

**ISRO-IISc Space Technology Cell  
Indian Institute of Science  
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**ISTC**

**Nanostructured Chemoresistive Gas Sensor**  
(Final Technical Report)

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*April, 2014*



Project Title: <b>Nanostructured Chemoresistive Gas Sensor</b>	Project Code: <b>ISTC/MCE/VS/286</b>
	Date of Commencement: <b>01/04/2012</b>
	Date of Closure: <b>31/03/2014</b>
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Type of Project: <b>Research</b>	
Security classification if any: <b>Open</b>	
Short Abstract: <b>Nanostructured-palladium based gas sensors with potential for sensing hydrogen have been fabricated using an inkjet printer. Results of process development aimed at optimizing hydrogen sensing performance on paper/plastic substrates are presented in this report.</b>	
Keywords: <b>Inkjet printing, Palladium nanostructures, Hydrogen sensor</b>	

## **Acknowledgements**

The efforts of the following students/research scholars involved in the development of the inkjet printing process are gratefully acknowledged: Mr. Shravankumar Parmar, Mr. Pushkaraj Joshi, and Mr. Abhishek Panigrahi. We also thank Mr. Ingersol from ISRO and Dr. M. M. Nayak from IISc for their valuable inputs regarding hydrogen sensor design and expected performance characteristics.

## Abstract

A simple process for fabricating resistive palladium nanostructures on paper has been developed. A Print-Expose-Develop cycle was used to pattern conductive silver nanostructures on paper using a desktop inkjet printer. Galvanic displacement of silver with palladium was used to fabricate resistive palladium nanostructures. Such palladium nanostructures are promising candidates as hydrogen sensors. Preliminary experiments indicate that the hydrogen adsorption induced transformation of palladium to palladium hydride can be detected using these nanostructures as an increase in resistance. Currently, efforts are underway to fabricate such nanostructures on a flexible plastic substrate and to optimize the sensor morphology to improve response time, recovery time, and repeatability.

The use of palladium coated gold nanoparticle arrays as a platform for sensing hydrogen was also pursued. Protocols for synthesizing palladium coated gold nanoparticles and self-assembling them as monolayer arrays were developed. Electrically contacting such nanoparticle arrays by stamping onto pre-patterned electrodes as well as forming patterned electrodes on top of the self-assembled nanoparticle arrays have been pursued. Currently, efforts are underway to form robust and reliable electrical contacts to nanoparticle arrays.

## Contents

### Chapter 1 Introduction

#### 1.1 Motivation and Objective

In the original proposal, we planned to design a sensor that combined the molecularly-specific interactions of metalloporphyrins with the transducing capability of Ligand Protected Nanoparticle (LPN) arrays to detect changes in the electronic energy levels of molecules interconnecting neighbouring nanoparticles. The key aspect of the proposed design being the use of a monolayer of nanoparticles to avoid signals arising from swelling caused by analyte partitioning into the organic matrix of multilayered films. Based on interactions with Dr. Nandakumar during the initial stages of the project, we decided to focus on the development of a hydrogen sensor. Hydrogen carrying pipelines at LPSC span a length of few hundred metres, and represent a significant safety concern. Commercial hydrogen leak detectors are expensive and impose a significant cost burden for continuous monitoring. Moreover, the standard detectors are rigid which limits their ability to monitor joints in pipelines for incipient leaks. Therefore, it is essential to develop a cost-effective, flexible hydrogen sensing platform indigenously.

In this project, two different approaches have been pursued to fabricate palladium nanostructures capable of detecting hydrogen. The first one is based on a modification of the original proposal, and comprises of using palladium-coated gold nanoparticle arrays as transducers of interaction with hydrogen gas in the environment. The ordered nanoparticle monolayer array provides a large specific surface area for interaction and so, should lead to faster response times, when electrically contacted using micron-scale interdigitated electrodes. The second approach was based on a simple low-cost process to fabricate palladium nanostructures using an inkjet printer in conjunction with photographic chemistry and Galvanic displacement.

#### 1.2 Literature Survey

Available market products mostly rely on catalytic combustion induced temperature changes, thermal conductivity measurements or passivation of surface defects in semiconductor-metal oxide films as the principle of detection of Hydrogen [1]. Issues related to cross-sensitivity, reliability and robustness have been addressed by specialised engineering of the sensor, leading to complex designs that are not easily portable or cheap to fabricate. Metallic films, on the other hand, esp. palladium alloy based resistors have a more specific and selective interaction with Hydrogen under typical sensing conditions and so, can be easily fabricated. Thin palladium films respond to hydrogen very slowly by an increase in resistance [2]. Upon exposure, the surface of palladium metal becomes saturated with dissociated hydrogen, as hydrogen is adsorbed strongly in comparison to other species present in ambient air. The proton then diffuses into the crystal lattice of palladium to form Pd-Hx. The hydride has a higher lattice constant and higher resistivity than Pd. Therefore, the metal swells with an increase in resistance. The sequence of steps involved in the formation of Pd-Hx is shown in Fig. 1.

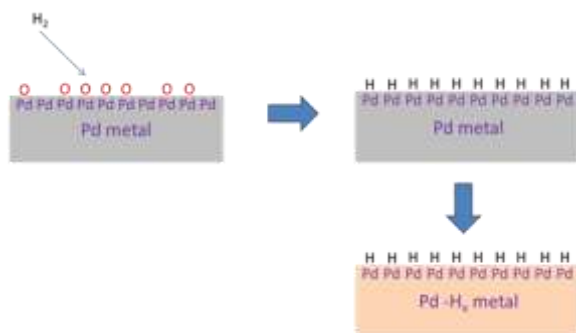


Figure 1: Schematic representation of the various stages of formation of Pd-H<sub>x</sub>, when palladium nanostructures are exposed to hydrogen. Initially, the surface palladium atoms are covered with oxygen molecules from the ambient atmosphere. After exposure to Hydrogen in the gas phase, the hydrogen molecules are catalytically dissociated and hydrogen atoms are preferentially adsorbed on the palladium surface. Upon continuous exposure, the hydrogen permeates into the bulk of the palladium film to form palladium hydrides.

The mechanism of formation of Pd-H<sub>x</sub> involves saturation of surface of palladium with hydrogen atoms formed by dissociation of hydrogen molecules. Therefore, increasing the surface to volume ratio should improve the sensitivity, while decreasing the size to nanoscale regime would minimize the diffusion timescales to form Pd-H<sub>x</sub> and hence vastly decrease the response time of the sensor. Also, the reversibility of the sensor depends on the ability of the sensing film to relieve mechanical stress

accumulated during the expansion and contraction cycle without delamination or fracture. Therefore, a mesh of mesoscale/nanoscale - palladium/palladium alloy nanowires would be an ideal platform for manufacturing fast, reversible and robust hydrogen sensors. Palladium meso-wires [3], comprising of “beads on a string” morphology, have been fabricated by electroplating on templates from solutions of palladium salt. This architecture when exposed to hydrogen forms Pd-Hx, which swells and closes the nano-gap between palladium nanoparticles. This increases the number of percolating pathways resulting in decrease in resistance. The swelling of palladium occurs at the time scale of diffusion of proton into the palladium nanoparticle, viz. < 1s. These devices have fast response, but the fabrication process is prone to large variations leading to irreproducible behaviour amongst sensors. Single palladium nanowires [5] subjected to hydrogen environment respond faster compared to thin films as well as nanoparticle films. However, they cannot be fabricated over a large scale. Palladium metal and alloy nanoparticle films (MPC - monolayer protected cluster films)[4] have been tested for response to hydrogen. The organic capping hinders the access of metallic surface to hydrogen, thus reducing their response. An improvement was sought by ozone and/or thermal treatment of these devices to remove the organic layer. However due to lack of control over the process parameters, the response was irreproducible. Also, Pd-Hx exists in two phases,  $\alpha$  and  $\beta$  at low and high H<sub>2</sub> concentrations. These phases have different lattice constant leading to different electrical resistance, thereby leading to a hysteretic behaviour when exposed to cyclic hydrogen concentrations. However, alloying palladium nanostructures with other metals like silver or gold helps to limit hysteretic behaviour[6]. Hence in order to produce a robust hydrogen sensor, we must address the issue of large scale manufacturing of bare and robust palladium alloy nanostructures to ensure faster response and reliable performance.

### *1.3 Scope of the Project*

The scope of the project was the development of a simple, low-cost process for fabricating hydrogen gas sensors on flexible substrates like paper and plastic sheets.

## Chapter 2 Results and Discussions

### 2.1 Self-assembled arrays of Palladium coated gold nanoparticles

Gold nanoparticles of size  $5.1 \pm 0.8$  nm and  $6.6 \pm 0.7$  nm were synthesized using tannic acid protocol developed in our group. Dodecanethiol (DDT) replaced tannic acid by ligand exchange in a 1mM solution of DDT in ethanol. The solution was left undisturbed for about 6 hours and then centrifuged at 3000 rpm for 45 minutes to precipitate the nanoparticles. The precipitate was further washed in ethanol and centrifuged twice to remove excess DDT. After drying the precipitate for 6 hours, the nanoparticles were dispersed in an appropriate solvent for self-assembly. Close packed nanoparticle monolayer films were formed with the aid of self-assembly on air-water interface. Two methods were used for self assembly – Teflon cell method, and petridish method. Fig.2 shows the details of the self-assembly methods.

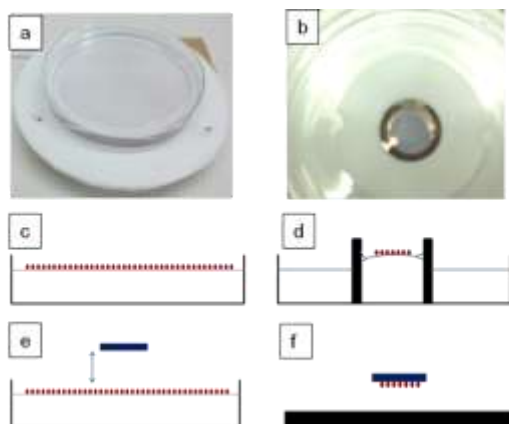


Figure 2: Self assembled monolayer by Petridish method. [(a) and (c)]Teflon cell [(b) and (d)] and. Langmuir-Schaefer transfer of monolayer [(e) and (f)] to a PDMS stamp pad for transfer printing onto desired substrates.

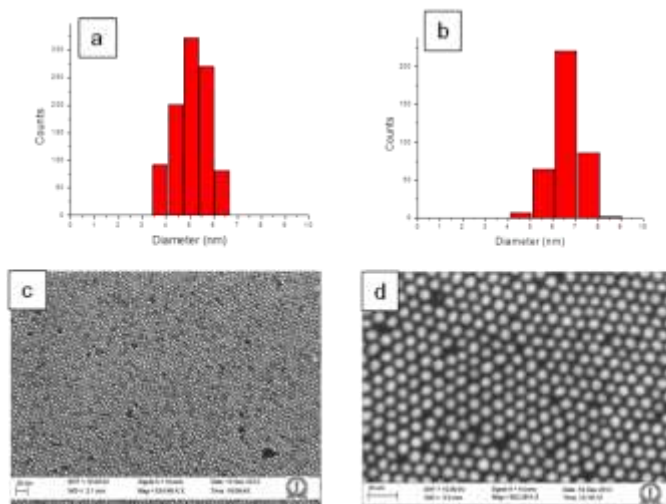


Figure 3: (a) and (b) show the size histograms of 5 nm and 7 nm particles respectively. Representative FESEM images of 5 nm (c) and 7 nm (d) gold nanoparticle array capped with dodecanethiol. Scale bar in both the images represent 20 nm.

The monolayer was transferred by Langmuir-Schaefer technique using a PDMS stamp. Representative field emission scanning electron microscopy (FESEM) images (Ultra-55, Zeiss) are shown in Fig. 3 (c), (d). For particle sizing, the FESEM images of particles were analyzed using ‘ImageJ’ software. The thresholding of the images to capture particle edges was done manually and further eroding and filling was done to smoothen the edge. Fig 3 (a), (b) show the size histograms obtained by this procedure.

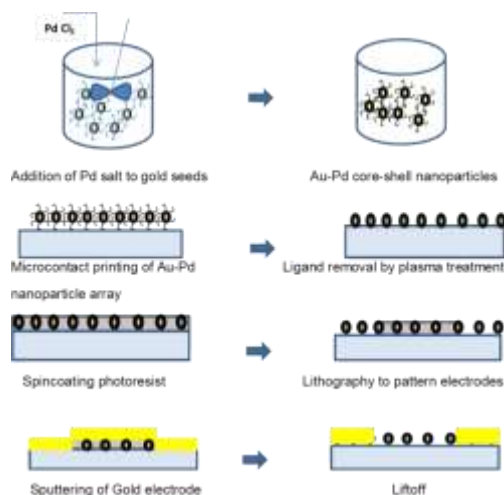


Figure 4: Schematic of steps involved in fabrication of hydrogen sensor based on self-assembly of Au@Pd nanoparticles.

A modified tannic acid protocol was used for synthesis of Au-Pd core shell nanoparticles. Tannic acid protocol was used to synthesize  $5 \text{ nm} \pm 0.7 \text{ nm}$  gold seeds. To grow a 2 nm shell of Palladium on the gold seeds, 75  $\mu\text{L}$  of (50 mM)  $\text{PdCl}_2$  salt solution in 0.2 N HCl was added dropwise after adjusting the pH of the solution to  $\sim 10$ . The color of the solution turned dark immediately after adding  $\text{PdCl}_2$ . Fig. 5 shows the seed solution (red) and the core-shell particle (dark brown/black) solution.



Figure 5: Digital photograph of seed solution containing 5 nm gold nanoparticles (red) and Au-Pd core-shell nanoparticles (dark brown/black).

Tannic acid at basic pH turns dark brown in color with time. Hence, UV-Vis spectrometry of the core-shell particles is performed to verify the suppression of surface plasmon resonance of the gold seeds. Fig. 6 shows a comparison of UV-Vis spectra of the Au-Pd solution with the gold seed, seed at pH 10 and tannic acid solutions. It shows that the surface plasmon peak at  $\sim 520 \text{ nm}$  of gold seed disappears only in Au-Pd solution. This provides a clear indication of coating of Pd on gold seeds. However, it is necessary to verify if all the Pd is coated on the seeds. A dropcast solution of DDT coated Au-Pd solution was viewed under FESEM. Fig. 7 shows representative FESEM images of the drop-cast sample after plasma treatment. The FESEM indicates two modes in the size distribution of particles. This indicates that some of the Pd might be nucleating to produce smaller particles.

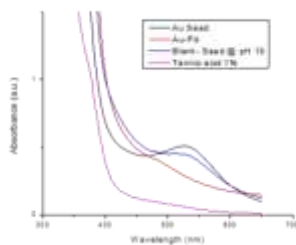


Figure 6: UV-visible spectra comparison of aqueous solutions of Au-Pd, gold seeds, gold seeds at pH 10 and tannic acid.

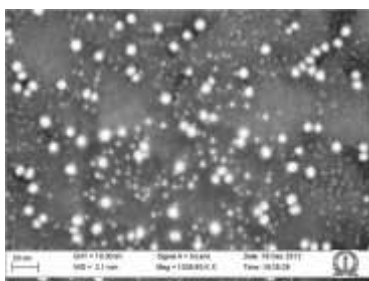


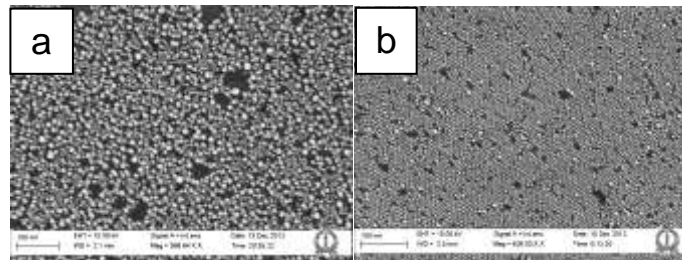
Figure 7: Representative FESEM image of particles dropcast from a solution of Au-Pd.



**Substrate preparation** - The substrate used for printing the monolayer is a nominally 100 nm thick SiO<sub>2</sub> film on Si wafer. It was prepared by oxidation of Si wafer. For this n-type Si (100) substrate was cleaned using RCA (Radio Corporation of America) protocol followed by HF (Hydrofluoric acid) dip for removal of native oxide. The wafer was then subjected to thermal oxidation process (dry oxidation) at 1000°C for 3 hours. To improve the oxide quality, the wafer was annealed at 1100°C for 10 minutes. The thickness of the oxide layer was measured using Ellipsometry (Accurion) and found to be around 113 ± 2 nm.

**Ligand removal** - Recently Sivaraman and Santhanam have shown that ligands can be removed without disturbing the nanoparticle array using ordinary RF plasma. The resulting array is chemically as well as thermally robust. The same protocol for ligand removal was followed. RIE (Milman Thin Film Systems Pvt. Ltd.) was used for removing ligand at optimized conditions. After the hydrogen plasma treatment, the substrate was washed in ethanol/water to remove physisorbed remnants of ligands.

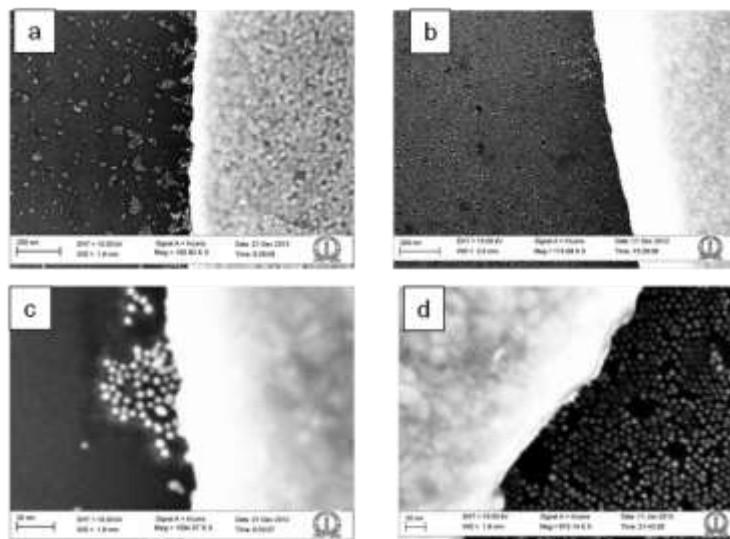
**Preheat treatment** - To pattern interdigitated gold electrodes on top of the array, photolithography was performed. Before spincoating the photoresist onto the substrate, the substrate was preheated to about 120°C for 1.5-2 hours. This removes bound moisture present on the substrate. Presence of moisture / ethanol prevents proper adhesion of the photoresist with the substrate. Fig. 8 shows representative FESEM images of substrates of 5 nm array with and without ethanol wash.



*Figure 8: Representative FESEM images of 5 nm gold nanoparticle array washed with ethanol after plasma treatment (a) and without ethanol wash (b). Scale bar in both the images represent 100 nm.*

The array after plasma treatment and cleaning in ethanol/water mixture is reported to be stable against solvents. However, ethanol washing of this sample caused the particles to coalesce. DDT capped particles are known to coalesce in ethanol. This implies that ligand removal is incomplete. This can occur due to drift in the RIE chamber conditions. Therefore, conditions for complete ligand removal need to be optimized, and this task is currently held-up due to a breakdown of the RIE equipment.

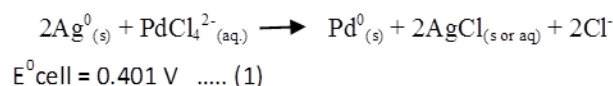
**Lithography** - Interdigitated electrodes (IDE) were patterned on the substrates using photolithography. The stability of the nanoparticle array with and without ligand removal due to plasma treatment was studied. Fig. 9 shows that when the array is untreated it dissolves away during the process of photolithography. Whereas plasma treated array can withstand lithography process. To avoid any contact resistances, good contact of electrode with the array is essential. The FESEM images show that there is a good physical contact between the array and the electrode in this sample.



*Figure 9: Representative FESEM images of electrodes fabricated without plasma treatment (a), (c) and with plasma treatment (b), (d). Scale bar in (a) and (b) represents 200 nm, for (c) 30 nm and for (d) 20 nm.*

## 2.2 Large scale fabrication of Ag–Pd nanostructures

Silver nanowires were formed *in situ* on paper by depositing a silver bromide film using an office inkjet printer, followed by exposure to actinic light and development in a commercial photographic developer solution. The resultant silver nanowire networks on paper (Fig. 10) were transformed into palladium silver alloy nanostructures by galvanic displacement reaction, upon immersion of the silver nanowires in a bath of palladium salt at room temperature. The concentration of palladium salt used and duration of immersion were varied to obtain different compositions of palladium-silver alloys. Eq. (1) describes the chemical reaction involved in the galvanic displacement process.



Microscopic and spectroscopic characterization of the nanostructures on paper after palladium displacement confirmed the presence of palladium and the formation of a palladium silver alloy, which would be useful in avoiding hysteretic behaviour upon hydrogen dissolution and release from palladium nanostructures. FESEM and TEM images (Fig.11) showed that hollow nanostructures were generated after galvanic displacement. This is in concord with the fact that silver atoms diffuse faster than palladium atoms and so, the displacement of silver by palladium atoms occurs at the nanowire-solution interface. The XRD results confirm the formation of an alloy structure based on the intermediate position of the (111) reflection between that of pure silver and pure palladium. XPS spectra confirm the predominant presence of the reduced form of palladium in these samples. The resistance of the samples increased by three orders of magnitude after the galvanic displacement reaction, which alluded to the formation of nanoscale gaps (see Fig. 13) between the Pd-Ag alloy filaments, as the specific resistivity of the alloy is only slightly lower than that of bulk.

The sensing performance of a Pd-Ag nanostructure was carried out in a testing set-up available at CeNSE, IISc. A 1000 ppm test gas of hydrogen in synthetic air was passed at 1000 sccm into the chamber, maintained at room temperature (25 °C). The current decreased rapidly upon introduction of hydrogen gas, while it took a considerably longer time to recover. This response suggests that compositional changes in the palladium film are responsible for the observed changes and that the morphology is not suited for swelling induced resistance percolation mechanism, which would have a better response time. These results are promising in terms of cost of fabrication of hydrogen sensors, although their response characteristics need to be optimized further for field-deployment. Presently, investigations are ongoing to optimize the extent of alloying and morphology to attain responses similar to swelling-bridged nanogaps, which should improve the sensitivity and response times substantially. The underlying drift in the current response (Fig. 12) has been recently traced to a fault in the current measurement unit used at CeNSE and measurements using another electrical measurement unit did not show any drift in current with time. During the demo/interaction with ISRO personnel in June 2013, it was suggested to modify the design and fabricate the sensor on a plastic substrate, to ward off safety concerns about using paper, a flammable material, as the substrate. After optimising the surface properties of a standard inkjet transparency, Ag nanostructures have now been successfully formed on plastic substrates (Fig. 13) and converted to palladium nanostructures. We are currently in the process of characterizing their sensor response.

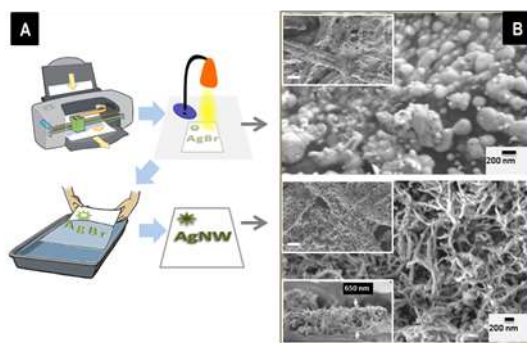


Figure 10. Print-Expose-Develop scheme for *in situ* formation of conductive silver nanowires on paper using a desktop inkjet printer.

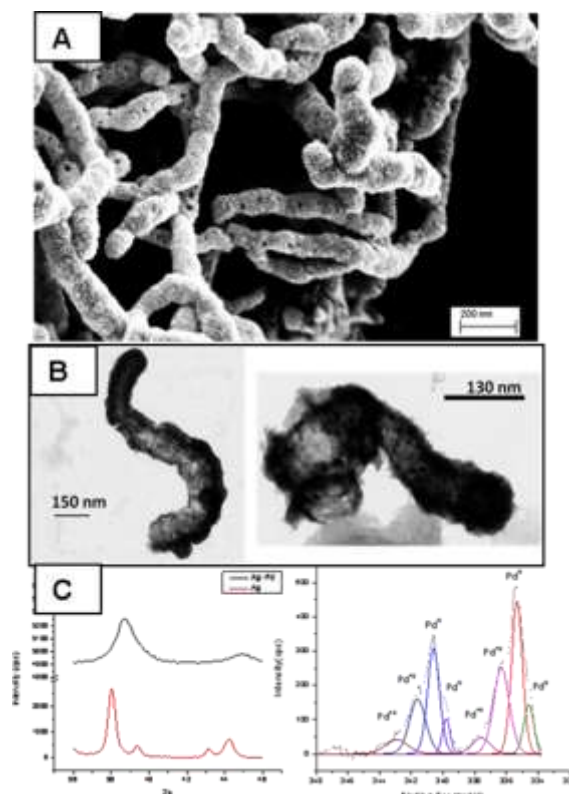


Figure 11. Microscopic and spectroscopic characterization of a 1:1 Pd:Ag sample formed by galvanic displacement of silver nanowire networks on paper. a) FESEM image showing a roughened filamentary structure, b) TEM images of nanofilaments suggesting hollow nature of these structures, c) XRD and XPS characterization of the sample.

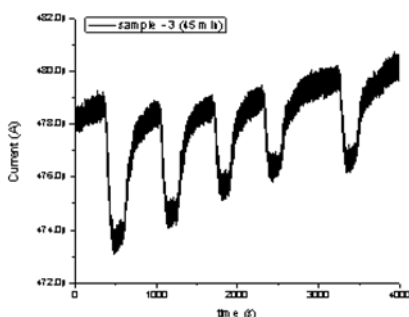


Figure 12. Current change across a Pd-Ag nanostructure on paper at a constant applied voltage of 1 V. The sensor response shows an immediate decrease in current upon introduction of hydrogen gas(response time~ 6s), while it takes much longer to recover. There is also a drift in the baseline response with time that is attributed to a fault in the electrical characterization set-up used for these measurements.

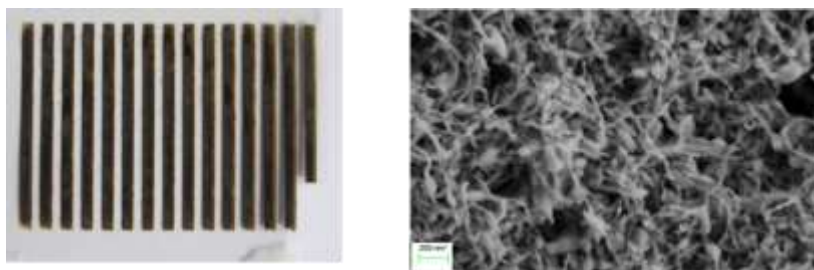


Figure 13 (a) Stripes of 1.5''x0.08'' are printed on a transparency sheet. (b) Representative FESEM of Ag nanofilaments on transparency. Scale bar corresponds to 200 nm.

## Chapter 3 Conclusions

A simple process for fabricating flexible, paper-based silver-palladium alloy nanostructures was developed. Structural and spectroscopic characterizations clearly demonstrate the successful formation of a Pd-Ag alloy. The response of these nanostructures to hydrogen gas indicates that palladium hydride formation with concomitant increase in electrical resistance is the mechanism of sensing. Further efforts are underway to optimize the nanostructure morphology and improve the response as well as recovery characteristics by optimizing the gaps between palladium nanostructures so that swelling induced resistance decreases can be measured leading to faster response times. The development of flexible hydrogen sensors using a low-cost fabrication process will pave the way for improved safety while handling hydrogen gas, an issue of growing importance to ISRO as well as the developing fuel cell based 'hydrogen economy'. Fabrication of Ag nanofilaments over a plastic substrate is successful. Future efforts would go into optimizing the performance of sensor by varying different ratios of Ag and Pd.

### Deliverables

- Low-cost process for fabricating palladium nanostructures on paper/plastic substrates.

### Future Direction

- Optimizing the sensor response of palladium nanostructures to detect low concentrations of hydrogen in a rapid and reliable manner.

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