Chapter 1

Introduction

1. General Introduction

This is an introductory chapter which provides a general idea on nanoparticles (NPs) and their diverse applications in various areas. Metallic NPs play a dominant role in heterogeneous catalysis and therefore attract current research prospects. The present chapter is mainly focused on the applications of Pd- and Cu-based NPs. Especial emphasis has been paid towards application of catalysts in fuel cell (FC) oxygen reduction reaction (ORR; for energy related issues) and various nitroaromatic reduction reactions (for chemicals and pharmaceuticals).

1.1 Overview

NPs are the simplest form of structures with a diameter smaller than 100 nm and exhibits novel properties that are related to its scale. The first evidence of nanotechnology dates back to ~2000 B.C., where silver and gold NPs were used to create beautiful stained glass windows due to their unique optical properties [1]. The Romans mixed solutions of nano-gold and silver to make a variety of painted glasses [2]. Today NPs are used to fight cancer [3–5], catalyze various reactions [6,7], and as chemical and biological sensors [8]. Over the two decades, significant advances have been made in the field of nanotechnology; particularly for metal NPs, whose properties differ from their bulk counterparts. NPs are aggregation of a few to many millions of atoms or molecules. They may consist of identical atoms, or molecules, or two or more different species. If the NP was the size of football, a virus would be as big as a person, a red blood cell would be the size of rugby field, and a doughnut would be as big as the world. The word ‘nano’ is derived from the Greek word ‘nanos’, means draft or extremely small. Now-a-days nano is denoted by 10^{-9} m in S.I. units. The word nanoscience denotes the study of manipulation and engineering of material, particles and systems in the nanoscale (0.1 to 100 nm). It comprises the understanding and development of new methods for the synthesis of nanomaterials (NMs), whose properties are significantly improved as well as different than from bulk materials [9], e.g., nanoscale gold can have different electrical, optical, mechanical properties to that of its bulk scale. The term nanotechnology refers to the technological development of nanoscience which associates with the use of new nanosize materials and components in useful products. Nanotechnology will eventually involves the use custom-made

NMs and products with new improved properties, in various areas such as nanoelectronics components, medicines, sensors, textile industries and biotechnology to provide better technologies to the society [10]. Although the seed of modern nanotechnology was planted by the famous physicist and Nobel laureate Richard Feynman in 1959, but its entire idea was developed during the days of ancient Romans. History reveals that metal NPs in the form of colloids and sols have been used traditionally in dye fabrics, colouring glasses, and ornamental decoration etc. in medieval times and during the days of ancient Romans. It is known that alchemists used colloidal form of Au and Ag NPs in water for the treatment of arthritis. During the Greek and Roman days tiny PbS NPs were used for hair dyeing [11]. The Lycurgus cup is an another man-made example of the Roman times in fourth century A.D., which is currently in the British Museum, show unusual optical effect. The glass appears in two different colours i.e., deep wine red in transmitted light and green in reflected light as shown in Figure 1.1**.** The chemical analysis of this glass revealed that the unusual colour change is due to the surface plasmon resonance of nano size Au and Ag where Cu NPs were re-dispersed throughout the glassy matrix [12].

Figure 1.1: The Lycurgus cup in reflected light (left) and in transmitted light (right) [12].

This discloses in what way the people in ancient times used colloidal Au and Ag NPs to succeed the color-shifting effect. Damascus steel is one another example of the use of nanotechnology in ancient time. This used to make sword made from Damascus steel at about 500 AD in Damascus [13,14]. It becomes famous due to the extreme strength, sharpness, elasticity and the glory of their typical surface design [13]. The interesting myth story told that, it can cut clean through rock and still remain sufficiently sharp to cut through a silk scarf dropped on the blade. Recently researchers have discovered that, these special properties are due to multi-walled carbon nanotube (MWCNTs) in steel [13]. This may be the oldest example of man-made MWCNT. The first scientific investigation of the connection between the colour and the size of the particles was reported by Michael Faraday in 1857 [15]. He prepared Au colloids by reducing an aqueous solution of $HAuCl_4$ in the presence of phosphorus and CS_2. This gave ruby fluids of dispersed Au colloids due to minute size of the Au NPs as shown in the Figure 1.2.

Figure 1.2: Five original bottled samples prepared by Michael Faraday [15].

He presented this work in Philosophical Transactions entitled “Experimental relations of gold and other metals to light” in 1857 [16]. Another example of nanotechnological advances in the field of transportation is carbon black discovered by a tire manufacturing company in 1928. The addition of right amount of carbon black (latter found to be with diameter about 25 nm) to the tire manufacturing rubber unexpectedly increased mileage of the vehicles. There is a wide application of modern nanoscience and technology in present time due to their unique physical and chemical properties. Therefore, the era and the pioneer idea of nanotechnology was began after a visionary lecture by Nobel laureate Richard P. Feynman, in his famous lecture at the annual meeting of American Physical Society held at The California Institute of

Technology (Caltech), 29th December 1959 USA by the vision, 'There's plenty of room at the bottom', and described the probability of nanosized devices and related technologies. Feynman expected that 'it would be possible to put the 24 volumes of Encyclopedia Britannica on the head of a pin'. Although nanoscience is a growing branch of science, but, the concept of technology is very old. What has been different over the years is our understanding to predict. Now a day, we can manufacture and employ materials in the nanoscale. This is actually possible due to the discovery of some sophisticated analytical tools in the field. The discovery of scanning tunnelling microscope (STM) in the early 1980s was very first step towards the journey [17]. The successive invention of atomic force microscope (AFM) started new prospects for observing, characterizing, and deploying materials at the nanoscale region [18]. Additionally, the discovery of transmission electron microscope (TEM) and scanning electron microscope (SEM) pays more to the understanding and familiarity with the materials at atomic scale. The isolation of Buckminster fullerene (C_{60}), a carbon cluster, in 1985 is considered as one of the utmost successes in the field of nanotechnology. Even though, NPs have been used a long time ago, but nobody realized that it reached nanoscale.

1.2 Types of Nanomaterials

Based on the nature of materials, the NMs are classified in to four categories:

1.2.1 Carbon Based Material

These types of NMs are comprised of carbon and usually found in the form of a hollow spheres, ellipsoids, or tubes. Cylindrical type of carbon NM is called nanotubes, while spherical and ellipsoidal carbon one is known as fullerenes [19], [Figure 1.3]. Carbon nanotube belongs to the one dimensional material and has very superior properties than those of the steel wire, such as stronger than steel wires, conduct thousand times more electricity and bear million times more weight than their own weight. Graphene is the another form of two dimensional carbon based NM comprising layers of carbon atoms organized in six-membered rings [Figure 1.3]. Graphene has very unique properties and commonly used to make sensors, electrochemical devices, transistors and broadly in the field of catalysis [20,21]. These carbons based NMs have numerous possible applications, such as to improve films and coatings, to make tougher and lighter smart materials, in field of modern electronics and energy devices etc.

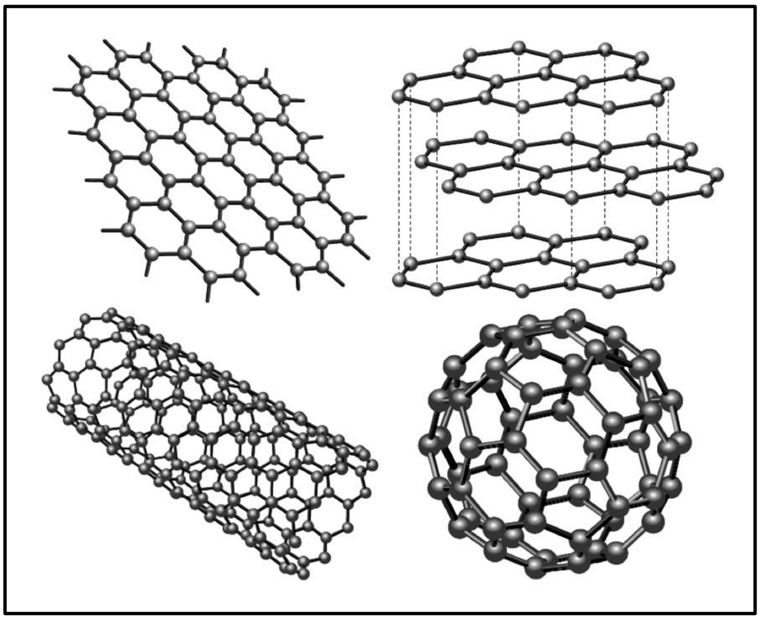


Figure 1.3: Various types of carbon based materials.

1.2.2 Metal-Based Materials

These types of NMs are broadly categorized into three major classes which include, (i) quantum dots (e.g., CdSe, CdS, etc.), (ii) metals (e.g. Au^0, Ag^0, Pd^0, etc.), and (iii) metal oxides (MOs), such as TiO_2, ZnO, etc.

(i) Quantum Dots: Quantum dots (QD) are very small closely packed semiconductor particles, with only a few nanometres in size, they have very rich optical and electronic properties due to their high extinction co-efficient. They are a central theme in nanotechnology [22].

(ii) Metals: Metals with dimensions in the range one to few nanometers are termed as metallic NPs. Metallic NPs possess distinct properties from those of individual atoms and molecules or bulk matter. They possess large surface-to-volume ratio as compared to their larger counterparts and have high surface energy. Hence they are catalytically more active. Metal NPs catalyze various reactions. The unique chemical and physical properties of metal NPs are size-dependent and the most important challenge about NPs is to control accurately the particle size and overall particle size distribution [23]. Metal NPs may be monometallic or polymetallic. Monometallic NPs are composed of only one type of metal elements. On the other hand polymetallic NPs are composed of more than one metal. Polymetallic NPs may be bimetallic, tri-metallic etc. The generation of bimetallic NPs (A_mB_n) can be done with, more or less, controlled size (m + n) and composition (m/n). The method and conditions (like temperature, pressure, type of cluster source, etc.) applied for the generation of the nanocluster determines the cluster structures and degree of A-B segregation or mixing The importance of bimetallic NPs is more compared to the monometallic NPs. It is because bimetallic NPs possess enhanced thermal, optical, and catalytic properties. The enhancement in the catalytic properties of bimetallic NPs is due to synergistic effect. Moreover the catalytic behavior of bimetallic NPs is directed by two special effects. One is the dilution of the surface of one metal by the other known as the ensemble effect. And the other is the electronic structure modification which arises due to orbital interaction and charge transfer between constituent metals known as ligand effect [24,25]. One of the major advantages of bimetallic NPs is the fact that by varying the composition and atomic ordering as well as the size of the nanoclusters their chemical and physical properties can be altered. These are widely use in electronics, engineering and catalysis because of their rich variety of composition, structure and enhanced properties.

(iii) Metal Oxides (MOs**)**: MO NPs and their applications are recently the world’s one of the most important topics. MOs are compounds formed by a metal and oxygen in which the oxygen has an oxidation number -2 (SnO_2, TiO_2, CeO_2, Al_2O_3 etc.). The metals are able to form a large diversity of oxide compounds [26].These can adopt a vast number of structural geometries with an electronic structure that can exhibit semiconductor or insulator character. MO NPs deal with materials design, modelling, synthesis, fabrication, processing, structure-property relationships and their device application at nanoscale. Oxide NPs can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites.

Structural and electronic properties obviously drive the physical and chemical properties of the solid, the third group of properties influenced by size in a simple classification. In their bulk state, many oxides have wide band gaps and a low reactivity. A decrease in the average size of an oxide particle does in fact change the magnitude of the band gap with strong influence in the conductivity and chemical reactivity. In the case of MO NPs, surface properties are strongly modified with respect to 2D-infinite surfaces, producing solids with unprecedented sorption or acid/base characteristics. Furthermore, the presence of under-coordinated atoms (like corners or edges) or O vacancies in an oxide NPs should produce specific geometrical arrangements as well as occupied electronic states located above the valence band of the corresponding bulk material, enhancing in this way the chemical activity of the system. MOs are used for both their redox and acid/base properties in the context of absorption and catalysis. In a simple classification, oxides having only ‘s’ or ‘p’ electrons in their valence orbitals tend to be more effective for acid/base catalysis, while those having d or f outer electrons find a wider range of uses.

1.2.3 Dendrimers: Dendrimers are spherical nano-sized polymeric molecules, formed through an ordered self-assembly process. The dendrimers are very much useful in catalysis because the the surface of dendrimers has several chain ends, which can be tailored to achieve exact chemical reactions. Also, three-dimensional dendrimers molecules can be used in drug delivery system owing to its ability to carrier nanoscale molecules. Dendrimers have many potential used in day to day life, such as water with ultra-filtration techniques, sensors materials etc [27,28].

1.2.4 Nanocomposite Materials: Nanocomposite materials are combined phase of solid materials where one of the phases has one, two or three dimensions in the nanometer range [29]. The result of the addition of nanosized material into a matrix of standard material, the original material gain drastic improvement in their properties. These mainly include hardness, mechanical strength, and thermal or electrical conductivity. In this process normally only between 0.5 and 5% by weight of the nanosized material is added. Nanocomposites can effectively enhance properties of material such as: mechanical properties comprising strength, modulus and dimensional solidity, electrical and thermal conductivity, decreased gas, water and hydrocarbon permeability, flame retardancy, thermal stability, chemical resistance, surface appearance, optical clarity etc. Figure 1.4 represents some of the core areas of applications of metal NPs.

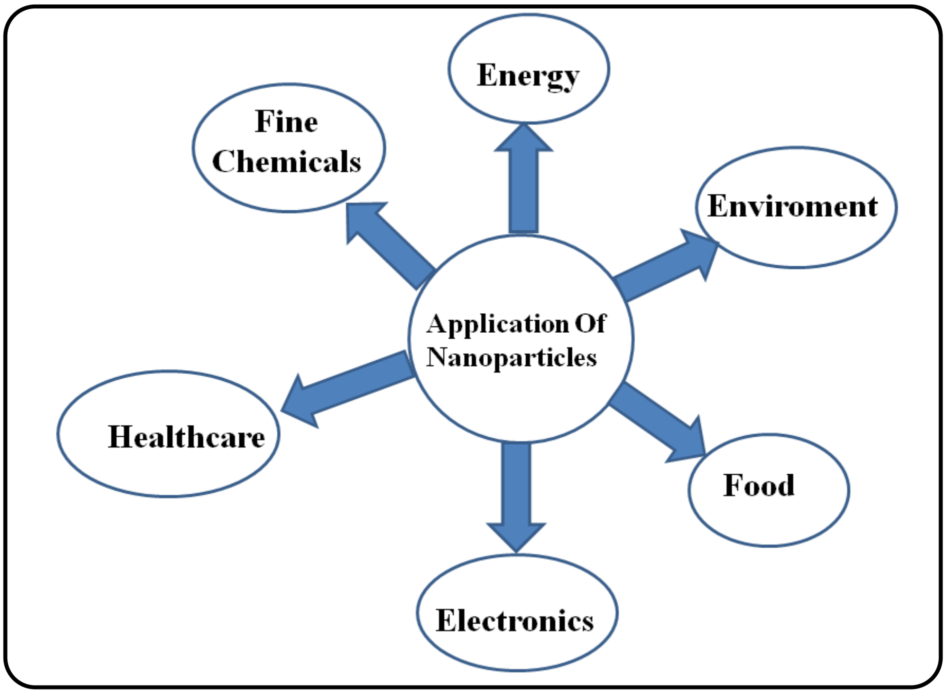
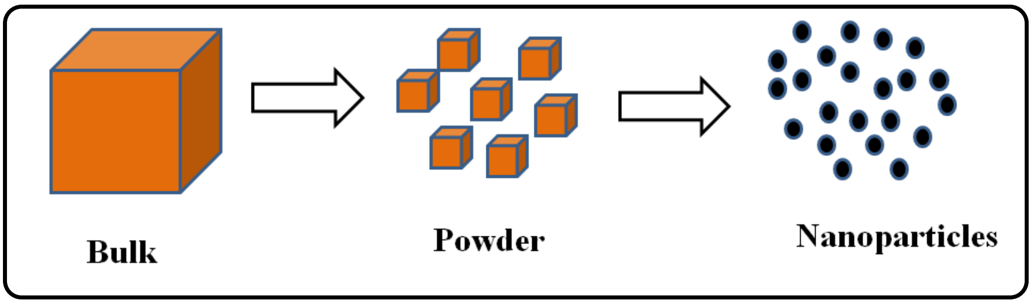


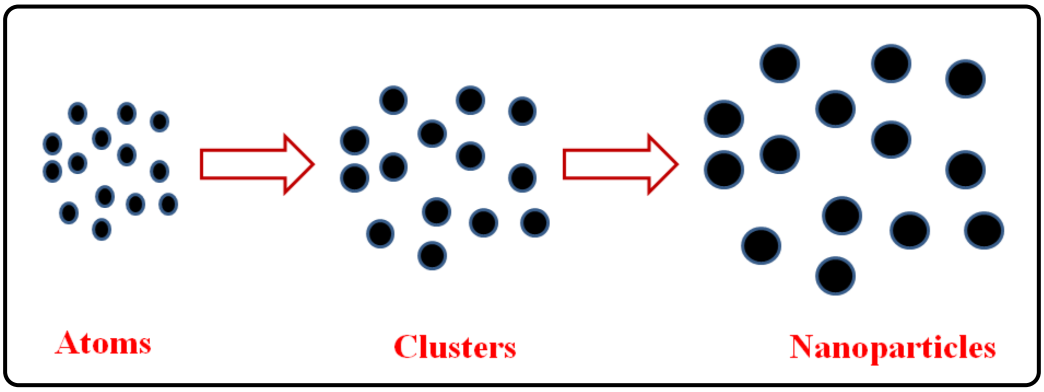
Figure 1.4: Some of the core areas of applications of metal NPs.

1.3 Synthesis of Nanomaterials

There are several synthesis methods for preparation of NPs including physical and chemical methods. The synthesis methods normally follow two approaches, ‘top-down’ and ‘bottom-up’ approach. In the top down approach, NPs are obtained from large materials which are broken by several techniques until desired shape and size particles (Scheme 1.1). In top down approach various types of physical methods are (i) arc discharge method [30], (ii) ball milling, (iii) electrodeposition, (iv) laser ablation, (v) aerosol synthesis, (vi) plasma synthesis, (vii) inert gas condensation, (viii) chemical vapour deposition, (ix) chemical beam epitaxy etc., which have been implemented for the successful production of NPs in a variety of environments.



Scheme 1.1: Schematic representation of 'Top-down' approach.



Scheme 1.2: Schematic representation of 'bottom-up' approach.

In the bottom-up approach, NPs are synthesized from atom or molecules (Scheme 1.2). In this approach obtained NPs have less defect, more homogeneous chemical composition, and improved long and short range ordering. There is a variety of chemical methods or bottom up method to obtained NPs, including (i) chemical reduction, (ii) photochemical, (iii) hydrothermal/solvothrmal, (iv) sonochemical, (v) electrochemical, (vi) microemulsion, (x) sol-gel, (xi) co-precipitation, (xii) seed mediated method etc. A few synthetic methods relevant to the thesis work are summarized below for the synthesis of NPs.

1.3.1 Hydrothermal Synthesis: This is a method to produce different chemical compounds using a closed-system. Physical and chemical processes flowing in aqueous solutions at temperatures above 100 °C and pressures above 1 atm are employed. The method is based on the ability to dissolve the insoluble substances into water at high temperature and pressure, which are practically insoluble under normal conditions: some oxides, silicates, sulphides, etc. The synthesis is carried out in autoclaves, which are sealed steel cylinders that can withstand high temperature and pressure for a long time. NPs are generally produced by means of either high temperature hydrolysis reactions of various compounds directly in the autoclave or hydrothermal treatment of reaction products at room temperature; the latter case is based on the sharp increase in the rate of crystallization of many amorphous phases in hydrothermal conditions [31].

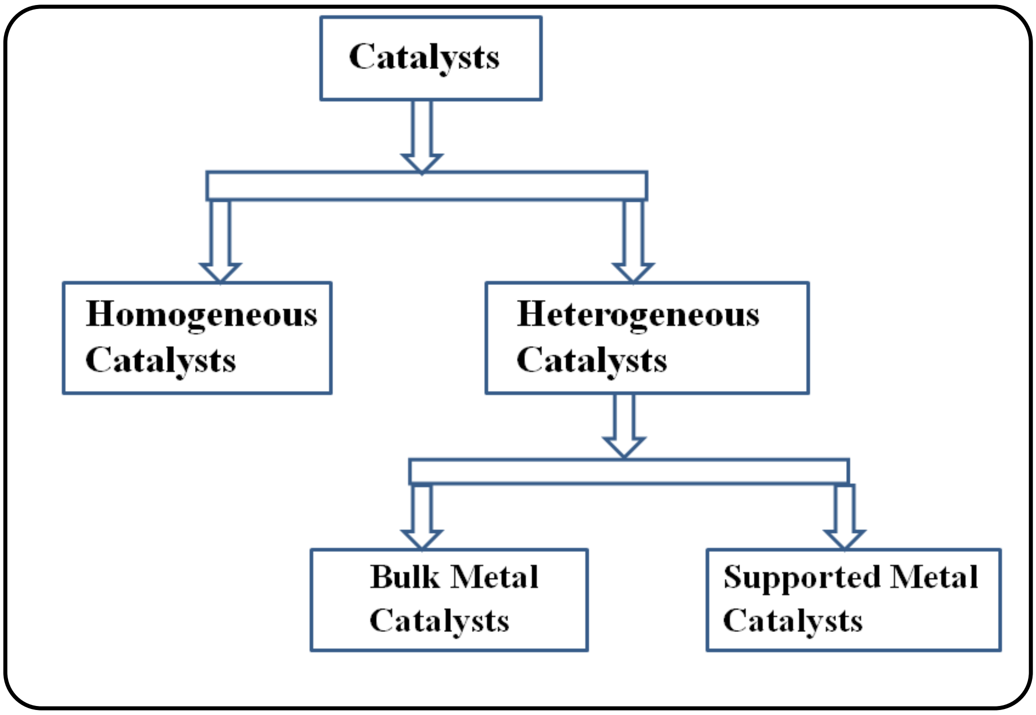
1.3.2: Solvothermal Synthesis: This process involves the heating of organic solvents and metal compounds at high temperatures. It is comprised of usually three stages: (i) heating of the solution or slurry suspension during which dissociation of the metal precursor occurs; (ii) aging of the solution at a desired temperature for further particle nucleation and growth that determines the final size and surface properties of the particles; and (iii) particle separation and collection from the unreacted material and the solvent [32].

1.3.3. Co-reduction Method: This is the simplest and the most commonly used bulk-solution synthetic method for metal NPs by the chemical reduction of metal salts. The synthesis of various metal NPs with different morphologies and sizes using chemical reduction of different metal salt have been reported. This synthetic method involves reduction of an ionic salt in an appropriate medium in the presence or absence of surfactant using various reducing agents [33].

1.3.4. Microwave Assisted Method: The method is similar to solvothermal method. In this method thermal energy is supplied by microwave radiation. Using this method, microwave-assisted heating enables the convenient preparation of polymer capped NPs with improved mono dispersity, morphological control, and higher crystallinity, compared with samples heated conventionally under otherwise identical conditions. Microwave irradiation was found to provide more uniform seeds for the subsequent growth of larger nanostructures of desired size and surface structure. NP growth kinetics is also markedly different under microwave heating [34].

1.4 Nanomaterials as Catalysts

Catalysis is a process of altering the rate of chemical transformations by means of adding some foreign material called catalyst. The ‘catalysis’ is a Greek word which was first introduce by Berzelius in 1836, the prefix, ‘cata’ meaning down, and the verb ‘lysis’ meaning to split or break [35]. According to Berzelius, the catalyst is a material added to the reaction to alter the rate of reaction without being consumed in this chemical process. A catalyst also changes the pathway or mechanism of a reaction by choosing the lowest activation energy path. Catalysts are extensively used in nature, in industry application and laboratory for valuable conversions. It is approximately predicted that catalysis industries contributing one sixth of the value of all manufactured goods in the world. The catalytic activity and selectivity depends on its size, composition and morphology of the catalyst. Many years later in 1895 Ostwald came up with a definition “A catalyst is a substance that changes the rate of a chemical reaction without itself appearing into the products” according to which a catalyst could also slow down a reaction. Scheme 1.3 represents various types of catalysts.



Scheme 1.3: Schematic representation of different catalysts.

Catalysts are basically of two types such as homogeneous and heterogeneous depending on whether it exists in the same or different physical state as compared to reactant. Homogeneous catalysts are present in the same phase to that of reactants and all the catalytic sites are available because they are dissolved in the solvents, thereby it is highly selective towards the formation of a desired product. The benefit of homogeneous catalysis is not only in superior yields but also to have high regio-enantioselectivity. Hence, these catalysts are used in a number of large scale industrial processes. Along with the all mentioned advantages, the homogeneous one find difficulty in separation from the product, owing to which, their impact is restricted. The existence of even trace amount of catalyst in the final product is very objectionable for some industries, mainly the pharmaceutical industry, restraining their usage. Under this context, heterogeneous catalysts come into the role, where the reagents phase is different from those of the catalyst phase. Currently, heterogeneous catalysts are attaining growing importance in the field of chemical conversions due to its definite industrial advantages. For example, in petroleum refinery heterogeneous catalysts play an important rule as cracking, which is the one of the largest process among the industrial processes. The main advantage of the heterogeneous catalytic process is that the separation of the catalyst from the final reaction product is also quite easy than that of the homogeneous catalyst. The heterogeneous catalysts are further categorized to bulk and supported ones. Supported catalysts are more advantageous over bulk catalysts where the active component is precious metals, MOs, and other compounds. To maximize the activity, selectivity and stability, required active components are dispersed over suitable supports, which in turn also reduce the overall cost of catalyzed processes.

1.4.1 Metal NPs as Catalyst: The use of metal NPs as catalyst in various processes is mainly due to their unique large surface-to-volume ratios and quantum-size effects. NPs are effectively used as a both homogeneous and heterogeneous catalyst as NPs are well solubilised by majority of the regular solvents and can frequently be characterized by NMR, infrared, UV-vis spectroscopy and cyclic voltammetry. Therefore, NPs can also be used as homogeneous catalysts or then again they can be converted into heterogeneous by dispersion onto a heterogeneous support, such as alumina, silica, other oxides or carbon based materials. As a result, metal NPs are used in both homogeneous and heterogeneous catalysis, therefore NPs are often called as "semi heterogeneous” [37,38]. On the other hand, metal NPs in the form of heterogeneous catalyst has involved in almost all type of catalytic reactions. Heterogeneous system has many unique properties like selectivity, efficiency, recyclability and hence they meet the modern needs in catalysis. Due to above mentioned advantages metal NPs used in the various fields like production of renewable energy, remediation of environmental pollutants and the synthesis of fine chemicals, such as, hydrogen storage, hydrogenation, FC, ammonia decomposition, catalytic reforming, and wastewater treatment and so on [39,40].

1.4.2. Emerging Applications of Pd and Cu-based NPs

Pd and Cu-based NPs have been playing significant role in the field of catalysis. Due to various classes of applications they are considered as next generation materials in the field of catalysis. These applications can be divided into two broad categories such as energy concerned and environmental applications. The thesis works are mainly focused on the application of hybrid Pd-based NPs and Cu/MO_x-based interfacial catalysts (MO_x = $CuFe_2O_4$ or $CuCo_2O_4$) toward ORR in FCs. Furthermore Cu-based NPs are employed for the reduction reactions of various nitroaromatics that are most important in chemical and pharmaceutical applications. Accordingly, in the next sections we highlight the recent literatures on the ORR in FCs and reduction of nitroaromatics over various Pd- and Cu-based catalysts.

1.4.2.1. Pd-based NPs

Pd-based hybrid NPs has generated significant interest as heterogeneous catalysts due to their versatile compositional and structural properties [41]. The fabrication of these hybrid NPs delivers improved catalytic activity, selectivity, and stability of metal NPs [42]. The catalytic activity of hybrid NPs are tuned or modified by controlling the electronic structure of two metals, surface elemental distribution, inter-metallic charge transfer, and lattice strain [43]. Hybrid NPs of Pd and non-precious metals are especially important from the economic and environmental perspective for lowering production costs and attaining sustainability. Apart from displaying improved catalytic ability, the hybridization of Pd with non-precious metals also increases their resistance towards poisonous ingredients [44]. It can be hybridized with various transition metals (e.g., Cu, Ni, Co, Fe) and MOs to improve its catalytic properties [45]. Specifically, the Pd-Ni hybrid NPs displays excellent catalytic efficiency due to their profound synergistic effect [46]. This is primarily due to the good miscibility between Pd and Ni due to their identical electron configurations and crystal structures [47]. Moreover, the density functional theory calculations shows d-band shifts in Pd, which improves the catalytic activity [48]. The idea of hybridizing two different metals was devised during 1970s and later extended by Toshima and his group [49] who employed polyvinylpyrrolidone (PVP) to stabilize Pd-Au NPs. Various methods have been employed to synthesize hybrid NPs [50-53]. Now-a-days, the use of supported metal NPs are gaining much attention, as the metal immobilized on solid supports remains insoluble in solvents, thereby reducing residual metal in final products [54], thus improving efficiency/quality as well as decreasing the production costs. Thus, various biopolymers and inorganic materials were investigated as supports for the immobilization of Pd NPs for improved catalytic performance [55]. In recent years, Pd-MO hybrid NPs has been extensively explored for various catalytic and sensing application including photocatalytic and electrocatalytic applications [42a-c,56,57].

Because of the increasing population and rapid industrialization, the fossil-fuel resources are decreasing day by day, hence there is a critical need for the use of non-fossil-fuel resources. Sustainable alternative, such as wind, solar, wave energy power, geothermal, and FCs are being explored [58]. Along with other such alternatives, FCs are actively developed for the purpose as they have several advantages like zero emissions, high power density, high efficiency, noiseless operation etc. Among all the existing FCs, the proton exchange membrane FC (PEMFC) has been actively developed for use in vehicles, portable electronics systems due to its simplicity, high power density, quick start-up and low working temperature [59]. However PEMFC faces several difficulties, primarily the sluggish kinetics of the ORR, and thermodynamic instability of cathodes under unsympathetic electrochemical conditions [60]. Figure 1.5 shows the schematic presentation of PEMFC.

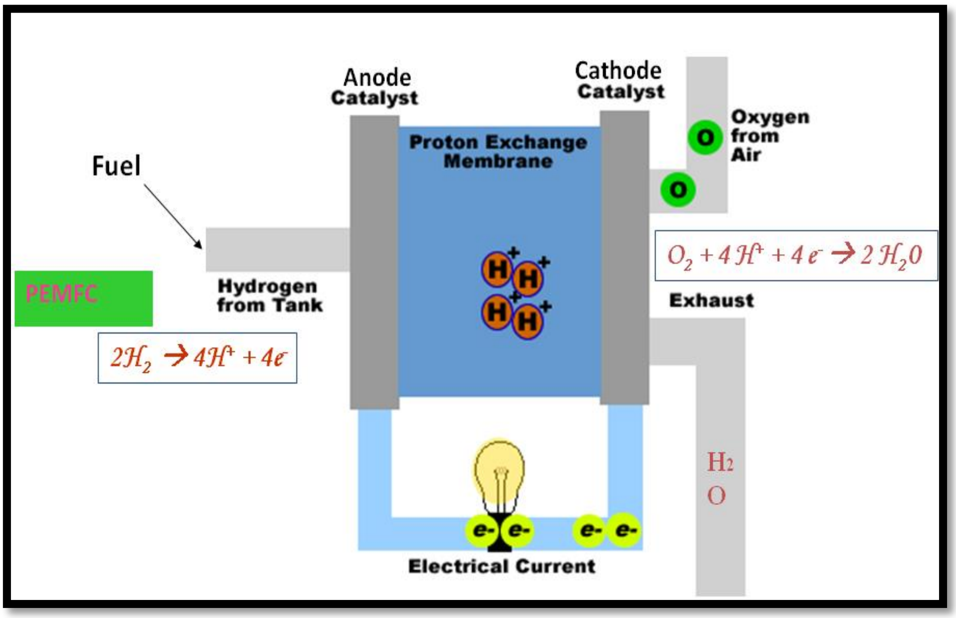


Figure 1.5: Schematic presentation of proton exchange membrane fuel cell.

ORR is a multi-electron reaction that proceeds via several elementary steps involving various intermediates and suitable mechanisms on the cathode surface of FCs. In acidic media, O_2 reduction proceeds as follows:

(i) A direct 4*e*⁻ reduction pathway where O_2 is converted into H_2O.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(ii) A partial 2*e*⁻ reduction pathway that involves formation of H_2O_2 as intermediate.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

Similarly, O_2 reduction in alkaline media also proceeds via 4*e*⁻ pathway to give OH^- as follows:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Or, by a 2*e*⁻ pathway to give HO_2^- as intermediate and then OH^- as shown below:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$$

The slow kinetics of the ORR is among the most limiting factors in the energy conversion efficiency of FCs. For these reason the Pt based catalysts have been extensively used for the desired ORR [61]. However, the high-ceilinged price and low abundance of Pt in resources leads to its high cost of its corresponding devices [62,63]. Moreover, when Pt is used as cathode, kinetic limitations of the ORR, as well as the low alcohol tolerance in direct alcohol FCs become pertinent obstacles in the commercialization of low-temperature FCs [64]. Therefore it is an urgent necessity to develop non-Pt based ORR catalysts with low cost, superior efficiency and high alcohol tolerance. In this context, Pd and Pd-based NPs has become an area of intense attention [65] as a capable alternative for ORR due to its low price, high abundance and comparable properties with Pt such as the identical crystalline structure and close lattice parameters [66]. Although, the inherent catalytic property of Pd for the ORR is still inferior to that of Pt [67], recent works that utilizes Pd-based hybrid catalysts show much promise.

For ORR, the catalysts are supported onto variety of materials. Carbon black is the most common support material due to its high conductivity, large surface area, and low price. Other materials such as carbon nanotubes (CNTs), graphene (G), graphitic carbon nitride (CN_x), MOs, biochar etc. have also been eomployed in recent years. The support material can control the efficiency of the catalysts in several directions. For example, it prevents the agglomeration of NPs, may change conductivity of supported metal via electronic effects and the stability of a catalyst is greatly influenced by preventing the metal leaching. Kumar et al. [68] showed the influence of chemical pretreatment of Vulcan XC-72R carbon support for ORR on Pd NPs in acidic electrolyte. The kinetics of ORR on these electrocatalysts predominantly involves a $4e^-$ process. However, the observed ORR activity is greatly influenced by the pre-treated carbon support and superior to that of standard E-Tek 20% Pd/C. Moreover Pd/Ketjen black and Pd/Vulcan also exhibits good ORR activity and provide stability during chronoamperometric tests [69]. To study the morphology dependent ORR activity, Pd/C with various morphologies using carbonyl chemical route with various metal loading were explored which resulted in variable electrocatalytic activity [70]. Pd/C was also synthesized by using $NaBH_4$ and NH_3 as reducing and complexing reagent, respectively. Twinned and polycrystalline structures of Pd/-$NaBH_4$-NH_3 shows high activity for ORR with a maximum power density of 508 $mWcm^{-2}$ [71]. Carbon paper was also employed as support for the improved ORR activity. Rego et al. used electroless deposition methods for deposition of Pd NPs on porous carbon paper. The new material exhibited superior ORR activity compared to the standard Pt/carbon paper [72]. Doping of non-metal like, N, P, B in G is another strategy to improve ORR activity [73]. Ramaprabhu and his co-worker synthesized triangular shaped Pd NPs decorated nitrogen-doped G by pyrolysis method. It shows high ORR activity with high methanol tolerance in acidic media due to the strong cooperation between Pd NPs and N-G support [74]. Figure 1.6 presents the schematic illustration of SEM, TEM and HR-TEM images of Pd/N-G.

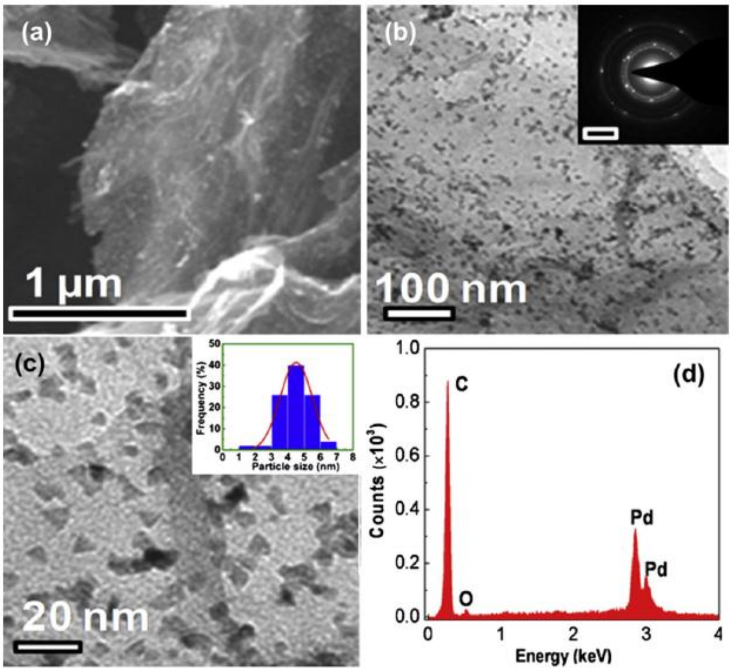


Figure 1.6: (a) SEM image of Pd/N-G, (b, c) Low and high resolution TEM images of Pd/N-G. Inset in (b) shows the diffraction pattern of Pd/N-G and the scale bar corresponds to 5 nm^{-1}. Inset in (c) shows the histogram of the Pd NPs distribution in Pd/N-G electrocatalyst. (d) EDX spectra of Pd/N-G. [Reproduced from 74]

Alkaline electrolytes give a less corrosive environment to the catalysts so that the ORR kinetics is faster in alkaline electrolyte than that in acidic electrolyte. Pd/G QDs was synthesized using thermolytic reduction of $PdCl_2$ in 1,2-propanediol which exhibited good ORR activity in alkaline media[75]. Barman and his co-worker observed superior ORR activity of Pd NPs-CN_x hybrid in both acidic and alkaline media than benchmarked Pt/C with methanol tolerance [76]. Figure 1.7 shows the ORR performance over Pd-CNx hybrid nanocatalyst.

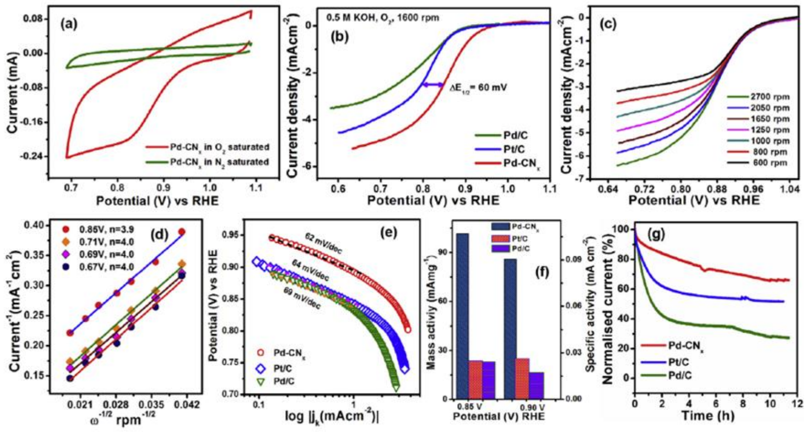


Figure 1.7: ORR on Pd-CN$_x$ composite in 0.5 M KOH medium: (a) CVs of Pd-CN$_x$ composite in O$_2$- and N$_2$-saturated 0.5 M KOH solution with scan rate 100 mV/s, (b) Comparison of LSV curves of porous Pd-CN$_x$, Pt/C and Pd/C modified GC electrode in O$_2$-saturated 0.5 M KOH with 1600 rpm rotation at 100 mV s^{-1} scan rate, (c) LSV curves of Pd-CN$_x$ modified electrode in O$_2$-saturated 0.5 M KOH solution with rotating speed varying from 600 rpm to 2700 rpm, (d) The corresponding K-L plots at different potentials, (e) Mass transfer corrected Tafel slope of Pd-CN$_x$ composite in comparison with Pt/C and Pd/C catalyst in basic medium, (f) The mass activity and specific activity of Pd-CN$_x$, Pt/C and Pd/C modified electrode at different potentials, (g) Steady state chronoamperometric response of Pd-CN$_x$ composite, Pt/C and Pd/C at a constant potential of 0.7 V. [Reproduced from 76]

The ethanol/methanol tolerance for ORR catalysts is a major challenge because ethanol/methanol infiltration to the cathode material will significantly decrease the fuel cell's efficiency. As a result, it is very much important to practical application of the cathode electrocatalysts to possess high ethanol/methanol tolerance ability. The photo-assisted Pd/g-C$_3$N$_4$ exhibits ORR activity via 4e^- pathway in 0.1 M KOH solution which exhibited significant methanol tolerance as well as enhanced stability in comparison to the benchmark Pt/C [77]. CNT is also used as support due to its high surface area, porous structure, good conductivity, and stability [78]. Jukk et al. prepared Pd NP/MWCNT hybrids by magnetron sputtering and applied for ORR in both acidic and alkaline solution. [79]. Transition MOs are also used to improve the ORR activity and methanol tolerance. The hypo d-electron transition MOs has good corrosion-resistance, high chemical-stability, high surface area and strong metal-support interaction, which can improve the performance of the catalysts. MOs, as catalyst supports, are able to stabilize and disperse effectively a number of active phases, as well as to retain a high surface area [80, 81]. Sun et al. synthesized

Pd@MnO_2 hybrid nanocatalysts by depositing Pd on the surface of β-MnO_2 nanorod. The activities of the Pd@MnO_2 NPs for ORR were 2.5 times higher than that of the Pd/C catalyst. The better activity of the catalyst is due to the Pd layer on the surface of the MnO_2 nanorod [57]. Other report by using different form of MnO_2 as support material has also found enhanced activity than the commercial Pt/C [82,83]. WO_3 and TiO_2 are also explored for fabrication of hybrid catalysts with superior ORR activity and methanol tolerance ability than the benchmark Pt/C [84-86].

1.4.2.2: Cu-based NPs

This part provides an overview of Cu-based NPs, especially in the field of environmental catalysis. The growing world population with their intensification of agricultural and industrial activities are responsible for the contamination of air, soils and aquatic ecosystems and also for global climate change [87].

Cu is attractive because of its high natural abundance and low cost [88]. They can promote and catalyze a variety of chemical reactions due to varied oxidation states of Cu (Cu^0, Cu^I, Cu^{II}, and Cu^{III}) [89]. Cu-based NPs have been widely employed in organic transformations, reduction/oxidation, photocatalysis, electrocatalysis, and so on [90-96]. Additionally, Cu has high boiling point that makes it compatible with high-temperature reactions such as continuous flow reactions, microwave-assisted reactions, vapor phase reactions, and various organic transformations [89,93]. Due to such unique properties, Cu-based NPs are suitable for the development of reactive and selective catalytic systems. Metallic Cu NPs have demonstrated different catalytic, electronic and/or surface enhanced plasmonic resonance properties [94,95]. In 2014, Deka et al. reported [97] in situ generation of Cu NPs via a precursor mediated route. Figure 1.8 represents the characterization and catalytic activity of the in situ generated Cu NPs.

Reduction of nitroaromatics to their corresponding amines is industrially significant. For example, 4-nitrophenol (4-NP) is a common ‘water pollutant’ whereas 4-aminophenol (4-AP) is an important substrate in the preparation of several analgesics and antipyretic drugs [99–101]. Hence, the reduction of 4-NP to 4-AP finds wide consideration and consequently several heterogeneous nanocatalysts are developed in recent years which functions in the presence of suitable reducing agent

[102–104]. Nasrollahzadeh et al. [90] reported a facile synthesis of environmentally benign Cu NPs/perlite composites which showed favourable activity and separability for the catalytic reduction of 4-NP. Bhaumik and co-workers [105] reported selective synthesis of Cu nanorods/nanospheres using a saturated fatty acid as template for chemoselective reduction of nitrobenzenes.

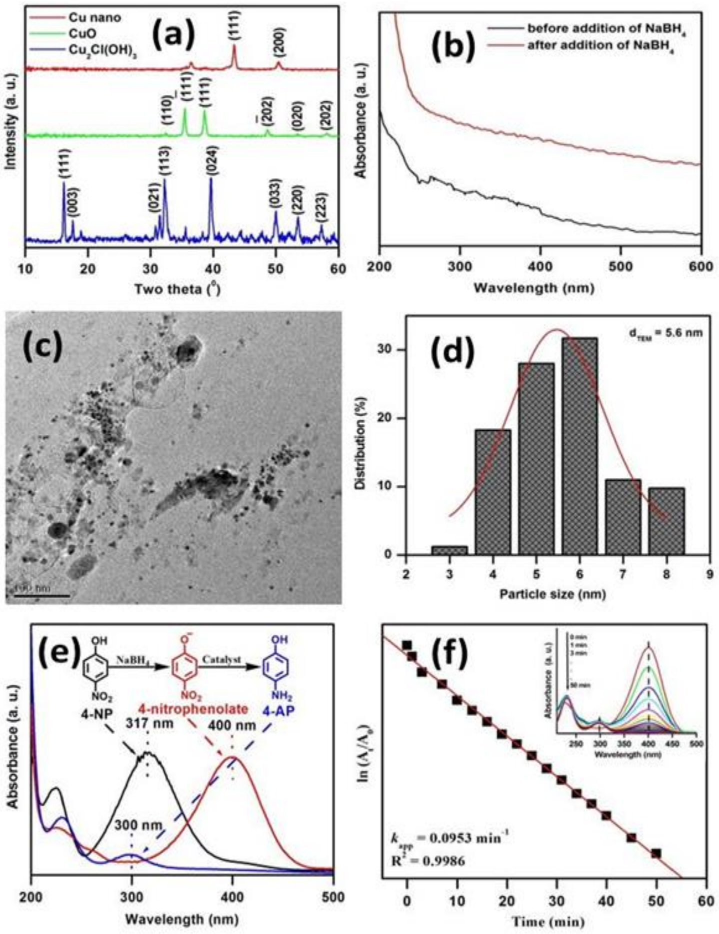


Figure 1.8: XRD pattern of different Cu-compounds (a); UV-visible spectra of $Cu_2Cl(OH)_3$ (b); TEM image of in-situ generated Cu NPs (c); particle size distribution of Cu NPs (d); UV-visible absorption spectra (e) of 4-nitrophenol before (black line) and after (red line) addition of $NaBH_4$ and 4-aminophenol (blue line) and plot of $\ln(A_t/A_0)$ against reaction time (f) derived from absorption spectra (inset) of 4-nitropehnol reduction in presence of in-situ Cu nanocatalyst. [Reproduced from: 88]

The bimetallic NPs preferred over monometallic counterparts because of improved activity. Noble metal bimetallics are studied more frequently [106]. However, high cost and scarcity of the noble metals limit their practical applications in large scale processes. Therefore, in very recent time, attention turns towards the cost effective transition metals that has almost similar electronic properties compared with the noble metal counterparts [107]. In this context, Cu-based bimetallics with second metals e.g., Fe, Co, Ni etc are particularly find importance due to their high natural abundance as well as low cost [89].· Zhai and co-workers reported [108] dendritic Cu-M (M = Fe, Co and Ni) microstructures synthesized via a facile, environment-friendly, and rapid electrodeposited route at room temperature.

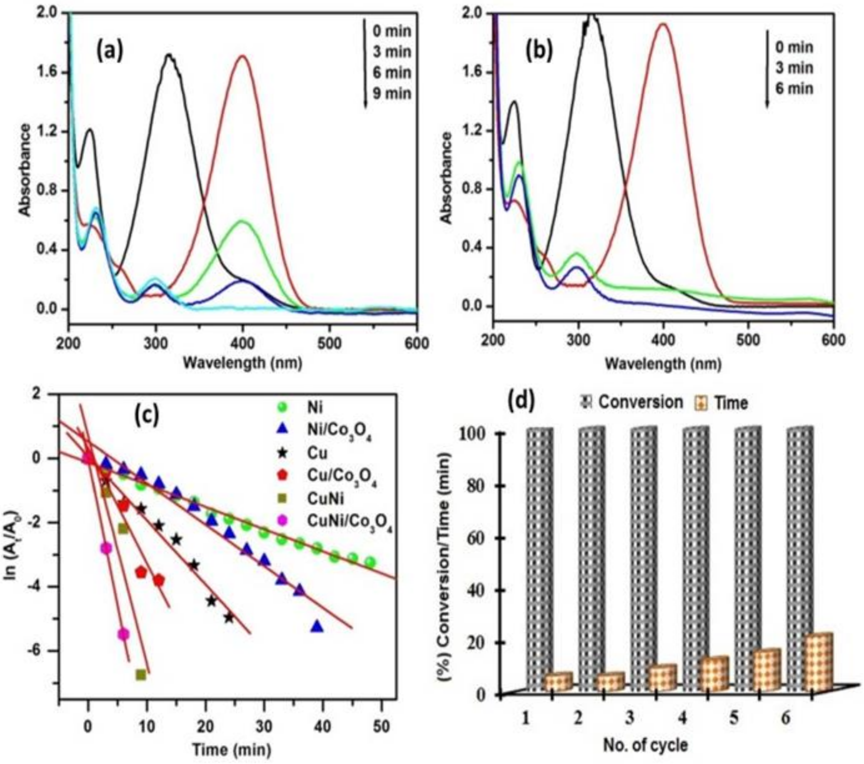


Figure 1.9: Time dependent UV-visible absorption spectra over CuNi (a) and CuNi/Co_3O_4 (b); plots of ln (A_t/A_0) against reaction time derived from absorption spectra (c) and recyclability test over CuNi/Co_3O_4 nanocatalyst for the 4-NP reduction, respectively. [Reproduced from 88]

The Cu-M dendrites exhibited excellent catalytic activity for the reduction of 4-NP to 4-AP in excess $NaBH_4$. Chen and co-workers [109] reported CuNi nanocrystals supported on RGO synthesized by co-reduction of Cu^{2+}, Ni^{2+} and GO. The synthesized RGO–CuNi nanocomposite exhibited high catalytic activity and recyclability toward the reduction of 4-NP. Furthermore, due to the ferromagnetic property of nanocomposite the catalyst could be easily separated by an external magnetic field. Krishna et al·[110] reported Cu@Ni/RGO using simple two step method and employed for catalytic reduction of 4-NP. Li and co-workers [111] synthesized G/CuNi nanocomposites by electrostatic-adsorption and explored for 4-NP reduction Nasrollahzadeh and co-workers [112] synthesized Cu/Fe_3O_4/eggshell nanocomposites via a green and economical method using aqueous extract of the leaves of *Orchis mascula L.*. The nanocomposites exhibited good activity towards the reduction of various dye including 4-NP. Guo et al. synthesized magnetic core–shell C-dot@MFe_2O_4 (M = Mn, Zn and Cu) hybrid materials through a facile ultrasonic method [113]. The catalytic activity for reduction of 4-NP followed an order of C-dot@$CuFe_2O_4$ > $CuFe_2O_4$ > C-dot@$MnFe_2O_4$ > C-dot@$ZnFe_2O_4$ > $MnFe_2O_4$ > $ZnFe_2O_4$ > C-dots. In 2016 Bharali and his co-workers reported synthesis of supported CuNi NPs over Co_3O_4 by surfactant aided co-reduction method for nitroaromatics reduction [114]. Figure 1.9 represents the catalytic reduction of 4-NP over bare and Co_3O_4 supported CuNi NPs. Wang and co-workers[115] reported Cu/Co@NPCC for the reduction of 4-NP. Goyal et al. [116] fabricated transition metal doped cobalt ferrite ($CoM_{0.2}Fe_{1.8}O_4$ (M= Co, Ni, Cu, Zn) NPs with quasi-spherical shape using the sol-gel method. The catalytic efficiency of the synthesized ferrite samples were investigated for the reduction of various substituted nitrophenols. $CoCu_{0.2}Fe_{1.8}O_4$ showed superior catalytic activity for the reduction of nitrophenol than the other metal (M= Co, Ni and Zn) ferrite.

1.5 Objectives of the Present Work

The final objectives for the present work are succinctly given below:

I. To synthesize bimetallic or trimetallic NPs of type $Pd_{4-x}M'_x/C$ and $Pd_{4-x}CuM''/C$ (M' = Cu, Ni, Fe; M'' = Fe, Co, Ni; x = 1-3), $Cu/MO_x/C$ ($MO_x = CuFe_2O_4$ and $CuCo_2O_4$) and CuM (M = Ni and Fe) by hydrothermal/solvothermal method.

II. To study the physicochemical properties of the synthesized NPs by various analytical techniques, such as, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray analyses (EDX), inductively coupled plasma-optical emission spectrometry (ICP-OES), ultraviolet-visible spectroscopy (UV-Vis), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area and vibrating sample magnetometer (VSM).

III. To study the electrocatalytic activity of $Pd_{4-x}M'_x/C$ and $Pd_{4-x}CuM''/C$ (M' = Cu, Ni, Fe; M'' = Fe, Co, Ni; x = 1-3), $Cu/MO_x/C$ ($MO_x = CuFe_2O_4$ and $CuCo_2O_4$) NPs toward oxygen reduction reaction.

IV. To evaluate the catalytic activity of CuM (M = Ni and Fe) NPs for reduction of nitroaromatics.

References

[1] Daniel, M-C. and Astruc, D. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews*,104:293−346, 2004.

[2] van Albada, G. A., and Schreck, J. O. Alchemy and philately. *Journal of Chemical Education*, 64(10):869, 1987.

[3] Bhattacharya, R., Patra, C. R., Earl, A., Wang, S., Katarya, A., Lu, L., Kizhakkedathu, J. N., Yaszemski, M. J., Greipp, P. R., Mukhopadhyay, D., and Mukherjee, P. Attaching folic acid on gold nanoparticles using noncovalent interaction via different polyethylene glycol backbones and targeting of cancer cells. *Nanomedicine: Nanotechnology, Biology and Medicine*, 3(3):224−238, 2007.

[4] Wang, D., and Li, Y. Bimetallic nanocrystals: liquid-phase synthesis and catalytic applications. *Advanced Materials*, 23(9):1044−1060, 2011.

[5] Neuberger, T., Schöpf, B., Hofmann, H., Hofmann, M., and von Rechenberg, B. Superparamagnetic nanoparticles for biomedical applications: Possibilities and limitations of a new drug delivery system. *Journal of Magnetism and Magnetic Materials*, 293(1):483−496, 2005.

[6] Liotta, L. F., Gruttadauria, M., Di Carlo, G., Perrini, G., and Librando, V. Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity. *Journal of Hazardous Materials*, 162(2-3):588−606, 2009.

[7] Chu, Y. Y., Qian, Y., Wang, W. J., and Deng, X. L. A dual-cathode electro-Fenton oxidation coupled with anodic oxidation system used for 4-nitrophenol degradation. *Journal of Hazardous Materials*, 199-200:179−185, 2012.

[8] Luo, X., Morrin, A., Killard, A. J., and Smyth, M. R. Application of nanoparticles in electrochemical sensors and biosensors. *Electroanalysis*, 18(4):319−326, 2006.

[9] Mott, D., Galkowski, J., Wang, L., Luo, J., Zhong C. J. Synthesis of size-controlled and shaped copper nanoparticle. *Langmuir*, 23(10):5740−5745, 2007.

[10] Meek, S. T., Greathouse, J. A., and Allendorf, M. D. Metal-organic frameworks: a rapidly growing class of versatile nanoporous materials. *Advanced Materials*, 23(2):249−267, 2011.

[11] Walter, P., Welcomme, E., Hallegot, P., Zaluzec, N. J., Deeb, C., Castaing, J., Veyssiere, P., Breniaux, R., Leveque, J. L. and Tsoucaris, G. Early use of PbS nanotechnology for an ancient hair dyeing formula. *Nano Letters*, 6:2215−2219, 2006.

[12] Horikoshi, S. and Serpone, N. Microwaves in NP Synthesis: Fundamentals and Applications; Wiley-VCH, Heidelberg, 2013.

[13] Reibold, M., Paufler, P., Levin, A. A., Kochmann, W., Pätzke, N., and Meyer, D. C. Carbon nanotubes in an ancient Damascus sabre. *Nature*, 444(7117):286−286, 2006.

[14] Perttula, J. Wootz Damascus steel of ancient orient. *Scandinavian Journal of Metallurgy*, 33(2):92−97, 2004.

[15] X. The Bakerian Lecture. Experimental relations of gold (and other metals) to light. *Philosophical Transactions of the Royal Society of London*, 147:145−181, 1857.

[16] IX. Electro-physiological researches. Physical and chemical phenomena of muscular contraction.Tenth series. Part I. *Philosophical Transactions of the Royal Society of London*, 147:129−143, 1857.

[17] Binnig, G., Rohrer, H., Gerber, C., and Weibel, E. Surface studies by scanning tunneling microscopy. *Physical Review Letters*, 49(1):57−61, 1982.

[18] Binnig, G., Quate, C. F., and Gerber, C. Atomic Force Microscope. *Physical Review Letters*, 56(9):930−933, 1986.

[19] Rao, C. N. R., Kulkarni, G. U., Thomas, P. J., and Edwards, P. P. Metal nanoparticles and their assemblies. *Chemical Society Reviews*, 29(1):27−35, 2000.

[20] Novoselov, K. S., Geim, A. K., Morozov, S. V, Jiang, D., Zhang, Y., Dubonos, S. V, Grigorieva, I. V, and Firsov, A. A. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666−669, 2004.

[21] Schedin, F., Geim, A. K., Morozov, S. V., Hill, E. W., Blake, P., Katsnelson, M. I., and Novoselov, K. S. Detection of individual gas molecules adsorbed on graphene. *Nature Materials*, 6(9):652−655, 2007.

[22] Lin, C.-A. J., Liedl, T., Sperling, R. A., Fernández-Argüelles, M. T., Costa-Fernández, J. M., Pereiro, R., Sanz-Medel, A., Chang, W. H., and Parak, W. J.

Bioanalytics and biolabeling with semiconductor nanoparticles (quantum dots). *J. Mater. Chem.*, 17(14):1343−1346, 2007.

[23] Ferrando, R., Jellinek, J., and Johnston, R. L. Nanoalloys: from theory to applications of alloy clusters and nanoparticles. *Chemical Reviews*, 108(3):845−910, 2008.

[24] Chang, C.-R., Long, B., Yang, X.-F., and Li, J. Theoretical studies on the synergetic effects of Au–Pd bimetallic catalysts in the selective oxidation of methanol. *The Journal of Physical Chemistry C*, 119(28):16072−16081, 2015.

[25] Gao, F., and Goodman, D. W. Pd–Au bimetallic catalysts: understanding alloy effects from planar models and (supported) nanoparticles. *Chemical Society Reviews*, 41(24):8009−8020, 2012.

[26] Qin, H., Li, W., Xia, Y., and He, T. Photocatalytic activity of heterostructures based on ZnO and N-Doped ZnO. *ACS Applied Materials & Interfaces*, 3(8):3152−3156, 2011.

[27] Bhushan, B *Introduction to Nanotechnology*, in: B. Bhushan (ed.) springer Handbook of Nanotechnology, Berlin: Springer-Verlag, 2004.

[28] Ozin, G. A. and Arsenault, A. C. *Nanochemistry: A Chemical Approach to Nanomaterials*, RSC Publishing, 2005.

[29] Goesmann, H., and Feldmann, C. Nanoparticulate functional materials. *Angewandte Chemie International Edition*, 49(8):1362−1395, 2010.

[30] Gong, X., Milic, T., Xu, C., Batteas, J. D., Drain, and C. M. Preparation and characterization of porphyrin nanoparticles. *Journal of American Chemical Society*, 124:14290−14291, 2002.

[31] Schäf, O., Ghobarkar, H., and Knauth, P. Knauth, P. and Schoonman, J., *Nanostructured Materials: Selected Synthesis Methods, Properties and Applications*, 23–42, Kluwer Academic Publishers, Boston, 2002.

[32] Soultanidis, N., Zhou, W., Kiely, C. J., and Wong, M. S. Solvothermal synthesis of ultrasmall tungsten oxide nanoparticles. *Langmuir*, 28(51):17771−17777, 2012.

[33] Cheng-Min, S., Chao, H., Tian-Zhong, Y., Cong-Wen, X., Shu-Tang, E., Hao, D., and Hong-Jun, G. Monodispersive CoPt nanoparticles synthesized using chemical reduction method. *Chinese Physics Letters*, 25(4):1479−1481, 2008.

[34] Zhang, H., Fei, C., Zhang, D., and Tang, F. Degradation of 4-nitrophenol in aqueous medium by electro-Fenton method. *Journal of Hazardous Materials*, 145(1-2):227−232, 2007.

[35] Wikipedia Contributors. Catalysis. Retrieved on 12 May. 2017 from https://en.wikipedia.org/wiki/Catalysis, july,2019.

[36] Altavilla, C. and. Ciliberto, E. *Inorganic Nanoparticles: Synthesis, Applications, and Perspectives*, 2011.

[37] de Vries, J. G. A unifying mechanism for all high-temperature Heck reactions. The role of palladium colloids and anionic species. *Dalton Trans.*, (3):421−429, 2006.

[38] Feng, J., Chen, L., Song, P., Wu, X., Wang, A., and Yuan, J. Bimetallic AuPd nanoclusters supported on graphitic carbon nitride : One-pot synthesis and enhanced electrocatalysis for oxygen reduction and hydrogen evolution. *International Journal of Hydrogen Energy*, 41(21):8839−8846, 2016.

[39] Liu, Y., and Walker, A. R. H. Monodisperse gold-copper bimetallic nanocubes: facile one-step synthesis with controllable size and composition. *Angewandte Chemie International Edition*, 49(38):6781−6785, 2010.

[40] Singh, S. K., Singh, A. K., Aranishi, K., and Xu, Q. Noble-metal-free bimetallic nanoparticle-catalyzed selective hydrogen generation from hydrous hydrazine for chemical hydrogen storage. *Journal of the American Chemical Society*, 133(49):19638−19641, 2011.

[41] Shimizu, K., Sawabe, K. and Satsuma, A. Unique catalytic features of Ag nanoclusters for selective NO_x reduction and green chemical reactions. *Catalysis Science & Technology*, 1:331–341, 2011.

[42] Xiao, C., Wang, L. L., Maligal-Ganesh, R. V., Smetana, V., Walen, H., Thiel, P. A., Miller, G. J., Johnson, D. D. and Huang, W. Intermetallic $NaAu_2$ as a heterogeneous catalyst for low-temperature CO oxidation. *Journal of the American Chemical Society*, 135(26):9592–9595, 2013.

[43] Sinfelt, J. H. Catalysis by alloys and bimetallic clusters. *Accounts of Chemical Research*, 10(1):15–20, 1977.

[44] Serov, A. and Kwak, C. Review of non-platinum anode catalysts for DMFC and PEMFC application. *Applied Catalysis B: Enviromental*, 90(3-4):313–320,

2009.

[45] Liu, S., Zhang, Q., Li, Y., Han, M., Gu, L., Nan, C., Bao, J. and Dai, Z. Five-fold twinned Pd_2NiAg nanocrystals with increased surface ni site availability to improve oxygen reduction activity. *Journal of the American Chemical Society*, 137(8):2820–2823, 2015.

[46] Nakagawa, Y.and Tomishige, K. Total hydrogenation of furan derivatives over silica-supported Ni–Pd alloy catalyst. *Catalysis Communications*, 12(3):154–156, 2010.

[47] Wu, Y., Wang, D., Zhao, P., Niu, Z., Peng, Q. and Li, Y. Monodispersed Pd-Ni nanoparticles: Composition control synthesis and catalytic properties in the Miyaura-Suzuki reaction. *Inorganic. Chemistry*, 50(6):2046–2048, 2011.

[48] Demirci, U. B. Theoretical means for searching bimetallic alloys as anode electrocatalysts for direct liquid-feed fuel cells. *Journal of Power Sources*, 173(1):11–18, 2007.

[49] Toshima, N., Harada, M., Yamazaki, Y.and Asakura, K. Catalytic activity and structural analysis of polymer-protected Au-Pd bimetallic clusters prepared by the simultaneous reduction of $HAuCl_4$ and $PdCl_2$. *The Journal of Physical Chemistry*, 96(24):9927–9933, 1992.

[50] Kuttiyiel, K. A., Sasaki, K., Choi, Y., Su, D., Liu, P. and Adzic, R. R. Nitride stabilized PtNi core–shell nanocatalyst for high oxygen reduction activity. *Nano Letters*, 12(12):6266–6271, 2012.

[51] Chen, J., Wiley, B., McLellan, J., Xiong, Y., Li, Z. Y. and Xia, Y. Optical properties of Pd-Ag and Pt-Ag nanoboxes synthesized via galvanic replacement reactions. *Nano Letters*, 5(10):2058–2062, 2005.

[52] Sarkar, A., Murugan, A. V.and Manthiram, A. Pt-encapsulated Pd-Co nanoalloy electrocatalysts for oxygen reduction reaction in fuel cells. *Langmuir*, 26(4):2894–2903, 2010.

[53] Coutts, M. J., Zareie, H. M., Cortie, M. B., Phillips, M. R., Wuhrer, R. and McDonagh, A. M. Exploiting zinc oxide re-emission to fabricate periodic arrays. *ACS Applied Materials & Interfaces*, 2(6):1774–1779, 2010.

[54] Zaccheria, F., Ravasio, N., Psaro, R.and Fusi, A. Heterogeneous selective catalytic hydrogenation of aryl ketones to alcohols without additives.

Tetrahedron Letters, 46(21):3695–3697, 2005.

[55] Karim, A. A., Tie, A. P.-L., Manan, D. M. A. and Zaidul, I. S. M. Starch from the sago (*Metroxylon sagu*) palm tree properties, prospects, and challenges as a new industrial source for food and other uses. *Comprehensive Reviews in Food Science and Food Safety*, 7(3):215–228, 2008.

[56] Zhang, Y., Wang, Q., Xu, J. and Ma, S. Synthesis of Pd/ZnO nanocomposites with high photocatalytic performance by a solvothermal method. *Applied Surface Science*, 258:10104–10109, 2012.

[57] Sun, W., Hsu, A. and Chen, R. Palladium-coated manganese dioxide catalysts for oxygen reduction reaction in alkaline media. *Jounal of Power Sources*, 196:4491–4498, 2011.

[58] Yu, X. and Pickup, P. G. Recent advances in direct formic acid fuel cells (DFAFC). *Journal of Power Sources*, 182:124−132, 2008.

[59] Nie, Y., Li, L. and Wei, Z. Recent advancements in Pt and Pt-free catalysts for oxygen reduction reaction. *Chemical Society Reviews*, 44:2168−2201, 2015.

[60] Seo, M. H., Choi, S. M., Lee, D. U., Kim, W. B. and Chen, Z. Correlation between theoretical descriptor and catalytic oxygen reduction activity of graphene supported palladium and palladium alloy electrocatalysts. *Journal of Power Sources*, 300:1−9, 2015.

[61] Meku, E., Du, C., Wang, Y., Du, L., Sun, Y., Kong, F. and Yin, G. Concentration gradient Pd-Ir-Ni/C electrocatalyst with enhanced activity and methanol tolerance for oxygen reduction reaction in acidic medium. *Electrochimica Acta*, 192:177−187, 2016.

[62] Stauffer, D. B., Hirschenhofer, J. H., Klett, M. G. and Engleman, R. R. Fuel Cell Handbook (No. DOE/FETC-99/1076). Federal Energy Technology Center (FETC), Morgantown, WV, and Pittsburgh, PA. 1998**.**

[63] Brouzgou, A., Song, S. Q.and Tsiakaras, P. Low and non-platinum electrocatalysts for PEMFCs: Current status, challenges and prospects. *Applied Catalysis B: Environmental*, 127:371−388, 2012.

[64] Antolini, E. Alloy vs. intermetallic compounds: Effect of the ordering on the electrocatalytic activity for oxygen reduction and the stability of low

temperature fuel cell catalysts. *Applied Catalysis B: Environmental*, 217:201–213, 2017.

[65] Bianchini, C. and Shen, P. K. Palladium-based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells. *Chemical. Reviews*, 109:4183–4206, 2009.

[66] Antolini, E. Palladium in fuel cell catalysis. *Energy & Environmental Science*, 2:915–931, 2009.

[67] Shao, M. Palladium-based electrocatalysts for oxygen reduction reaction. *In Electrocatalysis in fuel cells. Springer, London*. 513–531, 2013.

[68] Kumar, S. S., Herrero, J. S., Irusta, S. and Scott, K. The effect of pretreatment of Vulcan XC-72R carbon on morphology and electrochemical oxygen reduction kinetics of supported Pd nano-particle in acidic electrolyte. *Journal of Electroanalytical Chemistry*, 647:211–221, 2010.

[69] Alegre, C., Stassi, A., Modica, E., Vecchio, C. L., Aricò, A. S.and Baglio, V. Investigation of the activity and stability of Pd-based catalysts towards the oxygen reduction (ORR) and evolution reactions (OER) in iron–air batteries. *RSC Advances*, 5:25424–25427, 2015.

[70] Luo, Y., Mora-Hernández, J. M., Estudillo-Wong, L. A., Arce-Estrada, E. M. and Alonso-Vante, N. Nanostructured palladium tailored via carbonyl chemical route towards oxygen reduction reaction. *Electrochimica Acta*, 173:771–778, 2015.

[71] Rego, R., Oliveira, C., Velázquez, A. and Cabot, P. L. A new route to prepare carbon paper-supported Pd catalyst for oxygen reduction reaction. *Electrochemical Communications*, 12:745–748, 2010.

[72] Rego, R., Oliveira, M. C., Alcaide, F. and Álvarez, G. Development of a carbon paper-supported Pd catalyst for PEMFC application. *International Journal of Hydrogen Energy*, 7:7192–7199, 2012.

[73] Lin, H., Chu, L., Wang, X., Yao, Z., Liu, F., Ai, Y., Zhuang, X. and Han, S. Boron, nitrogen, and phosphorous ternary doped graphene aerogel with hierarchically porous structures as highly efficient electrocatalysts for oxygen reduction reaction. *New Journal of Chemistry*, 40:6022–6029, 2016.

[74] Vinayan, B. P., Sethupathi, K. and Ramaprabhu, S. Facile synthesis of

triangular shaped palladium nanoparticles decorated nitrogen doped graphene and their catalytic study for renewable energy applications. *International Journal of Hydrogen Energy*, 38:2240−2250, 2013.

[75] Deming, C. P., Mercado, R., Gadiraju, V., Sweeney, S. W., Khan, M. and Chen, S. Graphene quantum dots-supported palladium nanoparticles for efficient electrocatalytic reduction of oxygen in alkaline media. *ACS Sustainable Chemistry & Engineering*, 3:3315−3323, 2015.

[76] Bhowmik, T., Kundu, M. K., Barman, S. Highly active and durable Pd nanoparticles-porous graphitic carbon nitride composite for electrocatalytic oxygen reduction reaction. *International Journal of Hydrogen Energy*, 41:14768−14777, 2016.

[77] Konda, S. K., Amiri, M., and Chen, A. Photoassisted deposition of palladium nanoparticles on carbon nitride for efficient oxygen reduction. *The Journal of Physical Chemistry C*, 120:14467−14473, 2016.

[78] Lin, Y., Cui, X. and Ye, X. Electrocatalytic reactivity for oxygen reduction of palladium-modified carbon nanotubes synthesized in supercritical fluid. *Electrochemical Communications*, 7:267−274, 2005.

[79] Jukk, K., Alexeyeva, N., Sarapuu, A., Ritslaid, P., Kozlova, J., Sammelselg, V.and Tammeveski, K. Electroreduction of oxygen on sputter-deposited Pd nanolayers on multi-walled carbon nanotubes. *International Journal of Hydrogen Energy*, 38:3614−3620, 2013.

[80] Takenaka, S., Susuki, N., Miyamoto, H., Tanabe, E., Matsune, H.and Kishida, M. Highly durable Pd metal catalysts for the oxygen reduction reaction in fuel cells, coverage of Pd metal with silica. *Chemical Communications*, 46:8950−8952, 2010.

[81] Takenaka, S., Susuki, N., Miyamoto, H., Tanabe, E., Matsune and H., Kishida, M. Highly durable carbon nanotube-supported Pd catalysts covered with silica layers for the oxygen reduction reaction. *Journal of Catalysis*, 279:381−388, 2011.

[82] Dong, H. Q., Chen, Y. Y., Han, M., Li, S. L., Zhang, J., Li, J. S., Lan, Y.Q., Dai, Z.H. and Bao, J. C. Synergistic effect of mesoporous Mn_2O_3-supported Pd nanoparticle catalysts for electrocatalytic oxygen reduction reaction with

enhanced performance in alkaline medium. *Journal of Materials Chemistry A*, 2:1272−1276, 2014.

[83] Zhang, Z., Wang, X., Cui, Z., Liu, C., Lu, T. and Xing, W. Pd nanoparticles supported on WO_3/C hybrid material as catalyst for oxygen reduction reaction. *Journal of Power Sources*, 185:941−945, 2008.

[84] Lu, Y., Jiang, Y., Gao, X., Wang, X. and Chen, W. Strongly coupled Pd nanotetrahedron/tungsten oxide nanosheet hybrids with enhanced catalytic activity and stability as oxygen reduction electrocatalysts. *Journal of the American Chemical Society*, 136(33):11687−11697, 2014.

[85] Li, J., Zhou, H., Zhuo, H., Wei, Z., Zhuang, G. L., Zhong, X., Deng, S., Li, X and Wang, J. G. Oxygen vacancy on TiO_2 promoted the activity and stability of supported Pd nanoparticles for oxygen reduction reaction. *Journal of Materials Chemistry A*, 6:2264–2272, 2018.

[86] Yousaf, A. B., Imran, M., Uwitonze, N., Zeb, A., Zaidi, S. J., Ansari, T. M., Yasmeen, G. and Manzoor, S. Enhanced electrocatalytic performance of Pt_3Pd_1 alloys supported on CeO_2/C for methanol oxidation and oxygen reduction reactions. *The Journal of Physical Chemistry C*, 121(4):2069−2079, 2017.

[87] Perreault, F., Fonseca de Faria, A., and Elimelech, M. Environmental applications of graphene-based nanomaterials. *Chemical Society Reviews*, 44(16):5861−5896, 2015.

[88] Deka, P., Borah, B.J., Saikia, H. and Bharali, P. Cu-based nanoparticles as emerging environmental catalysts, *The Chemical Record*, 19:462 – 473, 2019.

[89] Gawande, M. B., Goswami, A., Felpin, F.-X., Asefa, T., Huang, X., Silva, R., Zou, X., Zboril, R., and Varma, R. S. Cu and Cu-based nanoparticles: synthesis and applications in catalysis. *Chemical Reviews*, 116(6):3722−3811, 2016.

[90] Nasrollahzadeh, M., Sajadi, S. M., Rostami-Vartooni, A., Bagherzadeh, M., and Safari, R. Immobilization of copper nanoparticles on perlite: Green synthesis, characterization and catalytic activity on aqueous reduction of 4-nitrophenol. *Journal of Molecular Catalysis A: Chemical*, 400:22−30, 2015.

[91] Zou, X., Fan, H., Tian, Y., and Yan, S. Synthesis of Cu_2O/ZnO hetero-nanorod arrays with enhanced visible light-driven photocatalytic activity. *CrystEngComm*, 16(6):1149−1156, 2014.

[92] Li, Z., Liu, J., Wang, D., Gao, Y., and Shen, J. $Cu_2O/Cu/TiO_2$ nanotube Ohmic heterojunction arrays with enhanced photocatalytic hydrogen production activity. *International Journal of Hydrogen Energy*, 37(8):6431−6437, 2012.

[93] Shaygan Nia, A., Rana, S., Döhler, D., Jirsa, F., Meister, A., Guadagno, L., Koslowski, E., Bron, M., and Binder, W. H. Carbon-supported copper nanomaterials: Recyclable catalysts for Huisgen [3+2] cycloaddition reactions. *Chemistry - A European Journal*, 21(30):10763−10770, 2015.

[94] Yang, X., Zhong, H., Zhu, Y., Jiang, H., Shen, J., Huang, J., and Li, C. Highly efficient reusable catalyst based on silicon nanowire arrays decorated with copper nanoparticles. *Journal of Materials Chemistry A*, 2(24):9040−9047, 2014.

[95] Guo, X., Hao, C., Jin, G., Zhu, H.-Y., and Guo, X.-Y. Copper nanoparticles on graphene support: an efficient photocatalyst for coupling of nitroaromatics in visible light. *Angewandte Chemie International Edition*, 53(7):1973−1977, 2014.

[96] Kale, M. J., Avanesian, T., and Christopher, P. Direct photocatalysis by plasmonic nanostructures. *ACS Catalysis*, 4(1):116−128, 2014.

[97] Deka, P., Deka, R. C., and Bharali, P. In situ generated copper nanoparticle catalyzed reduction of 4-nitrophenol. *New Journal of Chemistry*, 38(4):1789−1793, 2014.

[98] Sun, Y., Xu, L., Yin, Z., and Song, X. Synthesis of copper submicro/nanoplates with high stability and their recyclable superior catalytic activity towards 4-nitrophenol reduction. *Journal of Materials Chemistry A*, 1(39):12361−12370, 2013.

[99] Jiang, Z., Xie, J., Jiang, D., Jing, J., and Qin, H. Facile route fabrication of nano-Ni core mesoporous-silica shell particles with high catalytic activity towards 4-nitrophenol reduction. *CrystEngComm*, 14(14):4601−4611, 2012.

[100] Fenger, R., Fertitta, E., Kirmse, H., Thünemann, A. F., and Rademann, K. Size dependent catalysis with CTAB-stabilized gold nanoparticles. *Physical Chemistry Chemical Physics*, 14(26):9343−9349, 2012.

[101] Layek, K., Kantam, M. L., Shirai, M., Nishio-Hamane, D., Sasaki, T., and Maheswaran, H. Gold nanoparticles stabilized on nanocrystalline magnesium

oxide as an active catalyst for reduction of nitroarenes in aqueous medium at room temperature. *Green Chemistry*, 14(11):3164−3174, 2012.

[102] Wu, K.-L., Yu, R., and Wei, X.-W. Monodispersed $FeNi_2$ alloy nanostructures: solvothermal synthesis, magnetic properties and size-dependent catalytic activity. *CrystEngComm*, 14(22):7626−7632, 2012.

[103] Li, J., Liu, C., and Liu, Y. Au/graphene hydrogel: synthesis, characterization and its use for catalytic reduction of 4-nitrophenol. *Journal of Materials Chemistry*, 22(17):8426−8430, 2012.

[104] Kuroda, K., Ishida, T., and Haruta, M. Reduction of 4-nitrophenol to 4-aminophenol over Au nanoparticles deposited on PMMA. *Journal of Molecular Catalysis A: Chemical*, 298(1-2):7−11, 2009.

[105] Patra, A. K., Dutta, A., and Bhaumik, A. Cu nanorods and nanospheres and their excellent catalytic activity in chemoselective reduction of nitrobenzenes. *Catalysis Communications*, 11(7):651−655, 2010.

[106] Liu, S., Amada, Y., Tamura, M., Nakagawa, Y., and Tomishige, K. Performance and characterization of rhenium-modified Rh–Ir alloy catalyst for one-pot conversion of furfural into 1,5-pentanediol. *Catalysis Science & Technology*, 4(8):2535−2549, 2014.

[107] De, S., Zhang, J., Luque, R., and Yan, N. Ni-based bimetallic heterogeneous catalysts for energy and environmental applications. *Energy & Environmental Science*, 9(11):3314−3347, 2016.

[108] Zhang, H., Ni, Y., Zhong, Y., Wu, H., and Zhai, M. Fast electrodeposition, influencing factors and catalytic properties of dendritic Cu–M (M = Ni, Fe, Co) microstructures. *RSC Advances*, 5(117):96639−96648, 2015.

[109] Yang, J., Shen, X., Ji, Z., Zhou, H., Zhu, G., and Chen, K. In situ growth of hollow CuNi alloy nanoparticles on reduced graphene oxide nanosheets and their magnetic and catalytic properties. *Applied Surface Science*, 316:575−581, 2014.

[110] Krishna, R., Fernandes, D. M., Ventura, J., Freire, C., and Titus, E. Novel synthesis of highly catalytic active Cu@Ni/RGO nanocomposite for efficient hydrogenation of 4-nitrophenol organic pollutant. *International Journal of Hydrogen Energy*, 41(27):11608−11615, 2016.

[111] Fang, H., Wen, M., Chen, H., Wu, Q., and Li, W. Graphene stabilized ultra-small CuNi nanocomposite with high activity and recyclability toward catalysing the reduction of aromatic nitro-compounds. *Nanoscale*, 8(1):536−542, 2016.

[112] Nasrollahzadeh, M., Sajadi, S. M., and Hatamifard, A. Waste chicken eggshell as a natural valuable resource and environmentally benign support for biosynthesis of catalytically active Cu/eggshell, Fe_3O_4/eggshell and Cu/Fe_3O_4/eggshell nanocomposites. *Applied Catalysis B: Environmental*, 191:209−227, 2016.

[113] Guo, Y., Zhang, L., Liu, X., Li, B., Tang, D., Liu, W., and Qin, W. Synthesis of magnetic core–shell carbon dot@MFe_2O_4 (M = Mn, Zn and Cu) hybrid materials and their catalytic properties. *Journal of Materials Chemistry A*, 4(11):4044−4055, 2016.

[114] Deka, P., Choudhury, R., Deka, R. C., and Bharali, P. Influence of Ni on enhanced catalytic activity of Cu/Co_3O_4 towards reduction of nitroaromatic compounds: Studies on the reduction kinetics. *RSC Advances*, 6:71517–71528, 2016.

[115] Li, H., Yue, F., Yang, C., Xue, P., Li, N., Zhang, Y., and Wang, J. Structural evolution of a metal–organic framework and derived hybrids composed of metallic cobalt and copper encapsulated in nitrogen-doped porous carbon cubes with high catalytic performance. *CrystEngComm*, 19(1):64−71, 2017.

[116] Goyal, A., Kapoor, S., Samuel, P., Kumar, V., and Singhal, S. Facile protocol for reduction of nitroarenes using magnetically recoverable $CoM_{0.2}Fe_{1.8}O_4$ (M = Co, Ni, Cu and Zn) ferrite nanocatalysts. *RSC Advances*, 5(63):51347−51363, 2015.