Annexure-IX

PROJECT COMPLETION REPORT

1. **Title of the project:** Nanowire array based dye-sensitised solar cells (DSSC)

2. **Principal Investigator(s) and Co-Investigator(s):** S. Venugopal and Sanjeev Kumar Gupta.

3. **Implementing Institution(s) and other collaborating Institution(s):** Department of Chemical Engineering, Indian Institute of Science, Bangalore-560012

4. **Date of commencement:** 15/03/2010

5. **Planned date of completion:** 14/03/2013

6. **Actual date of completion:** 14/03/2013

7. **Objectives as stated in the project proposal:**

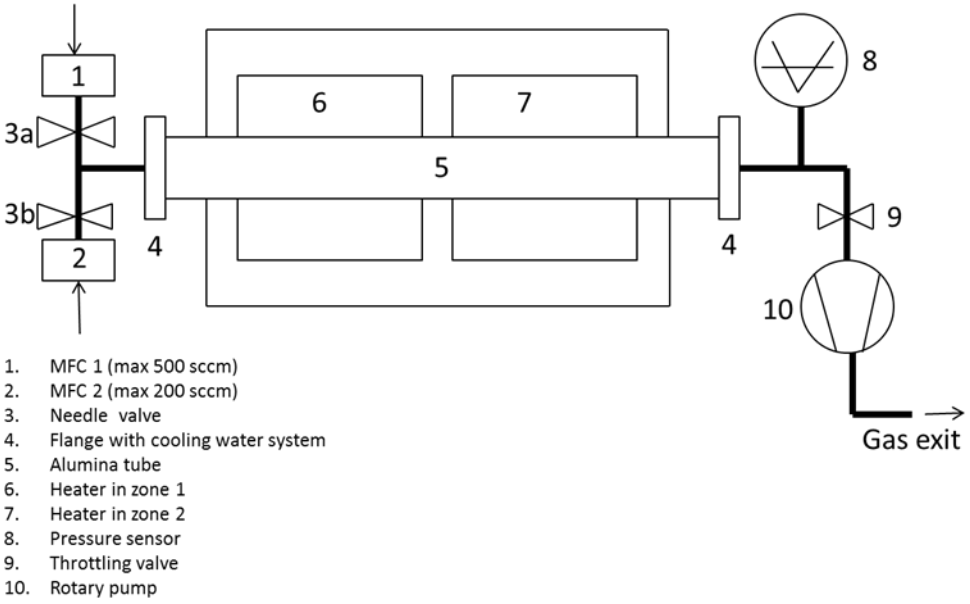
    - The use of thermally stable bare metal nanoparticle arrays as site-specific templates for the growth of ZnO nanowire arrays by VLS mechanism.
    - Fabrication of DSCs based on ZnO nanowire array photoanodes and characterization of their photovoltaic performance.
    - Optimization of ZnO nanowire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

8. **Deviation made from original objectives if any, while implementing the project and reasons thereof:**
    - The characterization of photovoltaic performance of ZnO nanowire array photoanodes and optimization of ZnO array geometry could not be carried out:- Accurate control of vacuum level during temperature ramp-up and cooling down of the furnace is required for eliminating unwanted growth processes. The principal reason being the inability to implement an automatic vacuum control system for the tube furnace due to budgetary constraints.

9. **Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:**

VLS growth system

Photograph of High temperature tubular two zone furnace

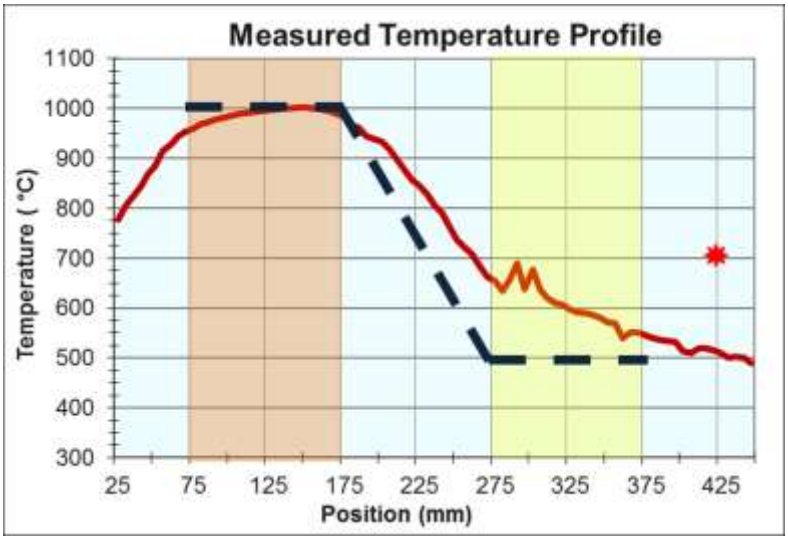


1. MFC 1 (max 500 sccm)
2. MFC 2 (max 200 sccm)
3. Needle valve
4. Flange with cooling water system
5. Alumina tube
6. Heater in zone 1
7. Heater in zone 2
8. Pressure sensor
9. Throttling valve
10. Rotary pump

Schematic of the two zone system setup for growing ZnO nanowires

The system setup comprises of the gas input units (1, 2, 3), cooling units (4), growth units (5, 6, 7) and gas output units (8, 9, 10). The input gas is pure Ar or N_2 (99.99%) flowing

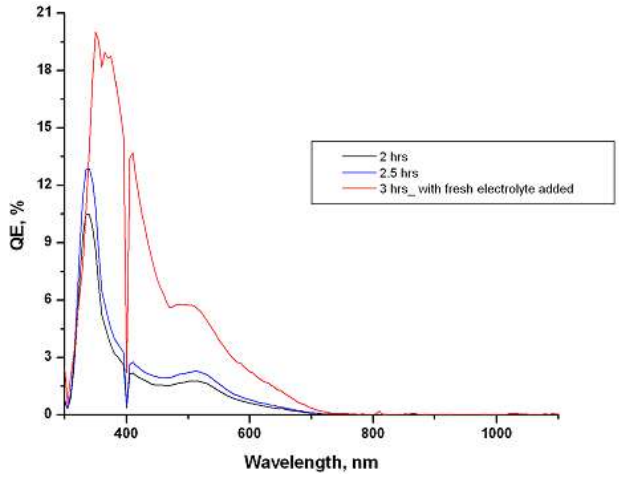
through a mass flow controller No.1 followed by a needle valve No. 3. Another input unit is provided to flow O_2 through mass flow controller No. 2. The mass flow controllers have maximum flow rates of 500 sccm and 200 sccm respectively. In our case, we are investigating the growth of ZnO without flowing reactive O_2 as Ar/N_2 contains 0.002% O_2 as impurity. The needle valve can be used as final gate between the input gas and the rest of the growth system. An alumina tube (No. 5, 7 cm inner diameter and 100 cm length) placed inside the two zone furnace (No. 6 & 7). ZnO NWs can be grown in the alumina tube. The output unit composes a pressure sensor (Hind High Vacuum), and a manual throttling valve. The gas is pumped by a 2-stage rotary vane pump (adixen, 2010C1), with a maximum pump rate of 10 m^3/h.



Characterization of temperature profile in a Two-zone tubular furnace

Photovoltaic characterization

Photograph of photovoltaic efficiency characterization system



Quantum efficiency spectra of standard 'Graetzel' cells measured using the solar simulator set-up.

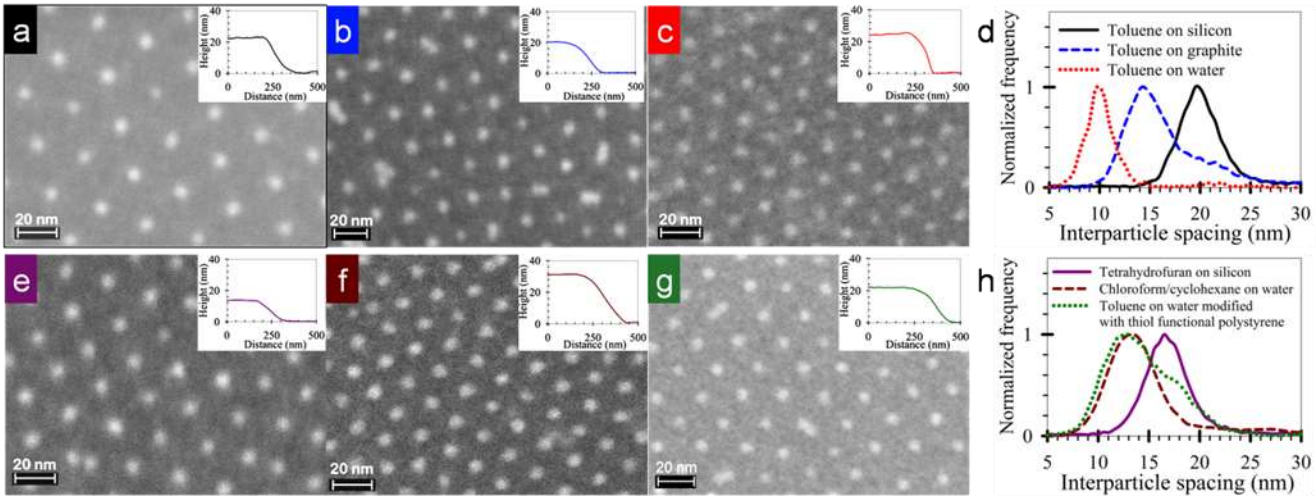
Nanoparticle array fabrication

Aqueous gold colloids of size 7 ± 0.7 nm were synthesized at room temperature using tannic acid as both reducing and stabilising agent, as reported earlier1. Briefly, 30 mL of 0.64 mM aqueous chloroauric acid was added to 45 mL of 0.9 mM aqueous tannic acid dropwise. The pH of the reaction mixture was always maintained above 6.4 by the addition of requisite amounts of 1 % (w/v) KOH solution intermittently. Polymer grafting to gold nanoparticle was achieved by mixing 7 mL acetone solution (containing 0.02% (w/v) thiol terminated polystyrene, molecular weight: 20000 g/mol, Polymer Source Inc.) with 5 mL of aqueous gold colloid. The solution was left undisturbed overnight, and then centrifuged at 3500 rpm for 30 minutes. The precipitate was then washed with 5 mL acetone twice to remove excess thiol terminated polystyrene molecules. The final precipitate was re-dispersed in the desired organic solvent prior to fabricating nanoparticle arrays. Thermo Gravimetric Analysis, TGA (Perkin Elmer, Pyris6000) measurements indicated that the nanoparticle surface is saturated with polystyrene thiol after this procedure, with the thiol coverage corresponding to 1.57 molecules/nm2. p-type silicon substrate (with native oxide) was cleaned using standard RCA method2, followed by UV-Ozone cleaning using a commercial UVO cleaner® (Jelight-42). Graphite substrates (~ 100-200 nm thick) were generated by cleaving a graphite block with scotch-tape. HPLC grade organic solvents were used as received without any further purification. Deionized water from a Millipore Milli-Q® system was used throughout.

Field-Emission Scanning Electron Microscope (FESEM) images were obtained using Ultra-55, Zeiss NTS GmbH, at an operating voltage of 10 KV. Multiple images taken at different locations were used for image analysis. The interparticle spacing, i.e. the distribution of the edge to edge distance of nearest neighbours (for >100 particles across several images from different areas of the film), is determined using a customised code written in IGOR Pro™ environment. In the case of the samples formed on the graphite substrate and polystyrene thiol modified water surface, the vacancy defects were higher and resulted in bimodal curves; the values reported in the text are for the dominant

mode. The standard deviation of these distributions are in the range of 1-2 nm, which is reasonable given the errors associated with thresholding[3] and the resolution of the FESEM. Zetasizer Nano (Malvern Ltd.) was used for DLS measurements. AFM characterization was performed using MFP-3D (Asylum Research) in a clean room environment, maintained at 21°C and 45% RH. A set of silicon nitride tips (Olympus, OMCL-AC-240 TS, spring constant: 20-40 N/m, resonant frequency: 340 kHz) were used for imaging and force spectroscopy. The heights of the nanoparticle films were obtained by averaging across several cross-sections from images spread across the sample (typically several mm's across), and the standard deviations of the measured values (n>100 cross-sections) were approximately 1 nm. The force-displacement curves reported were repeatable across several areas, and were further verified by intermittently checking the reproducibility of force-displacement curves on bare silicon substrate. In the case of the array formed on polystyrene thiol modified water, the force-displacement curves were almost identical everywhere on the substrate, except for reproducible differences in adhesive force, possibly due to transfer printing of the polystyrene thiol layer along with the nanoparticle array. This was further confirmed by the phase image of the sample, which showed that the phase lag was similar both on top of the array and on the 'reference' plane.

Thiol-functionalized polystyrene grafted gold nanoparticles were dispersed in toluene, and 5 µL drops were cast on three different substrates; namely, silicon, graphite and water. The toluene drops spread rapidly into a uniform thin film (due to favourable vdW interactions and large spreading coefficients), and resulted in the formation of a monolayer of gold nanoparticles after solvent evaporation (~1 minute), over macroscopically large areas. The monolayer formed on the water surface was transferred onto a silicon substrate by microcontact printing for further characterization. Representative FESEM images are shown. The average interparticle spacings (edge to edge distances) were determined to be 20.0, 14.5 and 10.0 nm on silicon, graphite and water respectively. The average thicknesses of the thin-films were found to be 23.0, 21.0 and 23.3 nm respectively. These values are only slightly lower than the mean hydrodynamic size (dh) of thiol-functionalised polystyrene grafted gold nanoparticles in toluene (29 nm based on Dynamic Light Scattering (DLS) measurements).



Representative FESEM images of self-assembled 2D arrays of thiol-functionalized polystyrene grafted gold nanoparticles (a-c, e-g) and their corresponding interparticle spacing distributions (d, h). The insets in the images show representative cross-sectional profiles measured using AFM. These 2D arrays were formed by drop-casting gold nanoparticles from: a) toluene solution onto silicon substrate (with native oxide), b) toluene solution onto freshly cleaved graphite, c) toluene solution onto water, e) tetrahydrofuran solution onto silicon (with native oxide), f) 50% (v/v) chloroform/cyclohexane solution onto water, g) toluene solution onto a water surface that was *a priori* modified with a thin film of thiol functionalised polystyrene.

10. **Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:**

11. **Conclusions summarizing the achievements and indication of scope for future work:**

12. **S&T benefits accrued:**

i. **List of Research publications**

S No	Authors	Title of paper	Name of the Journal	Volume	Pages	Year
1	G. Muralidharan, S. K. Sivaraman, and V. Santhanam	Effect of substrate on particle arrangement in arrays formed by self-assembly of polymer grafted nanoparticles	Nanoscale	3	2138-2141	2011
2	G. Muralidharan, Navakanta Bhat, and V. Santhanam	Scalable processes for fabricating non-volatile memory devices using self-assembled 2D arrays of gold nanoparticles as charge storage nodes	Nanoscale	3	4575–4579	2011

ii. **Manpower trained on the project**

a) **Research Scientists or Research Associates** - none

b) **No. of Ph.D. produced-** One

c) **Other Technical Personnel trained -** Three (M.S -1; P.A -1; M.Tech-1)

iii. **Patents taken, if any**

13. **Financial Position:**

No	Financial Position/ Budget Head	Funds Sanctioned	Expenditure	% of Total cost
I	Salaries/ Manpower costs	398000	231500	7.71
II	Equipment	2010000	2009746	66.98
III	Supplies & Materials	315000	312815	10.43
IV	Contingencies	100000	99950	3.33
V	Travel	50000	46600	1.55
VI	Overhead Expenses	300000	300000	10.00
VII	Others, if any			
	Total	3173000	3000611	**100%**

14. **Procurement/ Usage of Equipment**

a)

S No	Name of Equipment	Make/Model	Cost (FE/ Rs)	Date of Installation	Utilisation Rate (%)	Remarks regarding maintenance/ breakdown
1	Tube furnace	Delta Power Controls	Rs.3,35,707	3/2011	80	Currently being upgraded with an automatic vacuum control system
2	Solar Simulator	Newport, QE system	Rs. 16,74,039	10/2011	30	

b) Plans for utilising the equipment facilities in future

We are now upgrading the vacuum tube furnace with a home-built vacuum controller and appropriate flanges to enable pressure control during temperature ramp-up, growth and ramp-down periods

The Newport system is currently being used to characterize the photovoltaic performance of standard TiO2 based DSSCs and in the future will be used to characterize ZnO nanowire array based DSSCs

Name and Signature with Date

a._____
(Principal Investigator)

b._____
(Co-Investigator)