CHAPTER 5

METAL/POSS NANOPARTICLES FOR MICROBIAL
AND BIOFUEL CELL APPLICATIONS

Research and development in the past decade have shown that once materials are synthesized in the form of very small particles, they change significantly their physicochemical properties, sometimes to the extent that a completely new phenomena will be reestablished. Nanosized inorganic particles, of either simple or composite nature, display unique physical and chemical properties and represent an increasingly important material in the development of novel nanodevices, which can be used in numerous physical, biological, biomedical and pharmaceutical applications. The preparation of uniform nanosized drug particles with specific requirements in terms of size, shape and physico-chemical properties are of great interest in the formulation of new pharmaceutical products. Resistance of bacteria to bactericides and antibiotics has increased in recent years due to the development of resistant strains. Some antimicrobial agents are extremely irritant and toxic and there is much interest in finding ways to formulate new types of safe and cost-effective biocidal materials. Previous studies have shown that antimicrobial formulations in the form of nanoparticles could be used as effective bactericidal materials.

Recently, Klabunde et al (1996) demonstrated that highly reactive metal oxide nanoparticles exhibit excellent biocidal action against gram-positive and gram-negative bacteria. Thus, the preparation, characterization, surface modification and functionalization of nanosized inorganic particles
opens the possibility for the formulation of a new generation of bactericidal materials. It is well known that metal ions and metal-based compounds are highly toxic to microorganisms (Slawson et al 1992, Zhao and Stevens Jr 1998) showing strong biocidal effects on as many as 16 species of bacteria including *E.coli*. Thus, metal ions, as an antibacterial component, have been used in the formulation of dental resin composites, fibrous materials and as coatings for medical devices. The present study was carried out to investigate the biocidal action of these particles against gram positive and gram negative organisms. Such metal nanoparticles can be used for the electrooxidation of glucose, since the POSS derivatives are used as stabilizing agents for the preparation of metal nanoparticles.

The electrochemical oxidation of glucose has potential applications in sensors and fuel cells. The electrochemical oxidation of glucose has been a fascinating subject in electrochemistry for several decades because of the intimate relation between glucose oxidation and biological applications. A number of studies on various electrodes have been reported and the current generation is relatively low compared to the oxidation of other small organic molecules. Though the current generation is relatively low compared to small organic molecules, it has an important role in chemical and biosensor applications. Hence, the present section describes the synthesis of amine functionalized POSS and various metal nanoparticles/POSS composites. The preparation of Ag/POSS, Au/POSS and Pt/POSS composites and their antimicrobial properties were tested. Further, nanoparticles stabilized POSS (NPs/POSS) composites were then used as a probe for investigating the electrooxidation of biologically important molecule, glucose. The working Ag/POSS/graphite, Au/POSS/graphite and Pt/POSS/graphite electrodes were made by mechanical immobilization method on the graphite electrode to form a thin film of the catalyst on the electrode surface.
5.1 SPECTRAL ANALYSIS OF POSS AND NPs/POSS COMPOSITES

The POSS derivatives and nanoparticles/POSS (NPs/POSS) are characterized by UV-visible, FT-IR and NMR spectroscopy. The size of nanoparticles was determined using HR-TEM analysis.

5.1.1 UV-Visible Spectroscopy

Figure 5.1 shows the UV-visible spectrum of Ag/POSS, Au/POSS and Pt/POSS.

Figure 5.1 UV-Vis spectra of Ag/POSS, Au/POSS and Pt/POSS nanocomposites
A broad peak was obtained at 448 nm for Ag/POSS nanocomposite, 547 nm for Au/POSS and a weak tail in the case of Pt/POSS composite, all of which corresponds to the plasmonic absorption of the respective metal nanoparticles. This is also further confirmed using TEM analyses (Figures 5.4, 5.5 and 5.6) that show an average size of less than 7 nm.

5.1.2 FT-IR Spectroscopy

Figure 5.2a-d shows the FT-IR spectrum of POSS, Ag/POSS, Au/POSS and Pt/POSS respectively. The amino group in POSS molecule was confirmed by the presence of a sharp peak at 3357.8 cm\(^{-1}\).

![FT-IR spectrum of POSS, Ag/POSS, Pt/POSS, and Au/POSS](image)

**Figure 5.2** (Continued) FT-IR spectrum of (a) POSS, (b) Ag/POSS, (c) Pt/POSS, and (d) Au/POSS
Figure 5.2 FT-IR spectrum of (a) POSS (b) Ag/POSS (c) Pt/POSS and (d) Au/POSS

The peak at 1120.6 cm\(^{-1}\) was due to the -Si-O-Si- bond in the POSS structure, while in the case of Ag/POSS, the peak at 3357.8 cm\(^{-1}\) was broadened, shifted to a higher value of 3389.1 cm\(^{-1}\), which indicates the complex formation through \(-\text{NH}_2\) group of POSS with metal nanoparticles. Similarly, in the case of Pt/POSS and Au/POSS, the peak values are shifted to 3419.6 and 3420.8 cm\(^{-1}\) for \(-\text{NH}_2\) group, respectively (Figures 5.2c and 5.2d).

5.1.3 NMR Spectroscopy

The \(^1\text{HNMR}\) spectra for Octa(nitrophenyl)silsesquioxane (ONPS) and Octa(aminophenyl)silsesquioxane (OAPS, also denoted as POSS) are shown in Figure 5.3a-c.
Figure 5.3  (a) $^1$H NMR spectrum of ONPS (b) $^{29}$Si NMR spectrum of ONPS and (c) $^1$H NMR spectrum of OAPS
In ONPS, the peaks for aromatic protons appeared in the range of 7.0-9.0 ppm, while in the case of OAPS the aromatic protons are observed in the range of 6.5-7.5 ppm. The amino protons are seen in the range of 4.0-5.0 ppm and are in the ratio of 2:1 which are in good agreement with the results of Tamaki et al (2001).

$^{29}$Si NMR spectra of ONPS is presented in Figure 5.3b and the appearance of two bands at -79 ppm and -82 ppm indicates that ONPS comprises two isomers containing meta and para disubstituted species.

5.1.4 Surface Morphology of NPs/POSS Composites

Figures 5.4 - 5.6 show the HR-TEM images of Ag/POSS, Au/POSS and Pt/POSS, respectively. Most of the particles are found to be spherical in shape. Very small number of rods and other shapes are also observed in all the three cases.

![Figure 5.4 HR-TEM images of Ag/POSS composite](image-url)
Figure 5.5 HR-TEM images of Au/POSS composite

Figure 5.6 HR-TEM images of Pt/POSS composite
5.2 ELECTROCATALYTIC OXIDATION OF GLUCOSE (CHEMICAL SENSORS)

The oxidation of glucose by nanoparticles/POSS (NPs/POSS) composites in strongly alkaline to acid electrolyte have been investigated and were found to yield higher currents in alkaline electrolyte compared with the neutral pH range or acidic pH. Hence, glucose oxidation was performed in alkaline pH based electrolyte.

5.2.1 Ag/POSS Composites for Glucose Oxidation

Figure 5.7 shows the glucose oxidation in different electrolytes using Ag-POSS composites as anodic electrode. For Ag nanoparticles modified electrodes (Figure 5.7), oxidation and reduction responses for Ag nanoparticles were obtained in both basic and phosphate buffer (PBS) medium (pH 7.4). Therefore, prior to using Ag nanoparticle modified electrodes, the electrochemical measurements were repeated for ten cycles in order to identify exact redox potential of Ag(0) electrode in an alkaline or buffer solution in the absence of glucose. At Ag/POSS nanocomposite modified electrodes in phosphate buffer, typical voltammetric curves displayed an oxidation wave at ca. 0.28 V extending to the potential limit in the absence of glucose.

This oxidation peak is attributed to the oxidation of Ag(0) to Ag(I) in the absence of glucose. In the presence of glucose, the catalytic oxidation current was observed at ca. 0.43 V, and the peak potential was 0.15 V positive compared to that in the absence of glucose. The result obtained was similar to the behavior observed at silver electrodes. These results indicate that glucose was oxidized catalytically at Ag/POSS nanoparticle electrode.
Figure 5.7 Cyclic voltammogram of Ag/POSS electrode (a) 0.5 M NaOH and 10 mM glucose (b) 0.5 M NaOH and 10 mM glucose and Different scan rates of forward sweeps in (c) 0.5 M NaOH and 10 mM glucose (d) 0.5 M PBS and 10 mM glucose

Using Ag/POSS nanocomposite modified electrodes in 0.5 M NaOH, typical voltammetric curves displayed an oxidation wave at ca. 0.24 V extending to the potential limit in the absence of glucose as seen in phosphate buffer solution. This oxidation peak is attributed to the oxidation of silver (0) to silver (I) in the absence of glucose. In the presence of glucose, the catalytic oxidation current was observed at ca. 0.34 V and its peak potential was 0.10 V positive compared to that in the absence of glucose. The oxidation of glucose at nanoparticles modified POSS composites on graphite electrode was
studied at various pH solutions and the results obtained from cyclic voltammograms clearly show that in alkaline media, glucose are oxidized at relatively negative potentials, however, when pH was decreased towards the acidic electrolyte medium, a positive shift in the oxidation potential was observed. Results mentioned in this work were carried out using 10 mM glucose dissolved in 0.5 M NaOH solution and 0.5 M phosphate (pH 7.4). From the results, it is inferred that, Ag/POSS composite electrodes are 10 times more active in basic medium than compared to neutral phosphate medium. Further, it is concluded that the presence of POSS prevents the aggregation of silver nanoparticles and improved the catalytic ability of the nanoparticles.

5.2.2 Au/POSS Composites for Glucose Oxidation

Figure 5.8 shows the cyclic voltammogram obtained with Au/POSS electrode in 0.5 M NaOH solution and 10 mM glucose. Oxidation of glucose started around 0.06 V (vs SCE) on a Au/POSS electrode. In the case of gold nanoparticle/POSS composite coated graphite electrode, oxidation and reduction peaks at lower potentials were observed pertaining to the formation and reduction of Au oxide monolayer on the Au/POSS electrode (Fig. 5.8a) in the absence of glucose. Figure 5.8 shows significant oxidation current density around 0.06 V at 50 mV pertaining to the oxidation of glucose in 0.5 M NaOH electrolyte. In the negative scan, oxidation of glucose does not occur until the surface oxides are reduced thus reactivating the electrode surface for further glucose adsorption and electro-oxidation. The catalytic activity pertaining to Au(0)/POSS modified electrodes towards glucose oxidation was found to be significantly enhanced in basic medium. There is no significant catalytic activity pertaining to Au(0)/POSS modified electrodes towards glucose oxidation in neutral phosphate (pH 7.4) or acid electrolyte (0.5M H$_2$SO$_4$) in the potential range studied in all the three systems. However, the
bare Au surface would remain (as a defect of the surface) to form a number of AuOH sites at which oxidation of glucose would take place.

**Figure 5.8** Cyclic voltammogram of Au/POSS electrode in the presence of 0.1 M NaOH and 10 mM glucose at various scan rate (υ = 20, 50, 100, 150, 200 and 250 mVs⁻¹) and in the absence of glucose at υ=20 mVs⁻¹ (a)

On the other hand, at more positive potentials, oxidation of gluconolactone take place around -0.1 to +0.1 V vs SCE, the population of the AuOH sites should increase on the electrode surface, and one glucose or gluconolactone molecule can interact with more than one AuOH site on the electrode surface, to give products of more than two electron oxidation with carbon-carbon bond cleavage. Actually, oxidation of gluconolactone around 0.12 V (vs SCE) gave formate as a main product (more than 50% in current yield) in solution. This voltammetric behavior was similar to a polycrystalline Au electrode. A high catalytic activity for glucose oxidation in alkaline media takes place at ca. 0.126 V (vs SCE). The oxidation current increases with an increase in the scan rate of the reaction.
5.2.3 Pt/POSS Composites for Glucose Oxidation

The oxidation of glucose at Pt/POSS nanoparticle composites in strongly alkaline to acid electrolyte have been investigated. Figure 5.9 shows the cyclic voltammogram of Pt/POSS/graphite electrode in 0.1 M NaOH and 10 mM glucose. Three oxidation peaks (a, b and c) appeared in the positive-going scan, and a cathodic peak d appeared in the negative-going scan (Figure 5.9) consistent with the literature reports (Lei et al 1995). The peak at -0.74 mV (peak a) has been assigned to the chemisorptions of glucose at the platinum electrode with a C-H bond cleavage as the initial step (equation 5.1) based on vibrational spectroscopy of the adsorbed products.

\[ \text{R-CH-OH} \rightarrow \text{R-C-OH}_{\text{ads}} + \text{H}_{\text{ads}} \]  

(5.1)

The small feature in the double layer region at -0.26 mV (peak b) has been ascribed to further oxidation to gluconate followed by slow desorption. Because of product adsorption, neither signal is useful for the determination of concentrations. The broad signal between -0.096 and 0.34 mV which was centered at around 0.086 (Peak c) is ascribed to the formation of d-gluconolactone, which overlaps in the platinum oxide region. Gluconate is formed after desorption and hydrolysis from weakly adsorbed d-gluconolactone. An oxidation signal is also found in the negative scan at about -0.392 mV (peak d). The anodic currents in the negative scan at about -0.392 mV are observed after the platinum oxides have been reduced. The glucose oxidation is completely irreversible. No reduction of products have been observed.
Peak c is due to the complete oxidation of glucose moiety from the solution phase, which agrees well with the experimental data. Pt/POSS composite materials does not show any significant oxidation current in neutral phosphate with the potential region selected in the present studies.

Figure 5.9 Cyclic voltammogram of Pt/POSS electrode in 0.1 M NaOH and 10 mM glucose

In all Pt/POSS, Ag/POSS and Au/POSS nanocomposites modified graphite electrodes, there is an enhancement in the oxidation current in basic medium, which suggests that Pt/POSS, Ag/POSS and Au/POSS composites are potent catalysts in alkaline biofuel cells (biofuel such as glucose). Thus a simple method has been elucidated for the electrocatalytic oxidation of glucose using Pt/POSS, Ag/POSS and Au/POSS composites modified electrodes in the absence of enzymes.
5.3 NPs/POSS NANOCOMPOSITES AS BACTERIOCIDES

In addition to the study of POSS supported nanoparticles for electrochemical oxidation of glucose, the present work has also been extended to probe their antibacterial activity. This is because, when bulk materials are converted to nanomaterial, their properties are extremely different from the bulk of the same material. These properties are also influenced by the nature of the stabilising agents. For example, aurothiolates inhibit HIV-1 infectivity by gold(I) ligand exchange with a component of the virion surface and effect of gold sodium thiomalate on murine acquired immunodeficiency syndrome.

Figure 5.10 shows the antibacterial activity of Ag/POSS composites. Significant results were obtained in the case of Ag/POSS, where the antibacterial activity was found to be even higher than the standard ciprofloxacin drug. The different zone of inhibition obtained for 25 µL, 50 µL and 100 µL of (5 mg dissolved in 10 mL DMF) NPs/POSS composite solution is shown in Figure 5.10.

Figure 5.10  Images of the petri dishes showing the antibacterial activity at various concentration of Ag/POSS composites
Normally, metal nanoparticles such as gold and platinum are inactive towards microorganisms. As per the previous reports, by changing the stabilising agent, it is possible to make the metal nanoparticles as antibacteriocides (Sondi and Salopek-Sondi 2004, Stoimenov et al 2002). The present study indicated that Pt/POSS and Au/POSS nanoparticles are found to inhibit the growth of microoganism. This may be due to the synergistic effect of the interaction between metal and POSS molecules in NPs/POSS composite nanoparticles.

The antibacterial activity of Au/POSS and Pt/POSS composites with different zone of inhibition obtained for 25 µL, 50 µL and 100 µL of NPs/POSS composite solution are shown in Figure 5.11. A comparative studies was done using standard antibiotic drug ciprofloxacin (5 mg). Result indicates that the NPs/POSS composite nanoparticles are found to be good antibiotics.

Figure 5.11  Images of the petri dishes showing the antibacterial activity of (A) Au/POSS and (B) Pt/POSS composites