

Research Proposal for STC

Project Title:

NANOSCALE CHEMORESISTIVE GAS SENSOR

Submitted to:

ISRO – IISc Space Technology Cell
Indian Institute of Science
Bangalore 560 012

Investigator(s) from IISc:

Dr. VENUGOPAL SANTHANAM

Co-investigator(s) from ISRO (LPSC):

Dr. NANDAKUMAR K



*Department of Physics
Indian Institute of Science
Bangalore 560 012
September, 2011*

APPLICATION FOR GRANT OF RESEARCH / DEVELOPMENT PROJECT

SECTION –A

- | | | |
|---|--|--|
| 1 | Title of research/ development Proposal | Nanoscale chemoresistive gas sensor |
| 2 | Name of the Principal Investigator
Designation and Address | Dr. VENUGOPAL SANTHANAM
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| | Name of the Co- Investigator (s) from IISc
Designation and Address, Phone, Fax, Email, Mobile Numbers | NIL |
| | Name of the Co-Investigator(s) from ISRO
Designation and Address, Phone, Fax, Email, Mobile Numbers | Dr. N.K GUPTA
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E-mail: nkgupta1950@gmail.com |
| 3 | Proposed duration of the research/development proposal | 2 years |
| | Proposed date of commencement of project | April 1, 2012 |
| 4 | Amount of grant proposed for | Rs 13 63 200 |
| 5 | Department of the institution where R & D project will be carried out
Other department if any, which will co-operate in this study
Details of financial support sought/obtained from other agencies | Dept. of Chemical Engineering, IISc

PI: DST No: SR/S3/CE/073/2009, Rs 32.79 Lac, till Mar 2013
Co-PI: DST No: IR/S3/EU-04/2006, Rs 492.47 Lac, till May 2012 |
| 6 | Specific Aim of the Project
Summary of Proposed research/facilities and objectives (brief statement about the proposed investigation, its conduct and the anticipated results in not more than 300 words)
Key words
Classification of the project | Appendix B (Attached)
Appendix B (Attached)

Appendix B (Attached) |
| 7 | Background and justification
(Basis for the proposal with a brief review of the state of | |

	the art in the subject, followed by an outline of the relevance and importance of the project, in particular, towards research/development/design related to ISRO programs	Appendix C (Attached)
8	Approach (details of the actual approach indicating how each of the objective listed in item 6 (a) will be achieved); deliverables, Task schedule and bar chart	Appendix C (Attached)
9	Previous work done in this or related fields Describe briefly any work done that is particularly pertinent to the proposal & list: (I) your personal publications in this & related areas	Appendix C (Attached)
10	Expected Contributions from ISRO collaborators	Appendix C (Attached)
11	Additional information	Appendix D (Attached)

I certify that a detailed technical report describing the research work/ procedure and its findings will be submitted before the closure of the project.

Date: 29/08/2011

Signature of the Principal Investigator

APPENDIX – A

Project Title:

Nanoscale chemoresistive gas sensor

Amount of Grant Proposed: **Rs 13 63 200**

Grants (in Rs)	I Year	II Year	Total
(a) Salary [#] @ Rs 14000 PM	1 68 000	1 68 000	3 36 000
(b) Equipment [⊗]	NIL	NIL	NIL
(c) Working Expenses*	6 50 000	1 50 000	8 00 000
Sub-Total	8 18 000	3 18 000	11 36 000
(d) IISc Overheads @ 20%	1 63 600	63 600	2 27 200
Total	9 81 600	3 81 600	13 63 200
Grand Total			13 63 200

#Salary for number (specify no. of position) of project associates/project assistants/others

1. Project Assistant: (One) @ Rs 14 000 PM.

⊗List of Equipments (Give below)

NIL

***Working Expenses** include Stationary, Consumables and components, chemicals, minor fabrication costs (which ever is needed), TA/DA, etc. (Give a list of important consumable/components with approximate cost).

List of important consumables:

Schottky filament for FESEM (Rs 5 00 000) — required for acquiring electron microscopy images of nanoparticle arrays and sensors,

High purity chemicals: chloroauric acid, Ligands for encapsulation and sensing (Porphyrins and thiol functionalized polystyrene), cylinders, flow controllers and gases for testing, Photoresists for patterning interdigitated electrodes.

APPENDIX – B

Project Title:

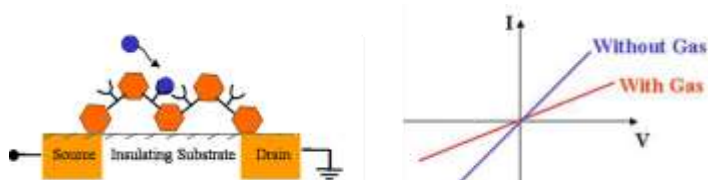
Nanoscale chemoresistive gas sensor

1. SPECIFIC AIM/ OBJECTIVE OF THE PROJECT:

- 1) To fabricate chemoresistive sensor elements consisting of mono/multilayer ordered films of gold nanoparticles interconnected by different organic interconnect molecules
- 2) To evaluate the response characteristics and selectivity of different interconnecting molecules in the presence of common gases and volatile organic compounds

2. SUMMARY OF PROPOSED RESEARCH:

We propose to fabricate a chemoresistive sensor for gas/vapour molecules using arrays of ordered gold nanoparticles interconnected by appropriate organic ligands such as porphyrins. The electrical conductivity of monolayer/bilayer assemblies of molecularly interconnected nanoparticles are strongly influenced by the electronic energy levels of the molecular layer that interconnects the metallic cores and are weakly dependent upon swelling/contraction of the film. Metallated porphyrins have been shown to interact selectively with gas/vapour molecules and hence, show promise as molecular interconnects. These features can be combined to form selective and sensitive chemoresistive gas sensors by using an array of nanoparticles interconnected by porphyrins to transduce specific analyte binding interactions into an electrical signal (see schematic below). The amplification of such binding interactions by a lithographically defined micron-scale chemoresistive sensor should enable the detection of even a few thousand analyte molecules.



Schematic cross-sectional view of the proposed chemoresistive sensor and sketch of an expected response

Keywords:

Chemoresistive sensor, Gold nanoparticles, 2D array, Porphyrins, Gas sensor

APPENDIX – C

Project Title

Nanoscale chemoresistive gas sensor

Background and justification:

Ligand Protected Nanoparticle (LPN) array based chemoresistive sensors offer a route to rapid, sensitive and highly portable identification of toxic gases and vapours. Nanoparticle array based sensors have several advantages over conventional conductive polymer based sensors, such as the ability to detect analytes without the need for preconcentration, and the enhanced sensitivity associated with the large surface area of nanoparticles. LPN arrays have been used to detect a wide variety of compounds, oxidants, reductants, and even relevant biomarkers associated with lung cancer by analysing breath samples. However, the sensors reported so far have used non-specific ligands, and are based on using thick multi-layered films of LPNs that are prone to swelling induced signal changes. On the other hand, colorimetric sensors based on using powders of porphyrins and their metallated derivatives have been developed as specific and selective probes for a wide variety of gases and volatile organic compounds, including sulfur dioxide, chlorine and ammonia. However, their ability to detect trace quantities is compromised by the need to use adequate amounts for transducing the binding interactions into a detectable change in fluorescence signal. Till now, there is no report that combines the exquisite sensitivity of organic molecules with the ability of nanoparticles to act as transducers of their environment.

In this proposal, we plan to use a micron-scale interdigitated electrode to probe a porphyrin coated 2D nanoparticle array, which will simply act as an electrical transducer. This chemoresistive sensor architecture also allows for altering the specificity by varying the structure of the interconnecting ligand. Another advantage of the proposed design is that it can enable the detection of even a few thousand molecules. This is because, within the micron-scale gap between two electrodes, only a few thousand nanoparticle junctions will be present. Although, similar architectures have been proposed earlier, they haven't fructified into a working prototype due to several formidable challenges. The key challenge being that

the LPNs can only be self-assembled into thin films or ordered arrays using monofunctional ligands, which then have to be exchanged with the bifunctional ligands to enable sensing. This step is hindered by the fact that both LPNs and the bifunctional ligands (typically organic) are both soluble in similar solvents, and thus the integrity of the nanoparticle thin film is lost during the ligand exchange process.

In our group, we have already addressed this challenge by developing an F based plasma process to selectively remove the ligands from a 2D LPN array without disturbing the nanoparticles. The plasma treated arrays adhere well with the substrate and do not dissolve in typical organic solvents, thereby enabling ligand exchange. Thus, we are uniquely placed to develop this proposed chemoresistive sensor design. Such a device should enable rapid, portable, and cost-effective sensing of toxic gases and volatile organic compounds with applications ranging from security perspective to industrial safety and even medical diagnostics.

In the context of ISRO, such rapid, portable and sensitive gas detection platform should find applications ranging from leak detection and process safety to monitoring the health of crew in space.

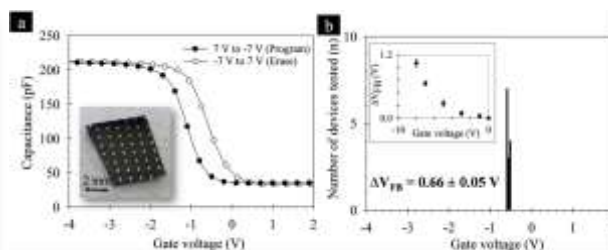
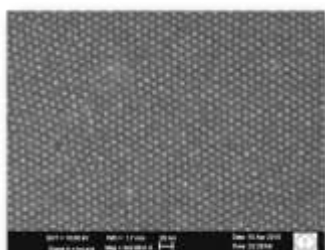
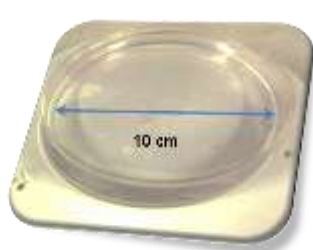
Approach

- 1) Colloidal solution of thiol protected nanoparticles will be self-assembled on a water surface and transferred onto a silicon/plastic substrate by microcontact printing.
- 2) The thiol coating will be removed by a specifically designed RF plasma treatment process.
- 3) If required, the above steps can be repeated to fabricate multiple layers to improve the conduction properties of the nanoparticle array.
- 4) Micron-scale interdigitated electrodes will be formed by lithography on top of these nanoparticle arrays using maskless photolithography.
- 5) Porphyrins or other desired interconnecting ligands will then be incorporated into the nanoparticle array by exposure to a solution of the ligand molecules.

6) Finally, electrical characterization of the arrays under various atmospheres will be carried out to characterize their resistance changes and to determine their sensitivity and detection limits.

Previous work done in this area

Our group has been working in the area of nanoparticle engineering and device fabrication for the last six years at IISc. Over these years, we have developed processes for synthesizing monodisperse gold nanoparticles and fabricating large scale ordered arrays of gold nanoparticles. Such regular and ordered nanoparticle arrays show reproducible memory windows, when incorporated as the floating gate in a MOS capacitor structure.



Digital photograph of wafer scale, ordered monolayer of gold nanoparticles formed by self-assembly on a water surface

FESEM image of an ordered monolayer of 7 nm gold nanoparticles, transferred onto a silicon substrate

Capacitance-Voltage characteristics of a floating gate capacitor fabricated using gold nanoparticles as the charge storage layer. The memory window (hysteresis) is reproducible and repeatable across several devices

Facilities Available and Equipment to be procured:

In our laboratory we have the facility for synthesizing gold nanoparticles and their ordered assemblies, and characterizing these using Dynamic Light Scattering (DLS), Atomic Force Microscope (AFM), and Field Emission Scanning Electron Microscope (FESEM). We also have access to a maskless lithography system, e-beam evaporator and electrical probe station with enclosed head space for fabricating interdigitated electrodes and electrical characterization of sensor response.

REFERENCES:

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Task schedule (Important Milestones for research reviews/completion of tasks – Please indicate Milestones that will be presented at Annual in House Seminar)

Deliverables (To include the interim and Final Technical report)

- 1st year: Optimization of protocols for forming interconnected nanoparticle arrays and their spectroscopic and structural characterization
 Fabrication of interdigitated electrodes capable of probing the molecularly interconnected nanoparticle arrays
 Submission of interim technical report
- 2nd year: Electrical characterization of interconnected nanoparticle arrays and optimization of their response to various gases and volatile organic compounds
 Submission of final technical report

APPENDIX – D

Additional Information (if applicable)

(Note: This information is being collected to update information on prior projects with STC and will not be a part of the evaluation process)

1. List of projects (Title/Principal Investigator/Co-investigator/duration/amount) handled previously by IISc PI/Co-PI under STC.

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