Summary

The thesis "Studies on nanocomposites of TiO_2/WO_3 with organically modified silicate for electroanalytical application" has been divided into following four chapters-

1. General Introduction
2. Synthesis and applications of Ormosil film in the presence of TiO_2 and Pd-linked glycidoxypropyltrimethoxysilane.
3. Synthesis and applications of Pd-TiO_2-SiO_2 nanocomposite.
4. Synthesis and applications of Pd-WO_3-SiO_2 nanocomposite.

Chapter 1 described the literature survey on the chemistry of sol-gel process, structure of sol-gel glass materials and organically modified silicate (Ormosil). The role of metal oxide during the sol-gel processing of these materials has been reviewed. The development of electrochemical sensor based on nanocomposite of metal oxide and organically modified silicate has been critically reviewed followed by inclusion of the origin of present research program and its objectives.

Chapter 2 described the synthesis, characterization and application 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. Major conclusions drawn from this chapter are as follows, (i) The presence of TiO_2 and Pd control the thickness of Ormosil films; (ii) The effect of titania and palladium facilitate the redox electrochemistry of ferrocene methanol and potassium ferricyanide; (iii) The redox behaviour of electron transfer mediators present within nanostructured domain useful in electrochemical sensing (iv) the presence of TiO_2-Pd in ormosil shows better catalytic activity as compared to that of made with only TiO_2 toward ascorbic acid (AA)

oxidation; (v) Ferrocene-methanol encapsulated ormosil has been found relatively more efficient mediator as compared to that of potassium ferricyanide toward AA oxidation. The findings justify the approach on the fabrication of ormosil films for electroanalytical applications.

Chapter-3 described the synthesis and applications of Pd-TiO_2-SiO_2 nanocomposite. The composite was made by mixing titanium isopropoxide and palladium-linked glycidoxypropyltrimethoxysilane (3-GPTMS) followed by calcination at optimum temperature to get anatase phase of TiO_2. The presence of SiO_2 enables the formation of ordered spherical geometry of Pd-TiO_2-SiO_2 nanocomposite. The phase transformation of TiO_2 (rutile to anatase) at 900 ºC in composite material has been observed as evidenced from X-ray diffraction pattern of Pd-TiO_2-SiO_2 nanocomposite. The electrocatalytic activity of TiO_2 nanoparticle and Pd-TiO_2-SiO_2 nanocomposites justified electrocatalytic oxidation of ascorbic acid. Pd-TiO_2-SiO_2 Modified electrode exhibits good sensitivity towards AA (10.22 μA/mM) with a linear range of 1 μM -1 mM.

Chapter-4 described the synthesis and applications of WO_3, Pd-WO_3-SiO_2 and Pd-WO_3-SiO_2-PB nanocomposites. The Pd-WO_3-SiO_2 is made from a homogeneous mixture of tungstic acid sol and palladium linked 3-Glycidoxypropyltrimethoxysilane sol. The homogenized sol is allowed to form gel under ambient conditions and calcinated at 600˚C. The as synthesized calcinated Pd-WO_3-SiO_2 nanocomposite powder was mixed with Prussian blue suspension made as described earlier [Electrochimica Acta. 87 (2013) 1-8] followed by sonication and drying at 65 ˚C. The Pd-WO_3-SiO_2-PB nanocomposite shows spheroids morphology with average particle size of 85 nm. The nanocomposites show both peroxidase mimetic and electrocatalytic activity for the sensing of the biologically active analytes with following findings: (i) The PB act as an excellent redox materials behaving as continuous conducting relay with the porous metal oxide matrix, thereby providing an electronic conduction pathway which improves the process of charge transfer through the matrix (ii) WO_3, Pd-WO_3-SiO_2 and Pd-WO_3-SiO_2-PB shows biocompatibility and peroxidase mimetic behavior justifying catalytic efficiency in the order of Pd-WO_3-SiO_2-PB > Pd-WO_3-SiO_2 > WO_3; (iii) HRP-modified Pd-WO_3-SiO_2-PB shows 7 fold enhanced analytical sensitivity as compared to that of Pd-WO_3-SiO_2-PB system; (iv) Pd-WO_3-SiO_2-PB nanocomposite exhibits excellent electrocatalytic activity for H_2O_2 sensing with catalytic rate constant to the order of 7.5×10^4 M^{-1} s^{-1}. These findings justify the role of WO_3 and Pd-WO_3-SiO_2 nanostructure material for improving the catalytic character of PBNPs.

Excellent sensitivities with improved detection limit and stability of the present electrochemical sensors provide scope for the practical use of these sensors in the determination of the analytes accurately.