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Review

Electrochemical Detection of 4-Nitrophenol by Using Graphene Based Nanocomposite Modified Glassy Carbon Electrodes: A Mini Review

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Abstract: This article describes the fabrication of electrochemical devices for the detection of a key environmental pollutant, 4-Nitrophenol (4-NPh). 4-NPh is a requirement for the synthesis of organophosphate pesticides. These pesticides are mostly used in the agricultural sector to obtain a high yield of agricultural products. The use of 4-NPh in the agricultural field results in poisonous levels of this compound in the soil and water. Different techniques have been used for its transformation by biological and chemical degradation. However, these strategies not only created highly toxic pollutant but also need fast operation and time consuming processes. In this background, we have reported a broad and efficient review of the electrochemical reduction of 4-NPh as a feasible alternate method. In this review paper, graphene oxide (GO), reduced graphene oxide (rGO), N-doped graphene oxide, functionalized graphene oxide, metallic nanoparticles coated graphene oxide, metal oxides covered on rGO, polymer functionalized graphene oxide and hybrids materials functionalized with graphene oxide (hydroxyl apatite and β-cyclodextrin) which have been fabricated on a glassy carbon electrode (GCE) to enhance the electrocatalytic reduction and increase the sensor activity of 4-NPh are discussed. We have also described the effects of a few interfering phenolic pollutants such as aminophenol, hydroquinone, o-nitrophenol (o-NPh), trinitrotoluene, trinitrophenol, 2, 4-dinitrophenol (4-DNPh) and nitrobenzene. In the paper, easy and more effective electrochemical methods for the detection of 4-NPh with graphene- based nanocomposites modified on GCE for 4-NPh detection are summarized and discussed.

***Keywords*:** graphene nanocomposite, electrochemical sensor, 4-Nitrophenol

1. Introduction

Hazardous pollutants result in a polluted environment and have an effect on humans and other living organisms [1-2]. A huge amount of toxic heavy metals are present in soil, water, air and plants. These toxic heavy metals are incorporated into food chain, biomagnify into food and effectively result in severe health effects [3]. Nitrates, ammonia, phosphates, salinity and electrical conductivity were used to manufacture fertilizers and are comparable with other fertilizers on the market. Microalgae and macrophytes removed 4.4% of the chemical organic demand (COD) when compared to nitrates (12.5%), ammonia (11.3%) and phosphates (70.47%). The nitrates, ammonia and phosphates were compared with other common fertilizers removing of 95 mg/g, 39.5% and 62.5%, respectively. L. minor was used in the preparation of fertilizer and L.minor and C.inerta were used to eliminate organic pollutant nutrients from palm oil mill effluent (POME) [4]. Pyrene was degraded by fungi to isolate new species to biodegrade remazol brilliant blue R (RBBR).

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The biodegradation method has been developed with various parameters like agitation, concentration of glucose, temperature and salinity [5].

Environmental pollution is fashioned by means of the release of natural compounds waste from industries and a variety of dangerous wastes have contaminated the soil and water [6-7]. Consequently, the monitoring of pollutants is very important in soil and water and protects the surroundings from dangerous waste. The removal of organic compounds is very challenging to maintain water and soil resources. Even though, sensor methods have provided a good means of environmental protection such as water and soil [8]. However, simple and low-cost sensors for the evaluation organic pollutants such as nitrophenols (NPh) in water are needed [9]. Nitrophenols are toxic pollutants in human and animals. Nitrophenols are very crucial chemical substances for the manufacturing of pesticides, pigments, rubber chemical compounds, explosives and prescribed drugs [10]. They are continuously bleaching soil and damaging water environments, so in this sense they are among the foremost toxic chemicals [11]. Nitrophenols possess different properties such as they are toxic, inhibitory and bio-refractory natural chemicals. Amongst them, 4-NPh is the most important toxic and hazardous chemical that is detrimental to the health of living organisms in both soil and water environments [12]. If 4-NPh is continuously inhaled it causes health issues such as nausea, cyanosis, complications in humans and the Environmental Safety Corporation indexed and restricted its concentration to 0.43 µM in water environments [13-14]. Most fertilizers manufacturing industries use 4-NPh for the production of insecticides in agricultural use and act as intermediate compounds in fertilizers [15]. The plastic, paper, dyes, rubber industries are also major contributors to the presence of this pollutant in the environment. The effluents of these industries therefore contain small amounts 4-NPh which is released into the environment [16-18]. Despite the fact that, a low amount of 4-NPh is present in soil and it still can cause diseases in humans and residing organisms. 4-NPh is without difficulty highly stable in the environment [19-22]. 4-NPh which is present in industrial wastewater, home wastewater and agricultural wastewater can cause infections in humans and other living organisms as shown in Figure 1.

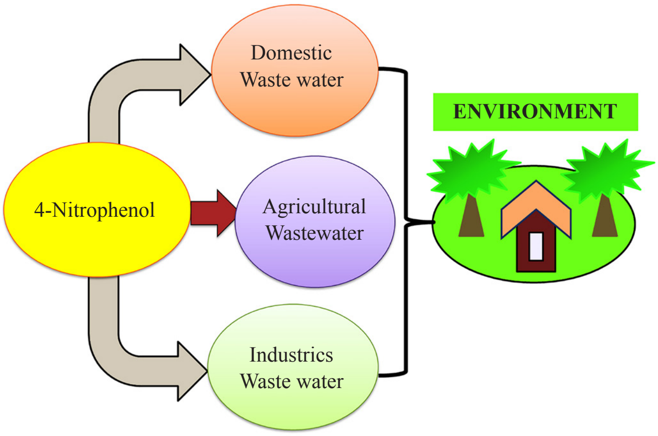

Figure 1. 4-NPh discharged into environment from industrial waste water, domestic waste water and agricultural waste water

Numerous techniques have been explored for the complete oxidation of 4-NPh such as biodegradation [23], microbial catabolism [24], Fenton reagents [25], photocatalytic degradation [26] and electrochemical techniques [27]. However, these methods can make different aromatic compounds like p-benzoquinone, 4-nitrocathechol, hydroquinone and phenol and they have shown higher toxicity than 4-NPh [28-29]. Recently, the degradation of 4-NPh has been performed by a chemical reduction method. However, the chemical reduction method is used with good reducing agents and is more toxic than transition metals [30]. Furthermore, the chemical reduction technique needs high power operating conditions for the degradation of 4-NPh [31]. Electrochemical reduction of 4-NPh is a better alternate method for eliminating hazardous pollutants and it also produces toxic byproducts. The intermediate products are used in different chemical industries and are used in various applications [32-33]. Therefore, electrochemical reduction techniques can be applied for the electrochemical degradation of 4-NPh into 4-Aminophenol (4-APh) and it was also shown to be easy and less time-consuming for the reduction of 4-NPh into 4-APh.

In this review article, we have therefore focused on the electrochemical reduction of 4-NPh with various experimental procedures. The effective reduction of 4-NPh was conducted with various modified glassy carbon electrodes (GCE). Different graphene based modified GCE electrodes have been reported for the electrocatalytic reduction of 4-NPh.This review also discusses the modification of GCEs with some phenolic compounds with graphene based nanocomposites by electrochemical processes. Generally, effective and simple electrochemical processes for the reduction of 4-NPh by GCEs modified with graphene are discussed.

2. The major uses of 4-NPh

4-NPh is widely utilized in the pharmaceuticals, insecticide, explosive and dye industries [34-36]. The majority of 4-NPh arises from the manufacturing of fertilizers like organophosphorus. Organophosphorus acts as an insecticide which includes parathion, methyl parathion and methamidophos and they are all poisonous agricultural chemicals create severe damages to humans, plants and other living organisms. 4-NPh is used as an intermediate to produce herbicides and pesticides. This has rendered it a major pollutant in water and is effortlessly soluble in water which also results in it becoming a cancer causing agent [37]. Pesticides also create problems for humans and plants and their 4-NPh intermediate has also created problems in the environment. The European environmental agency has set the maximum permissible limit of 0.1 g/l for pesticides in drinking water [38]. 3-methyl-4-NPh, 4, 6-dinitro-ocresol, parathion-methyl, fenitrothion are examples of compounds containing the 4-NPh intermediate and they are used in vegetation (wheat, corn and potatoes). These compounds enter the surface of water and sedimentations and they are able to easily persist in water [39]. These derivatives of 4-NPh are without problems soluble in drinking water [40]. The proposed mechanism for the conversion of of organophosphate into 4-NPh is shown in Figure 2.

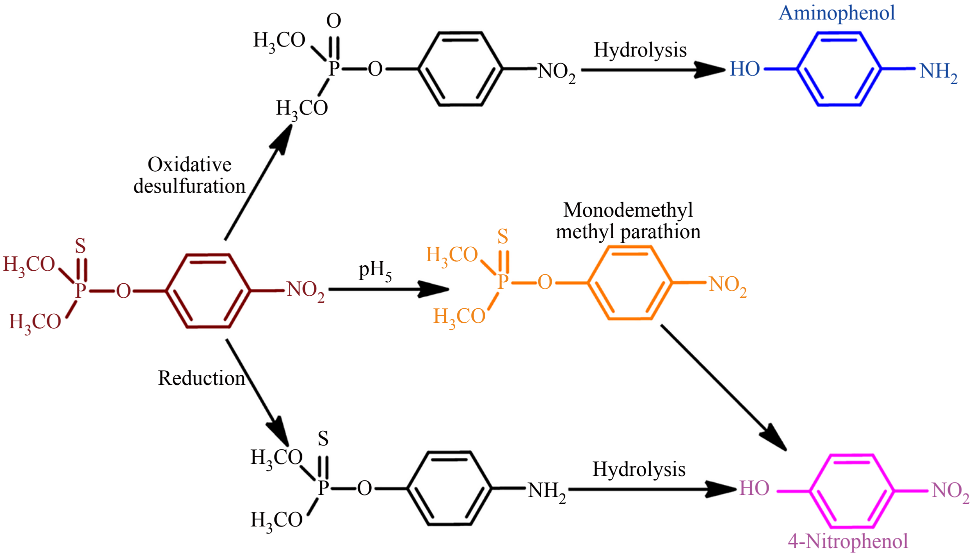

Figure 2. The proposed mechanism path ways of organophosphate to 4-NPh

3. Analytical methods for 4-NPh detection

In the last ten years, different analytical methods have been recognized and used for the sensing of 4-NPh as shown in Figure 3. These methods include Capillary electrophoresis [41], High-Performance Liquid Chromatography [42], Spectrophotometry [43], Float-injection analysis [44] and Enzyme-related immune sorbent assay [45]. Even though, most of the analytical methods are expensive and demand longer time analysis, these drawbacks can be overcome.

Electrochemical methods are becoming increasingly popular for the detection of 4-NPh. The electrochemical approach offers the advantages of low cost, easily handling, good sensitivity and selectivity and in-situ detection [46-47]. The electrochemical analysis of 4-NPh using a bare GCE offers lower sensitivity, excessive over potential and interference problems [48]. Therefore, modified GCEs have been used to solve these problems and to improve the electrochemical detection of 4-NPh [49-51].

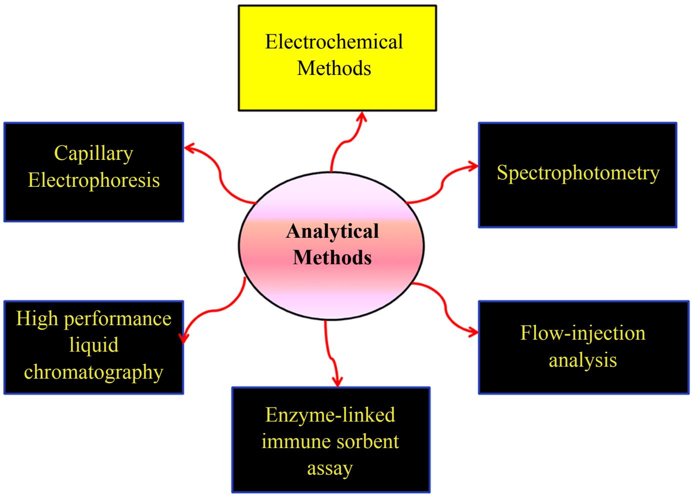

Figure 3. Analytical methods for the determination of 4-NPh from wastewater samples

4. Electrochemical sensor principle

The electrochemical sensor is referred to as a growing chemical sensor in analytical chemistry. A chemical sensor has without difficulty been incorporated into devices and provides additional information on the environment. This sensor has also been validated to directly identify the chemical substances in environmental samples. Such sensors are also able to identify the physical state of the analyte [52]. The electrochemical sensor is a crucial device because of its excellent delectability simplicity, low cost and easy operation and it can be also used to analyse a wide variety of samples including industrial, clinical, environmental and agricultural samples. Electrochemical sensors can be divided into three types which include Potentiometric, Conductometric and Amperometric. The Potentiometric sensor works on the principle of equilibrium between the sensor interface and sample potential. The signal is measured between two electrodes. Conductometric sensors measure the conductivity of the sample with collection frequencies. An Amperometric sensor measures the potential of the sample between the reference electrode and working electrode for the duration of oxidation and reduction of samples and subsequently gives a current reading as a signal. The electrochemical sensor is consequently becoming more popular in Analytical Chemistry [53-57].

The chemically modified GCE has demonstrated a greater ability for the detection of 4-NPh than the biologically modified GCE. The biological substrate does not give a good signal and demonstrates poor sensing due to fouling and the formation of an electrochemical polymerization film on the GCE [58]. Electrochemical sensor applications in biological samples include the detection of ascorbic acid, dopamine, glucose, hydrogen peroxide and metallic ion sensing via using the chemical sensor [59]. Electrochemistry converts an electrical sign into a digital signal for the detection of the analyte as shown in Figure 4. Typically, the cyclic voltammetry approach has produced the signal from chemical substrates and electricity and the associated signal is likewise associated with Linear Sweep Voltammetry, Potentiometric, Amperometric and Conductivity measurements [60]. The important processes of the electrochemical sensor have enhanced the electrocatalytic properties, sensitivity, selectivity and interference.

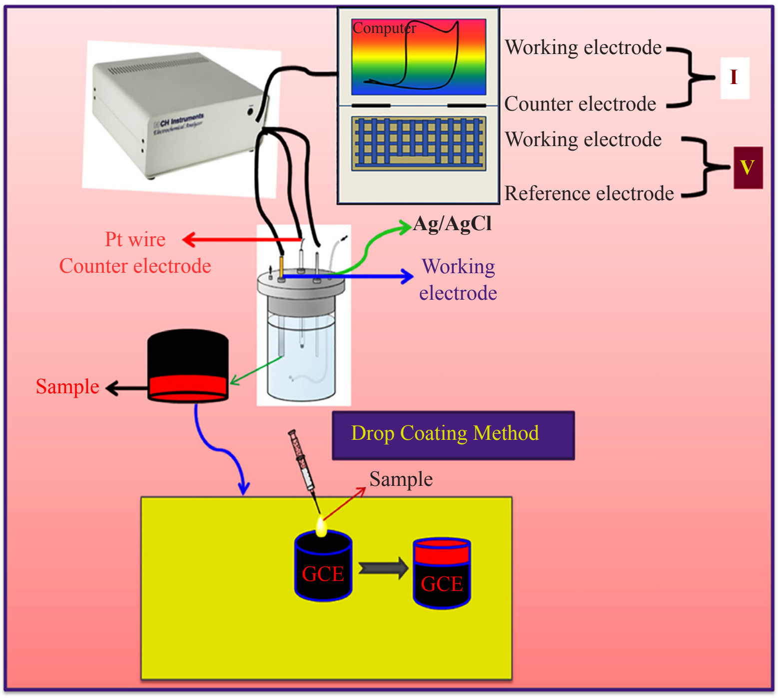

Figure 4. Principle and modified route in the function of an electrochemical application

5. Electrochemistry of 4-NPh

Generally, 4-NPh has electrochemical properties that lead to the electrocatalytic reduction of 4-NPh to 4-APh at a GCE. At the electrode surface 4-electrons and 4-protons are transferred resulting in the conversion of 4-NPh into hydroxyl aminophenol an intermediate compound [61-62]. Further, the hydroxyl aminophenol is reduced to benzoquinone imine and the elimination of water occurs after which the final product of aminophenol is acquired from benzoquinone imine by the intermediate of hydroxyl aminophenol [63-64]. The electrocatalytic reduction mechanism of 4-NPh into 4-APh is proposed. But, the floor amendment technique on the electrode has solved the problems including poor kinetic rate of the modified electrode and excessive overvoltage potential. This is an essential technique for boosting the sensitivity and selectivity of 4-NPh [65].

6. Different modified electrodes for 4-NPh

Electrochemical detection of 4-NPh has been performed with different GCE sensors by various electroactive nanomaterials. These nanomaterials include metallic nanoparticles, metallic oxides and metal oxide nanocomposites, polymer nanocomposites and carbon nanocomposites. Metallic nanoparticles are mainly silver nanoparticles [66] but bimetallic Au-CuNPs nanoparticles have also been applied for the electrocatalytic conversion of 4-NPh [67]. ZnONPs, CuONPs, Cu_2ONPs, Alpha-MnO_2NPs and Fe_3O_4NPs have been utilized as modified electroactive materials in the detection of 4-NPh [68-72]. Chitosan nanocomposites, polyaniline nanocomposite, poly (p-aminobenzene sulfonic acid) nanocomposites and poly(methylene blue) nanocomposites have also been applied for the electrocatalytic reduction 4-NPh [73-76]. The carbon substances and metallic nanoparticles composites include CNTs, AgNPs/CNT, Mesoporous, Graphene oxide (GO), molecularly imprinted Graphene, AgNPs/rGO, AuNPs/rGO, MnO_2NPs/GO, RGO/PSA and GO-Chit as shown in Figure 5 [77-87]. The electrochemical methods include Cyclicvoltammetry, Linear Sweep Voltammetry, Differential Pulse Voltammetry, Square Wave Voltammetry (SWV), Amperometry and Impedance Spectroscopy and all of these methods have been used for the detection of 4-NPh. Different nanomaterials have been classified for the electrocatalytic reduction of 4-NPh as shown in Table 1 [88-102].

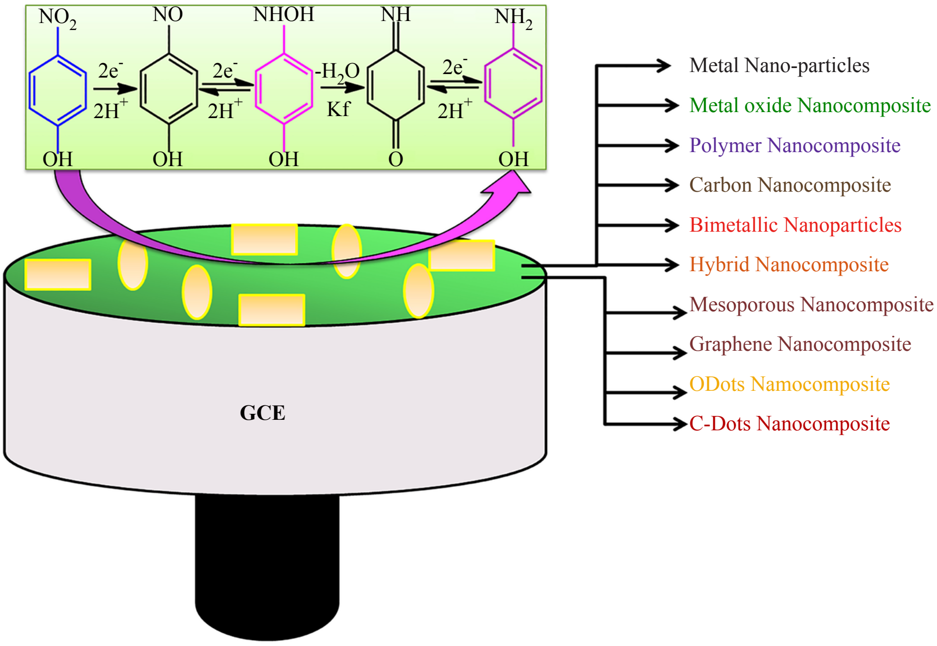

Figure 5. Different nanomaterials modified GCE for electrochemical detection of 4-NPh

Table 1. The different nanomaterials are classified for electrocatalytic reduction of 4-NPh

S.NO	Modified GCE	Linear range (µM)	Detection limit (µM)	References
1	PDDA-G	0.06-110	0.02	88
2	Ag-rGO	1-1100	0.32	89
3	GO/TiO2/GCE	0.02-80.57	3.9	90
4	GCE-AuNPs-rGO	0.05-2	0.02	91
5	Green Ag-NPs/GCE	0.09-82.5	60	92
6	GCE/Ag-chitosan	0.07-2.0	70	93
7	Cu-curcumin/GCE	0.1-030	68.2	94
8	GCE/rGO	50-800	200	95
9	NMP-Graphene	0.5-5.6	0.15	96
10	GCE-rGO-CD-CS	0.06-40	16	97
11	ZnO-chitosan	0.5-400	0.23	98
12	GCE-Green AgNPs	0.5-3000	0.5-3000	99
13	GCE-chitosan-BMIMBF-MWCNT	0.3-20	0.1	100
14	GCE-Au NPs	10-1000	8	101
15	GCE-PANi-GITN	0.03-3	0.0052	102

PDDA-G: poly (diallydimethylammonium chloride)-graphene;
NPs: nanoparticles;
BIMIMBF: 1-butyl-3-methylimidazolium tetrafluoroborate;
MWCNT: multi-walled carbon nanotube;
rGO: reduced graphene oxide;
PANi-G-ITN-Integrated polyaniline with graphene oxide-iron tungsten nitride nanoflakes;
rGO-CD-CS Reduced graphene oxide-cyclodextrin-chitosan;
NMP-N-methylphenazoniummethyl sulfate.

7. Graphene materials for electrochemical sensors

Graphene is a kind of carbon material with a unique structure when compared to other carbon materials. Graphene comprises a 2D dimensional sheet of sp^2 hybridizede carbon atoms. The dense arrangement of carbon is in a honeycomb crystal lattice. This carbon sheet layers are bonded with weak Van der Waals Forces [103]. Graphene has unique electrical conductivity when compared to other carbon materials. GO is synthesized by numerous methods which include heat, chemical conversion and electrochemical methods as shown in Figure 6. GO facilitates fast electron transfer between the edge of oxygen and defects [104-106]. Consequently electrochemical sensors can be prepared with graphene-based materials [107-109]. Chemically modified rGO has exhibited better electrochemical sensing due to oxygen-containing functional groups. This is without difficulty modified with special functionalization which include modification with biological molecules and polymers [110-112]. 4-NPh is easily detectable using metal nanoparticles, metallic oxide nanoparticles, carbon nanocomposites and polymer nanocomposites with graphene as shown in Figure 7. This graphene nanocomposite has delivered a fast electrochemical sensor with unique analytes such nitrophenols, trinitrotoluene, picric acid (PA), nitrobenzene, H_2O_2 and dihydroxy benzene isomers.

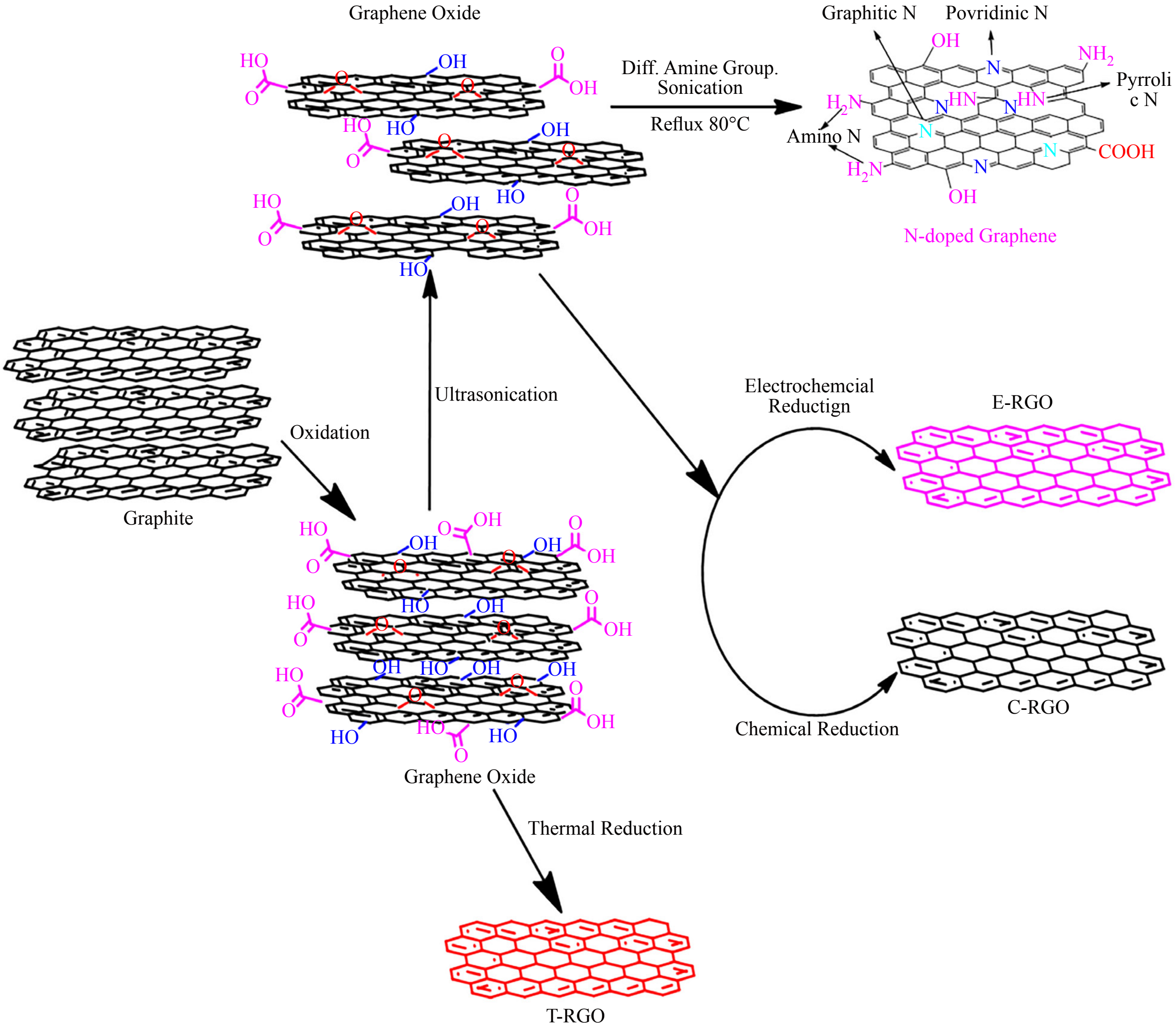

Figure 6. Different ways of synthesis of GO, graphite oxide with thermally, chemically and electrochemically

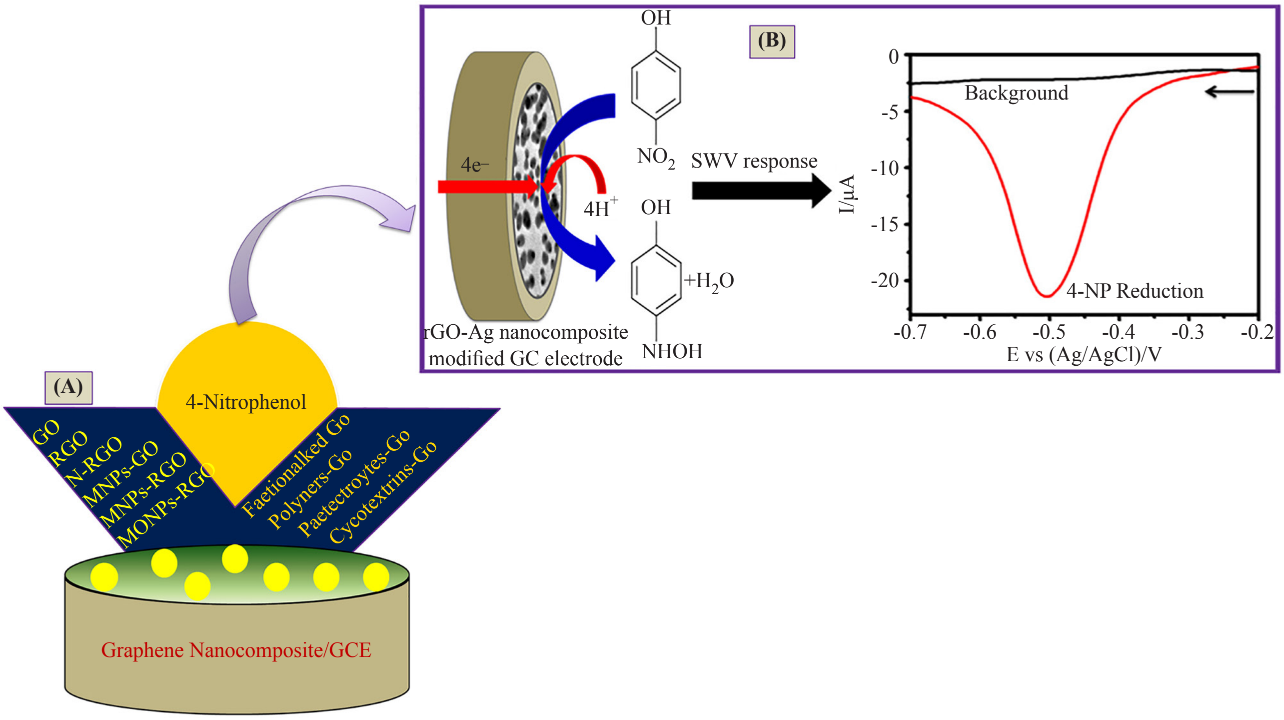

Figure 7. (A) Different graphene and graphene nanocomposites modified GCE for detection of 4-NPh. (B) Schematic representation of the electrocatalytic reduction of 4-NPh at rGO-Ag nanocomposite-modified GCE. (B) Figure only reprinted with permission from ref. 83, Copyrights (2014) Elsevier Publications

8. Electrochemical sensors of 4-NPh by using graphene materials nanocomposite

Metal nanoparticles, Metallic oxide nanoparticles, Polymers nanocomposites and Carbon nanocomposites are in high demand for the electrochemical detection of 4-NPh. These show superior accuracy with electrocatalytic sensing and selectivity with different analytes. GO has a 2D lattice shape and has significantly developed as an electrocatalyst and electrochemical sensor. It has a better electron transfer abilities due to the large number of functional groups such as COOH, OH and the epoxy group. The functional groups of GO can improve fast electron transfer between the electrode and analyte. This also involves heterogeneous electron transfer between the GO modified electrode and analytes. GO is also capable of faster electrochemical sensing when compared to other materials. GO has shown good electric conductivity, stability, sensitivity and kinetic electron transfer rate due to nano graphite impurities in carbon nanotubes [113]. Li, et al. fabricated a GO modified GCE (GO/GCE) and it showed good catalytic capability to reduce 4-NPh. The modified GO/GCE has a strong adsorptive capability and clear electronic characteristics due to hydrogen bonding and hydrophobic forces between GO and 4-NPh [114-115]. Since 4-NPh has an aromatic group, it can also engage in π-π stacking interactions with GO. There may also be electrostatic interactions between GO and 4-NPh where the N atom in 4-NPh can become positively charged. These properties have resulted in high electrochemical detection of 4-NP on GO. In contrast to different NPh chemical sensors based on chemically rGO substances, studies on the electrochemical detection of 4 NPh do not show better stability and reproducibility, but rather result in the selective reduction of 4-NPh once this is electrochemically detected. The reduction peak current concentration range is from 0.1 to 120 μM for 4-NP and its limit of detection (LOD) is 0.02 μM**.**

Electrochemical procedures have reported the electrodeposition of GO on GCE surface and formation of electrochemical reduction graphene oxide (ERGO) films is exhibited as crumpled, wrinkled and flake-like shapes [87-90]. In recent years, researchers have improved the stability and sensitivity of modified ERGO on GCE films, which can be used to enhance electrochemical sensors [116-121]. In ERGO film formation a few defects are found such thickness management, inability to separate the films and analyte and the analytes are mostly present on the surface of ERGO films [122]. Hence, an easy route for synthesizing ERGO films on GCE has been developed and these can be directly attached on GCE from GO dispersion with single step. Wu et al. reported the simple preparation of ERGO nanocomposite films by using a co-electrodeposited method [123]. Further, ERGO modified electrodes have been designed with single step electrodeposition methods. This system is used to assemble the ERGO films on GCE and result in good rapid electron transfer for the electrochemical sensor. Since this electrodeposition technique has been confirmed to be very significant it has been applied for ERGO based nanocomposite sensors for the electrochemical detection of analytes.

Rao et al. used electrochemically rGO films on GCE (ERGO/GCE) for the detection of 4-NPh [124]. This kind of modified electrode was used for the electrocatalytic reduction of 4-NPh because of edge plane defect of ERGO for the electrocatalytic reduction of 4-NPh. Therefore, ERGO/GCE are promising for the electrochemical sensing of 4-NPh. ERGO/GCE films were confirmed as electroactive substrates for sensing analytes. ERGO can be without difficulties shaped on the film on GCE with a one-step electrochemical approach and electrocatalytic activity through 4-NPh reduction and oxidation due to amino and hydroxyl groups. Chen et al. suggested that the modified ERGO/GCE film is formed by the electrodeposition technique. This technique has facilitated the use of ERGO films from GO due to fast electron transfer and the green approach [125]. Here, the graphene films are synthesized on GCE directly from GO with single steps of the electrodeposition method [126]. This modified ERGO electrode delivered a terrible fouling effect, desirable balance, sensitivity and higher electrochemical sensing of 4-NPh.

Oliveira et al employed the novel nanocomposite of N-methylphenazonium methyl sulfate (NMP) adsorbed on graphene for the electrocatalytic reduction of 4-NPh. This NMP/RGO is fabricated on a GCE electrode to facilitate the powerful electrochemical detection of 4-NPh. N-methylphenazonium methyl sulfate acts as an electron transfer mediator between RGO and GCE and has high stability, and results in the fast electrochemical redox reaction in 4-NPh determination [127-128]. This nanocomposite exhibits a non-covalent linkage between the RGO and NMP to enhance the electrocatalytic reduction of 4-NPh. NMP/RGO/GCE electrode detects 4-NPh at a concentration of up to 0.3 nM through DPV and 0.15 nM with the aid of Amperometry, (S/N = 3). NMP/GO/GCE electrode is viable, stable, sensitive and results in rapid determination of 4-NPh.

9. Electrochemical sensor of 4-NPh by N-doped RGO nanocomposite

Enhanced electrical conductivity, electrocatalysis and electrochemical sensors are needed with modified GO containing heteroatoms such as S, N, P and B [129-130]. Amongst them, a N-doped graphene oxide structure may be involved in extraordinary applications [131-132]. N-doped graphene oxide supplies a quick electron transfer rate and reduces the band gap for electrochemical applications [133]. The nitrogen atom is smoothly doped with different chemical materials because of its atomic size and lone pair electron and it is able to without difficulty be doped with carbon materials consisting of carbon atoms with strong bonds [134]. The lone pair of electrons on the nitrogen atom is doped on rGO carbon materials that have aromatic moieties, increase electric conductivity and change the band gap of rGO [135-136]. GO has not exhibited any activity improvement, so N-doped graphene oxide can be utilized for the numerous applications of electrocatalysis and electrochemical sensors [137]. N-doped graphene oxide can be prepared by different methods including nitrogen plasma process [138], arc-discharge [139], segregation growth [140], chemical vapour deposition [141-142], thermal annealing [143-144], hydrothermal techniques [145-146] and solvothermal methods [147].

However, modification has been used on GCE and has more suitable electrochemical sensors and electrocatalysis [148]. The connectivity of the N-doped graphene oxide consisting of graphitic N, pyridinic-N and pyrrolic N have specific properties which increase the surface area and enhance the electrocatalytic activity with the thermal remedy of melamine and 2-methyl imidazole [149] as shown in Figure 8. Exceptional kinds of N-doped graphene oxide materials have shown the tremendous electrochemical behavior which is closer to the 4-NPh sensor. Zhang and coworkers prepared the N-doped graphene oxide with urea combination by using solvothermal methods [150]. Giribabu and coworkers prepared N-doped graphene oxide by using the solvothermal method of GO and sodium diethyldithiocarbamate mixture [151]. Dadkhah and coworker synthesized N-doped graphene oxide which was prepared by the solvothermal method of GO and 3-aminopropyltriethoxysilane (APTES). This improvement of N-GO has resulted in crucial issues together with structural modifications. Hydrogen bonding is formed the N atom and GO and π-π bond interplay of N-GO and analytes [152-153]. N-GO modified GCE is implemented for electrochemical application

4-NPh.

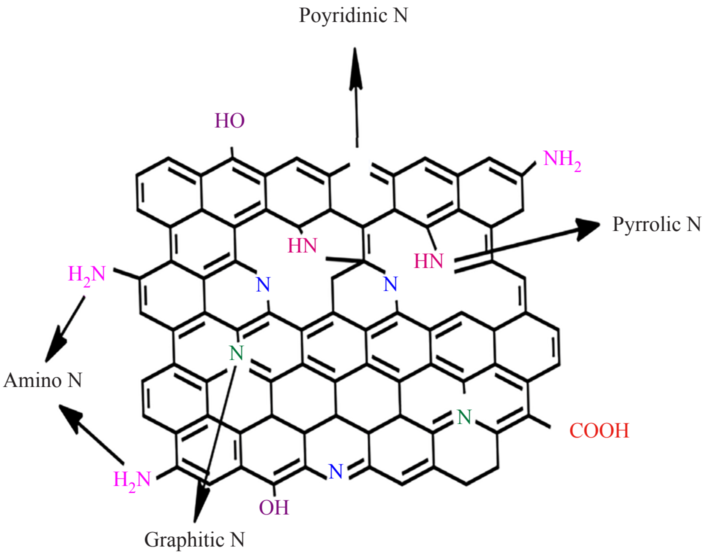

Figure 8. Synthesis process of nitrogen-doped graphene and illustration of types nitrogen configurations in N-doped graphene. Green, blue and red colour represents graphitic N, pyridinic N and pyrrolic N respectively

10. Electrochemical detection of 4-NPh using functionalized on GO nano-composite

GO is an attractive material and its properties are utilized in electrochemical applications. The GO is without difficulty agglomerated by chemical conversion techniques and it easily gets graphitized from GO due to van der walls forces and π-π stacking interplay [154]. These substances have controlled utility, so issues are involved in opposition to graphitization and agglomeration. The modification of GO substances are wanted with covalent and non-covalent bonds by using functionalization techniques. In which non-covalent strategies onto GO are special properties consisting of the blockage of the agglomeration of the layer of GO with the hydrophilic or hydrophobic organization, increased solubility and increase electrochemical application examine than covalent technique [155-156]. Therefore, polymers, non-covalent- polyelectrolyte and macromolecules are used to alter GO [157]. Peng et al. posted the research on a modified electrode via the usage of polyelectrolyte (poly (diallyldimethylammonium chloride) (PDDA))-functionalized GO for the electrochemical detection of 4-NPh [158]. Poly (diallyldimethylammonium chloride), PDDA is engaging in an ionic polymer and it can be bonded to GO sheets [159-162]. Therefore, PDDA is functionalized with GO to create a positive charge and so that it can without difficulty attract negative materials for different applications [163-164]. This electrostatic attraction of materials has reduced the electrochemical catalyst's activity and resulted in low detection of 0.02 µM of 4-NPh [165-166].

Bharath et al. proposed the synthesis of edge-carboxylated GO from graphite powder and magnetite-hydroxyapatite (m-HAp) which is coated on nicely defined GO through the use of the hydrothermal method. m-HAp onto GO nanocomposite offers an effective electrochemical detection of phenolic natural pollution for environmental protection [167]. m-HAp-GO nanocomposite confirmed the adsorbing behavior and it can't be reused and recycled after treatment. The technique is wanted severely to solve the problems. So the guided side-carboxylated GO sheet is utilized by ball mill techniques. m-HAp nanocomposites covered on GO is conducted by way of hydrothermal approaches. The resulting m-HAp/ECGO is modified on GCE for the electrocatalytic reduction of 4-NPh [168]. The modified m-HAp/ECGO/GCE sensor offerssuitable sensitivity, selectivity and the low detection limits which is 0.27 µM. Arfin et al. produced graphene oxide-poly (ethyleneimine) dendrimer (GO-PEI) functionalized modified GCE electrode through a drop-cast approach [169]. The modified GO-PEI/GCE shows better electrochemical sensing of o-NPh and good redox properties is observed. GO-PEI/GCE offers the concentration of o-NPh from 5-155 μM and limit of detection is 0.10 μM (S/N = 3). GO-chitosan nanocomposite on the GCE is fabricated for the electrochemical sensor of 4-APh by using using the voltammetry approach [170]. GO with polyaniline nanocomposite (GO-PANI) was prepared and applied in the electrochemical determination of 4-APh. GO-PANI nanocomposite was fabricated on GCE to faciliate the electrocatalytic sensing of 4-APh through the cyclicvoltammetry approach. GO-PANI/GCE electrode has performed a higher electrochemical reaction in 4-APh with low detection limit, suitable sensitivity, better stability and simultaneous determination of 4-APh. This GO-PANI/GCE electrode is used as sensor and biosensor based on the method [171]. GO-PANI nanocomposite GCE film is able to perform an effective electrocatalytic reduction of 4-APh and has a detection limit of 6.5×10^{-8} M.

10.1 *Electrochemical sensor for NPh by using GO-MIP nanocomposite*

Liu, et al proposed the electrochemical application of 2, 4-DNPh with the molecular imprinted polymer (MIP) with GO nanocomposite modified GCE electrode. 2, 4-DNPh is used as a template to prepare MIP [172]. MIP-GO has an extraordinary surface area, great selectivity and shows better electrocatalytic determination of 2, 4-DNPh. GO-MIP/GCE electrode has exhibited a low detection limit is 0.4 μM (S/N = 3) with DPV and GO-MIP/GCE resulted in the good sensitivity.

10.2 *Electrochemical sensor for 4-NPh by using GO-chitosan nanocomposite*

Deng et al advanced a newly modified electrode based on the acetylene black paste electrode graphene-chitosan composite film (GO-chit/ABPE) and it is able to electrochemically determine 2-NPh and 4-NPh simultaneously [173]. This resulted in detection limits of 200 nM for 2-NPh and 80 nM for 4-NPh, respectively. GO-Chit/ABPE electrode was successfully used for the electrocatalytic determination of 2-NPh and 4-NPh. The fabricated GO-Chit/ABPE electrode gave desirable stability, sensitivity and reproducibility and higher electrochemical detection of o-NPh and p-NPh. Tang et al introduced the graphene-chitosan composite film modified GCE (GO-Chit/GCE) become prepared for the simultaneous detection of p-NPh and o-NPh. GO-CS/GCE confirmed better electrocatalytic interest for the reduction of p-NPh and o-NPh. The detection limit (S / N = 3) of 0.09 μM at GO-CS/GCE for o-NPh and detection limit of 0.1 μM. GO-CS was validated as a promising sensor for the simultaneous detection of NPhs isomers [174].

Yin et al reported that a graphene-chitosan composite is immediately coated on GCE electrode and it is capable of using the modified electrode for electrocatalytic reduction of 4-APh. GO-Chitosan nanocomposite has unique properties like excessive surface area easily made film shapes of chitosan polymers, good electrical conductivity and best electrocatalytic reduction of 4-APh. GO-chitosan has exhibited the efficient electrochemical utility of 4-APh with detection limit is 0.057 μM (S/N = 3) [175]. Fana et al proved that a graphene oxide polyaniline (GO-PANI) nanocomposite was used for an electrochemical application of 4-APh. GO-PANI nanocomposite is prepared through an in situ polymerization approach and this nanocomposite film is coated on GCE for the electrochemical determination of 4-APh with the cyclicvoltammetry method. This GO-PANI nanocomposite sensor exhibited a low detection limit 6.5×10^{-8} M, excessive sensitivity and better stability for the electrochemical detection of 4-APh [176].

10.3 *Electrochemical sensor for 4-NPhs by using poly(sulfosalicylic acid)/GO*

Zheng et al proposed a new developed rGO-poly (sulfosalicylic acid (PSA) nanocomposite which was synthesized by a single step of the electrochemical approach. PSA/rGO nanocomposite was successfully fabricated on GCE for the electrochemical determination of acetaminophen. PSA/rGO/GCE electrode exhibited an extraordinary electrochemical detection of limit is of 0.041 μm (S/N = 3), high reproducibility, high stability and anti-interference capacity. The PSA/rGO/GCE electrode suggests a fantastic electrochemical behavior of acetaminophen with a synergistic effect between the PSA and rGO film to increase the electrochemical detection of acetaaminophen [177].

11. Electrochemical sensor of 4-NPh by using MNPs with GO nanocomposite

Metals and Metallic oxide nanocomposites modified GCE are extensively used as electrochemical sensors. These nanomaterials are coated on GO to show the best electrocatalytic behavior, great conductivity, selectivity and electrochemical sensing after modification with GCE. These nanomaterials give the better reduction peak current in 4-NPh detection and low interference effects.

Yang reports the synthesis of a GO/AgNPs nanocomposite via a hydrothermal method and AgNPs were uniformly coated on the GO sheet. AgNps/GO nanocomposite was coated on GCE and it can be tested for the super electrochemical sensingof 4-NPh with the low detection limit of 0.114 µM. This nanocomposite exhibited the following characteristics such as stability, anti-interference and sensitivity [178]. Mohamed Noor et al. reported the preparation of a reduced graphene oxide-silver (rGO-AgNPs) nanocomposite by using a microwave method and the rGO-AgNPs nanocomposite was modified on a GCE to provide rGO-AgNPs/GCE. This rGO-AgNPs/GCE was used for the electrocatalytic reduction of 4-NPh and additionally exhibited the limit of detection 0.32 µM. These observations confirmed that the rGO-AgNPs nanocomposite exhibited desirable selectivity toward the detection of 4-NPh even in the presence of different interfering molecules [179].

Ikhsan et al conducted a simple synthesis of a silver nanoparticle-coated GO AgNPs-rGO nanocomposite with Tollen's reagent at different time intervals. AgNPs-rGO nanocomposite modifies GCE to give AgNPs-rGO/GCE. This modified AgNPs-rGO/GCE was able to engage in the electrochemical detection of 4-NPh bythe use of SWV with a detection limit of 1.2 nM [180]. Karuppiah et al verified that the green method of preparation of silver nanoparticles with *justicia Glauca* leaf extract as a reducing agent. In addition, the silver nanoparticles were dispersed on GO to provide the AgNPs-rGO nanocomposite and this AgNPs-rGO nanocomposite was modified on the GCE to apply the electrochemical software for the detection nitrobenzene [181]. AgNPs-rGO/GCE showed a low limit of detection of 0.261 µM and showed the best selectivity and anti-interference.

Tang et al organized an unconventional sensor of AuNPs/rGO nanocomposite and it can be made on the GCE film electrode for the electrochemical detection of 4-NPh. The AuNPs/rGO/GCE sensor is prepared by using the electrochemical deposition cyclicvoltammetry technique. The AuNPs/rGO/GCE sensor exhibited the good electron change between the electrolyte and electrode and effortlessly improved the electrocatalytic response of 4-NPh. This sensor showed a low detection of 4-NPh with 0.01 µM and 0.02 µM by using Difference Pulse Voltammetry and SWV, respectively. AuNPs/rGO/GCE showed anti-interference activity, reliability and effective electrochemical of detection of 4-NPh [182]. Jiao et al. verified the synthesis of gold nanoparticles coated with GO nanocomposite (AuNPs/rGO) film by the electrochemical technique. AuNPs/rGO nanocomposite performed as a sensor with the aid of GCE and this AuNPs/rGO/GCE is implemented for the electrochemical dedication of 4-NPh with electrochemistry techniques. AuNPs wereimmobilized on rGO materials to improve the peak current and shifted the reduction potential of 4-NPh with the cyclicvoltammetry approach. It was well determined that the AuNPs/rGO/GCE films showed a good electrochemical signal for 4-NPh. AuNPs/rGO/GCE showed a low detection limit of 1.0×10^{-8} M, excessive sensivity, repeatibilty and stability in 4-NPh detection [183]. Wenbei et al showed the unconventional technique of modifying GO with gold nanoparticles (AuNPs/GO), wherein AuNPs is loaded in a very small amount of 10% and AuNPs is dispersed on the grpahene oxide sheet without any aggregation. AuNPs-GO nanocomposite is fabricated on GCE to present AuNPs/GO/GCE and it can be capable of detecting the 4-NPh by means of the Amperometric method with low detection of 0.47 µM. Au-GO/GCE can be effectively used as a powerful sensor material for the detection of 4-NPh [184-185].

Ezhil Vilian confirmed the environmentally friendly sensor of Pd-GA/rGO nanocomposite which is prepared with GA as a reducing agent. Pd-GA/rGO nanocomposite resulted in higher electrocatalytic and catalytic reduction of nitrophenol [186]. The catalytic abilities of Pd-GA/rGO nanocomposite are improved for GO to offer the good electrostatic interaction of rGO and 4-NPh. PdNPs exhibited more surface with GA-rGO and it is able to effortlessly unfold out on the GA-rGO surface to cause rapid electron transfer and electrocatalytic reduction of 4-NPh. Pd-GA/rGO nanocomposite modified GCE electrode gave a lower overpotential, excessive sensitivity and limit of detection is 9 fm (S/N = 3) with SWV. Pd-GA-rGO nanocomposite suggests higher catalytic activity with 4-NPh and the synergistic effect produced between the rGO and PdNPs to enhance the electrocatalytic and catalytic of 4-NPh as proven in Figure 9.

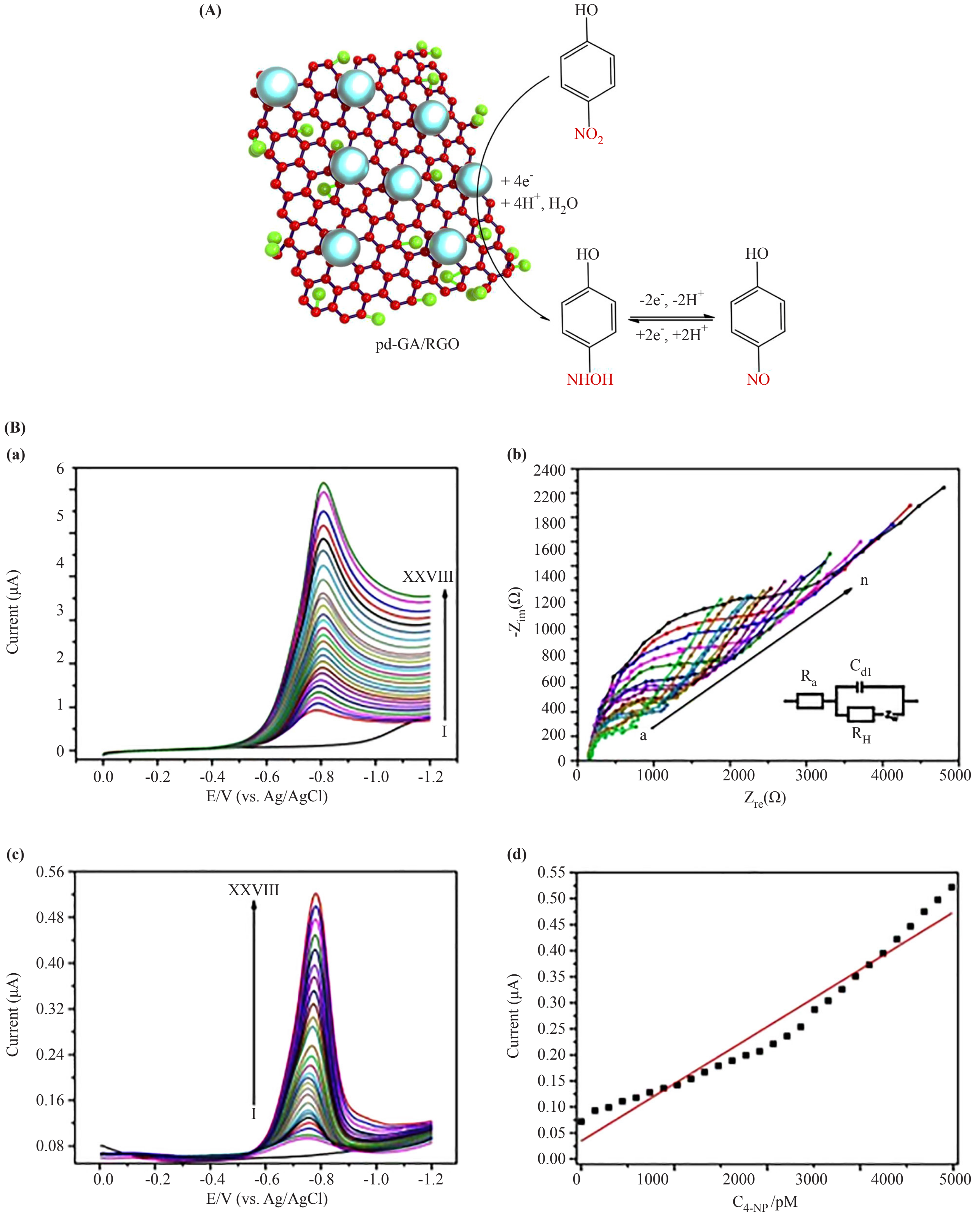

Figure 9. (A) Schematic illustration of 4-NP electrochemical reduction at Pd-GA/RGO/GCE. (B) (a-d) LSV curves of 4-NP on Pd-GA/RGO in 0.05 M PBS with various concentrations (from curve I to xxviii = 0-400 pM). (b) EIS of the Pd-GA/RGO with various 4-NP concentrations (from curve a to n = (0-300 pM) in PBS (pH = 7) containing 5 mM $Fe(CN)_6^{3-/4-}$ with 0.1 M KCl. (c) SWV curves of increasing different (0-80 pM) concentrations of 4-NP obtained with a Pd-GA/RGO sensor in a pH 7.0 solution. (d) Consequent calibration plot for cathodic peak currents and 4-NP concentrations. Conditions: 0.05 M PBS (pH 7.0). Reprinted with permission from ref. 186, copyrights (2014) Elsevier Publications.

12. Electrochemical sensor of 4-NPh by using MONPs with GO nanocomposite

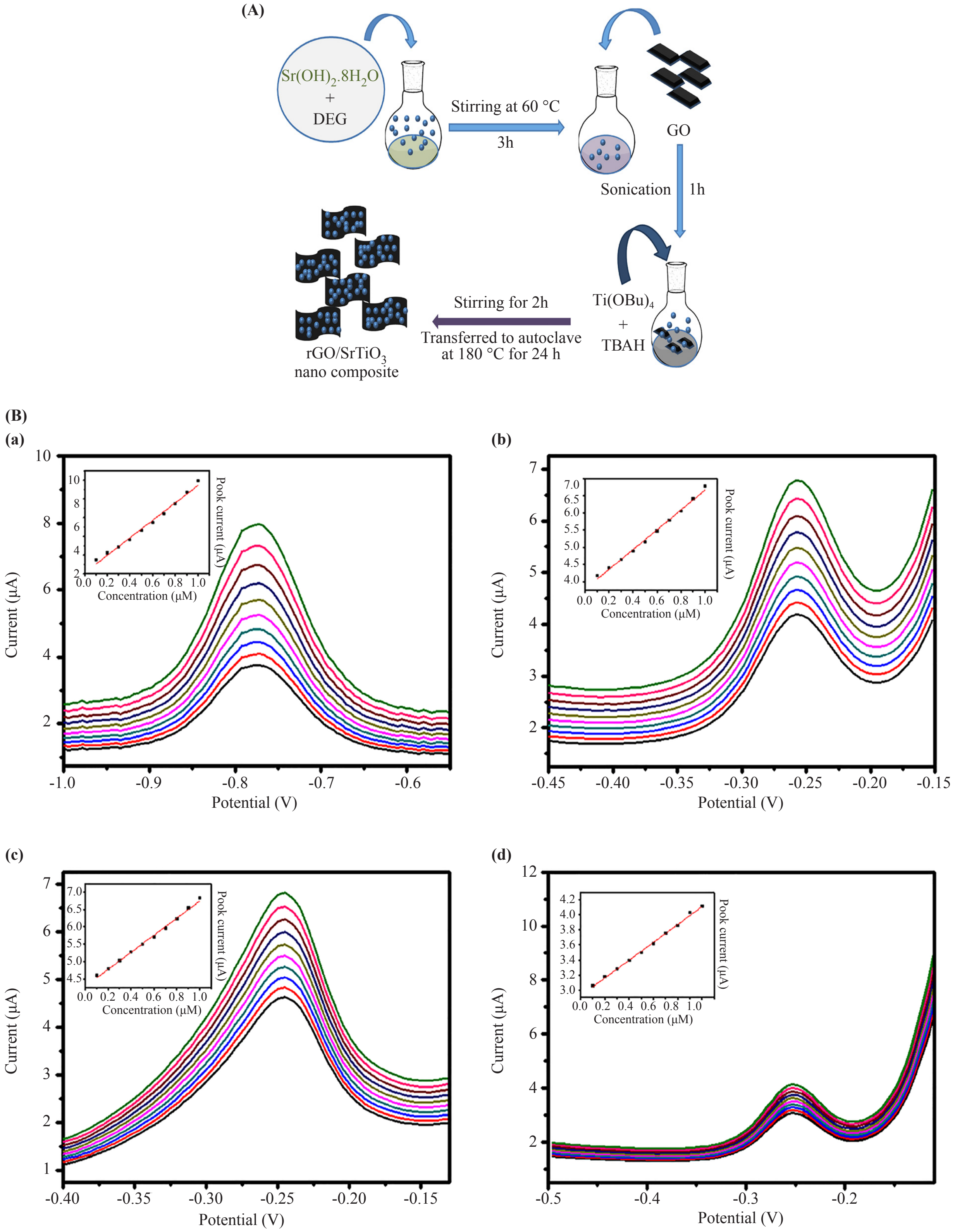

Figure 10. (A) Schematic representations for in-situ grown rGO/$SrTiO_3$. B(a-d) Differential pulse voltammograms of MGCE (a) for p-NP, (b) for 2,4-DNP, (c) for 2,4-DNT and (d) for TNP at different concentration (0.1-1 mM) in PBS (pH 7.0) with a scan potential of 100 mV/s. The inset showing the calibration plots of peak current versus concentration. Reprinted with permission from ref. 190, copyrights (2014) Elsevier publications

MnO_2-reduced GO nanocomposite is utilized as a modified electrode on GCE for the electrochemical application of 4-NPh. Right here, MnO_2 nanoparticles is loaded on reducing GO by means of the electrodeposition method. MnO_2-rGO/GCE has remarkably showed the best electrocatalytic reduction of 4-NPh with the limit of detection of 10 nM. This sensor nanocomposite exhibited better stability, high selectivity, speed of electron transfer and reproducibility in 4-NPh detection [187]. Haldorai et al suggested the alpha-MnO_2-Reduced GO nanocomposite can be prepared by using a residue free method. MnO_2-Reuced GO nanocomposite is at once, bound without any binding agent within the electrocatalytic reduction of 4-NPh. This sensor displays a low detection limit of 0.017 μm through SWV. This MnO_2-rGO/GCE electrode resulted in higher sensitivity, anti-interference capacity, and powerful electrocatalytic detection of 4-NPh [188].

Alam et al. showed that a reduced graphene oxide-Zinc oxide (rGO/ZnO) nanocomposite is prepared by a simple chemical reduction method with polyethylene glycol. The rGO/ZnO nanocomposite is effectively performed onto GCE for electrochemical application of 2-NPh. This r-GO/ZnO nanocomposite is modified on GCE a thin layer of nanocomposite and increases the electrochemical sensing abilities, results in high sensitivity and a low detection limit of 0.27 nM. This rGO/ZnO nanocomposite suggests a new approach for the improvement of better electrochemical sensing of 2-NPh [189].

The synthesis of rGO/$SrTiO_3$ nanocomposite is performed with the aid of a simple wet chemical approach with an in-situ technique. The rGO/$SrTiO_3$ nanocomposite is covered onto GCE with drop casting method. rGO/$SrTiO_3$ nanocomposite exhibited fast electron transfer among the active substances and analytes and development of electrode substances and electrolytes. It has been implemented for the electrochemical detection of nitro-substituted phenols such as 4-NPh, 2, 4-DNPh, 2, 4-dinitrotoluene (2, 4-DNT) and 2, 4, 6-Trinitrophenol (TNP) with low detection of (LOD) 110 nM, 134 nM, 128 nM and 146 nM, respectively [190]. rGO/$SrTiO_3$ showed the excellent activity such as stability, reliability and anti-interference in the nitro aromatic pollutants results. The modified rGO/$SrTiO_3$/GCE exhibited a good electrochemical sensor of 4-NPh within the nitro-aromatic pollution as proven in Figure 10. Mahyar suggested brand new sensor of PtNPs-rGO nanocomposite on GCE for the electrochemical sensor of PA. PtNPs-rGO/GCE electrode is efficaciously applied the selective and sensitivity electrochemical sensor for PA with low detection limit of 1 μM [191].

Electrochemical determination of nitrophenol derivative of acetaminophen has used the sensor of Fe_3O_4NPs coated PDDA-GO nanocomposite. Fe_3O_4NPs-PDDA-GO nanocomposite film is fabricated on GCE as a modified electrode for the sensitive detection acetaminophenol with cyclicvoltammetry. Fe_3O_4NPs-PDDA-GO/GCE film sensor can be capable of determining the electrocatalytic activity of acetaminophenol with the aid of the usage of differential pulse voltammetry approach. The modified Fe_3O_4NPs-PDDA-GO/GCE electrode resulted in significant detection of acetaminphenol with low detection of 3.7×10^{-8} M (S/N = 3). The proposed electrochemical sensor also exhibited good reproducibility and stability and has been used to discover acetaminophen [192].

13. Electrochemical detection of NPhs by using cyclodextrin based GO nanocomposite

Liu et al pronounced a β-cyclodextrin functionalized on reduced graphene oxide sheets (β-CD-RGO) nanocomposite which is used as a sensor for 4-NPh derivatives including p-NPh, o-NPh and m-NPh [175]. (β-CD-RGO) nanocomposite is coated on GCE to supply the modified (β-CD-RGO/GCE) electrode and is implemented in the electrocatalytic detection of NPhs. Here, RGO is a high surface region substance and easily accepts the host-guest group of cyclodextrin compounds. β-CD-RGO/GCE electrode has performed a higher electrocatalytic reduction in NPh and offers better redox peak current with the cyclicvoltammetric technique. β-CD-RGO/GCE was discovered for the electrochemical detection of NPhs to show good low detection limits of 0.05 μM, 0.02 μM and 0.1 μM with p-NPh, o-NPh and m-NPh, respectively. β-CD-RGO/GCE has brought appropriate sensitivity, true adsorptive, selectivity and anti-interference in the direction of NPhs.

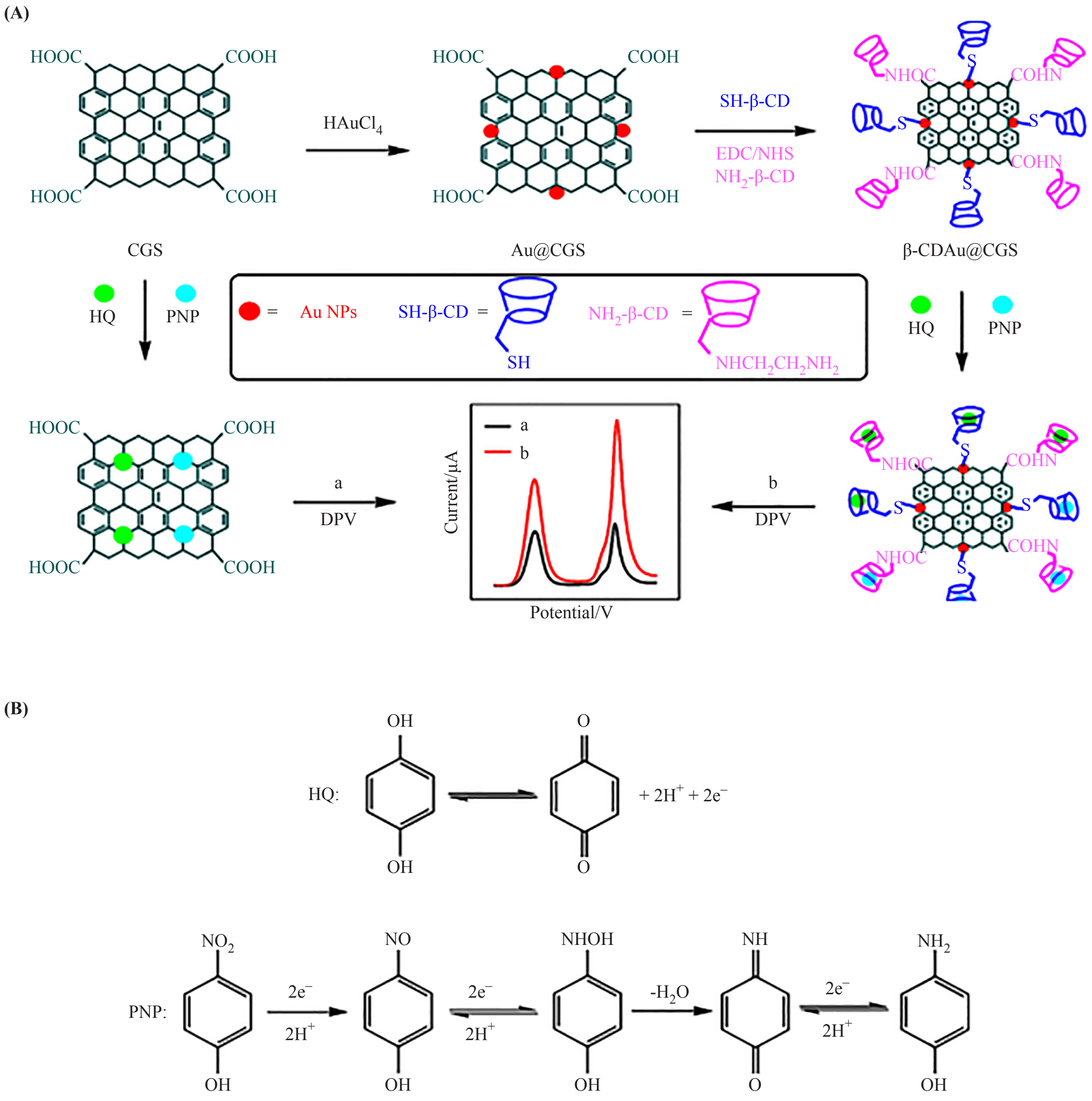

Figure 11. (A) *β*-CD-Au@CGS nanohybrids simultaneous sensing HQ and PNP by an electrochemical strategy. (B) The mechanisms of electron generation for HQ and PNP. Reprinted with permission from ref. 194, copyrights (2014) Elsevier publications

Li et al proposed a newly developed sensor of cyclodextrin functionalized with chitosan-reduced graphene oxide (CD-CS-RGO) for electrochemical utility of o-NPh and p-NPh by use of cyclicvoltammetry techniques [176]. CD-CS-RGO nanocomposite is conducted on GCE to give CD-CS-RGO/GCE sensor in o-NPh and p-NPh simultaneous detection. This CD-CS-RGO hybrid nanocomposite has an existing synergetic effect among CS-RGO and CD and it is feasibly combined to enhance the electrocatalytic reduction of NPhs. CD-CS-RGO nanocomposite also exhibited the electrostatic interaction force among cyclodextrins (CDs) and chitosan. This attraction force has been improved the electrocatalytic determination of o-NPh and p-NPh modified CD-CS-/GCE electrode. CD-CS-RGO/GCE is a satisfactory sensor in the determination of o-NPh and p-NPh with the limits of detection of 0.018 μM (S/N = 3) and 0.016 μM (S/N = 3) respectively. CD-CS-RGO/GCE electrode showed good stability, sensitivity, reproducibility and higher electrochemical detection of o-NPh and p-NPh.

Table 2. Electrochemical sensing of 4-NPh using GCE modified with various nanomaterials

S.NO	Materials	Analytical technique	Limit of detection (μM)	Linear range (μM)	Correlation coefficient (R^2)	pH	Ref.
1	GO	LSV	0.02	0.1-120	0.9975	4.8	46
2	RGO	DPV	42	50-800	0.9942	4.2	81
3	[a]GR/MIP	DPV	0.005	0.01-100, 200-1000	0.9970	4.0	82
4	rGO-AgNPs	SWV	0.0012	0.01-0.1, 0.1-1.0, 1.0 -11.0, 11.0-101.0,	0.998	7.2	83
5	AuNP/RGO	DPV	0.01	0.05-2.0 & 4.0-100	0.9981	5.0	84
6	AuNP/RGO	SWV	0.02	0.05-2.0	0.9961	5.0	84
7	MnO$_2$-RGO	LSV	0.01	0.02-0.5 & 2-180	0.991 & 0.995	7.5	85
8	[b]Gr-Chit/ABPE	LSV	0.08	0.1-20 & 20-80	0.9976	1.0	87
9	[c]EGS	DPV	0.04	0.2-20	0.998	5.6	127
10	[d]ERGO	DPV	0.55	3.3-34.4	0.9952.	7.0	128
11	[e]NMP/Gr	DPV	0.0003	0.001-1.17	0.998	5.0	132
12	NMP/Gr	Amp	0.15	0.50-5.60	0.999	5.0	132
13	N-rGO	LSV	0.007	0.020-0.5	0.9953	6	155
14	[f]PCZ/N-GE	CV	0.062	0.8-20.0	0.9971	4.6	156
15	[g]PDDA-G	LSV	0.02	0.06-110	0.9964	7.0	162
16	[h]AuNPs/TWEEN/GO	Amp	0.078	5-300	0.999	7.4	169
17	[i]m-HAp/ECG	DPV	0.27	0.2-994	0.9913	5.0	172
18	GR-CS	DPV	0.09	0.1-140	0.9891	4.5	179
19	RGO-Ag	Amp	0.114	1-500	0.9981	4.0	181
20	rGO-Ag	Amp	0.32	1-1110	-	6.0	182
21	rGO-Ag	SWV	0.0012	0.1-1.0	0.998	7.2	183
22	AuNP/RGO	DPV	0.01	0.05-2.0	0.9981	6.0	184
23	AuNP/RGO	SWV	0.02	4.0-100	0.9975	6.0	184
24	[j]ERG-AuNP	LSV	0.01	0.036-90	0.9983	4.0	185
25	[k]G-Au 10 %	Amp	0.47	0.47-1075	0.9943	Low pH	186
26	[l]Pd-GA/RGO	SWV	0.0009	0.00002-0.0008	0.9564	7.0	187
27	MnO$_2$-RGO	LSV	0.01	0.02-0.5 & 2-180	0.991 & 0.995	7.5	188
28	αMnO$_2$-RGO	SWV	0.017	1-100	0.9995	7.0	189
29	[m]rGO/SrTiO$_3$	DPV	110	0.3-0.8	-	7.0	190
30	[n]CD-RGO	DPV	50	1000-10000	0.997	4.0	191
31	RGO-CD-CS	DPV	0.016	0.06-0.16 & 5-40	0.9870	5.0	193
32	β-CD-Au@CGS	DPV	0.0038	0.01-5 & 5-200	0.998	6.0	194

[a] Molecularly imprinted graphene (GR/MIP);
[b] Acetylene black paste electrode modified with a graphene-chitosan composite;
[c] Graphene nanosheets (GS);
[d] Electrochemical reduction graphene oxide (ERGO);
[e] N-Methylphenazonium methyl sulfate and graphene;
[f] Polycarbazole (PCZ)/nitrogen-doped graphene (N-GE);
[g] Poly(diallyldimethylammonium chloride) (PDDA) functionalized graphene (PDDA-G) composite film;
[h] Polyoxyethylene sorbitol anhydride monolaurate (TWEEN 20) graphene oxide;
[i] Magnetite-hydroxyapatite (m-HAp) (m-HAp/ECG);
[j] Electrochemically reduced graphene oxide-gold nanoparticles;
[k] Graphene with gold nanoparticles (G-Au 10%);
[l] Pd-gum arabic/reduced graphene oxide (Pd-GA/RGO);
[m] Perovskite (SrTiO$_3$) and reduced graphene oxide (rGO) (rGO/SrTiO$_3$);
[n] β-Cyclodextrin functionalized reduced graphene oxide (RGO-CD-CS).

This sensor is also utilized in the electrochemical detection of o-NPh and p-NPh in environmental samples. Liu et al exhibited the new improvement of a cyclodextrin functionalized graphene nanosheets CD-GNS sensor which is applied for electrochemical detection of o-NPh. CD-GNS nanocomposite was fabricated on a GCE to improve the electrochemical determination of o-NPh. CD-GNS/GCE electrode has mostly contributed to the electrochemical detection of o-NPh because the cyclodextrin is without problems resulted in a massive surface of GO nanosheets. This CD-GNS/GCE sensor confirmed a better detection limit of 0.3 µM (S/N = 3) in addition to proper selectivity, excellent stability and reproducibility for the detection of o-NPh [193].

Xu et al discovered that the synthesis of hydroxypropyl-β-cyclodextrin (HP-β-CD) functionalized with GO modified on GCE enhanced the selectivity and sensitivity for 4-NPh [170]. CD increases the water solubility, chemical-physical properties and improvesthe electrocatalysis with GO. CD-GO nanocomposite is modified with GCE to give CD-GO/GCE for the electrocatalytic reduction of NPh derivatives. CD-GO/GCE electrode results in quick electron transfer and also the fast electrocatalytic activity of 2-NPh due to CD converting properties after functionalization on RGO. The prepared CD-GO/GCE showed good stability, selectivity and sensitivity in the determination of 2-NPh with cyclicvoltammetry methods of o-NPh with the detection limit of 1×10^{-8} M (S/N = 3). CD-GO/GCE has been tested for anti-interference in the presence of cresol, o-chlorophenol, 2, 4, 6-trichlorophenol, o-aminophenol and catechol.

Yang et al reported a green approach of AuNPs bound on carboxylic graphene nanosheets (AuNPs-CGS) without an external reducing agent [194]. This AuNPs-CGS nanocompsoite is similarly modified with CDs to give β-CD-Au@CGS nanocompsite. The CDs with thiol and amine functional groups easily forms an Au@CGS nanocomposite. β-CD-Au@CGS/GCE nanocompsite is efficiently coated on GCE to offer β-CD-Au@CGS/GCE which is applied for simultaneous electrochemical detection of 4-NPh and hydrqunione as shown in Figure 11. The β-CD-Au@CGS/GCE delivered a low detection limit of 4-NP and HQ are 6.5 nM and 3.8 nM (S/N = 3), respectively. β-CD-Au@CGS/GCE sensor offers advantages such as high surface area, excellent conductivity, selectivity, high-host-guest molecular capability and anti-interference. Table 2 shows the electrochemical sensing of 4-NPh using GCE modified with various nanomaterials.

14. Conclusions and future outlook

In this review the recently published literature for the electrocatalytic application of 4-NPh using graphene based nanocomposite has been discussed. The electrochemical determination of 4-NPh has been achieved by cyclicvoltammetry methods and enhancement of sensitivity and selectivity has been observed with GO nanocomposites modified on GCE. Although, GO materials showed a low detection limit in the electrochemical sensing of 4-NPh by using modified GCE with electrochemical techniques method. Graphene based nanocomposites have delivered the good interaction between the modified GCE and 4-NPh, stability of the modified electrode, reproducibility of the modified on GCE electrode, selectivity and sensitivity of the modified GCE electrode and finally modified electrode to apply for electrochemical sensing of other interference such as HQ, TNP, TNT, APh, o-NPh. The aim of the review was to show that, Graphene nanocomposite materials are utilized for the electrochemical determination of 4-NPh with selectivity and sensitivity toward the 4-NPh in environmental samples. A variety of GO based nanocomposites have been used for the electrochemical application of 4-NPh and the GO based nanomaterials such GO and rGO. Metal nanoparticles with GO, Metal oxide with GO materials, polymer with GO, N-doped graphene oxide materials, cyclodextrin functionalized with graphene oxide. These materials have developed the new modified sensor to increase the electrochemical determination of 4-NPh and long time stability, sensitivity, selectivity and reproducibility. For the aim of future work, more novel GO based materials are needed for the development of electrochemical detection of 4-NPh sensing with good sensitivity and selectivity for sensors in practical applications. These materials can result in a good modified GCE electrode and good sensor system for the determination of 4-NPh in the near future.

Acknowledgements

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