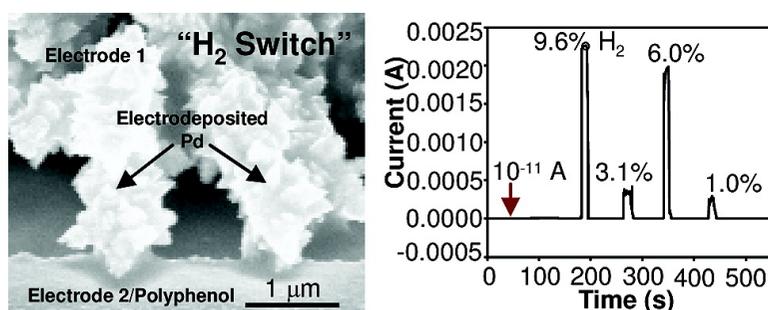## Communication

Hydrogen Switches and Sensors Fabricated by Combining Electropolymerization and Pd Electrodeposition at Microgap Electrodes

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Hydrogen Switches and Sensors Fabricated by Combining Electropolymerization and Pd Electrodeposition at Microgap Electrodes

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Here we describe a simple, highly reproducible electrochemical method for fabricating Pd-based H_2 sensors and switches. This work was inspired by Penner and co-workers,[1] who electrochemically synthesized an array of Pd mesowires on the step edges of highly oriented pyrolytic graphite and studied their resistance change in the presence of H_2. They observed a significant decrease in resistance due to the connection of break junctions within the mesowires upon volume expansion of PdH_x.[1] This mechanism led to devices with larger and faster responses compared to traditional Pd-based H_2 sensing devices, which exhibit a resistance increase in the presence of H_2 due to the formation of PdH_x.[2] Our group and others reported H_2 sensing with films of Pd nanoparticles[3,4] containing nanoscale gaps that operate on similar principles.

The approach described here importantly leads to Pd/electrode junctions with controlled responses to H_2 by uniquely combining Pd electrodeposition and phenol electropolymerization at microgap electrodes with the benefits of (1) a direct contact formed between the Pd structures and the electrodes during synthesis, eliminating the need for multistep processes involving transfer, assembly, lithography, and contact formation common in electronic-based micro/nanosensing devices that lead to long fabrication times and device failures, (2) a simple, fast, highly parallel process with a 100% success rate, and (3) general applicability toward fabricating a wide range of metal/organic/metal junctions.

Scheme 1 illustrates the two methods used to electrochemically fabricate devices on Au interdigitated array (IDA) electrodes (10 or 14 fingers) separated by a 5 μm gap. Procedure A, referred to as a "H_2 Sensor", involves electrodeposition of 1.2×10^{-3} coulombs of Pd on one set of electrodes (Electrode 1, E1) from a 5 mM $PdCl_4^{2-}$ solution at -0.1 V vs Ag/AgCl. Procedure B, referred to as a "H_2 switch", involves electropolymerization of phenol on one set of electrodes (Electrode 2, E2) by cycling from 0.0 to 1.2 V at 100 mV/s in a 5 mM phenol solution in 0.1 M H_2SO_4 for 4 to 10 cycles followed by the same Pd electrodeposition procedure on E1 used in Procedure A.

Figure 1A and B show scanning electron microscopy (SEM) images of a portion of 10-finger IDA electrode devices containing an E1/Pd/E2 and an E1/Pd/polyphenol (10 cycles)/E2 junction of a "H_2 sensor" and "H_2 switch", respectively (see Figure S1 of the Supporting Information for image of the entire array). Pd electrodeposited on E1 crossed over to E2 with a dendritic or flower-like structure. Frames C and D show the corresponding current–voltage plots. The "H_2 sensor" is ohmic, exhibiting a current of 13.0 mA at -1.0 V ($R = 77$ Ω). The "H_2 switch" exhibits a current of 2.09 nA at -1.0 V ($R = 478$ MΩ), but there is significant hysteresis in the plot. Current–time plots of a H_2 sensor and switch (Figure S2) show that the current is constant in the mA range with time for the former but exponentianlly decays by 1 to 2 orders of magnitude down to the 10 to 100 pA range with time for the latter (close to the device background). The high resistance of the "H_2 switch" is due to the low electronic conductivity of the polyphenol film

Scheme 1. Methods for Forming H_2 Sensors and Switches
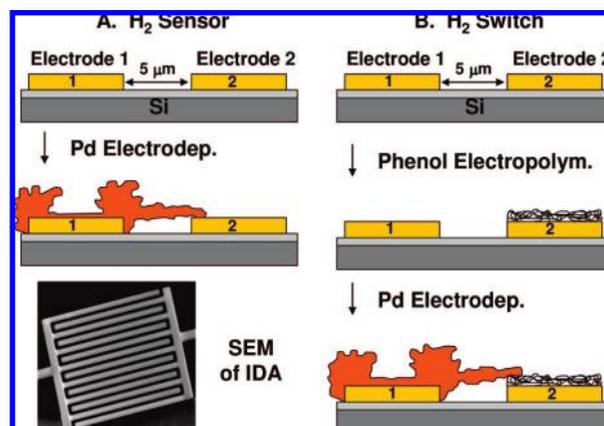
between E2 and the Pd (Scheme 1B), while the hysteresis and exponentially decaying current–time plot reveals some stray ionic conductance within the film.[5] Based on the known conductivity of Pd (94 800 Ω^{-1} cm^{-1}), the current observed for the "H_2 sensor" device corresponds to a contact area of only 83 nm $\times$ 83 nm. This value is much smaller than the apparent contact area observed from the top view SEM images. Side-view SEM images of "H_2 switch" devices in Figure S3 reveal that the Pd deposits vertically and horizontally from E1 preferentially at the edges of the electrodes and apparent connections viewed from the top as in Figure 1 may not actually be in contact with E2. This and possible high contact resistance likely explain the small contact area calculation. Table S1 provides information about the device current, resistance, number of apparent connections from the top view, and contact area based on the resistance for the devices studied. The number of apparent connections varied while the device current was within 1 order of
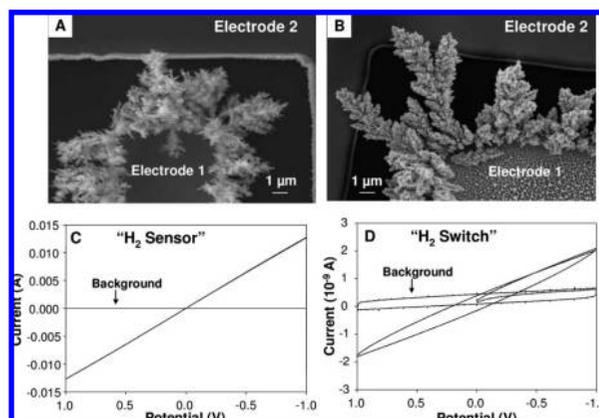
Figure 1. SEM images of (A) H_2 sensor device and (B) H_2 switch device and corresponding i–V curves in (C) and (D), respectively.
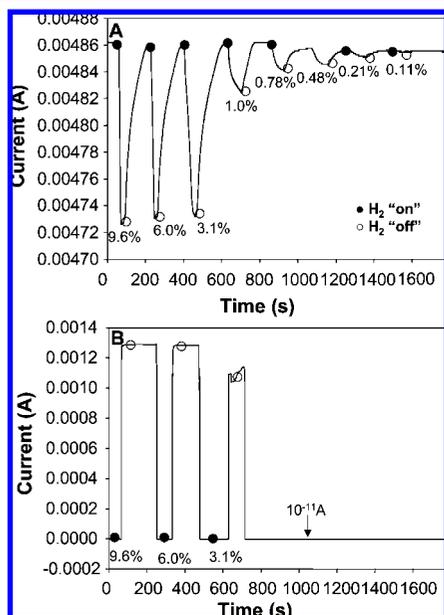
Figure 2. Current−time plots of (A) "H₂ sensor" device and (B) "H₂ switch" (10 cycles of phenol) measured at −0.3 V in the presence of N₂ initially and of various concentrations of H₂ (H₂ on) and 100% N₂ (H₂ off) as indicated.

magnitude for at least three samples of each type of device. These differences did not qualitatively affect the highly reproducible response to H₂.

Figure 2A shows the current at −0.3 V as a function of time for a 10-finger IDA "H₂ sensor" in the presence of 100% N₂ (H₂ "off", ○) and various H₂ concentrations (H₂ "on", ●) as indicated. The current was initially stable in N₂ and then decreased reversibly in the presence of H₂ due to the formation of PdH$_x$, which is more resistive compared to Pd.[2] The nonlinear response between 1.0% and 3.1% H₂ is due to the well-known α- to β-phase transition that occurs during PdH$_x$ formation,[2] and above 3.1% the sensor approaches H saturation. Calibration curves from 0.0 to 0.78% H₂ (Figure S4) for three devices reveal an average slope and theoretical limit of detection of 0.58 ± 0.11 and 0.04 ± 0.03% H₂, respectively (Table S2). The average response and recovery time range from 20 to 60 s (Table S3). Note that the 3% change in the Pd resistance for our H₂ sensor at 9.6% is smaller than the ∼20% change previously reported by Sakamoto et al.[2a] We believe the resistance increase of PdH$_x$ is counteracted by a resistance decrease caused by an increase in contact area upon volume expansion of PdH$_x$. This leads to a smaller increase in resistance than expected (see Scheme S1A).

Figure 2B shows the dramatically different behavior of the "H₂ switch", where the current increases a remarkable 7−8 orders of magnitude in the presence of 1.0% H₂ or larger (see Figure S5 for 1.0% H₂). For example, at 3.1% the current increased from about 1.0×10^{-11} to 1.1×10^{-3} A. We believe the large increase in current is due to the volume expansion of PdH$_x$ through the 4−10

nm thick polyphenol layer (Figure S6), leading to direct contact with E2 (see Scheme S1B). This likely occurs through pores present in the polyphenol film. This proposed mechanism, which is similar to that described by Penner and co-workers for Pd mesowires containing nanoscale break junctions,[1] is supported by three facts. First, we observe a similar threshold detection of ∼1.0% H₂, which is where the transition from α-phase to β-phase Pd occurs.[1,2] Below this threshold, the volume expansion of PdH$_x$ is not sufficient to form a direct connection to E2. Second, the current of the "H₂ switch" device above 1.0% H₂ is the same order of magnitude as the current (10^{-3} to 10^{-4} A) of the directly connected Pd in the "H₂ sensor" (Figure 2 and Table S4−S5), which strongly suggests that direct contact occurs for the "H₂ switch". Third, current−voltage curves of the "H₂ switch" in the presence of H₂ exhibit symmetric, linear curves as does the directly connected Pd in Figure 1C, making it unlikely that changes in Schottky barriers lead to the switching behavior.

Devices fabricated with polyphenol using 4 or 5 electrochemical cycles also operated as "H₂ switches" (Figure S7), but with <100% success. The response and recovery times are generally shorter than 10-cycle devices (Table S6−S7), which we attribute to faster penetration of PdH$_x$ through the thinner, more porous polyphenol film.

In summary, we demonstrate a combination of Pd electrodeposition and polyphenol electropolymerization at microgap electrode arrays for controlled H₂ sensing and switching behavior. While the results here are specific to the Pd/H₂ system, the general strategy of electrochemically controlling metal/organic/metal junctions at microgap electrodes should find broad use in a number of sensing, nanoelectronics, and molecular electronics[6] applications.

Supporting Information Available: SEM images of devices, tables of device characteristics, plots of response versus hydrogen concentration, and current−time plots of hydrogen switch devices. This material is free of charge via the Internet at http://pubs.acs.org.

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