

**Functionalized gold, silver and semiconductor nanoparticles as  
fluorescent sensors for the determination of toxic chemicals**

Final Technical Report of Major Research Project Submitted to the  
University Grants Commission, New Delhi

(Reference No. F. 42-283/2013 (SR), dated 12.3.2013)



By

**S. ABRAHAM JOHN**

Principal Investigator  
Department of Chemistry  
The Gandhigram Rural Institute-Deemed University  
Gandhigram-624 302. Tamil Nadu

**October 2017**

## **ACKNOWLEDGEMENT**

I wish to thank the University Grants Commission, New Delhi for its financial assistance to carry out this research work (Sanction Letter No. F. 42-283/2013 (SR) Dt: 12.3.2013).

(S. ABRAHAM JOHN)  
Principal Investigator

## **Annexure details**

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## **Final Report of the work done on the Major Research Project (2013-2017)**

1. Project report No: Final
2. UGC Reference No: F. 42-283/2013(SR)
3. Period of report: from April 1, 2013 to March 31, 2017
4. Title of research project: Functionalized gold, silver and semiconductor nanoparticles as fluorescent sensors for the determination of toxic chemicals
5. (a) Name of the Principal Investigator: Dr. S. ABRAHAM JOHN  
(b) Deptt: CHEMISTRY  
(c) University where work has progressed: The Gandhigram Rural Institute-DU
6. Effective date of starting of the project: April 1, 2013
7. Grant approved and expenditure incurred during the period of the report:
  - a. Total amount approved Rs. 7,05,000
  - b. Total expenditure Rs. 6,39,863
  - c. Report of the work done: **see Annexure-II**
- i. Brief objective of the project
- ii. Work done so far and results achieved and publications, if any, resulting from the work  
(Give details of the papers and names of the journals in which it has been published or accepted for publication)
- iii. Has the progress been according to original plan of work and towards achieving the objective: **YES**

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

**Contingency grant is not allotted in the budget. Therefore, the PI finds it very difficult to meet out the expenses due to stationary/Xerox/postal expenses.**

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

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) Manpower trained (b) Ph. D. awarded (c) Publication of results: **see Annexure I**

**PRINCIPAL INVESTIGATOR**

**REGISTRAR**

## Annexure-I

### **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: Functionalized gold,silver and semiconductor nanoparticles as fluorescent sensors for the determination of toxic chemicals
2. Name and address of the principal investigator: Dr. S. Abraham John, Department of chemistry, The Gandhigram Rural Institute, Gandhigram,
3. Name and address of the institution: The Gandhigram Rural Institute-DU, Gandhigram, Tamilnadu-624302
4. UGC approval letter no. and date: F.42-283/2013/(SR), dt: 12.03.2013
5. Date of implementation: 16.04.2013
6. Tenure of the project: March 2013-March 2017
7. Total grant allocated: Rs. 7,75,800
8. Total grant received: Rs. 7,05,000
9. Final expenditure: Rs. 6,39,863
10. Objectives of the project - see Annexure II
11. Whether objectives were achieved – YES. see Annexure II
12. Achievements from the project - see Annexure II
13. Summary of the findings - see Annexure III
14. Contribution to the society - see Annexure III
15. Whether any Ph.d. enrolled/produced out of the project: Yes (one)
16. No. of publications out of the project: Sevan (see Annexure IV)

**PRINCIPAL INVESTIGATOR**

**REGISTRAR**

**Report of the work done**

(i) Brief objectives of the project

- (i) Synthesis of functionalized heterocyclic ligands capped Au, Ag
- (ii) Characterization of the synthesized metal colloids by TEM, AFM, IR and XPS methods
- (iii) Characterization of metal particles coated electrode substrates by spectral and electrochemical methods
- (iv) Electrocatalytic reduction and oxidation of small molecules using metal particles coated electrodes
- (v) Determination of neurotransmitters in the presence of interferents
- (vi) Interpretation of the results and writing manuscripts
- (vii) Preparation of final technical report

(ii) Objectives done on the project

Introduction

Nanomaterials exhibit distinctive physical, chemical and catalytic properties because of their size, shape and high surface to volume ratio in contrast to bulk materials. The use of metal nanoparticles (MNPs) is becoming a part of daily life in the form of biomedicine, biosensors and drug delivery systems and also NPs received much attention because of their shape and size dependant optical properties and quantum confinement effects. The NPs are extensively used in the fields of cancer therapy, cell imaging, electronic devices, biochemicals, toxic chemicals and drug sensors. Although a number of approaches have been developed to prepare NPs using different ligands, the synthesis of stable NPs, particularly with tunable size and controllable morphology, still faces challenges. Because of

that NPs tend to aggregate because of vander waals attraction. Ligands such as alkanethiols, phosphines and amines are typically used to protect the NPs against aggregation. However, most of these kind of ligands are insoluble in water and need organic solvents for the synthesis of NPs. The usage of organic solvents for the synthesis raises environmental issues like instability and poor solubility in water which significantly limits their use in biological applications. Therefore synthesis of stable NPs in aqueous solution with controllable morphology has gained momentum in recent years. Among the different kind of metal nanoparticles gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) are received much attention due to excellent optical properties, good conductivity, chemical stability and catalytic activity. Further, AuNPs and AgNPs have been used extensively as an antibacterial agent, food storage, textile coatings and toxic chemicals sensor. We have synthesised various ligand capped nanoparticles such as 2-mercapto-4-methyl-5-thiazoleacetic acid cadmium sulfide nanoparticles (MMTA Cds NPs), Folic acid capped gold nanoparticles (FA-AuNPs), p-Aminophenyl diazonium gold nanoparticles (AP-AuNPs), 4-amino-6-hydroxy-2-mercaptopyrimidine capped gold nanoparticles (AHMP-AuNPs) and Chitosan capped silver nanoparticles (Chi-AgNPs). Further, these nanoparticles utilised in various applications both optochemical and electrochemical sensing. The details studied using these nanoparticles were discussed in attached published papers and few results are outlined in the following pages.

### *Synthesis of NPs*

#### Synthesis of MMTA capped CdS NPs

The colloidal solution of MMTA capped CdS NPs was prepared by the following procedure. 4.33 mg of MMTA was added to 25 mL of tris buffer (pH=7.2) under argon atmosphere. To this solution, 25 mL of aqueous solution of cadmium nitrate was added. Then, 0.4 mM Na<sub>2</sub>S solution was slowly added dropwise into the vortex of the solution. The solution was stirred for 12 h at room temperature followed by 20 min of flushing with argon

to remove the unreacted sulfide. To remove MMTA–Cd complexes from the solution, cold ethanol was added to the reaction mixture at room temperature to precipitate MMTA–CdS NPs. The resulting CdS NPs were further purified by dissolving them in double distilled water and precipitated again with cold ethanol. Finally, the MMTA–CdS NPs were dried in water bath at 80°C.

#### Synthesis of FA-AuNPs and AP-AuNPs

The FA-AuNPs were prepared as follows. 0.5 ml of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (0.137 M) was added to 42 ml of water in a round bottom flask with constant stirring. To this solution, 1 ml of FA (1 mM) followed by 6.5 ml of (0.25%)  $\text{NaBH}_4$  was added, and the stirring was continued for another 30 min. The color of the solution turned into wine red immediately after the final addition, indicating the formation of AuNPs. The colloidal solution of AP-AuNPs was prepared by adding 250  $\mu\text{L}$  of 31.7 mM  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  solution into 25 mL of water. Then, 200  $\mu\text{L}$  of 0.3 M freshly prepared ice cold  $\text{NaBH}_4$  was added with constant stirring. The yellow color of the solution was changed to wine red color indicating the formation of AuNPs. After stirring for 3 h, the solution was centrifuged at 10,000 rpm for 10 min to remove the excess of reducing agent present in the colloidal solution of AuNPs. The AuNPs precipitate was collected and washed with double distilled water for three times. 1 equivalent cold  $\text{NaNO}_2$  was added drop wise to generate the APD in the electrochemical cell. To the stirred AuNPs solution, 250  $\mu\text{L}$  of 100  $\mu\text{M}$  APD was added to prepare the AP-AuNPs.

#### Synthesis of AHMP-AuNPs

0.5 ml of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (31.7 mM) and 0.25 ml of 1 mM AHMP solution were added into 23.5 ml of water. Then, 2 ml of freshly prepared ice cold  $\text{NaBH}_4$  (0.125%) was added with constant stirring for 20 min. The color of the solution was changed into wine red immediately after the final addition of  $\text{NaBH}_4$ , indicating the formation of AuNPs. The synthesized AHMP-AuNPs were stored in a bottle at 4°C.

## Synthesis of Chi-AuNPs

5 mL of AgNO<sub>3</sub> (7 mM) and 1 mL of 1% chitosan in acetic acid were added to 86 mL of water in a round bottom flask with constant stirring. To this solution, 8 mL of 0.05 M NaBH<sub>4</sub> was added and the color of the solution turns into yellow immediately after the final addition, indicating the formation of AgNPs. The stirring was continued for another 30 min. The synthesized Chi-AgNPs were purified by centrifugation at 10,000 rpm and then the filtrate was dissolved in Millipore water. The purified Chi-AgNPs were used for further studies.

## *Instrumentation*

Absorption spectra were measured by using JASCO V-550 UV-vis spectrophotometer. Fluorescence spectral measurements were performed on a JASCO FP-6500 spectrofluorimeter equipped with a Xenon discharge lamp, 1 cm quartz cell at room temperature (about at 298 K). The FT-IR measurements of the solid were taken by using JASCO FT-IR 460 plus Fourier Transform Infrared Spectrophotometer. A large volume of NPs was synthesized and the particles were separated by centrifuging at 10,000 rpm and repeatedly washed with water and dried in vacuum. The dried NPs powder was used for X-ray diffraction (XRD) and FT-IR measurements. The XRD analysis was carried out with X-ray diffraction unit using Ni-filtered radiation. Inductively coupled plasma atomic emission spectral (ICP-AES) measurements were performed on a thermo electron IRIS intrepid II XSP DUO model ICP-AES. XPS measurements were carried out by using Shimadzu Axis 165 high performance multi technique analysis using an Al Ka source with pass energy of 80 eV, where the pressure in the analysis chamber was lower than 110 Torr. Raman spectra were recorded on a Horiba JY Lab-RAM HR800 Raman spectrometer coupled with microscope in reflectance mode with 633 nm excitation laser source and a spectral resolution of 0.3 cm<sup>-1</sup>. All the electrochemical measurements were carried out with CHI model 634B (Austin, TX,

USA) Electrochemical Workstation. The detailed objectives and results were achieved discussed in the published papers (see Annexure IV)

*Achievements from the projects*

- The determination of protamine and heparin in the presence of 1000 and 1040-fold higher concentration of common interferences using FA-AuNPs.
- ‘Turn-on’ chemosensor for Cu(II) using FA-AuNPs as the fluorophore and first report with high selectivity and sensitivity for the determination of Cu(II) in an aqueous medium.
- “Off-on” and “on-off” chemosensor for Hg(II) and Cu(II) by using MMTA and MMTA–CdS NPs fluorophores.
- The determination of thiamine and cysteine in the presence of common interferences using AHMP-AuNPs.
- Chi-AgNPs fluorophore for the determination of malathion.
- The electrocatalytic activity of the AP-AuNPs modified electrode was demonstrated by studying the oxidation of dopamine.

### *Summary of the findings*

Demonstrated a chemosensor for protamine and heparin using FA-AuNPs as fluorophore. On adding picogram amounts of protamine, the emission intensity decreased. However, after the addition of heparin into the same solution, the emission intensity was enhanced. Based on the decrease and increase in emission intensities, the concentrations of protamine and heparin were determined. The detection limits were found to be 4.8 and 12.6 fg/L. Further, 1000 and 1040-fold higher concentration of common interferences did not interfere with the determination of 25 and 65 pg of protamine and heparin, respectively.

We have demonstrated a ‘turn-on’ chemosensor for Cu(II) using FA-AuNPs as the fluorophore. On adding picomolar Cu(II) into FA-AuNPs, the emission intensity was enhanced. The enhancement of emission intensity was mainly due to the binding of Cu(II) with –COO groups of FA-AuNPs. This was confirmed by zeta potential studies. Based on the enhancement of the emission intensity, the concentration of Cu(II) was determined, and the detection limit of Cu(II) was found to be 50 fM/L (S/N=3). Further, the selective determination of 10 nM Cu(II) was accomplished in the presence of 10000-fold higher concentration of common interferences. The present method was successfully utilized to determine Cu(II) in different water samples and brass. The results were validated with the ICP-AES method. To the best of our knowledge, this is the first report with high selectivity and sensitivity for the determination of Cu(II) in an aqueous medium.

Also, we have developed “off-on” and “on-off” chemosensor for Hg(II) and Cu(II) by using MMTA and MMTA CdS NPs fluorophores, respectively and the detection limit was found to be 100 for Hg(II) and 0.5 pg/L for Cu(II) (S/N=3). Further, the selective determination of 10 nM of Hg(II) and Cu(II) was accomplished in the presence of 20,000 and 10,000-fold higher concentration of common interferences, respectively. The present

method was successfully utilized to determine Hg(II) and Cu(II) in different water samples. The obtained results were validated with ICP-AES method.

Further, demonstrates the highly sensitive and selective determination of thiamine in the presence of other vitamin complexes using AHMP-AuNPs as fluorophore. The AHMP-AuNPs were more stable and highly fluorescent with a large stock shift. The emission intensity of fluorophore was enhanced while adding thiamine even in the picomolar range. Based on the enhancement of emission intensity, the concentration of thiamine was determined. Further, the selective determination of 100 nM thiamine was accomplished in the presence of 10000 fold higher concentration of common interferences. Then, determination of cysteine (Cys) using AHMP-AuNPs was done. The AHMP-AuNPs were highly fluorescent with a large stock shift. The emission intensity of the fluorophore was enhanced while adding Cys even in the picomolar range. The enhancement of emission intensity was mainly due to the strong binding between Cys and AHMP-AuNPs. Further, the selective determination of 100 nM Cys was accomplished in the presence of 10,000-fold higher concentration of all other L-amino acids.

Also, we have developedd Chi-AgNPs fluorophore for the determination of malathion in lake water and fruit samples. The emission intensity of Chi-AgNPs was decreased at 536 nm with redshift. Based on the decrease in emission intensity, the concentration of malathion was determined. The lowest detection limit was found to be 94 fM/L. The presence of 1000-fold common interferences such as chloropyrifos, methyl parathion, endosulfon, imidacloprid and alphamethrin do not interfere in the determination of 10 nM malathion.

Also, we demonstrated the spontaneous grafting of aminophenyl groups on AuNPs by reaction with in situ generated APD in an aqueous medium. The spontaneous grafting was proceeded by electron transfer from AuNPs to the APD cations to form an

aminophenyl radical and subsequent attachment with AuNPs. The crystalline nature of the AuNPs was confirmed by XRD. The absence of characteristic vibrational band at  $2300\text{ cm}^{-1}$  due to diazonium group in the IR spectra confirmed the spontaneous reduction of the APD at the surface of AuNPs. The presence of aminophenyl layers on AP-AuNPs were confirmed by XPS. SERS spectrum reveals the strong evidence for the existence of Au-C bond on AuNPs. The amino groups present on the surface of the AP-AuNPs were used to self-assemble them on GC electrode. UV-vis spectrum showed the SPR band at 533 nm, which confirms the attachment of AP-AuNPs on ITO substrate. The SEM studies reveal that the attached AuNPs were spherical in shape with narrow size distribution. The modified electrode showed greater electrocatalytic activity towards the oxidation of dopamine by enhancing its oxidation current than bare GC electrode.

#### *Contribution to the society*

- ✓ We have determined malathion in polluted lake water and fruit samples such as grapes and mangos. The proposed method was successfully applied for the determination of malathion in water and fruit samples.
- ✓ The proposed method was successfully utilized using FA-AuNPs to determine heparin and protamine drugs in human blood serum samples.
- ✓ The practical application of the proposed method was evaluated by determining Cu(II) in tap water, river water, pond water, and industrial effluent water samples. The present method was successfully utilized to determine Cu(II) in different water samples and brass.
- ✓ The practical application of the present method was evaluated by determining Cys in human blood serum and urine samples. The obtained good recovery and RSD values indicated that the present method could be successfully used for the determination of Cys and thiamine in real sample analysis.

### Papers Published

1. Sensitive and highly selective determination of vitamin B1 in the presence of other vitamin B complexes using functionalized gold nanoparticles as fluorophore  
*S. Shankar and S.A. John*  
**RSC Advances 5 (2015) 49920.**
2. 4-amino-6-hydroxy-2-mercaptopyrimidine capped gold nanoparticles as fluorophore for the ultrasensitive and selective determination of L-cysteine  
*S. Shankar and S.A. John*  
**Sensors and Actuators B: Chemical 221 (2015) 1202.**
3. Spontaneous grafting: A novel approach to graft diazonium cations on gold nanoparticles in aqueous medium and their self-assembly on electrodes  
*S. Kesavan and S.A. John*  
**Journal of Colloid and Interface Science 428 (2014) 84.**
4. Off-on and on-off chemosensors for ultratrace mercury(II) and copper(II) using functionalized thiazole and cadmium sulphide nanoparticles fluorophores  
*N. Vasimalai and S.A. John*  
**Sensors and Actuators B: Chemical 190 (2014) 800.**
5. A turn-on highly selective and ultrasensitive determination of copper(II) in aqueous medium using folic acid capped gold nanoparticles as probe  
*N. Vasimalai and S.A. John*  
**Nanotechnology 24 (2013) 505503.**
6. Aggregation and de-aggregation of gold nanoparticles induced by polyionic drugs: Spectrofluorimetric determination of picogram protamine and heparin drugs in the presence of 1000-fold major interferences  
*N. Vasimalai and S.A. John*  
**Journal of Materials Chemistry B 1 (2013) 5620.**
7. Biopolymer capped silver nanoparticles as fluorophore for ultrasensitive and selective determination of malathion  
*N. Vasimalai and S.A. John*  
**Talanta 115 (2013) 24.**

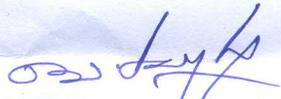
UNIVERSITY GRANTS COMMISSION  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI – 110 002

EVALUATION CERTIFICATE

It is certified that the report entitled "Functionalized gold, silver and semiconductor nanoparticles as fluorescent sensors for the determination of toxic chemicals" by Dr. S. Abraham John, Department of Chemistry, Gandhigram Rural University has been evaluated to the University Grants Commission, New Delhi for final support under the scheme of Major Research Project (F. 42-283/2013(SR)).

Details of Expert Committee

The objectives mentioned in the proposal were completed. The results are published in international journals with good impact factors. Overall, the outcome of the project is very good. The report is as per the guidelines.

  
Signature with seal

**Dr. V. Ganesan**  
Associate Professor  
Department of Chemistry  
Institute of Science  
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Mobile: 09452072138

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

EVALUATION CERTIFICATE

It is certified that the report entitled "Functionalized gold, silver and semiconductor nanoparticles as fluorescent sensors for the determination of toxic chemicals" by Dr S. Abraham John, Department of Chemistry, Gandhigram Rural University, Gandhigram-624 302 has been evaluated to the University Grants Commission, New Delhi for final support under the scheme of Major Research Project (F. 42-283/2013(SR)).

Details of Expert Committee:

The objectives mentioned in the Research proposal entitled "Functionalized gold, silver and semiconductor nanoparticles as fluorescent sensors for the determination of toxic chemicals" were completed satisfactorily.

The obtained results are published in peer reviewed International journals with good impact factor.

**Overall, the outcome of the Research project is very good.**

The report is as per the guidelines.



Signature with seal

**Dr. T. SELVARAJU, M.Sc., M.Phil., Ph.D.**  
Associate Professor  
Department of Chemistry  
Bharathiar University  
Coimbatore - 641 046. India.

THE GANDHIGRAM RURAL INSTITUTE – DEEMED UNIVERSITY  
GANDHIGRAM-624 302, DINDIGUL DISTRICT, TAMIL NADU

(Ministry of Human Resource Development, Govt. of India)  
Accredited by NAAC with 'A' Grade (3<sup>rd</sup> Cycle)

Dr.K.SOMASUNDARAM  
Registrar i/c



EPABX No. 2452371 - 2452376

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Ref: GRI-DU/FS-II/C4/Refund /2017-2018 /194

28-09-2017

To  
The Secretary  
University Grants Commission  
Bahadur Shah Zafar Marg  
New Delhi – 110 002.

Sir,

Sub: GRI-DU-UGC-MRP Project on “Functionalized gold, silver ..... Toxic Chemicals”  
- Dr. S.Abraham John, Principal Investigator, Department of Chemistry, GRI (DU) –  
sending of unspent balance of **Rs.80,434/-** reg.

Ref: Your letter F.No.42-283/2013 (SR) dated 12-03-2013

\*\*\*\*\*

With reference to your letter cited above, the grant received for the UGC MRP on “  
Functionalized gold, silver and semiconductor nanoparticles as fluorescent sensors for the determination  
of toxic chemicals” sanctioned to Dr. S.Abraham John, Principal Investigator, Department of Chemistry,  
has been utilized and the balance amount of Rs. 80,434/- (Rupees Eighty thousand four hundred and  
thirty-four only) remaining as such unspent as on 31-03-2017 has been refunded to the A/c No.  
8627101002122 Canara Bank, UGC Office, in the name of the Secretary, UGC New Delhi through  
account transfer on 27-09-2017. This account may be treated as settled and closed.

Kindly acknowledge the receipt of the letter with enclosure.

Yours faithfully,

REGISTRAR i/c 28.9.17

Encl.: As above.

Copy to. 1. Dr.S.Abraham John,  
Principal Investigator, UGC-MRP,  
Department of Chemistry,  
GRI, Gandhigram

2. File.

The Gandhigram Rural Institute – Deemed University  
Gandhigram - 624 302

UGC-MRP Project on "Functionalized gold, silver and semiconductor nanoparticles as fluorescent sensors for the determination of toxic chemicals"

Dr.S.Abraham John, Professor, Dept.of chemistry.

University/Institution : The Gandhigram Rural Institute-Deemed University, Gandhigram-624 302  
Sanction Letter No. and Date of UGC, New Delhi : F.42-283/2013/(SR),dt: 12.03.2013  
Statement of Actual Expenditure during : 16.04.2013 to 31.03.2017

Item of Expenditure	Total Grant approved	Actual Grant Received				Total (3 to 6)	Actual Expenditure incurred				Total (8 to 11)	Excess/Saving diff. of Co.7 & 12
		2013-14	2014-15	2015-16	2016-17		2013-14	2014-15	2015-16	2016-17		
1	2	3	4	5	6	7	8	9	10	11	12	13
<b>(A) Non-Recurring</b>												
1. Equipment	0	0	-	-	-	0	0	0	-	-	0	0
2. Books and Journals		0	-	-	-	0	0	0	-	-	0	0
<b>Total (A)</b>	<b>0</b>	<b>0</b>	<b>-</b>	<b>-</b>	<b>-</b>	<b>-</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
<b>(B) Recurring ( Per Annum)</b>												
1.Project Fellow - 2 Years	5,28,000	2,64,000	-	-	2,11,200	4,75,200	1,31,600	1,68,000	0	1,68,000	4,67,600	7,600
2.Chemical/Glassware/Consumable	1,00,000	50,000	-	-	40,000	90,000	70,133	0	0	0	70,133	19,867
2.Hiring Services	50,000	25,000	-	-	20,000	45,000	11,236	15,198	1,000	5,000	32,434	12,566
3.Contingencies	0	0	-	-	-	0	0	0	0	0	0	0
4.Travel/Field Work	30,000	15,000	-	-	12,000	27,000	1,896	0	0	0	1,896	25,104
5.Overhead Charges	67,800	67,800	-	-	-	67,800	67,800	0	0	0	67,800	0
<b>Total (B)</b>	<b>7,75,800</b>	<b>4,21,800</b>	<b>-</b>	<b>-</b>	<b>2,83,200</b>	<b>7,05,000</b>	<b>2,82,665</b>	<b>1,83,198</b>	<b>1,000</b>	<b>1,73,000</b>	<b>6,39,863</b>	<b>65,137</b>
<b>Total (A) + (B)</b>	<b>7,75,800</b>	<b>4,21,800</b>	<b>-</b>	<b>-</b>	<b>2,83,200</b>	<b>7,05,000</b>	<b>2,82,665</b>	<b>1,83,198</b>	<b>1,000</b>	<b>1,73,000</b>	<b>6,39,863</b>	<b>65,137</b>
Interset on Grant received		9,954	4,529	421	393	15,297		0	0	0	0	15,297
<b>Total</b>	<b>7,75,800</b>	<b>4,31,754</b>	<b>4,529</b>	<b>421</b>	<b>2,83,593</b>	<b>7,20,297</b>	<b>2,82,665</b>	<b>1,83,198</b>	<b>1,000</b>	<b>1,73,000</b>	<b>6,39,863</b>	<b>80,434</b>
Unspent Balance												80,434

Total Grant received with interest 7,20,297  
Less: Expenditure 6,39,863  
Unspent Balance as on 31.03.2017 80,434

Certified that the grant has been utilized for the purpose for which it was sanctioned and in accordance with terms and conditions attached

**PRINCIPAL INVESTIGATOR**  
UGC - MRP (Functionalized)  
Department of Chemistry  
Gandhigram Rural Institute  
Gandhigram - 624 302. Tamil Nadu

**Special Officer (Finance)**  
Gandhigram Rural Institute

**REGISTRAR**  
Gandhigram Rural Institute

**For A.V. SUBRAMANIAN & CO.,**  
**CHARTERED ACCOUNTANTS**

C.A. J. S. Mathi  
M. No: 029617, Partner  
ICAI: FRN: 010643S

**UNIVERSITY GRANTS COMMISSION**  
**UTILIZATION CERTIFICATE – From 16.04.2013 to 31.03.2017**

It is certified that the amount of **Rs.6,39,863/-** (Rupees Six lakhs thirty-nine thousand eight hundred and sixty-three only) out of the grant of **Rs.7,05,000/-** (Rupees Seven lakhs and five thousand only) Sanctioned to Dr.S. Abraham John, Professor and PI, Department of Chemistry by the University Grants Commission vide its letter No.42-283/2013/(SR),dated.12.03.2013 towards UGC-MRP on **“Functionalized gold, silver and semiconductor nanoparticles as fluorescent sensors for the determination of toxic chemicals ”** under UGC-MRP scheme has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions as laid down by the commission.

If as a result of check or audit objection some irregularities are noticed at a later stage, action will be taken for refund, adjustment or regulation.

Signature   
 Registrar / Principal with seal

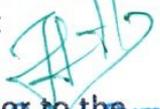
**REGISTRAR**  
*Gandhigram Rural Institute*

Signature   
 Coordinator of the Programme /  
 Head of the Department  
 (As the case may be)  
**PRINCIPAL INVESTIGATOR**  
**UGC - MRP (Functionalized)**  
 Department of Chemistry  
 Gandhigram Rural Institute  
 Gandhigram - 624 302. Tamil Nadu

Signature  
 Finance Officer with seal

  
**Special Officer (Finance)**  
 Gandhigram Rural Institute

**For A.V. SUBRAMANIAN & CO.,**  
**CHARTERED ACCOUNTANTS**

Signature, Chartered Accountant  
 with seal and Registrar No.   
 (If the accounts were audited prior to the  
 audit of Statutory Auditors) **M. No: 029617, Partner**  
**ICAI: FRN: 010643S**

Note: The University/ Institution will submit an audited statement of accounts, duly audited by the Statutory Auditors of the University / Institution as soon as the accounts of the University / Institution are audited.