A review on graphene based transition metal oxide composites and its application towards supercapacitor electrodes

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Abstract

Two-dimensional (2D) graphene and its outstanding properties such as, enormous conductivities, mechanical strength, optical and electrical properties brought it one of the most studied materials for the production of energy using renewable resources. The composites of graphene with the same morphological materials such as layered transition metal oxides will be the most aspiring combination to boost their conducting, optoelectronic and mechanical properties. Furthermore, the transition metal chalcogenides materials attracted significant attention due to their atomically thin layers and enormous optical, conducting and electrical properties. The layered materials offer mostly atomically thin 2D plane to the charge carrier with superior conducting properties. The thickness at atomic level, band gap, spin orbit coupling electronic and optoelectronics properties of transition metal dichalcogenides makes them one of the promising entities in energy harvesting technologies. The review suggests some strategies to improve the transition metals-composites stability conducting properties to be tailored in various applications.

Keywords Graphene · Supercapacitor · CV · PEC

1 Introduction

Carbon is without any suspicion the most adaptable element known to man, because of the fact it is the foundation of life on earth. Carbon is the fundamental construction unit of all organic chemistry and of the 20 million known molecules. Graphene is a carbon allotropic form which consist of carbon atoms forming a monolayer [1]. All graphite materials are formed from graphene. The length bond of carbon bonded atom is 0.142 nm [2]. Layers of graphene arranged together forming graphite with inter-planer distance of 0.33 nm [3]. The sheets are stick together by Vander-wall's interaction which can be further exfoliated by different methods [4]. The thinness material known to man is graphene about single atom thick, the mild material recognized with 1 m² weighing about 0.77 mg and the strongest material ever found about 300

times stronger than steel [5]. Despite of the invincibility graphene is an good conductor of heat, electricity and optically transparent [6, 7]. Because of the amazing characteristics graphene has been selected for a broad range of applications ranging from electronics to optics bio-devices and sensors [8–10]. Recently Nano-technologists are quite enthusiastic about graphene. Scientists have been studied that graphene has the ability to conduct electricity even at zero carrier concentration because of Heisenberg uncertainty principles [11]. The electron buzzing around the carbon atom which interact with the periodic potential of graphene hexagonal lattice [12] which produce new quasi-particles that's why graphene never stop conducting. The reasons that makes graphene interesting both as individual and as composites is due to the outstanding properties such as stiffness, strength [13] and toughness [14]. Throughout the world research

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groups working on the development of industrially fabricated graphene layers that have high stiffness used as graphene based composites for optoelectronics and neural implants [15, 16]. Graphene is the first 2D-material which consist of single atomic sheet of carbons atoms arranged in a honey comb lattice [17]. The as-discussed properties of graphene arises due to the long range π bond conjugation which results high values of young modulus (1 Tpa)³. High thermal conductivity (5000 w/mk)⁴ high carrier mobility about (200,000 cm² v⁻¹ s⁻¹)⁵ [18, 19]. Graphene bounds together to form graphite lattice crystals which is arranged in the form of highly ordered pyro-lytic graphite (HOPG) [20]. In the outer shell of carbon atom there are four electrons, three sigma (σ) and one pie (π) bond for graphene. The pie bond is sp² hybridized which provide a strong binding force for atomic neighbors. The P_z orbital as for π bond, these results half field band improving free moving electrons demonstrate metallic characteristics [21]. Graphene material normally called zero gapes semiconductors because of the absence of any measureable band- gap in both single and double layers. The serious limitation to use graphene in electronics as switching off any device is because of lack of band gap. There is dramatic effect on the transport property of the graphene due to the addition of substrate. For traditional graphene devices silicon dioxide SiO₂/Si were used as a substrate [22]. But however due to the surface roughness SiO₂ could not demonstrate any impressive improvement over more initial designs [23]. Therefore other substrate substances such as hexagonal boron nitrate [24] and now dichalcogenides have been tried as support [25]. On the atomic scale of graphene system, recently few observations reported particularly for suspended graphene [26]. To eliminate substrate effect, suspended graphene have been used. This suspended geometry allows exfoliating directly the impressive characteristics of graphene [27, 28]. Combined study has shown over the past 50 years that electrons and holes at electron graphene point or (Dirac point) (Intersection point of the linear dispersion curve is called Dirac point) have zero efficient mass. Two symmetric Dirac point are being there due to two sub-lattices of graphene [29]. The cause of this zero effective mass is the energy momentum relation. These electrons/holes are called Dirac fermions or graphinos [30]. Experiments have provided that the electron mobility of graphene is ultimately high as previously reported above. Because of the zero mass, graphene electron act like photons. Charge carrier have the ability to cover sub-micrometer distances, without dispersion and this phenomena is called ballistic transport [31]. The strength of graphene is permanent from the beginning. In 2007, atomic force microscopy (AFM) were performed on graphene single-layer that were suspended over SiO₂ cavities, these experiment showed that graphene had

very much strong and uniform young modulus of 0.5 Tpa [32]. In the optical characteristics, graphene has also capability to absorb rather large 2.3% of the white light is a thorough characteristic of graphene. Recently it was proved that the absorption of white light is the cause of fine design constant. Due to these fascinating properties, saturated absorption takes place when once optical intensity approaches a certain critical point [33]. Graphene can be functionalized which result various substances such as graphene oxide or fluorinated graphene [34]. At present, overwhelming attention has started to the electronic and framework features of carbon-based materials as well as graphene are now hottest topic in condensed matter physics. This is not only due to the outstanding properties of graphene regarding its mechanical stability, thermal conductivity, and 2-dimensional layers but also unusual electronic properties such as Dirac-particles with linear dispersion transport energy gap and simple absorption coefficient of light [12]. So, it could have a unique practical application due to these unique properties. Graphene monolayers have been fabricated by exfoliating graphene flakes from the bulk graphite and depositing them on SiO₂/Si substrate.

To address some of the TMDCs, One of the most studied and widely used layered transition metal dichalcogenides (LTMDs) is molybdenum disulfide (MoS₂). It has wonderful electrical, optical, chemical and mechanical properties which makes it a suitable candidate to be used as a catalyst in hydrogen evolution reaction (HER) as active material or transport material in solar cells photo catalyst, as electrodes in lithium batteries. Similar to other LTMDs bulk MoS₂ is indirect band gap of magnitude 1.2 eV. When exfoliated to a monolayer the value of band gape changes to 1.9 eV. These effects make MoS₂ a strong candidate in the field of 2D devices [35]. 2H-WS₂ is a semiconductor having indirect band gap of 1.3 eV. After exfoliation of monolayer WS₂ indirect band gap become direct band gap. These monolayers of WS₂ are connected by Vander Waal interaction which turn makes it a thin 2D layer. The 2H- WS₂ is n-type semiconductor having charge carrier density of 10¹⁴ cm⁻³ at room temperature. The crystal size of WS₂ is hexagonal having lattice parameters of a = b = 0.315 cm, c = 1.22, $\alpha = \beta = 90$ and $\gamma = 120$, which is characterized by Raman spectroscopy and hall measurement [36]. Molybdenum diselenide is a unique type of transition metal dichalcogenides (TMDCs) which has been special in the mind of researcher due to its extraordinary applications in photoluminescence devices, lubricants, solar cells, field effect transistors and super-capacitors [37]. In the family of TMDCs NiSe₂ is one of the materials that can be studied for the production of control over nanostructure. Because of the extraordinary morphologies the nickel selenide has been expected for the application

of energy research, such as storage, electrochemistry and catalytic activity in the hydrogen evolution reaction (HER) [38]. NbS_2 is a 2D conducting material belongs to the family of TMDCs. It can be said that to made ohmic relation with 2D semiconductors materials due to its high work function and Vander Waal interface which make it suitable for semiconductor. Regardless of the importance of NbS_2 as an electrode, the previous methods of production could not control the thickness, size and consistency of niobium disulfide (NbS_2). NbS_2 can be used as electrode material in super-capacitors. Tas_2 is one of the TMDC which shows attractive combination of valuable structure, mechanical, chemical and electronic properties. Its electronic properties and structure are very useful for high power applications such as micromechanical system, superconductors and super-capacitors.

2 Graphene-based composites

Materials created by mixing two or more components with various characteristics to produce a final product with extraordinary characteristics are called composite materials. As was mentioned before, graphene has countless of new attributions, any amount of which could be used to produce outstanding composites. Composites with superb qualities can be made by the presence of graphene which ultimately improve the strength and conductivity of bulk material [39]. Graphene can be attached to metals, polymers and ceramics to manufacture heat and pressure resistant composites. Graphene composites have a variety of applications and a great deal of research is underway to produce unique and interesting materials. The endless uses of graphene-composites in photo-catalytic process are worthy of being light, versatile and best electrical conductors. However, in the following section authors are going to discuss graphene based transition metal oxides composites.

2.1 Transition metal oxides-graphene composites

There are many plans to produce composites of graphene-metal. The un-usual structural and excellent mechanical properties of transition metal graphene composites are related to the strengthening mechanism of graphene, and excellent interaction between the metal matrix and the graphene. With traditional metallurgical process to get graphene contain metal matrix composites, due to the big difference in density between graphene Nano-platelets and metal matrix, there are numerous issues [40]. The huge interest in this area is growing because of the countless applications of transition metal- graphene composites. Following are some different types of graphene

reinforced-transition metal composites. Recently, the composite of graphene and magnesium reinforced were fabricated by the combination of ball-milling and hot pressed sintering techniques [41–43]. The impact of graphene on the microstructure and mechanical characteristics was investigated by scanning electron microscope (SEM) and using energy dispersive spectroscopy (EDS) to explore composite crystal structure [44]. The mechanical characteristics of the composite also enhanced with the addition of graphene owing to standardized graphene production. Magnesium and its alloys have wide range of uses in the area of aero-space and automotive industry due to their low mass density and outstanding damping capacity, but due to low strength and ductility its uses are limited [45]. Therefore by the addition of graphene all these properties were trigger [46]. Chen et al. [47] have extracted the Mg composite strengthened with graphene Nano-platelets by combining ultrasonic liquid state processing and solid state stirring and obtained amazing improved properties. Furthermore Magnesium produced metal matrix composite enhanced by the use of graphene Nano-platelets (GNPs) by powder metallurgy [43, 48, 49] Rashad et al. SEM images for graphene- magnesium composite indicate that graphene Nano-particles are equally distributed in the magnesium matrix and dark black areas reveals oxidation during sintering process. The mechanical strength of magnesium increased from 57.5 to 68.5 when combined with graphene. The resulted tensile strength increased to 197 and 238 MPa (Fig. 1).

The first studied graphene-based composite among metal-graphene composites is graphene-reinforced aluminum matrix composite. Bartolucci et al. asserted in 2011 that graphene platelet composites and Al powder were generated by ball milling, warm iso-static pressing and extrusion [51]. The development of Al carbide described the inferior mechanical characteristics of the composite during the consolidation and subsequent heating and extrusion phase. In 2012, Wang et al. recorded aluminum composite strengthened with graphene Nano-layers using peel powder metallurgy [52]. The impact on tensile strength of aluminum composite was only 0.3 wt% GNS is 249 MPa. It was 62% better than the standard Al matrix. The composite and corresponding Al tensile characteristics are shown in Fig. 2a, b. Also graphene reinforced Al was fabricated by mixing graphene-Cu powder into melted Aluminum [53]. The picture of the Al composite with graphene-cu through scanning electron microscopy is shown in Fig. 2. In addition, the composite graphene-Al (6061) was generated by ball milling, by semi-solid thermal compaction [53].

Copper-graphene composite were synthesized by jagannadham in 2011 [54]. It was found appropriate by dropping the graphene oxide (GO) on the Cu surface

Fig. 1 SEM broken surface pictures; **a** unalloyed Magnesium, **b** magnesium/0.3 wt % GNPs composite with clear picture [50]

Fig. 2 **a** 0.3 wt % GNS/Al composite tensile characteristics and the respective flaky Al sample; **b** 0.3 wt % GNS/Al composite fracture structure; the inset indicates the GNS drawn out [52]

and then drying a thin sheet of Cu was placed on top of the graphene oxide by laser physical vapor deposition. Figure 3 shows the SEM picture of graphene on the Cu substrate. It is clear from Fig. 3 that graphene is highly agglomerated, which decrease the mechanical properties. After reinforcement of graphene the hardness of aluminum composite increased by 40% as compared to pure Al. Jagannadham subsequently revealed in 2011 that graphene-reinforced Cu matrix composite was also produced by CuSO_4 electrochemical co-deposition and graphene oxide solution [55]. A paper on the preparing of Cu-graphene composite was released in 2012 [56], in which graphene was firstly produced on the layer of the micron sized Cu-powder by chemical vapor deposition. The as-produced materials were then compressed by cold rolling reported by Kaltosva et al. to obtain bulk composite. After the structural study of the composite it was seen that the strength is increased by 39% as compared to unreinforced Cu. For the preparation of graphene enhanced Cu matrix by Hwang et al. in 2013, molecular level blending technique and spark plasma sintering (SPS) process were used [57].

SEM image of the Cu-graphene sheet can be shown in the Fig. 4. The grey areas are copper and the dark regions are graphene. It is predicted that the cross-plane thermal conductivity of the copper was affected due to low thermal conductivity of graphene perpendicular to ab plane.

Nickel is an important industrial and also carbon-stable material. The nickel graphene composites was firstly studied by Hu et al. in 2012 [59]. It was made from graphene oxide sheets using Ni-plating in NiSO_4 solution without electricity. The microstructure of Ni-graphene composites is shown in Fig. 5. It was believed that the as-prepared composite could be used as catalysts owing to the big particular region, the permeable shape and constant absorption of Ni particles on the film surface of the graphene. Kumar et al. revealed Ni graphene composite coating on stainless steel plates in 2013 [60]. They used electro-deposition method to fabricate it. The author's research indicates that the coating material graphene increases the nucleation rate and stops the development of crystals. The electro-deposition of 0.12 wt% was also reported by Kuang et al. [61]. Where the composite was manufactured using nickel sulphamate solution blended with graphene.

Fig. 3 SEM picture of Al composite by mixing with graphene–Cu [53]

Fig. 4 SEM picture of the Cu-graphene sheets. [58]

After the procedure, the composite's thermal conductivity was 15 percent higher than ordinary Ni. The composite strength was 4 times greater than mere material. Ren et al. [60] reported similar work with different mechanical outcomes. The composite in the Kuang technique has 6.85 GPa hardness and 252.76 GPa elastic modulus, while the findings were 4.6 and 240 GPa respectively in Ren's job.

So far there are very less reports and studies on the iron-graphene composites. However graphene oxide–iron composites was reported by Lin et al. in 2014 [64]. The laser sintering process was employed for the production. The hardness of the iron-graphene composites was found to be 93.5% of the pure material. The interfacial structures and strengthening mechanism of the composites were also investigated as shown in Fig. 6. The documented

Fig. 5 **a** Synthesized films of Ni/graphene [62]. **b** Dried Ni/graphene sheets at 383 K for 12 h [63]

Fig. 6 **a** Cross sectional TEM images of GOs; **b** HRTEM of Fe (iron) combination and GO [64]

laser coating micro-hardness of 2 wt% GO composite was 600 HV, which is 93.5 percent higher than the basic material. The transmission electron microscopy (TEM) image of GO and HRTEM picture of its composite with iron (Fe) are shown in Fig. 6. However there are various studies on the transition metal-graphene composites. These composites can be used as catalysts, photo-catalysts, materials for battery storage and conversion, biosensors and many more. Some of the common graphene based composites are Fe–Ni graphene composites [65], Ag–graphene composites [66], Au–graphene composites [67–69], Pt–graphene composites [70], Pb–graphene composites [71], Cd–graphene composites [72] and so on.

Tungsten oxide is an electrochemically sustainable metal oxide of type n with implementations in different sectors. Because of their superior effective applications in energy storage devices, gas detectors, photo-catalyst, field-emission devices, and electro-chromic, nanostructured tungsten oxide (WO_3) products have gained growing interest [73–75]. Due to their significant surface area and low charge movement resistance, nanostructured tungsten oxides (WO_3) as electrode components are anticipated to exhibit improved electrochemical efficiency [76, 77]. Among some of the different nanostructures, one-dimensional (1D) components such as nanowires and nanotubes are particularly appealing in terms of dimensionality and shape, considered to be exogenous constituents that can deliver new and outstanding characteristics. WO_3 has been investigated to be an interesting electrode component for super-capacitor and other energy storage devices because of the interpolation/de-interpolation of protons and electrons into oxide [78]. But its applications

are limited for pseudo-capacitors due to low conductivity and less rate of performance [79]. It is researched that to enhance the performance and features of WO_3 is to make hybrid material of WO_3 with various carbon fibers, conducting polymers and reduced graphene oxides [80]. However a lot of work has been carried out on WO_3 as positive electrode material than negative. To fabricate composite of WO_3 and graphene various methods were deployed, but the most reliable technique was hydrothermal method [81, 82]. Transmission electron microscopy and field emission scanning electron microscopy were used to study the morphologies and microstructure mechanism of the sample. Various particles of metal oxides like WO_3 and Ce-O_x (cerium oxide) were placed on the surface of every graphene layer. The specific capacitance of the device was improved when the metal oxides were placed on the surface of graphene. The high specific capacities 377.5 mFg^{-1} , 368.75 Fg^{-1} , 331 Fg^{-1} and 325 Fg^{-1} at a scan rate of 2 mVs^{-1} were obtained from deposition of Ce-O_x and WO_3 for W_2 , W_4 , W_3 and W_1 respectively. Both the Nano-composites showed advantageous electrochemical redox properties and reactivity of ions. The following table shows various values of specific capacitance when the fabrication methods, crystal structure and morphologies of the sample are different (Table 1).

Titanium di-oxide has been considered to be one of the best compounds for super-capacitor electrodes. The reasons that make it excellent option are best chemical stability, low fabrication cost, non-toxic in nature, huge availability and large surface area, which gives a capacity value of 235.6 Fg^{-1} at current density of 0.5 Ag^{-1} [91, 92]. This capacitance value, nevertheless, should only be

Table 1 Relation of WO₃ made super-capacitor's electrochemical characteristics and its various crystal configuration

Sample	Morphology	Crystal structures	Fabrication techniques	Specific capacitance	Cycling stability	Ref
WO ₃	Microspheres	Hexagonal	Hydrothermal	538 Fg ⁻¹ at scan rate of 5 mVs ⁻¹	85% capacitance retention after 2000 cycles	[84]
h-WO ₃	Aligned nano pillar bundles	Hexagonal	Hydrothermal	488.78 Fg ⁻¹ at scan rate 0.5 mVs ⁻¹	Retained almost 84.75% within 10,000 cycles	[76]
WO ₃	Nano fibers	Hexagonal	Hydrothermal	536.72 F g ⁻¹ at scan rate of 10 Ag ⁻¹	Retained 92.3% of initial capacitance after 2000 cycles	[85]
H-WO ₃ . n H ₂ O	Nano rod	Hexagonal	Hydrothermal	342 Fg ⁻¹ at scan rate of 5 mVs ⁻¹	N/A	[86]
WO ₃ -WO ₃ . 0.5 H ₂ O	Disordered nano rods	Hexagonal and cubic	Microwave-assisted hydrothermal	44 Fg ⁻¹ at current density of 0.5 Ag ⁻¹	N/A	[87]
m-WO ₃ -x	Meso-porous	Cubic	Template-assisted	302 Fg ⁻¹ at current density of 10 Ag ⁻¹	N/A	[88]
WO ₃ ·2H ₂ O	Amorphous	Amorphous	Microwave irradiation	391 F g ⁻¹ at current density of 0.5 Ag ⁻¹	82% retention after 10,000 cycle	[89]
WO ₃	Irregular rods	Monoclinic	Hydrothermal	436 Fg ⁻¹ at current density of 1 Ag ⁻¹	93% of initial capacitance after 5000 cycles remained	[90]

achieved at an ideal size below 10 nm with ultrathin sheets or Nano-scaled particles [93, 94]. Due to their extreme specific capacity and maximum power rate sensitivity with different microstructures, TiO₂ has been researched for use in wide scale energy storage. A preferred 3D structure with adequate active frameworks to resolve the low ion diffusion coefficient (10^{-13} – 10^{-17} cm²/s) [92] and heavy electrical resistance is crucial to realizing the value of super-capacitors based on TiO₂. The production of titanium dioxide nanotube arrays [95, 96] or nanoparticles [97] are therefore a usual process to assisting ion transport and enhancing electrolyte-active surface interaction. Also practical applications of TiO₂ are less because of low volumetric density and less conductivity. In order to enhance the electrical conductivity of TiO₂ coating or insertion of conducting polymer or carbon decoration has been carried out [98, 99]. Due to this composition process the electrical behavior was far improved. However to make further enhancement the coating should be done with porous conductive material and also deposition techniques to carried out the process. Recently graphene has been considered one of the best conductive and porous materials that can be used as substrate to coat TiO₂. Graphene's adaptable mesopore and macropore structures enable the surface to be covered by Nano scale components yet at the same time maintaining conduction networks for electron transport. To fabricate graphene Nano-composites various methods have been used like hydrothermal, sol-gel and electroplating. Neither of these method can completely use the elevated graphene surface area or regulate the

accumulation of metal oxide in the nanometer scheme. However TiO₂-graphene has shown some improvement but size controlling remains a challenge [100]. In contrast atomic layer deposition (ALD) is considered one of the efficient approach to carried out the mechanism [101]. The TiO₂-G composites established using ALD exhibit unique electrochemical reliability with good maintenance capacity at a rapid scan rate. The manufactured TiO₂ Nano-membrane was used for high capacitance of super-capacitor. The experimental result had showed a specific capacity of 2332 Fg⁻¹ at 1 Ag⁻¹ with 100 TiO₂ ALD cycles and energy density of 81 whkg⁻¹. As the ALD cycles increase, the capacity decreases. In contrast to previous studies on TiO₂ there is a great improvement in specific capacity of TiO₂. The capacitance has increased 400% with composition of TiO₂ as compared to graphene. Different studies were carried out by various researchers. Reddy et al. extracted a specific capacity of 160 Fg⁻¹ by hydrothermal method for TiO₂/MWCNTs (multiwall carbon nanotubes) Nano-crystalline composite with 99% detention [102]. TiO₂ prepared by in situ microwave irradiation method shows elevated specific capacitance value of 585 Fg⁻¹ at a uniform current density of 1 Ag⁻¹ [103]. The SEM, TEM and HRTEM images of the product are shown in the following Fig. 7 with ALD cycles.

SnO₂, because of its unique characteristics, has received a lot of attention as a transparent semiconductor. Tin oxide (SnO₂) can also be used as electrode material in super-capacitor. Tin oxide with various structural morphologies containing 1D nan-rods, 2D Nano-layers and 3D shapes

Fig. 7 **a:** (a) SEM images of (b) composite $\text{TiO}_2\text{-G}$ produced using 50 ALD cycles and (c) (d) composite $\text{TiO}_2\text{-G}$ produced using 100 ALD cycles. **b:** (a) TEM and (b) $\text{TiO}_2\text{-G}$ hybrid material HRTEM image produced using 100 ALD cycles [104]

can display speedy charge transportation, which made them unique candidate for fabrication of electrodes [105]. Tin oxide has fascinating properties like high power density and low cost which expands its applications in various areas for instance lithium ion batteries, solar cells, sensors and super-capacitors [106–109]. However poor charge transportation and less electrical conductivity makes its uses limited [110]. To improve these characteristics we need to create composite material of SnO_2 with graphene. Since graphene has large surface area and good electrical conductivity [111, 112]. To fabricate such type of hybrid electrode material various techniques have been deployed like hydrothermal synthesis, one step synthesis and pulse microwave deposition method etc. which has different consequences in specific capacitance. Li et al. accumulated SnO_2 on graphene sheets in the presence of hydrochloric acid and urea by reducing graphite oxide with SnCl_2 . The fabricated product has good capacitive properties. Kim et al. revealed a simple and direct strategy for the production of graphene- SnO_2 composites with elevated lithium storage capacity by incorporating NH_4OH and hydrazine to RGO and oxidizing tin-particles with HCl [105]. Field emission scanning electron microscopy (FESEM) was carried out to study the morphology of as-produced composite. Figure 8 shows the structural behavior of SnO_2 and SnO_2 Nano-composite. Furthermore, findings of electrochemical coupling spectroscopy (ECS), cyclic voltammetry (CV) and galvanostatic load discharge affirm unique electrochemical characteristics of the super-capacitor graphene- SnO_2 Nano-composite. The formulated FLG/ SnO_2 Nano-composite's basic capacitance showed outstanding strong

capacitance capacitive efficiency (365 Fg^{-1}), outstanding cyclic appearance relative to Pure SnO_2 Nano-particles [113].

Copper oxide (Cu-O) is one of the low price intercalation materials in contrast to other noble metals or metal oxide Nano-structures. Because of its fascinating features like huge availability, low price, best capacitive properties and less toxicity to environment expand its applications to many areas like, active anode material, heterogeneous catalyst, superconductors and sensors [105, 114]. Graphene- Cu-O Nano-composite has been fabricated through hydrothermal method assisted by ammonium solution by many researchers for application of super-capacitors. To study the surface morphology of the as-produced product, high resolution transmission electron microscopy (HR-TEM) and scanning electron microscopy (SEM) were carried out. Furthermore, reduced graphene oxide-copper sulfide was also studied as electrode material because of its elevated theoretical capacity and best electro-conductivity. RGO/ CuS composite shows high capacitance values of 946 Fg^{-1} at 10 Mvs^{-1} and 906 Fg^{-1} at 1 Ag^{-1} , respectively. The cycling stability was also super it maintains 89% after 5000 cycles at current density of 5 Ag^{-1} [115]. A three-dimensional graphene oxide aerogel/copper oxide (3DGOA/ CuO) cylindrical composite substance has been effectively manufactured as a super-capacitor electrode material using a comfortable one-step self-assembly hydrothermal procedure. The as prepared product exhibit improved specific capacity of 211 Fg^{-1} at current density of 1 Ag^{-1} [116]. Also the high specific capacity was obtained from Nano-composite

Fig. 8 **a, b** TEM image of G-SnO₂ **c–g** TEM and HR-TEM images of SnO₂/G Nano-composite and **f** Elemental structure of SnO₂/G Nano-composite [105]

foam layer of copper oxide and graphene is 238.3 Fg^{-1} [117]. The surface morphology was examined by scanning electron microscopy (SEM) as shown in figure. Moreover when nickel-copper foam is combined with graphene oxide it shows an elevated capacitance of 1320.2 Fg^{-1} at a discharge rate of 2 Ag^{-1} and energy density of 30.01 Whkg^{-1} at power density of 10.2 kwkg^{-1} [118] (Figs. 9, 10).

Three dimensional decreased graphene oxide Nano-sheet containing iron oxide nanoparticle (Fe_3O_4 NPs) hybrid (3D Fe_3O_4 /RGO) produced by one-pot microwave approach. Figure 11 shows scanning electron microscopy pictures of Fe_3O_4 /RGO nanostructure and different magnification rate [119].

By using galvanostatic charge/discharge method and cyclic voltammetry, the calculated the specific capacitance of 3D hybrid Fe_3O_4 is 455 Fg^{-1} and 317 Fg^{-1} at a scanning rate of and 27 mVs^{-1} respectively [119], which is better than all previous graphene- Fe_3O_4 based supercapacitor electrode [120–122]. The 3D hybrid illustrates great cycling stability with a retention ratio of 91.4% from around 190 cycles to 9600 cycles.

A stand-alone hybrid film combining Nano-flakes of graphene and zinc oxide used as electrode substrate was prepared by through an easy self-assembly filtration and heat reduction techniques. Thy hybrid film can be used effectively for super-capacitors as binder-free and self-supported electrode material [123].

The maximum capacity of prepared zinc oxide is almost 167.2 Fg^{-1} at a tracking rate of 5 mVs^{-1} , while RGO-ZnO prepared by hydrothermal method have a specific capacitance of 156 Fg^{-1} at a scan rate of 5 mVs^{-1} . The graphene-ZnO electrode exhibit excellent cycling ability, maintenance of the initial capacity over 90% after 2000 cycles [123]. The electrochemical impedance spectroscopy analysis shows low electrical resistance and improving ion diffusion capacity [123]. Figure 11a, b shows the reduced graphene oxide and zinc oxide films and specific capacity as a function of tracking rate respectively [123].

CV of the hydrous RuO_2 /G composite with different Ru loads with a scanning rate of 10 mVs^{-1} shows that the integrated area, corresponding to the specific capacity, increases up to 55.8% as shown in Fig. 12a. The specific capacitance of RuO_2 /G shows in Fig. 12b, corresponding

Fig. 9 Scanning electron microscopy (SEM) images of GOA (graphene oxide aerogel) **a** and 3DCuO/GOA **b** at less and elevated magnification [116]

Fig. 10 **a** and **b** Shows SEM picture of RGO/Fe₃O₄ at magnification rate of 50 mm and 20 mm respectively [119]

to different current densities ranging from 0.1 to 20 Ag⁻¹. Figure 12c shows that the capacitance retention of 80.5% of RuO₂/G composite with 44.6 wt% of Ru, even at a high current rate of almost 20 Ag⁻¹. The volumetric capacitance of 1485 Fg⁻¹ at a current density of 0.1 Ag⁻¹ is shown in Fig. 12d [124].

Figure 13 shows the ragone plot which demonstrates outstanding performance of RuO₂/G composite. A maximum volumetric energy density of 50.6 WhL⁻¹ can be achieved for the RuO₂/G composite with a 44.6 wt% Ru charge at a power density of 32.9 WL⁻¹ based on the amount of active material [124].

V₂O₅ Nano-rods prepared by sol–gel technique, while graphene oxide is prepared by Hummer's method [125, 126]. The prepared V₂O₅ and GO powders is taken in 1:1 ratio, the V₂O₅ dissolved in distilled water then GO is added. The mixed solution is stirred at 80 °C until the solution fully evaporated [127], the obtain Nano composite is RGO/V₂O₅. The specific capacitance of RGO/V₂O₅ is 290 and 186 Fg⁻¹ at a scanning rate of 5 and 10 Ag⁻¹ respectively which is higher than that of bare V₂O₅ which is 144 and 93 Fg⁻¹ at same tracking rate [127]. The ragone plot for bare V₂O₅ and RGO/V₂O₅ is shown in Fig. 14.

Fig. 11 **a** It shows RGO/ZnO film. **b** Specific capacitance at different scanning rate [123]

Fig. 12 **a** CV curves at scan rate of 10 m versus **b** Gravimetric capacitance of composites with different Ru loading at various current densities. **c** Shows the volumetric of composites. **d** Gravimetric and volumetric capacitance [124]

To sum up the graphene based composites on the basis of improved features various kinds of reinforcements with distinct characteristics are accessible for use in metal matrix Nano-composites (MMNCs) particularly,

based on aluminum, copper and magnesium. Based on the metal matrix, manufacturing method and required properties, the choice of reinforcement is executed. The primary necessary reinforcement features based on

Fig. 13 Hydrous RuO₂/G & pure RuO₂/G ragaone plot [124]

Fig. 14 It demonstrate the ragone plot for V₂O₅ and RGO/V₂O₅ [127]

composite application may be a mixture of some of the following characteristics, relatively low specific gravity, elevated Young's modulus, high strength, chemical and mechanical matrix compatibility, high heat and electrical conductivity, and low thermal expansion coefficient [128]. As mentioned previously, magnesium is, in theory, rather light and its modulus is somewhat small, while its power is not sufficiently high. In addition, its thermal expansion coefficient is quite large, while it is electrical and heat characteristics are medium. Similarly aluminum has same limitations therefore, in order to create a new aluminum-based composite with greater mechanical and physical characteristics and a desirable low heat expansion coefficient, high strength and high modulus, at least adequate strengthening is essential. In order to extend

the applications of aluminum, copper, magnesium and Nickel in the electronic packaging industry and meet the criteria in this field, it is necessary to use very high thermal conductive reinforcements with a low coefficient of thermal expansion. Also gold-Nano-composites have stunning properties when added to graphene, Au-graphene composites are low cost material used in super-capacitor electrodes. It displayed stable capacity values of 100 and 500 Fg⁻¹ for the chemically synthesized Nano-composite electrodes and using ionizing radiation, which stayed continuous over 5–500 mVs⁻¹ potential scan speed. Furthermore, the reinforcement chosen should be sufficiently light to maintain the composite as light as possible. Under these conditions, it is possible to use carbon-based reinforcement materials as reinforcements to create fresh composite materials with superior mechanical, physical and thermal characteristics.

In the spectrum of above discussion we are going to use graphene based materials in the fabrication of super-capacitor electrodes and how the graphene materials enhanced the storage capability of super-capacitors.

A super-capacitor has very high value of capacitance more than other capacitors [129]. The storage ability of super-capacitors is 10 to 100 times more than electrolytic capacitors. It can get and release charges in much high rate than batteries. Super-capacitors are also called super-cap, ultra-capacitors, gold-cap or electrostatic double layer capacitors (EDLCs) [130]. There are two main differences between super-capacitors and ordinary capacitors. The area of super-capacitors plates is very large and the separation between the plates is very small. The sheets of super-capacitors made of metal covered with absorbent materials such as powder, activated charcoal, which eventually raises the surface area to increase the load [131]. There is no dielectric between the plates of super-capacitors, however, both sheets are wetted in an electrolyte and segregated by a very slender carbon insulator, paper or plastics as shown in Fig. 15. As the area of the plate increases and the distance between the plates decreases, the capacitance of the capacitors increases. Specific capacitance of super-capacitors is heavily influenced by carbon electrodes with a significant surface space available to electrolyte ions, porous carbon materials such as activated carbon [132], carbide-derived carbons [133, 134], arranged meso-porous carbons [135, 136], carbon aerogels and carbon nanotubes have been investigated as large-surface electrodes [137]. Graphene-based materials are desirable because of their elevated theoretical volume ratio (2630 m²g⁻¹ and electrical conductivity) [138] as electrode materials for super-capacitors. Numerous graphene-based materials with unique chemical structures and morphologies such as chemical-modified graphene [139], microwave enhanced graphite oxide

Fig. 15 Internal structure and working principle of super-capacitors [142]

(MEGO) [140] and curved graphene [141] were studied as super-capacitor's electrode components. This large portion of microwave broadened graphite oxide (a-MBGO) of micro- and meso-porous that provides a big and available region to accommodate charges and thus increases the specific capacity of organic and ionic liquid electrolytes to obtain a remarkably elevated spectroscopy density. The first super-capacitors were created in the first of 1950s using activated charcoal as labels, but over time progress in material science resulted to the growth of much more efficient carbon nanotubes plates, barium titanate, aerogels and graphene. The internal structure and mechanism of super-capacitor is shown in the following Fig. 15.

The energy density for V_2O_5 is 31.25 Whkg^{-1} and 20.18 Whkg^{-1} and that for RGP/ V_2O_5 is 62.93 Whkg^{-1} and 40.36 Whkg^{-1} respectively at a scan rate of 5 and 10 Ag^{-1} [127]. The calculated power density for V_2O_5 1.814 kWkg^{-1} and 2.075 kWkg^{-1} and that for RGO/ V_2O_5 is 1.862 kWkg^{-1} and 2.201 kWkg^{-1} [126, 127].

To date, numerous materials such as new carbon fabrics [143], conductive polymers, hybrid metals oxides have been deployed as super-capacitors electrodes [144–146]. Carbon was generally used in its various forms as super-capacitors of electrode components, due to High specific capacity and elevated production density [147, 148]. Although permeable carbon components have a big specific surface area, their operation in super-capacitors with high energy density is limited by the low conductivity of porous carbon materials. Since 1997, carbon nanotubes (CNTs) have been manufactured for super-capacitors with exceptional electrical conductivity and elevated surface fields. However, the anticipated performance was not met by CNT-based super-capacitors; the measured contact resistance between the electrode and the current

collector is probably one reason. Graphene is a notable carbon material with the ability to use electrochemical energy storage devices owing to its outstanding chemical stability, high electrical conductivity and strong surface features. Graphene has recently been suggested as a sustainable material for super-capacitor application [149], and two graphene super-capacitor implementation studies with a specific capacity of 135 Fg^{-1} in aqueous electrolyte and 117 Fg^{-1} in aqueous H_2SO_4 [139, 150] based on a multi-sheeted graphene matrix have been recorded. The effective size of graphene parts as condenser electrode parts does not depend on the distribution of solid-state pores, unlike conventional high-surface products [139] which is distinct from the present super-capacitors made of activated carbon and carbon nanotube [146, 151, 152]. Definitely, the effective surface area of graphene materials should be highly dependent on the substrates, i.e. one or several layers of graphene with less aggregation should be presumed to have more effective surface area and therefore better supercapacitor outcomes. So in this work we are going to review graphene and different other materials for the electrodes of super-capacitor. The reason that researchers use graphene or graphene based materials for electrodes because they have high surface area and light weight. Recently, there are many records of super-capacitors based on graphene to enhance specific capacity using different electrolytes such as potassium hydroxide, organic electrolyte and ionic liquids [153]. Chenguang et al. indicated high power density graphene-based super-capacitor. This was accomplished with twisted morphology for a large surface graphene. Moreover, their estimated discharge capacitance value (154.1 Fg^{-1}) at 1 Ag^{-1} is still comparatively small and the release period at 76.3 Whkg^{-1} is 120 s. Afterward, Yanwu

et al. [154] examined graphene super-capacitors, capacitance characteristics with the same ionic liquid. In addition, pseudo-capacitors with metal oxide and polymer graphene composites have been observed by many study organizations with enhanced efficiency involving faradic reactions [155]. But the strength and mechanical stability of the electrode during electrochemical responses in such pseudo-capacitors is low, resulting development in the polymer-based electrode area that needs to be resolved before real-time operations occur. Composites of metal oxide graphene used to enhance capacity contain Mg–O, Fe_3O_4 , MnO_2 , and cobalt oxide [156–160]. Graphene can be used in many different designs, i.e. zero dimensional materials or points, odd-dimensional strand or yarns, 2D films and 3D graphene materials.

Chemical graphite exfoliation into GO can manufacture graphene dots and droplets, followed tunable reduction in GO (with reducing agent such as hydrazine hydrate). The associated chunks of graphene are easily solubilized and by the preceding decrease the rGO becomes hydrophobic, affecting more water development or aqueous circumstances. GO, Just from the other hand, there is a special amphiphile with negatively charged hydrophilic edges and hydrophobic cell membrane [161]. This distinctive feature makes it possible for GO to combine selectively with certain solvents capable of tuning GO's amphiphilicity and regulating rGO formation. Zhang et al. used multiple detergents to explore surfactant-stabilized graphene-based products, such as tetra-butylammonium hydroxide (TBAOH), bromide of cetyltrimethylammonium, and sulfonate of sodium dodecyl benzene [162, 163]. They discovered that surfactants might intercalate the rGO sheets. The experimented specific capacity from stabilized TBAOH graphene was 194 Fg^{-1} . For example, at the current density of 1 Ag^{-1} of super-capacitor electrode, which result to a reduced degree of rGO re-stacking and enhanced wettability in the manner of the preservative intercalation? Super-capacitor electrodes produced from graphene powders usually display elevated power density, superb electrical conductivity owing to high surface area and rapidly charging [164]. In terms of the small capacity value ($\sim 200 \text{ Fg}^{-1}$), they are limited. Consequently, the device's energy density and general effectiveness are generally dissatisfied. Furthermore, the quasi-capacity acquired from other transition metal oxides (i.e. Ruthenium oxide (RuO_2), manganese dioxide (MnO_2), NiO , CO_3O_4 and Fe_3O_4) or hydroxides ($\text{Ni}(\text{OH})_2$ and Cobalt(II) hydroxide $\{\text{Co}(\text{OH})_2\}$) as well as highly conductive polymers (i.e., PANI, poly-pyrrole and poly-thiophenes) as a byproduct of diagnosable faradaic redox reactions on the electrode coating, important accurate capabilities are demonstrated. The main electrolytic ingredients in EDLCs are carbon-based materials, i.e. graphene [165–169]. By using metal oxides/

hydro-oxides or some conductive polymer is also best way is to fabricate hybrid electrodes with the graphene wires to scale the EDLC and pseudo-capacity effectively sequentially. Graphene will work as a conductive charge transfer membrane in the hybrid electrodes and thus enhanced overall conductivity, while metal oxides/hydroxides or conductive polymers produce pseudo-capacity. Graphene- MnO_2 composites were extensively researched among the metal oxide composites [159, 170]. Yang et al. created a clear strategy to the preparing of hydrothermal reduction graphene- MnO_2 Nano-composites. Graphene- MnO_2 Nano-composite powders demonstrate un-usual capacitance value of 211.5 Fg^{-1} . The charge discharge rate is 1000 load/discharge cycle in Na_2SO_4 electrolyte with uniformity in capacitance is 75% at a prospective scanning rate of 2 mVs^{-1} [171]. Ni-(OH) $_2$ Nano-sheets on graphene layers were synthesized by Dai et al. High specific capacity of 1335 Fg^{-1} at current density of 2.8 Ag^{-1} and $\sim 953 \text{ Fg}^{-1}$ at 45.7 Ag^{-1} was achieved from modified electrode material [172]. To maximize the graphene sheet potential, an approach is to effectively load some of the Nano-crystal graphene skin oxide/hydroxide, which will have the dual procedure of pseudo-capacity and spacers between the graphene shades.

Novel manufacturing techniques, including spin-coating, for graphene-based sheets and papers, Langmuire Blodgett, sheet-by-layer placement, auto-assembly design and vacuum ventilation [173, 174], have been researched. In a comparable scenario as with the manufacturing of graphene less size films and papers is prevented by other graphene-based products by aggregation and repacking of graphene sheets. The reduction in surface area and spreading of electrolyte among graphene walls arising from inter-planar contact and van der Waals force. Appropriate spacer isolation is an efficient strategy to improving graphene sheet stacking. Pseudo-capacitive materials (e.g. transitional metal oxides, hydroxides and conductive polymers), carbon particles, CNT), metals (e.g., Pt, Au) or metal oxides (e.g., SnO_2) have been widely used as a spacer between layers [175–177]. Furthermore carbon black nanoparticles were injected to graphene layers as a spacer by wang et al. A qualified consequences were obtain (i, e). enhancement in electrochemical efficiency (i.e. a specific capacitance of 138 Fg^{-1} in liquid electrolyte with a scanning rate of 10 mVs^{-1} and a loss of capacitance of only 3.85% after 2000 cycles with a current density of 10 Ag^{-1}). To stop restoring the inner sheet Li et al. introduced a versatile graphene film paper that utilizes CNTs as a stabilizer. Which result high specific capacitance 140 Fg^{-1} at current density of 0.1 Ag^{-1} . Many researchers have reported different types of separator between graphene sheets to improve the capacitance and energy density. Like Pt, SnO_2 , $\text{Ni}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, MnO_2 [172, 175, 176, 178]

Fig. 16 “Graphene sheets intercalated with $\text{Ni}(\text{OH})_2$ Nano-plates is characterized by anatomical features and composition **a–c** Boundary-sectional GNIF SEM pictures with distinct magnifications, inset GNIF optical pictures displaying their flexibility, **d** Side profile of the

GNIF focused-ion beam in equal orientation to the layers of graphene **e** In-plane regarded GNIF’s SEM and TEM (inset) diagonal to graphene sheets, **f** GNIF’s XRD structure and XPS spectra” [182]

and also transition metals are used as spacers in graphene sheets such as Co_3O_4 , Fe_3O_4 , $\text{Cu}-\text{O}$, $\text{Ni}(\text{OH})_2$, MnO_2 , RuO_2 and conductive polymers such as polyanilines (PANI), polypyrrole (PPy) and polythiophene (PT) [179–181]. The structural morphologies of intercalated graphene with $\text{Ni}(\text{OH})_2$ are shown in Fig. 16.

Nano-composite graphene thin-films involving visiting nanoparticles in 2D graphene sheets can help to reduce graphene expenditure. To address this further, many attempts have been made to create Nano-structures based on graphene with 3D narrow materials like, porous ultra-light material, graphene spume and surf [183–185]. All such 3D graphene-based substances are made of micro-meso and macro-connected pores, huge surface regions and high rate of ion/electron transport channel. To improve efficiency these factors are essential for research into high power and energy as well as overall super-capacity improvements [186, 187]. Around most of these 3D graphene buildings showed outstanding electrochemical behavior for energy storage and other functional properties such as physical and catalytic [188]. Innumerable production techniques for preparing super-capacitor electrodes based on 3D graphene have been verified. For instance, to synthesize 3-dimensional macro-porous bubble graphene soap a template-driven insertion technique was deployed. The as produced 3D bubble graphene materials show controllable and relatively constant macro-pores outstanding microstructure, which leads to high capacity rate of 67.9% with a scrutinize speed of up to 1000 mVs^{-1} . Graphene aerogels (GAs) and hydro-gels are a

distinctive group of super-light, permeable carbon-based goods with higher strength-to-weight and large volume proportions [189, 190]. Mullen et al. exhibited a sophisticated model machine of elevated-performance electrode parts co-doped with boron and nitrogen relying on 3D mono-lithic graphene aerogels (BN-GAs) (see Fig. 17). An improved density of $\sim 8.65 \text{ Whkg}^{-1}$ to $\sim 1600 \text{ Wkg}^{-1}$ are consequences of BN-GAs derived electrodes having a uniform mechanical strength of $\sim 62 \text{ Fg}^{-1}$ and outstanding ability [183].

Among super-capacitor electrode materials, MnO_2 has been widely researched owing to its low price, natural availability, high theoretical capability (almost 1370 Fg^{-1}) and low toxicity [191]. In 1999, Lee and Goodenough first used amorphous MnO_2 and H_2O as possible electrode for super-capacitors in a light KCl liquid solution, with a capacity of about 200 Fg^{-1} was achieved [192]. MnO_2 -based electrodes capacity can be enhanced by various techniques have been used to explore the synthesis of nano-structured MnO_2 -based electrodes, with revolutionary morphologies, permeable monolithic structures, large quantities of pores and high particular thickness. Until now, manganese oxides have been manufactured with different structures and morphologies such as Nano-sheets, [193] Nano-spheres, [194] Nano-flowers [195] nanowires/ Nano-rods, [196] thin films, [197] and Nano-tubes [198], and their electrochemical features have been explored. Studies have shown that MnO_2 -based Nano-materials with manageable particle size, morphology, crystallinity, high-specific thickness, and excellent electrical conductivity are

Fig. 17 HGH preparedness and description. **a** Aqueous distribution photographs (2 mg/mL) of HGO and synthesized image of HGO. **b** Design of various sizes of a series of HGHs. **c** Large- and **d** less-mag-

nification scanning electron microscopic images of freeze-dried HGH inside microstructures. **e** Specific capacity compare to present density [183]

critical to enhancing capacity, speed, and cycling strength. Another efficient strategy to enhancing the efficiency of MnO_2 -based electrodes is the structure of compounds based on MnO_2 using superbly conductive substances such as flexible metal substrates, [199] conductive polymers, [166] Nano fibers/sphere, carbon nanotubes, [200, 201] and graphene [202] as substrates. In addition, due to the terrible electrical conductivity and gradual proton and cation diffusivity of the solid MnO_2 stage, the large pseudo-capacitive reaction is limited to, for example, a thin underground layer of MnO_2 , approximately 420 nm in width as per the B'elanger survey [147]. Electrochemical features of MnO_2 -based electrodes are affected by the crystallinity, the structure of crystals, the structure and function, the conductivity, the mass-charge of the active substance and the electrolyte used in the electrode.

3 Discussion

In this paper, we discuss structure, properties, fabrication and application of graphene based materials. Graphene prepared by epitaxial growth, CVD, Plasma enhanced and combustion method have the following advantages, it has high quality and high compatible with electronics, large graphene films high quality and large-scale production, relative low temperature and short reaction time, simple facility and quick synthetic process respectively. Graphene

prepared by top down techniques that's mechanical exfoliation, micromechanical cleavage, electrochemical reduction etc. have the following advantages, large size and unmodified graphene sheets, inexpensive, single step functionalization and exfoliation, high electrical conductivity of functionalized graphene respectively.

The effective implementation of graphene and/or other 2D materials in products depends not only on identifying the right products for new and existing applications, but also on making one of the materials at a lower cost in huge quantities. The progress made over the previous few years in creating new material procedures has been remarkable, particularly considering the wide demands of materials, from single crystal graphene to graphene clumps. It is possible to remove the cultivated graphene from the ground using an electrochemical tread separation from the copper substructure. As result, substrate of copper can be used constantly. Arrays of single-crystal graphene islands over 10 mm in size were achieved [203, 204]. Graphene wet-transferred room temperature Raman spectra on three separate substrates (Cu, SiO_2/Si) shows the basic Raman modes of graphene at about 1580 cm^{-1} due to the inner vibration of C-C bond. Small differences can be ascribed to substrate doping impacts in the room temperature peak locations and full-width-to-half maxima in the G and 2D peaks [205]. Researchers used the graphene TEC (thermal expansion coefficient) from Mounet et al. theoretical work to get the theoretical

frequency change due to strain, while the SiO_2 and Cu TEC values are extracted from the literature [206, 207]. The CVD process that scientists use for the production of graphene only takes 66 min without making use of vacuum pumps. The process is completed in four stages (cleaning, precursor injection, reaction time, and cooling). The use of saturated and unsaturated hydrocarbons is crucial for CVD graphene synthesis [208, 209]. C_2H_2 has a favorable free energy development of Gibbs with a value of approximately $= 209 \text{ kJ/mol}$, suggesting that reactants are favored in the following reaction: $2\text{C} + \text{H}_2 = \text{C}_2\text{H}_2$ [209]. Using dark and light field illumination mode, typical micrographs can be achieved by electron beam microscopy. The findings indicate sheets pulled up during sonication from Cu substrates. This impact can be ascribed to the balancing of carbon particles in nucleation centers that prevent graphene sheet epitaxial development. Likewise, carbonaceous agglomerates are observed in process at 800°C on a graphene sheet indicating the low-temperature accumulation hypothesis. Raman spectroscopy was performed to assess the graphene film growth structure under distinct circumstances. This spectroscopy method was used to test the structural and physical characteristics of graphic products, giving useful data on the atomic edge structure, disorder presence, faults, loads and strain [210]. In the applications of graphene, we discuss Super-capacitor. Stimulated microwave expanded graphite oxide have a big portion of micro and meso-porous so when this graphene use in super-capacitor, it provides big and available region to accommodate charges, which in turn increase the specific capacity of super capacitor. There is a greater influence of graphene and graphene-based materials on the energy density of super-capacitors. Every material has different values of energy capacity. By using graphene, the specific capacity obtained is 117 Fg^{-1} . The specific capacity property can be enhanced by doping different materials in graphene. Composite materials can be used to improve the energy density like, Mg-O , Fe_3O_4 , MnO_2 and cobalt oxides. Graphene can be folded into many shapes for example quantum dots, 1D, 2D or 3D which shows different values of energy density. Zhang et al. used graphene dots with various detergents and obtained a specific capacity of 194 Fg^{-1} . Some transition metals oxides have also shown dramatic capacity i.e. MnO_2 , RuO_2 , NiO , CO_3O_4 and Fe_3O_4 . Yang et al. developed an obvious way for the production of MnO_2 , which display a specific capacity of 211.5 Fg^{-1} . Similarly, Dai et al. use nickel hydro-oxide ($\text{Ni}(\text{OH})_2$) Nano-layer on graphene films showing a strong specific capacity of 1335 Fg^{-1} . A study group led by Tokyo University in Japan has created new materials with greater voltage and greater stability than other materials for super-capacitors. Activated carbons are used in condensers for electrodes, but they are constrained in single cells by low voltage,

the building blocks that make up condensers. The new material is a layer made of a constant three-dimensional graphene meso-sponge structure, a carbon-based material that contains pores of Nano-scale. Using electron microscopy and a variety of physical exams, including X-ray diffraction and vibrational spectroscopy methods, the scientists explored the physical characteristics of their new material. They demonstrate that the material had outstanding flexibility in a standard organic electrolyte at elevated temperatures of 60°C and high voltage of 3.5 V . It demonstrated ultra-high stability at 25°C and 4.4 V , 2.7 times greater than standard activated carbons and other materials based on graphene [211].

4 Limitations

When graphene is used as a catalyst its susceptibility is oxidative to environment. For growth of graphene, toxic material is used at high temperature due to this it exhibits some toxic qualities. Graphene has super-sharp edges that can readily penetrate the cell membrane, enter the cell and interfere with ordinary functions, production of large graphene sheets is difficult to achieve [212].

Graphene by itself is unsuitable for interaction with polymers chain because graphene is hydrophobic [213], so there is a high probability of graphene to pile in a polymer matrix, so to remove this agglomeration of graphene in polymer matrix modification of graphene using chemical, electrochemical, π - π interaction [214] is usually needed. Organic molecules can be the functional groups connected to graphene or polymer chains [214, 215]. To remove the accumulation of graphene from Al sheets, accumulative roll binding process [216]. Another set was prepared with same process in the absence of graphene coating. The main aim of these two samples is to study the effect of graphene. After that, sample was subjected to SEM, by observation it concludes that agglomeration of graphene is found less in this process. Transition metals as super-capacitor electrodes have great influence on capacitance. For example RuO_2 shows elevated capacitance and reliable life range, however it is very expensive to use. Next MnO_2 has super properties like low cost, elevated specific capacity, long life cycle, but its low electrical conductivity and unstable mechanical structure make its use limited. Furthermore Mn_3O_4 as super-capacitor electrode material has limitation because of less conduction. There are certain kinds of limitations in graphene based Nano-composites that can be great challenge to overcome like stability of structure, low conductivity, corrosion, transition in phase. Complication process was used to fabricate Cu_2O on graphene oxide sheet. The as-produced product have showed initial capacity of 1100 mAhg^{-1} . While

bad cycling makes this material unreliable in its present shape. Copper mixtures will be complicated because the Cu^{+2} oxidation state in several organic solvents is quickly disproportionate. Graphene based metallic materials were found agglomerated on graphene surfaces. To overcome these issues graphene based metal matrices composites prepared via by ball milling and hot-press sintering can produced homogenous mixture [217]. In these composites main problem is very low bonding between graphene and metallic matrices and limitation of full densification for bulk matrix composites, this hardship is depend on its preparation method, most useful method is powder metallurgy [218].

5 Conclusion

Regarding the outstanding and unusual characteristics of graphene, it is one of the best materials known which can be used for different purposes. Many areas are inspired by graphene like industrial areas, electronics, optoelectronics, flexible electronics and wearable electronics. Particularly for energy storage devices like batteries and super-capacitors, where graphene can be deployed as electrode material to absorb, store and release huge amount of energy for uses. Furthermore, graphene-based metal composites also have the property to enhance the capacity and energy density of super-capacitor. Various techniques has been used to fabricate scalable and best product like, chemical vapor deposition (CVD) chemical exfoliation, mechanical exfoliation and growth on different substrate materials like copper (Cu), nickel (Ni) graphene composites fabricated through plasma enhanced chemical vapor deposition are very expensive and need high temperature. Also roll to roll method with microwave assisted CVD technique is used to produce large scale composites, but due to its less efficiency it is not that much reliable. Graphene composites prepared through micromechanical cleavage cannot be used industrially because this process is time consuming. The best quality graphene can be obtained through CVD process having feature of manageable layers and CVD has also the ability to fabricate huge amount of graphene. Graphene shows capacitance of 135 Fg^{-1} and 117 Fg^{-1} when used in aqueous electrolyte and aqueous H_2SO_4 respectively. MgO_2 , Mg-O , FeSO_4 , MnO_2 cobalt oxide was studied and capacitance of 76.3 whkg^{-1} . TBAOH based graphene was examined which shows 194 Fg^{-1} of capacitance by intercalation of more graphene the capacity was increased to 200 Fg^{-1} . At a current density of 2.8 Ag^{-1} , $\text{Ni}(\text{OH})_2$ Nano-sheets on graphene layer shows high capacity of 1335 Fg^{-1} . Also different dimension of graphene based materials can be used for the electrodes of

super-capacitors like zero dimensional dots, 1D yarn, 2D and 3D respectively.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests

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