatalytic process that takes place at the cathode of electrolyzes employed in the process of water splitting. The process is of utmost importance in facilitating the generation of hydrogen gas (H_2) through the utilization of water. Two distinct reaction pathways lead to the HER, known as the Volmer-Tafel mechanism and the Volmer-Heyrovsky mechanism. The determination of the possible reaction way and rate-determining step (RDS) at an active site can be achieved by the application of experimental Tafel slope analysis [20]. The general rate of the HER reaction depends considerably on how well the adsorbed H* species bind to the surface. According to the Sabatier principle, an effective catalyst for the hydrogen evolution reaction (HER) should have weak binding interactions between the hydrogen species (H*) and its active sites. In recent years, significant progress has been achieved in the development of alternative electrocatalysts that do not rely heavily on Pt or contain reduced levels of Pt [21].

Numerous breakthroughs in this field have been achieved using knowledge about active sites and reaction mechanisms of HER on various catalysts. Graphene-based catalysts have exhibited superior environmental compatibility in terms of reduced heavy metal contamination and cost-effectiveness, as compared to conventional catalysts [22, 23]. Graphene-based catalysts commonly demonstrate four fundamental structural advantages in the context of the HER: (I) Efficient delivery of electrolytes to the active sites is facilitated by a significant surface area. (II) A significant level of electrical conductivity is necessary to provide rapid catalytic reaction kinetics. (III) Graphene-based catalyst exhibits a notable degree of chemical stability, enabling its structural integrity to be maintained even under the harsh conditions encountered during electrocatalysis. (IV) The presence of oxygen-containing groups in GO contributes to its improved dispersibility in different solvents. Additionally, these groups can establish chemical interactions with other materials, leading to the formation of desirable designs characterized by high conductivity and stability.

The incorporation of metal NPs and alloys with graphene is facilitated by the exceptional electrical conductivities, robust mechanical strengths, and efficient charge transfer that occurs between the catalyst and graphene material. The electrochemical features of graphene-based catalysts can be modified effectively by

different methods such as doping with heteroatom. Doping can be accomplished through two methods: carbonization of heteroatom-enriched compounds in an inert atmosphere, or post-treatment involving the use of toxic gases. Nitrogen as a dopant has garnered attention. In their groundbreaking study, Wenxin Li et al. successfully synthesized a novel core shell structure known as $NiSe_2$@nitrogen-doped graphene ($NiSe_2$@NG). This structure consists of $NiSe_2$ NPs that are enclosed within ultra-thin graphene shells, which have been doped with nitrogen. The graphene shells are generated from a Ni-based metal−organic framework. In both alkaline and acidic conditions, the hybrid has a relatively low onset potential of −163 mV (or −171 mV) compared to the RHE. Additionally, it demonstrates a minor overpotential of 201 mV (or 248 mV) vs. RHE at a current density of −10 mA cm^{-2}. Notably, it possesses a low Tafel slope of 36.1 mV dec^{-1} (or 74.2 mV dec^{-1}). The exceptional catalytic performance of the hybrid can be ascribed to its distinctive core−shell structure. This architecture not only enhances conductivity and generates a multitude of active sites to boost electrocatalytic activity, but also ensures the chemical and structural stability of the $NiSe_2$ core, thereby enhancing the overall stability of the electrocatalyst [24].

Mohd. Khalid et al. have reported a method for the simultaneous electro-reduction of GO, ruthenium chloride, and gold chloride precursors in a single step. This method does not require any pre- or post-mechanical, hydrothermal, or carbonization processes. The objective of this study was to prepare a homogeneous structure by anchoring ruthenium (Ru) and gold (Au) NPs onto RGO, which serves as an efficient electrocatalyst for the HER. The Ru Au-RGO catalyst has remarkable HER activity, as evidenced by an overpotential of 56 mV at a current density of 10 mA cm^{-2} [25].

In the future decades, fossil fuels will probably remain the predominant energy source. The inordinate consumption and subsequent emissions of carbon dioxide (CO_2) have resulted in significant challenges relating to resources, the environment, and climate change, also known as global warming [26]. The utilization of direct electrochemical CO_2 reduction (ECR) for the production of fuels and chemical substrates, such as hydrocarbons, shows potential as an early-stage technique to mitigate the adverse effects and decrease the atmospheric CO_2 concentration. Graphene is commonly used as a support for active phases (NPs or nanosheets) due to its large accessible surface areas and high conductivity. It has been discovered that the incorporation of metallic species (such as Ni, Fe, Co, Zn, Mn, Ru, Rh, Ir, Os, Ag, Cu, and Pt) into graphene significantly enhances the electrocatalytic activity of CO_2 redaction. In this study, Tooba et al. reported a highly effective electrocatalyst composed of copper (Cu) and tin (Sn) supported on nitrogen-doped graphene (NG). This catalyst demonstrates remarkable performance in the reduction of carbon dioxide (CO_2) across a broad range of potentials. The CuSn alloy NPs were synthesized on a substrate of NG using a hydrothermal approach to achieve a homogeneous distribution of the alloy nanoparticles. The electrocatalytic reduction of CO_2 into C1 products was conducted using a CuSn NP catalyst with a Cu/Sn ratio of 0.175. The catalyst exhibited a high faradaic efficiency (FE) of around 93% at an overpotential of 1.0 V versus RHE. This efficiency was significantly greater than that observed for the individual Cu and Sn catalysts, which were 32% and 58%, respectively. This study

describes a novel approach that employs inexpensive non-noble metals as electrocatalysts with exceptional efficiency for the reduction of CO_2 in aquatic environments [27].

2.3 Anodic Reaction: OER

The current leading approach to produce hydrogen is the process of water splitting. The crucial complementary reaction for these processes is the OER, which entails the production of oxygen at the anode. The reaction kinetics of OER are inherently slow due to the involvement of many proton-coupled electron transfer stages. To overcome this limitation, an efficient electrocatalyst is necessary to enhance the pace of the reaction. The electro-oxidation chemical reactions that occur in acidic and alkaline environments exhibit minor variations due to the involvement of different reactive species [28]. In acidic settings, the reactive species involved is H_2O, while in alkaline conditions, it is OH^-.

To establish design principles for OER catalysts that exhibit improved activity and stability, it is crucial to undertake thorough mechanistic investigations on the surfaces of the catalysts, regardless of the operational conditions in which OER electrocatalysts are utilized. The RDS can be assessed by analyzing the Tafel slope derived from the polarization curve. There is a prevailing pattern wherein the latter stage of the reaction induces a heightened transfer coefficient, subsequently resulting in a diminished Tafel slope and accelerated kinetics. The correlation between the activity and stability of OER catalysts poses a challenge. Typically, materials that possess enhanced catalytic activity for the OER tend to display heightened susceptibility to surface structural instability during OER, which frequently leads to the dissolution of cations. Graphene and related materials have the potential to enhance the stability of these catalysts.

In 2023, Ibrahim Khan et al., present the development of water-splitting electrodes that are both self-supported and exhibit long-term stability. As can be seen clearly in Fig. 3, this is achieved through the decorating of NPs onto a 3D porous structure known as laser-induced graphene (3D-LIG). The 3D-LIG electrodes are uniformly decorated with CuO and Pt NPs by an electrochemical technique that does not require the use of binders. The electrodes are subjected to individual analysis to determine their long-term performance in terms of OER and HER activities. This paper shows such a design, HER reaction on Cu-3D-LIG paired with OER reaction over Pt-3D-LIG. The 3D-LIG has a porous and wrinkled architecture, which results in a significant increase in surface area. This unique structure also promotes the easy flow of electrolytes via the channels. The electrodes demonstrate exceptional electrochemical durability when subjected to demanding alkaline conditions [29].

An electrocatalytic OER process of tri-metal atoms (Ni, Fe, Co) embedded nitrogen-doped graphene monolayer and coordinated with pyridine nitrogen atoms was investigated by Chen Ma et al. The objective of this study is to evaluate the stability of dual-metal and tri-metal sites and to quantitatively analyze the charge
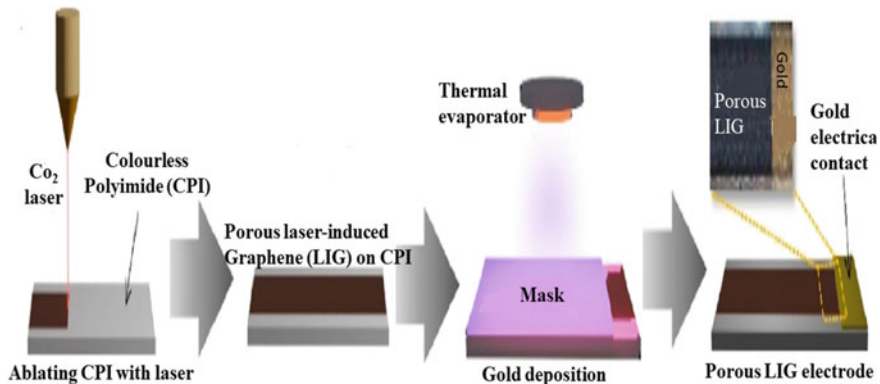
Fig. 3 Schematic image of the process of fabricating a three-dimensional laser-induced graphene (3D-LIG) electrode. Adapted with permission [30], Copyright (2023), Elsevier

redistribution of doped structures by the utilization of Bader charge analysis. The aforementioned discoveries provided significant insight into the relationship between metal-active sites and catalytic activity. [30].

2.4 Energy Storage Device: Supercapacitors

Supercapacitors (SCs) have substantial potential in facilitating the conversion and storage of electrochemical energy. SCs are electrochemical instruments that possess the ability to store energy and subsequently discharge it with notable power capacity and elevated current density within a brief temporal duration [31]. The fundamental concept underlying energy storage in a supercapacitor is either: (I) The accumulation of electrostatic charge at the electrode–electrolyte interface (electric double-layer capacitance) or (II) charge transfer to the layer of redox molecules that sit on the surface of the electrode (also known as pseudo capacitance) [32]. The efficacy of these systems is intrinsically linked to the properties of the materials utilized. Hence, the integration of material technology assumes a crucial role in enabling the advancement of SCs [33].

Extensively investigated materials for SCs electrodes encompass CBMs, metal oxides, and conducting polymers. The study of electrochemical devices has focused a lot of attention on CBMs because they enhance the electrode's electrical conductivity by increasing the mobility of the electron produced during the redox reaction. The latter will increase the electrode's ability to absorb electrolytes, hence reducing the polarization effect. Electrode materials made of CBMs have been used due to their extensive surface area, improved conductivity corrosion resistance, which allows them to operate based on electric double layer capacitance [34].

CBMs extraordinary chemical stability over a broad temperature range in both acidic and basic environments makes them highly desirable for use as electrodes in electrochemical energy devices. Due to the distinctive properties exhibited by graphene, significant attention has been directed to exploring the potential applications of graphene in the field of high-performance SCs. With a theoretical surface area of 2.63×106 m^2 kg^{-1}, graphene is a viable material for SCs electrodes due to its superior conductivity, tunable microstructure, and thermal/mechanical durability. Nithin Joseph Panicker et al. demonstrated a novel supercapacitor electrode material consisting of a band-gap controlled h-BN/rGO wrapped CdS/PPy. This material demonstrates exceptional performance in terms of specific capacitance, power density, and cycling stability. The compound was produced using a hydrothermal technique in conjunction with a chemical oxidative polymerization mechanism. The use of the h-BN/rGO-CdS core–shell structure effectively mitigates the phenomenon of swelling and shrinking in CdS, hence enhancing the electrochemical performance and stability of the SCs electrode [35]. Another study conducted by Jilei Liui's group fabricated NiCo$_2$S$_4$/nitrogen and sulfur dual-doped 3D holey-reduced GO (NiCo$_2$S$_4$/N, S-HRGO) composite structures using a two-step hydrothermal method for synthesis. As displayed in Fig. 4, TEM and HRTEM of the final stages of the composite show excellent distribution of this material. The enhanced super capacitive performance of the NiCo$_2$S$_4$/N, S-HRGO composite can be attributed to the utilization of 3D interconnected and highly conductive holey-reduced GO with a mesopore-rich structure, which facilitates fast electron/ion transport [36].

2.5   Sensors and Biosensors

An electrochemical sensor refers to a device or apparatus utilized to ascertain the observable existence, concentration, or amount of an analyte. The measurement of the electric current that is generated by chemical reactions within the electrochemical system is the fundamental principle underlying the detection of analytes by electrochemical sensors. The fundamental components of an electrochemical sensor consist of two essential elements: a chemical recognition system, which is accountable for the identification of the analyte species, and a physicochemical transducer, which facilitates the conversion of chemical interactions into electrical signals. The detection and display of these signals can be simply achieved through the utilization of modern electrical devices. The electrochemical reactions taking place at the electrode's surface interface between the recognition element and the target/binding analyte result in the formation of an electrical double layer. This potential is subsequently quantified by converting the chemical reactions into a measurable electrochemical signal using a recognition element and a sensor transducer. Electrochemical sensors have notable characteristics such as heightened sensitivity, rapid response time, affordability, instrumental simplicity, the potential for downsizing, and incorporation into portable devices.
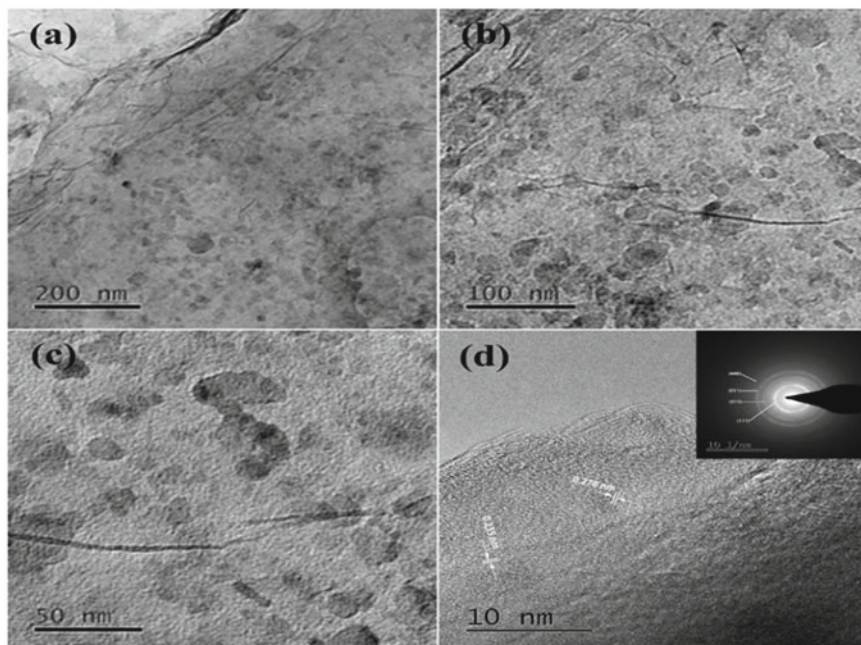
Fig. 4 a–c TEM pictures captured at various magnifications of the $NiCo_2S_4/N$, S-HRGO sample. **d** HRTEM picture of the $NiCo_2S_4/N$, S-HRGO sample, and the inset is corresponding SAED pattern. Adapted with permission [35], Copyright (2021), Elsevier

Additionally, electrochemical systems can detect a diverse array of substances, encompassing organic, inorganic, ionic, and neutral molecules, as well as metal ions [37]. The combination of CBMs and their characteristics has led to powerful electrochemical sensing platforms using "CBMs-modified electrodes" for determining various analyte species. The electrochemical sensor has undergone significant advancements over time due to its notable efficiency, straightforward functionality, and particularly, its adaptability to various chemical, physical, and biological attributes. The categorization of electrochemical sensors is based on the specific electroanalytical technique employed for the quantification of chemical interactions. The main categorizations encompass conductometric, voltammetric, and potentiometric sensors. The utilization of graphene-based nanohybrids has been widely recognized as a highly promising approach in the field of electrochemical sensing. When they were used as modifiers, the combination of these intriguing features has the potential to not only augment the kinetics of electron transfer and reduce overpotential but also boost sensitivity by increasing the peak current. Graphene has been widely used to detect and determine many analytes, including pharmaceutical formulations, biological species, and heavy metals, because of their superior properties. Usually, it is vital to apply alterations to graphene to produce GO or RGO. The underlying justification

behind this is: (I) the surface functional group of the original graphene is too minuscule to form strong bonds with other substances and, (II) the compound possesses a delocalized p-electron system and exhibits a significant surface area, rendering it prone to agglomeration and resistant to dispersion. Considering this, the functionalization and dispersion of graphene nanosheets are of the utmost significance for the application to which they will ultimately be put. As previously stated, hybrid CBMs, such as RGO composites, have already demonstrated enormous potential for electrochemical sensor construction due to their exceptional catalytic capabilities, making them emerge high-performance materials in the electrochemical sensor area. Sanaz Ghanbari et al. conducted an experimental procedure wherein RGO was subjected to functionalization through an amidation reaction with l-arginine (l-Arg), resulting in the bonding of the support and amino acid. The addition of a strong ligand, l-Arg, onto the electrode surface, resulted in the fabrication of a highly efficient catalytic sensor capable of detecting Pb(II) ions by differential pulse anodic stripping voltammetry (DP ASV). The findings of this study have emphasized the potential of RGO as a viable substrate for optical and electrochemical sensors. The electrochemical sensor that was proposed exhibits a broad linear range and a limit of detection of 0.06 nM, enabling the convenient identification of Pb(II) even in the presence of other cations [38].

Graphene-based modified electrodes have detected and determined organic pollutants and carcinogenic compounds like pesticides, anti-bacterial and anti-fungal agents, phenolic compounds, organophosphate insecticides, and toxic pharmaceutical and personal care ingredients. From the perspective of the graphene-based nanocomposite, electrochemical sensors may be categorized into two groups: "nonenzymatic sensors" and "biosensors". Electrochemical biosensors possess the capability to identify a diverse range of biomolecules within the human body, including but not limited to glucose, cholesterol, uric acid, lactate, DNA, hemoglobin, blood ketones, and other relevant substances. To accomplish this objective, it is imperative to establish a proficient electrical connection between the active redox centers (enzymes, DNA, antigen, and so on), and the surface of the electrode. The first case pertains to electrodes that have been modified with graphene-based nanocomposite and are utilized for the analysis of samples connected to biology. The second situation involves sensing platforms that incorporate bioreceptors, such as enzymes and aptamers, capable of detecting certain biological substances. The utilization of graphene as an electron mediator in the development and production of biosensing platforms incorporating redox proteins is facilitated by their redox properties, high electrical conductivity, and biocompatibility.

Yusuf Dilmac et al. investigated a study wherein they deposited gold nanoparticles (AuNPs) onto carboxylated graphene oxide (GO-COOH) for the purpose of electrochemical oxidation, as well as enzyme-free voltammetric and amperometric measurement of glucose. The GO-COOAu modified glassy carbon electrode (GCE) demonstrated superior sensitivity and stability when used for glucose electro-oxidation in alkaline environments. The working electrodes were subjected to electrochemical characterization through the utilization of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and amperometry techniques. The GO-COO

Au/GCE sensor exhibited exceptional electro-catalytic efficiency in the oxidation of glucose, demonstrating a linear range from 0.02 to 4.48 mM (R^2 = 0.9919) at a potential of +0.35 V shown in (Fig. 5). Additionally, the sensor had a low limit of detection (LOD) of 6 µM and a high sensitivity of 20.218 µA mM^{-1} cm^{-2} [39]. In this study, Sopit Phetsang et al. successfully established a straightforward electrochemical synthesis method for producing a nanocomposite film consisting of Pt, RGO, and poly (3-aminobenzoic acid) (Pt/rGO/P3ABA) on a screen-printed carbon electrode (SPCE). Furthermore, explored the potential application of this nanocomposite film in the construction of highly sensitive amperometric biosensors. Electro polymerization of P3ABA, co-electrodeposition of rGO and Pt, and GO reduction to rGO were done using cyclic voltammetry. A Pt/rGO/P3ABA-modified SPCE demonstrated effective electrocatalytic oxidation of H_2O_2 and can be used to produce glucose and cholesterol biosensors by integrating glucose oxidase (GOx) and cholesterol oxidase (ChOx). Under the optimized experimental parameters, specifically at a working potential of +0.50 V, the biosensors that were proposed exhibited highly desirable linear responses to glucose and cholesterol. These linear responses were observed within the concentration ranges of 0.25–6.00 mM for glucose and 0.25–4.00 mM for cholesterol. The biosensors demonstrated sensitivities of 22.01 and 15.94 µA mM^{-1} cm^{-2} for glucose and cholesterol, respectively. Additionally, the biosensors exhibited low detection limits (LODs) of 44.3 and 40.5 µM for glucose and cholesterol, respectively [40].

In 2022, Mantian Xue et al. fabricated a robust array of bioelectronic sensors based on graphene comprised of more than 200 integrated graphene-based sensing devices, custom-built speeds readout circuits, and portable, and trustworthy measurements. The platform provides a reversible, highly sensitive, and real-time response for sodium, potassium, and calcium ions in complex solutions despite variations in device performance [41]. In 2018, Thiago C et al. demonstrated the procedure for
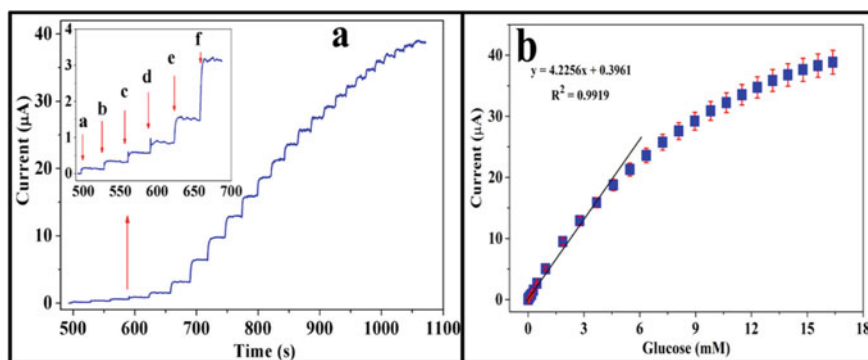

Figure. 5. Amperometry responses of the GO-COOAu/GCE electrode to different concentrations of glucose (0.02 (**a**), 0.04 (**b**), 0.06 (**c**), 0.08 (**d**), 0.1 (**e**), and 0.2 mM glucose (**f**)) were measured at a potential of + 0.35 V. (b) The calibration curve was generated for the amperometry technique of glucose measurement. Adapted with permission [38], Copyright (2020), John Wiley and Sons

synthesizing GO and then reducing it utilizing carbon NPs, without the use of standard chemical reducing agents or external energy sources. The endocrine disruptor bisphenol A was detected by using a printed carbon electrode coated with the rGO-CNPS nanomaterial. The SPE-rGO-CNPS electrode presented an excellent response for bisphenol A at concentrations varying from 7.5×10^{-9} to 2.6×10^{-7} mol L^{-1} in PBS, pH 7 with sensitivity 189.5 μmol L^{-1} and a detection limit of 1×10^{-9} mol L^{-1}. The electrode demonstrated exceptional performance, even when exposed to significant phenolic interferences. Consequently, it was employed to quantify the concentration of bisphenol A in drinking water stored in plastic bottles [42].

3 Conclusion

To accomplish efficient electrochemical energy storage and conversion, it is essential to develop electrocatalysts with both high activity and low cost. Graphene-based materials have distinctive structures and characteristics, rendering them potentially suitable electrocatalysts. This study primarily examines the current advancements in graphene materials for electrocatalysis. The scope of the chapter encompasses several aspects, including catalytic properties, functional modification, and electrocatalytic applications specifically ORR, OER, HER, CO_2RR, SCs, supercapacitors and sensors, and biosensors.

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