**Annexure – VIII**

**UNIVERSITY GRANTS COMMISSION**
**BAHADUR SHAH ZAFAR MARG**
**NEW DELHI – 110 002**

**Final Report of the work done on the Major Research Project**
**(Report to be submitted within 6 weeks after completion of each year)**

1. Project report No. : Final report
2. UGC Reference No. : F.No.40-2/2011
3. Period of report : 01.07.2011 to 30.06.2014
4. Title of research project : Synthesis of $WO_3$ and $TiO_2$ Nanomaterials and Fabrication of Gas Sensors.
5. (a) Name of the Principal Investigator : Dr. C. Sekar
   (b) Department : Bioelectronics & Biosensors
   (c) University where work has progressed : Alagappa University, Karaikudi, Tamilnadu
6. Effective date of starting of the project : 01.07.2011
7. Grant approved and expenditure incurred during the period of the report:
   a. Total amount approved : Rs. 12,32,328/- ; amount Received Rs. 11,65,475/-
   b. Total expenditure : Rs. 11,47,289/-
   c. Report of the work done : (Please attach a separate sheet)

i. Brief objectives of the project:

(i) To synthesize nanostructured metal oxides ($WO_3$, $TiO_2$ & $SnO_2$) in pure and doped form (Co, Mn, Ni etc.) and characterize them using XRD, SEM, TEM, VSM, XPS, etc.

(ii) To fabricate sensors for biomedical, food and environmental applications.

ii. Work done so far, and results achieved and publications:

▪ Successfully synthesized $WO_3$, $TiO_2$ & $SnO_2$ nanoparticles by microwave irradiation, chemical precipitation and hydrothermal methods

▪ Characterized extensively to confirm their structural, morphological, and magnetic properties by XRD, SEM, TEM, VSM, XPS, cyclic voltammetry and impedance spectroscopy methods.

1. A mediator-free horseradish peroxidise based $H_2O_2$ biosensor was fabricated using Ni doped $SnO_2$ NPs synthesized by microwave irradiation method. Direct electrochemistry of horseradish peroxidase (HRP)/1wt% Ni-$SnO_2$ modified glassy carbon electrode (GCE) exhibited excellent electron transfer properties for the detection of $H_2O_2$. The fabricated biosensor exhibits good

affinity, fast response, wide linear range ($1.0\times10^{-7}$ to $3.0\times10^{-4}$ M), lower detection limit (43 nM), high sensitivity, operational convenience, storage stability and acceptable reproducibility. The fabricated Ni-$SnO_2$ based electrochemical sensor can be used for analyses of clinical samples.

**Publication:** Fabrication of hydrogen peroxide biosensor based on Ni doped $SnO_2$ nanoparticles
N Lavanya, S Radhakrishnan, C Sekar (Biosensors & Bioelectronics 36 (2012) 41-47).
(Impact factor: 10.257).

2. A Riboflavin (vitamin B2) sensor has been fabricated based on Cr doped $SnO_2$ nanoparticles. Compared with undoped $SnO_2$ the 3 wt% Cr doped $SnO_2$ exhibit improved catalytic activity toward the detection of riboflavin. The fabricated sensor showed an excellent anti-interference ability against electroactive species and metal ions and proved to be useful to estimate RF content in the pharmaceutical samples with satisfactory recovery.

**Publication:** Fabrication of Cr doped $SnO_2$ nanoparticles based biosensor for the selective determination of riboflavin in pharmaceuticals
N Lavanya, S Radhakrishnan, C Sekar, M Navaneethan, Y Hayakawa
Analyst 138 (2013) 206 (Impact Factor: 3.864).

3. A novel folic acid biosensor has been fabricated using Cu-$SnO_2$ NPs synthesized by a simple microwav irradiation method. Cu (20 wt%) doped $SnO_2$ NPs are proved to be a good sensing element for the determination of folic acid. Cu-$SnO_2$ NPs (20 wt%) modified glassy carbon electrode (GCE) exhibited the lowest detection limit of 0.024 nM over a wide folic acid concentration range of $1.0\times10^{-10}$ to $6.7\times10^{-5}$ m at physiological pH of 7.0. The fabricated sensor is highly selective towards the determination of FA even in the presence of a 100-fold excess of common interferent ascorbic acid. The sensor proved to be useful for the estimation of FA content in pharmaceutical sample with satisfactory recovery.

**Publication:** Fabrication of folic acid sensor based on the Cu doped SnO2 nanoparticles modified glassy carbon electrode, N Lavanya, S Radhakrishnan, N Sudhan, C Sekar, SG Leonardi, C Cannilla, G Neri, Nanotechnology 25 (2014) 295501
(Impact Factor: 3.55).

4. A chemo resistive gas sensor was fabricated by depositing the nanostructured Cu-$SnO_2$ on a ceramic substrate provided with interdigited electrodes. The synthesis and the morphological-microstructural characterization of the sensing material were first investigated. The electrical and CO sensing experiments showed good performance of the fabricated sensor when operated in air

and nitrogen atmosphere, i.e. high sensitivity in a wide range of CO concentrations with very fast response/recovery time.

**Publication:** Development of a CO Sensor for Hydrogen Fuel Cell Powered Vehicles.
G. Neri, G. Leonardi, M. Parthibavarman, V. Hariharan, C. Sekar.
**Vehicle Engineering (2013), Academy publisher**

**5.** Tungsten trioxide ($WO_3$) is an n-type indirect type semiconductor with wide band gap ($E_g$~ 2.5 to 3.6 eV) and structural polymorphism. Owing to its outstanding optical and electrical properties, $WO_3$ has been widely used in various applications such as electrochromic devices, solar cells, lithium secondary batteries, gas sensors and catalysis. We have synthesized $WO_3$ NPs using simple household microwave oven. Precursor was prepared by mixing appropriate amount of starting materials ($H_2WO_4$ and NaOH), stirred well and then exposed to microwave under 180 W for 15 min. Powder XRD confirmed that the as-prepared sample is $WO_3$ with monoclinic structure (γ-$WO_3$) and the average crystallite size estimated to be 33 nm. Upon subsequent annealing at 600°C for 6 h under ambient conditions monoclinic γ-$WO_3$ got transferred to orthorhombic (β-$WO_3$) phase and that the average crystallite size increased to 38 nm. Further, this phase was confirmed by Electron Energy Loss (EEL) spectra. Structural changes and electronic properties were investigated by Raman, PL and UV-Visible spectroscopy. Electrochemical investigations revealed that the γ-$WO_3$ NPs modified GCE has excellent electrocatalytic activity towards the oxidation of dopamine (DA) in the presence of ascorbic acid (AA) at pH 7.0. Differential pulse voltammetry (DPV) studies of the γ-$WO_3$/GCE exhibited linear response over a wide concentration range of 0.1 µM to 600 µM of DA with the detection limit of 24 nM. The fabricated sensor showed an excellent anti-interference ability against electroactive species and metal ions with good stability and reproducibility. Finally, the developed sensor was applied to determine DA concentration in dopamine hydrochloride injection which indicates that this electrode can be effectively used for real sample analysis.

**Publication:** $WO_3$ nanoparticles based direct electrochemical dopamine sensor in the presence of ascorbic acid, AC Anithaa, N Lavanya, K Asokan, C Sekar *Electrochimica Acta* 167 (2015) 294-302. (Impact Factor: 6.216).

iii. Project has been completed as per original plan: **01.07.2011 to 30.06.2014**

iv. Please indicate the difficulties, if any, experienced in implementing the project

**There were no difficulties in implementing the project**

v. If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet.

**Not applicable**

vi. If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants commission.

**Final report of work done is attached**

vii. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Man power trained (b) Ph.D. awarded (c) Publication of results (d) other impact, if any

(i) Ms. N. Lavanya (Project Fellow) registered for Ph.D. programme in the Dept. of Bioelectronics & Biosensors. Register No.449/2010 dt.20.10.2012.

(ii) Mr. A. Arulram (Project Fellow) registered for Ph.D. programme in the Dept. of Bioelectronics & Biosensors. Register No. 0956/2014-15 dt.17.07.2014.

Based on the work done under this scheme, five original research papers have been published. Sensors developed during the project period will be helpful for the society.

**SIGNATURE OF THE**
**PRINCIPAL INVESTIGATOR** **REGISTRAR**

**Annexure – IX**

**UNIVERSITY GRANTS COMMISSION**

**BAHADUR SHAH ZAFAR MARG**

**NEW DELHI – 110 002**

**PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT**

1. TITLE OF THE PROJECT : Synthesis of $WO_3$ and $TiO_2$ Nanomaterials and Fabrication of Gas Sensors.

2. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR : Dr. C. Sekar, Dept. of Bioelectronics And Biosensors, Alagappa University, Karaikudi- 630003, TN

3. NAME AND ADDRESS OF THE INSTITUTION : Alagappa University Karaikudi – 630003, TN

4. UGC APPROVAL Letter & DATE : F.N0. 40-2/2011(SR), Dated: 29.06.2011.

5. DATE OF IMPLEMENTATION : 01.07.2011

6. TENURE OF THE PROJECT : 01.07.2011 to 30.06.2014

7. TOTAL GRANT ALLOCATED : Rs. 12,32,328/-

8. TOTAL GRANT RECEIVED : Rs. 11,65,475/-

9. FINAL EXPENDITURE : Rs. 11,47,289/-
   TITLE OF THE PROJECT : Synthesis of $WO_3$ and $TiO_2$ Nanomaterials and Fabrication of Gas Sensors.

10. OBJECTIVES OF THE PROJECT:

(i) To synthesize nanostructured metal oxides ($WO_3$, $TiO_2$ & $SnO_2$) in pure and doped form (Co, Mn, Ni etc.) and characterize them using XRD, SEM, TEM, VSM, XPS, etc.

(ii) To fabricate sensors for biomedical, food and environmental applications.

11. WHETHER OBJECTIVES WERE ACHIEVED: Yes

12. ACHIEVEMENTS FROM THE PROJECT :

1. Fabrication of hydrogen peroxide biosensor based on Ni doped $SnO_2$ Nanoparticles, N. Lavanya, S. Radhakrishnan, C. Sekar Biosensors and Bioelectronics 36 (2012) 41-47).(IF: 10.257)

2. Fabrication of Cr doped $SnO_2$ nanoparticles based biosensor for the seletive determination of ribodlavin in pharmaceuticals, N. Lavanya, S.Radhakrishnan, C. Sekar, M. Navaneethan and Y. Hayakawa, Analyst (2013, 138,206 (IF: 3.864).
3. Development of a CO Sensor for Hydrogen Fuel Cell Powered Vechicles, G.Neri, G. Leonardi, M. Parthibavarman, V. Hariharan, C. Sekar. A chapter in the book entitled "Vehicle Engineering" (2013), Academy Publishers.
4. Fabrication of folic acid sensor based on the Cu doped $SnO_2$ nanoparticles modified glassy carbon electrode N. Lavanya, S. Radhakrishnan, N. Sudhan C. Sekar, S. G. Leonardi, C. Cannilla, G. Neri Nanotechnology, 25 (2014) 295501 (IF: 3.55)
5. $WO_3$ nanoparticles based direct electrochemical dopamine sensor in the presence of ascorbic acid, *Electrochimica Acta* 167 (2015) 294-302 (IF: 6.216)

13. SUMMARY OF THE FINDINGS :

Sensors have become an indispensable part of our technology driven society and detection/quantification of chemical or biological species is of utmost importance for pharmaceutical, food, biomedical, environmental, security, industrial safety, clinical and indoor monitoring applications. The recent advances in the nanotechnology enabled the development of smart sensors that can detect even very low-level concentrations of analyte with high precision and miniaturization of the devices have become feasible. Despite all of these positive developments, there is a great demand for further improvement in the performance of the sensors in terms of its sensitivity, selectivity, reproducibility, simultaneous detection of a family of compounds, and to make the cost effective and user-friendly portable devices.

Nanostructured metal oxides semiconductors (NMOs) based chemical sensors endows an ambit for various innovative and novel functions with a variety of desired applications. Among various metal oxides, tin dioxide ($SnO_2$) is a versatile material with a wide band gap (3.6 eV at 300 K) in its stoichiometric form, but it becomes an n-type semiconductor due to lattice imperfections and intrinsic oxygen vacancies. Detailed literature survey revealed that the nanostructured $SnO_2$ have been extensively used as sensing material for the development and technological implementation of gas sensor for various applications. $SnO_2$ NPs are known to exhibit high surface reactivity, good catalytic activity and strong adsorption ability making it suitable candidate material for electrochemical sensing applications.

In this perspective, the main objective of this research work was to fabricate novel electrochemical sensors based on nanostructured $SnO_2$ for precise and rapid detection of

biomolecules, food constituents, contaminants, pollutants and toxic gases. We had successfully prepared good quality $SnO_2$ nanoparticles (NPs) in pure and chemically doped form by a simple microwave irradiation method and its applicability for the development of various sensors for selective and simultaneous detection of either single or two to three different kinds of molecules of the same family like (i) hydrogen peroxide, (ii) riboflavin, (iii) ascorbic acid, uric acid, folic acid, (iv) carbamazepine, (v) epinephrine and norepinephrine, (vi) hydroquinone and catechol. The $SnO_2$ NPs modified by chemical doping were further applied for the detection hydrogen and carbon monoxide gases by chemo-resistive method. A few results are highlighted below.

**Fabrication of $H_2O_2$ biosensor using Ni doped $SnO_2$ NPs**

This chapter describes the fabrication of a mediator-free horseradish peroxidise based $H_2O_2$ biosensor using Ni doped $SnO_2$ NPs synthesized by microwave irradiation method. The Ni-$SnO_2$ NPs were characterized using a variety of techniques such as powder XRD, HRTEM, VSM, ESR, UV-Vis absorption, CV and EIS. Direct electrochemistry of horseradish peroxidase (HRP)/1wt% Ni-$SnO_2$ modified glassy carbon electrode (GCE) exhibited excellent electron transfer properties for the detection of $H_2O_2$. The fabricated biosensor exhibits good affinity, fast response, wide linear range ($1.0\times10^{-7}$ to $3.0\times10^{-4}$ M), lower detection limit (43 nM), high sensitivity, operational convenience, storage stability and acceptable reproducibility. The fabricated Ni-$SnO_2$ based electrochemical sensor can be used for analyses of clinical samples.

**Vitamin sensors based on Cr and Cu doped $SnO_2$ NPs**

The first part of this work describes the construction, optimization and characterization of Cr doped $SnO_2$ NPs based electrochemical sensor for sensitive and selective detection of riboflavin (RF). The $VB_2$ is a water-soluble and essential vitamin to human health for converting carbohydrates, fats and proteins into energy and it supports the body during the stress of daily living. We have fabricated a new electrochemical sensor based on chromium (Cr) ion doped $SnO_2$ NPs for rapid detection of RF with high sensitivity, wide response range and the lowest detection limit of 107 nM. The developed sensor showed an excellent anti-interference ability against potential electroactive species (L-ascorbic acid and uric acid) and metal ions ($Fe^{3+}$, $Mg^{2+}$ and $Ca^{2+}$) and proved to be useful to estimate RF content in the riboflavin tablet and milk powder with satisfactory recovery.

We have also fabricated a novel folic acid (vitamin B9) sensor using Cu doped $SnO_2$ NPs. The 20wt% Cu doped $SnO_2$ modified GCE is proved to be a good sensing element for the determination of folic acid (FA) with the lowest detection limit of 0.024 nM over a wide concentration range of 1.0

$\times 10^{-10}$ to $6.7 \times 10^{-5}$ M at physiological pH 7.0. The ascorbic acid (AA) always coexists with FA in human body fluid and its concentration is much higher than that of FA. Therefore the determination of FA in the presence of high concentration of AA is very important. We have demonstrated that the newly fabricated electrode is highly selective towards the determination of FA in the presence of even 100-fold excess of AA. The sensor is further applied for the estimation of FA content in folic acid tablet.

**Fabrication of Dopamine Sensor using Tungsten Trioxide ($WO_3$)**

Tungsten trioxide ($WO_3$) is an n-type indirect type semiconductor with wide band gap ($E_g$~ 2.5 to 3.6 eV) and structural polymorphism. Owing to its outstanding optical and electrical properties, $WO_3$ has been widely used in various applications such as electrochromic devices, solar cells, lithium secondary batteries, gas sensors and catalysis. We have synthesized $WO_3$ NPs using simple household microwave oven. Precursor was prepared by mixing appropriate amount of starting materials ($H_2WO_4$ and NaOH), stirred well and then exposed to microwave under 180 W for 15 min. Powder XRD confirmed that the as-prepared sample is $WO_3$ with monoclinic structure (γ-$WO_3$) and the average crystallite size estimated to be 33 nm. Upon subsequent annealing at 600°C for 6 h under ambient conditions monoclinic γ-$WO_3$ got transferred to orthorhombic (β-$WO_3$) phase and that the average crystallite size increased to 38 nm. Further, this phase was confirmed by Electron Energy Loss (EEL) spectra. Structural changes and electronic properties were investigated by Raman, PL and UV-Visible spectroscopy. Electrochemical investigations revealed that the γ-$WO_3$ NPs modified GCE has excellent electrocatalytic activity towards the oxidation of dopamine (DA) in the presence of ascorbic acid (AA) at pH 7.0. Differential pulse voltammetry (DPV) studies of the γ-$WO_3$/GCE exhibited linear response over a wide concentration range of 0.1 µM to 600 µM of DA with the detection limit of 24 nM. The fabricated sensor showed an excellent anti-interference ability against electroactive species and metal ions with good stability and reproducibility. Finally, the developed sensor was applied to determine DA concentration in dopamine hydrochloride injection which indicates that this electrode can be effectively used for real sample analysis.

The key findings of these extensive interdisciplinary research accomplishments have been compiled neatly as a thesis for the award of Ph.D. degree by Alagappa University, Karakudi.

14. CONTRIBUTION TO THE SOCIETY :

Sensing materials with superior properties have been identified and characterized $SnO_2$ and $WO_3$ NPs were used to modify/fabricate electrodes for electrochemical sensing

applications. The developed sensors were tested towards the detection of various biomolecules such as hydrogen peroxide ($H_2O_2$), vitamins (riboflavin & ascorbic acid, folic acid), drug (carbamazepine), neurotransmitters (epinephrine and norepinephrine), pollutants (hydroquinone, catechol) by electrochemical methods. The fabricated electrochemical sensors were further applied for analysis of real sample applications like pharmaceutical products, fruits, tap water and urine samples.

Chemo-resistive gas sensors were fabricated and successfully tested for the detection of hydrogen and carbon monoxide with high precision. By making use of the sensing elements developed in the present work, high performance sensors can be fabricated at low cost. The future objective is to produce such sensor**s** under Make in India scheme.

15. WHETHER ANY Ph.D. ENROLLED/PRODUCED OUT OF THE PROJECT:

(i) Ms. N. Lavanya (Project Fellow) registered for Ph.D. (No. 449/2010 dt. 20.01.2012) under the guidance of PI.

(ii) Mr. A. Arulram (Project Fellow) registered for Ph.D. (No.0956/2014-15 dt.17.07.2014) under the guidance of PI.

16. NO. OF PUBLICATIONS OUT OF THE PROJECT: 5

**PRINCIPAL INVESTIGATOR** **REGISTRAR**

**Publication:**

Biosensors and Bioelectronics 36 (2012) 41–47

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Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

# Fabrication of hydrogen peroxide biosensor based on Ni doped $SnO_2$ nanoparticles

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ABSTRACT

Ni doped $SnO_2$ nanoparticles (0–5 wt%) have been prepared by a simple microwave irradiation (2.45 GHz) method. Powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies confirmed the formation of rutile structure with space group ($P_{42}/mnm$) and nanocrystalline nature of the products with spherical morphology. Direct electrochemistry of horseradish peroxidase (HRP)/nano-$SnO_2$ composite has been studied. The immobilized enzyme retained its bioactivity, exhibited a surface confined, reversible one-proton and one-electron transfer reaction, and had good stability, activity and a fast heterogeneous electron transfer rate. A significant enzyme loading ($3.374 \times 10^{-10}$ mol cm$^{-2}$) has been obtained on nano-Ni doped $SnO_2$ as compared to the bare glassy carbon (GC) and nano-$SnO_2$ modified surfaces. This HRP/nano-Ni–$SnO_2$ film has been used for sensitive detection of $H_2O_2$ by differential pulse voltammetry (DPV), which exhibited a wider linearity range from $1.0 \times 10^{-7}$ to $3.0 \times 10^{-4}$ M ($R$=0.9897) with a detection limit of 43 nM. The apparent Michaelis–Menten constant ($K_M^{app}$) of HRP on the nano-Ni–$SnO_2$ was estimated as 0.221 mM. This excellent performance of the fabricated biosensor is attributed to large surface-to-volume ratio and Ni doping into $SnO_2$ which facilitate the direct electron transfer between the redox enzyme and the surface of electrode.



## 1. Introduction

Nanostructured metal oxide semiconductors possesses high surface area, nontoxicity, good biocompatibility, sensitivity, and chemical stability that can easily be modified for immobilization of biomolecules for biosensor applications (Ansari et al., 2010). Among the metal oxide semiconductors, tin oxide ($SnO_2$), an n-type semiconductor with a wide band gap of 3.6 eV at 300 K, has been investigated for various applications such as gas sensors, solar cells, transparent conductive electrodes, spintronics and biosensor etc. (Chu et al., 2011; Ahn et al., 2004). One of the most important methods to modify the materials is the introduction of dopants into host system. A numerous experimental investigations have been performed on $SnO_2$ doped with transition metal ions such as Co, Mn, Fe, Ni, and Cr. Among these, Ni is of special interest because of its capability of grain growth inhibition within the $SnO_2$ matrix (Jain et al., 2006). Pure and doped $SnO_2$ have been produced using various techniques such as sol gel method (Sambasivam et al., 2011), solid state reaction method (Ahmed. 2010), spray pyrolysis (Korotcenkov and Do Han, 2009), chemical vapor deposition method (Zhang et al., 2010), solvothermal method (Kang et al., 2007), polymer precursor method (Aragon et al., 2010), etc.

In recent years, sensitive and accurate determination of hydrogen peroxide ($H_2O_2$) is of great importance, because $H_2O_2$ is not only a byproduct of several selective oxidases but also an essential mediator in food, industry, pharmaceutical laboratories and environmental analyses (Lin et al., 2010). Many techniques have been employed for the determination of $H_2O_2$, which includes spectrophotometry (Lobnik and Cajlakovic 2001), chemiluminescence (Janasek et al., 1998), and electrochemistry (Kafi et al., 2008). Among these, electrochemistry has been widely applied for accurate determination of $H_2O_2$. Many proteins have been employed to construct the potential $H_2O_2$ biosensors, such as HRP, cytochrome C, myglobin and hemoglobin which are capable of reducing $H_2O_2$ electro catalytically. HRP is the most commonly used enzyme for the construction of $H_2O_2$ biosensors due to its high purity, sensitivity and low cost (Ferapontova et al., 2002). Cao et al. investigated the direct electrochemistry of heme protein immobilized on $Fe_3O_4$ nanoparticles for highly reproducible $H_2O_2$ sensing (Cao and Hu, 2006). Li et al. reported the Sb doped $SnO_2$ nanowires to possess excellent electron transfer properties for the enzymes than that of pure $SnO_2$ nanowire (Li et al., 2010a, 2010b). The electro catalytic ability of HRP–$TiO_2$ nanotube arrays had different sensitivities to $H_2O_2$ due to their different conductivity (Xiao et al., 2007). Ansari et al. have applied

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http://dx.doi.org/10.1016/j.bios.2012.03.035

Ni–$SnO_2$ modified electrode in $N_2$-saturated PBS (pH = 7.0) show no obvious changes after 20 cycles, and then it decreases (2.835%) slowly with the increase in cycles up to 100 (data not shown here). The reproducibility of the biosensor was investigated using 100 μM $H_2O_2$, with a series of five DPV experiments and the relative standard deviation (R.S.D) of 4.26% was achieved. These results indicated that the immobilized HRP possesses high enzymatic activity and nano-Ni–$SnO_2$ provided favorable microenvironment for HRP to perform direct electron transfer at the modified electrode.

## 4. Conclusions

Single phase Ni doped $SnO_2$ nanoparticles were successfully synthesized by a simple microwave irradiation method. Powder XRD and TEM analyses confirmed the phase purity and nanometric dimension of the samples. The grain sizes have been found to get reduced with increase in Ni concentration. Magnetic measurements revealed that the 1 wt% Ni doping into $SnO_2$ did not affect its diamagnetic behavior, but the higher Ni concentration (5 wt%) caused ferromagnetism in $SnO_2$. This result is important in view of the fact that the higher Ni doping did not promote the sensing characteristics of nano-Ni–$SnO_2$. Using this metal oxide nanoparticles incorporated with HRP, we have fabricated a simple and novel differential pulse voltammetric hydrogen peroxide biosensor. The electrochemical behavior of HRP at the nano-Ni–$SnO_2$ modified electrode demonstrated the direct electron transfer reaction of HRP. The fabricated biosensor exhibits good affinity, fast response, wide linear range, lower detection limit, high sensitivity, operational convenience, storage stability and acceptable reproducibility. The results indicated that the Ni doped $SnO_2$ nanoparticles can provide a favorable microenvironment for the enzyme and promote the direct electron transfer at the electrode surface.

## Acknowledgment

The authors thank the University Grants Commission (F.no. 40-2/2011) for financial support.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.bios.2012.03.035.

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# Fabrication of Cr doped $SnO_2$ nanoparticles based biosensor for the selective determination of riboflavin in pharmaceuticals†

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We report the fabrication and testing of a riboflavin (RF) biosensor based on the use of Cr doped $SnO_2$ nanoparticles. The Cr–$SnO_2$ nanoparticles with chromium concentration from 0 to 5 wt% were synthesised by a microwave irradiation method. Magnetic studies revealed that only 3 wt% Cr doped nano-$SnO_2$ has ferromagnetic behaviour at room temperature. This Cr–$SnO_2$ nanoparticles modified electrode responded to RF linearly over a concentration range of $0.2 \times 10^{-6}$ to $1.0 \times 10^{-4}$ M with a detection limit of 107 nM. The fabricated sensor showed an excellent anti-interference ability against electroactive species and metal ions and proved to be useful for the estimation of the RF content in pharmaceutical samples with satisfactory recovery.

## 1 Introduction

Nanostructured metal-oxide semiconductor based nanosensors have wide applications in biological, environmental and analytical chemical sciences. Among the oxide semiconductors, tin oxide ($SnO_2$) is one of the most promising candidates as a host material which has been used in gas sensors, dye-sensitized solar cells, electrochromic windows, transparent conducting electrodes, transistors, catalysts, supercapacitors, and so forth.[1,2] $SnO_2$ is a versatile material with a wide band gap (3.6 eV at 300 K) in its stoichiometric form, but due to lattice imperfections and oxygen vacancies arising during its production, it becomes n-type and conductive.[3] $SnO_2$ has been of considerable interest because of its combined properties of plentiful oxygen vacancies, high optical transparency, chemical and electrochemical stability, good electrocatalytic activity, nontoxicity, good biocompatibility, and high electron communication features when doped.[4] Chemical doping with appropriate elements (Fe, Cr, Co, Mn, Ni, *etc.*) is widely used as an effective method to tune surface states, energy levels of semiconductors and transport performance of carriers, and enhance the electrical, electrochemical and magnetic properties of materials.[5] Among these, Cr is the only elemental solid which shows antiferromagnetic ordering at room temperature and below. The ionic radius of Cr(III) is close to that of $Sn^{4+}$, which means that $Cr^{3+}$ can easily penetrate into the $SnO_2$ crystal lattice or substitute the $Sn^{4+}$ position in the crystal.[6] Various methods have been used to synthesize the $SnO_2$ nanostructures; sol–gel method,[7] co-precipitation,[8] pulsed laser deposition,[9] spray pyrolysis,[10] solid state reaction method,[11] polymeric precursor's route,[12] hydrothermal method,[13] *etc.* However, it still remains a great challenge to develop a simple method for fabricating nano-$SnO_2$, particularly metal ion doped $SnO_2$ nanostructures with controlled morphology. Herein we report the synthesis of Cr doped $SnO_2$ nanoparticles by a simple microwave irradiation method for the first time. Microwave assisted synthesis is a clean modern technique widely used for green chemistry. It takes only a few minutes to complete the reaction and it prevents agglomeration.

Riboflavin ($VB_2$) is a water-soluble B-group vitamin essential to human health which helps the body convert carbohydrates, fats and proteins into energy and supports the body during the stress of daily living.[14] Riboflavin is converted to 2 coenzymes, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD), which are necessary for normal tissue respiration. These coenzymes are involved in several reduction oxidation reactions and take part in the metabolism of other vitamins, *e.g.*, folate and vitamin $B_6$.[15] Riboflavin is very stable during thermal processing, storage or food preparation, but it is susceptible to degradation after exposure to light. Lack of riboflavin may lead to itching and burning eyes, sensitivity of eyes to light, sore tongue, itching and peeling skin on the nose and scrotum, and sores in the mouth. Riboflavin is found in various foods, including milk and dairy products, fish, meats, green leafy vegetables, and whole grain and enriched cereals and bread.[16] For the determination of riboflavin, several techniques have been developed, including liquid chromatography,[17] chemiluminescence,[18] spectrophotometry,[19] mass spectrometry[20] and

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† Electronic supplementary information (ESI) available: XRD parameter in Table S1 and comparison of our sensor performance with literature reports in Table S2. See DOI: 10.1039/c3an36754a

are summarized in Table 1. The data shows that the RF content in the examined tablets and milk powder fall within the tagged amount suggesting the good applicability of the proposed voltammetric method.

## 4 Conclusions

We have successfully synthesized Cr (0, 1, 3, and 5 wt%) doped $SnO_2$ nanoparticles by the microwave irradiation method. The rutile structure of $SnO_2$ was confirmed by X-ray diffraction and TEM studies, and no presence of Cr metals or other magnetic phases could be detected. The 3 wt% Cr doped $SnO_2$ nanoparticles exhibit room temperature ferromagnetism which was attributed to the possible enhancement of oxygen vacancies in the parent compound $SnO_2$. We have fabricated a highly sensitive RF sensor based on a Cr doped $SnO_2$ nanoparticles modified electrode for the first time using DPV. Compared with undoped $SnO_2$, the Cr (3 wt%) doped $SnO_2$ modified electrode exhibits improved catalytic activity toward the detection of RF. Excellent performance in sensitivity, stability, selectivity, reproducibility and freedom from interference was achieved when the sensor was exposed to RF solution. All these advantageous features can make the proposed sensor applicable in medical, food or other areas.

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# Fabrication of folic acid sensor based on the Cu doped $SnO_2$ nanoparticles modified glassy carbon electrode

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**Abstract**

A novel folic acid biosensor has been fabricated using Cu doped $SnO_2$ nanoparticles (NPs) synthesized by a simple microwave irradiation method. Powder XRD and TEM studies confirmed that both the pure and Cu doped $SnO_2$ (Cu: 0, 10, 20wt%) crystallized in tetragonal rutile-type structure with spherical morphology. The average crystallite size of pure $SnO_2$ was estimated to be around 16 nm. Upon doping, the crystallite sizes decreased to 9 nm and 5 nm for 10 and 20wt% Cu doped $SnO_2$ respectively. XPS studies confirmed the electronic state of Sn and Cu to be 4+ and 2+ respectively. Cu (20wt%) doped $SnO_2$ NPs are proved to be a good sensing element for the determination of folic acid (FA). Cu-$SnO_2$ NPs (20wt%) modified glassy carbon electrode (GCE) exhibited the lowest detection limit of 0.024 nM over a wide folic acid concentration range of $1.0 \times 10^{-10}$ to $6.7 \times 10^{-5}$ M at physiological pH of 7.0. The fabricated sensor is highly selective towards the determination of FA even in the presence of a 100 fold excess of common interferent ascorbic acid. The sensor proved to be useful for the estimation of FA content in pharmaceutical sample with satisfactory recovery.

Keywords: Cu doped $SnO_2$ NPs, x-ray photoelectron spectroscopy, folic acid sensor, differential pulse voltammetry, pharmaceutical products

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Folic acid (Vitamin B9), a water soluble vitamin, is a very significant compound for normal human metabolic function. Its deficiency in human beings causes different diseases such as gigantocytic anemia, mental devolution, leucopoenia, colon cancer, heart attack and congential malformation. Also, the folic acid (FA) is important for synthesis of DNA and RNA which are primary events for cell growth and division and it is one of the essential coenzymes of the haematopoietic system which controls the formation of ferrohaeme [1, 2]. Therefore, it is of great importance to monitor FA accurately in pharmaceutical and food samples. A wide variety of analytical techniques such as high performance liquid chromatography (HPLC), colorimetry, spectrophotometry, fluorometric, chemiluminescence and microbial methods have been reported for the determination of FA [3–8]. Some of these methods are unsuitable for routine analysis in food industries due to their expensive equipments, time consuming and complicated analytical processes. Hence it is of great significance to develop sensitive and simple method for FA detection. Electrochemical sensors have attracted wide attention due to their facile fabricating processes, low cost, high sensitivity, selectivity, fastness, compatibility and reproducibility. In particular, several FA electrochemical sensors such as salmon sperm dsDNA modified pencil graphite electrode, electrospinning prepared $\alpha$-$Fe_2O_3$ nanofiber modified GC electrode, MWCNT/poly(brilliant cresyl blue)

 

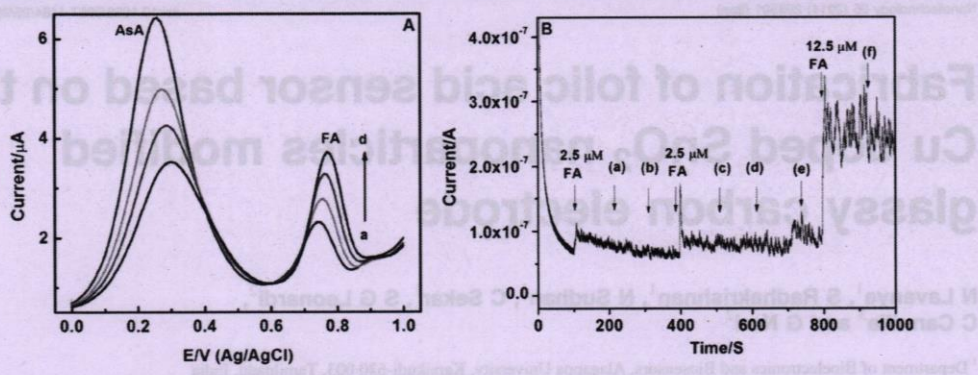


**Figure 9.** (A) DPVs obtained for the increment of FA from 10–50 $\mu$M in the presence of 1000 $\mu$M ASA in 0.1 M PBS at Cu-$SnO_2$ modified GC electrode. (B) Amperometric response of the Cu-$SnO_2$ modified electrode for the addition of FA and successive additions of interferents (12.5 $\mu$M) in the sequence of (a) glucose, (b) NaCl, (c) lactose, (d) KCl, (e) riboflavin and (f) urea in 0.1 M PB solution.

**Table 1.** Comparison of the detection limit of FA sensing by various modified electrodes.

| Electrodes | Method | pH | Linear range ($\mu$M) | Detection limit ($\mu$M) | Reference |
|---|---|---|---|---|---|
| DNA-PGE | DPV | 4.8 | 0.1–10 | 0.0106 | [9] |
| $\alpha$ $Fe_2O_3$ | i-t curve | 7.0 | 0.06–60 | 0.000 112 | [10] |
| MWCNTs-PBCB | DPV | 7.0 | 900–2310 | 96 | [11] |
| SWCNT | CV | 5.5 | 0.01–100 | 0.001 | [12] |
| $ZrO_2$-CPE | DPV | 7.0 | 20–2500 | 9.86 | [23] |
| Polymer immobilized sol-gel PEG | DPCSV | 2.5 | 20–300 | 0.005 | [24] |
| p-AMT | i-t curve | 7.2 | 0.1–800 | 0.0002 | [25] |
| $PMo_{12}$-PPy | DPV | <3.0 | 0.01–0.1 | 0.0001 | [26] |
| Ni-POA/CPE | CV | 13 | 100–5000 | 91 | [27] |
| MWCNT | ASV | 6.4 | 0.3–80 | 0.13 | [28] |
| Cu-$SnO_2$ | DPV | 7.0 | 0.01–67 | 0.000 024 | Present work |

**Table 2.** Determination of FA in pharmaceutical sample using Cu-$SnO_2$ electrode.

| Samples | Labelled content (mg/tablet) | Observed Content (mg/tablet)) | Recovery% |
|---|---|---|---|
| Folvite | 5 | 4.968 | 98.3 |
| Foligen | 5 | 4.842 | 100.1 |

also enhanced its oxidation current when compared to undoped $SnO_2$ modified and bare GC electrodes. The DPV current increased linearly while increasing the concentration of FA from $1.0\times10^{-10}$ to $6.7\times10^{-5}$ M with the lowest detection limit of $2.4\times10^{-11}$ M. The practical application of the fabricated electrode was demonstrated in pharmaceutical tablet by the recovery test. All these advantageous features make the proposed Cu-$SnO_2$ nanoparticles based FA biosensor applicable in food, pharmaceutical and other relevant areas.

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# $WO_3$ nanoparticles based direct electrochemical dopamine sensor in the presence of ascorbic acid

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ABSTRACT

Tungsten trioxide ($WO_3$) nanoparticles with monoclinic (γ) and orthorhombic (β) structures were synthesized by a simple microwave irradiation method and characterized using powder X-ray diffraction (XRD), electron energy loss spectroscopy (EELS), Raman spectroscopy, field emission scanning electron microscopy (FESEM), UV–vis absorption and photoluminescence (PL) spectroscopy studies. The γ-$WO_3$ nanoparticles modified glassy carbon electrode (GCE) showed an excellent electrocatalytic activity towards the oxidation of dopamine (DA) in the presence of ascorbic acid (AA) at pH 7.0. Electrochemical kinetic parameters of γ-$WO_3$/GCE such as electroactive area A (0.045 $cm^2$), electron transfer coefficient α (0.71) and electron transfer rate constant $k_s$ (1.121 $s^{-1}$) were calculated and compared with that of β-$WO_3$/GCE. Differential pulse voltammetry (DPV) studies of the γ-$WO_3$ modified GCE exhibited a linear response over a wide concentration range of 0.1 μmol $L^{-1}$–600 μmol $L^{-1}$ of DA with the lowest detection limit of 24 nmol $L^{-1}$. The fabricated dopamine sensor showed an excellent anti-interference ability against electroactive species and metal ions with good stability and reproducibility. Finally, the developed sensor was applied to determine DA concentration in dopamine hydrochloride injection which indicates that this electrode can be effectively used for real sample analysis.



## 1. Introduction

Dopamine (DA, 3,4-dihydroxy phenylalanine), one of the most important catecholamine, plays a significant role in the functioning of the central nervous, renal, hormonal and cardiovascular systems [1]. Detection and quantification of DA is important for diagnosis, monitoring, prevention and treatments of neurological disorders like Schizophrenia, Parkinson's disease, Alzheimer's disease and HIV infection [2]. In physiological samples, DA ($10^{-8}$ to $10^{-6}$ mol $L^{-1}$) usually coexists with high concentration of AA (0.2–0.5 mmol $L^{-1}$) which strongly influences the selectivity and sensitivity of DA detection. Moreover, the DA oxidises at almost the same potential as that of AA, resulting in an overlapping of voltammetric responses towards oxidation of DA and AA in the mixed samples. Consequently, the development of a simple, rapid and selective method is essential for the determination of DA in the presence of AA in routine clinical analysis. Although, the DA can be determined by chromatography [3], fluorometry [4], electrochemiluminescence [5], calorimetric [6] and high performance liquid chromatography (HPLC), electrochemical method is widely employed owing to its fast detection, simplicity, reproducibility, cost-effectiveness, potential for miniaturization and capability of in-situ detection.

In recent years, nanostructured metal oxides (NMOs) have been widely applied as sensing material in chemosensors and biosensors because of their high chemical stability, biocompatibility, structural flexibility, higher catalytic behaviour, and strong adherence to substrates [7–9]. The NMO based electrodes such as $MnO_2$/chitosan [10], SWCNT/$Fe_2O_3$ [11], $Cu_2O$/graphene [12] and $SiO_2$/$ZrO_2$/methylene blue [13] have been explored for the detection of DA in the presence of AA. Among various metal oxides, tungsten trioxide ($WO_3$), an n-type indirect wide band gap semiconductor (2.4–3.6 eV) has been used for chemical sensing of gases like $NH_3$, $H_2S$, $N_xO_x$, $SO_2$ and CO [14,15]. But there are only limited reports on the application of $WO_3$ nanoparticles (NPs) for biomolecule detection. Hariharan et al. have synthesized $WO_3.H_2O$ NPs by microwave irradiation method and demonstrated its applicability for the selective and sensitive detection of L-dopa, a chemical precursor of dopamine [7]. Ye Ma et al. have explored 3D graphene network @ $WO_3$ nanowire sensor for the electrochemical biosensing of DA with the lowest detection limit of 238 nmol $L^{-1}$ [6]. The $WO_3$ exists in different polymorphic forms with intriguing physical and chemical properties depending on the preparation

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# Development of a CO Sensor for Hydrogen Fuel Cell Powered Vehicles

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## ABSTRACT

The development of a CO resistive sensor for application in PEM fuel cells, based on Cu-doped $SnO_2$ thick film as a sensing layer, has been reported. The synthesis and the morphological-microstructural characterization of the sensing material were first described. A resistive sensor was fabricated depositing the nanostructured Cu-$SnO_2$ on a ceramic substrate provided with interdigited electrodes. The electrical and CO sensing behavior experiments showed the good performance of the fabricated sensor when operated in air and nitrogen atmosphere, i.e. high sensitivity in a wide range of CO concentrations with very fast response/recovery time. The sensor behavior and the sensing mechanism under simulated reformate fuel conditions (i.e.$CO/H_2/H_2O$ mixtures) were presented and discussed.

## INTRODUCTION

Proton-exchange membrane (PEM) fuel cell powered vehicles have the potential to significantly reduce harmful emissions and dependence on fossil oil fuels [Wee, 2007]. A hydrogen-based fuel cell could provide the electrical power necessary for a modern gasoline powered vehicle. However, there are still many obstacles that prevent PEM fuel cells from playing a major role in electrical power production for transportation purpose. One of the problems is the supply of hydrogen feed to fuel cell [Dunn, 2002]. The ideal fuel cell vehicle would operate on pure hydrogen stored on-board. However, storing hydrogen on-board the vehicle is currently not feasible for technical reasons. Reforming is an easy way to obtain hydrogen on board the vehicle (Fig. 1), directly from gasoline [Wipke et al., 2003], or other liquid hydrogen carriers such as methanol.