

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

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

103. Sub Area: (i) Chemical Engineering, (ii) Materials, Mining and Mineral Engineering and (iii) Condensed Matter Physics and Materials Science.

104. Duration in months: 36 months

105. Total cost: Rs. 54,60,000.00

106. FE Component: \$750

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

mail: venu@chemeng.iisc.ernet.in

e-

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
mail: sanjeev@chemeng.iisc.ernet.in

e-

125. Co-Investigator: NA

126. Designation: NA

127. Department : NA

128. Institute Name: NA

129. Address: NA

130. Date of Birth: NA **Sex (M/F):** NA

131. Telephone Fax Gram e-mail

132. Co-Investigator: NA

133. Designation: NA

134. Department: NA

135. Institute Name: NA

136. Address: NA

137. Date of Birth: NA **Sex (M/F):** NA

138. Telephone Fax Gram e-mail

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

Registration No:

Principal Investigator: S. Venugopal

Institution: Indian Institute of Science

191. Project summary:

This proposal envisions the fabrication of a functional template comprising of patterned and ordered monolayer/multilayer arrays of metal nanoparticles. Recently, a scalable and robust process utilizing directed self-assembly in combination with soft-lithography was able to fabricate patterned and ordered monolayers/multilayers of molecularly protected metal nanoparticles (MPN's) over a 1 sq. cm area. The conversion of such an MPN array, under the action of low energy oxygen plasma, into the desired array of bare metal nanoparticles will be investigated systematically in this project. This step will serve to not only remove the organic coating but also immobilize the nanoparticles preventing their agglomeration into larger grains. Such ordered bare metal nanoparticle arrays are directly suited as platforms for applications such as chemresistive multi-spectral bio/chemical sensors and in floating-gate memory devices. Of particular future interest is their capacity to act as templates for fabricating functional nanoscale architectures consisting of patterned and ordered arrays of nanorods or semiconductor nanowires by using them either as dry etching masks or as catalysts.

192. Key words:

Directed assembly, Soft-lithography, Plasma, Metal nanoparticle arrays, Functional nanoscale architectures.

200. Technical details

210. Introduction

211. Origin of the proposal:

This project proposal has its origins in my goal to start a research group that is involved in process development for fabricating functional architectures using nanoscale building blocks. This particular proposal is a result of my desire to build upon the knowledge and skills gained over the last six years in process development activities involving patterned arrays of monolayer protected gold nanoparticles. 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://serc-dst.org>).

212. Definition of the problem:

The development of scalable and robust processes for the fabrication of ordered metal nanoparticle arrays is critical for applications in nanoelectronics and photonics. To date fabrication of large-area (sq.cm) patterned and ordered mono/multilayer of bare metal nanoparticles has not been accomplished. The feasibility of forming such ordered and patterned arrays of bare gold nanoparticles, upon technologically relevant hard and soft substrates will be investigated in this proposal. This will be achieved in two stages: 1) employing soft-lithography in combination with directed self-assembly to form ordered and patterned arrays of MPN's, 2) plasma processing to selectively remove the molecular layer coating the nanoparticles without disturbing their order. Finally, the ability of such bare nanoparticle arrays to retain their local ordering at higher temperatures, critical for catalytic applications, will be studied.

213. Objectives:

1. Development of a plasma processing route for the fabrication of uniform, patterned, and ordered arrays of bare gold nanoparticle mono/multilayers from MPN arrays.
2. Optimization of plasma parameters using spectroscopic characterization of the rate of removal of alkanethiol monolayers from the surface of gold nanoparticles.
3. Thermal stability analysis of bare gold nanoparticle arrays on various substrates.

220. Review of status of Research and Development in the subject (Metal Nanoparticle Arrays)

The following is a list of general reviews regarding the fabrication of nanoparticle arrays and their applications.

1. Collier, C. P.; Vossmeier, V.; Heath, J. R. *Annu. Rev. Phys. Chem.* 1998, 49, 371.
2. Murray, C. B.; Kagan, C. R.; Bawendi, M. *Annu. Rev. Mater. Sci.* 2000, 30, 545.
3. Rao, C.N.R.; Kulkarni, G. U.; Thomas, P. J.; Edwards, P. P. *Chem. Soc. Rev.*, 2000, 29, 27.
4. Shipway, A.N.; Willner, I. *ChemComm.*, 2001, 2035.
5. Fendler, J. H.; *Chem. Mater.*, 2001, 13, 3196.

6. Maenosono, S.; Okubo, T.; Yamaguchi, Y. *J. Nanopar. Res.*, 2003, 5, 5.
7. Santhanam, V.; Andres, R.P. *The Dekker Encyclopedia of Nanoscience and Nanotechnology*, Eds. J.A. Schwarz, C. Contescu, K. Putyera, Marcel Dekker Inc., New York, 2004, 1829.

221. International status:

The preliminary work on forming nanoparticle arrays were based on island formation during the early stages of thin film deposition and resulted in a wide distribution of island sizes and also in a random disordered arrangement of these islands. Such substrates were ideal for studying the physics of quantum dots such as coulomb charging [1] and have also been recently used to catalyze the growth of semiconductor nanowires [2]. Recently, efforts have been made to generate beams of bare metal nanoparticles in an aerosol reactor and form patterned arrays by depositing it onto a FIB (Focused Ion Beam) or e-beam templated graphite substrate [3]. However, such aerosol deposition techniques have not yet been able to form large-area monolayer arrays of metal nanoparticles with reliable ordering. The ability to form such ordered arrays using parallel processes on technologically relevant semiconductor substrates is critical for proposed applications in nanoelectronics, photonics and plastic electronics [4].

Self-assembly provides an attractive alternative parallel-processing route from solution phase to achieve this goal. In order to facilitate solution processing and prevent agglomeration such metal nanoparticles are typically encapsulated by a monolayer of surfactant molecules. To date there have been several techniques pursued for fabricating large-scale ordered monolayer protected nanoparticle arrays by self assembly. These predominantly fall into four categories; 1) Self-assembly on a solid substrate; this includes drop-casting [5] and spin coating [6], 2) Self-assembly at a fluid interface; in a Langmuir trough [7], at a water-organic interface [8], 3) Templated synthesis with pores or nucleation sites forming a 2D lattice; inorganic porous membranes [9], biological substrates [10], and self-assembled latex colloidal crystals [11] have been used as templates for in-situ reduction or shadow evaporation of metals, and 4) Field-enhanced deposition or molecular interaction aided equilibrium deposition onto solid substrates; this includes electrophoretic deposition [12], ultrasonic rearrangement [13], and layer by layer epitaxial methods [14]. All these techniques have been successful in establishing self-assembly as an attractive tool for assembling nanoscale objects, but they all suffer from some or all of the following disadvantages: inability to reproducibly form an uniform macroscopic scale array, inability to form an uniform multilayer, inability to scale-up, and the large time scales involved in the fabrication.

Recently, a directed self-assembly scheme was developed that allows for the fabrication of large-area ordered monolayer and multilayer arrays of alkanethiol encapsulated gold nanoparticles on a water surface [15]. The arrays that are floating on the water surface have also been successfully transferred as patterned thin films onto desired solid substrates by using soft-lithographic techniques [16].

1. B-Sadeh, E.; Goldstein, Y.; Zhang, C.; Deng, H.; Abeles, B.; Millo, O. *Phys. Rev. B*, 1994, 50, 8961.
2. Law, M.; Goldberger, J.; Yang, P. *Annu. Rev. Mater. Res.* 2004, 34, 83.
3. Perez, A.; Bardotti, L.; Prevel, B.; Jensen, P.; Treilleux, M.; Melinon, P.; Gierak, J.; Faini, G.; Mailly, D. *New J. Phys.* 2002, 4, 76.1.
4. (a) Andres, R. P.; Averback, R. S.; Brown, W. L.; Brus, L. E.; Goddard III, W. A.; Kaldor, A.; Louie, S. G.; Moscovits, M.; Peercy, P. S.; Riley, S. J.; Siegel, R. W.; Spaepen, F.; Wang, Y. J.

- Mater. Res.* 1989, 4, 704. (b) Schön, G.; Simon, U. *Colloid Polym. Sci.* 1995, 273, 202. (c) Roychowdhury, V. P.; Janes, D. B.; Bandyopadhyay, S. *Proc. IEEE.* 1997, 85, 574. (e) Iannaccone, G.; Coli, P. *Appl. Phys. Lett.* 2001, 78, 2046.
5. (a) Huang, S.; Sakaue, H.; Shingubara, S.; Takahagi, T. *Jpn. J. Appl. Phys.* 1998, 37, 7198. (b) Schmid, G.; Bäuml, M.; Beyer, N. *Angew. Chem. Int. Ed.* 2000, 39, 181. (c) Murray, C. B.; Sun, S.; Gaschler, W.; Doyle, H.; Betley, T. A.; Kagan, C. A. *IBM J. Res. & Dev.* 2001, 45, 47. (d) Lin, X. M.; Jaeger, H. M.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B.* 2001, 105, 3353.
 6. Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science.* 1996, 273, 1690.
 7. (a) Lee, W. Y.; Hostetler, M. J.; Murray, R. W.; Majda, M. *Isr. J. Chem.* 1997, 37, 213. (b) Bourgoïn, J. P.; Kergueris, C.; Lefevre, E.; Palacin, S. *Thin Solid Films.* 1998, 329, 515. (c) Markovich, G.; Collier, C. P.; Henrichs, S. E.; Remacle, F.; Levine, R. D.; Heath, J. R. *Acc. Chem. Res.* 1999, 32, 415. (d) Huang, S.; Tsutsui, G.; Sakaue, H.; Shingubara, S.; Takahagi, T. *J. Vac. Sci. Technol. B.* 2001, 19, 115. (e) Chen, S. *Langmuir.* 2001, 17, 2878. (f) Brown, J. J.; Porter, J. A.; Daghlán, C. P.; Gibson, U. J. *Langmuir.* 2001, 17, 7966.
 8. (a) Schmid, G.; Beyer, N. *Eur. J. Inorg. Chem.* 2000, 835. (b) Sawitowski, T.; Franzka, S.; Beyer, N.; Levering, M.; Schmid, G. *Adv. Funct. Mater.* 2001, 11, 169. (c) Šloufová-Srnová, I.; Vlčková, B. *Nano Lett.* 2002, 2, 121.
 9. (a) Winningham, T. A.; Gillis, H. P.; Choutov, D. A.; Martin, K. P.; Moore, J. T.; Douglas, K. *Surf. Sci.* 1998, 406, 221. (b) Sawitowski, T.; Miquel, Y.; Heilmann, A.; Schmid, G. *Adv. Funct. Mater.* 2001, 11, 435. (c) Besson, S.; Gacoin, T.; Ricolleau, C.; Jacquiod, C.; Boilot, J. - P. *Nano Lett.* 2002, 2, 409.
 10. (a) Pum, D.; Sleytr, U. B. *Trends Biotechnol.* 1999, 17, 8. (b) Yamashita, I. *Thin Solid Films.* 2001, 393, 12. (c) Lee, S. -W.; Mao, C.; Flynn, C. E.; Belcher, A. M. *Science.* 2002, 296, 892.
 11. (a) Hulteen, J. C.; Van Duyne, R. P. *J. Vac. Sci. Technol. A.* 1995, 13, 1553. (b) Tessier, P. M.; Velev, O. D.; Kalambur, A. T.; Lenhoff, A. M.; Rabolt, J. F.; Kaler, E. W. *Adv. Mater.* 2001, 13, 396. (c) Han, S.; Shi, X.; Zhou, F. *Nano. Lett.* 2002, 2, 97.
 12. (a) Giersig, M.; Mulvaney, P. *Langmuir.* 1993, 9, 3408. (b) Bailey, R. C.; Stevenson, K. J.; Hupp, J. T. *Adv. Mater.* 2000, 12, 1930.
 13. Sasaki, M.; Hane, K. *J. Appl. Phys.* 1996, 80, 5427.
 14. (a) Grabar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D.; Natan, M. J. *Langmuir.* 1996, 12, 2353. (b) Schmid, G.; Peschel, S.; Sawitowski, T. *Z. Anorg. Allg. Chem.* 1997, 623, 719. (c) Sato, T.; Brown, D.; Johnson, B. F. G. *Chem. Commun.* 1997, 1007. (d) Okamoto, T.; Yamaguchi, I.; Kobayashi, T. *Opt. Lett.* 2000, 25, 372. (e) He, H. X.; Zhang, H.; Li, Q. G.; Zhu, T.; Li, S. F. Y.; Liu, Z. F. *Langmuir.* 2000, 16, 3846.
 15. Santhanam, V.; Liu, J.; Agarwal, R.; Andres, R. P. *Langmuir* 2003, 19, 7881.
 16. Santhanam, V.; Andres, R. P. *Nanolett.* 2004, 4, 41.

222. National status:

The use of reconstructed alumina surfaces having regular ridges as templates to produce ordered metal nanoparticle decorated surfaces using aerosol deposition techniques is being actively pursued at IISc [1]. The chemistry and physics of materials unit at JNCASR has been involved in self-assembly of metal nanoparticles at the interface of two liquids and also utilized dip-pen methods to form patterned arrays of metal nanocrystals [2]. The nanomaterials science

and technology group at NCL, Pune is also involved in assembling nanoparticles at the liquid-air interfaces and in thermally evaporated lipid matrices [3].

1. Ravishankar, N.; Carter, C. B. *J. Mater. Res.* 2002, 17, 98.
2. (a) Rao, C. N. R.; Kulkarni, G. U.; Thomas, P. J.; Agarwal, V. V.; Saravanan, P. *J. Phys. Chem. B*, 2003, 107, 7391. (b) Thomas, P. J.; Kulkarni, G. U.; Rao, C. N. R. *J. Mater. Chem.*, 2004, 14, 625.
3. Mandal, S.; Sainkar, S. R.; Sastry, M. *Nanotech.*, 2001, 12, 358.

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

This proposal aims to form large-area patterned and ordered gold nanoparticle mono/multilayer arrays on semiconductor or plastic substrates. Such arrays have not yet been fabricated in a reliable, robust and scalable process. Patterned and ordered bare metal nanoparticle arrays provide an excellent platform for fabricating multi-spectral bio/chem sensors by using appropriate bridging molecules and for catalyzing the growth of size-controlled vertically ordered semiconductor nanowire arrays (see figure 1). Presently, several devices such as diodes, transistors, lasers, and sensors have been demonstrated using individual carbon nanotubes and semiconductor nanowires made of different materials. These demonstrations have led to the hope that vertically aligned semiconductor nanowires will find use in applications that enhance the quality of life such as cheap household lighting devices, efficient solar energy conversion, and future nanophotonic and electronic devices.

An important hurdle facing development of these devices for practical applications is the need to arrange individual nanotubes/nanowires into densely packed ordered and electrically addressable architectures. In order to incorporate nanowires into functional architectures, a two-step approach is predominant in current practice. It consists of nanowire synthesis followed by dispersion in suitable solvents, which is then used to form arrays via fluidic self-assembly, microcontact printing or in Langmuir troughs resulting in arrays that lie flat on the final substrate. This approach surrenders the miniaturization advantage of the nanowires as its ultimate pitch will be determined by the size of the contacts used to address them and it also fails to utilize the third dimension. The bare and immobilised metal nanoparticle arrays proposed in the current project is a promising step towards circumventing these issues as it can not only catalyse the growth of a patterned, ordered array of uniform-size semiconductor nanowires but also provide individual electrical contacts to each nanowire by dint of the gold nanoparticle that remains on top of the nanowire grown by the VLS mechanism.

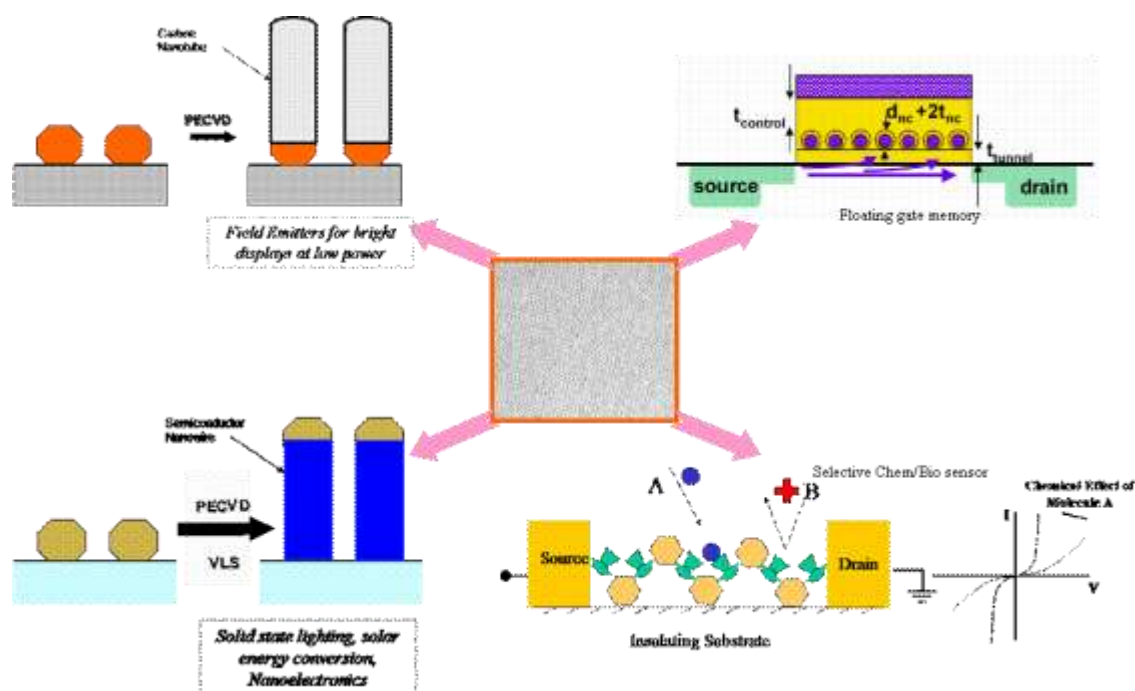


Figure 1. Schematic illustration of the potential applications of patterned and ordered arrays of metal nanoparticles.

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

The principal investigator developed a robust and scalable process to form patterned and ordered MPN arrays on any desired substrate by combining directed self-assembly and soft-lithographic techniques during his dissertation. This will be the basis for fabricating the proposed bare gold nanoparticle pattern in the PI's research group being set-up in the department of chemical engineering. Apart from this, the PI has experience in using a plasma etcher and forming molecular self-assembled monolayers during his post-doctoral research.

225. Patent details (domestic and international)

1. R. P. Andres, V. Santhanam, R. Agarwal, 'Fabrication of nanoparticle arrays', W.O. Patent-Pending, PCT # WO 2005015792.
2. G. Schmid, U. Simon, D. Jaeger, V. Santhanam, "Microelectronic component", Patent-Pending, Application no: US 2005218394.

230. Work plan

231. Methodology

Size-selected alkanethiol 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 and then stamped onto any desired solid substrate (silicon/quartz die) by conformal contact with the elastomeric stamp (see figure 2).

This array is then placed in Oxygen/Hydrogen plasma operating under low power conditions in order to break the alkanethiol segments whilst immobilising the particles to prevent agglomeration that has been observed upon thermal treatment of MPN arrays. This approach is based on preliminary experimental results from my dissertation that indicated a substantial decrease in alkanethiol coverage upon oxygen plasma treatment, although particle agglomeration could not be prevented due to the limitations on reducing plasma energy. The confidence in achieving the objective at lower plasma energies stem from recently published results [1] on the effects of low energy electron beam scanning upon self-assembled MPN arrays and [2] the use of low energy Hydrogen/Oxygen plasma to facilitate the deposition of gold nanoparticles from a thin film of di-block copolymer and nanoparticles. These results indicate that organic molecules coating the nanoparticles can be removed without disturbing the local ordering of the metal nanoparticles or inducing agglomeration, if the energy dose is low.

The development of a plasma route will provide for the more technologically appealing parallel processing route as compared to serial electron beam processing techniques in order to achieve this objective. Plasma processing parameters like RF input power, operating pressure and gas composition affect key plasma properties such as ion bombardment energy and ion concentration, which in turn will determine the rate of removal of organic coating, the anisotropic character of the plasma and more importantly the energy imparted to the nanoparticle monolayer. These parameters along with the processing time will be varied systematically and their effects on the nanoparticle monolayer studied by using TEM and spectroscopic characterization tools. This will provide the basis for finding the optimum operating conditions for removal of alkanethiol coating without disturbing the nanoparticle order.

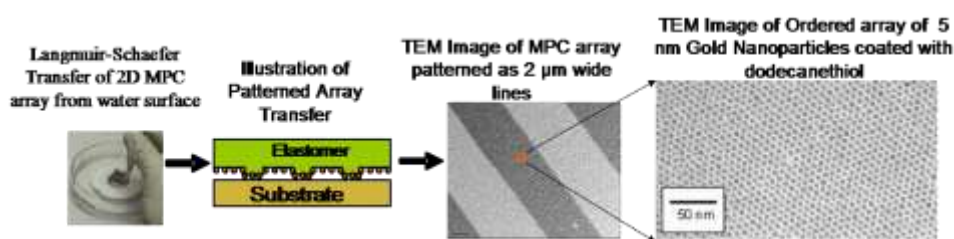


Figure 2. Illustration of process for forming Patterned 2D array of MPC's (Average particle size of 5 nm)

The thermal stability of the local ordering of such plasma processed nanoparticle arrays will be studied and a maximum processing temperature found for further applications as catalysts. If higher operating temperatures are desired then the nanoparticle arrays will be printed onto a thiol-terminated silane SAM [2] to enable better adhesion to the substrate and limit lateral mobility of the nanoparticles upon heating.

(1) (a) Lin, X. M.; Parthasarathy, R.; Jaeger H. M. *Appl. Phys. Lett.*, **2001**, 78, 1915. (b) Werts, M. H.V.; Lambert, M.; Bourgoin, J.-P.; Brust, M.; *Nano Lett.* **2002**, 2, 43-47.

(2) Mizuno, M.; Sasaki, Y.; Yu, C. C. A.; Inoue, M. *Langmuir*, **2004**, 20, 11305.

232. Organisation of work elements

Technical work elements:-

- Colloid synthesis and size-selective precipitation.
- Particle size analysis.
- Array formation.
- Plasma processing.
- Thermal stability analysis.
- TEM characterization of arrays.

Administrative work elements:-

- Selection of equipment and processing purchase order.
- Fabrication and installation of RIE equipment.

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 -- 1 month after sanction of funds. I have already made enquiries regarding the availability of plasma etchers and obtained quotes for the same from both Indian and foreign manufacturers. The only Indian company able to fabricate and demonstrate a RIE system is Milman thin film systems, Pune. The other manufacturers are outside India and their quoted values are more than double the Indian manufacturer for similar configurations. Also, the quality of the Indian manufacture has been vouched for by the personnel at FCIPT, the industrial affiliate of IPR, Gandhinagar. Therefore, this equipment will be purchased from Milman thin film systems, Pune and it will require about 1 month to process the purchase order after DST approval.
- Fabrication and Installation of Plasma equipment:- Time required — 9 months. Based on preliminary enquiries, it takes about 6-7 months for Milman to assemble plasma equipment built to my specifications. The additional two months will facilitate the transportation, installation and start-up of the equipment in my lab at IISc.
- Colloid Synthesis and Size-selective Precipitation:- Time span – 1-30 months. This is not a continuous activity, but will be performed as and when required to synthesize arrays. Based on my previous experience, about two weeks of synthesis and size-selection experiments can sustain the fabrication of about 12-18 arrays and subsequent experimentation (typically a 2-3 month activity).
- Particle size analysis:- Time span – 2-31 months. This is typically done subsequent to colloid synthesis by drop casting solutions on TEM grids and analysing their sizes. I also plan to utilize the Dynamic Light Scattering (DLS) instrument available in the chemical engineering department to analyse the colloid and provide for more rapid size distributions.

- **Array Formation:-** Time span – 6-32 months. The formation of array requires the fabrication of an experimental cell made of Teflon disks. This will take a few months. After that, arrays can be formed as and when required for experimentation.
- **Plasma Processing:-** Time span – 10 - 34 months. This is the most important work element of this proposal and entails knowledge generation by systematic experimentation to optimize power, density and other operating parameters of the plasma process to selectively remove the organic coating without disturbing local nanoparticle ordering.
- **Thermal Stability Analysis:-** Time span – 20-35 months. This is the next crucial step of this proposal. Tentatively, I expect that plasma processing will be optimized after about 10 months of research and I plan to check for thermal stability after this. Probably, there will be a need to find alternative routes like utilising additional SAM layer to improve adhesion of the nanoparticles with the substrate. Then there will be a feedback into the plasma processing step to optimize the conditions.
- **TEM characterization of Arrays:-** Time span – 6-36 months. This is a continuous characterization effort as this is the principal diagnostic tool to characterize the local ordering of nanoparticles within the array before and after various treatments. Some spectroscopic characterizations will be performed to ascertain the removal of alkanes.

Important Milestones:-

1. Installation of the plasma equipment (1st year).
2. Fabrication of bare nanoparticle arrays (2nd year).
3. Determination of maximum processing temperature (3rd year).

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

The successful development of the plasma processing route is a patentable discovery as it will be the first time large-area patterned and ordered bare metal nanoparticle arrays would be fabricated and also as it is an important step towards producing functional nanoscale architectures involving nanoparticles and subsequently nanowires. The results of this project will also be submitted to reputed journals in the field to help disseminate this information.

Generally, these results should be of interest to persons involved in nanodevices and sensors, specifically those interested in studying electron transport in ordered systems, those involved in the field of molecular and nanoelectronics, and those working on alternative architectures for replacing current VLSI style design.

300. BUDGET ESTIMATES: SUMMARY

	Item	BUDGET			(in Rupees)
		1st Year	2nd Year	3rd Year	Total
A.	Recurring				
	1.Salaries/wages	1,20,000	1,20,000	1,20,000	3,60,000

	2. Consumables	Rs.50,000	Rs.50,000	Rs.50,000	Rs. 1,50,000
	3. Travel	Rs. 50,000	Rs. 20,000	Rs. 20,000	Rs. 90,000
	4. Other costs	Rs. 1,00,000	Rs. 50,000	0	Rs. 1,50,000
B.	Equipment	Rs. 38,00,000	0	0	Rs. 38,00,000
C.	Institute overhead @ 20%	Rs. 8,24,000	Rs. 48,000	Rs. 38,000	Rs. 9,10,000
	Grand total (A+B) Total FEC*	Rs. 49,44,000 (\$750)	Rs. 2,88,000	Rs.2,28,000	Rs. 54,60,000 (\$750)

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.10,000	Rs. 1,20,000 (12)	Rs. 1,20,000 (12)	Rs. 1,20,000 (12)	Rs. 3,60,000 (36)
Total	Rs.10,000	Rs. 1,20,000 (12)	Rs. 1,20,000 (12)	Rs. 1,20,000 (12)	Rs. 3,60,000 (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 RIE facility.

320. BUDGET FOR CONSUMABLE MATERIALS

		BUDGET	(in Rupees)
--	--	--------	-------------

Item		1 st Year	2nd Year	3rd Year	Total
Silicon Nitride Membrane windows	Q*	50 nos.	0	0	
	B**	Rs. 33,000	0	0	Rs. 33,000
	F***	\$750	0	0	
General TEM consumables eg. Gloves, Tweezers, Carbon grids, and Gas supplies for Plasma system	Q*				
	B**	Rs. 17,000	Rs. 50,000	Rs. 50,000	Rs. 1,17,000
	F***				
Total	B	Rs. 50,000	Rs. 50,000	Rs. 50,000	Rs. 1,50,000
	F	\$750	0	0	\$750

***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)

Silicon nitride membrane window grids are required for TEM characterization of plasma/thermal processing upon micro-contact printed (μ cp) arrays, as normal grids using carbon thin films are easily damaged upon contact with the stamp. The number requested is an estimate based on previous experience with process optimization for chemical exchange on arrays. They are all being shipped directly from USA at one time to save on shipping costs and also direct shipment using foreign currency is cheaper than procuring it from local redistributors using Indian currency by about 60-70%.

330. BUDGET FOR TRAVEL

		BUDGET			(in Rupees)
Reason		1st Year	2nd Year	3rd Year	Total
To attend monitoring meetings.	Travel (Only inland travel)	Rs.50,000	Rs.20,000	Rs.20,000	Rs.90,000

331. Justification for intensive travel, if any. – During the first year travel to the manufacturer's site is needed for inspection of components and also for training and that is the reason for a higher budget in the first year.

340. BUDGET FOR OTHER COSTS/CONTINGENCIES

		BUDGET			(in Rupees)
Reason		1st Year	2nd Year	3rd Year	Total
To cover cost/tax fluctuations	Other costs/Contingency costs	Rs.1,00,000	Rs.50,000	0	Rs.1,50,000

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 (in Foreign Currency also)*	Spare time for other users (in %)
1	Reactive etching system, Milman - M-RIE-1A [s]	Indigenous manufacturer (Milman thin film systems)	Rs.38,00,000	50%

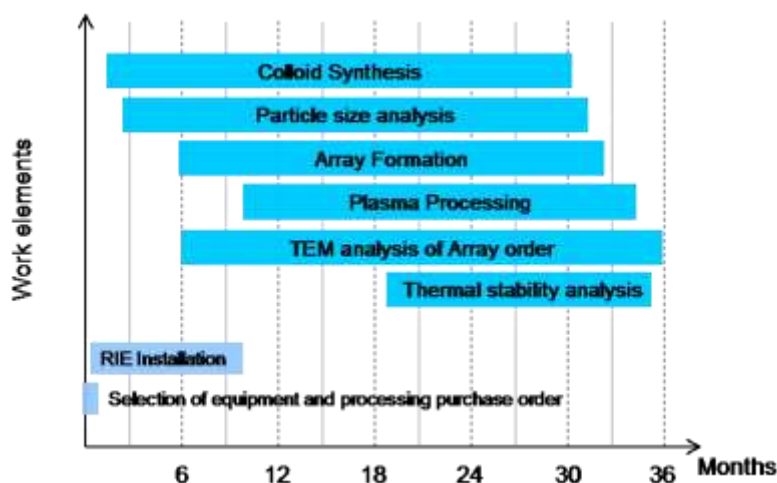
*** includes transport, insurance and installation charges.**

351. Justification for the proposed equipment.

The proposed plasma etching system is the critical component of this proposal. It provides the ability to control the RF power input into the system, while allowing variability in the gas density, composition and time of etching. This system provides a range of RF input power from 1-300 Watts at 13.56 MHz frequency with automatic matching to reduce RF reflection and operating pressures of 1-100 Pa. It has mass flow controllers on input gas lines, water cooled substrate holders and appropriate safety interlocks. Plasma etching of the organic

monolayer is one way of introducing energy (by accelerated species present in the plasma) into the system to break the chemical bonds without significant temperature increase. Also, this processing cannot be done in typical barrel etchers used for stripping photoresist as they are limited in their operating parameters for input power, substrate cooling etc.

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



- *Selection of equipment and processing of purchase order:* - Time required -- Time required -- 1 month after sanction of funds. I have already made enquiries regarding the availability of plasma etchers and obtained quotes for the same from both Indian and foreign manufacturers. The only Indian company able to fabricate and demonstrate a RIE system is Milman thin film systems, Pune. The other manufacturers are outside India and their quoted values are more than double the Indian manufacturer for similar configurations. Also, the quality of the Indian manufacture has been vouched for by the personnel at FCIPT, the industrial affiliate of IPR, Gandhinagar. Therefore, this equipment will be purchased from Milman thin film systems, Pune and it will require about 1 month to process the purchase order after DST approval.
- *Fabrication and Installation of Plasma equipment:-* Time required — 9 months. Based on preliminary enquiries, it takes about 6-7 months for Milman to assemble plasma equipment built to my specifications. The additional two months will facilitate the transportation, installation and start-up of the equipment in my lab at IISc.
- *Colloid Synthesis and Size-selective Precipitation:-* Time span – 1-30 months. This is not a continuous activity, but will be performed as and when required to synthesize arrays. Based on my previous experience, about two weeks of synthesis and size-selection experiments can sustain the fabrication of about 12-18 arrays and subsequent experimentation (typically a 2-3 month activity).
- *Particle size analysis:-* Time span – 2-31 months. This is typically done subsequent to colloid synthesis by drop casting solutions on TEM grids and analysing their sizes. I also plan to utilize the Dynamic Light Scattering (DLS) instrument available in the chemical

engineering department to analyse the colloid and provide for more rapid size distributions.

- *Array Formation:-* Time span – 6-32 months. The formation of array requires the fabrication of an experimental cell made of Teflon disks. This will take a few months. After that arrays can be formed as and when required for experimentation.
- *Plasma Processing:-* Time span – 10 - 34 months. This is the most important work element of this proposal and entails knowledge generation by systematic experimentation to optimize power, density and other operating parameters of the plasma process to selectively remove the organic coating without disturbing local nanoparticle ordering.
- *Thermal Stability Analysis:-* Time span – 20-35 months. This is the next crucial step of this proposal. Tentatively, I expect that plasma processing will be optimized after about 10 months of research and I plan to check for thermal stability after this. Probably, there will be a need to find alternative routes like utilising additional SAM layer to improve adhesion of the nanoparticles with the substrate. Then there will be a feedback into the plasma processing step to optimize the conditions.
- *TEM characterization of Arrays:-* Time span – 6-36 months. This is a continuous characterization effort as this is the principal diagnostic tool to characterize the local ordering of nanoparticles within the array before and after various treatments. Some spectroscopic characterizations will be performed to ascertain the removal of alkanes.

Important Milestones:-

- 1) Installation of the plasma equipment (1st year).
- 2) Fabrication of bare nanoparticle arrays (2nd year).
- 3) Determination of maximum processing temperature (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	TEM characterization at IISc

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			
PI's Department	DLS-Particle size measurement	Brookhaven, Goniometer based, 2003	Typically used for micelle size determination
	UV-Vis Spectrophotometer	Shimadzu, 2002	Typically used for concentration measurement
IISc	TEM	Tecnai F-30 300 kV , FEI, 2004	Central user facility being set-up as part of IISc Nanoinitiative

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.
Advisor: Prof. Ronald P. Andres GPA: 4.00/4.00

M.S. Chemical Engineering, Louisiana State University, December 1998.
Thesis: OH PLIF Imaging of Swirl-Stabilized Combustor.
Advisor: Prof. Carl F. Knopf GPA: 3.9/4.00

B.Tech. (Hons.) Chemical Engineering, IIT-Kharagpur, June 1996.
Thesis: Scrubbing of Diesel Fumes Using an Ejecto-Venturi Fume Scrubber.
Advisor: Prof. M. N. Biswas GPA: 8.49/10.00

RESEARCH EXPERIENCE

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

- ❖ Developed a novel process utilizing selective wet etching of MBE grown GaAs/AlAs heterostructure and NanoImprintLithography to fabricate 5-20 nm wide embedded metal lines for electrically addressing 1 & 2-Dimensional arrangements of quantum dots.

Graduate Research Assistant, August 1998-December 2002, Purdue University.

- ❖ Designed and developed an apparatus to produce large area ordered 2-D gold nanocrystal superlattices for use in nanoelectronic device fabrication.
- ❖ Developed a scalable, additive, parallel process using 'soft' lithography to form patterned ordered arrays of gold nanoclusters for use in device fabrication, and patterned substrates for binding biologically active molecules.
- ❖ Synthesized gold nanocrystals in an aerosol reactor for crystal structure determination using HRTEM and developed a model for the production of non-stoichiometric bimetallic clusters.

Graduate Research Assistant, August 1996-July 1998, Louisiana State University.

- ❖ Implemented a Planar Laser Induced Fluorescence (PLIF) imaging set-up for detection of coherent flame structures in a swirl-stabilized spray combustor.
- ❖ Developed a calibration unit for quantifying OH radical mole fraction using PLIF data.

PATENTS

- ❖ R. P. Andres, V. Santhanam, R. Agarwal, 'Fabrication of nanoparticle arrays', W.O. Patent-Pending, PCT # WO 2005015792.
- ❖ G. Schmid, U. Simon, D. Jaeger, V. Santhanam, "Microelectronic component", Patent-Pending, Application no: US 2005218394.

PUBLICATIONS

- ❖ V. Santhanam and R.P. Andres, "Microcontact Printing of Uniform Nanoparticle Arrays", Nanoletters, Vol.4 (1), Jan 14th 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), Sep 15th 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), Jul-Aug 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.

431. Detailed Bio-data of the Co-Investigator

Name: Sanjeev Kumar Gupta

Contact Information:

Associate Professor,
 Department of Chemical Engineering,
 Indian Institute of Science,
 Bangalore, India-560012.
 e-mail: sanjeev@chemeng.iisc.ernet.in
 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

- ❖ Singh, Reetu and Sanjeev Kumar, 2005, Effect of Mixing on Nanoparticle Formation in Micellar Route, *Chem. Engg. Sci.* in press
- ❖ Tulasi, G.L, Sanjeev Kumar, 2005, Aggregation vs. Breakup of the Organic Phase Complex, *Hydrometallurgy* in press.
- ❖ Sailaja, D., K. L. Suhasini, Sanjeev Kumar and K. S. Gandhi, 2003, Role of micelles in solubilization into surfactant solutions *Langmuir* **19**, 4014-4026.
- ❖ Singh, Reetu, M. Durairaj and Sanjeev Kumar, 2003, An Accelerated Monte-Carlo Technique For Simulation of Nanoparticles, *Langmuir* **19**, 6317-6328.

- ❖ Deshpande, Kiran and Sanjeev Kumar, 2003, A New Characteristic of Liquid-Liquid Systems-Inversion Holdup of Intensely Agitated Dispersions, *Chern. Engg. Sci.* 58, 3829-3835.
- ❖ Rajganes, P.S., B. Chanda, S. K Gupta, M. K Mathew, and J. Chandrasekhar, 2000, Modelling of ion permeation in calcium and sodium channel selectivity filters, *Proteins: Structure, Function & Genetics* 38 384-92.
- ❖ 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.
- ❖ Tulasi, G.L, Sanjeev Kumar, 1999, Amino-acid extraction using D2EHPA: New description of equilibrium behaviour, *AI.Ch.E. Jouna*145, 2534-2541.
- ❖ Sanjeev Kumar, S. Srinivas, R. Kumar and K.S. Gandhi, 1998, Alternative mechanisms of drop breakage in stirred vessels, *Chern. Engng. Sci.* 53,3269-3280.
- ❖ Sanjeev Kumar and D. Ramkrishna, 1997, Reply to comments 'On the maximum stable drop diameter in stirred liquid-liquid dispersions', *AI.Ch.E. J.*, 43,1374.
- ❖ 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, *IE&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/O 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.
- ❖ Sanjeev Kumar, R. Kumar and K S. Gandhi, 1993, A simplified procedure to predict d_{max} in stirred vessels, *Chern. Engg. Sci.* 48, 3092-3096.
- ❖ Sanjeev Kumar, R. Kumar and K S. Gandhi, 1993, A new model for coalescence efficiency of drops in stirred vessels, *Chern. Engg. Sci.* 48,2025-2038.
- ❖ Sanjeev Kumar, R. Kumar and K S. Gandhi, 1992, A multistage model for drop breakup in stirred vessels, *Chern. Engg. Sci.* 47,971-980.
- ❖ 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.

- ❖ Saneev Kumar, 2001-2002, Recovery of Carbon Particles from Filter Media Using Liquid Liquid Dispersions, *Hindustan Lever Research Center*, Rs. 9,50,000.
- ❖ Saneev Kumar, 2001-2004, Studies on Phase Inversion in Agitated Liquid-Liquid Dispersion, *DST*, Rs. 17,90,000.
- ❖ Saneev Kumar, 2004-2007, Coalescence of drops in centrifugal extractors, *Indira Gandhi Center for Atomic Research*, Rs. 18,49,000.

500. Any other relevant matter.

The PI is currently involved in setting-up a modern laboratory, using IISc start-up funds, which will be equipped with appropriate accessories to synthesize gold nanoparticles, perform size-selective precipitation, and form large-scale ordered monolayer protected nanoparticle arrays. The civil and electrical renovation of the laboratory is scheduled to be completed by the end of March 2006.

File No** _____

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

2. Proposed Budget for 3 years:

2.1 Total: Rs.54,60,000.00

2.2 Equipment: Rs.38,00,000.00 (Reactive Ion Etcher)

2.3 Staff (proposed research staff): One (Rs. 3,60,000.00)

2.4 Other Recurring costs:

Consumable : Rs.1,50,000.00

Travel : Rs.90,000.00

Contingency : Rs.1,50,000.00

Any other expenses : Institute overhead @20%
(Rs. 9,10,000.00)

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	Coalescence of drops in centrifugal extractors	Rs. 18,49,000	3 years (2004-2007)	IGCAR