Chapter 1

State-of-the-Art Electronic Devices Based on Graphene

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Additional information is available at the end of the chapter

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Abstract

Graphene can be considered as the material used for electronic devices of this century, due to its excellent physical and chemical properties, which have been studied and implemented from a theoretical basis and have allowed the development of unique and innovative applications. The need for an ongoing study of the state-of-the-art electronic devices is ultimately useful for the progress achieved so far and future project applications. To date, graphene has been used individually in composite, hybrid materials or functional materials. In this chapter, an overview of their applications in nanoelectronics, particularly with an emphasis directed to flexible electronics, is presented. The description of the advantages and properties of graphene at a level of materials science and engineering is presented, in order to spread its enormous potential. In addition, the future prospects of these applications arising from the developments made currently in the laboratory phase are examined.

Keywords: graphene, nanoelectronics, flexible electronics, electronic devices

1. Introduction

The main driving force of the electronics industry is the search of new materials, capable of fulfilling the compelling demand for a higher performance and lower power consumption in the electronic systems. Novel electronic devices based on two-dimensional materials are being designed as innovations for flexible electronics within new perspectives of the future technological developments [1, 2]. Numerous research groups around the world are introducing nanomaterials which can work individually, or used in combination with other materials to exploit the physicochemical properties of these materials either as composite materials, hybrid materials, or functional materials. In particular, carbon nanomaterials such as carbon nanotubes and graphene are impelling the innovation in the area of electronics through diverse devices making use of different technological strategies by exploiting the materials science and engineering.

Among the allotropes of carbon, graphene offers one of the best materials to develop applications in areas such as electronics, biological engineering, filtration, lightweight and strong composites and photovoltaic and energy storage applications [3, 4]. Since the isolation of graphene from graphite in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester, this electronic material has gained considerable interest in different fields of application in the last decade [2, 5]. Its strategic advantages are derived from the mechanical, chemical, electronic, optical, thermal, magnetic and biological properties. This material is 207 times stronger than steel by weight, conducts heat and electricity efficiently and is almost transparent. Graphene is an emerging material for future electronics directed into flexible electronics, photonics and electrochemical energy storage [6], as shown in **Figure 1**.

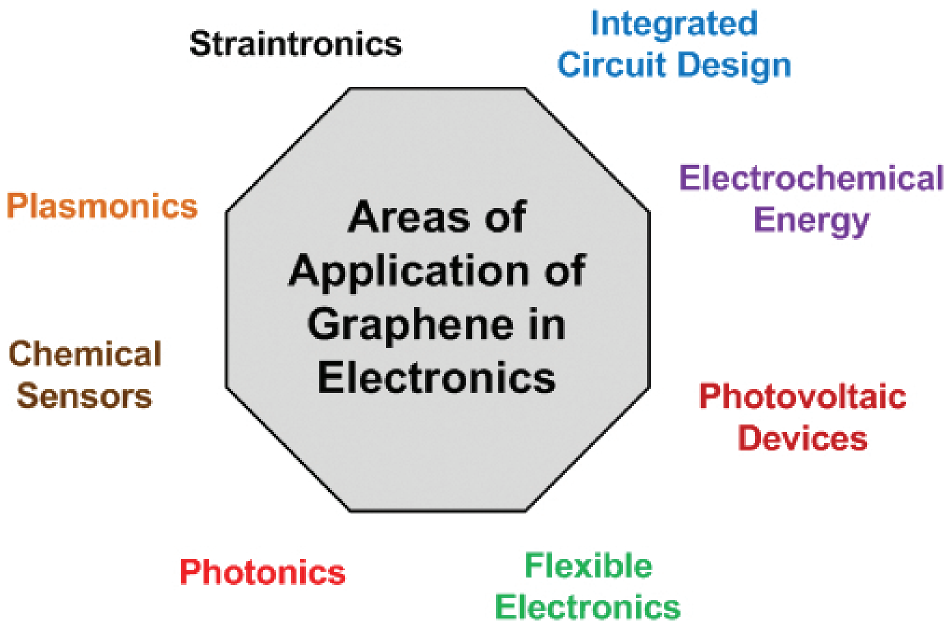

Figure 1. Technical areas of application of the graphene in electronics industry.

Different authors have published studies about the state-of-the-art graphene and its applications [4, 7]; however, it is impossible that all varieties of applications and innovations achieved to date can be covered in a unique work. In flexible nanoelectronics, graphene is primarily used in RF FETs, transparent conductive films, heat spreaders, acoustic speakers and mechanical actuators [7]. Commercial products bearing graphene are touch panels of smartphones by companies such as Samsung, Nokia and Sony. For example, hybrid materials have extended functionalities of graphene in different applications such as resonant tunnelling devices, light emission devices, photovoltaic devices, plasmonics, chemical sensors including gas sensors and flexible electronics [6], as shown in **Figure 2**. In this chapter, the main advantages of graphene in the electronics industry are analysed through their various technological applications. A brief description collecting relevant information about graphene and its applications is presented to summarize its extraordinary potential. A comprehensive review of the progress

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made and reported in the literature in the last decade is performed in order to predict its future applications.

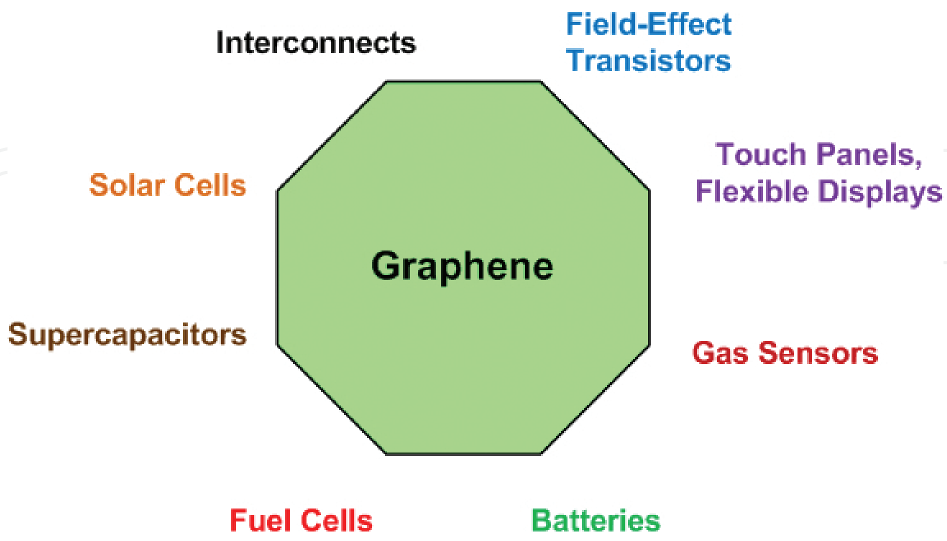

Figure 2. Main electronic devices fabricated based on graphene of the electronics industry.

2. Electrical properties of the graphene and basic devices

Graphene can be defined as a two-dimensional crystalline material composed of a graphite monolayer with a thickness of 0.34 nm, where carbon atoms present a sp^2 hybridization state since each atom is covalently bonded to three others and these form a honeycomb lattice composed of two intertwined triangular sublattices, as shown in **Figure 3**. Its mechanical properties such as extraordinary strength and flexibility are derived from the strong and rigid σ bonds formed by its sp^2 hybrid orbitals, while electrical properties are obtained due to the localization of the σ bonds and formation of π and π^* bonds by hybridization of the remaining p_z atomic orbitals of the nearest C atoms, thereby making that the electrons behave as a 2D electron gas [8–10]. Graphene has the ability to accept electrons from and donate to the strong electron donors or acceptors, respectively. These charge-transfer processes will lead to *n*- or *p*-doping of the graphene conducting to partially charged species at facilitating electrostatic interactions between them. Graphene can also establish strong van der Waals and π–π interactions with other moieties due to its insolubility and extreme aspect ratio [11]. Therefore, graphene has an enormous capability of adsorbing small molecules and therefore, it is extremely sensible to be used as a sensing material, although it also presents a very poor selectivity [10]. Graphene and its derivatives can react with a wide variety of chemical substances. These reactions, for example, chemical functionalization, are used to modulate the structures and properties of the graphene with the aim of extending their functionalities and practical applications [12]. Graphene functionalization is carried out either in a noncovalent or covalent manner. Weak interactions of the type π-π, van der Waals or electrostatic are observed in noncovalent functionalization, while an oxygen-containing functional group (carboxylic, epoxic and/or hydroxyl) is produced in covalent functionalization [13]. Chemical doping of the graphene facilitates the tuning of the electronic structure and properties by changing their electrical properties from metallic to semiconducting behaviour [14]. Dopants present at the interstitial site in graphene can be removed by a suitable heat treatment. When graphene is doped with heteroatoms (for example, N, B, P or S), more active sites are produced and its electronic properties are tuned, thus improving the interactions between graphene and oxygen molecules [15].

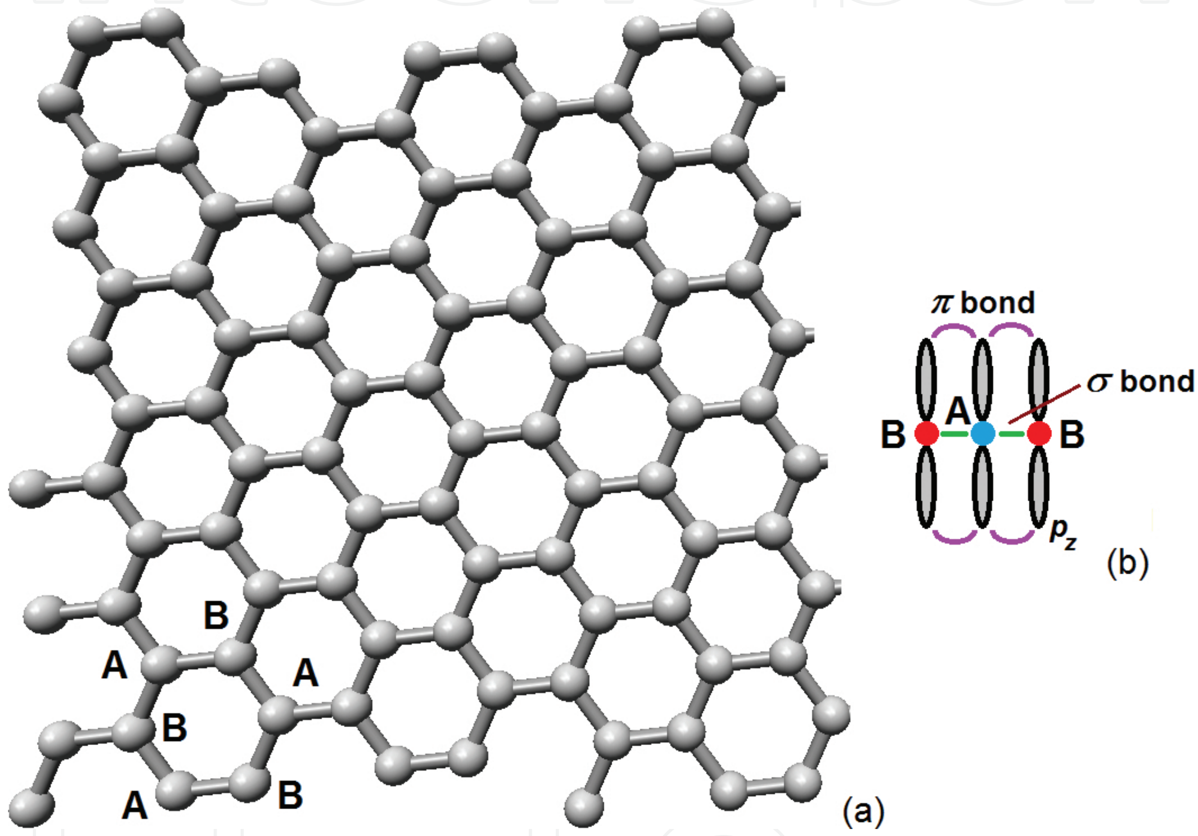

Figure 3. Basic aspects of graphene: (a) a sheet of graphene, and (b) types of chemical bonds presented in graphene.

Like carbon nanotubes, graphene has impressive electrical transport properties. Each intertwined triangular sub-lattice of the honeycomb lattice contributes to the wavefunction of charge carriers. Its unique conduction properties can be described by an energy dispersion equation, Eq. (1), which leads to the vanishing of the energy bandgap in the so-called Dirac points illustrated in **Figure 4**. The energy dispersion can be expressed as follows [9, 16]:

$$E(\boldsymbol{k}) = \pm t\sqrt{3 + 2cos\left(\sqrt{3}k_y a\right) + 4cos\left(\frac{\sqrt{3}k_y a}{2}\right)cos\left(\frac{\sqrt{3}k_x a}{2}\right)} \tag{1}$$

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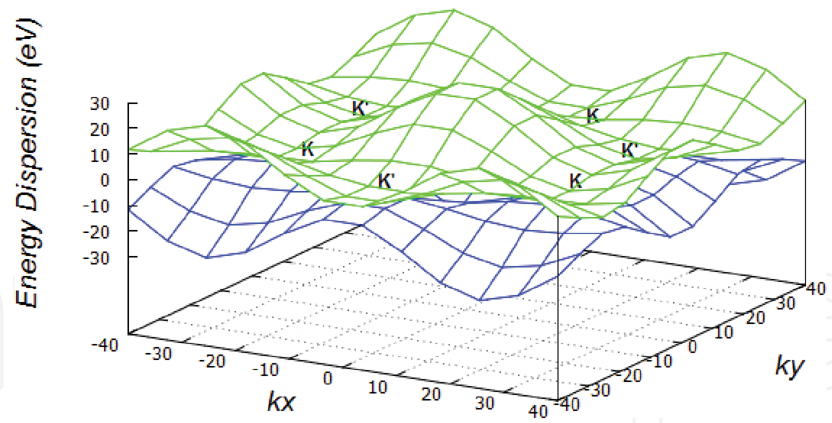

Figure 4. Energy dispersion in graphene.

where $\boldsymbol{k} = (k_x, k_y)$ is the wavevector of charge carriers relative to Dirac points, $a = 0.142$ nm is the distance between two C atoms, $t = 2.75$ eV is known as the hopping energy, plus and minus signs are associated with the upper (π^*) and lower (π) bands, which are referred as the electron and hole states, respectively [17]. The honeycomb crystal structure of single-layer graphene consists of two non-equivalent sublattices and results in a unique band structure for the itinerant π-electrons near the Fermi energy which behave as massless Dirac fermion. The valence and conduction bands touch conically at two non-equivalent Dirac points, called K and K' point, which form a time-reserved pair, i.e. opposite chirality [18, 19]. Moreover, electronic properties of graphene are invariant by interchanging the K and K' states, which means that the two valleys are related by time-reversal symmetry [8]. It can be observed in **Figure 2** that the electrical transport properties are equal for electron states or hole states due to the symmetry around the Dirac points.

The electrical transport in graphene is ambipolar, that is, it can be developed by electrons or holes, depending on the electrical voltage applied to the material either positive or negative, respectively. Both ambipolar transport and the lack of a bandgap at Dirac points have conducted to the so-called Klein paradox (Klein tunnelling), which implies that charge carrier transport leads to the complete transformation of electron states into hole states (or vice versa) [9, 17, 20]. The Klein paradox implies that the reflected electrical current is larger than the incident one and the reflection probability is larger than unity [11, 21].

Intrinsic graphene is a semimetal or zero-gap semiconductor. Monolayer graphene has a cone-like valence and conduction bands intersect at the Fermi level with no band gap, even a bilayer graphene without electrical field applied has the behaviour of the gapless semiconductor. Bilayer graphene shows a band gap when an electrical field is applied in a direction perpendicular to the σ-bond [22]. Graphene contains 100% sp^2 orbitals; however, if some of these orbitals are converted to sp^3 orbitals, then it presents a band gap and a semiconducting behaviour can be exploited. When graphene is subjected to twisting, it strongly affects the band structures of graphene, and electron localization is modified, and it changes the nature and magnitude of the electrical current passing through graphene.

Graphene conducts either electrons or holes with concentration as high as 10^{13} cm^{-3}. It has an extraordinary carrier mobility of ~500,000 cm^2/Vs and its electronic properties are strongly related to its thickness [22]. Due to its high electrical and thermal conductivity (5000 Wm/K) and low electrical noise, graphene is considered as an interesting alternative to copper for electrical interconnects in integrated circuits to connect electronic devices [23, 24]. Vertical and horizontal interconnections can be implemented using zigzag graphene nanoribbons, where horizontal connections are more feasible. The graphene presents a higher conductance with respect to Cu for interconnects in the range of nanometers. The following properties of graphene have been exploited in interconnects: high carrier mobility at room temperature, thermal conductivity, higher mechanical strength, reduced capacitance coupling between adjacent wires, width-dependent transport gap, temperature coefficient and ballistic transport. Graphene shows its work function dependence on the type of substrate used for its synthesis. It has a very large surface area 2630 m^2/g. Graphene has to be chemically modified according to the application as well as the design of different electronic devices. The electrical mobility in graphene depends completely on the physical properties of the substrate on which this material is deposited to be used in electronic applications [9, 11]. Particularly, this parameter establishes the performance that, for example, graphene-based field-effect transistors (GFETs) will achieve [25]. In addition, configurations such as those based on top gate (TG) and where materials for oxide with high dielectric constants (k) are used onto or under graphene [17, 26–29], configurations with suspended graphene [23, 28, 30–32] or substrate-less graphene, or at encapsulating (embedding) graphene in dielectric materials, such as boron nitride, with lattice matched [28, 33–35], have maximal mobility. When graphene is embedded in dielectric materials, the strong Coulomb scattering increases the electrical mobility [28]. In addition, suspended graphene eliminates substrate-induced carrier scattering. Hybrid structures based on the use of an ultrathin benzocyclobutane (BCB) polymer as a buffer layer to reinforce the top gate of graphene used in field-effect transistors [32].

GFETs [26, 27, 35] and negative differential resistance (NDR) devices [36–41] exploit the previously described outstanding physical properties. These devices can work in the sub-millimetre and terahertz region [8]. Four different configurations to implement GFETs were proposed, such as back-gate GFETs, top-gate GFETs, wrap-around GFETs and suspended GFETs to design electronic devices; unfortunately, wrap-around GFETs still have no real implementation [23]. The readers are suggested to read the previous work for more details about the GFETs. Flexible graphene field-effect transistors (GFETs) are being fabricated with graphene channels fully encapsulated in hexagonal boron nitride through a self-aligned fabrication scheme [35]. These devices present an outstanding DC and RF performance with high mechanical flexibility. Despite high mobility of the electrical carriers in graphene, the ambipolar conduction and quantum capacitance are the fundamental limitations of the graphene itself in the development of electronic devices [34]. In addition, device transconductance (g_m) and output conductance (g_{ds}) characteristics in GFETs until now have not achieved the performance of the silicon CMOS devices. Field-effect transistors (FETs) based on 2D-material-based heterostructures with MoS_2 channels, *h*BN as dielectric and graphene gate electrodes are being designed for logic circuits offering an adequate mobility and low power consumption, thereby replacing conventional materials such as silicon [42].

Negative differential resistance (NDR) is the essential mechanism of three-terminal electronic devices such as high-frequency oscillators, frequency multipliers, memories, quantum dots and fast switches [36, 37, 40]. These devices offer better properties that conventional two-terminal NDR devices such as independence of quantum tunnelling and the gate electrode can be used to control the current density and the output power of the AC oscillation [37]. Moreover, tunnel diodes and tunnelling FETs can be developed using graphene with the effect of negative differential resistance to design high-performance devices for either analogue or digital applications [39]. These devices exploit the peak current and the peak-to-valley ratio which are strongly enhanced and weakly sensitive to the length fluctuations of the transition region, owing to the graphene working as the active material. Moreover, vertical transistors based on multilayers of graphene can be developed for applications in logic circuits, high-speed electronics and as barristors [38]. Circuits based on GFETs exploiting the effects of negative differential resistance (NDR) at room temperature without any technological doping step can be integrated with silicon-based circuits in the same process [41]. These circuits can be applied for developing amplifiers, oscillators, memories, switches, etc.

An interesting technological alternative is the use of three-dimensional printing of graphene scaffolds for electronic applications from a liquid ink [43]. These structures make use of composite materials based on polymers and graphene, which have potential applications in wearable and implantable nanoelectronics, and in devices such as transistors, supercapacitors, transparent conductors, interconnects and gas sensors. Mathematical modelling is being used to predict the electrical behaviour of the graphene that will be used in the design of electronics devices [44–47]. Increasing the width of graphene nanoribbons used in field-effect transistors results in an increment in the leakage current and subthreshold swing and decrease in their I_{ON}/I_{OFF} ratio [44]. It is possible to increase the I_{ON}/I_{OFF} ratio and subthreshold swing in graphene nanoribbon field-effect transistors using single-vacancy defects [46]. These defects increase the band gap of the graphene, as is demonstrated by theoretical studies using computer simulation. Dual-gate graphene nanoribbon field-effect transistor (DG-GNRFET) under local uniaxial strain in source and drain regions as a device suitable for switching applications [45]. Models based on 2D Poisson atomistic mode-space approach and Schrödinger equations within the Non-Equilibrium Green's (NEGF) are used to predict a high on-current and on-off ratio which is necessary for digital integrated circuits. An exhaustive study of the mathematical expressions of the electrical parameters of devices based on graphene is achieved using computer simulation with the aim of knowing the importance of this tool to predict the behaviour of field-effect transistors based on graphene (GFETs) [47]. In this work, a frequency analysis is realized to know the cut-off frequency (f_T) and maximum frequency (f_{max}) of the RF field-effect transistors based on graphene using different mathematical models. Moreover, the negative differential resistance (NRD) effect presented in GFET is completely analysed in the same work.

Interconnects refer to the physical connecting medium between several electrical nodes in a semiconducting chip to transmit signals from one point to another without any distortion [5, 24]. Depending on the orientation of carbon atoms on the edge of the graphene sheet, graphene nanoribbons (GNRs) can be either armchair or zigzag. Zigzag GNR always has metallic behaviour, whereas armchair GNR can have either semiconducting or metallic depending on geometry (chirality). An illustrative schematic of the different types of graphene nanoribbons is presented by the author in [47] for the reader, where pathways of electrical conductivity are better understood. Several layers of interconnects are required between devices; these can be horizontal and/or vertical [24, 48]. A vertical interconnection is called via; it is used to make connections between different horizontal levels in an integrated circuit to connect device to device, device to system or system to system [23]. For interconnecting applications, zigzag GNR is proposed for the future generation of VLSI circuits, due to its metallic property [5, 48].

3. Applications in Analogue Radiofrequency (RF) Devices and Integrated Circuit Design

Graphene offers the better prospects for developing flexible transistors based on 2D atomic sheets with good electrical and mechanical properties to implement electronic devices such as analogue RF devices, with a performance similar to that of the Si-CMOS technology, but on arbitrary plastic substrates [17]. Graphene nanoribbons with reduced width exhibit a low electrical mobility and high electron energy levels which increase gate leakage current and the large contact resistance between them and the metal contacts. Thus, graphene is not an ideal candidate for digital applications; but graphene is suitable for radiofrequency because RF transistors do not necessarily need to be turned completely off [16]. RF devices based on graphene have received much attention due to the significant progress that has been achieved in the last decade to implement wafer-scale-integrated amplifier circuits with voltage amplification until 20 dB with field-effect transistors operating with an intrinsic cut-off frequency above 300 GHz [49]. Graphene-based RF field-effect transistors (FETs) can be used to implement RF circuits with both cut-off frequencies f_T and maximum oscillation frequencies f_{max} working slightly above a few GHz [50]. Graphene has the potential to offer third-order linearity, at least, comparable to carbon nanotube-based field-effect transistors (CNFETs) and metal-oxide semiconductor field-effect transistors (MOSFETs), but it, unfortunately, suffers from worse second-order linearity. In addition, its load-resistance dependency is intimately tied to the lack of a band gap and linear density of states (DOS) of graphene [51]. Strategies such as increasing the graphene quality lead to increasing mobility, reduce contact resistance, and a good electrostatic control of the channel, and therefore, its drain-source current (I_{DS}) and transconductance (g_m) of the field-effect transistor [52].

The set of analogue RF devices and circuits, where graphene can be used, includes a very wide variety of RF ICs, where the entire RF signal chain is covered from DC to beyond hundreds of GHz [53]. The use of the ambipolar transport properties and high carrier mobility of graphene are exploited to design nonlinear electronics for RF applications including high-speed transmitters and receivers in a sensor network, satellite communications and radar systems [54]. Moreover, graphene has a great potential in RF communication electronics in the development of low noise amplifiers, frequency multipliers and resonators [53]. Some applications are mixers of microwaves and millimetre waves [54, 55], wafer-scale integrated graphene amplifier circuit [49], filters, absorbers and antennas with high-impedance surface [56].

Different mixers have been developed based on GFETs operating in the range of MHz [49, 53–55]. Due to the symmetrical ambipolar conduction of the graphene, graphene-based mixers can effectively suppress odd-order intermodulation and lead to lower spurious emissions in the circuit [54]. Graphene offers competitive advantages in RF mixers such as high conversion loss (CL) over the frequency range in GHz, good current on-off ratio, narrow bandwidth and better linearity. A mixer was designed based on microstrip technology using an array of bow-tie-structured graphene with performance better than those fabricated with other technologies.

Graphene top-gate transistors can be used as amplifiers to generate signal amplification [6]. Graphene voltage amplifiers present better high-gain signal amplification on conventional loads at room temperature in a frequency range surpassing classical values of their technological predecessors. Even frequency multipliers based on graphene can operate at 1.4 GHz [6].

Graphene-based two-dimensional laky-wave antenna (LWA) allows both frequency tuning and beam steering in the terahertz band [56]. These antennas can be used in the development of smart systems such as tunable transceivers and sensors because of its high directivity and frequency reconfiguration. Radar applications are possible, as the operating frequencies are > 100 GHz [11], where synthesis method has a direct effect on maximum frequency achieved by electronic devices. Graphene plasmons, quanta of the collective charge-density waves excited by two-dimensional carriers in graphene, can dramatically increase the light (THz photons) and matter (graphene) interaction, leading to “giant THz gain” [25].

In particular, polymer composites containing graphene are being studied by the author to be used as electromagnetic interference (EMI) shielding due to their unique combination of electrical conduction, polymeric flexibility and lightweight [57]. These materials exhibit moderately high electrical conductivity and low permittivity. The aspect ratio, orientation and the weight percentage of graphene have a direct effect on electromagnetic interference shielding of the resultant composite. These electromagnetic waves are not desired as they modify the electrical and magnetic behaviour of the electronic devices.

4. Applications in electrochemical energy systems and photonics

Graphene and its derivatives can be used in electrochemical energy systems requiring conversion and storage function such as batteries, fuel cells, and supercapacitors [58]. Numerous studies have been conducted to describe the advances achieved by researchers in energy applications using graphene as an active material [59, 60]. Mechanical properties such as mechanical resistance and flexibility can be exploited to design bendable, foldable and/or stretchable devices for flexible energy conversion and storage. The main applications of the graphene are photovoltaic devices (solar cells) [60], fuel cells [61], nanogenerators [62], supercapacitors [59] and batteries [58–60, 63]. These devices are potentially applied in roll-up displays, electronic papers, touch screens, active radiofrequency identification tags, wearable sensors and implantable medical devices, which form part of the applications of wearable and portable electronics. In addition, those materials used in these applications should offer high electrical and/or ionic conductivities, large specific surface areas and excellent chemical, photochemical and/or electrochemical stabilities. Graphene, graphene derivatives, and their composites fulfil these requirements, and now they are being used to design novel electronic devices for energy applications [64].

Graphene-based materials are used as transparent conductive electrodes or electron acceptors in solar cells, or as current collectors, electrodes, active materials or conductive electrodes for energy storage devices [60]. Advantageous properties of the graphene with respect to conventional materials such as metals and ceramics are useful for these applications, such as lighter weight densities, adequate flexibility, better optical transparency, higher optical, chemical and/or electrochemical stabilities, larger specific surface areas and higher electrical conductivity [8]. A thin film of graphene is semitransparent to the visible and NIR regions, whereas thick films are opaque. The transmittance and electrical conductivity of the graphene can be tuned by varying the thickness of the films and the degree of chemical reduction [28]. An ideal sheet of graphene exhibits sheet resistance of 6kΩ/□″ with nearly constant optical transparency of 98% in the visible-IR range. Graphene compared with the indium tin oxide (ITO) films has high strength, flexibility and chemical stability, and its production is less expensive [14].

Graphene can be used as an active material in solar cells only in *n*- and *p*-type semiconducting behaviour where a band gap of 1.4 eV is used when solar energy is used for the illumination. Chlorine added on both sides of the surface of graphene generates a band gap of 1.2 eV, while hydrogen placed in the same way presents a band gap of 2.54 eV [22]. Photovoltaic (PV) devices require very demanding specifications such as optical transmittance (T > 85%) and sheet resistance (R < 50 Ω/□). Graphene has been proposed as an ideal material to replace transparently and conductive oxides such as zinc oxide (ZnO), indium-tin oxide (ITO) and tin dioxide (SnO_2). However, further studies must be carried out for fulfilling such technological requirements [59]. A Schottky junction solar cell with modified graphene films and silicon pillar arrays provide a conversion efficiency of up to 7.7%. Heterojunction solar cells based on graphene/semiconductor can achieve conversion efficiency up to 9.2% [22]. In the case of dye-sensitized solar cells (DSSC), a lot of work must be done to incorporate graphene: (1) the graphene surface must be functionalized without affecting its work function so that the active layer can be attached to the surface of the graphene layer, (2) since graphene is hydrophobic, it must be hydrophilic to be used in solution with organic dye or electrolytes, and (3) an ohmic-type contact must be created between active layer of the solar cell and the graphene in the electrodes [22]. Graphene has been used in electrodes of Schottky cells, CdTe cells, dye-sensitized cells, organic cells and hybrid solar cells [65]. Doping and tailoring of graphene are strategies very useful for tuning electronic structure and work function, which are the key approaches for graphene to be assembled into photovoltaic cells.

Graphene and its derivatives have a strong impact on the development of electrodes and electrode supports in energy storage devices, due to their high surface area, improved porosity, tunable electrical conductivity and high mechanical strength [58]. Fortunately, the development of graphene-based materials is in its infancy, and the actual deficiencies can be overcome with the aim of achieving better performance. Numerous techniques are being experimentally tested for fabricating precise nanostructures with defined dimensions, and self-assembly techniques allow improve their physicochemical and electrochemical properties [64].

Lithium-ion batteries must have high energy density, high voltage, long cycle life, light weight, and good environmental stability [58]. Graphene is used as an anode, owing to its amenability for reversible intercalation/deintercalation process with metal ions and in particular, lithium ions. The functional groups on graphene make it highly electronegative, thus resulting in selective interaction with cationic species. Graphene presents large capacity, high rate capability and excellent cycling stability, which facilitate the access of electrolyte and rapid diffusion of Li^+ ions and electrons and these deliver a large reversible capacity [13]. Rechargeable lithium-sulfur (Li-S) batteries to be optimized in their performance, such as high energy density, require novel materials such as graphene. This material is being used in sulphur positive electrodes, lithium negative electrodes and as an interlayer [63]. In the case of cathodes, now rarely can deliver a discharging capacity under high current densities, which is theoretically valued as 1673 mAh/g. However, there exists the possibility of improving its performance at synthesizing graphene sheets with controlled compositions, sizes and structures that can be required to obtain high electrical conductivity and high specific surface area possible only theoretically. With the aim of optimizing the cycling stability and rate capability of the Li-S batteries, functionalized graphene-based interlayers can be used for intercalating lithium ions among electrodes in the battery [64]. In a similar way, graphene is being used as a medium to load sulphur into battery during long cycle life to offer high energy density with an average voltage of 3.5 V. When graphene interlayers are used in batteries, there exists the possibility of restacking of these layers; for alleviating this problem, solid nanoparticles of Si, CuO, Fe_2O_3, SnO_2, Co_3O_4 or Mn_3O_4 can be used [15]. Graphene anodes experience significant irreversible capacity losses during charge/discharge cycling, mainly due to the restacking of graphene layers.

Supercapacitors serve as portable energy sources with smaller size, more flexible packaging, lighter weight, longer life, higher power capability, wide thermal operating range and more efficiency that conventional lead-acid or alkaline battery [66]. They store electrical energy in a capacitive form and where electrochemical double layer capacitors are formed at the electrode-electrolyte interface [58]. Specific capacitance and performance characteristics of graphene-based capacitors depend mainly on the route employed for preparing electrode material. Graphene has been used extensively as a material for electrodes used in supercapacitors. Efficient supercapacitors or hydrogen storage materials can exploit graphene, thanks to its high specific surface area (SSA) with theoretical values of 5000 m^2/g (considering the incorporation of holes into graphene), although the best state of the art is of only 3000 m^2/g [59, 64]. Graphene achieves an ideal capacitance of 200–500 F/g which depends on the surface area, pore size (both previous qualities are improved by chemical activation treated with alkali) and the electrical conductivity of the material (chemical doping to increase the carrier concentration) [22].

Fuel cells convert continuously supplied fuel to electricity, and particularly graphene is used as a catalyst support material for oxidation/reduction reactions [58]. Graphene and its derivatives have been considered as one of the most promising alternatives as electrode materials in energy-related devices, since they allow the oxidation of hydrogen and hydrogen-containing gases (e.g., methanol, ethanol, etc.) and/or the reduction of oxygen and oxygen-containing gases (such as air) in fuel cells [66]. Nitrogen-doped graphene has a good electrocatalytic activity for oxygen reduction and graphene loaded with Fe or Co enhances the electrocatalytic activity of the fuel cells [22]. This electrical activity involves the electron transfer out of or into the graphene sheets from the surrounding environment, due to the high electrical conductivity, large SSA, profuse interlayer structure and abounding functional groups involved [66]. Graphene is used as catalyst supports since it maximizes the availability of nanosized electrocatalyst surface area for electron transfer but also provide better mass transport of reactants to the electrocatalysts [65]. In addition, it facilitates efficient collection and transfer of electrons to the collecting electrode surface. The solubility of graphene oxide in different solvents allows it to be uniformly deposited onto a wide range of substrates in the form of thin films [61].

Graphene electrodes present high carrier mobility, which leads to high on/off ratio of the output current of graphene-based nanogenerators. Graphene provides electrical and structural stability under external mechanical loads such as bending and rolling. Graphene-based room-temperature (RT) nanogenerators can be used to develop self-powered RT device applications such as flexible self-powered touch sensors, wearable artificial skins, fully rollable display mobile devices and battery supplements for wearable cellular phones [62].

Graphene and its derivatives owing to their electronic and optical properties are ideal options for photonic and optoelectronic applications [67, 68]. The optical transparency and electrical conductivity of graphene can be exploited for many photonic devices [58]. Flexible and transparent optoelectronic devices based on graphene are transparent displays, solar cells and wearable electronics [21]. To ensure a good performance of these devices, it is necessary to integrate diverse classes of 2D materials, for example, graphene, with distinct physical properties. Graphene shows photonic properties such as absorption of a significant fraction of incident white light, strong tunable interband transitions and high contrast ratio [68]. In addition, it has a low broadband absorption which is ideal to transparent conductors [21]. Among different applications in these areas are transparent electrodes, touch screens, organic light emitting diodes (OLEDs), etc. Graphene-based transparent electrodes can be developed on flexible substrates for solar cells and the previously mentioned applications. In addition, graphene electrodes can be used in organic field-effect transistors (OFETs), resistive switching devices and molecular junction devices, thanks to the favourable interfacial contact between organic materials and electrochemical functionalization with graphene [69]. Touch screens require graphene-woven fabric to develop smart self-sensing elements based on piezo resistors directly transferred onto flexible substrates such as poly(dimethylsiloxane) (PDMS) [70]. Organic light-emitting diodes (OLEDs) are benefiting significantly from graphene-based transparent conducting electrodes (TCEs) where thin films of semiconducting metal oxides such as MoO_3 or WO_3 cover graphene [71]. The oxide coating provides effective graphene doping, ideal alignment of the transport levels at the graphene interface, effective wetting and graphene protection during etching and patterning.

5. Applications in gas sensors

Intensive research interest based on nanotechnology, for developing gas sensors more sensitive, with fast response and better stability, is being driven [72]. Gas sensors are based on chemiresistors (two-terminal graphene devices) and FETs with 1D nanostructures (three-terminal transistor-like structures). Graphene can play an important role in the development of chemical sensors due to its excellent chemical and surface properties derived from their chemical composition and the high-aspect ratio between its length and width [19]. Owing to these nanomaterials, it is possible to detect parts per billion or parts per trillion in comparison with their technological predecessors which could detect only part per million. With the aim of achieving it, defects or imperfections must be introduced to the sp^2 configuration of graphene to be used in the design of chemiresistors and chemical field-effect transistors (chemFETs) [22]. Gas sensors based on pristine graphene are less sensitive to analyte molecules because adsorbate binds to point defects, which have low resistance pathways around them [73]. Therefore, the conductance of graphene is more sensitive to the geometry and types of defects rather than their concentration. In addition, graphene must be cut into ribbons of width comparable to the line defect dimensions to offer superior performance as gas sensors. Graphene materials due to its superior properties such as thermoelectric conduction, surface area and mechanical strength, have inspired huge interest in sensing of various chemical species [74]. In addition, graphene can be modified to achieve high sensitivity and provide good selectivity for particular gases through methods such as using dopants and defects, decoration with metal/metal oxide nanoparticles and functionalization with polymers. The adsorption of a transition metal on graphene is one of the most studied due to the variety of promising materials for gas sensors [72]. Graphene's surface can be modified to lead to functional activity to increase the detection limit and response time at ambient temperatures, which are key parameters for an enhanced gas sensor. Unfortunately, the large-scale production of graphene-based gas sensors with high and uniform quality continues being a challenge in the electronic industry. Furthermore, novel strategies not explored to date must be exploited so that newer dopants, functional molecules and fabrication methods can be introduced.

Different graphene-based hybrids can be used in the development of chemiresistive gas sensors such as graphene with noble metals (such as platinum (Pt), palladium (Pd) and silver (Ag)), graphene with 3D, 2D, 1D or 0D metal oxides, graphene with conducting polymers (such as polythiophene (PTh), polyaniline (PANI) and polypyrrole (PPy)) and ternary graphene-based hybrids (where noble metal-metal oxide, noble metal-conducting polymers or metal oxide-conducting polymers are hybridized with graphene to jointly exploit their advantages) [75]. Metal oxides such as SnO_2, ZnO, WO_3, Cu_2O and Co_3O_4 are being used in hybrid materials based on graphene to develop toxic gas sensors for analytes such as CO, NO_x and NH_3 [76]. Some difficulties for its implementation on a large scale are a lack of reproducibility, nonuniform thickness of the graphene, high sheet resistance and relative inertness to hydrophilic atmospheres.

Water acts as an electron acceptor when adsorbed on the graphene surface which is accomplished by hole injection [28]. A *p*-type doping is used when the electron affinity of the adsorbate molecule (water) is greater than the work function of the substrate (graphene).

6. Prospects of graphene in electronics

Graphene is the cornerstone that experts in science and engineering materials have to implement innovative electronic devices and applications. A key to success in such applications is the development of novel methods to produce large quantities of graphene with high repeatability and quality. Researchers around the world are looking for alternative technological solutions for electronic devices to achieve maximum efficiency of all physicochemical properties that have the graphene. The modification of the bandgap is one of the main strategies to promote the extensive use of graphene. This advancement will allow a much wider range of applications not developed so far are reached, and where semiconductor materials have been exploited tremendously. The scalability of the production and processing convenience are important precursors to convert graphene and other two-dimensional materials (2D) in the material par excellence for the development of electronic devices in the XXI century. Aspects such as the control of the thickness of graphene, unusual rotational graphene stacking, and the relationship between the structure and electronic properties between graphene and its substrate must be clearly understood. Mathematical modelling of electronic devices based on graphene and its derivatives should be extended in order to broaden the understanding of the effects and physicochemical properties of the interaction between graphene and different materials such as metals, ceramics and polymers to produce hybrid materials, composite materials and functional materials, which have direct application in the development of innovative electronic devices.

7. Conclusions

A few decades ago, the potential of the electronics industry depended entirely on silicon; new materials have now been introduced to increase efficiency, capacity and speed of information processing in the electronics industry such as carbon allotropes such as carbon nanotubes and graphene. Actually, in electronics, graphene is used in the manufacture of supercapacitors, batteries, field-effect transistors, solar cells, light-emitting diodes, transparent, covered electrodes for electrostatic dissipation and/or electromagnetic interference shielding. Graphene's potential has not been fully associated with the development of materials science and engineering. The use of graphene in the electronic industry will be extended in the design of new electronic devices being applied either individually or as a component within a composite, hybrid or functional material. The cointegration of graphene and semiconducting

2D materials forming composite, hybrid or functional materials on the same flexible substrate will fulfil all electrical properties required by materials used in electronic industry at the thin-film limit. Although substantial progress has already been achieved to lead graphene to practical applications in electronic industry, however, a lot of work must be realized to consolidate the position of the graphene as the electronic material of this century. More studies for tuning electrical properties of the graphene and its derivatives (composites, hybrid, hierarchical or functional materials) could lead to the first large-scale applications based on graphene.

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