Semiconductor – Metal Nanocomposite Materials Embedded in Polymer Matrix and their Applications

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The thesis consists of six chapters. While the first chapter provides a general introduction on nanoscience and Nanotechnology, the second chapter provides the details about the materials and experimental methods employed in this study. Chapter III to Chapter VI present the results of the present study.

CHAPTER I: Introduction

Chapter I describes about the history of nanoscience and nanotechnology, the significance of this field and the current status of nanomaterials. The importance of bandgap, flat-band potential and electron–hole recombination process of the semiconductor are clearly stated. The advantages and limitations of semiconductor materials were also explained. The effects of silicate sol- gel matrix and secondary linker molecule in the composite material were justified. The influence of noble metals on the composite material was also explained in this part. Photoelectrochemical cells and electrochemical sensors applications were clearly explained. A brief outline of the scope of the present investigation was also presented.

CHAPTER II: Experimental methods

The experimental details such as chemicals and solvents, pretreatment and fabrication of electrodes are given in this chapter. This part also describes the analytical techniques, viz., diffuse reflectance spectrophotometer (DRS), photoluminescence spectroscopy (PL), Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometer (XRD), high resolution transmission electron microscopy (HRTEM), X-ray energy dispersive spectra (EDS), scanning electron microscope (SEM), selected area electron diffraction (SAED) techniques employed to

characterize the prepared composite materials. The electrochemical and photoelectrochemical applications of the prepared materials were studied.

<u>CHAPTER IIIA</u>: Photoelectrocatalytic Performance of a Titania–Keggin type Polyoxometalate–Gold Nanocomposite Modified Electrode in Methanol Oxidation

The 3-(aminopropyl)triethoxysilane (APS) and polyoxotungstate anions (PTA) based aminosilicate sol-gel matrix supported titania-keggin ions-gold nanocomposite materials (APS/(P25-PTA-Au)$_{NCM}$) were prepared by a simple chemical reduction method and were characterised by DRS, PL spectra, XRD, TEM and EDAX analyses. Less than 5 nm sized Au$_{nps}$ were found to be deposited on the APS/P25-PTA nanocomposites. The photoelectrocatalytic actvity of the APS/(P25-PTA-Au)$_{NCM}$ modified photoelectrode was investigated towards methanol oxidation. The APS/(P25-PTA-Au)$_{NCM}$ modifed photoelectrode showed higher photocurrent towards the oxidation of methonol when compared to the control photoelectrodes. We found that the modification of keggin ions and Au nanoparticles significantly boosts the photoelectrochemical cell performance *via* synergistic effect and thus improves the interfacial charge transfer processes. The influence of methanol concentration reveals that the steady state photocurrent is directly proportional to the concentration of methanol, indicating that the rate of methanol oxidation on the APS/(P25-PTA-Au)$_{NCM}$ is first order with respect to the low concentration range of methanol. The increase in the photocurrent started to level off at higher concentrations of methanol. This newly fabricated APS/(P25-PTA-Au)$_{NCM}$ modified photoelectrode could be a promising candidate for photoelectrochemical cells.

CHAPTER IIIB: Photoelectrocatalytic Oxidation of Formic Acid over Titania@Polyoxometalate/Gold Nanocomposite Material Modified Electrode

The photoelectrocatalytic oxidation of formic acid was studied at the APS/(P25-PTA-Au)$_{NCM}$ modified photoelectrode. The APS/(P25-PTA-Au)$_{NCM}$ photoelectrode showed synergistic photoelectrocatalytic behavior towards the oxidation of formic acid. The photoresponse observed at the APS/(P25-PTA-Au)$_{NCM}$ modified photoelectrode in a photoelectrochemical cell was higher than that of the APS/P25, APS/(P25-Au)$_{NCM}$ and APS/P25-PTA modified photoelectrodes. The present study demonstrates that the loading of Au$_{nps}$ on APS/P25-PTA is beneficial to enhance the charge separation and interfacial charge transfer processes. The Au$_{nps}$ act as an electron sink for the photoexcited electrons and minimizes the charge recombination process. The combination of PTA with Au$_{nps}$ further enhances the charge separation and improves the photocurrent generation due to the formic acid oxidation by the synergistic effect. The promising photoelectrocatalytic oxidation of formic acid observed at the APS/(P25-PTA-Au)$_{NCM}$ photoelectrode may find potential application in direct formic acid fuel cells.

CHAPTER IV: Titania/Keggin type Polyoxometalate/Silver Nanocomposite for the Photoelectrocatalytic Oxidation of Methanol

Aminosilicate sol-gel supported titania-polyoxometalate-silver nanocomposites APS/(P25-PTA-Ag)$_{NCM}$ were prepared by a simple chemical reduction method and were characterized by DRS, PL spectra, XRD, TEM and EDAX analyses. The photoelectrochemical studies of the APS/(P25-PTA-Ag)$_{NCM}$ modified photoelectrode was investigated towards the oxidation of methanol. The onset potential for the photoelectrocatalytic oxidation of methanol for APS/(P25-PTA-Ag)$_{NCM}$ starts at – 0.4 V which is a less positive potential than that of other

reported photoelectrodes. Also the prepared nanocomposite shows 17-fold enhancement of photocurrent than the APS/P25 photoelectrode. The incorporation of PTA and Ag_{nps} on the surface of the P25 significantly influences the photoelectrocatalytic performance of methanol oxidation via the synergistic effect of Ag_{nps} and PTA. The Ag_{nps} improves the interfacial charge transfer processes and thereby reduce the charge recombination. The newly fabricated APS/(P25-PTA-Ag)$_{NCM}$ modified photoelectrode could be employed as photoanode in direct methanol fuel cells.

<u>CHAPTER VA</u>: Silver Decorated Amino Silicate Functionalized Nanoporous TiO_2 Composite for Electrochemical Sensing of Hydrazine

The APS/(nanoporous TiO_2-Ag)$_{NCM}$ was prepared using simple chemical reduction method. The optical and morphological property of APS/(nanoporous TiO_2-Ag)$_{NCM}$ was studied by UV-visible diffused reflectance spectroscopy. The size and shape of the prepared composite were verified by SEM and HRTEM analysis. The size of the spherical APS/nanoporous TiO_2 was found to be nearly 400 nm and the size of the deposited Ag_{nps} was in the range of 10-50 nm. The crystalline nature of the composite material was analyzed by SAED analysis. The presence of Ag_{nps} in the composite was also confirmed by cyclic voltammetry. The prepared composite was studied toward the electrocatalytic oxidation of hydrazine. The lowest detection limit was found to be 0.26 µM. The sensitivity of the modified electrode was calculated to be 1.297 µA μM^{-1} cm^{-2}. The interference of various inorganic metal ions in the determination of hydrazine was also studied and the results are presented.

<u>CHAPTER VB</u>: Gold Decorated Amino Silicate Functionalized Nanoporous TiO_2 Composite for Enzymeless Determination of Hydrogen Peroxide

The APS/(nanoporous TiO_2-Au)$_{NCM}$ was prepared using simple chemical reduction method. The absorption characterisitics of APS/(nanoporous TiO_2-Au)$_{NCM}$ was studied by UV-visible diffused reflectance spectroscopy. The size and shape of the prepared composite were analysed by SEM and HRTEM analysis. The size of the spherical APS/nanoporous TiO_2 was found to be nearly 400 nm and the size of the deposited Au_{nps} was in the range of 10-50 nm. The presence of Au in the APS/(nanoporous TiO_2-Au)$_{NCM}$ was confirmed EDX and cyclic voltammetry. The crystalline nature of the composite material was investigated by SAED analysis. The prepared composite was evaluated towards the electrocatalytic reduction of hydrogen peroxide. The lowest detection limit was found to be 0.13 µM. The sensitivity of the modified electrode was calculated to be 0.9685 µA μM^{-1} cm^{-2}. The effect of various common physiological interferents in the determination of hydrogen peroxide was also studied. From the results, it was concluded that the prepared APS/(nanoporous TiO_2-Au)$_{NCM}$ could serve as a good electrocatalyst in sensor applications.

<u>CHAPTER VIA</u>: Silver Nanoparticles Supported on Graphitic like Carbon Nitride for the Electrochemical Sensing of Nitrobenzene and its Derivatives

The N-[3-(trimethoxysilyl)propyl]-ethylene diamine (EDAS) based EDAS/(g-C_3N_4-Ag)$_{NCM}$ was prepared by simple chemical reduction method and characterized using UV-vis diffused reflectance spectroscopy, FT-IR, EDX and HRTEM analyses. The absorption spectra of EDAS/(g-C_3N_4-Ag)$_{NCM}$ was studied by UV-visible diffused reflectance spectroscopy. The absorption edge at 430 nm and appearance of broad peak at 450 nm suggests the presence of Ag_{nps} and g-C_3N_4 nanosheets in the composite. The different vibrational bands observed in the FT-IR spectra confirm the

presence of g-C_3N_4 nanosheets. From TEM analysis, it is confirmed the size of the Ag_{nps} on g-C_3N_4 nanosheets is in the range of 10-15 nm. The presence of silver in the EDAS/(g-C_3N_4-Ag)$_{NCM}$ was also confirmed by EDX and elemental mapping analysis as well as by cyclic voltammetry. The application of prepared composite towards the electrocatalytic reduction of nitrobenzene was examined. The detection limit was found to be 2 µM. The prepared composite material was also studied towards the sensing of nitrobenzene derivatives such as nitroaniline, nitrobenzoic acid, nitrophenol and nitrotoluene.

<u>CHAPTER VIB</u>: Gold Nanoparticles Supported on Graphitic like Carbon Nitride for the Electrocatalytic Oxidation of Nitrite

The EDAS/(g-C_3N_4-Au)$_{NCM}$ was prepared using simple chemical reduction and characterized well. The absorption edge at 430 nm and appearance of broad peak at 550 nm suggests the presence of Au_{nps} and g-C_3N_4 nanosheets in the composite. From TEM analysis, it is confirmed that about 10 nm Au_{nps} are deposited on g-C_3N_4 nanosheets. The presence of Au_{nps} deposited on g-C_3N_4 nanosheets was also characterized by EDX and cyclic voltammetry. The electrocatalytic oxidation of nitrite using the prepared composite was studied. The lowest experimental detection limit was found to be 0.6 µM. The sensitivity of the modified electrode for the oxidation of nitrite was studied. The interference of various common physiological interferents and major inorganic ions in the determination of nitrite was also studied.

The salient results of the study are summarized in Chapter VII.