

# A Review: Advanced Electrochemical Detection Using Nanomaterials And Conducting Polymers As Sensing Probes

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*Abstract: The implication of nanomaterials in electroanalysis is due to very specific properties of nanomaterials, exhibited only at the nanoscale. These include enhanced diffusion based on convergent rather than linear diffusion, high active surface area, improved selectivity, catalytic activity, higher signal-to-noise ratio and unique optical properties. The use of nanomaterials also grants control over the local microenvironment. This can be vastly profitable while incorporating sensitive or biological material into a system. These exclusive possessions make nanomaterials supremely suited for electroanalytical applications. Improved convergent mass transport to nanoelectrodes assists the study of faster electrochemical processes. At the nanoscale, crystal planes can be exposed which are not accessible at the macroscale, in turn giving rise to enhanced current responses and catalysis. In terms of construction of nanomaterial based electrodes, costs can be reduced compared with the costs for manufacture of conventional macroelectrodes as only a fraction of the nanotubes is needed. Conducting polymers (CPs) are a class of polymeric materials that have attracted considerable interest because of their unique electronic, chemical and biochemical properties, making them suitable for numerous applications such as energy storage, memory devices, chemical sensors, and in electrocatalysis. Therefore, the electroanalytical application of such nanomaterials and conducting polymers has been found to be quite extensive which clearly indicate that there is a great deal of scope for further study in this area of electrochemistry.*

**Keywords:** Nanoparticles; Conducting Polymers; Electrochemical Detection; Sensors; Biological Fluids

## I. INTRODUCTION

Nanomaterials based sensing strategies offer a number of advantages over traditional molecular diagnostic and cellular analysis techniques, including signal amplification, improved sensitivity and speed, and versatile sensing schemes that can be tailored to a desired target. In this article, we highlight a variety of nanomaterials based sensors, and discuss the advantages of different nanomaterials compositions and probes of various classes. Recent advances in the development of electrochemical sensors are covered, with special regard to breakthroughs in sensitivity. The works reviewed herein emphasize the improvements that nanomaterials offer in the area of diagnostic assays and make a solid case for further advancement in the field of clinical and pharmaceutical industry.

## II. CARBON NANOPARTICLES

The subtle electronic properties of carbon nanotubes suggest that they have the ability to promote electron transfer reactions when used as an electrode in electrochemical reaction. This provides a new application in the electrode surface modification to design new electrochemical sensors and novel electrocatalytic materials<sup>1</sup>. As a new type of carbonaceous materials, carbon nanotubes (CNTs) possess some unique properties that are much different from the conventional scaled materials. Such properties include well-defined tubular structure of nanosizes, functional surfaces, modifiable ends and sidewalls, excellent chemical stability, strong electrocatalytic activity and excellent biocompatibility<sup>2</sup>. The three dimensional special architecture of the CNTs can lead to a high loading of electrocatalysis or biomaterial onto the solid substrate and thus can enhance the efficiency for

(bio) electrocatalysis. As tubular nanomaterials, the key advantages of CNTs are their small diameter and huge length to diameter ratio that allows them to be used as molecular wires for facilitating electron transfer between biomolecules and electrodes with ultra-sensitivity. These special properties foresee their promising applications in electroanalytical chemistry and make CNTs ideal candidates for constructing sensors with high performances. Both single wall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs) have been widely used in biosensing.

Peng et al. suggested that the intrinsic electronic properties of carbon nanotubes remain unaffected even when they are in direct contact with water by an *ab initio* study of water adsorbed on single walled carbon nanotubes and shows purely repulsive interaction without any charge transfer. This study revealed new avenues for application of carbon nanotubes modified sensors in aqueous medium. The modification of electrodes with CNTs has been observed to apparently improve the response of substrates from small  $H_2O_2$  molecules to huge redox proteins. The electron transfer and the direct electrochemistry of redox proteins at CNTs based electrochemical sensors are well reported. Excellent improvements in the electrochemical behavior of biologically important compounds such as dopamine and ascorbic acid, quercetin and rutine, tryptophan, tyrosine, procaine and metformine have been demonstrated at CNTs modified electrodes. CNTs modified electrodes were also utilized to determine hemoglobin in bovine blood<sup>15</sup>. Multi walled carbon nanotubes modified carbon paste electrode (MWNT/CPE) was used to study the electrochemical behavior of bergenin. The modified electrode showed excellent electrocatalytic activity in lowering the anodic over potential and remarkable enhancement in anodic peak current of bergenin as compared to the electrochemical performance obtained at CPE. Conventional electrodes are not suitable for the determination of catecholamines; epinephrine (EP) and norepinephrine (NE) due to the interference from ascorbic acid (AA) and uric acid (UA), which are co-existed in a real sample at 100 times higher concentration than EP and NE. These compounds can be easily oxidized at the similar potential of EP and NE and thus always interfere with EP and NE detection. Goyal et al. developed a MWNT modified EPPGE which can be used to monitor simultaneously different biomolecules. Ascorbic acid, dopamine, norepinephrine and uric acid showed oxidation peaks at -50, 80, 204 and 260 mV and do not interfere with the oxidation of epinephrine, confirming thereby that this voltammetric sensor is specific for the oxidation of epinephrine at 150 mV. The proposed sensor has also been utilized for the determination of epinephrine in human urine and plasma samples of smokers and non-smokers. Hydrogen peroxide ( $H_2O_2$ ) is a product of several biological, enzyme-catalyzed reactions. The detection of  $H_2O_2$  plays an important role in food industry, environmental protection, and in medical diagnostics. For the sensitive detection of  $H_2O_2$ , Tkac and Ruzgas have used an electrode modified with SWNT. The sensitivity was highly dependent on the dispersing agent in the organic solvents and charging status of polymers (e.g. Nafion and chitosan). It is found that the dispersion of both polymers is highly stable but the SWNT in the chitosan dispersion showed higher sensitivity for  $H_2O_2$  as compared to that in

Nafion. The single walled carbon nanotube modified gold detector for microchip capillary electrophoresis (CE) has been constructed and successfully used for the detection of *p*-aminophenol, *o*-aminophenol, dopamine and catechol. SWNT modified glucose biosensors exhibited a wider dynamic range and greater sensitivity in glucose determination. Rutin is a kind of flavonoid glycoside that has a wide range of physiological activities such as antiinflammatory, antitumor, and antibacterial. CNT modified electrodes have been successfully used for the determination of rutin. A gold electrode modified with SWNT was fabricated by Zeng et al., to investigate the voltammetric behavior of rutin. The anodic ( $E_{pa}$ ) and cathodic peak potentials ( $E_{pc}$ ) are 0.375 V and 0.328 V (vs. SCE), respectively, and the ratio of  $i_{pa}/i_{pc}$  is about 1, indicating that the electrode reaction is almost reversible under this condition. The linear range from 20 nM to 5.0  $\mu$ M and the detection limit of 10 nM were determined. The method can be applied to the determination of rutin medicinal samples. Based on the interaction of hemoglobin with rutin, this procedure can also be used for the indirect determination of hemoglobin. A nanocomposite of poly- Nile blue with SWNT modified glassy carbon demonstrated the ability to electrocatalyze the oxidation of NADPH at a very low potential (-80 mV versus SCE) with a substantial decrease in the overpotential by more than 700 mV as compared with the bare GCE.

Goyal et al. group is also actively studying the electrochemical determination of variety of biomolecules and drugs using CNT modified electrodes. Pyrolytic graphite electrode (PGE) has been explored as a substrate for the surface modification. The two planes of PGE namely edge plane (EPPGE) and basal plane (BPPGE) were modified with single-wall carbon nanotubes (SWNT) and were used as a sensor to determine triamcinolone, abused by athletes for doping. A comparison of the voltammetric behavior between SWNT modified PGE and fullerene -  $C_{60}$ -modified EPPGE indicated that SWNT modified EPPGE is more sensitive. The method was applied for the determination of triamcinolone in several commercially available pharmaceuticals and real urine samples obtained from patients undergoing pharmacological treatment with triamcinolone. A comparison of square wave voltammograms observed for triamcinolone at different electrodes is presented in Fig.1. SWNT appear to be a better surface modifier in comparison to fullerene for the reduction of triamcinolone, as it accelerates the rate of electron transfer faster.

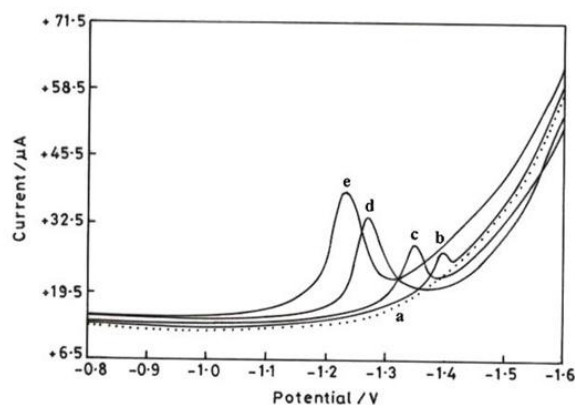


Figure 1: A comparison of square-wave voltammograms of 10 nM triamcinolone at pH 7.2 at bare BPPGE (b), bare EPPGE (c), fullerene modified EPPGE (d) and SWNT modified EPPGE (e). (a) is the background PBS (pH 7.2) at SWNT/EPPGE

Goyal et al. recommended that the SWNT/EPPGE showed great improvements in voltammetric response of guanine and 8-hydroxyguanine in terms of yields of large peak currents and lower peak potential as compared to bare EPPGE. Fig. 2 indicates that at bare EPPGE the oxidation of guanine and 8-hydroxyguanine occurs with broad peaks at 640 and 452 mV, respectively. After the modification, under the identical conditions the peak potential shifted negatively and oxidation occurred with well-defined peaks at 556 and 360 mV for guanine and 8-hydroxyguanine, respectively along with substantial increase in peak current.

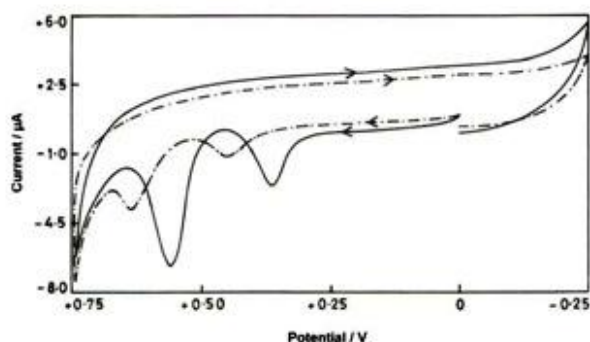


Figure 2: Cyclic voltammograms of homogeneous solution of guanine and 8-hydroxyguanine in PBS of pH 7.2 using (a) bare edge plane PGE (---) and (b) SWNT modified EPPGE (—) at scan rate of 20 mV/s

Two distinct surface regions exist in carbon nanotubes (CNTs): the sidewalls and the ends. Since carbon nanotubes can be seen as the graphene sheets rolled into tubes, the electrochemical properties of carbon nanotubes are comparable to the basal planes of pyrolytic graphite (BPPG). For intact carbon nanotubes, the defect-free structure makes the whole tubes possess almost the same properties to that of BPPG except that the cap regions may be more reactive due to the much higher curve strain than the sidewall. The opening of the ends by physical/chemical treatments on carbon nanotubes produces a variety of oxygen-containing groups, which possess the properties similar to the edge planes of PGE<sup>41</sup>. Due to the simple and well-defined responses at carbon materials, the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple has been widely used<sup>42</sup> to characterize the surface properties of all kinds of carbon electrodes (Fig. 3). Similarly, the electrochemical properties of carbon nanotube based electrodes are generally investigated by  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  as the probe. The electrochemical behaviour of aligned bundles of carbon nanotubes with other carbon electrodes of similar structures was compared by Nugent et al. The results indicated that  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  showed an ideal redox peak separation of 59 mV at the aligned multi-walled carbon nanotubes. In comparison, they reported  $\Delta E_p$  of more than 100 mV and 700 mV for the basal planes of highly oriented pyrolytic graphite (HOPG) with and without electrochemical pretreatments, respectively. In contrast to the ideal response reported by Nugent et al., Li et al. observed much

larger  $\Delta E_p$  at single-walled carbon nanotube modified electrode ( $\Delta E_p = 94$  mV). At aligned MWNT with heat pretreatment to remove impurities like amorphous carbon,  $\Delta E_p$  was observed 228 mV. Particularly, for aligned MWNT, the apparent electron transfer rate was found to correlate with both the area of the exposed sidewalls (with graphite basal-plane-like properties) and the density of graphite edge-plane-like defects. They attributed the small  $\Delta E_p$  at SWNTs which promoted electron transfer by the oxygen-containing defects produced during the acid purification step. In a word, the intact CNT sidewalls resemble the basal planes of pyrolytic graphite and can be regarded electrochemically inert to electroactive species. The apparent improved electron transfer at the intact nanotube sidewalls is attributed to the higher stains than the basal planes. As for the opened caps, the presence of defects and oxygen-containing functional groups make them possess similar electrochemical properties to those of edge planes of pyrolytic graphite. The introduction of edge-like defect sites and oxygen-containing functional groups at both the caps and the sidewalls by chemical or physical treatments can significantly improve the electrochemical properties of CNTs by changing the electronic structures, the surface states and the wet ability of the sidewall, reflected by the apparently facilitated electron transfer kinetics.

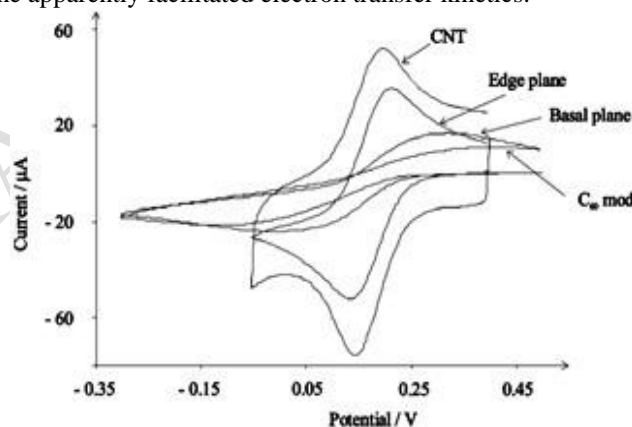


Figure 3: Cyclic voltammograms for the reduction of 1 mM ferricyanide for different carbon electrodes at a scan rate of 100 mV s<sup>-1</sup>

Fullerene science is one of the fastest growing areas of research in chemistry, physics, and material science. One imperative field of their application is their use as mediators in electrochemistry for the chemical modification of electrodes in electrocatalysis. Fullerene  $\text{C}_{60}$  or  $\text{C}_{70}$  modified electrodes catalyze the redox reaction of variety of compounds due to the formation of more conducting  $\text{C}_{60}^{n-}$  species during partial reduction of  $\text{C}_{60}$ , which help electron transfer at the interface<sup>44, 45</sup>. Fullerene anions (reduced fullerene) abstract proton from biomolecules and have some special properties like nano size and higher surface area to volume ratio. A very interesting feature of the partial reduction of fullerene films in aqueous solutions is the proposed 'sandwich like' reduction. Partially reduced fullerene films have a structure with a polar inner and outer surface, while the inside is non polar. The structure very much resembles to a biological membrane, thus raising the possibility of using fullerene as solid state modifiers to study the electrochemistry of biomolecules<sup>46</sup>. Therefore, fullerene modified electrodes meet the conditions essentially required

for the analysis of biomolecules which consist of excellent reproducibility, high sensitivity, wide potential range and high stability in biological samples. The performance of fullerene – C<sub>60</sub> – modified electrodes has been reported to produce electrocatalytic responses compared to the underlying electrode for certain target analytes. Jehoulet et al. demonstrated the formation of C<sub>60</sub> film casted on an electrode surface by evaporation of fullerene solutions unveiled the possibility to study the detailed aspects of its electrochemistry. Szucs and co-workers explored gold surfaces for the electrochemical determination of cytochrome c. Further, the electrochemical response of cytochrome c was determined by Csiszar et al. using fullerene C<sub>60</sub> modified electrodes with optimum results. Tan, Bond and co-workers reported the electrochemical oxidation of L-cysteine in aqueous solution using C<sub>60</sub>-modified glassy carbon electrode. Goyal et al. reported the electrochemical oxidation of uric acid to be mediated by C<sub>60</sub> supported on glassy carbon electrodes. The overlapping voltammetric response of uric acid and ascorbic acid observed at the bare glassy carbon electrode being resolved into two well-defined voltammetric peaks with a potential difference of ~150 mV facilitated through the introduction of C<sub>60</sub> on the glassy carbon electrode surface. Also, the same group further studied the effect of surface modification by C<sub>60</sub> for the voltammetric determination of various biomolecules and drugs and reported that the use of C<sub>60</sub> modified electrodes decreases the peak potential and increases the peak current alongwith improving detection limit and sensitivity. The unique structure of C<sub>60</sub> has a distinct lack of edge plane like- sites/defects consequently the origin of the reported electrocatalysis is quite curious. The elegant work by Compton and co-workers has clearly indicated that the origin of the electro-catalytic response observed at C<sub>60</sub> modified carbon electrodes as reported by Tan, Bond and co-workers for the electrocatalytic detection of cysteine<sup>51</sup> is unambiguously due to graphite impurities in C<sub>60</sub>. Recently, the electrocatalytic detection of adenine and guanine, nandrolone, adenosine and guanosine and most recently, salbutamol and the determination of dopamine in the presence of ascorbic acid<sup>61</sup> have been reported using C<sub>60</sub> – modified electrodes. The authors of these reports suggested that the observed electrocatalytic activity is due to the partially reduced conductive C<sub>60</sub> film rather than graphite impurities. The reduction of C<sub>60</sub> films in aqueous media is in fact the electrochemically reversible reduction of adventitious C<sub>60</sub>O<sub>n</sub>, with subsequent rapid loss of “O<sub>2</sub><sup>•-</sup>” in an irreversible chemical step. There is no evidence that C<sub>60</sub> itself is reduced within the potential window of aqueous electrolytes. In another attempt, in the case of the target analyte nandrolone, Goyal and co-workers have carefully examined the effect of metallic impurities in the C<sub>60</sub> and they found that the removal of embedded metals from fullerene shifts the peak potential of nandrolone to more positive potentials and peak current decreases as shown in Table 1. Thus, the untreated fullerene modified electrode exhibits enhanced catalytic effect as compared to the acid purified and super-purified C<sub>60</sub> modified electrodes.

Sample	Metallic content in (%)				Nandrolone	
	Fe	Cu	Co	Ni	E <sub>p</sub> (mV)	i <sub>p</sub> (μA)
Untreated fullerene	0.416	0.191	0.007	0.392	456	11.7
Purified fullerene	0.162	0.164	0.001	0.263	492	7.25
Super-purified fullerene	0.099	0.071	0.001	0.086	548	5.43

Table 1: Effect of metallic contents of fullerene on peak potential and peak current of nandrolone in phosphate buffer of pH 7.2

Although, the origin of the electrocatalysis has always been attributed due to partially reduced conductive C<sub>60</sub> film but recent reports have indicated that this is not the only reason. The presence of graphite impurities, metal impurities and the pretreatment employed may all be the origin or contribute significantly to the observed electrocatalysis at C<sub>60</sub> – modified electrodes depending on the experimental parameters, chosen not only during the electrochemical measurements, but also during the synthesis of fullerenes. It is likely that other over-looked parameters may also contribute to the electrocatalytic effect of C<sub>60</sub> modified electrodes and thus it is recommended that control experiments should be performed before electrocatalysis of C<sub>60</sub> modified electrodes is claimed. It must also be realized that it is practically impossible to get 100% pure fullerenes without breaking the structure as embedded metals in the cavities cannot be removed.

### III. METAL NANOPARTICLES

Metal nanoparticles (NP) have become one of the most emerging materials which have found broad applications in different kinds of electro analytical methods and can be used to construct novel and improved sensing devices particularly electrochemical sensors and biosensors. Owing to their small size (in order of 1-100 nm) metal nanoparticles exhibit unique chemical, physical and electronic properties. They can absorb biomolecules strongly and play an important role in the modification of electrodes to improve their electrocatalytic activities. Metal nanoparticles increase electrochemical activities as they exhibit higher catalytic efficiency per gram than the larger materials and reveal good performance, enhancement of mass transport and good biocompatibility. Bioactivity of biomolecules is retained onto the surface of nanoparticles due to their biocompatibility. Metal nanomaterials enhance the performance of the biosensors by enlarging the effective surface area. Large surface area of deposited metal nanoparticles permits an improvement of analytical performance in terms of low detection limit and short deposition time. Transition metal nanomaterials possess high catalytic activities and facilitate electron transfer for many electrochemical reactions. A wide variety of metallic nanoparticles have been studied to assess the applications of these materials in electroanalysis. Biosensors incorporating metal nanomaterials, including platinum black, copper, silver palladium and gold have exhibited well biocompatibility and enhanced performance. Nanoparticles of bismuth and iridium have also been synthesized recently.

Campbell et al. studied  $\text{H}_2\text{O}_2$  reduction at a silver nanoparticles (AgNPs) on basal plane pyrolytic graphite electrodes, which has shown that the voltammetric trace for  $\text{H}_2\text{O}_2$  reduction will vary with both nanoparticles size and the extent of surface coverage. A decrease in nanoparticles size causes a negative shift in the peak potential, whereas increasing coverage causes a positive shift. Additionally, nanoparticles size effects have been simulated by Ward -Jones et al. for the anodic stripping voltammetry of various sizes of AgNPs. Theory has been presented for modeling the voltammetry produced from stripping nanoparticles from the surface of an electrode. Radial diffusion and the proximity of the particles to each other were considered in the model. Electrochemical detection of hydrogen peroxide using an edge-plane pyrolytic-graphite electrode, a glassy carbon electrode, and a silver nanoparticle-modified glassy carbon electrode has been reported by Welch et al. As shown in Fig. 4 that in phosphate buffer hydrogen peroxide cannot be detected directly on either the EPPGE or GCE electrodes. However, reduction can be facilitated by modification of the glassy-carbon surface with nanosized silver assemblies.

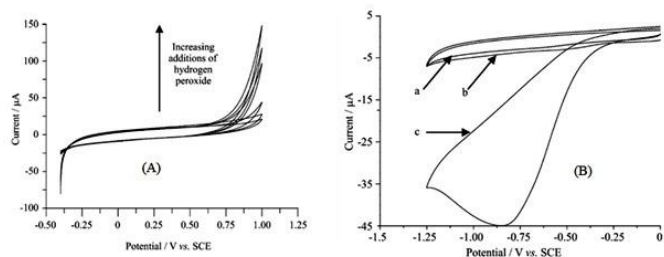


Figure 4: (A) Cyclic voltammograms detailing the response of an edge-plane pyrolytic-graphite electrode to additions of hydrogen peroxide (0, 5, 10, 15, 20 and 25  $\text{mmol L}^{-1}$ ), (B) The voltammetric response of (a) a bare glassy carbon electrode to 1  $\text{mmol L}^{-1}$  hydrogen peroxide, (b) a modified glassy-carbon electrode to blank phosphate buffer and (c) a modified glassy carbon electrode to 1  $\text{mmol L}^{-1}$  hydrogen peroxide in PBS of pH 7.4 at 50  $\text{mVs}^{-1}$ .

Screen-printed electrodes are planar devices with plastic substrates that are coated with layers of electroconductive and insulating inks at controlled thickness. The great versatility of screen-printed electrodes resides in their wide range of possible modifications. Such an electrode modified with silver nanoparticles by using electrochemical deposition has been utilized successfully by Calvo et al. Carbon screen-printed electrodes (CSPE) modified with silver nanoparticles present an interesting alternative in the determination of lamotrigine (LTG) using differential pulse adsorptive stripping voltammetry. The electrodes developed in this work present an environmental-friendly method for the analysis of LTG. The most important advantage is high sensitivity in the determination LTG in real samples. In fact, the detection limit obtained was less than the values found when LTG was measured with carbon and mercury-film carbon screen-printed electrodes.

Electrochemical study of sodium hypochlorite was carried out on dendrimer stabilized gold nano particles modified glassy carbon electrode. Deposition of gold nano particles on the surface of glassy carbon electrode was observed by transmission electron microscopy and X-ray photoelectron spectroscopy. Both anodic and cathodic peak currents were

found to increase after the deposition of these gold nano particles. This indicates that rate of electrolysis of sodium hypochlorite is enhanced by these gold nano particles. Gold nano particles modified glassy carbon electrode has also been used to detect Hg (II) in drinking water, sediments and pharmaceutical preparations by anodic stripping voltammetry. Mercury concentrations in the low range (ng/ml) were easily quantified with high accuracy and precision. Further, gold nano particles were deposited onto the surface of glassy carbon electrode and potential utility of electrode constructed was demonstrated by applying it for the analytical determination of As (III) with low detection limit of 2.5 ppb. Gold nano particles based nanostructured electrode was also developed for detection of ultra trace amount of carcinogenic Cr (VI). As gold is found to be very sensitive towards Cr (VI), it was a promising investigation towards the electrochemical behavior of Cr (VI) and importance of the method was evaluated for detection of Cr (VI) in ground water. Arsenic is highly toxic and exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic, and carcinogenic effects. A novel method for the detection of arsenic (III) in 1 M HCl at a gold nanoparticles modified glassy carbon electrode has been developed. The gold nanoparticles were electrodeposited onto the glassy carbon electrode via a potential step from +1.055 to -0.045 V vs. SCE for 15 s from 0.5 M  $\text{H}_2\text{SO}_4$  containing 0.1 mM  $\text{HAuCl}_4$ . The resulting electrode surfaces were characterized with both atomic force microscopy and cyclic voltammetry. After optimization, a LOD of 0.0096 ppb was obtained with linear sweep voltammetry (LSV). A high sensitivity of 95  $\mu\text{A}/\mu\text{M}$  is obtained using square wave voltammetry (SWV). The limit of detection of 0.0096 ppb and 0.014 ppb are achieved using linear sweep voltammetry (LSV) and square wave voltammetry (SWV), respectively. These results provide the possibility of applying the modified sensor for the detection of arsenic in natural water samples.

Simultaneous determinations of various biomolecules and drugs have vital importance in biomedical research. A gold nanoparticle-modified carbon paste electrode has been used successfully for the simultaneous determination of acetaminophen and atenolol. The modified electrode exhibited electrocatalytic properties toward acetaminophen and atenolol oxidation with a peak potential of 20.0 and 50.0 mV lower than that at the bare carbon paste electrode, respectively. Also, the enhanced peak current response is a clear evidence of the catalytic activity of gold nanoparticles modified carbon paste electrode towards oxidation of acetaminophen and atenolol. The large peak separations obtained using this electrode allows it to simultaneously detect these drugs. Moreover, high selectivity, good sensitivity, low detection limits with the low cost of the sensor, makes this method suitable for accurate determinations in pharmaceutical and clinical preparations. The individual and simultaneous electrochemical determination of various drugs and biomolecules including nandrolone methylprednisolone, atenolol, adenosine and adenosine-5'-triphosphate, 5-hydroxytryptamine and 5-hydroxyindole acetic acid has been successfully performed at gold nanoparticles modified indium tin oxide (NGITO) electrode. The method using NGITO is simple, fast and

accurate and opens new avenues for quick estimation of physiologically important compounds.

Platinum metal is widely used as industrial catalyst and can be found in the catalytic converters of vehicles, to remove pollutants from car exhaust fumes. Platinum is more expensive than both silver and gold; therefore, obvious economical advantages arise from use of platinum nanoparticles (PtNPs). Chang et al.<sup>87</sup> presented a method for the attachment and structural growth of PtNPs on indium tin oxide (ITO). Then, the PtNPs attached ITO (PtNP/ITO) has been applied for the study of electrochemical oxidation of methanol and the results are compared with those of bare ITO and platinum bulk electrodes as presented in Fig. 5.

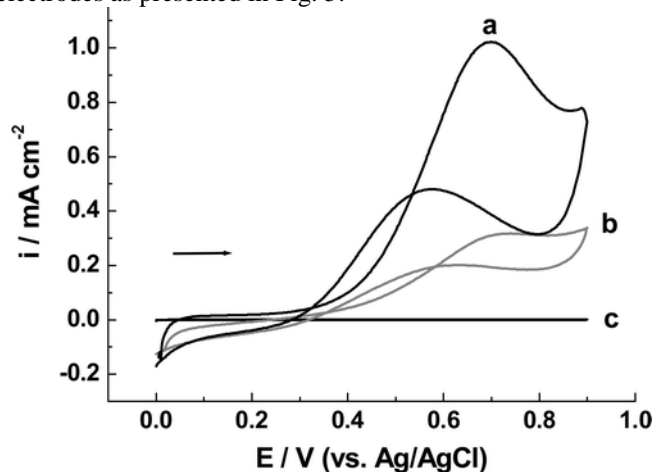


Figure 5: Cyclic voltammograms obtained for 0.1 M methanol oxidation in the N<sub>2</sub>-saturated 0.5 M sulfuric solution recorded with (a) the PtNP/ITO electrode prepared via 24 h of growth, (b) a Pt bulk electrode, and (c) a bare ITO electrode

#### IV. CONDUCTING POLYMERS

Conducting polymers (CPs) are polyconjugated polymers with electronic properties resembling those of metals, while retaining properties of conventional organic polymers. The award of the Nobel Prize in Chemistry in 2000 to H. Shirakawa, A. MacDiarmid and A. Heeger for their pioneering work on conducting polymers widely recognized the importance of these materials has prompted even more vigorous research in the field. Compared to saturated polymers, CPs have a unique electronic structure which is responsible for their electrical conductivity, low ionization potentials and high electron affinity. The most widely investigated conducting polymers include polyaniline, polyphenylenevinylene, polypyrrole and polythiophene as shown in Fig. 6.

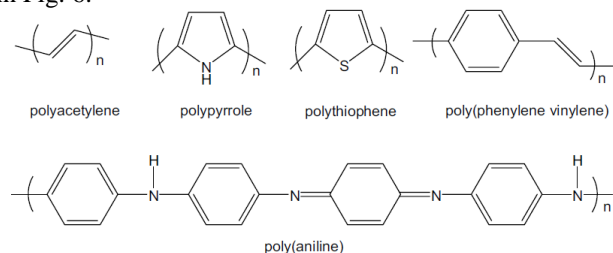


Figure 6: Structures of some of the most common conducting polymers

For CPs in the ground state (insulating or semiconducting state), p-bonds ( $p-p^*$ ) are partially localized due to a phenomenon called the Peierls distortion. During the doping process, the excitation across the  $p-p^*$  band gap creates self-localized excitations of conjugated polymers with localized electronic states in the gap region. These self-localized excitations are called polarons, bipolarons and solitons and underlay electrical conduction in CPs. The unique properties of CPs have led to a variety of applications for these materials, such as light emitting diodes (LEDs) electrochromic materials anti-static coatings solar cells batteries anti-corrosion coatings chemical sensors and biosensors.

In terms of biological applications, electrochemical polymerization is widely used because of several advantages: (i) it is performed at ambient temperatures and microelectrodes or electrodes with a large surface area can be used; (ii) the polymer film formed is confined to the electrode and its shape can thus be controlled by electrode design, while the thickness can be controlled in the nanometer to micrometer range; (iii) the properties of the CP film can be widely modulated by varying electrochemical polymerization conditions. Electrochemical polymerization can be carried out potentiostatically, amperometrically or with potential scanning and the whole process may only take a few seconds. During polymerization, the monomers are oxidized to form radical cations, followed by coupling reactions to form oligomers that eventually lead to deposition of the polymers on the electrode surface. Polypyrrole is one of the most extensively used conducting polymers in biosensor designs due to its good biocompatibility and polymerization at neutral pH. Wang et al. illustrated that short ss-ODN probes could be entrapped in a polypyrrole film as the dopant during film growth and still maintain an affinity for target ODNs. Alocilja et al. reported a DNA sensor for rapid detection of Escherichia coli prepared using same methodology. The recognition element was a 25-base pair oligonucleotide specific for E. coli derived from the uidA gene those codes for the enzyme b-D glucuronidase. A DNA concentration of  $1 \text{ mg mL}^{-1}$  was detected by cyclic voltammetry and the analysis was complete in 15 min. A pulsed amperometric detection of target DNA in PCR amplified amplicons with platinum electrodes modified by single stranded DNA (20 bases) entrapped within polypyrrole has also been reported. The detection time was 30–35 min and the sensor response to a complementary target was higher than for a non-complementary target by a factor of at least 6–8. Komarova et al. prepared ODN-doped PPy sensor films to detect the pathogen Variola major by means of chronoamperometry. It was established that thinner films with smaller or more highly concentrated dopant ions produced stronger amperometric signals. Blocking of the film surface with fragmented half thymus DNA resulted in complete disappearance of the non-specific signal when ultra-thin (Langmuir–Blodgett) films were tested, while the specific signal from complementary ODN remained unaffected. Additionally, lowering the potential during the hybridization reduced the nonspecific signal. Under optimal conditions a detection limit of 1.6 fmol of target ODN in 0.1 mL (16 pM) was achieved. For this type of DNA sensors, the obvious advantages are simplicity and fast detection, however, steric hindrance and poor accessibility of the probe entrapped within

the film to the analyte result in poor hybridization efficiency that greatly limits sensitivity and selectivity. In order to overcome these disadvantages, a variety of functionalized pyrrole monomers have been developed and used for DNA detection. Livache et al. developed a pyrrole monomer bearing an ODN and copolymerized this with pyrrole to realize addressable multiple probe immobilization.

## V. CONCLUSIONS AND FUTURE DEVELOPMENTS

This review discusses the ideology of electrochemical sensors and biosensors based on new engineering materials viz. carbon nanotubes, fullerenes, metal nanoparticles and conducting polymers. Subsequently, recent developments and major strategies for enhancing sensing performance and key challenges and opportunities of these sensors to further development are discussed. Besides a brief exposition of the properties of ionic liquids and their general applications based on these properties, this review focuses on the application of ionic liquids in electroanalytical sensors. New strategies for the synthesis of nanomaterials based sensors are likely to result in new bioelectronic sensing applications. The various conducting polymers used for DNA detection, along with different DNA immobilization and detection methodologies are presented. Current trends in this field and newly developed applications due to advances in nanotechnology are also discussed. Conducting polymer-based electrochemical DNA sensors have shown applicability in a number of areas related to human health such as diagnosis of infectious diseases, genetic mutations, drug discovery, forensics and food technology due to their simplicity and high sensitivity. Accent is given to direct electron-transfer reaction, origin of electrocatalysis effect of nanomaterials/conducting polymers and use of these sensors to determine the level of biomolecules, drugs/doping agents in biological fluids.

The use of nanoparticles in biodiagnostic assays offers potential fast readout and unprecedented sensitivity. The ability to functionalize nanostructured metal oxide-based sensors with the desired groups to bind target biomolecules, and doping these with electronically active materials to obtain enhanced charge transfer, may cover the approaches for innovative methods in sensor development. The synthesis of nanoparticles with various morphologies at the nano-domain level may offer a suitable environment for obtaining the oriented immobilization of desired biomolecules and thereby amplified signals. These nanostructured metal based sensors can be fabricated and tested in desired patterns for the development of functional integrated devices. The interface of nanomaterial based devices could also be used for parallel real-time monitoring of multiple analytes. It will be interesting to focus on new methods for the fabrication of innovative sensors with desired properties for health care and confining different biomolecules by using metal nanomaterials and their nano-structured oxides. This updated review aims to expand on this by covering the most recent trends and advances in the utilization of nanomaterials in electroanalytical techniques. It is anticipated that future efforts will continue to expand the probe/target library of nanoparticles-based assays, investigate

probe interactions towards enhanced specificity and sensitivity.

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