

## Platinum nanocomposites and its applications: A review

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**Abstract.** Platinum is a transition metal that is very resistant to corrosion. It is used as catalyst for converting methyl alcohol to formaldehyde, as catalytic converter in cars, for hydrocracking of heavy oils, in Fuel Cell devices etc. Moreover, Platinum compounds are important ingredient for cancer chemotherapy drugs. The nano forms of Platinum due to its unique physico-chemical properties that are not found in its bulk counterpart, has been found to be of great importance in electronics, optoelectronics, enzyme immobilization etc. The stability of Platinum nanoparticles has supported its use for the development of efficient and durable proton exchange membrane Fuel Cells. The present review concentrates on the use of Platinum conjugated with various metal or compounds, to fabricate nanocomposites, to enhance the efficiency of Platinum nanoparticles. The recent advances in the synthesis methods of different Platinum-based nanocomposites and their applications in Fuel Cell, sensors, bioimaging, light emitting diode, dye sensitized solar cell, hydrogen generation and in biosystems has also been discussed.

**Keywords:** Pt; nanocomposite; electrocatalyst; Pt NP; nanoparticles

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### 1. Introduction

Platinum (Pt) has 78<sup>th</sup> position in the modern periodic table with atomic weight of 195.084; it is a soft, dense, malleable, ductile, highly unreactive, precious, gray-white transition metal that is very resistant to corrosion. It can be found as a free element in alluvial deposits or combined with other elements. Some of the Pt is produced as a by-product of nickel and copper refining (Gouldsmith and Wilson 1963).

Pt possesses extraordinary properties which have been exploited for more than half a decade till now. It is used as a catalyst for various purposes like converting methyl alcohol to formaldehyde, as catalytic converter-a device found in cars which combines carbon monoxide and unburned fuel with oxygen to form carbon dioxide and water vapor. It is also used in many petroleum industries for hydrocracking of heavy oils and in Fuel Cell devices which combine hydrogen and oxygen to produce energy like electricity. Even in electronic industries Pt has been used in production of computer hard disks, thermocouples, optical fibers, LCDs etc. The application does not contain itself to just non-biological things; Pt compounds are important ingredient for cancer chemotherapy drugs such as cisplatin, carboplatin and oxaliplatin that are neutral Pt (II) complexes

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(Chen *et al.* 2013). It is also used for making pacemakers and dental filling. However, high cost and scarcity of Pt in the earth's crust limit its large scale applications globally.

In recent years attention has been diverted to Nanotechnology, especially use of nanoparticles because at nanoscale due to the interface that is not observed in the bulk or individual atoms, they exhibit new and unique properties. Use of nanoparticles of Pt provides increased surface area available for a reaction and also increases the percentage of platinum atoms available for contact with molecules involved in the reaction. Thus helping in use of smaller quantity of Pt that comes at a higher price.

## 2. Pt nano particles

Materials at nano scale are known to exhibit unique physico-chemical properties that are not found in its bulk counterpart. Pt NP due to their catalytic and optoelectronic properties are of interest is regarded as one of the high potential metal nanoparticles (NPs) for many practical applications (Kim *et al.* 2008, Hui *et al.* 2015, Narayanan and Al-sayed 2004, RonenBar-Ziv *et al.* 2015). Many properties of NP are size and structure dependent. Therefore, synthesis of Pt NP of desired size and shape is crucial for its applications. For example use of Pt containing films for enzyme immobilization (Gooding *et al.* 1998), optical applications (Vestberg *et al.* 2006) and catalytic activity (Kreb 1998). Enhanced catalytic activity of PtNPs play an important role in the reduction of pollutant gases exhausted from automobiles (Li *et al.* 2009). The size and shape effect on the catalytic efficiency of Pt NP is anticipated and under investigation, because if equal volume of element and its corresponding NP are considered, the catalytic activity of the NP would be much higher as the surface to volume ratio is very large. The stability of Pt NPs is another factor which is of great importance to the development of efficient and durable proton exchange membrane Fuel Cells (Dobrzanska-Danikiewicz and Kukowiec 2013, Zhang *et al.* 2012). The coalescence of PtNPs is responsible for reduction in the electrochemically active surface area that reduces cell performance (Hummers and Offman 1958). Furthermore, PtNPs is used widely in the electronics industry for the manufacture of conductive thick film circuits and internal electrodes of multilayer ceramic capacitors (Kempegowda *et al.* 2014). Formic acid and methanol are potential in the conversions between chemical energy and electric energy as the chemical fuels. Pt-based electro-catalysts have lowered the chemical barriers for this conversion (Kou *et al.* 2011). Pt has been recognized as an invincible catalyst for the electrochemical hydrogen evolution reaction (HER). Pt shows promising HER activity with very low over potential, small Tafel slope ( $\sim 30 \text{ mV}\cdot\text{dec}^{-1}$ ), and high exchange current density ( $10^{-3} \text{ A}\cdot\text{cm}^{-2}$ ) (Zhang *et al.* 2011). Unfortunately, the large-scale utilization of Pt catalysts in  $\text{H}_2$ -production electrolyzers is seriously hampered by its cost and scarcity. Sabatier's principle suggested (Paola Quaino 2014) a two-step catalytic reaction, passing through an adsorbed intermediate. This has been used to explain the effect of catalyst on hydrogen adsorption reaction. It states that adsorption energy can be either too high (i.e., endothermic process, which would be slow) or too low (i.e., exothermic process where desorption is slow). It is envisaged that at the equilibrium condition free energy for adsorption should be close to zero. Sabatier's concept is not the only method advocated to explain the hydrogen adsorption/desorption by several catalysts. Trasatti (1972) collected many experimental data and constructed a volcano curve for hydrogen evolution. During nineteen seventies, experimental or theoretical data for hydrogen adsorption were not available; hence, Trasatti used the energy of hydride formation instead. In his historic plot the reaction rate is expressed in terms

of the exchange current density (which is proportional to the reaction rate at the equilibrium potential) and is plotted versus the energy of hydride formation ( $\Delta G_H$ ). It is interesting to note that the ascending part of the curve contains mostly the metals like Ti, Pb, Zn, Cu, Au etc and the descending part of the curve contains the oxides of W, Mo, Nb Ta etc. Pt, as expected sits at the top of volcano, because it has lowest exchange current density i.e., at  $\Delta G_{ad} \sim 0$  formation of hydride. This plot gives information about the free energy required for the formation of hydride or for the evolution of hydrogen using different catalyst.

### 3. Platinum nanocomposites

Pt NPs are very promising for many practical applications; however, high cost and scarcity of Pt limit its large scale applications. To overcome this limitation and still be able to harness the incredible properties on Pt-NPs, researcher are trying and have, to some extent, been successful in making nanocomposites, which possess both the properties of individual nano-materials. Even in small quantities of Pt-NPs, the nano-composite exhibits good practical potential. Bar-Ziv *et al.* (2015), showed that methyl radicals react favorably with Pt NP as compared to Au and Ag NP giving a Pt-(CH<sub>3</sub>)<sub>n</sub>. It is reported that the Pt is coated by methyl radicals, which is stable in aqueous solutions. This experiment is carried out because Methyl and Alkyl radicals are important intermediates in heterogeneous catalytic processes, in electrochemical and electrocatalytic processes, CO<sub>2</sub> reduction etc.

In general terms, nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range (Lin *et al.* 2006). These nanocomposites materials have emerged as suitable alternatives to overcome limitations of individual NP and micro-composites. They are reported to be the materials of 21<sup>st</sup> century as they possess the design uniqueness and property combinations. Nanocomposites may offer new technology and business opportunities for all sectors in industry (Liu *et al.* 2010).

In this review we will be discussing about different types of Pt-based nanocomposites, their fabrication, application and the future scope of working with such nanocomposites materials along with some information about its potential use in oil drilling industry.

#### 3.1 Types of Pt nanocomposites

As mentioned above to overcome the limitations due to high cost and scarcity; and still be able to harness the incredible properties on Pt-NPs, researcher are trying and have, to some extent, been successful in making nanocomposites which possess both the properties of individual nano-materials. Even in small quantities of Pt-NPs, the nano-composite exhibits good practical potential. Pt nanocomposites can be categorized into two groups,

- (i) Pt conjugated with Organic material, which contains large number of carbon atoms as either part of the composite itself or as the substrate and
- (ii) Pt conjugated with Inorganic materials (metals or non-metals).

A very brief discussion of fabrication methods and its effect on the structural and functional properties of the nanocomposites is necessary in order to understand its potential application in various aspects of science.

##### 3.1.1 Organic compound conjugated Pt nanocomposites

One of the noticeable advantages of all the organic based Pt nanocomposites is the cost reduction owing to the use of polymers or carbon based matrix which is comparatively cheaper than other counterparts. Other advantages are high dispersion, low agglomeration thus better life and durability and stability. All the properties of Pt, may it be as electrocatalyst for methanol or formic acid oxidation or scavenging reaction oxygen species or as bio-sensor, are exploited even though amount is not more than 10%. This increases the potential application of Pt, which would not have been possible by just using Pt NP due to its scarcity in earth crust. A brief note on fabrication and features of some efforts on fabricating Pt nanocomposites are given forgoing sections,

#### Pt and Carbon Nano Fiber Nanocomposite (Pt/CNF)

Different forms of nano carbons such as Carbon nano fibers (CNF), Carbon nano tubes (CNT), Graphene, Carbon black and Carbon dots (CD) have been widely used in preparation of Pt nanocomposites for various applications.

Pt/CNF nanocomposite is fabricated by decomposition of CO on metal catalyst. Pt is deposited electrochemically onto the CNF. Various microstructures of Carbon Nano Fibers (platelet, fishbone and tube) have been successfully prepared and used for catalytic degradation of Methanol. It was concluded that Pt/CNF having plate like microstructure has very good electrocatalytic property and good stability at room temperature. Both these properties are attributed to the morphology of CNF which has many edge-active carbon atoms on the surface and also to the synergistic effects between CNF and Pt NP.

#### Pt and Carbon Nano Tube Nanocomposite (Pt/CNT)

Pt/CNT nanocomposite was synthesized by depositing Pt on CNT by ultra-sonication and chemical reduction method for its use as low cost cathode in high potential microbial Fuel Cell. The performance of Pt/CNT was judged in terms of power density generation in different concentrations and was found to be better than the cathode comprising of only Pt cathode, which might have been due to better interaction with oxygen in the cathode chamber and high catalytic activity of Pt/CNT for oxygen reduction reaction (Halakoo *et al.* 2015).

#### Pt, Ruthenium and Carbon Nano Tube Nanocomposite (Pt/Ru/CNT)

In a different approach Pt/Ruthenium was synthesized by supercritical fluid (supercritical CO<sub>2</sub>) at very high temperature, pressure condition thus changing the polarities and helping in deposition onto CNT. This Pt/Ru/CNT Nanocomposite was found to be very efficient electrocatalyst for low-temperature Fuel Cell application due to the fabrication method (Lin *et al.* 2006).

#### Pt and Multi Wall Carbon Nano Tube Nanocomposite (Pt/MWCNT)

Pt/MWCNT has been tried by many for different applications (Fig. 1). Using the same method as for the Pt/CNT; Pt/MWCNT was synthesized (Lin *et al.* 2006). For this purpose MWCNTs were synthesized by CVD method and then were functionalized with -COOH, -COH, -CO groups so as to facilitate the attachment of Pt on to them. TEM, HRTEM and XRD characterization of MWCNT showed 3-5 nm diam; Pt NPs were coated onto MWCNT in a wt ratio of 5%. These nanocomposites did not show any tendency to agglomerate. However, they did not report any

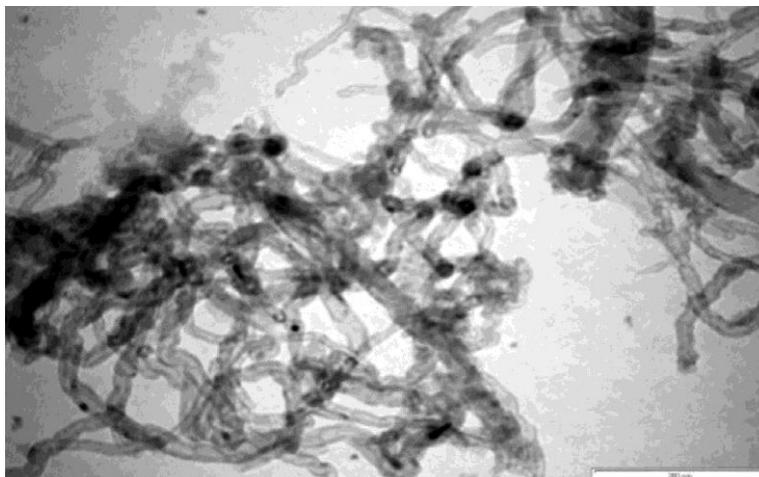


Fig. 1 STEM image of CNT with Pt NP

particular application of Pt/MWCNT.

#### Pt and Graphene Nanocomposite (Pt/Graphene)

Pt/Graphene nanocomposite has been tried by many (Zhang *et al.* 2012) for different purposes such as from graphene oxide from graphite by modified Hummer's method and synthesized Pt by chemical reduction method. For fabrication of Pt/Graphene nanocomposite they used one step microwave assisted method. This nanocomposite was used for detection of non-enzymatic  $H_2O_2$ , it exhibited high sensitivity, good selectivity, wide linear range and low detection limit for amperometric detection of  $H_2O_2$ .

In another attempt (Kempgowda *et al.* 2014) Pt/Graphene nanocomposite was synthesized for sensing arsenic at nanomolar level. Graphene was synthesized by exfoliation of graphite following Hummers method. Graphene was then chemically modified with Pt by reflux method. This nanocomposite was used as electrode which was quite stable and was used for repetitive analysis. It could detect very low amount of Arsenic in water. The reason was attributed to the superior electrocatalytic activity of Pt NP present on graphene layers.

#### Pt, Indium Tin Oxide and Graphene Nanocomposite (Pt /ITO/Graphene)

Pt has been subjected to formation of triple-nanocomposites also to enhance its performance (Kou *et al.* 2011). Fabrication of Pt/Graphene/ITO nanocomposite was done step wise, first ITO nanocrystals were directly synthesized on to the graphene sheet and then Pt NP were deposited on graphene-ITO hybrid by thermal method. Pt NPs were found to be more stable in this composite form. The further DFT calculations suggested that the defects and the functional groups on graphene also contributed to stabilizing the nanocomposite catalyst. When Pt/Graphene/ITO was tested for oxygen reduction potential applications in polymer electrolyte membrane Fuel Cell; it enhance the activity as well as stability.

#### Pt, Gold and Graphene Nanocomposite (Pt /Au/Graphene)

Zhang *et al.* (2011) presented a facile approach to synthesize ~5 nm PtAu alloy NP, in presence of sodium citrate and using poly (diallyldimethylammonium chloride) (PDDA) uniformly dispersed on graphene. According to them PDDA not only acted as “nanoreactors” for synthesis of PtAu alloy NP but also helped in uniform loading of PtAu on graphene. They have tested PtAu/Graphene nanocomposite for successful electrocatalytic oxidation of formic acid, thus suggesting it to be a promising anode electrocatalyst for direct formic acid Fuel Cell. Similar test was done (20) using Pt/Gold/PDDA-Graphene (Pt/Gold/PDDA-G).

#### Pt, Tin Oxide and Carbon (Pt / SnO<sub>2</sub>/C)

In the previous paragraphs it is mentioned that Pt based NP supported on various forms of carbon such as CNF, CNT, Graphene etc are used for Fuel Cell catalysis. Efforts are on to further improve it because such electro-catalysts suffer from the limited electrochemical durability due to inadequate resistance-corrosion of carbon materials (Liu *et al.* 2010). Pt/Tin/Carbon nanocomposite as electrocatalyst was fabricated by Zhang *et al.* (2014) for reduction of oxygen, which showed improved stability and activity. The process involved synthesis of nanocomposite of SnO<sub>2</sub>/Carbon by reflux method. Rather than using nano forms of carbon (CNT, CNF or graphene) they used Vulcan XC-72 carbon black. Then Pt NPs were deposited onto SnO<sub>2</sub>/C nanocomposite. Specific activity of this triple junction nanocatalyst towards oxygen reduction reaction and its electrochemical stability was 2.3 times and twice as compared to other counterparts respectively. This enhanced catalytic activity was attributed by them to three factors (i) electronic effect between Pt and SnO<sub>2</sub> that enabled the increased intrinsic activity of Pt, (ii) repulsion between OH on Pt active sites and on SnO<sub>2</sub> surface, can effectively weaken Pt-O bond, and promote ORR kinetics and (iii) carbon at Pt/SnO<sub>2</sub>/C triple junction can provide effective electron transfer path. Moreover, enhanced stability was due to simultaneous effective anchoring by SnO<sub>2</sub> NP and carbon.

#### Pt, TiO<sub>2</sub> and Carbon Black (Pt/C-Black/ TiO<sub>2</sub>)

Almost similar attempt was made by Sambandam *et al.* (2009) to get superior stability against corrosion under anodic polarization conditions as Fuel Cell electrocatalyst. However, instead of SnO<sub>2</sub> they attached TiO<sub>2</sub> NP. The fabrication was done chemically in a UV-photo-reactor with inert atmosphere.

#### Pt-Tungsten Trioxide and Carbon Black Nanocomposite (Pt/WO<sub>3</sub>/C)

Fabrication was done in 3 steps. First WO<sub>3</sub> was prepared by hydrolysis of tungsten hexachloride (WCl<sub>6</sub>) in dimethylformamide (DMF) and then were adsorbed onto carbon black to get WO<sub>3</sub>/C nanocomposite. Pt NP synthesized separately was annealed along with WO<sub>3</sub>/C nanocomposite at high temperature so as to decorate Pt NP on the WO<sub>3</sub>/C nanocomposite. This composite was tested for its methanol oxidation reaction, which was found to be very high and CO tolerant (Lin *et al.* 2014).

#### Pt-Quantum Dot Nanocomposite (Pt-e QD)

Attempts have been made (Lee *et al.* 2014) to synthesize quantum dot-Pt conjugate, by linking

QD to magnetic nano particle using DNA interaction with metal coordination bonding. Fabrication of Pt and QD was done separately and conjugation was done using linkers. QD-Pt complex was attached to the guanine residue in DNA. They have shown potential of application of QD-Pt(II) in staining chromosome and fluorescence in situ hybridization (FISH), thus being feasible for bio-sensing.

### 3.1.2 Polymer conjugated Pt nanocomposites

Polymers that have been tried for conjugation with Pt to enhance its activity includes Chitosan, Dendrimer, HIV-1-TAT, Poly (n-vinylcarbazole) (PNVC), Poly (o-Anisidine) (POA), Polyaniline, Polydopamine, Polymethylmethacrylate (PMMA), Polypyrrole and Saponin.

#### Chitosan Conjugated Pt Nanocomposites (Pt-CS)

Chitosan (CS) a linear polysaccharide composed of randomly distributed  $\beta$ -linked D-glucosamine and N-acetyl-D-glucosamine; is a strong chelating agent for metals. It has been used (Santos *et al.* 2004, Esumi *et al.* 2003) for stabilization of metal NP. That is why it is useful in developing sensors (Ou *et al.* 2007, Huang and Yang 2003). Moreover, synthesis of Pt-CS is a rather simple process; Pt NP is synthesized from Pt tetrachloride by reducing it with NaBH<sub>4</sub> (sodium borohydrate) in presence of CS to get Pt-CS nanocomposites, where CS molecules were adsorbed on the surface of Pt NP. In another method (Zhu and Ding 2013), Pt-CS composite was synthesized using one step synthesis method by electrodeposition and used as sensor for determining the nitrite.

#### Pt Dendrimer and Gold Nanocomposite

Dendrimers are highly branched spherical molecules of various polymers. They are synthetic polymer. All branches of a dendrimer are facing away from the core. The ends of branches have functional groups. They are different from other linear or branched polymers in their intrinsic viscosity, solubility, poly-valency and reactivity. That is why they are being used as a nano-container for encapsulating metal NP and medicinal drugs, as vector for genetic material, solubility enhancer, and even as a catalyst for chemical reactions. Pt encapsulated in carboxyl-terminated generation 4.5 PAMAM Dendrimer nanocomposite deposited on gold (used as electrode) surface through a self-assembled Cysteamine monolayer was fabricated (Sripada *et al.* 2007) and used for electrolysis. Pt/D is fabricated by chemical reduction method then coated on gold. Coating is done by covalent bonding of dendrimer on cysteamine functionalized gold surface. Novel linking strategy with affordable robust electrochemically active and catalytic thin films makes it a viable proposition.

#### Pt HIV-1-TAT Nanocomposite

TAT is a Human Immunodeficiency Virus (HIV) protein. It is transcriptional activator of HIV (Sakaue *et al.* 2010) and it was observed that Pt NP functionalized with a TAT fusion protein was internalized in both cytosol and mitochondria, where they exerted NADH oxidase activity. They concluded that this nanocomposite with the help of peptides has been envisaged to have a potential application in medicine (i) to improve symptoms caused by mitochondrial complex I defects and (ii) active targeting of this composite to mitochondrial matrix and/or inner membrane will be

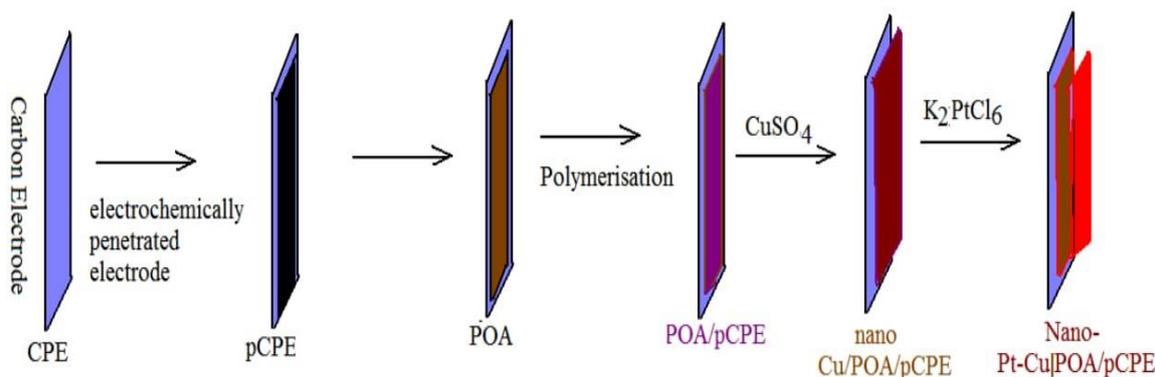


Fig. 2 Steps in preparation of Pt/POA/pCPE composite as mentioned above Polyaniine conjugated Pt NP

helpful in further development of its potency. They used a short peptide (DRTSTWR), which is known to have high affinity to Pt (Sarikaya *et al.* 2003) and a fusion peptide to conjugate the components to fabricate the nanocomposite.

#### Poly (n-vinylcarbazole) (PNVC) conjugated Pt NP

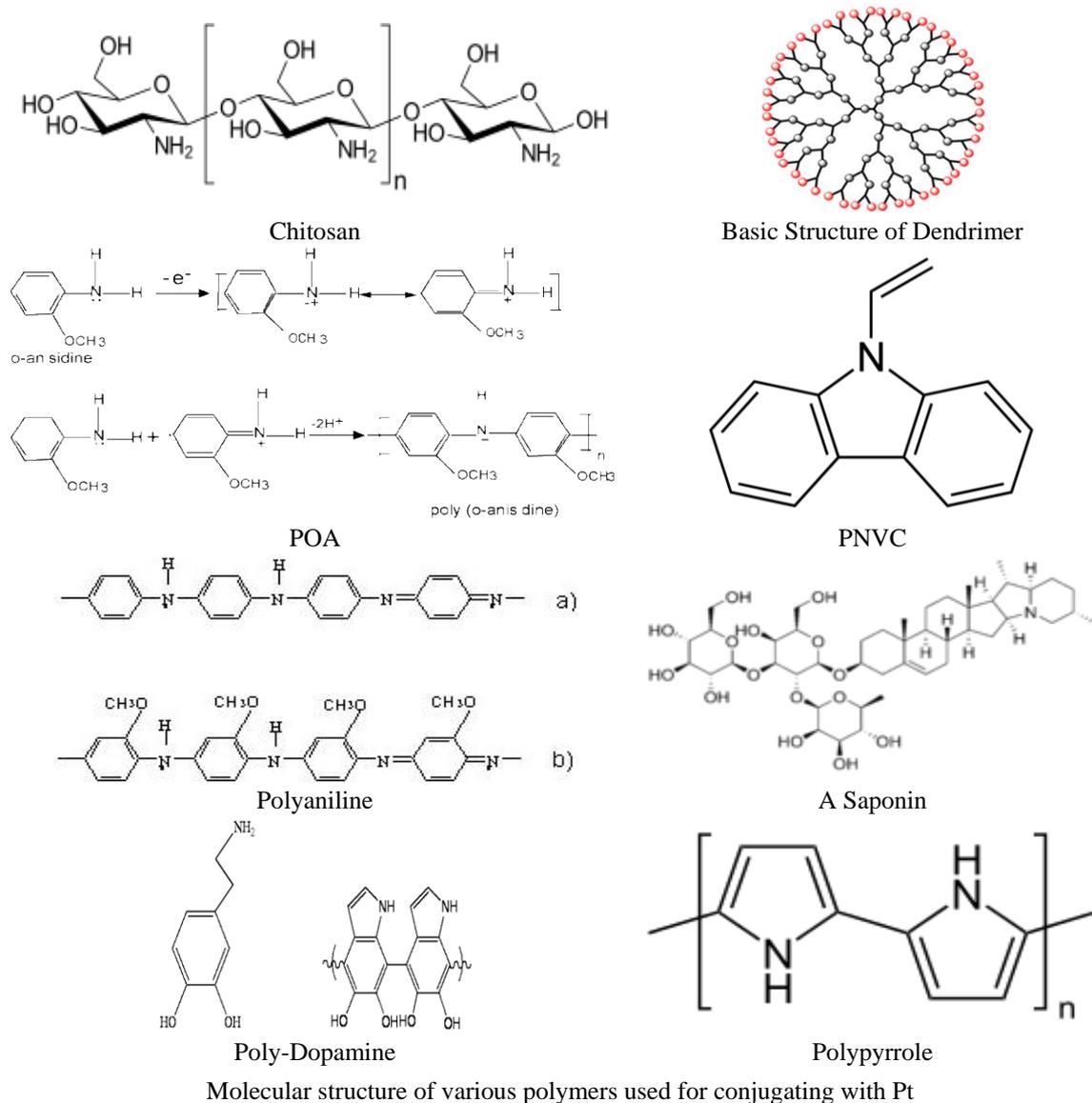
Polymers having specific properties such as  $\pi$  conjugated polymers that have high electrical conductivity and redox potential have been used to encapsulate inorganic NP for various applications ranging from batteries to light emitting devices (Zhou *et al.* 2010). Poly (n-vinylcarbazole) (PNVC) belongs to this family of specialty polymer. It was also fabricated by simple polymerization and redox reaction (Olujinmi *et al.* 2011), which exhibited Pt incorporation into the polymer matrix that had improved thermal stability. This fabrication technique did not require any oxidant because Pt metal precursor ( $\text{H}_2\text{PtCl}_6$ ) served as both oxidizer for polymerization and as a source of Pt that was encapsulated in PNVC.

#### Poly(o-Anisidine)(POA) conjugated Pt NP (Pt-Cu-POA) on Carbon Paste

Hosseini *et al.* (2015) for the first time did electropolymerization of POA on the carbon paste electrode without using any additive and template. They have fabricated Cu-POA composite on to electrochemically pretreated carbon paste electrode. Fabrication of Pt NP was done by first electrochemical reduction then galvanic replacement reaction between  $(\text{PtCl}_6)^{2-}$  and Cu NP. They have reported it to be a cheap and simple method with satisfactory methanol oxidation results. The POA film on carbon paste electrode showed high porosity with good stability. The procedure can be depicted as shown in Fig. 2.

Polyaniline is a conducting polymer. It is formed from the polymerization of aniline monomers. In another recent attempt Polyaniline-Pt nanocomposite having spherical and one dimensional morphology was prepared (Dutt and Siril 2015). Fabrication was done by micro-emulsion method. For fabrication of this composite they used swollen liquid crystals as soft template. The advantage of this method was that they could control the morphology by tuning the mode of mixing of reactant and soft liquid crystal. In this composite Pt NP were embedded in polyaniline matrix.

#### Saponin conjugated Pt NP



Saponin conjugated Pt NP synthesis was reported by Kim *et al.* in BMB Reports, for its use as a treatment for contact hypersensitivity. It is a well-known fact that search for antioxidant to scavenge reactive oxidant species, produced during metabolic disorders such as inflammatory diseases, ageing, cancer etc. has led to discovery of use of metal like Pt. Pt complexes are powerful antioxidant. One of the most common drug used for treatment of cancer is Cisplatin (*Cis*-diamminedichloro-Pt(II)). The Saponin-Pt conjugate was prepared by ethanol reduction of hydrogen hexachloroplatinate ( $H_2PtCl_6$ ).  $NaBH_4$  was used as reducing agent. All the assays conclude that this nano-conjugate is more efficient in scavenging reactive oxygen species.

Pt-Polydopamine @SiO<sub>2</sub> Nanocomposite

A glassy carbon electrode modified by Pt- Polydopamine @SiO<sub>2</sub> nanocomposite is prepared Manokaran *et al.* (2015) for electrochemical detection of Quercetin a flavinol found in many fruits, vegetables and grains. This preparation was done by polymerizing dopamine on SiO<sub>2</sub> and then loading Pt NP using NaBH<sub>4</sub> as reducing agent. Silica was synthesized by sol-gel method and further fabrication of nanocomposite was done using chemical reaction method. This Pt-Polydopamine@SiO<sub>2</sub> modified glassy carbon electrode showed very good selectivity (6.46 $\mu$ A/ $\mu$ M) to Quercetin due to its high synergistic effect, excellent reproducibility and stability.

#### Polypyrrole- Pt NP Multilayer Nanocomposite on ITO

In this novel approach to develop a impedimetric sensor to detect total cholesterol, a Polypyrrole- Pt NP multilayer nanocomposite on ITO electrode is developed by Chauhan *et al.* (2013). Fabrication was done by electropolymerization reaction and chronopotentiometry technique. Pt NPs were deposited between two pyrrole layers on indium tin oxide (ITO) glass plates, by electrochemical process. Thus, preparing a highly electro-active surface area and favorable micro-environment for immobilization of cholesterol esterase enzyme. Impedimetric studies showed excellent performance in terms of linearity (2.5 $\times 10^{-4}$  to 6.5 $\times 10^{-3}$ M/l), sensitivity (196 $\Omega$ /mM/cm<sup>2</sup>), detection limit (2.5 $\times 10^{-4}$ M/l), response time (25 sec), reproducibility and shelf life. This was due to the presence of Pt NP along with polypyrrole. This paper has presented a novel fabrication process and measurement technique, with reusability and minimum interference.

#### 3.1.3 Inorganic material conjugated Pt nanocomposites

##### Pt/TiO<sub>2</sub> Nanocomposite

In an attempt to develop hydrogen production method from water Roy *et al.* (2015) have demonstrated successful use of Pt/TiO<sub>2</sub> nanocomposite as catalyst; because, both the components have exhibited synergistic effect in increasing the hydrogen evolution reaction. Hydrothermal method was used for both synthesis and fabrication of NPs and nanocomposites respectively. Pt NP were then deposited onto faceted TiO<sub>2</sub>.

##### Pt/SiO<sub>2</sub> Nanocomposite

In another effort (Zidki *et al.* 2014) nano silica was used as a support for Pt NP for catalytic reduction of water. Pt NP alone do not catalyze water that is why many have tried to conjugate it with different inorganic material. Moreover, SiO<sub>2</sub>, which is also an inert support, has expressed very positive effect when conjugated with Pt.

##### Pt/Fe<sub>2</sub>O<sub>3</sub> Nanocomposite

Pt/Fe<sub>2</sub>O<sub>3</sub> nanocomposite is used to sense the hydrogen sensing properties of Pt (Pt) and Pt-iron (Pt<sub>3</sub>Fe) alloy NP decorated nitrogen doped graphene (Sripada *et al.* 2015). To synthesize this complex nanocomposite they first coated graphene with the nitrogen anionic polyelectrolyte followed by the pyrolysis in inert atmosphere, this process incorporated the nitrogen functional groups within the graphene matrix. Then the Pt and Pt<sub>3</sub>Fe NP were decorated on nitrogen-doped graphene (NG) by modified polyol reduction technique.

### Pt/MoS<sub>2</sub> Nanocomposite

Though use of ball milling is not very popular method for synthesizing nanocomposites, this technique was used (Lalande *et al.* 2000). Pt powder with powders of MoO<sub>2</sub> and MoO<sub>3</sub> was ball milled to synthesize CO-tolerant nanocomposite anode electrocatalyst for polymer electrolyte membrane Fuel Cells. They have shown that the ball milled Mo Oxides decompose into Mo based species and are leached away during lixiviation step. Their XPS analysis indicated that the Mo remains in the catalysts.

## 4. Various applications of Pt nanocomposites

In above paragraphs, we had a cursory glance at various Pt nanocomposites. These entire nanocomposites are specifically synthesized for a particular application. These nanocomposites have found applications as catalyst for chemical reactions, as catalytic converter in automobile industries, in oil/petroleum industries for hydrocracking of heavy oils, various nanocomposites are used in different types of Fuel Cell devices, which combine hydrogen and oxygen to produce energy like electricity, in electronic industries for production of computer hard disks, thermocouples, optical fibers, LCDs, as chemotherapeutic drugs for cancer treatment, Pt is used to make pacemakers and for dental filling.

### 4.1 Application of Pt composite in energy

Energy requirement of 21<sup>st</sup> century has increased many fold than what is produced to-day. It is also very certain that requirement of energy cannot be met by the fossil fuels as they are depleting very fast. Thus scientists are searching for some renewable sources of energy and amongst them; solar energy and hydrogen energy seems to take prominent place in the energy the requirements. In this article since we are concerned mainly with the application of Pt, hence, we shall restrict our discussions with those areas of energy where Pt and its composites are expected to give the answer to the problems. Some of the sources in Fuel Cells which are being considered are, Fuel Cell operating with hydrogen/oxygen, methanol, formic acid etc. Dye sensitized solar cell (DSSC) also utilizes electrocatalyst to initiate electrochemical reaction. Pt composites are finding some utilities in DSSC also. In the forgoing section we shall therefore, restrict our discussions on application of Pt composite on Fuel Cells operating with methanol, hydrogen and formic acid and its application in solar energy.

#### 4.1.1 DMFC fuel cell (FC)

In a FC there are basically two electrodes, one at which oxidation of fuel like methanol takes place and the other electrode where reduction of oxygen takes place. The cell can be operated either in acidic or alkaline media. The basic reactions which occur with methanol FC at the two electrodes in acidic/alkaline media are,



And in alkaline media,



In DMFC, a three body reaction takes place. At the anode, methanol in presence of water (or hydroxide ions) is oxidized to give  $\text{CO}_2$  (Eqs. (1) and (3)). The electrode must be able to allow the diffusion of methanol into the pores of the anode electrode where water or hydroxide ion should also get diffuse to facilitate the reaction. These two species must come in contact with some electro-catalyst. After the completion of the reaction the site at which these reactions have taken place should be able to expel  $\text{CO}_2$  out of the system. In addition, the electrode must be a good conductor of electricity to allow electron to move to the cathode. The pores of electrode should also be such that it does not allow water to fill all the pores, because if that happens then the system will be short circuited.

Similar is the situation at the cathode. Oxygen should be able to diffuse (Eqs. (2) and (4)) into the cathode where  $\text{H}^+$  ion or  $\text{H}_2\text{O}$  should also be able to diffuse and after the completion of reaction, water or hydroxide ion must diffuse out into the system. This poses a condition that water should not diffuse from the system to the electrode, which means the cathode should be hydrophobic in nature.

Unless these basic requirements are met, the efficiency of the entire process would be poor. Since the reactions are facilitated by the electro-catalyst, the morphology of the catalyst material should be such that it can permit ions to come near its site and at the same time should be able to prevent other electrolyte to diffuse into it. These requirements demands that electro-catalyst should have large surface area, large pore size, pores should be hydrophobic in nature and should be able to help the specific reaction to take place at its site. Catalyst should be stable in acidic media (if FC is to work in acidic media) or in alkaline media (if cell has to operate in alkaline media).

Pt is preferred as an electrode in such type of FC because it helps in dissociative adsorption of fuels like methanol, formic acid. However, there are few major drawbacks in using Pt either as an anode or cathode. Some of them are enumerated here; (i) poor utilization of Pt surface specially with bigger particles, (ii) with methanol or formic acid, Pt is poisoned very easily with a byproduct formed during the oxidation process (Eq. (5)), which makes the efficiency of the process low and (iii) high cost of Pt makes such Fuel Cell unaffordable for terrestrial application.

Several efforts have been made to overcome these difficulties namely (i) an alloy of nano size Pt particles and non-noble metal is made to reduce the quantity of Pt (ii) the alloy of Pt/metal is dispersed over materials which has large surface area and pore size as well as hydrophobic.

In this review it would be difficult to mention all types of nano-Pt alloy with different type of carbon nanomaterials. Hence, efforts are made to discuss few systems to explain the intricacy of the process.

Scientists are engaged in searching for non-noble metals which are stable at the operating potential, and are as good as Pt or palladium. Nano size Pt has also been tried and observed that most appropriate particle size for Pt-based electro-catalysts is in the range of 2-4 nm (Zhou *et al.* 2003, Arenz *et al.* 2005, Bonneman and Richards 2010).

Unfortunately no metals so far have been found to meet these requirements. As a compromise, scientists are searching for a composite of nano size Pt with other metals like Sc, Y, Cr, Mn, Fe, Co, Ni, Cu, Ir, Ru, Rh, Pd, Au,  $\text{MoS}_2$ ,  $\text{WO}_3/\text{C}$ , Cu/poly (o-Anisidine) etc. In order to induce a hydrophobic character and to increase the surface area and pore size along with nano-Pt/metal alloy, carbon nano materials like activated carbon, carbon black, graphitized carbon black, carbon

nanofibers, bamboo-shaped carbon nano fiber arrays (CNFAs), CNTs, graphene, functionalized graphene, GNS-wrapped MWCNT, etc have been used. Poisoning of Pt electrode due to CO formation has been prevented by making the alloy of nano-Pt/C with Ru, Pd, Au, PtSn, Pt-TiO<sub>2</sub>, Pt-WO<sub>3</sub>. But some more research is needed to confirm their application for developing terrestrial Fuel Cell (Lin *et al.* 2014, Zhou *et al.* 2003, Arenz *et al.* 2005, Bonneman and Richards 2010, Wang *et al.* 2004).

It has been demonstrated by Sripada *et al.* (2007) that immobilizing dendrimer-encapsulated Pt NP onto an electrode surface by linking it through a cysteamine monolayer on a gold electrode is useful as electrocatalyst activity for the oxidation of organic fuels like methanol, ethanol and ethylene glycol.

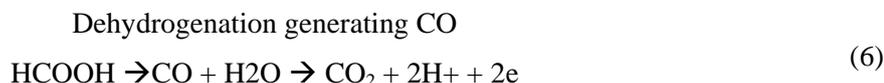
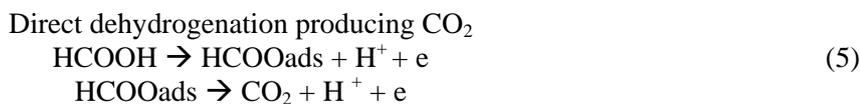
Unfortunately, till date no suitable economical and highly efficient Pt composites have been found, which could give efficiency as high as Pt and affordable cost. As a result search for such requirements is going on. Fortunately it has been established that composite of Pt-metal alloy with carbon materials does show a better performance than pure Pt-carbon composite or Pt-alloy. It is also observed that process of synthesis does affect the efficiency of the electro-catalyst. It is hoped that one day scientists will come up with a suitable synthesis process and composition of Pt (using very less amount of Pt) with carbon and a metal, which will be stable in either acidic or alkaline media and will be of affordable for terrestrial application (Li *et al.* 2009, Lin *et al.* 2006, Sambandam *et al.* 2009, Hossieni *et al.* 2015, Lalande *et al.* 2000, Awasthi *et al.* 2014).

We have not discussed the reduction of oxygen separately, which are the essential part of cathodic reaction of Fuel Cell, mainly because Pt-alloy with carbon composite have also been found to be useful as cathode (Seifitokaldani and Savadogo 2015, Kaewsai *et al.* 2016, Diloyan *et al.* 2012, Narayanmoorthy *et al.* 2014).

Recently application of nano size Pt grown over nano size graphene quantum dot of an average size of 2.79 nm as a cathode for the oxygen reduction process is reported by Yang *et al.* (2013), which suggests that the Pt/G quantum dot catalyst could reduce oxygen at 1.05V, that is 70 mV more positive than Pt/C electrode. The activity of Pt/G quantum dot showed nine times higher specific activity.

#### 4.1.2 Formic acid fuel cell

Formic acid oxidation, like methanol oxidation on Pt follows dual pathways (Maiyalagan *et al.* 2014).



Electrocatalyst has to be developed such that it either does not produce CO which can poison electrocatalyst and hence reduce the efficiency of formic acid oxidation processor or the difference in the window for CO<sub>2</sub> and CO formation are large so that Fuel Cell could be operated at the desired potential without poisoning the catalyst.

Fuel Cell with formic acid has been kept on a low gear because of this fact that most of catalyst get poisoned by CO gas. Some electrocatalyst are developed, which do not either get poisoned or suppresses the formation of CO. We enumerate few examples of such catalysts to explain the

intricacy of the oxidation process. Nanocomposite materials of the Au NP (Au/PDDA-G) and the bimetallic PtAu NP on poly-(diallyldimethylammonium chloride) (PDDA)-modified graphene sheets (PtAu/PDDA-G) are used for the oxidation of formic acid (Yung *et al.* 2015). A high electrocatalytic activity toward formic acid oxidation has been observed by using Graphene Decorated with PtAu Alloy NP (Zhang *et al.* 2011). They reported that this material needs low over potential of 170 as compare to Pt/C of 300 mV. Addition of graphene to Pt complex reduces the formation of CO and hence poisoning of electrode is minimized. Suppression of CO formation is believed to be due to strong interaction between graphene and NP of PtAu alloy.

Pt-Cu/P5CN/GC was used as catalysts for oxidation of both methanol as well as for formic acid in acidic media and observed the formation of CO took place at 350 mV more positive to that potential for direct formic acid oxidation to CO<sub>2</sub> (Li *et al.* 2015). This suggests that this composite is better than graphene Pt/Au nanocomposite investigated earlier (Zhang *et al.* 2011), which give a window difference of only 130 mV as compared to 350 mV. It is suggested that highest electrocatalytic activity for methanol and formic acid oxidation is due to the following factors, (i) P5CN provides an excellent electron and proton conducting polymer pores (ii) help in dispersing Pt/Cu nano clusters on its surface and (iii) the facile shuttle of electronic charges, and large surface area of Pt-Cu nano clusters, exposes the active sites of Pt for showing better catalytic performance. Since the reduction process of oxygen is well established there are some efforts made for such process (Li *et al.* 2015, Zheng *et al.* 2015, 2016, Puthusseri and Ramaprabhu 2016, Oh 2014).

It has also been reported that nanosized Pt/alloy with carbon materials are equally useful for oxygen reduction process (Sui *et al.* 2013). Pt NP impregnated on GNF-DNA composite (Pt/GNF-DNA) is observed to give high electro catalytic activity for oxygen reduction reaction (ORR). Fibrous structure of GNF and its effective functionalization process via  $\pi$ - $\pi$  interaction is believed to give better electroactivity for oxygen reduction process (Wang *et al.* 2016).

Recently a new Pt-free alkaline direct formate Fuel Cell is developed (Huang *et al.* 2016). This cell consists of commercial anion exchange membrane, a nano-structured Pd/C anode and a Fe-Co/C cathode. The cell can operate at room temperature as well as at 60°C. Energy efficiency is with high energy density fuel (4 M KCOOH and 4 M KOH). It is suggested that this can be a new alkaline Pt-free DFFC technology for portable electronic devices laptop, and for remote area power generation. It is suggested that a fuel load with 750 ml in a DFFC device operating at 60°C would be able to produce 90 W h of energy.

Simultaneously a highly dispersed PtCu/C catalyst on a carbon as a precursor is also developed (Huang *et al.* 2016), which showed that the method of preparation of this material has effect on its catalytic property. It is suggested that the method of preparation has effect on surface area of the material. PtCu/C as compared to commercial Pt/C is 2.5 times more effective in the oxidation of formic acid. It is also suggested that it is less poisoned with CO formation.

Pt NP (3 nm) dispersed in CNT at a room-temperature in an ethylene glycol/water mixed solvent (Zheng *et al.* 2016) exhibited excellent methanol oxidation and oxygen reduction activities.

#### 4.1.3 Dye sensitized solar cell (DSSC)

In spite of the fact that efficiency of DSSC solar cell has been achieved in the laboratory to the extent of 12%, this type of cell did not get commercial popularity. The main hurdle in making such commercially viable cells is the stability problem of organic dyes and polymer under the UV component of the solar rays. Scientists are making efforts to find a solution to this problem by searching for Pt based composite. In developing organic photovoltaics, Liao *et al.* synthesized two

organometallic alternating conjugated polymers, (i) TPT–TPyPt and TPT–TIqPt, consisting of indacenodithiophene (thiophene/phenylene/thiophene; TPT) and (ii) cyclometalated Pt (II) moieties. They compared their photovoltaic properties and reported that the absorption bands of the metal-based polymers significantly shifted to red as compared metal free polymers. They fabricated electrode for OPVs by incorporating blends of these polymers and (6,6)-phenyl-C<sub>71</sub>-butyric acid methyl ester and obtained a power conversion efficiency of 2.9% with short-circuit current of 7.7 mA/cm<sup>2</sup> and open circuit potential of 0.78 V (Liao *et al.* 2013). Six new solution process with Pt (II) acetylide donor-acceptor (D-A) triads end-capped by 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DTBT) have been synthesized. These materials show absorption in 400 and 700 nm. An organic photovoltaic cell was developed showing efficiency of 1.46% with the open-circuit voltage ( $V_{oc}$ ) of 0.70 V, short-circuit current density ( $J_{sc}$ ) of 6.17 mA cm<sup>-2</sup> (Liu *et al.* 2016, Zhan *et al.* 2011, Li *et al.* 2011).

The effects of size of carbon black–supported Pt NP (CB/PtNPs) on the reduction of triiodide ions (I<sub>3</sub><sup>-</sup>) in a dye sensitized solar cell were observed by Yeh *et al.* (2015) and they reported that 4nm size gave the best electrocatalytic effect.

#### 4.2 Application of Pt-nanocomposites as sensor

Sensors are required to detect the presence of toxic chemicals, sugar level in blood/urine, cholesterol level, Quercetin level in blood, H<sub>2</sub>O<sub>2</sub>, Nitrite, CO, laughing gas etc. Sensors should also be economical as well as detect the chemicals to its lowest concentration and quickly. Unfortunately for each type of requirements, specific type of sensors is developed. The basic principle on which sensors work is the exploitation of the chemical properties of materials to be detected and physical changes occurring with sensing material, which causes a specific change in the characteristic properties of sensing material. For example, when the material is adsorbed on the sensing material, it changes its electrical resistance. Thus it may be possible to establish a relationship between the resistance and the quantity of material adsorbed on the sensing material. In some cases, it is possible to quantitatively measure the magnitude of the anodic or cathodic current produced when sensor on to which material in question is adsorbed and is put under some specific d.c. potential. This technique is known as cyclic voltametry or chronopotentiometry. If material to be detected fluoresces under some specific light, then by measuring the magnitude of fluorescence peak, the quantity of material adsorbed on the sensor is detected. Like this there are many physical properties which are measured and material present on the sensor is detected.

Research is done to find out physical properties of the material in question which should be measured and which gives the satisfactory change with the least amount of the material. Therefore, the sensors have three following components, (i) base substrate over which the sensor is kept, (ii) carbon material, which is inactive but has large surface area so that material in question can be adsorbed in large quantity and (iii) finally the active electrocatalyst kept over the these materials that can show large variation in its physical properties by adsorbing least amount of material in question.

Noble metal NP especially Pt nanoparticle-attached surfaces has been utilized as a sensor materials for many chemicals such as hydrogen peroxide, nitrite, arsenic etc owing to their extraordinary catalytic activities. Several analytical techniques like spectrophotometry, chemiluminescence, cyclic voltammety, amperometric technique have been utilized to measure the presence of material in the solution. Enzyme- and non-enzymatic based electrochemical sensors have also drawn interest to detect material due to their high sensitivity and fast response

Table 1 Pt nanocomposites used as sensors for different materials and their sensitivity

COMPOSITION OF SENSOR	TO DETECT	DETECTION LIMIT ( $\mu\text{M}$ )	REFERENCE
Se/Pt nanocomposites	$\text{H}_2\text{O}_2$	3.1	Li <i>et al.</i> (2010)
Pt NP/ordered mesoporous carbon nanocomposite	$\text{H}_2\text{O}_2$	1.2	Bo <i>et al.</i> (2010)
Pt nanoparticle-loaded carbon nanofiber electrode	$\text{H}_2\text{O}_2$	0.6	Liu <i>et al.</i> (2011)
Pt/polypyrrole hybrid hollow microspheres	$\text{H}_2\text{O}_2$	1.2	Bian <i>et al.</i> (2010)
Mesoporous Pt Microelectrodes	$\text{H}_2\text{O}_2$	4.5	Evans <i>et al.</i> (2002)
Pt/graphene nanocomposite	$\text{H}_2\text{O}_2$	0.8	Zhang <i>et al.</i> (2011)
Pt-chitosan nanocomposite over glassy carbon	Nitrite	$1.5 \times 10^{-7} \text{M}$	Zhu <i>et al.</i> (2013)
Graphene-Pt nanocomposite	Arsenic	1.1 nM	Kempegowda <i>et al.</i> (2014)
Pt- polydopamine @ $\text{SiO}_2$ nanocomposite	Quercetin	16 nM	Manokaran <i>et al.</i> (2015)
Polypyrrole and Pt Nanoparticle Multi-Layer Nanocomposite	Cholesterol	$2.5 \times 10^{-4} \text{M/l}$	Chauhan <i>et al.</i> (2013)
Gold electrode ornamented by chitosan-Pt NP (CS-PtNPs) and grapheme-gold NP (GR-AuNPs)	Erythromycin	$2.3 \times 10^{-8} \text{mol./L}$	Lian <i>et al.</i> (2012)
Pt-Fe alloy NP dispersed N-doped graphene	Hydrogen	Very good	Sripada <i>et al.</i> (2015)

time. Pt based composite substituted over graphene sheet has also attracted scientists to use it as a sensor. Graphene provide large surface area for the adsorption. Thus over graphene sheet the material to be detected can be deposited and detected.

Pt seems to be best electrocatalyst because it is inert and stable both in acidic and alkaline media. It would be very expensive if Pt metal is used for the purpose. Hence, nano Pt powder or a composite of Pt NP is deposited over carbon nanomaterials (CNF or CNT) and this is deposited over some electrode like glassy carbon electrode (Table 1). In this way small quantity of Pt is used for this purpose and carbon nanomaterials provide large surface area for the adsorption of material in question. Scientists are trying to find out specific type of Pt composite that is suitable for the specific requirement. Some examples of such sensors are discussed in the foregoing section and are given in Table 1.

There are few sensors like Pt NP/graphene nanosheet composites for sensing  $\text{H}_2\text{O}_2$ , Pt/ionic liquid/graphene nanocomposite for ascorbic acid and dopamine (Li *et al.* 2010) and graphene-Pt nanoparticle hybrid material as cholesterol biosensor (Li *et al.* 2010; Dey and Raj 2010), which are getting popularity for detecting smaller quantity of materials (Dey and Raj 2010) Graphene oxide-PtNP composite has been used to detect the presence of arsenic in drinking water (Kempegowda *et al.* 2014).

Quercetin is a flavonoid that occurs in plant extract. This has antioxidant, antibacterial, anti-inflammatory and antitumor properties. This is used to prevent cancer, heart related diseases. Its determination is essential for human health and is detected in urine and blood. Pt supported polydopamine coated silica nanoparticle was used to detect Quercetin. Cyclic voltammetry was used to detect its presence to the limit of 16nM (Manokaran *et al.* 2015). Human serum contain

free and esterified cholesterol. It is important to determine its concentration in the blood to make any diagnosis related to heart disease, myocardial infarction and arteriosclerosis. Graphene/Pt NP/nafion nanocomposite modified electrode is developed to detect metoprolol (MTP) in nano molar amounts (Engin Er *et al.* 2016).

A gold electrode ornamented by chitosan-Pt NP (CS-PtNPs) and grapheme-gold NP (GR-AuNPs) nanocomposites is developed (Lian *et al.* 2012) for the determination of a drug erythromycin. The detection limit was  $2.3 \times 10^{-8}$  mol/L. The sensor had high selectivity, good stability and reproducibility. Reduced graphene oxide-carboxymethyl cellulose layered with Pt NP/PAMAM dendrimer/magnetic NP hybrids is used for the detection of xanthine in the 50 nM-12  $\mu$ M range. This biosensor showed high reproducibility and repeatability when used for detecting xanthine in fish samples (Boryana *et al.* 2016).

A temperature and pressure sensing Pt complex is developed by Iijima and Sakaue (2012). They used Pressure- and temperature-sensitive paint (two-color PSP) using a luminescent polymer of poly(1-(trimethylsilyl)phenyl-2-phenylacetylene) (PTMST) and Pt(II) tetrakis (pentafluorophenyl) porphyrin (PtTFPP). This polymer uses poly(1-trimethylsilyl-1-propyne) based polymer for this purpose. Time response is of the order of 10 ms.

It is reported (Sripada *et al.* 2015, Kamrul *et al.* 2016) that Pt<sub>3</sub>Fe/NG NPs composite and (Pt/Pd-ZnO NRs) shows high performance as hydrogen sensor at room temperature.

When nanocomposites of ethylene glycol protected Pt NP (1-2 nm size) onto different types of carbon nano materials (CNF, activated carbon, MWCNT) was dispersed and evaluated their utilities as non-enzymatic glucose sensing material. They observed sensitivity 1.07, 1.10 and 0.52  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> for Pt-C, Pt-MWCNT and Pt-CNF respectively (Rathod *et al.* 2010).

Some efforts were made Engin *et al.* (2013) to develop Pt composite with Zr and Hf, which can act as a chemical sensor at high temperature and harsh atmosphere.

Haridas *et al.* (2011) developed rf sputtered SnO<sub>2</sub> thin film (90 nm) with uniformly distributed Pt catalyst cluster for the detection of LPG. It can detect 200 ppm of LPG using 10 mm thick film. Stegmeier *et al.* (2010a and 2010b) have reported Pt composite with Ga<sub>2</sub>O<sub>3</sub> for detecting volatile organic compounds. It is suggested that due to the adsorption of organic chemicals there is an appreciable change in the resistance of the film, which can be calibrated for the quantitative evaluation of the chemical. This sensor can detect aldehyde, alcohols, esters, ketones, and hydrocarbons as well as toxic CO.

Polyaryl films grafted on Pt electrodes via the electrochemical reduction of diazonium tetrafluoroborates as blocking layers, can be used as glucose biosensors (Raicopo *et al.* 2016).

An efficient non-enzymatic biosensor electrode with a detection limit of 0.05 mg ml<sup>-1</sup> comprising of nitrogen-doped graphene (N-graphene) and Pt nano-flower (Pt NF) were fabricated on indium tin oxide (ITO) glass for detection of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (Tajabadi *et al.* 2016, Siriviriyanyum *et al.* 2013).

Polyvinylferrocenium based Pt composite was used for lysine detection, the response time of sensors was less than 30 s. Detection limit was in the range of  $6.5 \times 10^{-4}$  and  $5.0 \times 10^{-4}$  mM. The biosensor was able to determine lysine in pharmaceutical samples (Zeki *et al.* 2011).

Likewise nanosize Pt with different polymers and carbon composite has been used for the detection of xanthine, glucose, cholesterol, DNA etc. (Zeki *et al.* 2011, Kang *et al.* 2008, Tsai *et al.* 2008, Ferreira *et al.* 2011, Lu *et al.* 2008). Table 1 gives some of the nano-Pt composites which have been used as a sensor for detection of different materials.

#### 4.3 Nano Pt composites for production of hydrogen

Dwindling availability of petrol and diesel has attracted scientist to develop hydrogen based technology. Though several applications have been developed for the hydrogen, but major limitation in hydrogen based technology is the availability of this gas. Moreover, it is also observed that amount of energy used to electrolyze water is (~1.6V) which is more than what one would get by burning hydrogen (~ 0.9 V). Hence efforts are made to develop electrocatalyst which can electrolyze water at lowest possible potential (near to thermodynamic potential of 1.223V). Pure Pt however needs almost zero over potential, but its high cost has limited the use of Pt. Hence efforts are made to develop Pt composite with other metal, which could electrolyze water at least over potential (Zidki *et al.* 2014). For this purpose, as mentioned earlier, the activity of Pt can be improved by (i) nano-structuring (ii) alloying with some non-noble metals and (iii) depositing the nano Pt over sub nanometer size suitable support materials like carbon nanomaterial. Roy *et al.* (2015) have recently made some efforts in this direction. They developed nitrogen doped reduced graphene oxide based with Pt-TiO<sub>2</sub> nanocomposite. They reported over potential of 300mV as compared to experimentally observed more than 400 mV with non-noble metal.

Yonezawa and Toshima (1993) have developed polymer- and micelle-protected gold/Pt bimetallic systems for the detection of hydrogen. Visible light-induced hydrogen evolution method was used for this purpose. Kalisman *et al.* (2015, 2016) have improved the efficiency of photocatalytic property of nanoparticle-based Au-Pt bimetallic co-catalyst coated with CdSe@CdS. They reported 100% photon-to-hydrogen production efficiency, by illuminating the catalyst with visible light.

#### 4.4 Pt nanocomposites as filter

There are some stringent regulations to suppress the emission of particulate matters through the exhaust used in chemical and, automobile industries. Hence Pt-nanocomposites have found applications in different types of filters e.g., a low cost of nano-structured well-dispersed Pt particles on a MWCNT support is developed, which can act as a catalytic diesel particulate filter including gases like Nox (Zhou *et al.* 2015).

#### 4.5 Pt nanocomposites as a photocatalyst

Pt/PbWO<sub>4</sub> composite micro crystals are developed as nanocatalyst (Yu *et al.* 2015). Its photocatalytic properties were evaluated by studying the photocatalytic degradation of acid orange II dye. This composite showed high photocatalytic activity and stability. It is suggested that deposition of nano size Pt/Pt NPs created surface Plasmon resonance (SPR), which created harvesting of visible light. Nano size Pt expected to help in separation of photo-generated electrons and holes to initiate an effective photocatalytic effect.

#### 4.6 Pt nanocomposites as light emitting diode

Some efforts are being made to utilize the photoemitting properties of complex Pt materials for using it as light emitting diode (Hu *et al.* 2010). Novel Pt complex-a Pt(II) (2-(4',6'-difluorophenyl)pyridinato-N,C<sup>2'</sup>)(picolinate) was synthesized (Liang *et al.* 2013). They studied the optophysical, electrochemical and electroluminescent properties of this complex. This complex exhibited red-shifted photo-luminescence and higher quantum efficiency at room temperature. This complex can be used for white polymer light-emitting diode.

#### 4.7 Pt nanocomposites for drug detection

Avaji *et al.* (2014) have developed a polymer therapy system (100using a new monomeric Pt (II) complex (dach) Pt(HEDM) (dach, *trans*-(±)-1,2-diaminocyclohexane; HEDM, 2-hydroxyethoxydiethylmalate) with an object to use it for targeted delivery of oxaliplatin using polymer therapy. It was designed to include the antitumor moiety (dach)Pt and HEDM as a linker to the polyphosphazene backbone.

Recently an electrochemical determination of anti-tuberculosis drug, isoniazid (INH) using gold-Pt core-shell NP modified over glassy carbon electrode is developed by Gowthaman *et al.* (2016). They could successfully determine this drug present even in a mixture. Drug detection sensitivity was found to be  $26 \times 10^{-9}$  M and it could simultaneously detect the concentrations of INH and TP in human blood and urine samples.

#### 4.8 Pt nanocomposites for drug delivery

A review on various types of drug delivery system to deliver Pt anticancer drugs has been given by Oberoi *et al.* (2013).

#### 4.9 Pt nanocomposites for bioimaging

Water soluble Pt complexes (Pt(ppy)(en))Cl, (where ppy=2-phenylpyridine and en=ethane-1, 2-diamine) is synthesized for bioimaging by Pasha *et al.* (2016). This Pt complex give strong green luminescence in solution and is able to penetrate the cell membrane in both cancer (HeLa, U87MG and Nuro2a) and normal cells (CHO-K1 and 3T3-L1). But the cellular uptake of this Pt complex was very high in cancerous cells. This complex can therefore be used for Bioimaging.

### 5. Conclusions

Pt is the best noble metal which gives very promising results when used as electrocatalyst for applications as electrode in alkaline Fuel Cells, photoelectrode in dye sensitized solar cell etc. However, if Pt is to be used for terrestrial applications, cost becomes the major concerned. Considering these two aspects, in this review efforts are made to report various methods developed for synthesizing Pt composites with non-noble metals, polymers and carbon nanomaterials, with a view to get the final product giving better efficiency than pure Pt. Emphasis is also on for using very little of Pt in the composite. The second aspect of this review is to discuss the application of Pt composites with non-noble metal and carbon nanomaterial as an electro-catalyst in developing methanol, formic and hydrogen alkaline Fuel Cell, as a biosensors, as drug delivery vehicles, for bioimaging, in sensors, light emitting diode, photocatalyst, etc. It is observed from the results obtained by various scientists that composite of Pt/alloy with carbon nanomaterial has produced good results but there is still a need to develop the material, which could give as much efficiency as pure Pt so that material could be used for terrestrial application. It is also reported that the quality of Pt composite also depends on the method of synthesis, hence there is also a need to improve the process of synthesis to get desired result.

## References

- Arenz, M., Karl, J., Mayrhofer, K.J.J., Stamenkovic, V., Blizanac, B.B., Tomoyuki, T., Ross, P.N. and Markovic, N.M. (2005), "The effect of the particle size on the kinetics of CO electrooxidation on high surface area Pt catalysts", *J. Am. Chem. Soc.*, **127**(18), 6819-6829.
- Avaji, P.G., Joo, H.I., Park, J.H., Park, K.S., Joo, Y.J., Lee, H.J. and Sohn, Y.S. (2014), "Synthesis and properties of a new micellar polyphosphazene-Pt(II) conjugate drug", *J. Inorg. Biochem.*, **140**, 45-52.
- Awasthi, R.N. and Sharma, C.S. (2014), "Review, an overview of recent development of Pt based cathode materials for direct methanol fuel cell", *J. Electrochem. Sci.*, **9**, 5607-5639.
- Bar-Ziv, R., Michael, S., Vladimir, S. and Dan, M. (2015), "Coating Pt NP with methyl radicals: Effects on properties and catalytic implications", *Chem. Eur. J.*, **21**(52), 19000.
- Bian, X.J., Lu, X.F., Jin, E., Kong, L.R., Zhang, W.J. and Wang, C. (2010), "Fabrication of Pt/polypyrrole hybrid hollow microspheres and their application in electrochemical biosensing towards hydrogen peroxide", *Talanta*, **81**(3), 813-818.
- Bo, X., Ndamani, J.C., Bai, J. and Guo, L.P. (2010), "Nonenzymatic amperometric sensor for hydrogen peroxide and glucose based on Pt NP ordered mesoporous carbon nanocomposite", *Talanta*, **82**(1), 85-91.
- Bonnemann, H. and Richards, R.M. (2010), "Nanoscale metal particles-synthetic methods and potential applications", *Eur. J. Inorg. Chem.*, **2001**(10), 2455-2480.
- Boryana, B., Sánchez, A., Jiménez-Falcao, S., Martín, M., Salazar, P., Parrado, C., Pingarrón, J.M. and Villalonga, R. (2016), "Reduced graphene oxide-carboxymethylcellulose layered with Pt NP/PAMAM dendrimer/magnetic NP hybrids. Application to the preparation of enzyme electrochemical biosensors", *Sens. Actuat. B, Chem.*, **232**, 84-90.
- Chauhan, K.R., Solanki, P.R. and Basu, T. (2013), "Development of impedimetric biosensor for total cholesterol estimation based on polypyrrole and Pt NP multi later nanocomposite", *J. Org. Chem.*, **3**(4), 262-274.
- Chen, X., Wu, Y., Dong, H., Zhang, C.Y. and Zhang, Y. (2013), "Pt-based agents for, individualized cancer treatment", *Curr. Mol. Med.*, **13**(10), 1603-1612.
- Dey, R.S. and Raj, C.R. (2010), "Development of an amperometric cholesterol biosensor based on graphene-Pt nanoparticle hybrid material", *J. Phys. Chem. C*, **114**(49), 21427-21433.
- Diloyan, G., Marcus, S., Das, K. and Hutapea, P. (2012), "Effect of mechanical vibration on Pt particle agglomeration and growth in polymer electrolyte membrane fuel cell catalyst layers", *J. Pow. Source*, **214**, 59-67.
- Dobrzanska-Danikiewicz, A.D. and Kukowiec, D. (2013), "Synthesis and characterization of Pt/MWCNT nanocomposites", *Phys. Stat. Sol. B*, **250**(12), 1-6.
- Dutt, S. and Siril, P.F. (2015), "Controlling the morphology of polyaniline-Pt nanocomposites using swollen liquid crystal templates", *Synthet. Metal.*, **209**, 82-909.
- Engin, Ç., Sabolsky, K. and Sabolsky, E.M. (2013), "Pt thin film electrodes for high-temperature chemical sensor applications", *Sens. Actuat. B, Chem.*, **181**, 702-714.
- Engin, E., Hüseyin, Ç. and Erk, N. (2016), "A novel electrochemical nano-platform based on graphene/Pt NP/nafion composites for the electrochemical sensing of metoprolol", *Sens. Actuat. B, Chem.*, **238**, 779-787.
- Esumi, K., Takei, N. and Yoshimura, T. (2003), "Antioxidant-potentiality of gold-chitosan nanocomposites", *Coll. Surf. B*, **32**(2), 117-123.
- Evans, S.A.G., Elliott, J.M., Andrews, L.M., Bartlett, P.N., Doyle, P.J. and Denuault, G. (2002), "Detection of hydrogen peroxide at mesoporous Pt microelectrodes", *Anal. Chem.*, **74**(6), 1322-1326.
- Ferreira, V.C., Melato, A.I., Silva, A.F. and Abrantes, L.M. (2011), "Conducting polymers with attached Pt NP towards the development of DNA biosensors", *Electrochem. Commun.*, **13**(9), 993-996.
- Gooding, J.J., Praig, V.G., Hall, E.A.H. and Gooding, J.J. (1998), "Pt-catalyzed enzyme electrodes immobilized on gold using self-assembled layers", *Anal. Chem.*, **70**(11), 2396-2402.
- Gouldsmith, F. and Wilson S. (1963), "Extraction and refining of the Pt metals a complex cycle of smelting,

- electrocatalytic and chemical operations”, *Pt Met. Rev.*, **7**(41), 136-143.
- Gouse, P.S., Sahu, A.K., Arunchander, A., Nath, K. and Bhat, S.D. (2015), “Deoxyribonucleic acid directed metallization of Pt NP on graphite nanofibers as a durable oxygen reduction catalyst for polymer electrolyte fuel cells”, *J. Pow. Sour.*, **297**, 379-387.
- Gowthaman, N.S.K., Srinivasan K. and Abraham, J.S. (2016), “Monitoring isoniazid level in human fluids in the presence of theophylline using gold @ Pt core@shell NP modified glassy carbon electrode”, *Sens. Actuat. B, Chem.*, **230**, 157-166.
- Halakoo, E., Khademi, A., Ghohari, M. and Ismail, A.F. (2015), “Production of sustainable energy by carbon nanotube/Pt catalyst in microbial fuel cell”, *Proc. CIRP*, **26**, 473-476.
- Haridas, D., Chowdhuri, A., Sreenivas, K. and Gupta, V. (2011), “Effect of thickness of Pt catalyst clusters on response of SnO<sub>2</sub> thin film sensor for LPG”, *Sens. Actuat. B, Chem.*, **153**(1), 89-95.
- He, G., Yang, S., Liu, K., Walter, A., Chen, S. and Chen, S. (2013), “Oxygen reduction catalyzed by Pt NP supported on graphene quantum dots”, *ACS Catal.*, **3**, 831-838.
- Hosseini, S.Y., Raoof, J.B., Ghasemi, S. and Gholami, Z. (2015), “Synthesis of Pt-Cu/poly(o-Anisidine)nanocomposite onto carbon paste electrode and its application for methanol oxidation”, *J. Hydrog. Energy*, **40**, 292-302.
- Hu, Z., Wang, Y., Shi, D., Tan, H., Li, X., Wang, L., Zhu, W. and Cao, Y. (2010), “Highly-efficiency red-emitting Pt (II) complexes containing 4'-diarylamino-1-phenylisoquinoline ligands in polymer light-emitting diodes, synthesis, structure, photoelectron and electroluminescence”, *Dyes Pigm.*, **86**(2), 166-173.
- Huang, H.Z. and Yang X.R. (2003), “Chitosan mediated assembly of gold NP multilayer”, *Coll. Surf. A*, **226**(1-3), 77-86.
- Huang, Y., Zhao, T., Lin, Z., Peng, T. and Xu, J. (2016), “A facile approach for preparation of highly dispersed Pt-copper/carbon nanocatalyst toward formic acid electro-oxidation”, *Electrochim. Acta*, **190**, 956-963.
- Hui, M., Zhan, Y., Zeng, D., Zhang, X., Zhang, G. and Jaouen, F. (2015), “Factors influencing the growth of Pt nanowires via chemical self-assembly and their fuel cell performance”, *Small*, **11**(27), 3377-3386.
- Hummers, W.S. and Offman, R. (1958), “Preparation of graphitic oxide”, *J. Am. Chem. Soc.*, **80**, 1339-1342.
- Iijima, Y. and Sakaue, H. (2012), “Pt porphyrin and luminescent polymer for two-color pressure- and temperature-sensing probes”, *Sens. Actuat. A, Phys.*, **184**, 128-133.
- Jian, F., Zhou, R., Yao, Z., Du, Y., Xu, J., Yang, P. and Wang, C. (2011), “Facile fabrication of Pt-Cu nanoclusters-decorated porous poly(5-cyanoindole) with high electrocatalytic activity”, *J. Electrochem. Sci.*, **6**, 4114-4126.
- Kaewsai, D., Lin, H., Liu, Y. and Yu, T.L. (2016), “Pt on pyridine-polybenzimidazole wrapped carbon nanotube supports for high temperature proton exchange membrane fuel cells”, *J. Hydrog. Energy*, **41**(24), 10430-10445.
- Kalisman, P., Nakibli, Y. and Amirav, L. (2016a), “Perfect photon-to-hydrogen conversion efficiency”, *Nano Lett.*, **16**(3), 1776-1781.
- Kalisman, P., Lothar, H., Eran, A., Yaron, K., Maya, B.S. and Lilac, A. (2015), “The golden gate to photocatalytic hydrogen production”, *J. Mater. Chem. A*, **3**, 19679-19682.
- Kamrul, H., Uddin, A.S.M., Iftekhar, U., Kim, F. and Chung, G.S. (2016), “Pt/palladium bimetallic ultrathin film decorated on a one-dimensional ZnO nanorods array for use as fast response flexible hydrogen sensor”, *Mater. Lett.*, **176**, 232-236.
- Kang, X., Mai, Z., Zou, X., Cai, P. and Mo, J. (2008), “Glucose biosensors based on Pt NP-deposited carbon nanotubes in sol-gel chitosan/silica hybrid”, *Talanta*, **74**(4), 879-886.
- Kempegowda, R., Antony, D. and Malingappa, P. (2014), “Graphite-Pt nanocomposite as a sensitive and selective voltammetric sensor for trace level arsenic quantification”, *J. Smart Nano Mater.*, **5**(1), 17-32.
- Kim, J., Takahashi, M. and Shimizu, T. (2008), “Effects of a potent antioxidant, Pt nanoparticle, on the lifespan of *Caenorhabditis elegans*”, *Mech. Age. Dev.*, **129**(6), 322-331.
- Kim, Y.J., Kim, D., Lee, Y., Choi, S.Y., Park, J., Lee, S.Y., Park, J.W. and Kwon, H.J. (2008), “Effect of nanoparticulate saponin-Pt conjugates on 2,4-dinitrofluorobenzene-induced macrophage inflammatory

- protein-2 gene expression via reactive oxygen species production in RAW 264.7 cells”, *BMB Rep.*, 304-309.
- Kou, R., Shao, Y., Mei, D., Nie, Z., Wang, D., Wang, C., Viswanathan, V.V., Park, S., Aksay, I.A., Lin, Y., Wong, Y. and Liu, J. (2011), “Stabilization of electrocatalytic metal NP at metal-metal oxide-graphite triple junction points”, *J. Am. Chem. Soc.*, **133**, 2541-2547.
- Krebs, R.E. (1998), *Pt-The History and Use of our Earth's Chemical Elements*, Greenwood Press, 124-127.
- Lalande, G., Denis, M.C., Gouerec, P., Guay, D., Dodelet, J.P. and Schuls, R. (2000), “Pt based nanocomposites produced by high energy ball milling as electrocatalysts in polymer electrolyte fuel cell”, *J. New Mater. Electrochem. Syst.*, **3**, 185-192.
- Lee, J., Kim, H., Sim, T. and Song, R. (2013), “A new quantum dot-Pt conjugate for self-assembled nanoconjugates by coordination bonding mediated recognition”, *Chem. Commun.*, **49**, 6182-6184.
- Li, F.H., Chai, J., Yang, H.F., Han, D.X. and Niu, L. (2010), “Synthesis of Pt/ionic liquid/graphene nanocomposite and its simultaneous determination of ascorbic acid and dopamine”, *Talanta*, **81**, 1063-1068.
- Li, L., Chow, W., Wong, W., Chui, C. and Wong, R.S. (2011), “Synthesis, characterization and photovoltaic behavior of Pt acetylide polymers with electron-deficient 9, 10-anthraquinone moiety”, *J. Organometal. Chem.*, **696**(6), 1189-1197.
- Li, M., Wu, X., Zeng, J., Hou, Z. and Liao, S. (2015), “Heteroatom doped carbon nanofibers synthesized by chemical vapor deposition as Pt electrocatalyst supports for polymer electrolyte membrane fuel cells”, *Electrochim. Acta*, **182**, 351-360.
- Li, Y., Zhang, J.J., Xuan, J., Jiang, L.P. and Zhu, J.J. (2010), “Fabrication of a novel nonenzymatic hydrogen peroxide sensor based on Se/Pt nanocomposite”, *Electrochem. Commun.*, **12**(6), 777-780.
- Li, Z., Cui, X., Zhang, X., Wang, Q., Shao, Y. and Lin, Y. (2009), “Pt/carbon nanofibers nanocomposite as electrocatalysts for direct methanol fuel cells, prominent effects of carbon nanofibers nanostructures”, *J. Nanosci. Nanotechnol.*, **9**, 2316-2323.
- Lian, W., Liu, S., Yu, J., Xing, X., Li, J., Cui, M. and Huang, J. (2012), “Electrochemical sensor based on gold NP fabricated molecularly imprinted polymer film at chitosan-Pt NP/graphene-gold NP double nanocomposites modified electrode for detection of erythromycin”, *Biosens. Bioelectron.*, **38**(1), 163-169.
- Liang, A., Li, Y., Zhu, W., Wang, Y., Huang, F., Wu, H. and Cao, Y. (2013), “Novel cyclometalated Pt (II) complex containing carrier-transporting groups, Synthesis, luminescence and application in single dopant white PLEDs”, *Dyes Pigm.*, **96**(3), 732-737.
- Liao, C., Chen, C., Chang, C., Hwang, G., Chou, H. and Cheng, C. (2013), “Synthesis of conjugated polymers bearing indacenodithiophene and cyclometalated Pt(II) units and their application in organic photovoltaics”, *Sol. Energy Mater. Sol. Cells*, **109**, 111-119.
- Lin, C.L. and Wang, C.C. (2014), “Enhancement of electroactivity of Pt-tungsten trioxide nanocomposites with NaOH-treated carbon support toward methanol oxidation reaction”, *Energy Proc.*, **61**, 538-541.
- Lin, Y., Cui, X., Wang, J., Yen, C.H. and Wai, C.M. (2006), “Pt and Pt-Ru/carbon nanotube nanocomposite synthesized in super critical fluid as electrocatalyst for low temperature fuel cells”, *NSTI Nanotech*, **1**, 524-527.
- Liu, Q., Zhu, N., Ho, C., Fu, Y., Lau, W., Xie, Z., Wang, L. and Wong, W. (2016), “Synthesis, characterization, photophysical and photovoltaic properties of new donor-acceptor Pt (II) acetylide complexes”, *J. Organometal. Chem.*, **812**, 2-12.
- Liu, S.H., Chang, C.C., Wu, M.T. and Liu, S.B. (2010), “Electrochemical activity and durability of Pt NP supported on ordered mesoporous carbons for oxygen reduction reaction”, *J. Hydrog. Energy*, **35**, 8149-8154.
- Liu, Y., Wang, D.W., Xu, L., Hou, H.Q. and You, T.Y. (2011), “A novel and simple route to prepare a Pt nanoparticle-loaded carbon nanofiber electrode for hydrogen peroxide sensing”, *Biosens. Bioelectron.*, **26**(11), 4585-4590.
- Lu, Y., Yang, M., Qu, F., Shen, G. and Yu, R. (2008), “Seed-mediated growth of Pt NP on carbon nanotubes for the fabrication of electrochemical biosensors”, *Electrochim. Acta*, **53**(10), 3559-3565.

- Maiyalagan, T., Wang, X. and Manthiram, A. (2014), "Highly active Pd and Pd-Au NP supported on functionalized graphene nanoplatelets for enhanced formic acid oxidation", *RCS Adv.*, **4**, 4028-4033.
- Manokaran, J., Muruganatham, R., Muthukrishnaraj, A. and Balasubramanian, N. (2015), "Pt-Polydopamine@SiO<sub>2</sub> modified electrode for the electrochemical determination of Quercetin", *Electrochim. Acta*, **168**, 16-24.
- Narayanamoorthy, B., Pavan Kumar, B.V.V.S., Eswaramoorthy, M. and Balaji, S. (2014), "Oxygen reduction reaction catalyzed by Pt nanonetwork prepared by template free one step synthesis for polymer electrolyte membrane fuel cells", *Mater. Res. Bullet.*, **55**, 137-145.
- Narayanan, R. and El-Sayed, M.A. (2004), "Shape-dependent catalytic activity of Pt NP in colloidal solution", *Nano Lett.*, **4**(7), 1343-1348.
- Oberoi, H.S., Nukolova, N.V., Kabanov, A.V. and Bronich, T.K. (2013), "Nanocarriers for delivery of Pt anticancer drugs", *Adv. Drug Deliv. Rev.*, **65**(13-14), 1667-1685.
- Oh, J., Park, J., Kumbhar, A., Smith, D.J. and Creager, S. (2014), "Electrochemical oxygen reduction at Pt/mesoporous carbon/zirconia/ionomer thin-film composite electrodes", *Electrochim. Acta*, **138**, 278-287.
- Olujinmi, M.F., Sadiku, E.R. and Maity, A. (2011), "Preparation and characterization of poly(N-vinylcarbazole)/Pt nanocomposite via in situ solid state polymerization", *Can. J. Pure Appl. Sci.*, **5**(3), 1713-1719.
- Ou, C.F., Yuan, R., Chai, Y., Tang, M., Chai, R. and He, X. (2007), "A novel amperometric immunosensor based on layer-by-layer assembly of gold NP-multi-walled carbon nanotubes-thionine multilayer films on polyelectrolyte surface", *Anal. Chim. Acta*, **603**(2), 205-213.
- Pasha, S.S., Das, P., Rath, N.P., Bandyopadhyay, D., Jana, N.R. and Laskar, I.R. (2016), "Water soluble luminescent cyclometalated Pt(II) complex-a suitable probe for bio-imaging applications", *Inorg. Chem. Commun.*, **67**, 107-111.
- Puthusseri, D. and Ramaprabhu, S. (2016), "Oxygen reduction reaction activity of Pt NP decorated nitrogen doped carbon in proton exchange membrane fuel cell under real operating conditions", *J. Hydrog. Energy*, **41**(30), 13163-13170.
- Quaino, P., Fernanda, J., Santos, E. and Wolfgang, S. (2014), "Volcano plots in hydrogen electrocatalysis-uses and abuses", *Beilst. J. Nanotechnol.*, **5**, 846-854.
- Raicopol, M.D., Andronescu, C., Atasiei, R., Hanganu, A., Vasile, E., Brezoiu, A.M. and Pilan, L. (2016), "Organic layers via aryl diazonium electrochemistry, towards modifying Pt electrodes for interference free glucose biosensors", *Electrochim. Acta*, **206**, 226-237.
- Rathod, D., Dickinson, C., Egan, D. and Dempsey, E. (2010), "Pt NP decoration of carbon materials with applications in non-enzymatic glucose sensing", *Sens. Actuat. B, Chem.*, **143**(2), 547-554.
- Roy, N., Keung, K.T. and Pradhan, D. (2015), "Nitrogen doped reduced graphene oxide based Pt-TiO<sub>2</sub> nanocomposite for enhanced hydrogen evolution", *J. Phys. Chem.*, **119**(33), 19117-19125.
- Sakaue, Y., Kim, J. and Miyamoto, Y. (2010), "Effects of TAT-conjugated Pt NP on life span of mitochondrial electron transport complex I-deficient caenorhabditis elegans nuo-I", *J. Nanomed.*, **5**, 687-695.
- Sambandam, S., Valluri, V., Chanmanee, W., De Tacconi, N.R., Wampler, W.A., Lin, W., Carlson, T.F., Ramani, V. and Rajeswar, K. (2009), "Pt-carbon black-Titanium dioxide nanocomposite electrocatalyst for fuel cell application", *J. Chem. Sci.*, **121**(5), 655-664.
- Santos, D.S., Goulet, P.J. and Pieczonka, N.P. (2004), "Gold nanoparticle embedded, self-sustained chitosan films as substrates for surface-enhanced Raman scattering", *Langmuir*, **20**(23), 10273-10277.
- Sarikaya, M., Tamerler, C., Jen, A.K.Y., Schulten, K. and Banyex, F. (2003), "Molecular biomimetics, nanotechnology through biotechnology", *Nat. Mater.*, **2**, 577-585.
- Seifitokaldani, A. and Savadogo, O. (2015), "Electrochemically stable titanium oxy-nitride support for Pt electro-catalyst for PEM fuel cell applications", *Electrochim. Acta*, **167**, 237-245.
- Siriviriyanun, A., Imae, T. and Nagatani, N. (2013), "Electrochemical biosensors for biocontaminant detection consisting of carbon nanotubes, Pt NP, dendrimers and enzymes", *Analyt. Biochem.*, **443**(2), 169-171.

- Sripada, R., Nirmal, R.G., Mathiyarasu, J., Berchmans, S., Phani, K.L.N. and Yegnaraman, V. (2007), "Pt-dendrimer nanocomposite films on gold surface for electrocatalysis", *Catal. Lett.*, **119**, 40-49.
- Sripada, R., Parambath, M.B., Santhosh, P., Nair, N. and Ramaprabhu, S. (2015), "Pt and Pt-iron alloy NP dispersed nitrogen-doped graphene as high performance room temperature hydrogen sensor", *J. Hydrog. Energy*, **40**(32), 10346-10353.
- Stegmeier, S., Fleischer, M. and Hauptmann, P. (2010b), "Thermally activated Pt as VOC sensing material for work function type, gas sensors", *Sens. Actuat. B, Chem.*, **144**(2), 418-424.
- Stegmeier, S., Fleischer, M. and Hauptmann, P. (2010a), "Influence of the morphology of Pt combined with  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> on the VOC response of work function type sensors", *Sens. Actuat. B, Chem.*, **148**(2), 439-449.
- Sui, S., Zhuo, X., Su, K. Yao, X., Zhang, J., Du, S. and Kendall, K. (2013), "In situ grown nanoscale Pt on carbon powder as catalyst layer in proton exchange membrane fuel cells (PEMFCs)", *J. Energy Chem.*, **22**(3), 477-483.
- Tajabadi, M.T., Sookhakian, M., Zalnezhad, E., Yoon, G.H., Hamouda, A.M.S., Azarang, M., Basirun, W.J. and Alias, Y. (2016), "Electrodeposition of flower-like Pt on electrophoretically grown nitrogen-doped graphene as a highly sensitive electrochemical non-enzymatic biosensor for hydrogen peroxide detection", *Appl. Surf. Sci.*, **386**, 418-426.
- Trasatti, S. (1972), "Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions", *J. Electr. Chem. Interf. Electrochem.*, **39**(1) 163-184.
- Tsai, Y., Chen, S. and Lee, C. (2008), "Amperometric cholesterol biosensors based on carbon nanotube-chitosan-Pt-cholesterol oxidase nanobiocomposite", *Sens. Actuat. B, Chem.*, **135**(1), 96-101.
- Vestberg, R., Westlund, R., Eriksson, A., Lopes, C., Carlsson, M., Eliasson, B., Glimsdal, E., Lindgren, M. and Malmström, E. (2006), "Dendron decorated Pt(II) acetylides for optical power limiting", *Macromol.*, **39**, 2238-2246.
- Wang, L.Q., Bellini, M., Filippi, J., Folliero, M., Lavacchi, A., Innocenti, M., Marchionni, A., Miller, H.A. and Vizza, F. (2016), "Energy efficiency of Pt-free alkaline direct formate fuel cells", *Appl. Energy*, **175**, 479-487.
- Wang, M.Y., Chen, J.H., Fan, Z., Tang, H., Deng, G.H. and He, D.L. (2004), "Ethanol electro-oxidation with Pt and Pt-Ru catalysts supported on carbon nanotubes", *Carbon*, **42**, 3257-3260.
- Yeh, M., Chang, S., Lin, L., Chou, H., Vittal, R., Hwang, B. and Ho, K. (2015), "Size effects of Pt NP on the electrocatalytic ability of the counter electrode in dye-sensitized solar cells", *Nano Energy*, **17**, 241-253.
- Yonezawa, T. and Toshima, N. (1993), "Polymer- and micelle-protected gold/Pt bimetallic systems. Preparation, application to catalysis for visible-light-induced hydrogen evolution, and analysis of formation process with optical methods", *J. Molecul. Catalys.*, **83**(1-2), 167-181.
- Yu, C., Bai, Y., He, H., Fan, W., Zhu, L. and Zhou, W. (2015), "Characterization and photocatalytic performance of rod-shaped Pt/PbWO<sub>4</sub> composite microcrystals", *Chin. J. Catalys.*, **36**(12), 2178-2185.
- Yung, T., Liu, T., Huang, L.Y., Wang, K.S., Tzou, H.M., Chen, P.T., Chao C.Y. and Liu, L.K. (2015), "Characterization of Au and bimetallic PtAu NP on PDDA-graphene sheets as electrocatalysts for formic acid oxidation", *Nanos. Res. Lett.*, **10**, 365.
- Zeki, B.S., Gülce, S. and Yıldız, S. (2011), "Amperometric xanthine biosensors based on electrodeposition of Pt on polyvinylferrocene coated Pt electrode", *J. Molecul. Catalys. B, Enzymat.*, **72**(3-4), 282-288.
- Zhan, H., Wong, W., Ng, A., Djurišić, A.B. and Chan, W. (2011), "Synthesis, characterization and photovoltaic properties of Pt-containing poly(aryleneethynylene) polymers with phenanthrenyl-imidazole moiety", *J. Organometal. Chem.*, **696**(25), 4112-4120.
- Zhang, S., Shao, Y., Liao, H., Liu, J., Aksay, I.A., Yin, G. and Lin, Y. (2011), "Graphene decorated with PtAu alloy NP, facile synthesis and promising application for Formic acid oxidation", *Chem. Mater.*, **23**, 1079-1081.
- Zhang, F., Wang, Z., Zhang, Y., Zheng, Z., Wang, C., Du, Y. and Ye, W. (2012), "Microwave assisted synthesis of Pt/graphene nanocomposites", *J. Electrochem. Sci.*, **7**, 1968-1977.
- Zhang, N., Zhang, S., Du, C., Wang, Z., Shao, Y., Kong, F., Lin, Y. and Yin, G. (2014), "Pt/tin oxide/carbon

- nanocomposites as promising oxygen reduction electrocatalyst with improved stability and activity”, *Electrochim. Acta*, **117**, 413-419.
- Zheng, Y., Dou, Z., Fang, Y., Li, M., Wu, X., Zeng, J., Hou, Z. and Liao, S. (2016), “Pt NP on carbon-nanotube support prepared by room-temperature reduction with H<sub>2</sub> in ethylene glycol/water mixed solvent as catalysts for polymer electrolyte membrane fuel cells”, *J. Pow. Sour.*, **306**, 448-453.
- Zhou, Y., Itoh, H., Umemura, T., Naka, K. and Chujo, Y. (2002), “Synthesis of novel stable nanometer-sized metal (M Pd, Au, Pt) colloids protected by a  $\pi$ -conjugated polymer”, *Langmuir*, **18**, 277-283.
- Zhou, Q., Zhong, K., Fu, W., Huang, Q., Wang, Z. and Bei, N. (2015), “Nanostructured Pt catalyst coating on diesel particulate filter with a low-cost electroless deposition approach”, *Chem. Eng. J.*, **270**, 320-326.
- Zhou, Z.H., Wang, S., Zhou, W.J., Wang, G.X., Jiang, L.H., Li, W.Z., Song, S.Q., Liu, J.G., Sun, G.Q. and Xin, Q. (2003), “Novel synthesis of highly active Pt/C cathode electrocatalyst for direct methanol fuel cell”, *Chem. Commun.*, **3**, 394-395.
- Zhu, X. and Ding, A. (2013), “One step construction of sensor based on nanocomposite of Pt and chitosan formed by electrodeposition and its application for determination of nitrite”, *J. Electrochem. Sci.*, **8**, 135-148.
- Zidki, T., Bar-Ziv, R., Green, U., Cohen, H., Meisel, D. and Meyerstein, D. (2014), “The effect of nano-silica support on the catalytic reduction of water by gold, silver and Pt NP-nanocomposite reactivity”, *Phys. Chem. Chem. Phys.*, **16**, 15422-15429.