Chapter 1
General introduction

The term nanotechnology was coined by Professor Norio Taniguchi (Taniguchi., 1974; Handy et al., 2008). It is called nanotechnology because it has a scale of one billionth (10^{-9}) of a meter. As early descriptions of nanotechnology noted, this technique entailed precisely manipulating atoms and molecules in order to produce macroscale products, sometimes called molecular nanotechnology. A more general definition of nanotechnology was later developed by the national nanotechnology initiative, involving the manipulation of matter in more than one dimension, typically between 1 nm and 100 nm in size. Material properties can be controlled at a nanometric scale using nanotechnology, which entails modifying materials at the atomic scale based on a set of well-defined characteristics that are more adjustable than bulk material properties (Mauter et al., 2008; Thanh et al., 2014). The reduction potential, stabilization, and reactivity of noble metal nanoparticles play a vital role in the nanoscale analoguezation of their bulk phase counterparts. Noble metal nanoparticle synthesis has attracted much interest in the past few years because of their remarkable properties, such as size-dependent, optical, electronic, and catalytic characteristics. (Haruta et al., 1989; Du et al., 2018; Wang et al.,2011; Mak et al., 2012; Feng et al., 2018). Furthermore, nanoparticles can be used to produce high quality superlattices that display the cumulative characteristics of individual metal nanoparticles (Taleb et al., 1998; Yang et al., 2006; Lewandowski et al., 2014). The high surface area to volume ratio of nanomaterials is associated with their exceptional reactivity, which helps make them excellent catalysts (Siamaki et al., 2011**;** Shang et al.,2014; Singh et al 2014; Bilal et al.,2018). The innovation of nanometer-sized particles has been widely investigated due to the various scientific and technical interests associated with these nanoparticles (Wouters et al., 2004; Singh, et at., 2008;). Top-down or bottom-up approaches are commonly used in order to prepare nanosized colloidal suspensions of

nanoparticles (Mijatovic et al., 2005). Massive production of metallic nanoparticles can be accomplished by solubilized metal atom dispersion (An and A 2015; Zhao et al., 2019). Nanoparticles of noble metals can be produced using a variety of physical (mechanical ball milling, physical vapour deposition), chemical (wet chemical reduction, inverse micelles, and analytical approaches (electrochemical and chemical vapour deposition) (Choi et al., 2010; Dhand et al., 2014; Jeyaraj et al., 2019; Baig et al., 2021). Recently, developments in the synthesis of noble metal nanoparticles such as silver, palladium, and gold have been made, and these nanoparticles are used for extremely promising catalytic applications, including biosensing, fluorometric sensing, electrochemical sensing, cell imaging, dye degradation and organic reactions (Pandey et al., 2003b; Farzin et al., 2020; Fu et al., 2020; Rajeev et al., 2021). Recently numerous studies and research have been conducted on the synthesis and application of noble metal nanoparticles because of their diverse characteristics and catalytic properties. Noble metal nanoparticles like palladium, gold, and silver are also bimetallic nanoparticles and trimetallic nanoparticles that can be modified to make them better suited to specific applications by changing their size, shape, chemical composition, and environmental conditions (Pandey and Chauhan., 2012; Pandey and Pandey., 2014c; Sharma, et al., 2017; Loza et al., 2020). An introductory discussion of the NMNPs' synthesis and applications is described vide infra.

1.1. Noble metal nanoparticles: An introductory discussion

In the field of noble metal nanoparticles, research is active on the design and synthesis of nanoparticles. The synthesis of noble metal nanoparticles can be accomplished through a variety of physical, chemical, and more recently, biological methods. However, all the methods have some advantages and limitations. This section of the introduction covers the synthesis of

noble metal nanoparticles (Au, Ag, and Pd), as well as their properties and applications in various disciplines.

1.1.1. Synthesis approach of noble metal nanoparticles

1.1.1.1. Silver nanoparticles

One of the categories of noble metal nanoparticles is silver nanoparticles, justifying a variety of practical applications (Pandey and Chauhan., 2012). The possibility of utilizing silver nanoparticles (AgNPs) as highly dispersed supports for increasing the signals from organic compounds in Raman spectroscopy has sparked scientific and practical interest in silver nanoparticles (AgNPs) in recent years (Pandey and Singh., 2015a; Guo et al., (2016). The most frequent method for producing AgNPs with good stability and colloidal dispersibility in aqueous and organic liquids is chemical synthesis. In general, reducing agents for aqueous solvents include sodium borohydride, tri-sodium citrate, hydrazine, and ascorbic acid, but the most frequent organic solvent is ethanol, which Toshima and his colleagues employ (Islam et al., 2018). Additionally, AgNPs were synthesised using DMF, DMSO, and Formamide (Jebaranjitham et al., 2019). Silver ions (Ag^+) are reduced in various ways to form silver atoms (Ag^0), which combine into oligomeric clusters (Henglein et al., 1099). Vanhaesebroeck et al., Earlier research found that using a strong reducing agent resulted in relatively monodispersed tiny particles, but using a weaker reducing agent resulted in a slower reduction rate, although the average diameter remained large (Bastús et al., 2014). As a consequence, stabilising agents must be incorporated into the synthesis method to keep dispersed and stable AgNPs stable. A common method of protecting AgNPs is to use protective chemicals that can be absorbed into the nanoparticle's surface and attached to its surface, so that the particles will not agglomerate. (Hebbalalu et al., 2013) Poly (ethylene glycol) (PEG), poly (vinylpyrolidone) (PVP), poly

(methacrylic acid) and polymethyl methacrylate (PMMA)are the most utilised polymers for AgNPs stabilisation. Biosynthetic techniques that use polysaccharide, biological microorganisms such as fungi and bacteria, or plant-derived reducing agents as reducing agents have recently emerged as a simple and feasible option for AgNP synthesis. Nevertheless, the synthesis and application of stabilized silver nanoparticles for real-time practical applications has been a challenging task of research investigation.

1.1.1.2. Palladium nanoparticles

Palladium nanoparticles are another type of noble metal nanoparticle (Pandey et al., 2001a). These nanoparticles are used in a diverse number of relevant applications, including dye degradation, hydrogen evolution processes, fluorometric sensing, organometallic reactions, and electrochemistry sensing (Pandey et al., 1998; Cookson et al., 2012; Ammam et al., 2013; Li, et al., 2015). The dimension of the particles is important for catalytic efficiency, as colloidal dispersions of valuable noble metals are used as catalysts in a variety of chemical reactions (Kummer et al., 1986). Recent years have seen the development of approaches such as wet chemical synthesis as an extremely versatile and efficient method for controlling the size and shape of synthesised PdNPs (Biskos et al., 2008; Kulkarni et al., 2020). Using a variety of safe chemical stabilisation procedures for nanoparticle synthesis. Stabilization techniques that are successful incorporate electrostatic or steric interactions, or even both very well documented (Astruc et al., 2005 and Liguori et al., 2014). Until now, the most frequently utilised stabilizers have been organic ligands, surfactants, polymeric materials, and dendrimers (Jia et al., 2011; Deraedt et al., 2014). Phosphine derivatives are used as stabilising agents for the fabrication of nanoscaled materials. The average size found is about 3.5–7.5 nm as a function of the reaction conditions applied. 1,2-Bis(diphenylphosphino) ethane (DPPE) and tris(2-cyanoethyl)

phosphine (TCP) are two other phosphine derivatives used (Saldan et al., 2015). Amines group

is also associated with the stabilizer of palladium nanoparticles, such as oleylamine, porphyrins

and imidazole derivatives act as important ligands for the steric stabilisation of palladium

nanoparticles. Polymeric stabilizers support the dispersibility of nanoparticles in a variety of

solvent systems, including aqueous medium. The use of polymers is frequently related to the

polyol method (Cookson et al., 2012; Moumen et al., 2017). In this process, alcohol is used to

dissolve and reduce a metal precursor at high temperatures. Stabilizers are incorporated into a

wet chemical reduction path during the early phase of synthesis, together with the metal

precursor. Metal ions interacting with stabilizers and reducing agents cause prolonged stability

of homogeneous dispersion and constitute an exciting research area.

1.1.1.3. Gold nanoparticles

A gold nanoparticle is among the most extensively studied noble metal nanoparticles (Pandey

and Chauhan, 2012). During the last few decades, a great deal of research has been conducted

on the synthesis of AuNPs, including an emphasis on controlling their size, shape, dispersion,

and functionality. Michael Faraday conducted the first scientific analysis of AuNPs (Faraday

and Philos, 1857). He developed a biphasic synthesis approach that involved treating an

aqueous suspension of gold salt, sodium tetrachloroaurate, [Na(AuCl4)], with phosphorus

solubilized in carbon disulfide. After some brief reaction, the yellow solution of [Na(AuCl)4]

turned red red, indicating the synthesis of AuNPs. Since Faraday's time, a number of other

procedures for the production of AuNPs have been proposed, such as the Martin, Brust, and

Turkevisch approaches. Turkevisch invented this method in 1951 (Turkevisch et al., 1951). It

is still the most widely used way of producing AuNPs currently. Sodium citrate is used both

as a stabilising agent and a reducer throughout this approach. Due to electrostatic repulsion

between negatively charged oxygen on citrate, it serves as a reducer to $Au^{3+,}$ forming Au^+ and Au^0, and subsequently as a stabiliser. The Martin approach is also used to synthesise AuNPs by the interaction of $NaBH_4$ with an aqueous $HAuCl_4$ solution without the use of stabilizers such as citrate or alkanethiols. This approach produces monodispersed NPs with diameters ranging from 3.2 to 5.2 nm. The Martin technique is further refined to produce AuNPs stabilised using octanethiol (Martin 1994). Brust and Schiffrin (1994) came up with a way to synthesise AuNPs in organic solvents which usually distinguished from aqueous systems. The colour of organic media changes from yellow to dark brown when sodium borohydride is added. These NPs are more stable because they have stronger interactions between Au and thiol, which makes them more stable. Stabilization of AuNPs may be accomplished by the use of sodium citrate or by using the significant Au-thiol interactions. While thiol ligands were the most commonly used to functionalize AuNPs, a variety of other ligands were also used. Amines are significant as stabilizers due to their ubiquity, or their presence in all environmental and biological processes (Leff et al., 1996). Published the first report on using amine in the synthesis of Au nanoparticles. These researchers synthesised hydrophobic AuNPs by replacing dodecylamine or oleylamine with the dodecanethiol used in the Brust-Schiffrin technique. As a result, this approach is considered a modified variant of the Brust-Schiffrin method. AuNPs are formed when the precursor based on Au3+ interactions with a long sequence of primary amines [AuCl(NH2R)] decomposes in tetrahydrofuran (Gomez et al., 1945). Additionally, utilising amines such as Laurylamine and octadecylamine, phase transfer was performed to synthesise organically soluble monodispersed AuNPs (Kumar et al., 2003). Recently, the controllable synthesis of AuNPs through simple heating in ionic liquid was established, while quaternary ammonium-based room-temperature ionic liquids were used as solvents, reducing

agents, and stabilizers (Huang et al., 2010) and still constitute an interesting topic of further research.

1.1.2. Properties and applications of noble metal nanoparticles

Although the history of gold nanoparticles is relatively old, considerable attention has been paid during the last two decades (Pandey et al., 2014a; Pandey et al., 2014b). Researchers are extremely interested in noble metal nanoparticles because of their exceptional properties and potential applications (Jain et al., 2008; Zhang et al., 2018). Noble metal nanoparticles have been extensively studied in many interdisciplinary fields for their versatile properties. The effects of different reaction conditions and morphological features of nanoparticles on the behaviour of nanoparticles have been examined in a variety of important areas. The field is still very active despite the extensive examination of noble metal nanoparticles (Sau et al., 2010; Ndolomingo et al., 2020). The applications of noble metal nanoparticles in medicine, catalysis, sensing, and other fields are intensively researched. Due to their unique optical properties, noble metal nanoparticles are highly sensitive to electrodynamic changes in their environments. Noble metal nanoparticles are widely used in optics, electronics, and many other applications (Amendola et al., 2013; Deng et al., 2014; Link et al., 2014). There are still a variety of potential applications of these nanoparticles that are being explored for addressing targeted needs.

1.1.2.1. Properties of silver nanoparticles

A. Optical properties

Silver nanoparticles have a wide range of absorption wavelengths (380-450 nm) through the stimulation of localised surface plasmon resonance (LSPR), which allows them to be used in a variety of applications (Jiang et al., 2005; Cheng et al., 2011; Meng et al., 2013; Carnovale

et al., 2016; Mohaghegh et al., 2020; Atwan et al., 2020). In the previous study, it was found that thin film thickness can be an important factor that determines photoluminescence in Ag/ZnO nanocomposite. When the thickness increases, UV emission increases, but decreases again when the thickness is greater than six layers (Xu et al., 2017). As studied by Lee et al., the aqueous chemical reduction of gallic acid was used to produce AgNPs of different sizes. According to their research, 7 nm AgNPs have a surface plasmon resonance at 410 nm, whereas 29 nm AgNPs have one at 425 nm. Furthermore, 89 nm AgNPs had a broad band with a maxima at 490 nm (Lee et al., 2019). It was found that surface plasmon resonance is proportional to nanoparticle size, and if the symmetry of a nanoparticle is irregular, AgNPs can also exhibit multiple resonances. Thus, several results suggest that AgNPs might be used in sensor devices (Zhang et al., 2010). Their unique features have recently been used as efficient colorimetric sensors for chromium detection in surface waters, industrial wastes, and vegetable samples (Prosposito et al., 2020; Minh et al., 2020). AgNPs have good optical properties, so they were used to make an optical test strip for measuring the amount of hydrogen peroxide (H2O2) in aqueous solutions. Ajitha et al. (2016) evaluated PVA-capped AgNPs as LSPR-based optical hydrogen peroxide sensors with lower detection limits than conventional enzyme-based sensors.

B. Toxic properties

Silver nanoparticles (AgNPs) can be used in many different ways due to their unique chemical properties (Ahmed, et al., 2017). It has been used for killing bacteria, viruses, and some other microorganisms. These materials are also used in a lot of cosmetics and clothing that are harmful directly or indirectly to humans. AgNPs can slow down cell growth and chemotaxis of stem cells, enhance cytotoxicity and oxidative stress in human hepatoma HepG2 cells, and

do a lot of other negative things (Hussain et al., 2019). Their toxicity mechanisms are still debatable, however, several alternative routes have been suggested (Dos Santos et al., 2014).

C. Electrical properties

The specific electrical characteristics of AgNPs can be used in electronic devices. The electrical conductivity of AgNPs varied in size from 4 to 12 nm and was produced in glass-ceramic was studied (Syafiuddin et al., 2017). Various AgNP films were studied within a temperature range of 80 to 300 K for their DC electrical resistivity. According to the findings, surface resistivity increases linearly with temperature from 120 to 300K. Another key discovery from the research was that the actual Debye temperature increased with an increase in the AgNP size (Ma et al., 2017). In electroconductive adhesives (ECAs), AgNPs are used instead of polymer conductive materials. Results show that adding AgNPs to ECAs decreased the resistivity, which indicates that the medium is more conductive than before (Yu et al., 2012). The preceding studies suggest that AgNPs can be used in electrical devices. Zeta potential is a scientific term used to describe the electrical potential of a colloidal dispersion, which is typically written using the Greek letter ζ. This value indicates the charge of a particle in the suspension. Furthermore, it can be used to indicate the possible stability of the colloidal system. Dynamic light scattering (DLS) is the most extensively used approach for analyzing this characteristic (Waghmare et al., 2018). A strong negative or positive zeta potential of all the particles in suspension suggests that they tend to reject each other and that there is no propensity to flocculate. According to Singh et al., a low negative or positive value of this value indicates that the particles prefer to be flocculated. However, for this same reason, the zeta potential of the sphere and hexagon AgNPs was investigated. They observed that sphere and hexagon AgNPs exhibited a potential of-5.11 and -15.3 mV, respectively (Singh et al.,

2014). These findings suggest that hexagonal AgNPs are much more resilient than sphere ones. Anisotropic nanoparticles have more corners in comparison to isotropic, and their total area is significantly greater (Reguera et al., 2017). As a consequence, greater negative charge can usually be found to be anisotropic nanoparticles.

1.1.2.2. Application of silver nanoparticles

A. Catalytic application

AgNPs as effective catalysis agents have been used to degrade dyes such as Rose Bengal, methylene blue, eosin, rhodamine B, 4-nitrophenol, and methyl orange (Jacob et al., 2008; Veisi et al., 2019). The chemical method of synthesis of AgNPs resulted in the ability of these nanoparticles to act as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol. A reduction process without a catalyst could take 200 minutes). On the other hand, in the presence of the catalyst, the reduction was completed in just 105 seconds with the optimum parameters of 250 mM $NaBH_4$ and 10 mL AgNPs. There is a well-established reduction mechanism for various dyes using AgNPs in the presence of $NaBH_4$ and it appears to follow the Langmuir-Hinshelwood model (Malik et al., 2020). $NaBH_4$ acts as an electron donor and hydrogen donor. A positive charge is generated on the surface of the AgNP by this process before BH^{4+} is added, resulting in the dye being absorbed by the surface of the AgNPs concurrently. By receiving electrons from BH^{4+}, the AgNPs transfer them to the dye molecules. A large volume of hydrogen is also provided by $NaBH_4$ when AgNPs are present during the hydrogenation of azo dyes (Sreekanth et al., 2016; Saha et al., 2016). The large surface area of AgNPs makes them susceptible to desorption, resulting in a colorless final product.

B. Sensing application

Sensors and biosensors provide potent detection and analysis tools for use in pharmaceuticals, biomedical research, healthcare, environmental monitoring, homeland security, and the battlefield (Justino et al., 2010; Rad et al., 2011; Su et al., 2012; Wang et al., 2012; Zhu et al., 2015; Li et al., 2019; Shoaie et al., 2019). In biosensor development, numerous factors are considered, such as transduction signal generation, fluidic design, surface immobilisation chemistry, detection format, and data analysis. Noble metal nanoparticles, such as AgNPs, have consistently attracted attention as potential biosensors. Due to their exclusive physical and chemical properties, Sensors and immunosensors are used in a variety of fields in which a highly accurate, inexpensive, fast, and online measuring system is required. As the result of developing active nanostructures that perform a specific function, local environmental changes take place

C. Photovoltaic applications

During the last few years, the photovoltaic industry has seen a lot of growth driven by high and rising fossil fuel costs as well as a growing concern over the detrimental effects of such fuels (Liu et al., 2013; Charrier et al., 2013; Zhang et al., 2015). The devices created by hybrid photovoltaics are made up of polymers and metals. Photovoltaic devices have several characteristics enhanced by these metals, such as light absorption, charge carrier mobility, and physical and chemical stability, as seen in inorganic semiconductors. In addition to providing new opportunities for the development of photovoltaic devices and new device technologies, a hybrid system provides a platform for investigating 3D morphology (Salve et al., 2020). The AgNPs were used to provide direct paths of electrical conduction in hybrid photovoltaic devices. It has been demonstrated that thin Ag layers on the cathode and thick layers on the anode of organic photovoltaic devices enhance light transmission through the semitransparent

cathode and inhibit Ag growth, improving device stability (Wei et al., 2014; Ali et al., 2020). AgNPs are used in a variety of photovoltaic devices. In a study conducted by researchers, surface plasmons of metallic nanoparticles interacted with excitons in thin films of organic media

1.1.2.3. Properties of palladium nanoparticles

A. Electronic properties

The use of unsupported palladium nanoparticle catalysts is practical for preparing micropower devices as anodes for direct formic acid fuel cells, including cell phones, laptops, etc (Zhou et al., 2006;). Palladium nanoparticles with crystallographic orientations of 100 and 110 are useful as working electrodes for oxygen reduction reactions in an ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (Tang et al., 2016). Similarly, anisotropic nanostructured palladium dendrites are used as an electrocatalyst for the oxidation of formic acid (Kannan et al., 2013; Patra et al., 2010; Ding et al., 2019).

B. Catalytic properties

There have been numerous studies of palladium nanoparticles in a variety of catalytic applications, including oxidation, hydrogenation, carbon-carbon bond formation, dye degradation, electrochemical reactions in fuel cells, and several other reactions (Kwon et al., 2005; Wu et al., 2008; Deshmukh et al., 2011; Harraz et al., 2012; Saldan et al., 2015). The palladium is attached to the mesopores of mesoporous silica nanoparticles, resulting in enhanced catalytic efficiency and stability (Wang et al., 2014; Shen et al., 2015). Single atom palladium thin films stabilised by atomic layer deposition are catalysts for methanol decomposition by Feng (Feng et al., 2010). Palladium nanoparticles placed in magnetic carbon

nanocages have shown excellent catalytic activity towards the cleavage reaction of N-butyl-4-NHalloc-1,8naphthalimide (Sun et al., 2020; Yao et al., 2021).

1.1.2.4. Applications of palladium nanoparticles

A. Homogeneous and heterogeneous catalyst

There are various chemical and electrochemical reactions in which palladium can serve as a homogeneous or heterogeneous catalyst. Nanoparticles of palladium are small and are usually dissolved in reaction media, which enables them to interact with reactant molecules through catalysis. As a result, they are excellent homogeneous catalysts. Furthermore, one-phase reactions also control the stereochemistry and regiochemistry of the reaction products. Stevens and colleagues used a homogeneous palladium catalyst for the cross-coupling reactions of Suzuki, Heck, and Sonogashira (Jang et al., 2011; Balanta et al., 2011; Navalon et al., 2016). In their study, Rashim and coworkers used palladium nanoparticles encapsulated in PAMAM-dendrimers as homogeneous catalysts for the Heck reaction (Rahim et al., 2001). Palladium nanoparticles supported on a solid matrix are used in catalyzing reactions such as dye degradation, hydrazine decomposition reactions, hydrogenation of arenes, carbonylation of methanol, intramolecular reactions, and hydrogenation of alkenes. As reported by Bhattacharjee and Bruening (2008), the use of palladium nanocatalysts placed in multilayer polyelecrolyte films resulted in remarkable intramolecular selectivity in the hydrogenation of alkenes (Pacardo et al., 2014; Shylesh et al., 2014; Gawande et al., 2015; Kamel et al., 2021). Furthermore, new catalysts or precatalysts such as Pd–carbene complexes or phospha-palladacycles are increasingly used in carbon coupling reactions (Frey et al., 2005).

B. Polymer membrane components

Polymeric nanoparticles (PdNPs) in a monometallic palladium matrix provide granular stability and protect the PdNPs, while the polymers enhance the access of substrate molecules to the active sites of the nanoparticles (Wang et al., 2019; Topuz et al., 2019; Luo et al., 2019). The reduction of Pd cation within the polymeric membrane network allows both the fabrication and catalysis processes to take place simultaneously, which further speeds up the reactions. PSMNPs and materials, such as polyelectrolyte brushes, polystyrene microspheres, and polyelectrolyte multilayers, which are widely used as membrane materials, have been synthesized by using some common polymers, such as cellulose acetate, hydrophilized polysulfone, polyacrylic acid-modified polyethersulfone, and polyvinylidene fluoride (Dai et al., 2002; Kidambi et al., 2005; Domènech et al., 2011; Li et al., 2104; Yang et al., 2019). Nanoparticle immobilization can be successfully achieved by using porous membranes, and layer-by-layer adsorption is very attractive for catalysis (Wang et al., 2015; Ariga et al., 2019).

C. Sensors based on nanomaterials

The gas sensing properties of palladium-doped SnO_2 hollow nanofibers for 100 ppm H_2, 100ppm CO, 500 ppm CH_4, and 100 ppm C_2H_5OH were investigated (Cai et al., 2020). The use of nanoscale gaps in palladium nanowires to study hydrogen gas sensing (H_2) mechanisms has been widely reported (Shahzamani et al., 2019). These nanoscale gaps were also used to develop a reversible sensor design for gas detection (Sun et al., 2007; Yang et al., 2010; Weber et al., 2019). An innovative hydrogen gas sensor based on nanoscale gaps in palladium nanowires was developed by Lee and his coworkers (Lee et al., 2011). An efficient method for

non-enzymatic sensing of biological molecules that are important to life, such as glucose, using palladium NPs and their nanohybrid are well documented (Lu et al., 2011; Zhang et al., 2019).

D. SERS-active substrates

When vibrating molecules interact with metal surfaces and produce an oscillating electromagnetic field, Raman signals become stronger. (Wang et al., 2017, Al-Syadi et al., 2021; Daripa et al., 2021). Recently, nanostructured transition metal substrates have been developed that maximize the electromagnetic field near the analytes and further enhance their polarization. When nanoparticle surfaces are present, SERS has additional cross sections due to hot spots and resonating Raman effects (Liu et al., 2011; Indrasekara et al., 2014). Advances in synthetic strategies have provided a range of approaches to precisely tune nanoarchitectures to attain the desired functionality (Huang et al., 2018; Baig et al., 2021;) and structure. Several studies have been conducted to develop SERS nanosensors that integrate the anisotropy of particle morphology with improved surface properties for selective detection (Mubeen et al., 2007; Wang et al., 2014; Wang et al., 2020).

E. Nanosensitizers for fluorophore

Several studies have shown how a nanoscaled noble metal surface impacts chromophore properties (Zharov et al., 2005; Saeed et al., 2021). The optical properties of molecular molecules can be magnified by rugged metal surfaces and nanoclusters, particularly fluorescence emission intensity (Langer et al., 2015; Paramasivam et al., 2017). Metal-induced fluorescence has been widely studied as an interspace phenomenon as the amplitude of oscillations and fluorescence lifetimes depend on the distance between the fluorophore and the nanocluster (Jahn g et al., 2016). It has been proposed that the metal-enhanced fluorescence is

a function of plasmonic activity and the local field generated by collective oscillations of electrons induced by the metal nanoparticles (Sau et al., 2010). The surface plasmon resonance of weaker metals like palladium (Zhang et al., 2015; Spata et al., 2017), as well as platinum, is also crucial for fluorescence enhancement.

1.1.2.5. Properties of gold nanoparticles

A. Fluorescence quenching

Fluorescence quenching is defined as a reduction in the intensity of fluorescence emission (Landes et al., 2001). When the Plasmon band of AuNPs overlaps with the emission spectrum of fluorophores, fluorescence quenching occurs (Eustis et al., 2006; Wu et al., 2006; Doria et al., 2012; Saha et al., 2012; Zhao et al., 2020). It is necessary to add fluorophores to the surfaces of AuNPs in order to study this phenomenon. Researchers have used resonance energy transfers in biophotonics and materials sciences (Song et al., 2014; Deng et al., 2014; Malekzad et al., 2017). It has been shown that both radiative and non-radiative quenching pathways are particle size-dependent, with smaller nanoparticles quenching more efficiently (Mohamed et al., 2000; Ogilby et al., 2010; Wang et al., 2014). In a photo-induced electron transfer, AuNPs can accept electrons from fluorophores, restricting the fluorophores from illuminating (Dong et al., 2015; Lai et al., 2017).

B. Redox activity

There are discrete electron transition energy levels in AuNPs that result from a quantum size effect. AuNPs possess molecule-like redox behaviour demonstrated using 1.62 nm hexanethiol functionalized AuNPs (Su et al., 2006; Sardar et al., 2009; Antonello et al., 2007). Through experiments, it has been established that these possess redox behaviours at room temperature.

In electrochemical devices, AuNPs are used due to their quantized capacitance charging behaviour, which can be easily modified by manipulating the local environment of NPs (Chen et al., 199; Subramaniam et al., 2005; Boettcher et al., 2007).

C. Surface plasmon resonance (SPR)

AuNP SPR is produced by the collective oscillation of conduction electrons within the nanoparticles in response to incident photons. Various UV-Vis spectra exhibit a peak that corresponds to this excitation, which is designated the "Surface Plasmon Band". A study by Bijanzadeh (2012) explains how these phenomena begin. A small spherical particle interacting with an electromagnetic field was solved by Maxwell's electromagnetic equation. Visible light fulfils the resonant condition for AuNPs, explaining the intense coloration observed in AuNPs (Ghosh et al., 2007; Zhao et al., 2008; Alex et al., 2015; Jain et al., 2008). Very small nanoparticles will not display a surface plasmon band, nor will bulk materials, since the plasmon band depends not only on size but also on solvents, reducing agents, stabilizer temperatures, etc. The band shows red shifting as the AuNPs increase in size. As a consequence of AgNPs aggregation, red shifts are also induced by interparticle plasmon coupling, changing the color of AuNPs suspension from red to blue. This color change has been applied to colorimetric sensing (Aromal et al., 2012; El-Brolossy et al., 2008).

1.1.2.6. Applications of gold nanoparticles

A. Heavy metal ions detection

It is very important for environmental monitoring equipment to detect heavy metal ions, as they are hazardous to human health. The detection of heavy metal ions is also based on a heavy metal ion chelation technique, whereby the ligands are applied to the surface of AuNPs in order

to chelate heavy metal ions (Sugunan et al., 2005; Aragay et al., 2012; Ting et al., 2015). A very simple colorimetric technique for detecting heavy metal ions has been developed by Kim et al. (2001). The functionized-AuNPs containing mercaptoundecanic acid were used to cause the aggregation of AuNPs when exposed to heavy metal ions. The carboxylate group on the ligand had the capability of binding metal ions, including $Pb^{2+,}$ $Cd^{2+,}$ and Hg^{2+} (Sugunan et al., 2005; Zhang et al., 2016).

B. Colorimetric Sensing

The aggregation of small AuNPs results in the formation of a strong interparticle surface coupling, which causes a color change in suspension from red to blue, which can be visible to the naked eye. Color changes can provide a source of information regarding the aggregation and redispersion properties of AuNPs when they come into contact with the target analyte (Liu et al., 2006; Ghasemi).

C. Sensing based on fluorescence

The detection of metal ions using fluorescence resonance energy transfer (FRET) has been demonstrated by Huang and Murray (2002). For these experiments, they used tiopronin-coated AuNPs and the cationic fluorophore Ru $(bPy)_3^{3+}$. The electrostatic complexation of negatively charged AuNPs with positively charged $[Ru(bPy)_3^{3+}$ led to the quenching of $[Ru(bPy)_3^{3+}$ fluorescence. Chiu and Huang (2009) noted that the addition of an analyte (metal ions) reverses the electrostatic complexation, thus restoring fluorescence. Another interesting work was developed to simulate dopamine oxidation with the use of functionalised or protein-modified AuNPs, which is based on the quenching phenomenon and a mechanism for dopamine sensing followed by electron transfer pathways (Tao et al., 2013; Chellasamy et al., 2021).

D. Detection of small organic molecules

The competitive glucose assay demonstrated by Aslan et al. (2004) used assemblies of concanavalin A (Con A) and dextran-functionalized AuNPs. In addition to multivalent crosslinking of dextran-coated nanoparticles with Con A, glucose also releases the dextran-coated AuNPs, which can be characterized by UV-Vis spectroscopy (Aslan et al., (2004) with a glucose dynamic sensing range of mM. With a wide detection range combined with AuNP incorporated into molecularly imprinted polymers (Au-MIP), it is applicable both to diabetics and to healthy individuals (with a 3-8 mM and 2-40 mM detection range, respectively) (Ahmad et al., 2015). A colorimetric sensor for adrenaline was developed by Rypar et al. (2021).

E. Hydrogenation reaction

The reaction most studied in organic chemistry is the selective reduction of carbonyl bonds (C=O) when they are present with unsaturated bonds. Hydration of a C=C bond is preferable over a C=O bond by nearly 35 kJ mol^{-1}. Therefore, catalysts have been modified in order to maximize C=O reduction selectivity. A study conducted by Shibata et al. (1988) described gold's first application to the reduction of unsaturated carbonyls. In 1988, Shibata et al., using Au-Zr alloy, reduced crotonaldehyde to 2-butenal with 60% chemo-selectivity. Later, Hutchings and Bailie (1999) used supported Au catalysts over ZnO and ZrO2 for crotonaldehyde reduction**.**

F. Therapeutics

Gold nanoparticles are widely used for biomedical purposes since they are nontoxic and biocompatible (Shukla et al., 2005; Aminabad et al., 2019). When exposed to light with wavelengths of between 700 and 800 nm, AuNPs emit heat due to their tendency to absorb near-IR radiation. AuNPs possess this property and are therefore effective in eliminating

targeted tumors (Zhang et al., 2015). When gold nanoparticles accumulate near tumor cells, they quickly heat up when exposed to light, and when this happens, cancer cells are killed, a process known as hyperthermia therapy or gold nanoparticle therapy. A therapeutic agent can also be attached to the surface of AuNPs, ensuring that the drug accumulates in nearby tumor cells and preventing side effects on the healthy cells (Piktel et al., 2016; Francois et al., 201; Talekar et al., 2011; Wang et al., 201; Beik et al., 2019). A large surface area allows gold nanoparticles to be coated with thousands of molecules (such as therapeutics, targeting agents, and anti-fouling polymers).

G. Detection of Anions

In comparison to cations, detecting anions is difficult and challenging. This may be due to a combination of factors, such as a lower charge to radius ratio, pH sensitivity, a wide range of geometries, and solvent-dependent binding affinity and selectivity (Saha et al., 2012; Beer and Gale, 2001). In addition to detecting cations, AuNPs have also been shown to be effective for detecting anions. At pH 5.5, AuNPs with ethylene glycol attached isothiouronium units were used as a mediator to detect F-using 3-nitrophenylboronic acid (Minami et al., (2008). Furthermore, Itoh et al., (2004); Fei et al., (2006), applied ionic liquid functionalized AuNPs to the detection of anions like I- and PF6-. Researchers have used ionic liquids containing the imidazolium cation for colorimetric detection (Siedlecka et al., 2009).

1.2. Synthesis and application of multimetallic analogues of noble metal nanoparticles

Noble metal nanoparticles (NMNPs) or noble matals (NMs) combined with multiple metals to form bimetallic nanoparticles (BMNPs) and trimetallic nanoparticles (TMNPs), which have attracted more attention in recent years due to their exceptional catalytic properties compared

to their monometallic nanoparticles (Hoseini Chopani et al., 2020; Ali et al., 2021) as discussed in the following.

1.2.1. Bimetallic nanoparticles

It is interesting to examine bimetallic nanoparticles in comparison to their monometallic counterparts since they are characterized by distinctive catalytic, electronic, and optical properties (Pandey et al., 2015b; Zaleska-Medynska et al., 2016; Suwannarat et al., 2018; Sharma et al., 2019;). A bimetallic nanoparticle catalyst containing Au-Ag, Au-Pd, and Ag-Pd has been attracting great attention due to its similarities in the lattice parameters that allow them to be easily fixed in any ratio (Tang et al., 2014; Darabdhara et al., 2016; Liao et al., 2019). The electrochemical processes of methanol oxidation, 2-propenol oxidation, and formic acid oxidation have enhanced activity in the presence of bimetallic nanoparticles. Many different nanoclusters such as Au-Pd, Au-Ag, and Ag-Pd nanocatalysts are used for many different reactions, such as those involved in the reduction of 4-nitrophenol and dye degradation, as well as a variety of processes for eliminating organic and inorganic pollutants from water, soils, and many more. It has been found that bimetallic nanoparticles can be synthesized by two different processes: sequential and simultaneous approaches (Pei et al., 201; Srinoi et al., 2018). Metal ions are reduced according to their reduction potentials, resulting in a variety of structures simultaneously forming. The preparation of core shell structure bimetallic nanoparticles is usually carried out by sequential reduction (Mallik et al., 2001). Various reducing agents have been investigated that require their participation. According to Mallin et al. (2002), sodium borohydride and sodium citrate were used as reducing and capping agents for stabilizing Au-Ag bimetallic nanoparticles. Synthesized Au-Ag BMNPs using hydrazine as a reducing agent (Sharma et al., 2020). It has been possible to

synthesize BMNPs containing gold as one of the elements. A gold nanoparticle (AuNP) participated in the process as a counterpart to the silver.

1.2.2. Trimetallic nanoparticles

The properties of multimetallic nanoparticles are superior to those of monometallic nanoparticles (Pandey et al., 2016c; Sharma et al., 2017; Yadav et al., 2018; Ali et al., 2021). A multimetallic nanoparticle contains three or more elements. The size, shape, and stability of trimetallic nanoparticles have been extensively investigated in recent decades. Multicomposition core shell-structured trimetallic catalyst systems are prepared via a multistep seed-mediated growth process in which particle size and shape are typically unavoidable without prefabricated uniform seeds (Wang et al., 2011; Wu et al., 2019). Researchers Wang and Yamauchi synthesized triple-layered Au@Pd@Pt nanoparticles consisting of a core of Au, an inner layer of Pd, and an outer shell of nanoporous Pt in a poly(vinylpyrrolidone) (PVP)-based aqueous solution (Wang and Yamauchi, 2010; Zhang, et al., 2015)). As another example, Venkatesan and Santhanalakshmi (2012) report the synthesis of Au-Ag-Pd trimetallic NPs by simultaneous reduction of precursor salts containing CTAB as the capping agent. Catalysts based on ternary elements are highly active in many catalytic processes, such as the oxidation of methanol and formic acid. The fabricated dendritic Au@PtPd trimetallic nanoprobe was integrated into the sandwiched sensor to determine the presence of folate receptors on cell surfaces (Ge et al. 2015). Kondrat and his colleagues have also achieved base-free, selective oxidation of glycerol using trimetallic nanoparticles (Au-Pd-Pt). In another study, Gebre and Sendeku, prepared Ag-Au-Pt trimetallic nanoparticles by hydrothermal, solvothermal co-reduction, and seed-growth approaches and used them to focus their efforts on hydrogen evolution, alcohol oxidations, and oxygen evolution (Gebre and Sendeku, 2022).

1.3. Challenges in the synthesis and application of noble metal nanoparticles and their multimetallic analogues

In the literature, many traditional methods have been used to make noble metal nanoparticles. These methods have also been modified by including several other reagents like PVP, PAP, etc, to form NMNPs. However, in addition to providing valuable information on the synthesis and application of NMNPs, many of them limit their practical applications. As a result of aggregation, nanoscale metal particles in solutions are active and likely to coalesce because of Van-der Waals forces and high surface energies. Therefore, various chemical, thermal, and photochemical processes have been used to synthesize AgNPs, PdNPs, AuNPs, BMNPs, and TMNPs. A description in the previous section restricts the application of NMNPs to solid state configurations, allowing only aqueous phase application, controlled nucleation, solubilization in a variety of solvents, and functionalization. For NMNPs to be useful, a new synthetic protocol has to be developed that allows them to be prepared in a controlled manner while also obtaining (i) a narrow size distribution, as nanoparticle properties are highly dependent on their size, (ii) protection against aggregation, as well as functionality for further conjugation. Moreover, the insolubility of these nanoparticles in a variety of organic solvents is another issue that has hampered their direct manipulation for practical application. Therefore, nanodispersion technology must be developed to create monometallic and their multimetallic analogues dispersed in a solvent for the development of nanoparticle-based devices that are able to be designed with fine patterns in solid-state form. This research investigation intends to examine a systematic approach to investigate the synthesis of nanoparticles and provide a deeper understanding of the practical application of these issues, thereby exploring the possibility of developing a new synthetic route.

1.4. Origin of the present research programme

There has been a great deal of attention focused on the fabrication of sol-gel glasses on several occasions over the past decade, in electrocatalysis sensing, dye degradation, and other applications (Pandey et al., 1999; Paney et al., 2003a; Anitha et al., 2004; Liu et al., 2015; Asefa et al., 2016). Thin sol-gel films are produced to fabricate electrochemical biosensors and also ion sensors (Pandey et al., 2003b). Trimethoxysilane (TMS), 3-aminopropyltrimethoxysilane (3-APTMS) 2-(3,4-(epoxycyclohexyl) ethyltrimethoxysilane (EETMS), and 3-glycidoxypropyltrimethoxysilane (3-GPTMS), have been successfully used to form nanostructured matrix in a favorable ratio as a function of their hydrophilicity and hydrophobicity (Pandey et al., 2003b; Pandey et al., 2001a; Pandey et al., 2001b). Numerous research has been published in our laboratory based on this approach [Ph.D. thesis: Bhupendra Singh (2007), Arvind Prakash (2014), and Richa Singh (2015); and Gunjan Pandey (2016), Subhangi Shukla (2019) and Swarnima Shingh (2021). The nanoporous matrix allows for maximum exposure to analytes while limiting mass transfer kinetics. The use of water-leachable nanostructured materials within nanostructured domains, as well as electron transfer, relays like ferrocene monocaboxylic acid and potassium ferricyanide, is therefore being explored in order to facilitate the mass transfer and electron transfer dynamics across the ormosil film. There have been further efforts to integrate nanoelectrocatalysts like Pd, Au, and Ag into organically modified silicate networks to manipulate the sensing and catalytic processes for real applications. However, significant findings regarding the specific interaction of 3-GPTMS and the palladium cation revealed the formation of -Pd-C- linkage within the organically modified silicate matrix. When trimethoxysilane is combined with 3-GPTMS

during organically modified silicate formation, -Pd-C-and -Pd-Si-linkages are formed, which leads to the formation of a unique nanostructured matrix for commercial electrochemical biosensors. (Tripathi et al., 2006; Pandey et al., 2001a; Pandey et al., 2001b; Pandey and Shukla, 2020). In addition to its role as a constituent in ormosil, GPTMS with APTMS is shown to be a reducing agent for converting Au^{3+} into Au^0 (Pandey and Chauhan, 2012; Pandey and Pandey, 2014). Similar results have been observed in the preparation of gold, palladium, and silver nanoparticles using APTMS (Pandey and Pandey, 2016; Pandey and Singh, 2015; Pandey et al., 2015; Pandey et al., 2017). It acts as a capping agent by controlling the size and shape of nanoparticles due to its micellar behaviour. This is noteworthy provided the well-established and potential role of various functional alkoxysilanes in a variety of fields. The purpose of this research programme is to thoroughly explore the utility of 3-APTMS and 3-GPTMS in the controlled and rapid synthesis of noble metal nanoparticles and their multimetallic analogues, which have not been much explored so far and form the basis for future research.

1.5. Objective of the present research investigation

The use of functional trialkoxysilane has been first time introduced in palladium nanoparticles synthesis (Pandey et al., 2001b). The incorporation of functional trialkoxysilane into NMNPs synthesis was utilized to investigate the awareness of the functional trialkoxysilane moiety during NMNPs synthesis and its homogeneous heterogeneous fabrication. Furthermore, the majority of published procedures don't allow dispersibility in various solvents, thus restricting their application as a practical material. In addition, the previous reported method takes a long time to synthesize nanomaterials. Thus, the objective of this thesis is to synthesize NMNPs via a microwave-assisted controlled process within a few minutes and to use them as catalysts for

various analytes. A microwave provides an optimum temperature within a few seconds for the synthesis of noble metal nanoparticles, resulting the solvent, which has a low boiling point, being evaporated and solidified. Thus, previously used solvents, such as ethanol, methanol, or acetone, do not work adequately because they are volatile in nature and enable to solidify the nanoparticles. Thus, in order to prevent nanoparticles from solidifying, a solvent with a higher boiling point as well as the dispersibility of functional trialkoxysilane is best suited for the microwave-assisted rapid synthesis of noble metal nanoparticles. An ethylene glycol solvent or a mixture of previously used solvent and ethylene glycol was used as a solvent in the microwave-assisted rapid synthesis of noble metal nanoparticles and their multimetallic analogues. As a result, the coherent objectives of the proposed thesis are as follows:

- A study of 3-APTMS, 3-GPTMS, and silver nitrate was used to synthesize AgNPs under the microwave oven within a few minutes along with controlled nanogeometry.

- To synthesized AuNPs by using 3-APTMS, 3-GPTMS, and Chloroauric acid under the microwave oven. while controlling their solubility as well as their functionalities and nanogeometry.

- To investigate and synthesis of PdNPs by using 3-APTMS, HCHO, and potassium palladium chloride under the microwave oven.

- Study of synthesized bimetallic and trimetallic nanoparticles like Au-Ag/Au-Pd, Ag-Pd/Pd-Ni, and Au-Ag-Pd under the microwave oven, respectively.

- To investigate the synthetic incorporation of palladium and palladium-nickel bimetallic nanoparticles within a heterogeneous matrix (mesoporous silica/mesoporous silica nanoparticles).

- To understand the role of functional trialkoxysilane in stabilizing nickel nanoparticles in the absence and presence of known stabilizers (PVP).

- Optimization of functional trialkoxysilane during the synthesis of nanoparticles so as to achieve stable and well-dispersed nanosized materials for enhanced applications.

- To understand how functional trialkoxysilane changes the topography and catalytic properties of nanocrystals at different concentrations.

- To investigate the role of organic reducing reagents such as HCHO, cyclohexanone along with $NaBH_4$ in the presence of 3-APTMS and 3-GPTMS during the synthesis of noble metal nanoparticles and their multimetallic analogues. Additionally, we investigated the significant role of functional trialkoxysilane in the synthesis of various noble metal nanoparticle.

- To understand the effective role of functional trialkoxysilane on fluorescence emission intensity and synchronous fluorescence intensity.

- Study the catalytic efficiency of synthesized noble metal nanoparticles and their multimetallic analogues in various relevant applications.

- To investigated the importance of ethylene glycol solvent in the synthesis of various NMNPs via microwave oven.

1.6. Work plan of the thesis

Functional trialkoxysilane has been extensively studied in the synthesis of various noble metal nanoparticles. Microwave assisted synthesized noble metal nanoparticles have been assessed for their catalytic potential as well as the effect of functional trialkoxysilane in the fabrication process. The thesis work plan includes the following aspects:

The first section of the work plan is named "functional trialkoxysilane mediated synthesis of NMNPs via microwave assisted." The catalytic application of these nanoparticles for selective glucose sensing via synchronous fluorescence spectroscopy. In addition, functional trialkoxysilane has been extensively investigated in order to perform the synthesis. Throughout the fabrication process, the result of 3-APTMS with 3-GPTMS and HCHO was effectively demonstrated.

The second section of the work plan is titled "functional trialkoxysilane mediated controlled synthesis of fluorescent gold nanoparticles." The catalytic application of these nanoparticles for dopamine sensing using fluorescence emission spectroscopy. The intensity of the fluorescence emission characteristic is determined by the size of gold nanoparticles.

The third part of the work plan puts emphasis on the "synthesis of different sized gold nanoparticles and Pd-Ni incorporated within a heterogeneous matrix for selective sensing and decomposition of hydrous hydrazine, respectively, as well as the study of sensing and decomposition employing synchronous fluorescence spectroscopy."

The last work plan of the thesis focuses on the "synthesis of palladium nanoparticles and palladium-nickel bimetallic nanoparticles incorporated within a heterogeneous matrix." palladium-nickel bimetallic nanoparticles synthesised with different metal ratios and their applications for comparative study to degrade both Rh B and Congo red dyes.

Consequently, the entire study plan focuses mostly on aspects of the objectives suggested in section **1.5,** which are summarized below.

[1] In order to understand the role of the functional moiety present in 3-APTMS and 3-GPTMS for the reduction and stabilization of nanoparticle dispersion.

[2] In order to synthesis monometallic like AuNPs, AgNPs, PdNPs, bimetallic nanoparticles such as Au-Ag/Au-Pd, Ag-Pd/Pd-Ni and trimetallic nanoparticles Au-Ag-Pd in a homogeneous medium.

[3] To understand the effect of 3-APTMS and 3-GPTMS concentration on the nanogeometry and morphology of various nanoparticles.

[4] The application of homogeneously synthesized above nanoparticles to glucose sensing by synchronous fluorescence spectroscopy, and a comparison of their glucose sensing abilities

[5] Synthesis of small size AuNPs under the optimized concentration of 3-APTMS and its application for fluorometric sensing of Dopamine.

[6] To study the gold nanoparticle size dependent sensing of hydrous hydrazine.

[7] Study the application of Pd-Ni bimetallic inserted mesoporous silica nanoparticles for hydrous hydrazine decomposition reactions.

[8] Synthetic incorporation of palladium and palladium-nickel bimetallic nanoparticles within a heterogeneous matrix (mesoporous silica/silica nanoparticles).

[9] To investigate the role of PVP in synthesis and stabilization of Pd-Ni bimetallic nanaoparticles.

[10] In order to study how to influence the catalytic degradation with Ni concentration of Pd-Ni bimetallic inserted mesoporous silica nanoparticles.

[11] The application of Pd-Ni bimetallic nanoparticles for hydrazine decomposition reactions.

[12] The application of heterogeneous synthesized Pd and Pd-Ni bimetallic nanoparticles and successfully applied for the catalytic dye degradation of RhB and Congo red.

[13] To characterize the nanoparticles using several sophisticated techniques, namely, high resolution scanning electron microscope (HR SEM), transmission electron microscope (TEM), photoelectron spectroscopy (XPS), Braunauer-Emment-Teller (BET), and X-ray diffraction (XRD) characterization tools were used to investigate noble metal nanoparticles.

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