NANOSTRUCTURED GAS SENSOR BY INKJET PRINTING

Pushkaraj Joshi, Kalyan Nandakumar and Venugopal Santhanam

***Abstract*—A simple process for fabricating conductive 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 the conductive palladium nanostructures These 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 response characteristics in terms of response time, recovery time, and repeatability.**

I. INTRODUCTION

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 place a significant cost burden in terms of continuous monitoring. Moreover, the standard detectors are rigid which limits their ability to monitor joints in pipelines for incipient leaks. In this article, we describe a novel process for fabricating palladium-based nanostructures on flexible substrates using a desktop inkjet printer. This process has the potential to form low-cost hydrogen sensors on flexible substrates that could be easily wrapped around pipelines for continuous online monitoring.

Palladium based sensors have been the most popular choice for detecting hydrogen [1]. Palladium forms palladium hydride (Pd-H_x), an alloy wherein hydrogen atoms are formed by dissociation on the surface of Pd and diffuse into the interior and occupy the interstitial spaces, when exposed to hydrogen atmosphere. Palladium hydride has two different phases with vastly different lattice constants, corresponding to low and high hydrogen contents. This results in a hysteretic structural change, at room temperature, upon cycling the hydrogen concentration, which leads to hysteretic behavior in the electrical properties of the sensors based on palladium thin films [2]. Palladium alloy nanostructures, with a palladium rich shell, can avoid such hysteretic behavior due to confinement induced restriction on structural expansion [3]. Palladium-silver alloy nanostructures have been studied as possible alternatives to pure palladium nanowires to enhance the response characteristics in terms of reversibility and faster response times at room temperature [4].

Pushkaraj Joshi is a research scholar in the Department of Chemical Engineering, IISc, Bangalore-560012

Dr. Venugopal Santhanam is an assistant professor in the Department of Chemical Engineering, IISc, Bangalore-560012

Dr. Kalyan Nandakumar is head of the Combustion Division in the Liquid Propulsion Systems Centre, ISRO-Valiamala, Trivandrum 695 547

Project Code: **ISTC0286**

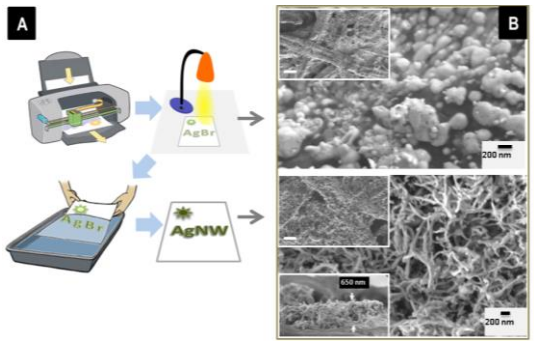

Fig. 1. Print-Expose-Develop scheme for *in situ* formation of conductive silver nanowires on paper using a desktop inkjet printer [5].

II. FABRICATION PROCESS

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. 1) were transformed into palladium silver alloy nanostructures by galvanic displacement reaction [6], 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.

$$2Ag^{0}_{(s)} + PdCl_4^{2-}{}_{(aq.)} \longrightarrow Pd^{0}_{(s)} + 2AgCl_{(s\ or\ aq)} + 2Cl^{-}$$

$$E^{0}cell = 0.401\ V \quad \ldots\ldots (1)$$

These paper-based conductive nanostructures were then placed inside a gas testing facility for sensor response characterization. A 1% Hydrogen in Nitrogen (1000 ppm) gas cylinder was used to obtain the results reported here.

III. RESULTS

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. FESEM and TEM images (Fig.2) 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.

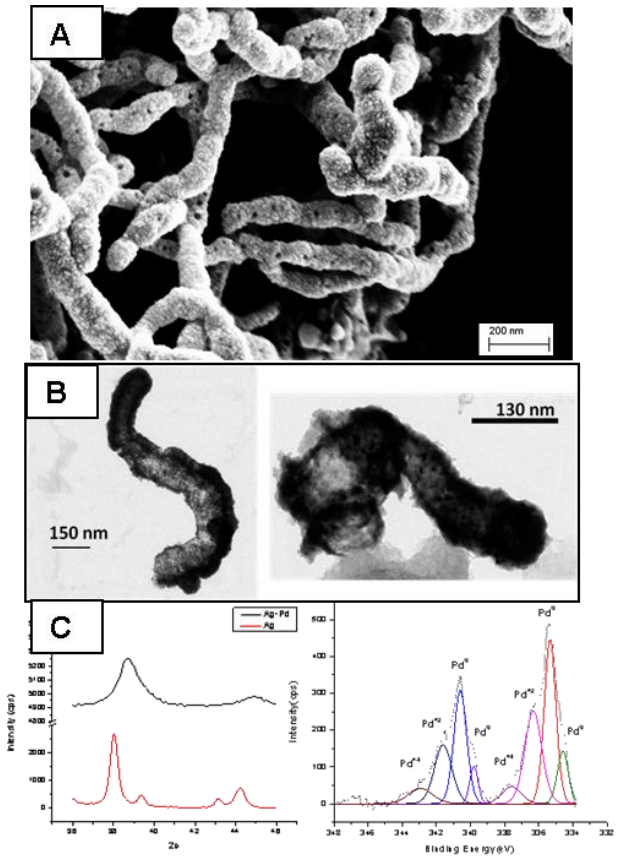

Fig. 2. Microscopic and spectroscopic characterization of a 1:1 Pd:Ag sample formed by galvanic displacement of silver nanowire networks on paper. a) FESEM image showing a roughened filamentary structure, b) TEM images of nanofilaments suggesting hollow nature of these structures, c) XRD and XPS characterization of the sample.

The resistance of the samples increased by three orders of magnitude after the galvanic displacement reaction, which alluded to the formation of nanoscale gaps between the Pd-Ag alloy filaments, as the specific resistivity of the alloy is only slightly lower than that of bulk. This is a promising characteristic in terms of hydrogen sensing capability, as hydrogen adsorption induced swelling and concomitant resistance decreases can lead to faster response times.

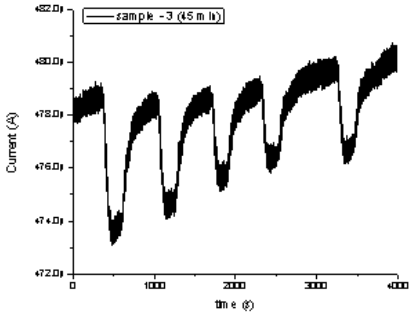

Fig. 3. Current change across a Pd-Ag nanostructure on paper at a constant applied voltage of 1 V. The sensor response shows an immediate decrease in current upon introduction of hydrogen gas(response time~ 6s), while it takes much longer to recover. There is also a drift in the baseline response with time that is attributed to electric field induced fusion of nanofilaments.

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 morphological changes in the palladium film are responsible for the observed changes and that the extent of alloying is not appropriate for suppressing the structural changes in the palladium layer. 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.

IV. SUMMARY

A simple process for fabricating flexible, paper-based silver-palladium alloy nanostructures was developed. Structural and spectroscopic characterizations clearly demonstrate the successful formation of an Pd-Ag alloy. The response of these nanostructures to hydrogen gas indicates that palladium hydride formation with concomitant phase transformation induced hysteretic electrical response is operative. Further efforts are underway to optimize the nanostructure morphology and improve the response as well as recovery characteristics. 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’.

REFERENCES

[1] T. Hübert, L. Boon-Brett, G. Black, and U. Banach, "Hydrogen sensors–a review," Sensors and Actuators B: Chemical, vol. 157, pp. 329-352, 2011..

[2] J.-S. Noh, J. M. Lee, and W. Lee, "Low-dimensional palladium nanostructures for fast and reliable hydrogen gas detection," Sensors, vol. 11, pp. 825-851, 2011.

[3] G. Monty, K. NG, and M. Yang, "palladium-silver alloy nanowires and nanoparticle columns for use as variable-range hydrogen sensors," EP 1552272 2011.

[4] X.-Q. Zeng, Y.-L. Wang, H. Deng, M. L. Latimer, Z.-L. Xiao, J. Pearson, T. Xu, H.-H. Wang, U. Welp, and G. W. Crabtree, "Networks of ultrasmall Pd/Cr nanowires as high performance hydrogen sensors," ACS nano, vol. 5, pp. 7443-7452, 2011.

[5] S. Parmar and V. Santhanam, "*In situ* formation of conductive silver nanowire networks", Manuscript in progress, 2013.

[6] J. F. Patton, S. R. Hunter, M. J. Sepaniak, P. G. Daskos, and D. B. Smith, "Rapid response microsensor for hydrogen detection using nanostructured palladium films," Sensors and Actuators A: Physical, vol. 163, pp. 464-470, 2010.