CHAPTER ONE

General Introduction

1. Introduction

The term “sol −gel” is used to describe a broad class of process in which gel is produced from colloidal suspension or sol. The sol-gel chemistry has rapidly developed over last few decades and is gaining popularity as a versatile general method for the production of inorganic-organic material [Ciriminna et al., (2013)]. The relative simplicity of sol-gel technology is responsible for its rapid proliferation.

The chemistry of ceramic science and technology is the key point in the evolution of modern nanostructured material derived through sol-gel process. During the last two centuries, developments in ceramic chemistry have triggered several domestic and technological applications. Ébelmen(1855) and Graham(1864) studied on silica gel, which indicated the productions of a glass like material in various form like fibers, monolithic optical lenses and composite glass [Graham, (1864)]. The major problem during the productions of ceramic material was long drying time of nearly one year duration that caused fracturing of silica gels into fine powder and consequently these investigations gained little technological interest. Major limitation of conventional ceramic material has been high temperature needed processing and limitation of technology in forming desired complex geometrical configuration of material.

Recent development in sol-gel technology has now permitted the formation of ceramic material in desired shapes at low temperature. During the down of the 20th centuries chemist got interested in the phenomena of Liesegang rings through sol-gel process. The phenomenon of periodic precipitation and crystal growth from gel was investigated in detail. In 1950 Iler’s work in silica chemistry led to commercial development of colloidal silica powder [Iler, (1955)]. R. Roy achieved a very high level of homogeneity in colloidal gels and synthesis ceramic oxide compositions involving Al, Si, Ti and Zr etc. which could not be achieved by tradition ceramic powder technology [Hench and West, (1990)]. This concept has led to the production of a wide variety of composites with the controlled morphologies and particle size [McCarthy et al., (1971)].

The sol-gel process yielded materials of high purity and homogeneity at low temperature. This process permits control of the surface and interfaces of materials during early stage of production. A quantitative comparison on the merits of sol-gel derived silica optics over the alternative high temperature processing methods has been reported [Orcel and Hench, (1984)]. The demonstration of potentially practical routes for production of new materials with unique properties coincided with the growing recognition that powder processing of materials had inherent limitation in homogeneity due to difficulty in controlling agglomeration. Sol-gel chemistry has been easily modified according to the various needs of society to produce fine-tuned sol-gel nanostructured porous materials for relevant applications. Some of the important applications range from, 1) thin films for optical coatings, protective and decorative coatings, and electro-optic components; 2) molded macrostructured bulk materials for use as economical lenses and beam splitters; 3) ultra fine ceramic powders as abrasives and multicomponent composites for dental and catalytic applications; 4) microfibers for fiber optic sensors and filters; 5) development of nanostructured material for fabrication of chemically modified electrode. Avnir and co-workers in 1984 reported the sol−gel entrapment of a dye, rhodamine 6G, in a silica matrix obtained by basic hydrolysis of a silicon alkoxide, tetramethoxysilane [TMOS, $Si(OCH_3)_4$], followed by room-temperature condensation. The sol−gel polycondensation was simply carried out in the presence of the dye in solution [Avnir et al., (1984)]. The resulting transparent doped silica glass was nonleachable in water and in methanol with enhanced photostability and thermal stability. The availability of organic functionality linked to alkoxysilane provides extra events during the formation of such materials as referred as organically modified silicate (Ormosil) and originate the need of current research program.

1.1. Organically Modified Silicates

Organic modification in sol-gel precursor provides better way of controlling nanoporous geometry of sol-gel glasses suitable for sensor design [Pandey and Singh, (2008); Pandey et al., (1999a)]. Such precursors allow the formation of organically modified sol-gel glass (ormosil). Organic functionality during sol-gel processing could be used to increase the degree of crosslinking, improve film adhesion to its support, reduces the concentration of surface silanol group and to introduce reactive functional group that can be subsequently used for anchoring of molecular recognition species of a prepared xerogels [Lev, O et al., (1995)]. The sol-gel process provides a convenient method for the production of organically modified surface by incorporating alkoxysilane monomers that contain desirable functional group in the starting polymerization mixture [Lev, O et al., (1995); Zhang, Jingzhong et al., (1999)].

Ormosils (organically modified silica) and ormocers (organically modified ceramic) can be tailored from commercially available organofunctional alkoxysilanes. The ratio of tetra alkoxysilane and organotrialkoxysilane can be used to control the cation exchange capacity and polarity of the porous surface [Sayari and Hamoudi, (2001); Walcarius, Alain and Delacôte, (2003)]. Cyanoalkyltrialkoxysilane or chloroalkyltrialkoxysilane monomers can be used either alone or in combination with tetra alkoxysilanes to acquire controlled surface polarity and reduced ion exchange capacity [Biernat et al., (1994)]. Monomers containing a Si-C bond and easily derivatized radical such as an amino, vinyl, epoxy or mercapto group can be used to prepare readily derivatized xerogels [Lev, O et al., (1995)]. These can be subsequently used as covalent anchors for specific chelating agents, redox mediator, or photometric reagents. The high molecular weight silica oligomers are more stable than smaller ones, which provide excellent condition for nucleophilic growth of large particles by feeding on low molecular weight-dissociated fragments. A direct way to introduce small organic moieties into a hybrid network through chemical bonding is to use functional alkoxysilanes

($R_nSi(OR')_{4-n}$ n=1=1-3, R=organic group, R'=alkyl) as one or more of the precursors for the sol-gel reaction.

The polymerization mechanism still involves the “hydrolysis-condensation” sequence, leading to the following global reaction for an initial 1:1 mixture of alkoxysilane and organo-alkoxysilane.

$$\mathbf{Si(OR')_4 + R_nSi(OR')_{4-n} + (8-n)H_2O \Rightarrow Si(OH)_4 + R_nSi(OH)_{4-n} + (8-n)R'OH}$$

$$\mathbf{Si(OH)_4 + R_nSi(OH)_{4-n} \Rightarrow (OH)_3\text{-}Si\text{-}O\text{-}SiR_n(OH)_{(3-n)} + H_2O}$$

By tailoring the nature and the structure of the organic group, R, chemical, mechanical, optical, or electrical properties of the resulting composite materials can be greatly modified. For example, it was possible to attach ferrocene groups by covalent binding to a silica xerogel, while maintaining their electroactivity after deposition of the hybrid material on a platinum electrode [Walcarius, Alain, (2001)]. Also, as compared to the grafting of organic groups on pure silica surfaces, the co-condensation procedure allows one to tune the distribution of these groups over the gel network or within the ceramic structure [Martin et al., (2014)], as well as an easier control of incorporated organics by varying the alkoxysilane to organo-alkoxysilane ratio. Another advantage of the sol-gel approach belongs to the possibility of grafting large organic molecules or organometallic complexes, as porphyrins [Markov et al., (2014)], to a silica matrix.

Beside the molecular approach, a hybrid material can also be synthesized via the in situ formation of inorganic species within a polymer matrix or, alternatively, by either the infiltration of previously formed oxide gels with polymerizable organic monomers of the mixing of polymers with a single or mixture of metal alkoxides in a common solvent[Schubert, (2011); Schubert et al., (1995)]. Simple entrapments of organics as a guest by impregnation within inorganic gel matrices, and formation of interpenetrating networks by simultaneous polymerization of both organic and inorganic phases, were also reported [Chung et al., (2007); Mohseni et al., (2014)].

Potential interest for the electrochemist are polymer-silicate hybrids displaying semiconductive properties, as the composites silicate-polyindole, -polythiophene, or –polyaniline [Pandey et al., (2012a); Pandey and Singh, (2011); Salinas-Torres et al., (2011)].

The sol-gel processing of organically functionalized alkoxysilanes provide dramatic opportunity for making nanocomposite with nanostructured materials yielding tremendous alteration of properties useful for technological innovations. The use of metal oxide play central role in innovating such materials and need to be reviewed herein.

1.2. An Overview of Nanostructured Metal Oxides

Metal oxides are performing very important role in many fields of physics, chemistry and materials science [Choi, Y. J. et al., (2014); Clapsaddle et al., (2004); Guiet et al., (2013); Zhang, G. and Lou, (2014)]. The metals have properties to form a variable range of oxide compounds [Greenwood and Earnshaw, (1997)]. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character [Fernandez-Garcia et al., (2004); Greenwood and Earnshaw, (1997)] . In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and also as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties in respect to those of bulk or single particle species [Guiet et al., (2013)]. Metal oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size. Particle size is expected to influence some important groups of basic properties in any material.

1.2.1 Physical Properties

Bulk oxides are usually tough and stable systems with definite crystallographic structures [Chopra, N. et al., (2007b)]. However, the rising importance of surface free energy and stress with decreasing particle size must be measured, changes in thermodynamic stability associate with size can induce by modification of cell parameters and structural transformations [Fernandez-Garcia et al., (2004)] and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and a high surface free energy [Liu, Jingyu and Hurt, (2010)]. In order to display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO_2 and Al_2O_3 oxides [Fernandez-Garcia et al., (2004); Goniakowski et al., (2008)]. Size-induced structural distortions associated with changes in cell parameters have been observed, for example, in nanoparticles of Al_2O_3, NiO, Fe_2O_3, ZrO_2, MoO_3, CeO_2, and Y_2O_3 [Rodriguez et al., (2007)]. As the particle size decreases, the increasing number of surface and interface atoms generates stress/strain and concomitant structural perturbations [Fernández-García and Rodriguez, (2007)]. Beyond this "intrinsic" strain, there may be also "extrinsic" strain associated with a particular synthesis method which may be partially relieved by annealing or calcinations [Fernández-García and Rodriguez, (2007); Rodriguez et al., (2007)]. Also, non-stoichiometry is a common phenomenon [Sebald et al., (2010)]. On the other hand, interactions with the substrate on which the nanoparticles are supported can complicate the situation and induce structural perturbations or phases not seen for the bulk state of the oxide [Fernandez-Garcia et al., (2004)]. The second important factor effect of size is related to the electronic properties of the oxide. In any material, the nanostruture produces the so called quantum size or confinement effects which essentially arise from the presence of discrete, atom-like electronic states. From a solid-state point of view, these states can be considered as being a superposition of bulk-like states with a concomitant increase in oscillator strength [Arora, (2014)]. Additional general electronic effects of quantum confinement experimentally probed on oxides are related to the energy shift of exciton levels and optical bandgap [Lee, Hee Sung et al., (2012)]. An important factor to consider when dealing with the electronic properties of a bulk oxide surface are the long-range effects of the Madelung field, which are not present or limited in a nanostructured oxide [Fernández-García and Rodriguez, (2007); Huang, Patrick and Carter, (2008)]. Theoretical studies for oxides show a redistribution of charge when going from large periodic structures to small clusters or aggregates which must be roughly considered to be relatively small for ionic solids while significantly larger for covalent ones. The degree of ionicity or covalency in a metal-oxygen bond can however strongly depend on size in systems with partial ionic or covalent character; an increase in the ionic component to the metal-oxygen bond in parallel to the size decreasing has been proposed. 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 [Fernández-García and Rodriguez, (2007)]. A decrease in the average size of an oxide particle do in fact change the magnitude of the band gap, [Peng et al., (2013)] with strong influence in the conductivity and chemical reactivity. Surface properties are a somewhat particular group included in this subject due to their importance in chemistry. Solid-gas or solid-liquid chemical reactions can be mostly confined to the surface and/or sub-surface regions of the solid. As mentioned above, the two dimensional (2D) nature of surfaces has notable structural, typically a rearrangement or reconstruction of bulk geometries, [Scopigno et al., (2011)] and electronic, e.g. presence of mid-gap states consequences. In the case of nano structured oxides, 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 nanoparticle 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 [Nilius et al., (2012)].

1.2.2. Chemical Properties

Metal oxides are used for both their redox and acid/base properties in the context of absorption and catalysis. The three key features essential for their application as absorbents or catalysts are; (i) The coordination environment of surface atoms (ii) The redox properties (iii) The oxidation state at surface layers. Both redox and acid/base properties are interrelated and may attempts to establish correlations of both properties in the literature [Arora, (2014)]. 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 [Huheey et al., (2006)]. The solid in a given reaction conditions that undergoes reduction and reoxidation simultaneously by giving out surface lattice oxyen anions and taking oxygen from the gas phase is called a redox catalyst [Ong, (2011); Rury et al., (2012)]. This process necessarily demands microscopy reversibility and implies dynamic operation. The commonly accepted mechanism was developed by Mars van Krevelen and essentially implies that redox systems require high electronic conduction cations to manage electrons and high oxygen-lattice mobility [Mars and Van Krevelen, (1954)]. Based on modern isotopic exchange experiments, the redox mechanism of chemical reactions can be more specifically divided in (i) extrafacial oxygen in which adsorbed (oxygen) species react (electrophilic reaction), and (ii) interfacial oxygen where lattice oxygen vacancies are created (nucleophilic reaction) [Haber, (2008)]. There are enormous evidence that nucleophilic oxygen is capable of carrying out selective oxidations while it seems that electrophilic species seems to exclusively work on non-selective ones. Latter, it was shown that hydrocarbon selective oxidation starts with H-abstraction steps and that the filling of oxygen vacancies require the cooperation of a significant number of cations [Arora, (2014)]. So, typically, an oxidation reaction demands to optimize three important steps: the activation of the C-H bond, molecular oxygen, and the desorption of products (to limit over-oxidation) [Davis et al., (2013)]. The effect of size on these key steps is unknown but can be speculated to be related to the oxidation state of surface cations and their ability to manage electrons and the influence of non-stoichiometry on the gas-phase oxygen species handling and activation [Leonidovna, (2008)]. Many oxides also display acid/base properties. Oxide materials can contain Bronsted and Lewis acid/base sites. Bronsted acid (A) and base (B) interactions consist of the exchange of protons. Lewis proposed a different approach to measure acid-base interaction. Latter, Petterson introduced the concepts of hard and soft acid and base but, usually, acid/base properties of solid are rationalized in terms of Bronsted and Lewis definitions. In any solid, two independent variables, the acid/base strength and amount (density per surface unit) need to be addressed to give a complete picture of its acid/base characteristics. Such characteristics are basically linked to the nature (valence/cation size) of the element present in the oxide and general views of the behaviour of Bronsted/Lewis acidity as a function of solid state variables have been published [Fernández-García and Rodriguez, (2007); Rodriguez et al., (2007)]. Essentially, Lewis acidity is characteristic of ionic oxides and practically absent (unless very aggressive out gassing treatments) in covalent oxides. The strongest Lewis acid oxides are Al_2O_3, Ga_2O_3. As a general rule, the stronger Lewis acid having few available sites (amount) due to the higher level of surface hydroxylation. As mentioned, because Lewis acidity is mostly associated to oxides with ionic character, Lewis basicity is mostly associated with them [Zecchina et al., (1998)]. This means that the stronger the Lewis acid sites, the weaker the basic sites and vice versa. On the contrary, most of the ionic metal oxides do not carry sufficiently strong Bronsted acidity to protonate pyridine or ammonia at room temperature although the more acid of them can do it at higher temperatures [Corma, (1995)]. In spite of this, the surface OH groups of most ionic oxides have a basic more than acid character [Dzombak, (1990)]. Covalent non-metal oxides (SiO_2, GeO_x, BO_x) having low valencey also show quite weak Bronsted acid properties. Finally, strong Bronsted acidity appears in oxides of elements with formal valencey five or higher (WO_3, MoO_3, N_2O_5 and V_2O_5).

Nanostructure metal oxides are convenient component, forming an appropriate environment for the immobilization of enzyme at the electrode surface and its interaction with metallic or conducting electrode surface [Ansari et al., (2010); Campuzano et al., (2014); Singh, Jay et al., (2012a); Zhao, Zhiwei et al., (2010)]. Stable immobilization of macromolecular biomolecules on semiconducting metal oxide nano-surface with complete retention of their biological recognition properties is a crucial problem for the commercial development of miniaturized biosensor [Ansari et al., (2010)]. Owing to large specific surface area and high surface free energy of nanoparticles can absorb enzymes strongly and play an important role in the immobilization of enzymes in construction of biosensor devices [Zhao, Zhiwei et al., (2010)]. Generally, the adsorption of enzymes directly onto naked surfaces of bulk materials may frequently result in their denaturation and loss of bioactivity [Luo et al., (2006)]. However, the adsorption of such enzymes onto the surfaces of nanoparticles can retain their bioactivity because of biocompatible nature of metal oxides nanoparticles [Luo et al., (2006)]. Since most of the metal oxide nanoparticles carry high isoelectric point (>IEP), they can electrostatically adsorb enzymes having different charges with low isoelectric point [Ansari et al., (2010); Iyer et al., (2014); Zang et al., (2007)]. In conclusion the results on metal oxide reveal unique properties relationship and may have potentiality to combine with sol-gel processing of ceramic materials. Accordingly, the findings on the formation of nanocomposite of metal oxide specifically with ormosil/sol-gel glasses need to be reviewed.

1.3 An overview on nanocomposite made with sol-gel glasses/organically modified sol-gel glasses

Nanocomposites are multiphase materials built up from a bulk matrix and one or more nanodimensional (1− 100 nm) phases, the intent of which is to achieve, through synergistic interactions between the components at their interfaces, enhanced properties (e.g., mechanical, electrical, thermal, optical, electrochemical, and catalytic) relative to either of the single homogeneous constituents [Camargo et al., (2009); Ciriminna et al., (2013)]. The presence of nanocomposite materials in nature is the structure of bones, teeth, and seashells [Chen, P-Y et al., (2008)]. Nanocomposite inks were already used almost 3000 years ago, while nanoscale organo-clays have been used as thickening agents of polymer solutions (e.g., as paint viscosifiers) or emulsions (e.g., as homogenizers in cosmetics) for more than 50 years [Ciriminna et al., (2013)].

Nanocomposite materials have a potential field of research. Everyday several new nanocomposite materials are introduced with enhance properties and used in the different field of research. Nanocomposite can be classified as inorganic, organic and hybrid material on the basis of phase. Metal oxide-silica nanocomposite materials have shown promising applications in several technological developments for commercial consequence particularly as electrochromic, energy storage, photocatalytic, electrocatalytic and sensing devices. Accordingly, the investigation has been conducted in the present thesis describe the studies of nanocomposites of metal oxide with organically modified silicate and their application in electroanalysis. The nanocomposite material are generally classified as follows on the chemical nature of the matrix and filler. Ceramic-matrix nanocomposites (CMnC) consist of a bulk ceramic with finely dispersed inorganic or organic nano filler(s), to achieve improved mechanical, optical, electrical, and magnetic properties, as well as corrosion-resistance and other protective capacities: Polymer-matrix nanocomposites (PMnC) have their enhanced performance due to an organic polymer matrix (responsible for flexibility, ductility, processability, and electric properties) and to metallic or other inorganic or nano fillers (for rigidity, thermal stability), even in extremely low concen-trations; Metal-matrix nanocomposites (MMnC) have a metal matrix reinforced either with a ceramic nano filler, carbon nanotubes or fibers, silicon carbide, or boron/carbon nitride.

The sol−gel technology marked a decisive point in the development of nanocomposites: (i) in the synthesis of ceramic matrixes, because it allows tailoring the inorganic final properties on account of its versatility, extending the range of organic nanofillers due to the mild conditions involved, and finally achieving a good dispersion of the nanophase; and (ii) in the synthesis of inorganic nanofiller, because it allows obtaining highly reproducible nanoparticles, with controlled size, structure, composition, and surface properties. Accordingly the various stages i.e. Chemistry of Sol-gel Process, Structure of Sol-Gel process based nanomaterials and Applications of organically modified silicate and their nanocomposite need to be reviewed.

1.3.1. Chemistry of Sol-gel Process

Brinker et al made detailed investigation on the chemistry of sol-gel process [Brinker, C Jeffrey and Scherer, (1990)]. The sol-gel process, as the name implies, involves the production of inorganic matrices through the formation of colloidal suspension (sol) and gelation of the colloidal suspension (sol) to form a wet gel (a globally connected solid matrix) which after drying forms the “dry gel” state (xerogel) [Brinker, C. J. et al., (1982); Hench and West, (1990)]. Sol is dispersions of colloidal particles in a liquid. Colloids are solid particles with diameter or colloidal particles in a liquid. Colloids are solid particle with diameter or 1-100 nm. A gel is an interconnected rigid network with pores of submicrometer dimensions and polymeric chain whose average length is greater than micrometer. A silica gel may be formed by network growth from an array of discrete colloidal particles or by formation of an interconnected 3-D network by simultaneous hydrolysis and polycondensation of an organomettalic precursor. When the pore liquid is removed as a gas phase from the interconnected solid gel network under hyper critical condition, the network does not collapse and a low density aerogel is produced. But when the pore liquid is removed at or near ambient pressure by thermal evaporation (called drying) and shrinkage occurs, the monolith is termed as xerogel. If the pore liquid is primarily alcohol based, the monolith is termed as alcogel. A gel is defined as dried when physically absorbed water is completely evacuated. This occurs between 100-180 ºC. Sol-gel materials display attractive properties such as ease of preparation, low temperature synthesis, controlled porosity and hydrophobocity [Lin, Jie and Brown, (1997)], capacity for chemical modification or entrapment of various components, optical transparency. Three approaches are used for the production of sol-gel monoliths: (1). Gelation of a solution into colloidal powders (2). Hydrolysis and polycondensntion of alkoxide precursors followed by hypercritical drying, (3) Hydrolysis and polycondensntion of alkoxide precursors followed by ageing and drying of gels under ambient atmospheres. The sol-gel processing steps involved in making silica monolith for methods (1-3) are associated to following steps. These steps are mixing, hydrolysis, condensation, ageing, drying, stabilization and densification.

a) Mixing

Sol is formed by mechanical mixing of colloidal particle in water at pH that prevents precipitation. A liquid alkoxide precursor, such as $Si(OR)_4$ where R is CH_3, C_2H_5 or C_3H_7 is hydrolyzed by mixing with water.

b) **Hydrolysis**

The alkoxide precursors undergo hydrolysis as follow:

$$R\text{-}Si(OR)_4 + 4H_2O \rightarrow RSi(OH)_4 + 4ROH \qquad \text{...... (1)}$$

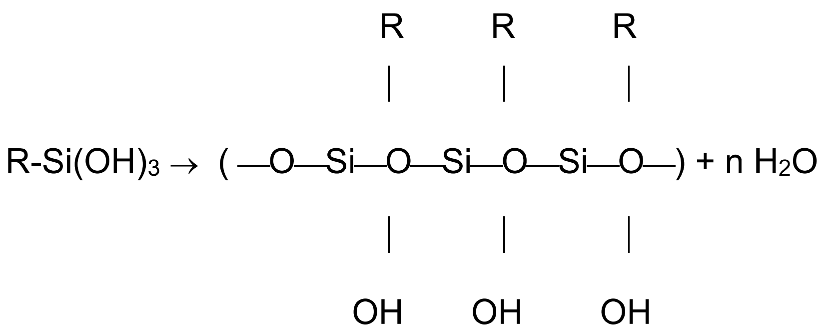
c) Condensation

The hydrated silica tetrahedral interacts in condensation reaction forming Si-O-Si bonds.

$$Si(OH)_4 + Si(OH)_4 \rightarrow (OH)_3\text{-}Si\text{-}O\text{-}Si(OH)_3 + H_2O \quad ...... (2)$$

d) Polycondensation

Further linkage of additional Si-OH tetrahedral occurs as polycondensation reactions which result in a SiO_2 networks.



$$R\text{-}Si(OH)_3 \rightarrow (-O-\underset{OH}{\overset{R}{Si}}-O-\underset{OH}{\overset{R}{Si}}-O-\underset{OH}{\overset{R}{Si}}-O-) + n\ H_2O \quad ...... (3)$$

e) Gelation

The colloidal particle and condensed silica species link together with time forming a 3 dimensional network. At gelation, the viscosity increases sharply and solid object result in shape of mold. The sol becomes a gel when it can support stress elastically. This is typically defined as gelation time t_{gel}. Gelation time can be nearly instantaneous for very acidic or basic solution of metal alkoxides. The anion and solvent also play role in kinetics of gelation which can be either acid or base catalysed. Longer and larger the solvent molecule, longer is the gelation time. Similarly longer and larger the alkoxy group longer the t_{gel}. The amount of water for hydrolysis of alkoxysilane has dramatic influence on gelation time. For low water content, generally an increase in the amount of hydrolysis water decreases t_{gel}, although there is dilution effect as well. It can be predicted that for higher water content t_{gel} increases with quantity of water. Further viscosity of sol-gel precursors significantly influences the physical forms e.g. fiber coating and monolith [Sakka and Kamiya, (1982); Strawbridge and James, (1986)].

f) Aging

Ageing of a gel, also called syneresis, involved maintain the cast object for a period of time, hours to days, completely immersed in liquid. During aging polycondensation continues along with localized solution and reprecipitation of gel network which increases thickness and decreases porosity. Thus the strength of gel is increased which develops sufficient resistance for cracking during drying.

g) Drying

The liquid is removed during drying from the interconnected pore network. The drying process is controlled by decreasing the liquid surface energy by addition of surfactant or by elimination of small pores, by hyper critical evaporation or by obtaining monodisperse pore size by controlling rate of hydrolysis and condensation.

h) Chemical stabilization/dehydration

The removal of surface silanol (Si-OH) bonds from the pore network results in chemically stable ultraporous solid. Porous gel made in this manner is optically transparent with interconnected porosity.

i) Densification

Densification occurs on heating the porous gel at high temperatures. The pores are eliminated and the density ultimately becomes equivalent to fused quartz of silica. The densification temperature depends considerably on the dimensions of the pore network. The purity and homogeneity of dense gel made are superior in quality due to their greater homogeneity and lower coefficients of thermal expansion.

Process such as aging, drying, stabilization and densification depend upon the gel structure. Since relative rate of hydrolysis and condensation determine the structure of the gel, it is essential to understand the kinetics of the hydrolysis (K_H) and condensation reaction (Kc) and the ratio of their rate constant (K_H/Kc). Hydrolysis and polycondensation occurs simultaneously. The variables of major importance are temperature, condensation of electrolyte (acid and base), nature of solvent and type of alkoxide precursor.

1.3.2. Structure of Sol-Gel process based nanomaterials

At mild thermal treatment in the process of sol-gel drying, a micro or mesoporous xerogel is obtained. Supercritical drying avoids shrinkage of the gel matrix and affords an aerogel. In both cases, the process is highly reproducible and can be scaled up to manufacture amorphous functional oxides in a wide range of compositions and shapes, including monoliths, coatings, disks, rods, powders, fibers, and porous membranes. Governing the sol−gel process at molecular level implies the ability to control the monomer → oligomer → sol → gel → xerogel transition affording a porous silicon oxide material with the desired textural, surface chemical and morphological properties. This is the ability to control the shape of porous materials, which affecting the chemistry of the resulting nanostructured (sol − gel) material. It is indeed the inner porosity of the resulting silica-based material that ensures accessibility, dispersion, and effective confinement of the entrapped molecules. Hence, the message conveyed by this approach is to look at doped silica-based sol−gels as porous solids filled with nanometer voids where all sorts of molecules can be entrapped, affording materials of large potential utility in widely different areas of application.

The characterization of sol-gel geometry is an important requirement and a few methods are available for the measurement of surface characters like thickness, porosity and structure at nanometer scale of sol-gel glass. The encapsulated sol-gel materials are taking part in electrocatalysis, therefore electrochemistry of sol-gel material also a matter of characterization. Following characterization procedure of sol-gel structure have now been adopted so for:

(a) Physico-chemical method

These methods are small-angle X-ray scattering (SAXS), neutron scattering (SANS) and light scattering (SALS), each of them giving complementary information and transmission electron microscopy of sol-gel geometry. SAXS allows the de- termination of a characteristic length of the particle (Guiniers radius of gyration or electronic radius of gyration) and a fractal dimension, which gives some information on the structure of the polymer (branched vs. linear) and on the growth mechanism. The application of SAXS to a number of gel systems has been reported [Brinker, CJ et al., (1984); Brinker, C. Jeffrey Clark David E. Ulrich Donald R. Materials Research Society Materials Research Society Meeting Symposium B., (1984); Orcel and Hench, (1984)] by various authors. SANS has also been applied to the study of silica sols [Zallen, (1998)]. Results similar to those from SAXS are obtained. But further development of the SANS technique may produce additional insight into the sol-gel process [Wright, (1985)]. SALS has received very little attention in the sol-gel literature. However, the characteristic dimension probed by visible light scattering is 710 nm, and therefore it cannot he used to characterize the early stage of the gelation process. Recent development of short-wave-length UV lasers may make it possible to extend light-scattering studies to 3 nm and thereby could follow most of the gelation process.

Carbon composite were characterized by scanning electron microscopy, BET adsorption experiment, differential thermo gravimetric analysis, and impedance spectroscopy to get information on the structure and properties of the material [Oskam and Searson, (1998)]. X-ray photoelectron spectroscopy was employed to evaluate the chemical stability of sol-gel film containing covalently bonded ferrocene moieties, coated on glassy carbon [Wang, Jiaxiong and Collinson, (1998)] and to monitor the chemical oxidation of tetra sulfur groups immobilized by covalent grafting to a silicate film coated on indium tin oxide electrode [Guo, Yizhu et al., (1998)]. The distribution of ZrO_2 particles with in sol-gel silica was studied by various techniques before incorporating the resulting material into carbon paste, including gas adsorption, scanning electron microscopy, x-ray diffraction and thermogravimatry [Alfaya and Gushikem, (1999)]. Composite film made with hybrid of nafion and silica were analyzed by TEM, EDS, modulated differential scanning calorimetry and electrochemical impedance spectroscopy using two stainless steel electrodes, revealing that the composite displays additional properties with respect to those of the isolated nafion and silica materials [Zoppi and Nunes, (1998)]. FTIR spectroscopy and UV-visible absorption spectrometry were extensively used for characterizing organically modified or pure silica modified electrode containing encapsulated organic or organometallic species [Fonseca et al., (2013); Guo, Yizhu et al., (1998); Ha and Kim, (1999); Makote and M. Collinson, (1999); Pawlik et al., (2014); Pessôa and Gushikem, (1999); Ribeiro and Gushikem, (1999); Song et al., (1999); Walcarius, A et al., (1999b)] developed TiO_2 matrix composites modified by sol-gel bioactive glasses, considering the physico-chemical and biological properties of the presented composites, the modification of TiO_2 with sol-gel bioactive glasses may prove useful strategy in several bone tissue related regeneration strategies.

(b) Electrochemical methods

Cyclic voltammetry oftenly applied to characterize the basis electrochemical behavior of silica modified electrode comprising electroactive centers or encapsulating electroactive components. The electrochemistry of Cu^{II} in ammonical medium at a silica gel-modified carbon paste electrode,[Walcarius, A. et al., (1999a)] showing that copper species were electrochemically accessible only because they retain enough mobility to diffuse out of the silica material on the time scale of the voltammetric measurement. Borgo et al agreed with a subsequent work [Borgo et al., (1999)] and reported redox behaviour for Cu^{II} initially loaded on aminopropyl-grafted silica similar to that usually observed for solution species. On the contrary, Bond et al have suggested an intra-silica charge transfer mechanism when studying the voltammetric reduction of several metal ions (Hg^{II}, Ag^{I}, Cu^{II},Pb^{II}) adsorbed onto a new thick-walled form of mesoporous silica [Bond et al., (1999)]. It was shown that silica gel with immobilized analytical regents (impregnated silica gel) can be used as an efficient sorvent for heavy metal ions by complex formation on the modified silica surface [Zaporozhets et al., (2001)]. The electrochemical characterization of CCCEs was mainly performed by the Lev's group [Lev, O. et al., (1997)]. They studied the influence of the carbon source (graphite, acetylene black or Ketjenblack), and compared the results to conventional carbon electrodes by using various organic and inorganic redox couples.

Electrochemical techniques were also exploited to evaluate the biocompatibility and porosity of sol-gel based materials as well as the associated mass transfer reactions. For example the ultra microelectrodes can be effectively used to probe molecular transport in microstructure gel material and provide an effective mean to get accurate values of diffusion coefficients of target molecules encapsulated within sol-gel derived silica monoliths[Collinson, (1998)]. Voltammetry was also directed to characterize mass transport in silica modified electrode, as well as to select the optimal experimental conditions to get a sensor device displying the highest sensitivity as possible [Walcarius, Alain, (2010); Walcarius, Alain and Kuhn, (2008)]. Note that beside the mass transfer limitations, the overall electrochemical reaction might also be limited by the heterogeneous rate of electron transfer, [Dryhurst, (2012); Markovich and Mandler, (2001)] via the electrochemistry of hexacynoferrate at an indium tin oxide electrode covered with an octadecylsilane monolayer.

1.3.3. Applications of organically modified silicate and their nanocomposite

Apart from many technological applications of such materials, limited used focused to current research program are reviewed. Sol−gel process is opening the route for practical applications in the field of biotechnology [Xu, Yuxi et al., (2010)] (such as biocatalysis, biosensing, bioremediation, and biomedical materials) that had remained annoyed due to lack of stability of most entrapping matrixes. Environmental and clean energy concerns were responsible for another impetus on the search for new sol−gel materials [Ciriminna et al., (2013)]. Recent results with doped sol−gels of long-lasting photobioreactors and biofuel cells, which can advantageously exploit solar radiation to convert polluting carbon dioxide into useful biofuels and electricity

[Ciriminna et al., (2013); Zhou et al., (2011)], constitute a significant advance toward the practical chemical exploitation of solar energy. The silica based matrixes, offer several advantages over organic polymer supports, including physical rigidity and high abrasion resistivity, negligible swelling in both aqueous and organic solution, chemical inertness, high biodegradable, photochemical and thermal stability, excellent optical transparency and low intrinsic florescence [ul Rehman and Pandith, (2013); Walcarius, Alain and Collinson, (2009)]. The actual strong emergence of silica modified electrodes could be explained by the revival and the huge development of sol-gel processing in numerous fields of chemistry, including electrochemistry, and the possibility to immobilize material by encapsulation within a silica network without preventing their activity [Avnir et al., (2006); Pandey et al., (2001c); Pandey and Upadhyay, (2005a); Walcarius, Alain et al., (2005)].

Metal oxide nanocomposite are outstanding materials for the modification of electrode surface and have been commonly used in the area of chemical sensor, gas sensor, bio sensors, optical sensors, pressure sensors, lithium ion batteries, electrochemical performance for energy storage, dye-sensitized solar cells, catalytic and photocatalytic, environmental remediation, field emission non-volatile memory and tunneling devices, bio-ceramic coating applications, nanogenerators, etc., [Brabec et al., (2014); Jang et al., (2013); Korotcenkov, (2014); Pessoa et al., (2014); Rhim et al., (2013); Sanchez et al., (2005)] have been elaborately discussed.

(A) Electrochemical sensors based on nanocomposite of Metal oxides and organically modified silicate

Metal oxides and organically modified silicate having several unique electrical, electrochemical, and optical properties are used to convert chemical information like concentration, activity and partial pressure into electrical or optical signals in the solid state, thus serve as a potential material for transducers in chemical sensors [Kango et al., (2013); Korotcenkov, (2014); Sharifi et al., (2013)]. One major requirement is to combine these transducers with selective molecular recognition to obtain a selective, durable and cost effective chemical sensor; this is further achieved by using metal oxide and organically modified silicate nanocomposites with improved properties to that of their parent materials.

a) Methods of electrode modification

Active layer is the specific part of a sensor. Various techniques have been developed to prepare modified electrode in order to adapt different sensing materials and different types of sensor configurations. Some of them are listed below [Bai et al., (2007); Nicollian and Brews, (1982)]:

- ***Electrochemical deposition***

It is the most convenient method to deposit sensing films. The thickness of the film can be controlled by the total charge passed through the electrochemical cell during film growth [Jiang et al., (2012); Xia et al., (2012)]

- ***Dip coating***

In this method, metal oxide thin film have been deposited on commercial aluminum and glass substrates using sol–gel dip-coating method [Amri et al., (2012)]. This process occurs on different substrates, and the thickness of the film is usually controlled by dipping time.

- ***Spin coating***

In this process, the metal oxide/composite solution is spread on a rotating substrate [Kim, Myung-Gil et al., (2011)]. After evaporation of solvent, a thin film was formed.

- ***Langmuir-Blodgett (LB) technique***

This technique is a famous method to produce a thin film [Malik and Tripathi, (2013)]. Two different ways are reported to deposit a sensing film by LB technique: vertical depositing and horizontal depositing on the substrate.

- ***Layer-by-layer (LBL) self-assembly technique***

The electrostatic layer-by-layer (LBL) self-assembly technique has provided an effective approach for the fabrication of a variety of ordered multilayer film materials with controllable architecture and properties [Li, Zhangpeng et al., (2011)].

- ***Thermal evaporation***

This method involves the heating of sensing film under vacuum, and the evaporated film deposits on the target substrate. The thickness of the film is determined by the duration of evaporation [Kim, Myung-Gil et al., (2011)].

- ***Vapor deposition***

This method is used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin film [Lokhande et al., (2011)]. This technique is useful not only for preparing a pure metal oxide film, but also in coating composite films of different CPs.

- ***Drop-coating***

This method is very simple and results in non-uniform films. It consists of putting the drops of the metal oxide solutions over a substrate [Fabbri et al., (2013)].

- ***Electrode modification with inorganic, sol-gel and composite materials***

Metal oxide, clays, zeolites and other inorganic, microcrystalline structured materials have also been used to modify electrode surfaces [Bard and Mallouk, (1992)]. These inorganic materials are of interest because they are ion exchangers, like ion exchange polymers; however, unlike polymers, clays and zeolites can withstand high temperatures and highly-oxidizing solution environments. Furthermore, these inorganic materials have well defined microstructures. For example, metal oxides have a spherical, rod-like, cube and many different structure and zeolites contain pores and channels of well-defined diameter. Ormosil and layered double hydroxides, displaying, respectively, cation and anion exchange properties, were found to be attractive material for electrochemical biosensor design because of their hydrophilic, swelling and porosity properties, and their mechanical and thermal stability [Qu et al., (2011); Zhao, Meng-Qiang et al., (2012)].

Another method involves the low-temperature encapsulation of recognition species within sol-gel films [Depagne et al., (2011)]. Such ceramic films are prepared by the hydrolysis of alkoxide or alkoxysilane under acidic or basic condensation, followed by polycondensation of a hydroxylated monomer to form a three dimensional interconnected porous network. The resulting porous glass-like material can physically retain the desired modifier but permits its interaction with the analyte that diffuses into the matrix. Besides their ability to entrap the modifier, sol-gel processes offer tenability of the physical characteristics e.g., porosity, thermal stability and mechanical rigidity. Sol-gel derived composite electrodes have also been prepared by dispersing carbon or gold powders in the initial sol-gel mixture [Wang *et al.* (1997)].

- ***Modified carbon paste electrodes***

Since the fabrication of carbon paste electrodes (CPE) by Adams (1958), a number of approaches have been employed for the modification of carbon paste electrodes. In general, the main reason to modify an electrode is to obtain qualitatively new sensor with desired, often predefined properties. Regarding this carbon pastes undoubtedly represent one of the most convenient materials for the preparation of modified electrodes [Svancara et al., (2012)]. In contrast to relatively complicated modifications of solid substrates the preparation of chemically modified carbon paste electrodes (CMCPEs) is very simple, typically by the means of various alternative procedures. The modifier can be dissolved directly in the binder or admixed mechanically to the paste during its homogenization. It is also possible to soak graphite particles with a solution of a modifier, and after evaporating the solvent use the impregnated carbon powder. The base of modified carbon pastes is usually a mixture of powdered graphite and non electrolytic binder. Modifying agent is usually one substance but the pastes can also be modified with two or even more components, which is the case of carbon paste-based biosensors containing enzyme (or its carrier) together with appropriate mediator or chemically modified carbon paste electrodes (CMCPEs).

b) Modes of sensing

Electrochemical sensors used in electroanalytical determination contain two basic functional units; receptor part, which transforms the chemical information into a form of energy and transducer part which transforms the energy, bearing chemical information, into a useful signal. Different kinds of electrochemical techniques can be used for this purpose. Some of the most common techniques are amperometry, potentiometry and conductometry etc. Based on these techniques the electrochemical sensors are divided into three main categories:

- ***Amperometric sensors***

This type of sensor is based on the measurement of the electrical current flowing through the sensor as a result of oxidation or reduction of the analyte or a reaction product from the analyte at a constant potential. Metal oxide and their composites provide surface for the direct oxidation or reduction of electroactive ions present in the solution (ion sensor) [Aricò et al., (2005); Safavi et al., (2009)]. Recently an amperomertic sensor was developed for the determination of NADH based on cobalt oxide (Co_3O_4) through flow injection analysis systemChen, C. H. et al., (2013a). The gaseous molecules may react chemically or through weak interaction with the selective layer of the sensor. A large variety of biological recognition elements including enzymes, antibodies, and antigens can be immobilized in material and their composite films to produce amperometric biosensor or immunosensors.

Amperomertic biosensors for a large variety of analytes, including hydrogen peroxide [Pandey et al., (2014); Pandey and Pandey, (2013b); Yagati et al., (2013)], glucose [Kacar et al., (2013); Pandey et al., (1999b); Patil, D. et al., (2012b)], glutathione [Pandey and Pandey, (2014)], Protein [Kirk et al., (2013)], creatine [Kacar et al., (2013)], DNA [Gao, A. et al., (2013)], hemoglobin [Chawla and Pundir, (2012)], Phenolic compound [Chawla et al., (2012)], Xanthenes [Devi et al., (2012)] and NADH [Teymourian et al., (2012)] by immobilization of different enzymes in selective layer are developed.

- ***Potentiometric sensors***

Potentiometric sensors are based on measurement of the electrical potential of the sensor versus a reference electrode with a constant potential, i.e., by the measurement of the electromotive force (EMF). Due to the excellent ion exchange property of metal oxide and their composite they are very promising solid contact materials in ion-selective electrodes for high precision potentiometric measurements [Du et al., (2013); Pandey et al., (2012b); Rudnitskaya et al., (2013); Yang, H. et al., (2013)]. Metal oxide and their composites can be applied as potentiometric sensors for gases, such as aromatic hydrocarbon, O_2, NO_2, CO and CO_2 [Izu et al., (2013); Li, M. D. et al., (2013); Liao et al., (2012); Washe et al., (2010)]. Potentiometric biosensors can be fabricated by immobilization of biological components into metal oxide and their composite films. Potentiometric biosensors for urea, glucose, antibody and creatinine [Pundir et al., (2013); Saeedfar et al., (2013); Tran-Minh et al., (1992); Yang, Z. et al., (2014)] can be obtained by immobilization of specific enzymes over the layer of biosensor.

- ***Conductometric sensors***

These sensors are based on the measurement of the electrical conductivity of the sensor material in contact with the analyte. The conductivity of metal oxide and their composites are very sensitive to the chemical structure as well as the morphology of metal oxide, which in turn are sensitive to the chemical compounds in contact with the metal oxide or it's composite. This makes them a potential material for the development of conductometric sensors. Conductometric ion sensors are developed by using metal oxide and their composites with ion receptors [Korotcenkov, (2014)]. The interaction of ion with ion receptor influences the conductivity along the metal oxide. Conductomertic gas sensors based on metal oxide and their composites utilize the interaction of metal oxide with gases which influence the mobility or number of charge carriers with the polymer chains. Gases that are electron acceptors like O_2, NO_2, SO_2, I_2 or electron donors like ammonia, hydrogen sulphide, hydrazine, triethylamine may oxidize or reduce the metal oxide and their composites thus influence its electronic conductivity [Atkinson et al., (2004)]. Conductometric biosensors are based on metal oxide and their composites are also developed for various important analytes [Mahadeva and Kim, (2011); Tsopela et al., (2014)].

1.4 Origin of research program

Earlier studies conducted in our laboratory opened a novel process on ormosil film formation from functionalized alkoxysilane using two different combinations [(system-1) and (system-2)] of sol-gel precursors. System-1 involve the role of hydrophilic (3-aminopropyltrimethoxysilane) and hydrophobic (2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane) precursors and whereas system-2 report the role of hydrophilic (Trimethoxysilnae) and hydrophobic (3-Glycidoxypropyltrimethoxysilane) during the formation of organically modified silicate (ormosil). The role of these films in electrochemical sensors design with special attention on the encapsulation of redox active protein, electron transfer relays have been demonstrated [Pandey P. C. et. al., (1999)]. The performances of ormosil based sensing devices were further improved by incorporating water leachable material like polyethylene glycol and conducting materials like graphite particles. [Tripathi, (2002)]. The different electron transfer mediators like ferrocene monocarboxylic acid, organic metal like TCNQ-TTF [Pandey P. C. et. al., (1999)]. The presence of glycidoxy residue in one of the alkoxysilane precursor (3-Glycidoxypropyltrimethoxysilane) yielded novel finding on the formation of palladium embedded ormosil for electrocatalytic applications. The presence of palladium within ormosil matrix yielded excellent redox electrochemistry of electron transfer relay present in same nanostructured domains [Pandey P. C. et. al., (2001)]. The interaction of $PdCl_2$ and 3-glycidoxypropyltrimethoxysilane has been identified based on XPS, NMR, Mass and UV-Visible spectrometry. It was found that palladium chloride opens the epoxide ringe of glycidoxy-residue and in trun gets reduced forming Pd-Glymo complex [Sharma (2002)]. Subsequent studies have been made in our laboratory to understand the property of ormosil film after encapsulating the organic moieties like ion-exchange (Nafion suspension) and ion-recognition sites (crown ethers) within ormosil matrix [Pandey P. C. et. al., (2004)]. The findings justified that the inherent property of these organic moieties within the resulting films was retained and revealing improved performances of ormosil film based sensing devices [Pandey et al., (2005b)]. The conversion of Prussian blue from potassium ferricyanide in the presence of cyclohexanone/tetrahydrofuran was also observed during sol-gel processing. The formation of Pd-Si linkage from the interaction of $PdCl_2$ with trimethoxysilane was also recorded [Pandey et al., (2001b)]. Such chemical reactivity of functional alkoxysilanes yielded in developing a library of electrocatalytic sited within nanostructured domains.[Singh, B., (2007)]. Four approaches causing manipulation in nano-structured domains were adopted: (a) increase in the molecular size of the components generating nanostructured domains; (b) modulation via chemical reactivity; (c) modulation by non-reactive moieties and known nanoparticles; and (d) modulation by mixed approaches (a–c). The results that are increase in the size of nanostructure domains or decrease in microporous geometry increases the efficiency of electrocatalysis. Although such approaches yielded excellent nanostructured matrixes for desired electrocatalysis however suffered from the problem of controlling the thickness of the ormosil film. An increase in film thickness caused decreases in electrocatalysis. According the present program was undertaken focusing on the findings that control the thickness of the same. Earlier report justified the effect of Ti molar fraction in ormosil film [Y. Sorek and R. Reisfelda, 1995]. The relatively low rise in the refractive index of the films as Ti content increase compared to inorganic glasses is a result of preparation at low temperature and the use of organic additives that reduce the glass density. The relation between film thickness and corresponding sol viscosity was investigated and found to be linear with the range of measured data [Bao-Ling and Li-Li, (2004)]. These findings directed our attention to understand the role of metal oxide during ormosil film formation. The role of metal oxide during sol-gel processing of ormosil not only control the thickness but yield many exceptional structure-activity relation as discussed in preceding section. Metal oxide has several limitations in potential applications especially in sensor design due to its low solubility and low conductivity as compared to that of metals. There are two important ways to make the metal oxide an effective material for various types of technological application: (i) Improvement in processibility through film formation and (ii) Improvement in electrocatalysis through nanocomposite formation. The present thesis is aimed to on the synthesis and characterization of nanocomposite of metal oxide with organically modified silicate derived from the use of organically functionalized alkoxysilane precursors i.e 3-Aminopropyltrimethoxysialne (3-APTMS), 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (ECETMS) and 3-Glycidoxypropyltrimethoxysilane and their use in the electroanalysis.

1.5 Objective of the present investigation

Following are the objectives for present investigation:

(1) The effect of titanium oxide (TiO_2) and Pd linked 3-Glycidoxypropyltrimethoxysilane during the formation of ormosil film from functional alkoxysilanes.

(2) Formation of Ormosil film encapsulating electron transfer mediators, i.e., potassium ferricyanide and ferrocene-methanol, in the presence of titanium oxide (TiO_2) and Pd linked 3-Glycidoxypropyltrimethoxysilane.

(3) Formation of TiO_2 and their nanocomposite with Pd linked 3-Glycidoxypropyltrimethoxysilane in powder form.

(4) Formation of WO_3 and their nanocomposite with Pd linked 3-Glycidoxypropyltrimethoxysilane. The as prepared nanocomposite was further modified Prussian blue and an enzyme horseradish peroxidase for the development of sensitive electrochemical hydrogen peroxide sensor..

(5) Characterization of the above synthesized nanomaterials using suitable techniques.

(6) Studies on the intrinsic peroxidase-like activity of metal oxide and their nanocomposite

1.6 Work plan for the present investigation

The work plan employed in the present thesis is as follows:

[1] Formation of ormosil films encapsulating two types of electron transfer mediators, i.e., potassium ferricyanide and ferrocene methanol, in the presence of titanium oxide (TiO_2) and Pd linked 3-Glycidoxypropyltrimethoxysilane.

[2] Synthesis of TiO_2 nanoparticles based on sol-gel process and their nanocomposite with Pd linked 3-Glycidoxypropyltrimethoxysilane.

[3] Synthesis of WO_3, Pd-WO_3-SiO_2, Pd-WO_3-SiO_2-PB nanocomposite by homogeneous mixing of precursors sols with Pd linked 3-Glycidoxypropyltrimethoxysilane and PBNPs.

[4] Characterization of as synthesized nanocomposites through electrochemical and microscopic techniques.

[5] Electrochemical sensing of hydrogen peroxide based on WO_3, Pd-WO_3-SiO_2, Pd-WO_3-SiO_2-PB nanocomposite.

[6] Investigation on peroxidase mimetic activity of as synthesized WO_3, Pd-WO_3-SiO_2 and Pd-WO_3-SiO_2-PB nanocomposite.