# **Recent Trends in Graphene based Electrode Materials for Energy Storage Devices and Sensors Applications**

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Graphene is a special allotrope of carbon with two-dimensional monolayered sheet network of sp<sup>2</sup> hybridized carbon. It possesses novel electronic, mechanical and conducting properties and these properties could be exploited in the field of scientific community in nanotechnology. Numbers of methods have been developed for the production of graphene such as micromechanical exfoliation, chemical vapor deposition, epitaxial growth, arc discharge method, intercalation methods in graphite, unzipping of CNTs, electrochemical and chemical methods. Graphene and graphene based composite materials are highly versatile materials and find wide applications in numerous fields of research. In this review, we discussed about different kind of graphene based electrode materials, which were applied in energy storage devices (supercapacitors, batteries, fuel cells and solar cells), electrochemical sensors, biosensors and pesticide sensors are discussed.

Keywords: graphene, nanotechnology, sensors, energy storage devices.

# **1. INTRODUCTION**

The three most important carbon based materials such as fullerene, carbon nanotubes and graphene were discovered from allotropes of carbon. These allotropes of carbon have different dimensions; fullerenes, carbon nanotubes (CNTs), graphene and graphite have 0D, 1D, 2D and 3D structures respectively. Fullerene was discovered in 1985 by R.E. Smalley [1] and carbon nanotubes were discovered in 1991 by Sumio Iijima [2]. Fullerene is entirely composed of carbon in the form of

spherical shape called bucky balls, whereas carbon nanotubes have tubular arrangements. Past two decades, fullerene and carbon nanotubes based electrode materials enjoyed widespread applications in diverse fields of research, such as electronics, batteries, supercapacitors, fuel cells, electrochemical sensors, bio-sensors and medicinal applications.

Recently, graphene become "raising star" material after its successful production by simple scotch tap approach from easily available graphite in 2004 by Andre Geim and his co-workers [3]. Principally, graphene is made up of single layer sheet of sp<sup>2</sup> bonded carbon atoms with densely packed honeycomb crystal lattice [4]. Its exceptional properties such as high surface area, room temperature Hall effect, tunable band gap, excellent electrical, thermal and conducting properties offered versatile platform to employ it as the active material for the preparation of various composite materials [3]. Recently, numerous efforts were made to review the structure, preparation, properties and applications of graphene and its composite materials [5-8]. Currently, graphene is one of the hottest materials and it can be applied for various energy storage and sensors devices. In this review article, we discussed about the synthesis, properties and applications of the graphene based composite electrode materials.

# 2. METHODS OF PREPARATION OF GRAPHENE

There were number of methods proposed for producing different kinds of graphene (electrode and composite) materials. Graphene is a promising electro active material which offered the important advantages of wide potential window and large electrode surface area. Micromechanical exfoliation, chemical vapor deposition, epitaxial growth, arc discharge method, intercalation methods in graphite, unzipping of CNTs, electrochemical and chemical methods were some of the important preparation methods available for graphene. Chemical methods involve strong oxidation of graphite and subsequent reduction to graphene by reducing agents or electrochemical methods [9]. Chemical methods involve use of graphene oxide (GO), an oxygenated derivative of graphene as an intermediate which can be prepared by Hummers method [10] and Staudenmaier's method [11]. A novel synthesis by dichromate oxidation of graphite followed chemical reduction with hydrazine also employed for the preparation of graphene [12]. A. Kumar *et al* reported the preparation of nitrogen doped graphene by microwave plasma chemical vapor deposition method [13]. Electrophoretic deposition (EPD) is one of the other interesting techniques to synthesis a nanosheet of graphene, for instance Y. Chen et al deposited graphene sheets onto nickel foams via EPD approach [14]. Likewise, M.S. Ata and coworkers prepared graphene by EPD method by aluminon as an organic charging and film forming agent [15]. Efforts were made to prepare graphene by direct current arc-discharge method in presence of hydrogen atmospheric pressure condition employing graphite rods as electrodes for the deposition [16]. Laser pyrolysis technique has been demonstrated to synthesize a multi-layer graphene in the presence of dilution gas [17]. Among these methods, chemical reduction is one of the efficient approaches for the large-scale synthesis, cost effective and environmentally friendly. Each method have its own advantageous and disadvantages. Among all of these methods, chemical method is the efficient and profitable method for the production of bulk quantity of graphene towards applications in electrochemical sensors and energy storage devices.

#### 2.1 Properties of graphene

The bond length of C-C bond in graphene is about 1.42 Å and specific surface area of single sheet of graphene is about 2630 m<sup>2</sup> g<sup>-1</sup> [18]. Graphene has unique optical properties with the band gap value is about 0 to 0.25 eV [19] and owns high electronic mobility of 15000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [20]. Graphene and its composite materials can be used as a semi-conductor, because of its extraordinary conducting properties. Graphene has been envisioned as the building block of all other important graphitic allotrope forms; fullerene-wrapped version of graphene, carbon nanotubes - rolled version of graphene and graphite stacked version of graphene. Enoki *et al* [21] investigated the unique magnetic properties of nanographene, such as spin glass states, magnetic switching, and edge-state spin gas probing for the possible applications in electronic and magnetic devices. S. Chen and co-workers reported brief experimental studies about the effects of isotope effects on the thermal properties of graphene and found that the ratio of <sup>12</sup>C and <sup>13</sup>C play an important role on the thermal conductivity of graphene [22].

Graphene have excellent mechanical properties, it is the strongest material known with high mechanical ability of hundred times stronger than steel. Zhang *et al* [23] discussed about the nonlinear refractive index value of graphene, and found that the nonlinear Ker effect coefficient value as  $10^{-7}$  cm<sup>2</sup> W<sup>-1</sup>, which is larger than bulk dielectrics by almost nine orders of magnitude.

# **3. APPLICATIONS**

#### 3.1 Supercapacitors

Supercapacitors attracted considerable attention as energy storage devices; they offer high power density, fast charge-discharge processes and excellent cyclic stability [24]. Generally supercapacitors were classified into two main types, namely electrical double-layer capacitors and pseuodocapacitors. Carbon based materials are widely used as electrode materials in double-layer capacitors owing to their excellent physic-chemical properties [25]. Similarly, various transition metal oxides and conducting polymers have been used as electrodes in pseuodocapacitors due to their large surface area,  $\pi$ -conjugated length and reversible redox processes. Likewise, graphene based composite materials were find extensive applications in supercapacitors research field. Graphene based nanocomposites with conducting polymers and metal oxides have been utilized for the applications in pseuodocapacitors.

Du *et al* [26] have synthesized two kinds of functionalized graphene sheets by adopting low temperature thermal exfoliation method. The first kind of functionalized graphene offered specific capacitance value of 230 F g<sup>-1</sup>, whereas the second kind of functionalized graphene sheet has the specific capacitance value of about 100 F g<sup>-1</sup>. Similarly, a graphene-activated carbon composite was prepared by chemical activation method and demonstrated for the supercapacitors applications which provided the specific capacitance of 122 F g<sup>-1</sup> [27]. Jaidev and Ramaprabhu [28] prepared poly(p-phenylenediamine)-graphene nanocomposites and obtained the maximum specific capacitance value of 248 F g<sup>-1</sup> at a specific current density of 2 A g<sup>-1</sup>, proving the versatile ability of the prepared composite

towards supercapacitors applications. Chen and co-workers constructed three-dimensional porous electrochemically reduced graphite oxide-polyaniline composite based supercapacitors and achieved the maximum specific capacitance value of 716 F g<sup>-1</sup> at 0.47 A g<sup>-1</sup> [29]. Hu et al [30] fabricated a nanorod-polyaniline (PANI)-graphene composite by in situ electrochemical polymerization method and which exhibited significantly improved performance with the maximum specific capacitance value of 878.57 F g<sup>-1</sup>. Recently, Zhang et al [31] prepared GO/PANI composite by electrochemical codeposition method and achieved the maximum specific capacitance value of 1136.4 F  $g^{-1}$  at lowest scan rate of 1 mV s<sup>-1</sup> (Figure 1). Figure 1 (b) showed, the plot of different scan rates against specific capacitance values, where the GO/PANI composite exhibited highest specific capacitance value than that of pure PANI electrode. The cyclic stability of GO/PANI composite and pure PANI electrode was displayed in figure 1 (c). As can be seen from figure, at the end of 1000th cycles only 11 % of capacitance value degrades from the first cycle indicating the excellent stability of the proposed supercapacitor. The charge-discharge curves recorded at different current densities of 1, 3, and 5 A g<sup>-1</sup> were displayed in fig 1 (d). Thus the prepared GO/PANI composite film modified electrode offered good capacity behavior at the current density of 5 A g<sup>-1</sup> and achieved significantly improved performance than the PANI electrode.



**Figure 1.** (a) Cyclic voltammetry curves of GO/PANI composite at different scan rates (b) The specific capacitance value of GO/PANI composite and PANI recorded at different scan rates (c) Cyclic stability of GO/PANI composite and PANI electrodes measured at the current density of 1.5 Ag<sup>-1</sup> and (d) charge-discharge curve recorded at different current densities (1 Ag<sup>-1</sup>, 3 Ag<sup>-1</sup> and 5 Ag<sup>-1</sup>) (Reproduced with permission from ref. [28]).

# 3.2 Batteries

Batteries are extensively used in automobiles (cars and bikes), aircrafts, boats, ships and electronic equipments [32,33]. In this connection, energy demands were considerably increasing every year and hence electrical storage devices having long life, good stability and safety are wanted to fulfill the energy demands [34]. Lithium-ion batteries are one of the promising energy storage devices which can be used in portable electronic applications [35]. The current focuses in rechargeable batteries have made reasonable improvements in terms of higher capacity and compact size for the convenient usage. Notably, the use of first made lithium-ion battery was launched in 1991 by Sony Corporation [36]. Recently, graphene and its composite materials were employed as novel electrode materials for the lithium-ion battery applications [37]. The excellent properties of graphene and ease of fabrication towards preparation of graphene based composites with metal, metal oxides and polymers make them extraordinary materials in the field of batteries.



**Figure 2.** Electrochemical discharge and charge curves of (a)  $CoFe_2O_4$ , (b) graphene, (c)  $CoFe_2O_4$ graphene (0.1) nanocomposite, (d)  $CoFe_2O_4$ -G (0.2) nanocomposite, (e)  $CoFe_2O_4$ -graphene (0.3), the applied potential range is 0.01 to 3 V at a current density of 100 mAhg<sup>-1</sup> and (f) comparison of the difference ( $CoFe_2O_4$ ,  $CoFe_2O_4$ -graphene (0.1) and  $CoFe_2O_4$ -graphene (0.2) ) nanocomposite electrodes (Reproduced with permission from ref. [39]).

A lilly-like graphene sheet wrapped nano-Si composite has been prepared by spray drying processes which afforded the reversible capacity value of 1525 mAh g<sup>-1</sup> [38]. Choi *et al* [39] reported, a Li-ion battery comprised of LiFePO<sub>4</sub> as cathode and TiO<sub>2</sub>/graphene composite as anode and demonstrated negligible degradation even after 700 cycles at 1 C<sub>m</sub> rate. Reduced graphene oxide and nickel oxide composite prepared via homogeneous coprecipitation and subsequent annealing approaches and utilized as anode materials for Li-ion batteries. The fabricated Li-ion battery exhibited the specific capacity of 1641 mAh g<sup>-1</sup> and 1097 mAh g<sup>-1</sup> for the first discharge and charge respectively [40]. Y.J. Mai *et al* prepared CuO/graphene composite by *in-situ* chemical method, which exhibited the reversible capacity of 583.5 mAh g<sup>-1</sup> and the reversible capacity retained capacity of 75.5 % even after 50 cycles, proved the excellent performance of the prepared composite towards applications in Lo-ion batteries [41].

CoFe<sub>2</sub>O<sub>4</sub>-graphene nanocomposite has been prepared by hydrothermal method and employed as an anode material for lithium-ion batteries (Figure 2) [42]. Pure CoFe<sub>2</sub>O<sub>4</sub> electrode (a) offered the first discharge and charge capacity values of 1606 and 960 mAh g<sup>-1</sup>, respectively. On the other hand pure graphene electrode exhibited 1200 and 426 mAh g<sup>-1</sup> of discharge and charge capacities respectively. CoFe<sub>2</sub>O<sub>4</sub>-graphene (10 wt% of graphene) nanocomposite offered the discharge and charge capacity values of 1531 and 952 mAh g<sup>-1</sup>. Similarly, CoFe<sub>2</sub>O<sub>4</sub>-G (20 wt% of graphene) exhibited the discharge and charge capacity values of 1388 and 906 mAh g<sup>-1</sup> respectively. Here, CoFe<sub>2</sub>O<sub>4</sub>-graphene composite having 20 wt% of graphene has high reversible capacity of 1082 mAh g<sup>-1</sup> along with excellent cyclic stability. This could be due to the facilitation of extra lithium storage attributed to the large surface area of incorporated graphene. High content of graphene in CoFe<sub>2</sub>O<sub>4</sub>-graphene (20 wt% of graphene) could facilitate the effective suppression of particle aggregation which in turn improve the cycling stability of the composite.

# 3.3 Fuel cells

Fuel cell are a kind of energy storage device, which converts chemical energy from a fuel into electrical energy by using oxygen and methanol. A green energy of fuel cells could be obtained from reduction of oxygen [43] and oxidation of methanol [44]. Most of the electrocatalytic performance is based on their selection in suitable electrode materials. Numerous efforts were made in the literature for the utilization of carbon based composite materials towards oxygen reduction reactions [45]. During the last two decades, carbon nanotubes were evolved as one of the most important nanomaterials towards fuel cell applications [46,47]. A chemical preparation of Au nanoparticles and multi-walled carbon nanotubes composite material provided a remarkable electrocatalytic activity towards reduction of oxygen in acid medium [48]. After the discovery of graphene, it finds widespread applications in fuel cells, where it can be used as an excellent electrode material ascribed to its excellent physicochemical properties. On the other hand, Pt act as an active cathode material and it can also be deposited onto the other electrode materials to improve their electrocatalytic properties towards methanol oxidation such as Pt oxides [49], Pt-Sn [50] and Pt-Ru [51].



**Figure 3.** (a) Cyclic voltammograms of Pt/carbon and Pt/graphene composite electrodes in 1 M methanol recorded at a scan rate of 50 mVs<sup>-1</sup>. (b) Electrode cyclic stability for methanol oxidation (Reproduced with permission from ref. [57]).

Kou et al [52] have synthesized Pt nanoparticle supported functionalized graphene sheets for the electrocatalytic reduction of oxygen. The composite has good catalytic activity and better stability in both electrochemical surface area and oxygen reduction activity. Smaller particles size and less aggregation of Pt nanoparticles onto the surface of functionalized graphene sheets could be probable for the improved performance of the composite. Long term stable Pt-loaded reason PEDOT/electrochemically reduced graphene oxide composite was prepared by electrochemical method and employed for oxidation [53]. The composite exhibited high mass peak current of 390 Ag<sup>-1</sup> and long term stability towards the ethanol oxidation. Zhang et al [54] have synthesized graphene/polyallylamine-Au nanocomposites and exploited it for the electrocatalytic reduction of oxygen. Microbial fuel cells are a type of fuel cells, utilizing microorganism to produce electricity by from organic wastes. Graphene/carbon cloth, graphene/PANI, graphene-modified stainless steel mesh and crumpled graphene electrodes have been demonstrated as microbial fuel cells [55-58]. Graphene nanosheet-CNT hybrid nanostructure provides numerous edge planes with strong electrochemical activity for the achievement of good performance in fuel cell applications [59]. Graphene-supported Pt electrocatalyst was prepared for methanol oxidation [60]. Moreover, the performance of Pt/graphene modified electrode has been compared with commercial Pt/carbon electrodes by cyclic voltammetric technique as shown figure 3 [60]. The onset potential value at the Pt/graphene (180 mV) was

considerably lower than that at the Pt/carbon electrodes (280 mV), in addition the catalytic activity of Pt/graphene electrode was much higher (1315 A  $g^{-1}$ ) than Pt/carbon (725 A  $g^{-1}$ ), indicated the superior electrocatalytic ability of the Pt/graphene towards methanol oxidation than commercial Pt/carbon electrodes.

#### 3.4 Solar cells

Solar cells (Polymer, bulk heterojunction and dye-sensitized) are most important promising devices for the conversion of sun light into electrical energy [61], offer the advantages of low cost and large scale production. Numbers of approaches were developed to improve the efficiency of the dye-sensitized solar cells (DSSC) by employing new composite materials, dyes and electrolytes. Platinum is widely used as cathode electrode materials for the DSSC applications. Though Pt has the advantage of having excellent electrocatalytic properties, it is highly expensive. Therefore, researchers have focused on alternative electrode materials i.e. inexpensive materials to facilitate the similar properties of platinum. Electrode materials based on carbon based materials such as, carbon nanotubes [62], activated carbon [63] and graphene sheets [64] have high electrocatalytic properties and they could replace the expensive Pt electrode in DSSC applications.

Metal oxides, Indium tin oxide and fluorinated tin oxide were extensively used in optoelectronic devices owing to their high conductivity and good transmittance properties but they have limited availably in nature. Efforts were made to replace these materials by finding alternative electrode materials such as transparent conducting oxides (TCO) [65], conducting polymer film [66] and carbon nanotubes [67] for the fabrication of organic light-emitting diodes and solar cell applications.

Graphene based carbon nanocomposite has been demonstrated as a counter electrode for the DSSC application [68] and the composite showed a conversion efficiency of 3.0%. Tjoa *et al* [69] demonstrated a facile photochemical synthesis method for the preparation of graphene-Pt nanoparticle hybrid composite by light assisted spontaneous coreduction of GO and chloroplatinic acid and employed it as a counter electrode for DSSC which yielded the efficiency of 6.77%. Photoelectron conversion efficiency of 7.5% was achieved by using graphene nanosheets incorporated activated carbon as the counter electrode [70]. Molybdenum sulfide (MoS<sub>2</sub>)/graphene composite electrode have been used as a counter electrode for dye-sensitized solar cell (DSSCs) as shown in figure 4 [71]. The composite modified electrode has highest current density than those of MoS<sub>2</sub>. The composite exhibited the power efficiency value of 5.98%, which was comparable to that of Pt electrode (6.23 %), revealed the good performances of the molybdenum based composite electrode the fabrication of low-cost DSSCs to get high efficiencies.



**Figure 4.** J-V curves of DSSCs with Pt counter electrode and MoS<sub>2</sub>/graphene counter electrode in different thickness (Reproduced with permission from ref. [98]).

#### 3.5 Electrochemical sensors

Sensors are widely used in our daily life and its applications becoming increasing in electrochemical, biological and environment detections. Sensors studies have been widely used in many fields, such as industry (pollutant), research institute (radiation measurements) and clinical diagnosis. In particular, electrochemical sensor offer selectivity and sensitivity with very low detection limits ranging from nanomolar to picomolar [72,73]. A number of electrochemical techniques including cyclic voltammetry [74], differential pulse voltammetry [75] and chronoamperometry [76] were employed to study the electrochemical sensors.

Graphene based materials have considerable attention for the fabrication of non-enzymatic sensors due to their low cost, high catalytic ability and good stability. Cuprous oxide-reduced graphene oxide nanocomposite was prepared by three different approaches and demonstrated as a non-enzymatic sensor towards sensitive determination of H<sub>2</sub>O<sub>2</sub> [77]. Graphene/PANI nanocomposite was prepared by in situ polymerization method and employed for the determination of 4-aminophenol via DPV technique [78]. Similarly, PANI/graphene composite thin film was synthesized by in situ electrochemical and utilized for the highly sensitive detection of hydrazine sensor [79]. Du et al [80] reported a non-enzymatic electrochemical uric acid sensor by used graphene-modified carbon fiber electrode. Amperometric determination of uric acid exhibited a wide linear range from 0.194 µM to 49.68  $\mu$ M with the limit of detection value is 0.132  $\mu$ M. A single walled carbon nanotubes-graphene hybrid (SWCNT-GNS) film modified electrode was fabricated and employed for the detection of acetaminophen by DPV (Figure. 4) [81]. Figure 4A shows the DPV curves of SWCNT-GNS/GCE in 0.1 M phosphate buffer (PBS) towards different concentrations of acetaminophen. Figure 4B shows the calibration curves of acetaminophen at the various electrodes, where SWCNT-GNS/GCE electrode showed high performance of wide linear range from 0.05 µM to 84.5 µM and low detection limit of 38 nM.



Figure 5. (A) DPVs at the SWCNT-GNS/GCE towards determination of acetaminophen at different concentrations of acetaminophen in 0.1 M phosphate buffer (pH = 7). (B) The corresponding calibration curves for acetaminophen at different electrodes (Reproduced with permission from ref. [67]).

## 3.6 Biosensors

Biosensors are one of the most important sections of sensors, which use biological components to detect the analytes [82]. Electrochemical biosensors developed based on graphene [83] and carbon nanotubes [84] were extensively studied. On the other hand, rapid analyses of enzyme based biosensors were widely used biological species in vivo and in vitro [85].

Graphene based biosensors were extensively studied owing to the large specific area, good electrical [3] thermal [86] and bio-compatibility [87] properties of graphene. Polypyrrole-graphene-glucose oxidase based biosensor was fabricated in which graphene sheets were covalently attached with glucose oxidase (GOx) and the resulting modified electrode has been employed for the determination of glucose [88]. Liu *et al* [89] fabricated a phenylethynyl ferrocene/graphene nanocomposite based dopamine biosensor for the sensitive and selective detection dopamine. The practical application of the proposed sensor has been studied in real samples such as serum and urine samples by using standard addition method. Chitosan dispersed graphene nanoflakes electrodes were

prepared utilized for the immobilization of direct electron transfer of Cytochrome *c* and achieved the direct electrochemistry. Besides, the modified electrode showed very good catalytic activity towards the biosensing of nitric oxide [90]. Thionine-graphene nanocomposite was developed for the electrochemical biosensing of DNA. The biosensor possess good selectivity and wide linear range of  $1.0 \times 10^{-12}$  to  $1.0 \times 10^{-7}$  M with very low detection limit of  $1.26 \times 10^{-13}$  M [91].



Figure 6. (A) Absorption curves of 3,3,5,5-tetramethyl benzidine catalyzed by the Hemine functionalized with different concentrations of  $H_2O_2$  in 25 mM PBS. Insert: linear calibration plot for  $H_2O_2$ . (B) The absorption curves for glucose detection with the calorimetric method to developed using glucose oxidase and Hemine functionalized graphene nanosheets, insert: Plot of linear calibration for glucose oxidation (Reproduced with permission from ref. [78]).

Figure. 6 showed the electrocatalytic activity of dual biosensor made by hemin functionalized graphene nanosheets for the biosensing of  $H_2O_2$  and glucose [92]. From the calibration curves for the electrochemical DPV determination of  $H_2O_2$  and glucose, the limit of detection was calculated to be 20 nM and 30 nM respectively.

# 3.7 Pesticide Sensors

Pesticide sensors were broadly used in the field of agriculture production and control of pests and insecticide. Organophosphorous pesticides pollute the environment, ground water and affect directly or indirectly through the food process and drinking water. It can cause short and long time health problems leading to death and therefore development of sensitive and selective pesticide sensors are very important. At first, pesticides were detected using analytical techniques such as gas/liquid chromatography with mass spectrometry [93] and fluorimetry [94]. But these techniques often associated with the main disadvantages such as expensive, involvement of complicated and requirement of highly skilled labors. Alternatively electrochemical methods such as cyclic voltammetry, chronoamperometry and differential pulse voltammetry offered simple and inexpensive routs for the sensitive detection of pesticides at nanomolar concentration.

In the past years, different electrodes were demonstrated such as, multi-walled carbon nanotube [95], metal oxide composites [96] and polymer nanocomposites [97] for the determination of

pesticides. Recently, graphene based composite materials find widespread fame among other carbon materials for the detection of pesticides. A disposable acetyl cholinesterase biosensor was constructed based on electrochemically reduced graphene oxide and nafion nanocomposite used for ultralow potential detection of organophosphate pesticide dichlorvos [98]. Acetyl cholinesterase was immobilized onto the nanocomposite and demonstrated as a biosensor which offered low detection potential, good selectivity, high sensitivity and low limit of detection of 2.0 ng mL<sup>-1</sup>. Yang *et al* [99] established a direct electrodeposition approach to synthesize graphene-Chitosan composite for the sensing of organophosphate pesticides, methyl parathion with limit of detection value is 0.8 ng mL<sup>-1</sup>.



**Figure 7.** (A) DPV curves of the  $\beta$ -CD-graphene/GCE after the solid phase extraction of mp with various concentrations of 0.3, 0.5, 0.8 and 1.0 ppb. (B) The DPV curves of graphene composite after the solid phase extraction of mp with different concentrations of 1, 5, 10, 50, 100, 200, 300 and 500 ppb in 0.1 M PBS (Reproduced with permission from ref. [87]).

A molecularly imprinted polymer-ionic liquid-graphene composite film deposited on the glassy carbon electrode has been presented for the sensing methyl parathion. The prepared graphene based composite modified electrode owns high stability, reproducibity and has the limit of detection of 6 nM towards determination of methyl parathion [100]. The electrochemically reduced  $\beta$ -cyclodextrin dispersed graphene electrode was fabricated for the sensing of methyl parathion, the electrode showed ultra-high sensitivity and good selectivity [101]. The electrode offered a limit of detection of 0.05 ppb and graphene is also utilized as a sorbent material for the detection of methyl parathion as shown in figure .7

#### **4. CONCLUSIONS**

In summary, preparation, properties and application of graphene has been presented and discussed. The unique properties of graphene make it highly versatile material for the applications in

various research fields and also numerous graphene based composite materials were prepared and characterized. The good properties pave a way to use it as a promising material in energy storage devices. Moreover, graphene and graphene based composite electrode materials exhibited high electrocatalytic properties towards, sensors, biosensors, solar cells and pesticides. In particular, graphene sheets act as a promising material for the sensitive, selective and good catalytic applications.

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