A proposal submitted to the
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Laboratory for Particle Engineering and Technology

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191. Project summary (maximum 150 words)

'Bottom-up' approach has opened new ways to control and manipulate processes in almost every discipline, including Chemical Engineering. The latter also has the opportunity to take up the role of enabling others to use 'bottom-up' approach by developing engineering level expertise to produce nanoparticles of desired sizes and polydispersity, and ordered arrays of nanoparticles. These represent the basic building blocks for many technological developments currently underway. We propose to initiate a program which takes us towards this role through the use of wet synthesis route for the synthesis of nanoparticles and evaporation induced self-assembly of nanoparticles for array formation. These energy efficient routes hold significant promise for future. The methodology adopted is to evolve quantitative understanding of the rate processes involved in the formation of these building blocks, supported by experimental explorations and concurrent validation. A novel flexible wall microchannel reactor which is excited by elecrical field to simultaneously pump and mix the reactant streams is proposed to be developed. Fixed wall microchannel reactors with optimized flow geometries, based on modelling, will also be explored. As a proof of concept of the above *bottom-up* theme, nanoparticles and their arrays produced by the robust techniques developed in this work will be used to develop a gas-sensor, capable of detecting gases at extremely low concentrations.

192. Key words (maximum 6)

nanoparticles, arrays, micrchannel reactors, mixing, gas-sensors.

200. Technical Details

210. Introduction

211. Origin of the proposal

'Bottom-up' approach is redefining and expanding scientific and technological activity in many fields. Chemical Engineering, by its broad scope and close proximity to chemistry, mathematics, and physics, is uniquely poised to make use of this development. Molecular simulations are being used to identify and design molecules for desired functionality at the macroscopic level, for example in personal and health care industry. Computational Fluid Dynamics tools are being used to design new process equipment 'from scratch' with miniaturization and process intensification as core objectives. Chemical Engineering is evolving by making inroads into emerging areas and also undergoing a paradigm shift in the areas already in its fold.

'Vision for R&D in Engineering Sciences—Chemical Engineering' document of SERC-DST (http://serc-dst.org/engineering.html#B1) also recognizes the above trends. This is evident from the inclusion of the following in the 'Areas of Focus' in this document: *Engineering of small systems* which includes the role of reverse micelles, nanoparticles and self-assembly, *Interfacial Phenomena* which includes precipitation, *Novel reactors*, and *New Modelling Tools*.

Closely tied with the above vision is the other manifestation of the 'Bottom-up' approach—*nanoscience* and *nanotechnology*. It is relevant to the Chemical Engineering community in two ways:

1. Use the capability to manipulate at nanoscale to redefine practices and standards in our current role in order to make them more conducive for the preservation of nature and its resources, and exploration of new possibilities,

2. As a *service discipline*, which is our identity since inception, enable others to play their roles in the new scenario.

The focus of the present proposal is to build capability to serve the emerging industry based on nanoscience and nanotechnology. Two bulk commodities which this emerging industry will require from others and where Chemical Engineering can play a role are: *synthesis of nanoparticles* of controlled size and poly-dispersity, and *ordered monolayers of nanoparticles*.

212. Definition of the problem

Among the many routes reported in the literature for the synthesis of nanoparticles, wet methods (using chemical salts as precursors) are gaining widespread use due to their energy

efficiency. These methods, demonstrated using small size batch systems (shake flasks), however, often fail to yield consistent product quality at the laboratory scale itself. An increase in number of applications involving nanoparticles and their ordered monolayers is expected to fuel their demand in near future. The Chemical Engineers are uniquely poised to play a key role at this stage and this proposal has three main components that can help us achieve this goal, namely—devising wet processes for engineering scale manufacture of nanoparticles of desired specification and polydispersity, developing robust processes for the formation of organized monolayers of nanoparticles, and demonstrate how the capability to manipulate the above two building blocks facilitates realization of new applications of nanoparticles in chemical engineering.

The first step required to realize the above goal is a quantitative understanding of the processes involved in nanoparticle synthesis and monolayer formation. As the particles nucleate almost instantaneously upon mixing of the reactants, the state of mixing in the vessel and the protocols followed to contact reactants play a significant role in controlling particle synthesis (also supported by the experimental data and the simulations carried out in our group).

Microchannels offer reproducible mixing of two streams albeit at low rates on account of laminar flow in channels. We propose to investigate and use in this project channels with flexible wall which can be excited using an external electric field. These channels can then be expected to pump and mix fluid streams simultaneously and reproducibly and used for nanoparticle synthesis.

Directed self-assembly of nanoparticles to form extended monolayers of particles is an attractive route (one of us was involved in the development of this technique). This process however needs to be understood quantitatively to evolve it as a robust and optimized process for controlled monolayer/multilayer formation. We propose to use this process to make nanoparticle based chemiresistive gas/vapour sensors, which use electronic nose technology. The latter refers to the ability of an array of gas/vapour sensors to analyse a molecule based on the composite electrical response of the entire sensor array, which is denoted as the analyte's 'fingerprint'. Such composite systems mimic the ability of the mammalian olfactory system to detect analytes and have garnered tremendous attention recently as they provide a cheaper, smaller, and more portable alternative to the traditional analytical tools, viz. gas chromatography, and also obviate the need for breeding and training animals to detect hazardous substances. The need for such systems spans the entire range of applications from medical diagnostics to bomb detection.

213. Objectives

In view of the foregoing, the objectives of the proposed work are to

1. develop quantitative understanding of synthesis of nanoparticles in bulk precipitation and reverse micellar routes.

2. development of flexible wall micro-channels which can mix and pump fluids simultaneously.

3. Investigate particle synthesis in rigid wall and flexible wall microchannels of various configurations to develop a robust continuous process for nanoparticle synthesis which permits control of particle size and polydispersity.

4. Quantitative understanding of formation of monolayer of particles and development of a robust process for monolayer formation.

5. Development of nanoparticle based chemiresistive gas/vapour sensor.

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

Laboratory scale synthesis of a variety of nanoparticles of different materials and composition, size, polydispersity, shape, and morphology has been reported in the literature. These have been reviewed in a number of journals [1, 2] as well as books [3]. Similar is the situation with respect to their properties and applications [4-6]. The latter range from traditional ones, such as catalysis, coloring agents (in colored glass windows), and reinforcement of rubber using carbon nano/sub-micron particles to more novel ones, such as drug delivery vehicles, hypothermic cancer therapy, contrast agents in magnetic resonance imaging and electron microscopy, magnetic and fluorescent tags in biology, solar photovoltaics, emission control in diesel vehicles, and the use of fine alumina particles for polishing semiconductor wafers. The production of organic active nanoparticles with a polymeric coating for pharmaceutical applications is also becoming increasingly important; it also counts among the nanoparticle enabled success stories [7, 8].

Nanoparticles can be manufactured either by extruding/grinding/sculpting bulk materials (top-down approach) or by initiating nucleation and growth of desired atomic precursors (bottom-up approach). The top-down approaches suffer from the following disadvantages: they are energy intensive, have a very broad particle size distribution, are limited in their capability to produce particles with diameters in the range of 1-20 nm, and can also introduce contamination due to the mechanical tools involved. The different routes for the bottom-up synthesis of inorganic nanoparticles can be classified into aerosol techniques and solution phase techniques.

Aerosol techniques [9] are based on a ‘inert gas condensation’ technique in which the desired atomic species are generated and mixed with an inert gas to achieve supersaturation and induce homogeneous and instantaneous nucleation of nanoparticles. The objective of saturating the gas phase with atomic species can be achieved through thermal evaporation using a resistive heat source, pulsed laser ablation of bulk target materials, spark discharge generation induced sputtering and ion beam induced sputtering of bulk targets, or through

the reaction of a precursor with an appropriate reducing agent in an inert gas atmosphere or within a flame or within plasma to produce the desired atomic species.

Solution techniques have undergone extraordinary developments over the last decade [10] and are currently capable of producing batch ($\sim$ few litres) quantities of a wide range of inorganic nanoparticle colloidal solutions. Typical techniques involve the reduction of inorganic salts by reducing agents either in the bulk of aqueous [11] or organic phase [12]. Another attractive route which has received significant impetus from Pileni's group [13] is based on the use of reverse micelles as microenvironments for confining nucleation and growth. It is worth pointing out here that the size of the nanoparticles however is not limited to that of the micelles before reduction, but is determined by several operating parameters such as mixing efficiency, micelle concentration etc. Presently, the particle size distributions of colloidal solutions produced by solvent techniques are comparable to, if not narrower than those produced by aerosol techniques. The mean particle size in these methods can be controlled by tuning the concentrations of the precursors and stabilizers, and more interestingly in the case of reverse micellar route by changing the size of micelles through water to surfactant mole ratio.

The main advantages of solution based techniques over aerosol based techniques are the control over the composition of multi-component systems, reduced energy demands and the increased yield. On the other hand there are increased complexities involved in sourcing appropriate inorganic salts as raw materials and in the purification of final product from reaction intermediates and other ingredients.

Recently, there have been reports on a process called *Digestive ripening* [14] that can be used for improving the monodispersity of the particles. The mechanism involved is however not clear.

Formation of arrays (monolayers) of a variety of particles has been reported in the literature [5]. The reason for a significant increase in activity in this field is the requirement of organised monolayers of particles as precursor in most of their applications. The investigations reported thus far reveal that the formation of well organised monolayers of nanoparticles is closely tied to the characteristics of nanoparticles (their poly-dispersity and stability) and the process of making monolayers. Self-assembly of particles which undergo colloidal interactions, capillary forces and Brownian motion into monolayers of particles on liquid-fluid interface has emerged as a useful technqiue which can be harnessed to develop a robust process for monolayer formation. A detailed understanding of the process is not available, and scale up the lab scale process is yet to begin in any serious way.

Electronic nose technology refers to the ability of an array of gas/vapour sensors to detect an analyte's presence in a gas mixture based on the composite electrical response of the entire sensor array. This response is denoted as the analyte's 'fingerprint'. Such sensor arrays mimic the ability of the mammalian olfactory system to detect analytes and have garnered tremendous attention recently as they provide a cheaper, smaller, and more

portable alternative to the traditional analytical tools, viz. gas chromatography. They also obviate the need for breeding and training animals to detect hazardous substances. The need for such sensor arrays spans the entire range of applications from medical diagnostics to chemical/biological warfare agent detection [15].

A variety of transduction methods have been exploited in the design of electronic sensors. They can be broadly classified under three categories: 1) Piezoelectric transducers [16] such as surface acoustic wave devices, quartz crystal microbalance (QCM), and microfabricated cantilever sensors, 2) Optical transducers [17] such as fluorescent and colorimetric devices, and 3) Chemiresistive sensors [18] such as those based on metal oxides, nanowires, carbon nanotubes, conducting polymer composites and nanoparticle films. Of these three categories, chemiresistive sensors whose conductivity changes in the presence of a vapor phase or gas analyte are more attractive for portable applications, as they require simpler instrumentation that can also be readily miniaturized.

Sensitivity, selectivity, reversibility, and multianalyte detection are important technical issues, when designing and considering the merits of a particular sensor. In this context, there are two main mechanisms by which chemiresistive gas sensors operate, namely analyte induced swelling/contraction and molecularly specific analyte binding. Of these two mechanisms, analyte induced swelling/contraction has been utilized so far in fabricating chemiresistive sensor arrays using nanoparticle films or carbon black-polymer composites [19]. The use of principal component analysis methods in conjunction with sensor arrays has alleviated some of the problems associated with multianalyte detection or detection of a single analyte in the presence of interference from other analytes using the swelling/contraction approach. However, it is successful only in classifying the analytes into broad classes. In order to achieve better selectivity and sensitivity, molecularly specific analyte binding approach coupled with an efficient transduction mechanism must be utilised.

With the above background, the rest of this section focuses on those aspects of nanoparticle synthesis, microchannels, monolayer formation, and gas sensor fabrication which are directly relevant for the present proposal.

221. International status

Modelling of synthesis of nanoparticle in well mixed systems

Synthesis of nanoparticles using bulk precipitation has been known for a long time starting with coloured ceramics to famous gold sol made by Faraday. First detailed study of nanoparticle synthesis is attributed to Turkevich et al. [11] who in 1951 made use of the then recently developed electron microscope to study the formation of gold nanoparticles. Scientific activity in the area of synthesis of nanoparticles witnessed a phenomenal increase in the late eighties and early nineties with three nearly simultaneous developments: gas phase synthesis of clusters of atoms, use of reverse micelles as micro-reactors, and

synthesis of ligand stabilized and protected clusters which can even be dried and kept as powder. Since then, synthesis of nanoparticles of a large variety of metals, semiconductors, and inorganic materials has been reported. Focus over these years has remained on synthesis. As a result, the mechanism of formation of nanoparticles and an understanding of the dynamic processes involved which should permit control and optimization of synthesis processes are beginning to be explored only in the recent past.

Reverse micellar route has been used to synthesize nanoparticle at laboratory scale (in well mixed small flasks) for about two decades [13, 25-28]. The experimental work geared towards the synthesis of calcium carbonate, calcium hydroxide [22-24], and lead sulfide [25] particles has also been modeled quite extensively. Two broad modelling approaches are available. They incorporate the same physical processes but with different simulation strategies. The system in one case is simulated by solving mean field population balance equations and in the other by using kinetic Monte-Carlo simulations.

Population balance models have been developed for several systems [29-35] in the literature. These models require number balance equations to be written for the variation of number of micelles of various types. The rate limiting steps in these models are taken to be fusion-fission of micelles which brings reactants together for supersaturation to build up. Nucleation within the micelles is considered to occur at a finite rate. Thus, a micelle, loaded with the required number of atoms, more than the minimum required to form a stable nucleus, can dissipate its supersaturation if it fuses with an unloaded micelle. Growth of already formed particles is taken to occur instantaneously. As detailed models accounting for population of a large type of micelles become too complex to handle, Poisson distribution is often assumed to simplify these equations. Detailed Monte-Carlo have been carried out to examine this assumption [34, 36], and it is found to be valid.

Population balance models are difficult to formulate but computationally efficient. They alone can be used for model based control strategies for controlling reactors for nanoparticle synthesis. Furthermore, this approach can be easily combined with the models for finite rate of mixing in reactors to study the effect of mixing on nanoparticle synthesis. First such model has been reported recently [36]. It predicts that the rate of mixing (agitation speed) affects particle synthesis in reverse micellar route significantly.

Monte-Carlo simulations, in comparison, are extremely simple to formulate and do not suffer from any assumptions that mean field equations implicitly make. Thus, the latter have a natural advantage for small population systems. Entirely Monte-Carlo simulation based models have also been reported in the literature [37-42].

The above models need two critical inputs: rate of nucleation in confined micelles and rate of fusion of reverse micelles. The latter is characterized through fusion efficiency, which when multiplied with Brownian collision frequency between the micelles yields rate of fusion of various micelle populations. Independent measurements of fusion efficiency have been reported using stopped flow apparatus, but only for just a very few surfactants.

There is a need to develop strategies to obtain these inputs so as to make these models completely predictive in nature.

Recently, a detailed model, first of its kind, for the synthesis of gold nanoparticles using bulk precipitation method of Turkevich et al. [11] has also been reported from our group [43]. The model successfully explains the steep dependence of particle size on precursor concentration in the low concentration range and very weak dependence at high concentration range. The model shows that contrary to expectations, the reason for this interesting behavior is the rapid degradation of di-carboxy acetone which brings gold atoms together before nucleation can occur.

Scaleup of nanoparticle synthesis processes

A few studies on scaleup of synthesis of nanoparticles have appeared in the recent past. The normal bench-top synthesis of manganese zinc ferrite (MZFO) nanoparticles using the reverse micellar route has been scaled by a factor of 40 and successfully adapted to a 30-L pilot plant [44]. While the product of this synthesis is similar to the bench-top sample, the primary difference in going from the bench-top level to the pilot-plant level lies in the clean-up time. It takes a total time of at least 2 days from initial mixing to the dried powder in the scaled up version, whereas in the bench-top mode, the total time required is just 4 hours.

Continuous mode synthesis is clearly a better option and since synthesis is normally carried out using small volumes of liquids (due to the problems associated with contamination and reproducibility), capillary tube reactors and microchannel reactors are being explored in the literature. Silver nanoparticles have been synthesized [45] in a continuous flow tubular microreactor using silver pentafluoropropionate as a single-phase reactant precursor. This is the simplest possible route to the formation of nanoparticles as product is formed by thermal reduction and no mixing of reactants is required for the reaction to occur. Finite rate of mixing in tubular flow thus affects only the competition between nucleation and particle growth processes. The same study reports that an increase in flow rate from 0.1 to 0.7 ml/min (a reduction in residence time from 60 to 6 seconds) results in an increase in particle size from 70 to 130 nm. The report however does not comment on the yield of the nanoparticles. It is therefore difficult to conclude whether dispersion in residence time or the availability of more precursor has caused such a significant increase in particle size with an increase in flow rate. The particles formed are claimed to be quite monodispersed though.

Synthesis processes that require chemical reaction between precursors, for example the synthesis of cadmium selenide and titanium oxide, have also been carried out in microfluidic channels. Normally a mixing element is required as the mixing of reactant streams is diffusion controlled and the reaction itself does not occur uniformly in the reactor. This leads to non-uniform buildup of supersaturation and hence non-uniform nucleation. To

overcome theses issues, Wagner et al. [46] seeded their reaction system for citrate method of gold particle synthesis with nanoparticles. However, the final particles obtained were polydisperse.

Experimental investigations with reaction being confined to droplets in microchannels have also been reported [48]. In this study, nanoparticles are formed in microchannel reactors, with precursors pre-mixed at low temperature (so that reaction does not occur to appreciable extent) and then introduced to the sections of the microchannel reactors maintained at high temperatures. However, the efforts to control particle size through precursor concentrations, residence time, and temperature ramp did not yield the desired control. Khan et al. [53] studied the effect of segmented flow on nanoparticle synthesis. They generated segmented flow by introducing bubbles into a microchannel reactor. Results on synthesis of colloidal silica show that segmented flow generates particles with narrow size distribution compared with the size distributions obtained for simple laminar flow with high axial dispersion.

Specially designed microchannel of PDMS (poly dimethyl siloxane) with three different feeds [47] have also been tried. Two of the side feeds bring the dispersed phases which contain different reactant precursors in them. The center feed which is an immiscible non-reactive oil phase prevents the two side feeds from coming in contact at the entry point and disperses them in the from of alternating droplets, which move one behind the other in the channel in a pattern which is repeated. Fusion of such drops containing the required reactants leads to nanoparticle formation in pico liter dimension reactors. This study shows that this elaborate configuration does results in smaller and more monodispersed CdS particles than those obtained with simple mixing of the reactant streams.

A reverse configuration with three input streams has also been tried [49]. In this configuration, a custom made microchannel (with two side and one straight input stream) is used to flow-focus a reactant containing stream with the help of two side streams of an immiscible inert phase which eventually becomes the continuous phase. The channel is shaped so as to form a nanojet of the stream of interest which breaks into uniform size drops as it traverses over a step downstream . The drops contain all the precursors in them from the beginning itself but the reaction between the precursors and the formation of nanoparticles commences only when the drops pass through high temperature zone (maintained at 250–300 ^{o}C) on the same microchip. The CdSe nanoparticles formed using this process were highly monodispersed and of size 3.8 nm.

When a similar process stream (trioctylphosphine with precursors needed to form CdSe) goes through hot section of a microchannel reactor as in a single phase homogeneous tubular reactor, particle size distribution depends on the flow rate [50, 51]. An increase in residence time (decrease in flow rate) results in formation of particles with larger mean size and larger polydispersity. The observed affect is attributed to an increase in the distribution of residence time for parabolic velocity profile in microchannels at high flow rates. In the

absence of a quantitative model, it is not clear if the residence time distribution is the direct cause for the observed changes or some other phenomenon which comes into effect due to the parabolic velocity profile. One such candidate is the competition between various rate processes which could be affected by diffusion/dispersion rates in different directions. The reason for the above speculation is that the relative distribution of residence times is independent of flow rates, whereas the relative polydispersity in particle size is not.

A change in flow rate is also reported [52] to influence crystal structure for the synthesis of Co nanoparticles in a single phase microchannel continuous reactor. However, the reasons for this change in crystal structure with flow rate are not known.

There is no model available in the literature to explain any of the experimental results mentioned above. A systematic model based effort is required to develop reactors which yield nanoparticles of desired mean size and polydispersity.

Pumping of fluids through microchannel reactors

Transport and mixing processes in fluids at the micron scale are qualitatively different from those at the macroscale, and so a different set of design criteria have to be evolved for designing equipment at the micron scale. Flow at the micron scale is laminar, and so the transport coefficients are much smaller than those for macroscopic applications where the flow is turbulent. The difference in the flow regime raises different issues with regard to fluid transport and mixing.

For transport of fluids through channels of micron scale, as the length scale of the conduits decreases, the ratio of surface area to volume increases. The friction loss per unit volume of fluid increases, since friction losses occur at the bounding surfaces, and the pressure drop required per unit length for pumping the fluid through channels also increases. Large pressure drops across micron size conduits could result in engineering problems with respect to controlling leakage, and would require high strength materials for the design of devices at the micron scale. One line of research is the use of positive displacement devices through chambers of fixed volume, which control the quantity of fluid transported, rather than the pressure drop. Different types of actuating mechanisms, such as motors driven by magnetic fields [54], pneumatic pumps driven by pressure pulses [55, 56], and the thermopneumatic effect obtained by the heating of a compressible fluid [57, 58], have been used in devices. These pumping mechanisms are localized and apply only at one point in the flow, and are not well suited to devices with long channels and tubes, which effectively create the pressure drop required for the flow to occur. However, the auxiliary mechanisms in these cases are bulky and much larger

Mixing in microchannel reactors

Mixing of fluids in macroscale devices is mostly turbulent mixing, and the transport is primarily due to turbulent eddies in the flow. The eddy diffusivity is much larger than the

molecular diffusion coefficient, resulting in enhanced transport coefficients. The flow at the micron scale is laminar, and so the mixing is due to molecular diffusion. This results in the requirement for longer residence times, and greater channel lengths, thereby increasing pumping requirements. There have been many attempts to increase the mixing coefficients in micron scale devices. Use of active devices, such as micro-rotors, is not efficient since the mixing generated due to these is localised at one location in space. In a large scale turbulent flow, the eddies generated by localised mixing would be carried downstream, but in laminar flows, the disturbances are damped over distances comparable to the channel width itself. Most earlier studies have attempted passive mixing mechanisms, such as the etching of grooves in the walls of the channels, or the use of a sinusoidal height modulations in the walls of the channel [59]. These mixing mechanisms have proved to augment the mixing significantly in channels, but since they are passive, they do not provide for active control over the mixing rates at different places in the channel. Another mechanism is to use electrolytes in the fluids that flow through the channel, and then use a transverse electric field to generate instabilities in the flow [60, 61]. The disadvantage with this mechanism is that it can be used only in the case of fluids with ions, and the mixing efficiency depends on the concentration of ions.

Work has also been carried out to augment mixing by creating interfaces within the fluid. For example, in a two-phase fluid, if the droplet diameter is comparable to the diameter of the channel, the droplets of the dispersed phase separated by a continuous phase could be passed through a tube in a sequential fashion, and mixing could occur due to molecular diffusion at the interface between the continuous and dispersed phase. However, the transport in this case is also due to molecular diffusion, though there is augmentation of transport due to the interfaces created within the fluid.

Methods for formation of nanoparticles monolayers

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

1. Collier, C. P.; Vossmeyer, 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.

Preliminary work on forming nanoparticle monolayers was 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 [62] and have also been used to catalyze the growth of semiconductor nanowires [63]. Recently, efforts have been made to generate beams of bare metal nanoparticles in an aerosol reactor and form patterned monolayers by depositing it onto a FIB (Focused Ion Beam) or e-beam templated graphite substrate [64]. However, such aerosol deposition techniques have not yet been able to form large-area monolayers of metal nanoparticles with reliable ordering. The ability to form such ordered monolayers using parallel processes on technologically relevant substrates is critical for proposed applications in nanoelectronics, photonics and plastic electronics [65].

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 several techniques have been pursued for fabricating large-scale monolayers of surfactant stabilized nanoparticles by self assembly. These predominantly fall into four categories; 1) Self-assembly on a solid substrate; this includes drop-casting [66] and spin coating [67], 2) Self-assembly at a fluid interface; in a Langmuir trough [68], at a water-organic interface [69], 3) Templated synthesis with pores or nucleation sites forming a 2D lattice; inorganic porous membranes [70], biological substrates [71], and self-assembled latex colloidal crystals [72] 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 [73], ultrasonic rearrangement [74], and layer by layer epitaxial methods [75]. 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 monolayer, 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 multilayers of alkanethiol encapsulated gold nanoparticles on a water surface [76]. 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 [77].

Current status of nanoparticle based gas sensors

Wohltjen and Snow were the first to report the use of surfactant stabilized nanoparticles for the detection of volatile organic compounds [78]. These sensors showed a fast, reversible and sensitive response to toluene vapours. Following this, several groups have reported the response of surfactant stabilized nanoparticles (same as molecularaly protected nanoparticles or MPN), with differing chemical functionalities, to the presence of polar and nonpolar vapour phase molecules [79]. Most of these studies reported a decrease in resistance upon vapour exposure due to analyte partitioning into the organic matrix resulting in swelling of the films. This caused the interparticle distances to increase, leading to lower conductivity of the film. Currently, the utilization of molecularly interlinked nanoparticle films for sensing is being pursued, as interlinked cluster films are mechanically more stable. Several types of interlinking molecules have been reported. This includes several polyfunctional molecules such as dithiols and dendrimers [80]. Cai et al. [81] have reported that scaling down the active area of MPN based sensor arrays did not have a significant impact on sensitivity. This suggests that chemiresistor sensor based on patterned MPN array are a viable option for portable gas and vapour sensors.

To date, all the devices reported in the literature have been based on thick films of molecularly protected nanoparticle (MPN) layers that were fabricated either by drop casting, spin coating or spray coating [78-81]. Such thick films, when compared to ordered monolayers of nanoparticles, suffer from the disadvantage of having a large number of parallel conduction pathways leading to the requirement of a greater number of interaction events to produce a significant change in the signal. This leads to a limit on the attainable detection limit. In the case of ordered nanoparticle monolayer/bilayers arrays lying between two electrodes placed a few microns apart, the detection limit can be of the order of a few thousand molecules. Ordered monolayer and bilayer arrays exhibit sheet resistances of the order of 10 Ohms/Square. Such resistances can be easily detected using current integrated circuit designs. The use of ordered bilayer arrays as compared to monolayer arrays leads to better signal to noise ratios. However, the use of increased number of layers, beyond two, does not lead to significant gain in signal to noise ratios [82].

222. National status

Most of the modelling work on nanoparticle synthesis has been carried out in India itself, in the Department of Chemical Engineering at IISc Bangalore [30, 31, 36, 39, 40, 43]. and at the Department of Chemical Engineering at IIT Bombay [29, 33, 41, 42, 88, 89]. These two departments continue to be active in this area, both from modelling and experimental studies view point. Recently, the Department of Chemical Engineering at IIT Kanpur has also joined this group with activity [34] on both experimental and modelling front. Synthesis of nanoparticle per se is being actively pursued at JNCASR, Bangalore, NCL, Pune,

and a few other departments at IISc itself.

To the best of our knowledge, microchannel and microcapillary reactors have not been tried for nanoparticle synthesis at any academic institution in India. A large number of groups in Chemistry and allied departments all over the country are actively pursuing nanoparticle at laboratory scale. As the focus of the present proposal is on engineering scale manufacture of nanoparticles, listing of these departments is not required.

Formation of monolayers of nanoparticles is also being investigated in the country, primarily at JNCASR, Bangalore, and the Materials Research Center at IISc Bangalore.

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 [83]. 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 [84]. 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 [85].

At the national level, research in the area of nanoparticle based sensors is gaining momentum. Hydrogen sensing ability of thick films of Zinc oxide nanoparticles, synthesized using sol-gel techniques, impregnated with different amounts of Platinum and Cobalt was investigated and found to be in the range of 10-1000 ppm [86]. Another report studied the effect of LPG and ethanol vapour environments on Palladium impregnated Zinc oxide nanoparticle film, synthesized using hydrothermal methods, and found that the resistance changes measurably at temperatures greater than 150^{o}C [87]. The sensor characteristics reported in both these publications are based on the semiconducting nature of the nanostructured metal oxide and the effect of gas molecules on the conductivity of electrons through it. There has been no report on the development of miniature chemiresistor arrays based on MPNs at the national level.

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

The true importance of the proposed project is the attempt to convert presently exotic processes, which require very specific and fragile protocols, into a scalable model-based procedures which are required if the benefits functional nanoscale architectures are to be realised. As discussed above, there is sufficient scientific evidence to indicate that monodisperse nanoparticles can be produced and they can be assembled into arrays, though most current approaches have been focussed on the chemistry of the synthesis and assembly procedures. However, large scale production of repeatable quality requires the resolution of basic chemical engineering issues of transport and reaction at the microscale. This involves two steps; one of which is the understanding of the fundamental processes involved, and then the integration of these processes in order to facilitate the production of large quantities at the minimum possible cost. Procedures for both the production of nanoparticles, as well as

their assembly into monolayers, have been currently based on extensive experimentation. As summarised above, many procedures have been devised for each of these processes, each of which have some advantages and disadvantages. There is as yet no comprehensive understanding of the basic chemical engineering principles of either of these processes, though attempts have been made within the country and internationally as well.

We propose to combine modeling and experimental validation of the synthesis of nanoparticles in micron scale devices, and their self-assembly into monolayers. Previous studies have shown that it is possible to achieve accurate size control of nanoparticles only if they are synthesised in micron scale devices. We plan to model the formation of nanoparticles in different configurations of microreactors, and to validate these with experiments. We also plan to initiate, for the first time, research on a novel mixing procedure which is to induce oscillations in flexible channels using electric fields. This method is promising because it offers the potential of much better control over flow and mixing in comparison to localised pumping procedures. The monodisperse nanoparticles produced by us will then be self-assembled into monolayers, and we will develop models for the transport processes involved in the monolayer assembly process. Finally, we also propose to develop an application, a gas sensor, which will be used to demonstrate the utility of functional nanoscale architectures.

Thus, the present project is an attempt at obtaining a comprehensive understanding of the fundamentals of nanoparticle synthesis and assembly from an engineering viewpoint. This is an essential step, if the commercial promise of nanoparticle synthesis and assembly is to be realised.

The present project, given an appropriate orientation, can nucleate research activity into the use of microchannels, nanoparticles, and nanostructure based ideas into traditional and emerging areas of Chemical Engineering in other Chemical Engineering Departments, which are otherwise currently engaged in research activity exclusively in the traditional areas. This task will be facilitated by providing to such departments an ability to make soft microchannels, which can then be used to revisit the traditional and venture into the emerging face of Chemical Engineering. It may be possible to enhance this activity to a new lavel by organising workshops for teachers so as to introduce the emerging and exciting face of Chemical Engineering to UG students, and thereby encourage them to seek higher education and pursue teaching and a research career. Presently, the research activity in emerging areas is confined to just a very few departments in the country.

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

V. Kumaran has been working in the area of fluid dynamics and hydrodynamic stability. He has made a comprehensive theoretical study of the instabilities in the flow past flexible surfaces, and has augmented this by carrying out experiments to verify the results of the

theory. He is currently working on the electric field induced oscillations at the interface between two fluids and between a fluid and a flexible surface.

Sanjeev K. Gupta has been working in the area of modelling of nanoparticle synthesis, micellar processes, and breakage and coalescence of drops in dispersions. He has developed models for synthesis of nanoparticles in reverse micelles and synthesis of gold nanoparticles in bulk precipitation, and is currently working on effect of mixing protocols on nanoparticle synthesis. Experimental program aimed at model validation and independent estimation of parameters is run concurrently.

S. Venugopal has developed a scalable process to form patterned and ordered MPN arrays on any desired substrate by combining directed self-assembly and soft-lithographic techniques. He has experience characterizing nanoparticles using Transmission/Scanning electron microscopy and Dynamic light scattering. He has worked in a clean room and fabricated micro/nanoelectronic devices using conventional and non-conventional lithographic processes. In the context of this proposal, he also has experience in using a plasma etcher for etching silicon dioxide, e-beam evaporator for electrode definition, mask aligner for defining patterns on photoresist, synthesizing nanoparticles, monolayer arrays and characterizing them using electron and scanning probe microscopic techniques.

225. Patent details (domestic and international)

1. R.P. Andres, V. Santhanam, R. Agarwal, 'Fabrication of nanoparticle arrays', US20060003097, Patent Pending.

2. V. Santhanam, G. Schmid, U. Simon, D. Jaeger, 'Single-electron transistor', US20050218394, Patent Pending.

230. Work plan

231. Methodology

Modelling of nanoparticle synthesis

As discussed in the previous section, nanoparticle synthesis in reverse micellar route has been modelled for many systems. A regular feature of these models, which have been quite successful in explaining the effect of various process parameter on particle size, is the treatment of rate of fusion of reverse micelles which has been taken to be a fitted parameter. This is a critical parameter of these models, not because it affects the time scale of the synthesis process but because it strongly influences the particle size and polydispersity. This parameter can be measured using fluorescence quenching [91]. It however requires stopped flow apparatus with low dead times and fast acquisition of transient spectroscopic data. We proposed to develop an alternative method which makes use of the strategies used to investigate mixing in homogeneous reactors using series-parallel reaction. This

development should facilitate an estimation of this parameter easily and independently. The model can then acquire a predictive character.

Modelling of nanoparticle formation in bulk precipitation, an area investigated experimentally at lab scale quite actively in the last ten years, is still in infancy possibly for two reasons: chemistry involved in the synthesis process is often not understood, and the urgency to develop models which will play a critical role in scale up, optimization of the process, and ability to seek alternative processes has not yet been felt. We have recently modelled [43] synthesis of gold nanoparticles for the widely used method of Turkevich et al. The model with fitted values for several reaction steps explains the data available over a period of fifty years and some interesting trends in the data (explained in an earlier section). We propose to obtain model parameters independently to validate the model with new protocols to synthesize nanoparticles. Models for other widely used protocols [12] for synthesis of metal, inorganic, and semi-conductor nanoparticles are also proposed to be developed with independently estimated parameters in the model.

The models for synthesis of nanoparticles using precipitation in bulk and reverse micelles will then be combined with models for finite rate of mixing both in tubular and channel reactors, and in small well mixed vessels. Simplified population balance model for nanoparticle synthesis will need to be developed, so that they can be combined with widely used models for finite rate of mixing. These models will be simulated for various mixing protocols and channel geometries, and also validated using experiments in custom made channels to develop robust methods for engineering scale synthesis of nanoparticles.

Mixing and Pumping in Microchannels

In the present project, we attempt to provide a non-localised pumping mechanism, where the soft flexible walls of the conduit themselves act to pump the fluid through the conduits. The objective is to have non-localised pumping, so that there is no sharp pressure drop across the micropump, and to achieve better control over the flow rates generated. We attempt to generate mixing by generating secondary flows due to the motion of the walls of the channel. Control is achieved by varying the frequency and the amplitude of the wall shape, and altering the secondary flow that is generated.

The coupling between the fluid flow and the wall dynamics in flow past flexible surfaces has been an area of active research in the group. It is known that the hydrodynamic instabilities can be induced in the flow past a flexible surface even in the limit of low Reynolds number, where viscous forces are large compared to inertial forces. The instability in a stratified fluid due to a transverse electric field has also been studied, and it has been shown that there is an interfacial instability due to a change in the dielectric constant across the interface between two fluids due to the application of an electric field [90]. All of these studies point to the feasibility of using a channel with flexible walls, and using electric fields to deform the walls of the channel. If this deformation due to electric fields

can be controlled, both spatially and temporally, the deformations generated could be used both for transporting fluids, as well as for generating secondary flows which will augment mixing. In this respect, the channel itself becomes the pump and the mixer.

The flexible materials used for the channel walls will be soft polymeric gels which have a modulus of the order of 1 kPa, which is about five to six orders of magnitude lower than that of metals. This permits the surfaces to deform significantly due to the presence of applied forces. The electric fields will be applied using wires that are embedded in the gels, and complex wave-forms can be obtained by making the wires individually addressable. This will enable us to manipulate the shape of the surface, provided the length scale is larger than the spacing between the wires. In order to cast the polymer gel in the shape of a channel, the negative of the channel (with a protruding indentation whose dimensions are the same as that of the channel) will be made in a silicon wafer. The polymer solution will be cast on the silicon wafer, and cross-linked, and then peeled off, in order to obtain a channel in the gel. The channel will then be covered with a glass plate in order to permit visualization, and if it is necessary to apply a potential across the glass plate, the plate will be coated with a conducting transparent material such as Indium Tin Oxide. The wires will be aligned in the cross-stream direction, with the wire spacing determined by the wavelength of the desired waveform of the surface. It is important to ensure that the spacing between the wires is larger than the channel width, so that the potential gradient is in the cross-stream direction across the channel, and not in the streamwise direction. While a constant potential in the wires would generate only a constant deformation in the channel, a spatially and temporally varying perturbation to the potential could be used to generate a traveling wave which could be used to transport fluid and to induce mixing.

Alternative ways to induce controlled mixing in microchannels

In addition to the above new method of simultaneous localized pumping and mixing, we propose to combine the proposed models for nanoparticle synthesis with flow field in channels of appropriate geometry and varying cross section (for improved mixing, as illustrated by deMello [92]) to control nucleation and particle growth. Interestingly, a stright capillary tube reactor with varying cross section is not expected to improve molecular mixing as the decreased mixing and residence time exactly compensate each other. We also propose to use our significant expertise with breakup and coalescence of drops to control particle synthesis process through the formation of drops containing different reactants in two different channels at high flow rate and then join the channel in ‘Y’ configuration to control the site and rate of reaction and subsequent nucleation of particles. These simulations and their experimental validation will go hand-in-hand to finally arrive at a robust process for nanoparticle synthesis in continuous mode.

Quantitative understanding of formation of ordered monolayers

A model will be developed for the formation of self-assembled monolayer for the method of Santhanam et al. [76], which perhaps is the only method available to self-assemble nanoparticles over a length scale running into a couple of millimeters. The model will consider interparticle forces, osmotic pressure changes due to the variation of concentration of particles on the interface and in the bulk, capillary forces between the particles locate on the interface, capillary force due to the curvature of the receding meniscus after a patch is formed at the center, and drag on particle due to flow of solvent around them (caused by the evaporation of solvent at the solvent-vapour interface). A detailed model is needed to resolve several competing hypotheses that can be proposed for the formation of ordered monolayer. Two of these are: (i) ordering is controlled by the competition between drag force on a particle as solvent evaporates on the surface and osmotic pressure buildup, and (ii) ordering is controlled by competition between the rate at which meniscus recedes after a nucleus of monolayer is formed due to the evaporation of solvent and the rate at which particles can migrate away from the center region due to their Brownian motion. New experiments that help to discriminate between various hypothesis will also be conducted. The model will be extensively verified using new experimental data as well as that available in the literature [76, 82].

The understanding of the formation of the ordered monolayer of particles will be used to devise simple and robust methods with suitable physical control parameters to obtain ordered monolayers of nanoparticles of different sizes and materials.

Development of Chemiresistive gas/vapour sensor

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 [20]. This feature can be utilised to form selective and sensitive chemiresistive gas sensors by using an array of MPNs to transduct specific analyte binding interactions into an electrical signal. If some gas molecules interact specifically with the molecular layer surrounding the nanoparticles, then this interaction will affect the electronic energy levels available for conduction through the molecular layer and thus produce a change in measured resistance (see figure 1). The advantage of such a transduction mechanism is that it provides an opportunity to tune the sensor response selectively to particular gas phase molecules by appropriately choosing the molecular layer that surrounds the nanoparticles.

We propose to fabricate such chemiresistive sensors using patterned bilayer assemblies of gold nanoparticles that are microcontact printed onto lithographically fabricated interdigitated electrodes. The two layers of nanoparticles will be interconnected using a bifunctional molecule that is selective to the analyte of interest. The use of patterned bilayer arrays is expected to provide enhanced sensitivity as compared to a thick coating

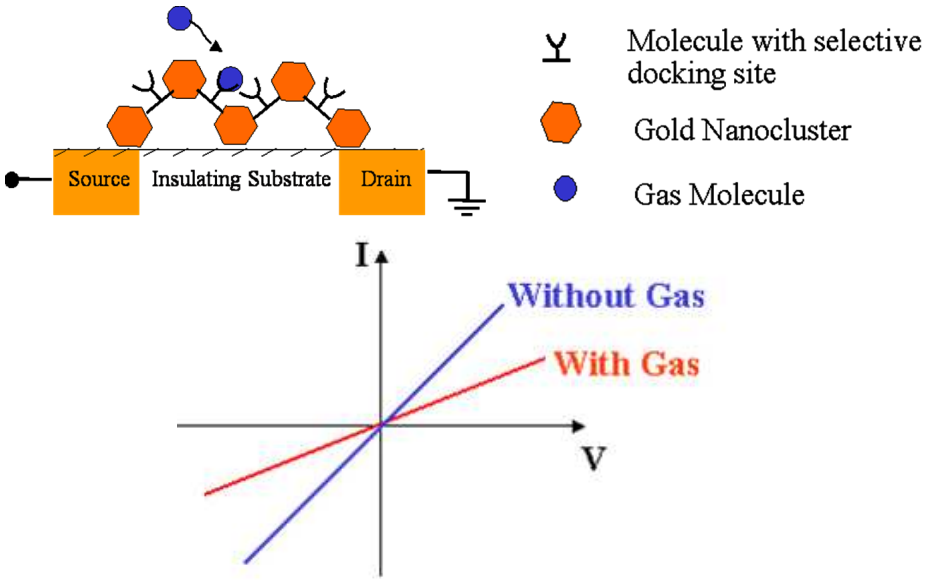

Figure 1: Figure 1. (top) Schematic illustrating nanoparticle array based chemresistive sensor device structure. (bottom) Illustration of the expected current vs. voltage (I-V) curves before and after exposure to gas that contains the molecule to be detected.

of nanoparticles; because of the smaller number of interaction events that are needed to produce a detectable change.

Microfabrication equipment is needed to miniaturize the size of an individual sensing element and also to form suitable interdigitated electrodes that are integrated with a heating element. Miniaturization of the sensing element is required to increase portability, perform sensing in confined spaces, reduce manufacturing costs, and to allow for multispectral detection by having numerous sensing elements on a single substrate. Lithographically patterned interdigitated electrodes are required to improve the signal level from a sensing element as they enable the application of very high electric fields at moderate voltages. The electrodes will also be embedded within the substrate (i.e. in-plane) to minimize contact resistances at the electrode nanoparticle assembly juncture that would otherwise dominate the electrical characteristics of the array [21]. Patterning will also aid in improving the detection limit as fewer interaction events are needed to trigger a net change in resistance.

The work plan is to use photolithography to produce electrically addressable interdigitated finger electrode patterns on a spin-coated photoresist layer that will then be transferred into the substrate using reactive ion etching and metal evaporation. A master for soft-lithography will be prepared using photolithography and used to form PDMS molds. These molds will be used to transfer nanoparticle assemblies, which are formed using the methods devised earlier, onto the substrate with the interdigitated patterns. The interconnecting molecules will be introduced either by vapour phase annealing or by contacting via a porous PDMS pad. The response of the sensor to various gas mixtures will then be characterised using an enclosed electrical probe station.

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232. Organisation of work elements

Administrative work elements

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

Technical work elements

- Modelling of pumping and mixing in flexible channels & Validation
- Modelling of nanoparticle synthesis & validation
- Modelling of array formation & validation
- Demonstration of field-modulated flexible channels
- Nanoparticle synthesis in microchannels
- Array formation using particles synthesized in microchannels
- Development of gas sensor

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

Administrative work elements

- Selection of equipment and processing purchase order:- Time required is 3 months. This time will be used to invite quotations and select the vendors by following appropriate institute rules. It is expected that the purchase orders can be released for most of the major equipment within this time-frame.
- Recruitment of personnel:- Time required is 3 months. The interview and selection of candidates for the different posts are expected be done during this time frame.
- Equipment Installation:- Time required is 15 months. This is a realistic estimate of the time required for design, installation and start-up of the various equipment needed to start fabricating microchannels routinely.

Technical work elements

- Modelling of pumping and mixing in flexible channels & Validation:- Time required is 30 months. This activity will require modelling and experimental validation of instability of flexible surface (system of two dielectrics) and the conditions when this instability can be sustained in modes useful for pumping and mixing of liquids in channels.

- Modelling of nanoparticle synthesis & validation:- Time required is 48 months. This activity is currently ongoing on a small-scale within our department and will receive a major impetus, when the project begins. It involves modelling and validation of the various transport and reaction processes during nanoparticle synthesis from precursors at the laboratory scale and within microchannels. Knowledge gained will be useful to complete other activities and feedback from such activities will also contribute to further model refinement.

- Modelling of array formation & validation:- Time required is 42 months. This activity will generate hypothesis and develop models to understand and optimize directed self-assembly technique. It will also be used to predict more robust parameter regimes for fabricating nanoparticle arrays using monodisperse and bi-modal particles in the size range of 5-50 nm.

- Demonstration of field-modulated flexible channels:- Time required is 18 months. This activity involves fabricating channels within flexible material, having appropriate modulus and dielectric constants, and integrating appropriate addressable electrode designs to control the pumping and mixing rates. Knowledge generated will include optimized parameters and designs for channel material and dimensions respectively.

- Nanoparticle synthesis in microchannels:- Time required is 36 months. This activity entails the use of modelling and validation knowledge to synthesize monodisperse nanoparticles of controlled sizes, employing flexible as well as quartz/silicon microchannel reactors. It will entail knowledge generation that includes optimized parameters for synthesizing different classes of nanoparticles.

- Array formation using particles synthesized in microchannels:- Time required is 30 months. This activity is expected to start a year after initiating experiments on nanoparticle synthesis in microchannels. It will carry on for the rest of the project duration and beyond to optimise the processes developed for different material systems, such as noble metals, semiconductors, and ferromagnetic materials encapsulated by either hydrophobic or hydrophilic ligands. This activity will rely upon our modelling and experimental know-how, both present expertise and those generated

earlier in the project. This activity is expected to generate both intellectual property and knowledge on directed self-assembly processes, which can feed into commercial ventures.

- Development of gas sensor:- Time required is 24 months. This activity will start after 3 years. By that time, we expect to be able to synthesize monodisperse metal nanoparticles in the size range of 5-20 nm based on expertise gained by modelling and validation effort. This activity will entail finding appropriate techniques and developing protocols to exchange the monofunctional ligands by molecular interconnects, such as aromatic dithiols etc, followed by characterization and optimization of their sensor response. This is an intellectual property generation exercise, predominantly. Knowledge generation, involving the kinetics of ligand exchange, is also entailed within this work element.

Note:- All the technical work elements are expected to sustain and be pursued even after the end of the project term, as more knowledge is generated and new ideas are conceived. The indicated time frames are the best current estimates of the time needed for these elements to be completed to a satisfactory level and to feed into subsequent work elements. They also indicate the priority of different work elements, during project implementation.

Major milestones

1. Microfluidic channel fabrication, 18 months.
2. Modelling and validation of pumping and mixing in flexible channels, 30 months.
3. Demonstration of electric-field modulated flexible channels, 36 months.
4. Modelling and validation of nanoparticle synthesis and array formation, 48 months.
5. Nanoparticle synthesis in microchannels, 54 months.
6. Array formation using nanoparticle synthesized in microchannels and demonstration of a nanoparticle based gas sensor, 60 months.

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

The development of processes for the bulk production of nanoparticles has a potential for many commercial applications, from dispersions and coatings to high surface area materials, and from functional nanodevices to consolidated materials. Other significant area to be impacted by nanoparticles is targeted drug delivery, gene therapy, and multifunctional coatings. New programs in these collaborative fields are likely to evolve, once the ability to manufacture nanoparticles with desired properties is developed. In the petroleum industry,

one potential application of nanoparticles is as additives in lubricants, in order to reduce the wear of solid surfaces in contact. The PIs are in contact with research division of HPCL and IOC for collaboration, and they have expressed interest in working out an umbrella agreement with the institute under which this research work will be taken up. Nanoparticle synthesis is currently an active area of research in the pharmaceutical industry, since controlled drug delivery can be better achieved if the particles are of controlled size.

Functional nanoscale architectures have significant potential applications in a variety of fields such as sensors and detectors, fabrication of quantum wires, efficient solar energy conversion, etc. However, these are new applications which cannot be easily assimilated by industry currently, and the monolayer arrays that we synthesise have to be further developed for use in real applications. The development of a gas sensor is one such envisaged within the project. The gas sensor developed here will have a significantly higher sensitivity in comparison to commercially available sensors, and the investigators plan to further take up the development and commercialisation of the sensor after the completion of this project. Further, growth of quantum nanowires from the monolayer arrays will also be pursued, and we will develop applications for ordered arrays of semiconductor nanowires, such as the efficient conversion of solar energy.

Micromixing and microtransport is likely to become a fundamental unit operation in the industry of the future, analogous to mixing and transport in large scale applications today. Current microreactors are small in dimension, but the pumping units required for these (syringe pumps and peristaltic pumps) are relatively large and bulky, and do not qualify for the adjective ‘micro’. The total device is truly microscale only if the reactor, pumping units and power supply put together are of micron scale. The benefit of the work on pumping and mixing by field actuation within the channel itself will, if successful, provide truly microscale reactors which do not require bulky side units. This will have applications in a variety of medical, pharmaceutical (drug delivery) and industrial applications, such as the controlled synthesis of nanoparticles.

300. BUDGET ESTIMATES: SUMMARY

	Item	BUDGET (in lakhs of rupees)					Total in lakhs
		1st year	2nd year	3rd year	4th year	5th year	
A	**Recurring**						
	1. Salaries/wages	4.5	4.5	4.5	4.5	4.5	22.5
	2. Consum-ables	2	3.5	3.5	3.5	2.5	15
	3. Travel	0.4	0.4	0.4	0.4	0.4	2
	4. Other costs	1	1	1	1	1	7
B	**Equipment**	351.74	0	0	0	0	351.74
C	Institute Over-head						
	20% of **A**	1.58	1.88	1.88	1.88	1.68	8.9
	Grand total (**A+B+C**)	361.22	11.28	11.28	11.28	10.08	405.14
	Total FEC (in USD)	621,880	4,000	4,000	4,000	2,000	636,880

(Note: - 1 USD = Rs. 48; 1 Euro = Rs. 58; 1 Euro 1.208 USD)

310. BUDGET FOR SALARIES/WAGES

		BUDGET					Total (m.m.)
		1st year (m.m.)	2nd year (m.m.)	3rd year (m.m.)	4th year (m.m.)	5th year (m.m.)	
Designation & number of persons	**Monthly emolu-ments**						
Post doc-toral fellow (one)	15,000	1,80,000 (12)	1,80,000 (12)	1,80,000 (12)	1,80,000 (12)	1,80,000 (12)	9,00,000 (60)
Research Assistants (two)	10,000	2,40,000 (24)	2,40,000 (24)	2,40,000 (24)	2,40,000 (24)	2,40,000 24	12,00,000 (120)
Temporary wage worker (one)	2500	30,000 (12)	30,000 (12)	30,000 (12)	30,000 (12)	30,000 (12)	1,50,000 (60)
Total		4,50,000	4,50,000	4,50,000	4,50,000	4,50,000	22,50,000

311. Justification for the manpower requirement

Provision has been made for a post-doctoral fellow and two research assistants to help us in achieving our research objectives. In addition, the service of a dedicated temporary wage worker is requested to maintain the cleanroom premises on a daily basis and to ensure the cleanliness of the support area. This post is required to wipe the clean room panels with acetone soaked tissues to remove particles adhered to the walls. Such maintenance action is needed in conjunction with constant circulation of filtered air through HEPA filters to maintain class 1000 and class 10000 areas.

320. BUDGET FOR CONSUMABLE MATERIALS

item		BUDGET					Total (in lakhs)
		1st year	2nd year	3rd year	4th year	5th year	
High grade chemicals: Photoresist, Developers, precursor salts, reducing agents, surfactants etc.	Budget	1	2	2	2	1	8
	FEC[a]	2000	4000	4000	4000	2000	16000
HPLC grade solvents	Budget	0.5	0.5	0.5	0.5	0.5	2.5
Gases and manifolds with regulators and mass flow Controllers for Reactive Ion Etching and Sensing experiments	Budget		0.5	0.5	0.5	0.5	2.0
General lab consumables like gloves, glassware, scintillation vials, etc.	Budget	0.5	0.5	0.5	0.5	0.5	2.5
Total		2	3.5	3.5	3.5	2.5	15

[a]Foreign exchange component in USD

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

The chemicals for precursors and photoresist need to be imported and have to be of high purity to enable reproducible and repeatable experimental outcomes. In the first year, precursor salts such as hydrogen tetrachloroaurate, Silver nitrate, Iron carbonyl salts etc along with reducing agents such as Hydrazine, sodium citrate and surfactants will be bought to validate mixing models in standard laboratory equipment and in 'off-the shelf' microfluidic channels. In subsequent years, these chemicals along with photoresist, developers and adhesion agents will be required to facilitate microchannel fabrication. Based on our experience, these chemicals need to be imported to ensure reproducible and repeatable results, as even trace impurities can lead to undesirable nucleation or defects. HPLC grade

solvents are required, during nanoparticle synthesis, to prevent undesirable heterogeneous nucleation due to particulate contaminants. Gases need to be purchased for characterizing the performance of the nanoparticle array sensor and also for use in processing equipment such as RIE and Maskless writer. Ultra high purity processing gases such as nitrogen, oxygen, hydrogen and Carbon tetrafluoride are required in conjunction with microfabrication processes to avoid particulate contamination and unwanted side-reactions. Also, gases such as carbon dioxide, nitric oxide, and trace amounts of hazardous mimics are needed to characterize nanoparticle array based gas sensor. Budget is also requested for procuring laboratory supplies for experimental work.

330. BUDGET FOR TRAVEL

	BUDGET					Total (in lakhs)
	1st year	2nd year	3rd year	4th year	5th year	
Travel (only inland travel)	40,000	40,000	40,000	40,000	40,000	2

331. Justification for intensive travel, if any

The funds requested are for PI's to attend review meetings and for students to travel to local conferences.

340. BUDGET FOR OTHER COSTS/CONTINGENCIES

	BUDGET					Total (in lakhs)
	1st year	2nd year	3rd year	4th year	5th year	
other costs/contingencies costs	1,00,000	1,00,000	1,00,000	1,00,000	1,00,000	5

341. Justification for specific costs

This amount is required to cover documentation, incidental expenses and any untoward currency exchange rate fluctuations.

350. BUDGET FOR EQUIPMENT

Sl. No.	Generic name of the Equipment along with make and model	Imported / Indigenous	Estimated Costs in Lakhs (in Foreign Currency also)[a]	Spare time for other users (in %)
1	Maskless writer, Heidelberg Instruments μPG101	Imported	87 (150,000 EUR)	20
2	Thin film evaporator, Milman metal evaporation system	Indigenous	50	20
3	Anodic Bonder, EV group, AB1-PV Anodic Bonder	Imported	20.3 (35,000 EUR)	20
4	Electrical probe station, MMR K20P4 and Keithley SCS 4200 characterization system	Imported	43.2 (90,000 USD)	20
5	Scanning Electron Microscope, Jeol JSM 6390	Imported	86.4 (180,000 USD)	40
6	Inspection Microscope, Olympus AX-70	Imported	9.6 (20,000 USD)	20
7	Grazing angle accesory for Perkin-Elmer FTIR	Imported	8.64 (18,000 USD)	40
8	Modular Clean room and Air Handling Units,Class 1000 (20 sq.ft) & Class 10000 (300 sq.ft)	Imported	28.8 (50,000 EUR)	20
9	Mass flow Controllers, Gas regulators	Imported / Indigenous	5.2 (8,000 USD)	0
10	Microfluidic kit-Protea standard toolkit	Imported	9.6 (20,000 USD)	0
11	Clean room compatible Hot plates, Sonicator, Baking oven	Indigenous	3	20

[a]includes transport, insurance and installation charges.

351. Justification for the proposed equipment

1. Maskless writer is an essential component for performing photolithography as it defines patterns on a photoresist layer. This step is critical for fabricating microfluidic channel of different shapes, defining electrode patterns at the micron scale for electrostatic actuation of flexible channels, and probing the electrical characteristics of nanoparticle arrays. The Heidelberg Maskless writer has a minimum resolution of 5 microns. This is appropriate for use in defining electrode patterns for field-modulated flexible channel studies and in- plane interdigitated electrode fabrication that will be used in gas sensor studies. It will also enable us to circumvent the general procedure of making a mask (mask writer) using a chromium coated quartz plate (typically out-

sourced to companies in Taiwan/USA, as it costs Rs. 1.2 crores for a mask writer alone) and then using it to expose the photoresist, using a mask aligner (cost Rs.1.1 crores), for fabricating microfluidic channels and integrated heaters based on our designs. The advantage of procuring a Maskless writer, in lieu of a mask writer and aligner, is that the Intellectual property, in the form of mask design, remains in-house.

2. Thin film e-beam evaporator system is required to deposit appropriate metal contact pads on substrates. The e-beam evaporator provides the ability to work at low vacuums with substrate cooling. These features are necessary for depositing electrode material through patterned trenches for fabricating in-plane electrodes, channels integrated with heaters, and defining the electrode patterns on flexible substrates. It will also minimize the loss of material, energy consumed, and more importantly the amount of substrate heating by radiation in comparison with thermal evaporation by resistive heating. The working vacuum level achievable in the system would be of the order of 10^{-6} torr, which is required to deposit smooth metal thin films with thicknesses ranging from 40 nm upwards. Higher pressures will cause the metal atoms to agglomerate in- flight, due to collisions, and the grains that form the film will be of the order of 30-40 nm in size, resulting in a rough and discontinuous electrode surfaces. This minimum thickness is required to minimize the depth that needs to be etched using RIE for in-plane electrodes, while forming electrodes with minimal resistance. Such thin film coaters can be manufactured by Indian companies such as Milman, Hind-High Vacuum etc., and so will be fabricated indigenously.

3. Anodic bonder is useful for bonding two quartz dies or a silicon with a quartz die. This is critical for forming a closed microfluidic channel. It electrostatically bonds two dissimilar materials together to form a strong, hermetic seal with little alteration in dimensions. The anodic bonder provides the ability to apply a force, while simultaneously applying a high voltage between two substrates to be bonded. This equipment allows one to achieve closed channels by bonding a glass plate to a silicon/quartz die and form leak-proof sealing at the micron scale. The AB-PV1 anodic bonder uses a high voltage supply to apply voltages in the range of 0.2-2 KV, contact forces in the range of 2-200 N, and temperatures upto 600 C. These ranges are sufficient to mobilise the ions on a quartz piece to form a hermetic seal. This equipment is not manufactured by any known indigenous manufacturer.

4. Electrical probe station and characterization system are essential for characterizing the current- voltage response of nanoparticle arrays in different environments. The MMR-K20P$ probe station in conjunction with a Keithley characterization system will allow for testing nanoparticle array coated interdigitated electrodes on a 1x1 cm die using four probes in a closed environment. The four probe technique is utilised to eliminate contributions from the internal circuit resistances to the measured resis-

tance. Two probes are used to inject a known current while the other two probes are used to measure the voltage drop across the device. The closed chamber is designed to eliminate dead time and improve the response characteristics of the chamber to changes in inlet concentration. The chamber design also allows for achieving different partial pressures of inlet gases by adjusting the pumping speeds. The keithley SCS 4200 system provides the ability to maintain a desired current value between two electrodes (in the range of a few fA to A) and measure the voltage drop across the other pair (few mV to V). It also provides the ability to directly record and plot these data either as current-voltage plots or as resistance changes with time. The response time of the characterization unit is of the order of nanoseconds and thus will not affect measurement of nanoparticle arrays (typically millisecond response times). This equipment is not manufactured by any known indigenous manufacturer.

5. Scanning electron microscope is critical for visualising the cross sections of various microfluidic channels that will be fabricated. The JEOL-JSM 6390 model has a 30kV filament that can provide a resolution of the order of 5 nm on metallic thin films. This will be useful to characterize the size and shape of nanoparticles that are above 10 nm in size. The advantage of SEM's in comparison with optical microscope is the excellent depth of focus of SEM images and this will be critical in evaluating the morphology of microfluidic channels over large areas, validating the integrity of fluidic interconnects via soft flexible materials, and characterizing the morphology of patterned nanoparticle arrays on silicon/quartz substrates. The JEOL SEM is supplied with fully loaded software that enables new users to image specimens with minimal training. The vacuum and electron gun optics are computer controlled and need not be aligned each time, thereby eliminating potential pitfalls for novices. The software has automatic stigmation and focusing capabilities, which again contributes to faster image acquisition time, with minimal training. It is also a low maintenance system, requiring only filament changes on a regular basis. The SEM's available on campus is heavily used by the institute members and currently it has a waiting period of the order of 1-1.5 months for a SEM slot. Such long waiting times will hamper the development of design and fabrication of microfluidic channels, for which the SEM characterization is an important feedback. This equipment is not manufactured by any known indigenous manufacturer.

6. Optical inspection microscope equipped with digital imaging abilities is useful for immediate inspection and verification of microfluidic channels and nanoparticle arrays at macroscopic length scales. The Olympus AX- 70 is a general purpose research microscope with infinity corrected lenses and magnification ranging from 4x - 60x. It allows the ability to image in Bright field, Dark field and Differential Interference Contrast modes. The DIC mode is critical for imaging transparent substrates

such as PDMS, as it enhances the contrast by using phase information. This ability will allow us to visualize flow within flexible PDMS microchannels and also record it, using a digital camera. The resolution (1 micron) is appropriate for capturing the flexing motion and inspection of microfabricated devices. This equipment is not manufactured by any known indigenous manufacturer.

7. Grazing angle accessory for Perkin-Elmer FTIR is needed to augment the capabilities of our department's FTIR. This accessory will enable us to verify and monitor ligand exchange kinetics on nanoparticle monolayers. This accessory will allow us to interrogate nanoparticle monolayer and bilayer at grazing incidence, thereby maximizing volume of interaction with the film, to record Infrared spectrum. IR characterization is essential to monitor and characterize the kinetics and dynamics of the insertion of gas-sensitive molecules and the displacement of alkane thiol molecules from nanoparticle monolayers. This is a critical component in the development of gas sensors, as it is the only option to interrogate ligand-exchange kinetics on a nanoparticle monolayer coated substrate. This equipment is not manufactured by any known indigenous manufacturer.

8. Modular clean room equipment are needed to protect environment sensitive instruments and also to provide micron-scale particle free atmosphere for fabricating/testing microfluidic and nanoparticle monolayer based devices. The modular clean room and air handling equipment are designed to fit within existing infrastructure and will provide an environment, of appropriate class, within which sensitive equipment (Maskless lithography system, SEM, chemical benches for processing photoresists etc.) can be housed along with a person or two. A class 1000 environment provides an environment in which there are only less than 1000 particles/ cu.ft of size 0.5 microns and above. This is only required for operating the Maskless writer (20 Sq.ft). A class 10,000 environment (less than 10,000 particles/cu.ft of size 0.5 micron and above) is required to prevent particle contamination while processing the patterned dies and before sealing. It will also be used to house the SEM, Inspection microscope and the wet benches. The class 1000 enclosure will be embedded within the class 10,000 environment. A modular unit of size 300 sq.ft is requested to house these instruments along with existing equipment such as RIE and spin coater. For comparison, an air-conditioned room is equivalent to a class 100,000 area. This equipment is not manufactured by any known indigenous manufacturer.

9. Mass flow controllers and gas regulators are needed to supply gases at controlled pressure and flow rates for processing equipment such as reactive ion etching, etc. and for drying dies and chips to prevent undesirable deposits on substrates. Mass flow controllers are also especially needed for sending in a known quantity of a gas or a mixture of gases, while characterising nanoparticle array based sensors. Bud-

get is requested for three mass flow controllers ($2000 apiece) to supply air (to verify humidity effects), inert gas (to get a baseline response) and gases of interest (CO/NO etc.) for the sensing experiments. Another MFC is requested to supply carbon tetrafluoride for RIE processing. Apart from this, provision has been made for gas regulators (Rs. 25,000 each) for all processing gases and required fittings, such as valves etc.

10. Microfluidic kit is needed for the initial start-up phase of the project. It consists of standard size and shape channels fabricated on quartz substrates and will also include capillary pumps and plumbing accessories. Typically, the shapes are either a double T junction or a mixing unit having different residence times, with width of 100 micron and depth of 20 micron. The accessories include luer-lock fittings, valves and capillary injection pumps needed to couple these chips to macroscopic world. This equipment is not manufactured by any known indigenous manufacturer.

11. Clean room compatible hot plates, ovens and sonicators are needed for wet processing after the lithographic process to convert the light intensity profile into a topographic profile on the photoresist. These can be procured indigenously.

410. Time Schedule of Activities through BAR Diagram

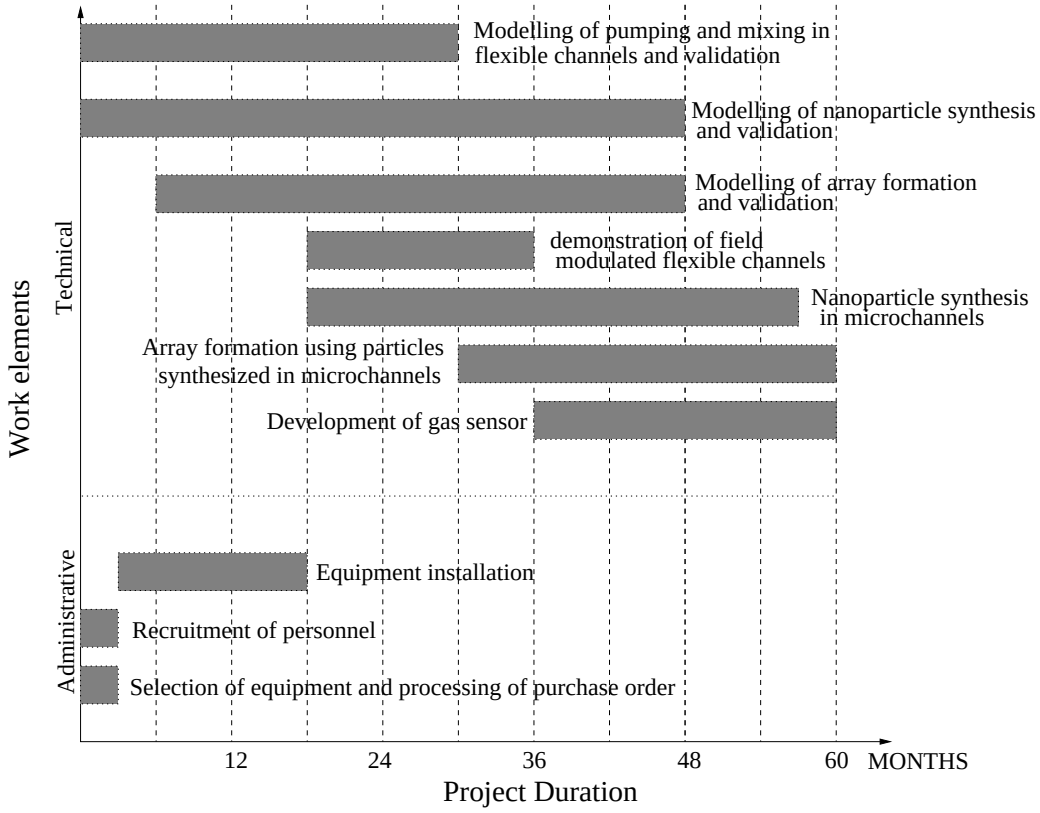

Figure 2: Time Schedule of work elements

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	yes
2.	Water & Electricity	yes
3.	Laboratory Space/ Furniture	yes
4.	Power Generator	yes
5.	AC Room or AC	yes
6.	Telecommunication including e-mail & fax	yes
7.	Transportation	yes
8.	Administrative/ Secretarial support	yes
9.	Information facilities like Internet / Library	yes
10.	Computational facilities	yes
11.	Animal/ Glass House	not req.
12.	Any other special faciity being provided	not req.

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's & their groups	UVO Plasma cleaner	Jelight, 42-220, 2005	Typically used for surface preparation and cleaning
	Spin coater	Milman Thin Films, 2005	Typically used for forming thin layers of polymers on solid substrates
	RIE & PECVD	Milman Thin Films, 2006	Etching of growing thin films of inorganic material on substrates
	Zetameter	Zetameter Inc. 2000	Used for measuring zeta potential of particle and drops
	Tensiometer	Dataphysics, 2004	Used for measuring interfacial tension,contact angle, and cmc.
	Rheometer	AR1000-N TA Instruments, England, 2004	Characterization of complex fluids
PI's Department	Atomic Force Microscope	Asylum Research MFP-3D, 2006	Used for nanoscale size characterization and imaging
	DLS-Particle sizer	Brookhaven Goniometer based, 2003	Used for particle and micelle size determination
	FTIR	Perkin-Elmer, 2002	Typically used for molecular characterization
	PIV	Solo-III-15 Hz New Wave Research, 2003	Fluid flow visualization
	Confocal Microscope	FV300, Optical Co. Ltd. Japan 2003	3-d imaging
	Stopped flow equipment	Biologic, France, 2006	Used to measure fast kinetics
Other Inst.	TEM	Tecnai F-30 300kV, FEI, 2004	Central user facility, generally used for materials characterization. Current waiting time 5 weeks
	SEM	Quanta 220 FEG, FEI 2004 SirionEBL 2004	Lower resolution than TEM. Has a waiting period of 4 weeks.

450. Details of Research Projects being implemented/ completed/ submitted by the Investigator(s)/Co-Investigators

1.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	S. Venugopal IISc, Bangalore Patterned and Ordered Metal Nanoparticle Arrays Templates for Functional Nanoscale Architectures ongoing 2006-09 DST 50 lakhs
2.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	Sanjeev Kumar IISc, Bangalore Coalescence of drops in centrifugal extractors ongoing 2005-2008 IGCAR, Kalpakkam 18.5 lakhs
3.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	V. Kumaran IISc, Bangalore Turbulent particle suspensions ongoing 2004-07 DST 10 lakhs
2.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	V. Kumaran IISc, Bangalore Dynamics of Granular Flows completed 2002-07 Swarnajayanthi Fellowship 31 lakhs
4.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	Sanjeev Kumar IISc, Bangalore Studies on Phase Inversion in Agitated Liquid-Liquid Dispersion completed 2001-04 DST 17.9 lakhs
5.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	Sanjeev Kumar IISc, Bangalore Redesigning of impellers for efficient breakup of drops completed 2000-2003 INSA 1.8 lakhs

6.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	Sanjeev Kumar IISc, Bangalore Recovery of Carbon Particles from Filter Media Using Liquid-Liquid Dispersions completed 2001-03 HLRC,Bangalore 9.5 lakhs
7.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	V. Kumaran IISc, Bangalore Flow past flexible surfaces - II completed 2000-02 DST 18 lakhs
8.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	V. Kumaran IISc, Bangalore Experimental studies on shear flows of granular materials completed 1998-01 INSA 5 lakhs
9.	Investigator(s) Name Institute Project Title Project Status: Duration Funding Agency Total Cost	V. Kumaran IISc, Bangalore Flow past flexible surfaces - I completed 1996-99 DST 12 lakhs