101. Project Title: Nanowire Array based Dye Sensitised Solar Cells

102. Broad Subject: Engineering Sciences;
and inclined towards -- Physical Sciences.

103. Sub Area: Chemical Engineering

104. Duration in months: 36 months

105. Total cost: Rs. 41,92,800.00

106. FE Component: $51,500

107. Project Category: Applied Research (Process/Product development)

111. Principal Inv. S. Venugopal

112. Designation: Assistant Professor

113. Department: Chemical Engineering

114. Institute Name: Indian Institute of Science

115. Address: IISc, Bangalore – 560 012

116. Date of Birth: 25-03-75. **Sex (M/F):** M

117. Telephone: (80) 2293 3113 **Fax:** (80) 2360 8121
Gram: SCIENCE BANGALORE 560 012 **e-mail:** venu@chemeng.iisc.ernet.in

118. Co-Investigator: Gupta, Sanjeev Kumar

119. Designation: Associate Professor

120. Department: Chemical Engineering

121. Institute Name: Indian Institute of Science

122. Address: IISc, Bangalore – 560 012

123. Date of Birth: 10-10-66 **Sex (M/F):** M

124. Telephone: (80) 2293 3110 **Fax:** (80) 2360 8121
Gram: SCIENCE BANGALORE 560 012 **e-mail:** sanjeev@chemeng.iisc.ernet.in

Project Title: Nanowire Array based Dye Sensitised Solar Cells

Registration No:

Principal Investigator: S. Venugopal

Institution: Indian Institute of Science

191. Project summary:

Presently, the application of Dye sensitised Solar Cells (DSCs or DSSCs) is limited to niche markets (e.g. building integrated photovoltaic panels etc.) by its overall low module efficiency. A promising approach for enhancing the efficiency of DSCs is to orthogonalize the directions of charge collection and light absorption functionalities. This proposal envisions the fabrication of a DSC comprising of ZnO nanowire arrays with very high roughness factors (i.e. ratio of available surface area for dye absorption to projected footprint area). Recently, a scalable and robust process utilizing directed self-assembly in combination with plasma processing was able to fabricate patterned and ordered monolayers of bare metal nanoparticles over a 1 sq. cm area. The conversion of such a catalyst array, using the Vapour-Liquid-Solid (VLS) growth mechanism into a ZnO nanowire array with high surface area will be investigated systematically in this project. This will be followed by DSC device fabrication and characterization to determine the photovoltaic efficiency. These results will be used as feedback to optimize the nanowire array geometry. Additionally, formation of a thin titanium dioxide film on the surface of ZnO nanowires will be explored to enhance the device performance. The expected increase in single-cell and concomitant increase of module efficiencies will enable DSCs to be economically viable for grid based applications.

192. Key words:

Dye sensitised Solar Cells, ZnO nanowire arrays, Vapour-Liquid-Solid, Photovoltaic efficiency.

200. Technical details

210. Introduction

211. Origin of the proposal:

This project proposal has its origins in the goals of our research group, which is process development for fabricating functional architectures using nanoscale building blocks. This particular proposal builds on the successful completion of an earlier project (Ref: SR/S3/CE/60/ 2005/17.2.06) to fabricate thermally stable gold nanoparticle arrays that can act as templates to grow nanowire arrays by the VLS process. The submission to DST is based on the information presented in the SERC website, wherein the objectives reflect the commitment to encourage young scientists to undertake challenging research, especially in the emerging interdisciplinary field of nanotechnology (http://www.serc-dst.org).

212. Definition of the problem:

To date, the use of sintered nanoparticle films of titanium dioxide has resulted in module efficiencies hovering about 3 to 5% ('record - 8.2%') due to limits on charge extraction efficiency. The development of scalable and robust processes for the fabrication of ZnO nanowire arrays with very high roughness factors (~1000 to 2000) is critical for further enhancements in the efficiencies of DSCs as they allow for orthogonalization of the directions of charge collection and light absorption, thereby simplifying design constraints. The roughness factors of nanowire array based photoanodes have been limited by fabrication processes to ~200 resulting in very low overall efficiencies although the charge extraction efficiency is higher. The use of thermally stable bare 5 - 10 nm gold nanoparticle arrays, with tunable interspacing in the range of 5-30 nm, as site specific catalytic templates for the growth of ZnO nanowire arrays using VLS approach to attain roughness factors of the order of 1000 to 2000 will be investigated in this project. Following this, the fabricated nanowire arrays will be used as photoanodes in a DSC configuration and their efficiencies will be characterized. Various means to enhance the overall photovoltaic efficiency such as using dyes in combination, reducing recombination losses and shunt resistances will also be explored.

213. Objectives:

1. The use of thermally stable bare metal nanoparticle arrays as site-specific templates for the growth of ZnO nanowire arrays by VLS mechanism.
2. Fabrication of DSCs based on ZnO nanowire array photoanodes and characterization of their photovoltaic performance.
3. Optimization of ZnO nanowire array geometry and architecture for improving photovoltaic efficiencies.

220. Review of status of Research and Development in the subject

The VLS growth mechanism based formation of crystalline ZnO nanowire arrays from metal nanoparticle templates is a well-established route and the following list provides references to authoritative recent reviews on the topic. The single crystalline nature of VLS grown nanowires, which allows for efficient electron transport is an important aspect in the context of DSC applications.

1. M. Law, J. Goldberger, P. Yang. *Annu. Rev. Mater. Res.* **2004,** 34, 83-122.
2. L. J. Lauhon, M. S. Gudiksen, C. M. Lieber. *Phil. Trans. R. Soc. Lond. A.* **2004**, 362, 1247–1260.

3. Y.W. Heo, D. P. Norton, L. C. Tien, Y. Kwon, B. S. Kang, F. Ren, S. J. Pearton. *Mat. Sci. Eng. R.* **2004**, 47, 1-47.
4. N. Wang, Y. Cai, R. Q. Zhang. *Mat. Sci. Eng. R.* **2008**, 60, 1-51.
5. K. W. Kolasinski. *Curr. Opin. Solid St. M.* **2006**, 10, 182-191.
6. K. Dick. *Prog. Cryst. Growth Ch.* **2008**, 54, 138-173.

The following is a list of general reviews and books [7-12] on the use of nanostructured materials for excitonic solar energy conversion and the use of 3-D nanostructured morphology for enhancing the efficiency of solar energy conversion. There are three main processes that occur in a DSC cell during photovoltaic operation. These are exciton (bound electron-hole pair) generation, exciton separation into electrons and holes at an asymmetric (in terms of electron and hole transport) interface, and charge collection. These three aspects have been looked into by various groups and several designs have been reported. The group led by Prof. M. Graetzel pioneered the use of a nanostructured TiO_2 based electrode (with 1000x enhanced roughness factors) to achieve meaningful photovoltaic efficiencies in the range of ~7% [13]. Over the past two decades, rapid strides have been made in improving and optimizing the various aspects of titanium dioxide nanoparticle based DSCs leading to the current record of 12.1% efficiency [14] for a single cell device. There have also been steady developments in the design of modules and the current record is 8.2% [15], although most groups report values in the range of 3-5%. Significant progress has occurred in coupling flexible substrates and cheaper processing techniques to fabricate DSCs. So, there has been enormous interest in the industrialization of the DSC concept, as attested to by the three biennial "international conferences on industrialization of DSC" (see www.dsc-ic.com for further details) already held. One of the abiding challenges identified in furthering this technology is the need to improve single-cell efficiencies to values higher than 15-20% by looking at alternative functional nanoscale architectures using materials such as ZnO, which can enhance electron transport rates considerably in comparison to titanium dioxide.

7. P.V. Kamat. *J. Phys. Chem. C.* **2006**, 111, 2834-2860.
8. G. W. Crabtree, N. S. Lewis. *Phys. Today.* **2007**, 37-42.
9. N. S. Lewis. *Science* **2007,** *315,* 798–801.
10. Nanostructured and Photoelectrochemical Systems for Solar Photon Conversion Nanostructured and Photoelectrochemical Systems for Solar Photon Conversion . Edited by M. D. Archer and A. J. Nozik. Imperial College Press: London. **2008**.
11. Z. Fan, H. Razavi, J.-w. Do, A. Moriwaki, O. Ergen, Y.-L. Chueh, P. W. Leu, J. C. Ho, T. Takahashi, L. A. Reichertz, S. Neale, K. Yu, M. Wu, J.W. Ager, A. Javey, *Nat. Mater* **2009**, 8, 648–653.
12. I. Gonzalez-Valls, M. Lire-Canti. *Energy Environ. Sci.* **2009**, 2, 19-34.
13. B. O. Regan, M. Graetzel. *Nature.* **1991**, 353, 737-740.
14. M. Graetzel. *DSC-IC 3, Nara, Japan* 23.4 - 25.4. **2009** (available on www.dyesol.com)
15. L. Han, A. Fukui, Y. Chiba, A. Islam, R. Komiya, N. Fuke, N. Koide, R. Yamanaka, M. Shimizu. *Appl. Phys. Lett.* **2009**, 94, 013305.

221. International status (ZnO nanowire array based DSCs):

This project proposal is focused on enhancing the charge separation and collection efficiencies by fabricating ZnO nanowire arrays with high roughness values and optimizing DSC geometry. So, the following section will focus on recent developments in this area.

The group led by Prof. P. Yang has pioneered the use of ZnO nanowire array based photoanodes in DSCs [16]. They enumerated several advantages associated with nanowire geometry namely: a fully interdigitated donor-acceptor interface allowing for optimization of light collection, charge separation, and charge transport in one design, and the ability to harness drift directed transport of electrons towards the electrode rather than depend on diffusive percolative transport across sintered networks. They achieved an

overall efficiency of 2.5% under AM 1.5 illumination (standardized condition) using a solution grown zincoxide nanowire array with a roughness factor of only 200. Since then, the group led by Hupp [17] has shown through careful electrochemical impedance studies that nanowire geometry does indeed exhibit 18x faster electron transport rates, while maintaining similar electron lifetimes as a nanoparticulate film. This implies that the thickness of nanowire array based photoanode can be about 150 μm as compared to the limit of ~10 μm on sintered nanoparticulate films due to recombination losses. Recently, Oosterhout et al. [18] used electron tomography to experimentally verify the linear dependence of efficiency on the fractional availability of direct electron transport pathways, thereby demonstrating the importance of drift enhanced electron transport. Also, recently a group from Sandia [19] has shown that the overall efficiency scales linearly with the roughness factor for ZnO nanorod array based DSCs. Despite these insights, the maximum efficiencies reported in the literature hovers around 2-3% for ZnO nanowire array based DSCs due to the inability of currently available fabrication techniques (such as hydrothermal growth [16], templated growth [20] etc.) to fabricate ZnO nanowire arrays with the desired nanoscale pitch and diameter over large areas [12].

There have also been several reports on the use of titanium dioxide overlayers on ZnO nanowires to alleviate problems associated with dye adsorption on ZnO surfaces, as most commonly available dyes have been optimized for use with titanium dioxide which has a lower pzc and so can tolerate the acidic dyes [21,22].

16. M. Law, L. Greene, J. C. Johnson, R. Saykally, P. Yang. *Nat. Mater.* **2005**, 4, 455-459.
17. A. B. F. Martinson, J. E. Mcgarrah, M. O. K. Parpia, J. T. Hupp. *Phys.Chem. Chem. Phys.* **2006**, 8, 4655-4659.
18. S. D. Oosterhout, M. M. Wienk, S. S. v. Bavel, R. Thiedmann, L. J. A. Koster, J. Gilot, J. Loos, V. Schmidt, and R. A. J. Janssen. *Nat. Mater.*, **2009**, 8, 818–824.
19. Y-j. Lee, M. T. Lloyd, D. C. Olson, R. G. Grubbs, P. Lu, R. J. Davis, J. A. Voigt, J. P. Hsu. *J. Phys. Chem. C.* **2009**, 113, 15778-15782.
20. H. J. Fan, W. Lee, R. Scholz, A. Dadgar, A. Krost, K. Nielsch, and M. Zacharias. *Nanotechnol.* **2005,** 16, 913–917.
21. Q. Zhang, C. S. Dandeneau, X. Zhou, G. Cao. *Adv. Mater.* **2009**, 21, 1-22.
22. M. Law, L. E. Greene, A. Radenovic, T. Kuykendall, J. Liphardt, P. Yang. *J. Phys. Chem. B.* **2006**, 110, 22652-22663.

222. National status (ZnO nanowire array based DSCs):

The group led by Prof. A. Pal at IACS has recently published their work on solution grown ZnO Nanowire array based DSCs using a novel Rose Bengal dye as sensitizer [23]. Their devices achieved an efficiency of 0.7%. Apart from this, Prof. Mehra from Univ. of Delhi has reported on the effect of electrolytes on DSC performance and Prof. V. Dutta from IIT, Delhi has reported on spray deposited ZnO nanoparticle based DSCs with 4.7% efficiency.

23. B. Pradhan, S. K. Batabyal, A. Pal. *Sol. Energ. Mat. Sol. C.* **2007**, 91, 769-773.
24. P. Suri, R. M. Mehra. *Sol. Energ. Mat. Sol. C.* **2007**, 91, 518-524.
25. A. R. Rao, V. Dutta. *Nanotechnol.* **2008,** 19, 445712.

223. Importance of the proposed project in the context of current status:

An important hurdle facing large-scale commercial deployment of DSC's is the low module efficiencies of 3-5% (recent 'record' is 8.2%), which is limited by the maximum achievable single cell efficiencies (12.1%) as on date. Nanowire array based photoanodes have been shown to be superior to sintered nanoparticle films due to their direct contact with the electrodes that help to reduce recombination losses and improve short-circuit current on a normalised roughness factor basis. However, till now no group has fabricated nanowire arrays with roughness factors that are similar to that of sintered nanoparticle films mainly due to the limitations on feasible nanowire diameter and spacing. The ideal diameter and spacing of nanowire arrays is expected to be in the range of 10-20 nm and 20-40 nm respectively, while the desired nanowire lengths are in the range of 50 μm [12]. The lower limit on the diameter of nanowires is placed by their ability to conduct electrons with minimal resistance and the interspacing is restricted by the mass transfer limitations on the electrolyte side. This project aims to improve single cell efficiencies by fabricating a nanowire array based photoanode with very high surface area using a bare gold nanoparticle template with nanoparticle sizes in the range of 5 to 10 nm and interspacing ranging from 10 to 30 nm. This should increase the single cell efficiencies to the order of 15-20%, which will make DSCs attractive for large-scale grid deployment in comparison to amorphous/polycrystalline silicon based solar cells.

224. Review of expertise available with proposed investigating group/institution in the subject of the project

The PI and Co-PI have been working on experimental and theoretical methods for the development of continuous scale processes for synthesizing monodisperse nanoparticles. Research in our group has led to the development of a rapid, green, room-temperature semi-batch protocol for the synthesis of size controlled metal nanoparticles. We have also developed and optimised protocols for fabricating large area metal nanoparticle arrays with controlled particle diameters and interspacing. For our previous DST project, we developed a plasma processing route that enhanced the thermal stability of ordered gold nanoparticle arrays at temperatures as high as 600°C. We have also setup a class 10000 cleanroom equipped with lithographic and characterization tools for exploring microfluidic/novel synthesis routes for energy-efficient, continuous production of nanoparticles. Research is also currently underway on utilizing ordered nanoparticle arrays in fuel cells, chemo-resistive sensors and floating gate nanoelectronic memory devices.

225. Patent details (domestic and international)

S.K. Sivaraman, and V. Santhanam, "A method for preparing metal or metal oxide nanoparticles", Patent-Pending, IPO Chennai -- 775/CHE/2009, US Patent being filed.

230. Work plan

231. Methodology

Size-selected ligand coated gold nanoparticles are spread as an organic thin film on a slightly convex shaped water surface and allowed to evaporate under appropriate conditions. This results in a uniform monolayer array (>1cm dia.) of hexagonally close-packed particles that are floating on the water surface. This is then transferred onto a patterned elastomeric stamp pad by gently contacting the water surface with the PDMS pad and then stamped onto any desired solid substrate (silicon/quartz die) by conformal contact with the elastomeric stamp. *We are now capable of tuning the size of the nanoparticle between 2 and 10 nm, while altering the interparticle spacing between 2 and 30 nm using appropriate surfactants/polymeric ligands.* These arrays will then be treated using Oxygen/Hydrogen plasma at optimal conditions, based on our

previous work. *After plasma treatment, these particle arrays retain their positional order for temperatures upto 600°C.* Such nanoparticle arrays will then be used as templates to seed the growth of ZnO nanowires.

During VLS growth, zinc vapours formed by the decomposition of a zinc-carbon source are adsorbed into the gold nanoparticle forming a gold-zinc alloy droplet into which further diffusion of zinc vapour results in phase separation into a gold-zinc alloy and zinc oxide nanowire (zinc is oxidised). Preliminary experiments in a single zone tube furnace indicate that there is a competition between the rate of vertical growth due to diffusion of zinc into the catalyst drop and the lateral diffusion and coagulation of the catalyst droplets on the substrate. These rates are temperature dependent and the research will be greatly aided by the use of a dual zone tube furnace, where the source and substrate temperatures can be independently controlled without compromising on the distance between the two, which adversely affects the concentration of zinc vapours at the sample surface. The temperatures and processing conditions (such as source charge and inert gas flowrate) will be optimized based on statistical design of experiments. The effect of catalyst loading (based on varying nanoparticle size and interspacing) on ZnO nanowire growth rates will also be investigated, resulting in phase maps with identified domains of vertical nanowire growth.

These vertical ZnO nanowire arrays will be sensitised with appropriate commercially available[26] dye molecules and optimal conditions reported in literature will serve as a starting point for these experiments. After appropriate sensitisation, a complete DSC device will be fabricated using commercially available[26] counter electrodes and electrolytes. The photovoltaic performance of these devices will be then characterised under standardised conditions using the solar simulator. The effect of nanowire array geometry (such as height, width and interspacing) as well as the presence or absence of a very thin shell of titanium dioxide will then be studied. The titanium dioxide shells will be grown using RF sputtering system being procured at the Institute. The growth of titanium dioxide shells using SILAR[27] technique will also be explored. The results of such characterizations will also feedback into the VLS optimization objectives (in terms of nanowire array geometry) to improve the overall process. The efficiency of the optimized device will be used to benchmark the effect of using a nanowire array based photoanode as opposed to a sintered nanoparticle network that is also commercially available[26].

26. See www.dyesol.com, www.solaronix.com, www.ecic.com
27. H.M. Pathan, S-K Min, J.D. Desai, K-D Jung, O-S Joo, Mater. Chem. Phys. 2006, 97, 5-9.

232. Organisation of work elements

Technical work elements:-

- Nanowire synthesis by VLS, and optimization of process and device geometry
- DSC fabrication and characterization

Administrative work elements:-

- Recruitment of project personnel
- Selection of equipment and processing purchase order
- Equipment installation

233. Time schedule of activities giving milestones (also append to bar diagram and mark it as Section 410)

- *Selection of equipment and processing of purchase order:* - Time required -- 2 months after sanction of funds. This is the minimum time taken to follow the institute procedures on purchasing equipment.
- *Equipment Installation:*- Time required — 9 months. Based on current practices and experience of time taken for equipment purchase and installation, this is the average time required to complete financial transactions following institute procedures, clear customs etc. and have the equipment installed in our lab.
- *Recruitment of personnel:*- Time required – 1-2 months. Depending on the availability of motivated personnel, this activity will take roughly 1-2 months after sanction of the project.
- *VLS synthesis:*- Time span – 9-35 months. Preliminary experiments will be carried out to explore the parameter space consisting of amount of source material, source temperature, sample temperature, distance between source and sample, and diameter and interparticle spacing of nanoparticle catalyst. Based on this exercise, the phase space over which nanowire growth is faster than lateral alloy diffusion will be identified and ZnO nanowire arrays will be synthesized with optimal spacing and size based on feedback from DSC fabrication and photovoltaic characterization.
- *DSC device fabrication and characterization:*- Time span – 15-36 months. Dye sensitised Solar Cells (DSCs) will be fabricated after the initial optimization of the VLS process for fabricating ordered nanowire arrays. These cells will be then characterized using the solar simulator to understand the effects of device geometry and dye loading conditions on electron recombination losses, photovoltaic performance indices such as fill factor, open circuit voltage and short circuit current. The aim is to improve single cell efficiencies to the range of 15-20% and also to characterize the enhancement in efficiency attributable to the use of nanowire array based architecture in comparison to that of a sintered nanoparticle film based photoanode that is currently used.

Important Milestones:-

1) Installation of the VLS equipment and preliminary exploration of processing parameters (1st year).
2) Fabrication of nanowire array based DSC (2nd year).
3) Optimization of VLS process and device fabrication to enhance the yield of DSCs (3rd year).

234. Suggested plan of action for utilization of research outcome expected from the project.

The successful development of an efficient DSC device using nanowire array architecture will call for further process development to enable mass production of such devices. The PI intends to focus on the development of appropriate large scale continuous processes to produce such nanowire arrays, based on the outcome of this research. Also, the successful development of a route for fabricating ordered vertical nanostructures with controllable pitch and geometry is critical for the development of various devices such as excitonic solar cells based on the concept of Extremely Thin Absorbing layer (ETA), cheap household lighting devices, and future nanophotonic and electronic devices. The results of this project will also be submitted to reputed journals in the field to help disseminate this information. There are quite a few conferences and meetings that feature DSC's on their agenda that will also provide appropriate fora for the dissemination of these results. Based on these interactions a national level meeting of researchers focussed on DSC device development can also be organised at an appropriate juncture.

300. BUDGET ESTIMATES: SUMMARY

	Item	BUDGET			(in Rupees)
		1st Year	2nd Year	3rd Year	Total
A.	Recurring				
	1.Salaries/wages	Rs. 1,68,000	Rs. 1,68,000	Rs. 1,68,000	Rs. 5,04,000
	2. Consumables	Rs.50,000	Rs.50,000	Rs.40,000	Rs. 1,40,000
	3. Travel	Rs. 15,000	Rs. 15,000	Rs. 20,000	Rs. 50,000
	4. Other costs	Rs. 1,00,000	Rs. 0	Rs. 0	Rs. 1,00,000
B.	Equipment*	Rs. 27,00,000	Rs. 0	Rs. 0	Rs. 27,00,000
C.	Institute overhead @ 20%	Rs. 6,06,600	Rs. 46,600	Rs. 45,600	Rs. 6,98,800
	Grand total (A+B) Total FEC**	Rs. 36,39,600 ($50,000)	Rs. 2,79,600 ($1000)	Rs.2,73,600 ($500)	Rs. 41,92,800 ($51,500)

*** DDP costs (INCO terms), ** FEC component is the DDU cost (INCO terms), conversion rate: 1 US$ = Rs. 50**

310. BUDGET FOR SALARIES/WAGES

		BUDGET			(in Rupees)
		1st Year(m.m.*)	2nd Year (m.m.)	3rd Year (m.m.)	Total (m.m.)
Designation & number of persons	Monthly Emoluments				
Project Assistant (One)	Rs.14,000	Rs. 1,68,000 (12)	Rs. 1,68,000 (12)	Rs. 1,68,000 (12)	Rs. 5,04,000 (36)
Total	Rs.14,000	Rs. 1,68,000 (12)	Rs. 1,68,000 (12)	Rs. 1,68,000 (12)	Rs. 5,04,000 (36)

311. Justification for the manpower requirement

Budget has been requested for one project assistant to assist with the set-up and maintenance of the VLS facility.

320. BUDGET FOR CONSUMABLE MATERIALS

		BUDGET			(in Rupees)
Item		**1st Year**	**2nd Year**	**3rd Year**	**Total**
Gas cylinders, Source materials and inert gases for VLS growth; Dye, O-rings, Counter electrolyte (imported) for solar cell characterization	**Q***				
	B**	Rs. 50,000	Rs. 50,000	Rs. 40,000	Rs. 1,40,000
	F***		$ 1000	$500	
Total	**B**	Rs. 50,000	Rs. 50,000	Rs. 50,000	Rs. 1,40,000
	F	0	$1000	$500	$1500

*Q: Quantity or number, ** Budget, ***F: Foreign Exchange Component in US$

321. Justification for costly consumable (if not provided for in Section 231 i.e. Methodology)

330. BUDGET FOR TRAVEL

		BUDGET			(in Rupees)
Reason		**1st Year**	**2nd Year**	**3rd Year**	**Total**
To attend monitoring meetings.	Travel (Only inland travel)	Rs.15,000	Rs.15,000	Rs.20,000	Rs.50,000

331. Justification for intensive travel, if any. –

Additional budget is requested in the third year to allow students to attend national conferences.

340. BUDGET FOR OTHER COSTS/CONTINGENCIES

		BUDGET			(in Rupees)
Reason		**1st Year**	**2nd Year**	**3rd Year**	**Total**
To cover cost and currency conversion fluctuations	**Other costs/ Contingency costs**	Rs.1,00,000	Rs.0	Rs. 0	Rs.1,00,000

341. Justification for specific costs under other costs– See above.

350. BUDGET FOR EQUIPMENT

Sl. No.	Generic name of the Equipment along with make & model	Imported/ Indigenous	Estimated Costs* (Foreign Currency component)	Spare time for other users (in %)
1	Dual zone quartz tube furnace with vacuum and gas control system, MTI – OTF-1200X2-3CLV	Imported (MTI Corporation)	Rs.10,00,000 (US $18,000)	20%
2	Solar simulator with cell accessories, ORIEL-92251A 150 W	Imported (Newport Corporation)	Rs. 17,00,000 (US $32,000)	30%

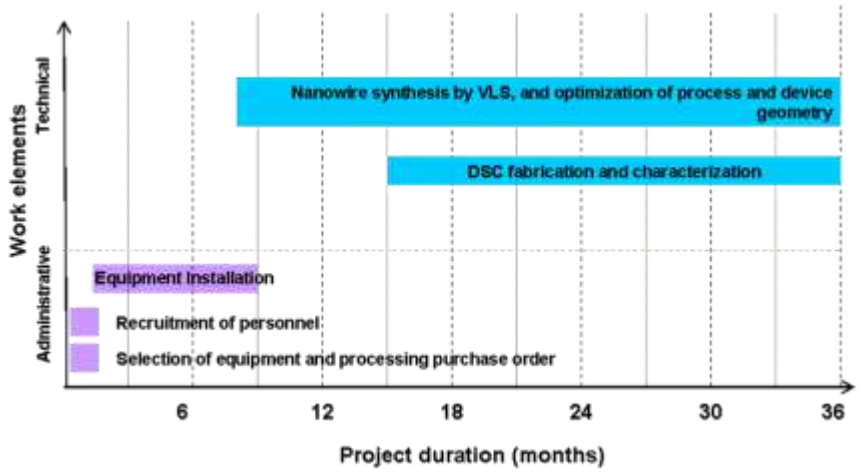
*** includes transport, insurance, import duties and installation charges.**

351. Justification for the proposed equipment.

The dual zone quartz tube furnace with vacuum and gas control system is required to carry out Vapour-Liquid-Solid (VLS) mechanism based growth of ZnO nanowire arrays using bare gold nanoparticle arrays as catalytic templates. In the initial stages zinc oxide vapours will diffuse into the gold nanoparticles and form an eutectic alloy that has a melting point of ~370°C. The dual zone nature is critical to maintain the source at ~900°C while the catalyst laden substrate is maintained at much lower temperatures (~400-500°C), for generating adequate flux of zinc vapours and reducing the lateral diffusivity of alloy drops respectively. This will ensure that each catalyst alloy drop seeds a vertical nanowire before it can spread laterally and become disordered. A single zone tube furnace cannot achieve such temperature differences over short enough distances to prevent excessive loss of zinc atoms to the tube furnace wall.

The solar simulator with cell accessories is important to characterize the photovoltaic performance of the nanowire array based DSC samples. A class 'A' certified solar cell simulator is required to scientifically characterize the photovoltaic performance indices (such as open circuit voltage, short circuit current and fill factors) and also to test long-term stability and robustness of the fabricated DSC devices. These tests require characterization in chunks of large time blocks and such a facility is not currently available in our institute. Immediate characterization is very critical to understand the implications of nanostructure geometry on the DSC performance indices and will be a significant feedback for optimizing the VLS synthesis parameters and device development.

410. Time Schedule of Activities through BAR Diagram (Append Section 233)



- *Selection of equipment and processing of purchase order:* - Time required -- 2 months after sanction of funds. This is the minimum time taken to follow the institute procedures on purchasing equipment.
- *Equipment Installation:*- Time required — 9 months. Based on current practices and experience of time taken for equipment purchase and installation, this is the average time required to complete financial transactions following institute procedures, clear customs etc. and have the equipment installed in our lab.
- *Recruitment of personnel:*- Time required – 1-2 months. Depending on the availability of motivated personnel, this activity will take roughly 1-2 months after sanction of the project.
- *VLS synthesis:*- Time span – 9-35 months. Preliminary experiments will be carried out to explore the parameter space consisting of amount of source material, source temperature, sample temperature, distance between source and sample and diameter and interparticle spacing of nanoparticle catalyst. Based on this exercise, the phase space over which nanowire growth is faster than lateral alloy diffusion will be identified and ZnO nanowire arrays will be synthesized with optimal spacing and size based on feedback from DSC fabrication and photovoltaic characterization.
- *DSC device fabrication and characterization:*- Time span – 15-36 months. Dye sensitised Solar Cells (DSCs) will be fabricated after the initial optimization of the VLS process for fabricating ordered nanowire arrays. These cells will be then characterized using the solar simulator to understand the effects of device geometry and dye loading conditions on electron recombination losses, photovoltaic performance indices such as fill factor, open circuit voltage and short circuit current. The aim is to characterize the enhancement in efficiency attributable to the use of nanowire array based architecture in comparison to that of a sintered nanoparticle film based photoanode that is currently used.

Important Milestones:-

1) Installation of the VLS equipment and preliminary exploration of processing parameters (1st year).
2) Fabrication of nanowire array based DSC (2nd year).
3) Optimization of VLS process and device fabrication to enhance the yield of DSCs (3rd year).

420. List of facilities being extended by parent institution(s) for the project implementation.

A) Infrastructural Facilities:

Sr. No.	Infrastructural Facility	Yes/No/ Not required Full or sharing basis
1.	Workshop Facility	Sharing basis
2.	Water & Electricity	Yes
3.	Laboratory Space/ Furniture	Yes
4.	Power Generator	Yes
5.	AC Room or AC	Not required
6.	Telecommunication including e-mail & fax	Sharing basis
7.	Transportation	Not required
8.	Administrative/ Secretarial support	Sharing basis
9.	Information facilities like Internet/ Library	Yes
10.	Computational facilities	Yes
11.	Animal/ Glass House	Not required
12.	Any other special facility being provided	Centre of excellence in nanoelectronics with common user facilities for nanoscale processing

B. Equipment available with the Institute/ Group/ Department/ Other Institutes for the project:

Equipment available with	Generic Name of Equipment	Model, Make & year of purchase	Remarks including accessories available and current usage of equipment
PI & his group	Class 10000 Cleanroom	Four-C-Tron (2008)	Used for providing a controlled environment for nanoscale device fabrication and characterization
	FESEM	Ultra55, Zeiss (2008)	Used to characterize nanoparticles and microstructures
	Maskless lithographic system	μpg-101, Heidelberg instruments (2008)	Fabricating micron scale patterns on photoresists
	Reactive Ion etcher	MRIE-1A, Milman thin films Pvt. Ltd (2007)	For removing ligands from nanoparticle monolayers
	Semiconductor characterization		For measuring currents in nA range and probing micro/nanoscale device

		Keithley SCS-4200 (2008)	characteristics
PI's Department	Atomic Force Microscope	MFP-3D, Asylum Reasearch (2006)	For nanoscale characterization and patterning
	Stop flow Reactor	SFM-400, Biologic SAS (2006)	For rapid kinetics measurement
	DLS-Particle size measurement	Brookhaven, Goniometer based, 2003	Typically used for hydrodynamic size determination
	UV-Vis Spectrophotometer	Shimadzu, 2002	Typically used for concentration measurement
IISc	TEM	Tecnai F-30 300 kV , FEI, 2004	Central user facility set-up as part of IISc Nanoinitiative
	RF sputtering systems	Procurement process is ongoing	Centre for excellence in Nanoelectronics

430. Detailed Bio-data of the Investigator

Name: S. Venugopal (Venugopal Santhanam)

Contact Information:

Assistant Professor,
Department of Chemical Engineering,
Indian Institute of Science,
Bangalore, India-560012.
e-mail: venu@chemeng.iisc.ernet.in
Fax no: 080-2360-8121; Phone no: 080-2293 3113

Date of Birth: 25-03-1975. **SEX:** Male

EDUCATION

Ph.D. Chemical Engineering, Purdue University, December 2002.
Thesis: Fabrication of Nanoelectronic Devices Using Self-Assembled 2D Arrays of Monolayer Protected Clusters.

M.S. Chemical Engineering, Louisiana State University, December 1998.
Thesis: OH PLIF Imaging of Swirl-Stabilized Combustor.

B.Tech. (Hons.) Chemical Engineering, IIT-Kharagpur, June 1996.
Thesis: Scrubbing of Diesel Fumes Using an Ejecto-Venturi Fume Scrubber.

RESEARCH EXPERIENCE

Research Scientist, April 2003-December 2004, RWTH Aachen.

AWARDS/HONOURS

- Associate Member, Indian Academy of Sciences, 2009.

PATENTS

- S.K. Sivaraman, and V. Santhanam, "A method for preparing metal or metal oxide nanoparticles", Patent-Pending, IPO Chennai -- 775/CHE/2009, US Patent being filed.
- G. Schmid, U. Simon, D. Jaeger, V. Santhanam, T. Reuter, "Microelectronic component with electrically accessible metallic clusters", **EP 1748501, US 7602069**.

PUBLICATIONS

- S. K. Sivaraman, I. Elango, Sanjeev Kumar, and V. Santhanam, "A green protocol for room temperature synthesis of silver nanoparticles in seconds", Curr. Sci. 97(7), 2009.
- V. Santhanam and R.P. Andres, "Microcontact Printing of Uniform Nanoparticle Arrays", Nanoletters, Vol.4 (1), 2004,pp 41-44.
- V. Santhanam, J. Liu, R. Agarwal and R.P. Andres, "Self-Assembly of Uniform Monolayer Arrays of Nanoparticles", Langmuir, Vol.19 (19), 2003, pp 7881-7887.
- V. Santhanam, F.C. Knopf, S.Acharya and E.Gutmark, "Fluorescence and Temperature Measurements in an Actively Forced Swirl-Stabilized Spray Combustor", AIAA J. Propul. Power, Vol.18 (4), 2002, pp 855-865.

BOOK CHAPTERS

- V. Santhanam, R.P.Andres, "Metal Nanoparticles and Self-assembly into Electronic Nanostructures", in the Dekker Encyclopedia of Nanoscience and Nanotechnology, Eds. J.A. Schwarz, C. Contescu, K. Putyera, Marcel Dekker Inc., New York, April 2004.

CONFERENCE PROCEEDINGS

- S. Sankar Kalidas, D. Mohana Rao, Sanjeev Kumar and Venugopal Santhanam, "Role of Coagulation in the Synthesis of Gold Nanoparticles by Citrate Reduction", The Fourth Asian Particle Technology Symposium (APT 2009), September 14-16, 2009
- D. Mohana Rao, M. Anusha, J. Chakraborty, S. Sankar Kalidas, Sanjeev Kumar, and S. Venugopal, "Kinetics and modeling of gold nanoparticle formation", CHEMFERENCE'09, Chennai
- S. Sankar Kalidas, Alok. Kr. Srivastava, and V. Santhanam, "Fabrication of Nanoparticle Arrays", CHEMCON - 2007, Kolkutta

FUNDED PROJECTS

- S. Venugopal, 2006-2009, Patterned and Ordered Metal Nanoparticle Arrays – Templates for Functional Nanoscale Architectures, *SERC-DST,* Rs. 50,00,000.

431. Detailed Bio-data of the Co-Investigator

Name: Sanjeev Kumar Gupta

Contact Information:

Associate Professor,
Department of Chemical Engineering,
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Fax no: 080-2360-8121; Phone no: 080-2293 3110

Date of Birth: 10-10-1966. **SEX:** Male

EDUCATION

Ph.D. Chemical Engineering, Indian Institute of Science, 1992.
Dissertation: *Breakage and Coalescence of Drops in Turbulent Stirred Dispersions.*

M.E. Chemical Engineering, Indian Institute of Science, 1989.
Thesis: *Studies on Phase Inversions.*

B.E. Chemical Engineering, University of Roorkee, 1987.

RESEARCH EXPERIENCE

Research Associate, 1993-1996, Purdue University.

AWARDS/HONOURS

- Young Scientist Medal of Indian National Science Academy, 1998.
- Young Associate of the Indian Academy of Sciences, 1997.
- Professor P.S. Narayana Medal for *the best thesis in Mechanical Science Division* given annually, 1992.
- Professor N. R. Kuloor Memorial Medal for *the best Ph.D. thesis in Chemical Engineering* given biennially, 1991-93.
- Professor N. R. Kuloor Memorial Medal for *the best Master of Engineering Student* in year 1989.

PUBLICATIONS

- Mahendra N. Nandanwar and Sanjeev Kumar, 2008, A new discretization of space for the solution of multidimensional population balance equations: Simultaneous breakup and aggregation of particles, *Chem. Engng. Sci.* **63**,3988--3997.
- Mahendra N. Nandanwar and Sanjeev Kumar, 2008, A new discretization of space for the solution of multidimensional population balance equations, *Chem. Engng. Sci.* **63**,2198--2210.
- Jayanta Chakraborty and Sanjeev Kumar, 2007, A new framework for solution of multidimensional population balance equations, *Chem. Engng. Sci.* **62**,4112--4125.
- Ramana Reddy and Sanjeev Kumar,2007, Dispersal of sticky particles, *Europhysics Letters* **80**, 56001.
- Sanjeev Kumar, K. S. Gandhi, and R. Kumar, 2007, Modeling of formation of gold nanoparticles by citrate method, *Ind. Engng. Chem.* **46**, 3128-3136.
- Reetu Singh and Sanjeev Kumar, 2006, Effect of mixing on nanoparticle formation in micellar route, *Chem. Engng. Sci.* **61**,192--204.
- Sanjeev Kumar and G. L. Tulasi, 2005, Aggregation vs. breakup of the organic phase complex, *Hydrometallurgy* **78**, 79--91.
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- Singh, Reetu, M. Durairaj and Sanjeev Kumar, 2003, An Accelerated Monte-Carlo Technique For Simulation of Nanoparticles, *Langmuir* **19,** 6317-6328.
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- Sanjeev Kumar, T. W. Pirog and D. Ramkrishna, 2000, A new method for estimating hindered creaming/settling velocity of particles in polydisperse systems, *Chern. Engg. Sci. 55,* 1893-1904.
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- Sanjeev Kumar and D. Ramkrishna, 1997, On the solution of population balance equations by discretization-III. Simultaneous nucleation, growth and aggregation, *Chern. Engg.* Sci. 52,4659-4679.
- Sanjeev Kumar, G. Narsimhan and D. Ramkrishna, 1996, Coalescence in creaming emulsions. Existence of a pure coalescence zone, *I&EC* 353155-3162.
- Andrew Lam, A. Sathyagal, Sanjeev Kumar and D. Ramkrishna, 1996, On the maximum stable drop diameter in stirred liquid-liquid dispersions, *AI.Ch.E. J. 411547-1552.*
- Sanjeev Kumar, 1996, On phase inversion behaviour of O/W and W *10* dispersions, *Chern. Engg. Sci.* 51, 831-834.
- Sanjeev Kumar and D. Ramkrishna, 1996, On the solution of population balance equations by discretization-II. A moving pivot technique, *Chern. Engg. Sci.* 51, 1333-1342.
- Sanjeev Kumar and D. Ramkrishna, 1996, On the solution of population balance equations by discretization-I. A fixed pivot technique, *Chern. Engg. Sci.* 51, 1311-1332.
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- Sanjeev Kumar, R. Kumar and K S. Gandhi, 1991, Alternative mechanism of drop breakage in stirred vessels, *Chern. Engg.* Sci. 46,2483-2489.
- Sanjeev Kumar, R. Kumar and K S. Gandhi, 1991, Influence of wetting characteristics of the impeller on phase inversion, *Chern. Engg.* Sci. 46,2365-2367.

FUNDED PROJECTS

- Sanjeev Kumar, 2000-2003, Redesigning of impellers for efficient breakup of drops, *INSA Young Scientist Award,* Rs.1,80,000.
- Sanjeev Kumar, 2001-2002, Recovery of Carbon Particles from Filter Media Using Liquid Liquid Dispersions, *Hindustan Lever Research Center,* Rs. 9,50,000.
- Sanjeev Kumar, 2001-2004, Studies on Phase Inversion in Agitated Liquid-Liquid Dispersion, *DST,* Rs. 17,90,000.
- Sanjeev Kumar, 2004-2007, Coalescence of drops in centrifugal extractors, *Indira Gandhi Center for Atomic Research,* Rs. 18,49,000.
- Sanjeev Kumar, 2007-2012, Laboratory for particle engineering and technology, *IRPHA-DST*, Rs. 4,92,47,000.

450. Executive Summary of Completed Research Projects

Title: Patterned and Ordered Metal Nanoparticle Arrays – Templates for Functional Nanoscale Architectures

The objectives of the proposal (given below) have been met and further progress in terms of process development for solar energy conversion has been undertaken.

- Development of a plasma processing route for the fabrication of uniform, patterned, and ordered arrays of bare gold nanoparticle monolayer from Molecularly Protected Nanoparticle (MPN) arrays.
- Optimization of plasma parameters using micro/spectro-scopic characterization of the rate of removal of alkanethiol monolayers from the surface of gold nanoparticles.
- Thermal stability analysis of bare gold nanoparticle arrays on various substrates.

Deliverables:

Technical Knowledge: The rate of polymer removal (as measured by an uniform decrease in the height of AFM cross sectional scans) is independent of the molecular weight of the ligand and this indicates that under the conditions used, the plasma enhances the degradation rate of organic ligands uniformly both in space and time. A novel, rapid, energy efficient and green protocol for metal nanoparticle synthesis has been developed as part of this work.

Process Development: The goal was to develop a fine-tuneable degradation of ligand, which requires maximization of treatment time at minimal power. In this respect, Pressure, RF power and gas composition (typically, H2 and/or O2) were optimized for the different ligands. An interesting observation that corroborated the uniform reactive nature of the plasma (in contrast to random ionic bombardment aspect) was that the use of hydrogen with polystyrene thiol ligands resulted in spherical aggregates, which is attributed to the hydrogenation of polystyrene rather than the expected degradation.

Publications / Patents:

- S. K. Sivaraman, V. Santhanam, "A method for preparing metal or metal oxide nanoparticles", IPO Chennai -- 775/CHE/2009 (patent pending)
- S. K. Sivaraman, I. Elango, S. Kumar and V. Santhanam, "A green protocol for room temperature synthesis of silver nanoparticles in seconds" Current Science (accepted for publication)
- S. K. Sivaraman, S. Kumar and V. Santhanam, "A Green, Room-temperature Protocol for the Rapid Synthesis of Gold Nanoparticles – Size-controlled Synthesis by Dropwise Addition" (Manuscript submitted to ACS Nano)
- S. K. Sivaraman and V. Santhanam, "Plasma enhanced thermal stability of nanoparticle monolayers" (Manuscript in preparation)

Future direction:

Presently, efforts are underway to utilise the enhanced thermal stability of gold nanoparticle monolayers to grow ordered arrays of zinc oxide nanowires by using a single zone tube furnace in collaboration with Prof. KKR Nanda, MRC-IISc. Such ordered arrays offer an attractive avenue to harness solar energy using dye sensitisation.

File No_____**

1. Title: Nanowire array based Dye Sensitized Solar cells

2. Proposed Budget for 3 years:

2.1 Total: Rs.41,92,800.00

2.2 Equipment: Rs.27,00,000.00

2.3 Staff (proposed research staff): One (Rs. 5,04,000.00)

2.4 Other Recurring costs:
Consumable : Rs.1,40,000.00
Travel : Rs.50,000.00
Contingency : Rs.1,00,000.00
Any other expenses : Institute overhead @20%
(Rs. 6,98,800.00)

3. Date of receipt:**

4. PI Name, Designation & Address: S. Venugopal, Assistant Professor, Department of Chemical Engineering, Indian Institute of Science, Bangalore 560 012.

5. Date of Birth: 25-03-75

6. Co-Investigator details: Gupta, Sanjeev Kumar

7. Date of Birth: 10-10-66.

8. Other projects with the PI/Co-PI:

Sr.No.	Title	Cost (in rupees)	Duration	Agency
1	Laboratory for Particle Engineering and Technology	Rs. 4,92,47,000	5 years (2007-2012)	SERC-DST