Single metal and conducting polymer nanowire sensors for chemical and DNA detections

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Abstract. Due to the small size, sensitivity, real time detection, and ultra-low power demands, nanowire sensors are being investigated for detection of a wide range of chemical and biochemical species. However, techniques used to fabricate these nanowire sensors have drawbacks of limited controllability and manufacturability. Reliable and controllable nanowire fabrication remains a significant challenge. In this work, we have developed a fabrication technique that is potentially capable of producing arrays of individually addressable nanowire sensors with controlled dimensions, positions, alignments, and chemical compositions and are in the process of fabricating sensor arrays to detect gases, and biochemicals. Fabrication of single Pd nanowires with diameters from 70 nm to 300 nm and up to 7 µm in length will be presented. These nanowires are used to sense hydrogen gas at concentrations as low as 0.02% and show a response time of 300 msec with an operating power of 350 nW. We also recently demonstrated the feasibility of fabricating single polypyrrole and polyaniline nanowires and their application as DNA sensor (1 nM). Currently, we are investigating single nanowire field effect transistors (SNWFET) for possible applications which include label-free DNA detection, early detection of disease signatures, and environmental monitoring.

1. Introduction
Nanotechnology involves the fabrication of materials, devices, and systems through the manipulation of individual atoms and molecules. Advances in this area are already opening in new applications that are leading to improved products across a broad realm of sectors, from textiles to electronics [1-7]. Some of these improved products are already available, including improved catalysts [1], stain resistant fabrics [2], better sunscreens [3], superior dental bonding materials [4], high resolution printer inks [5], digital camera displays [6], and high capacity computer hard disks [7], to name a few. In addition to making existing products and processes better, nanotechnology promises breakthroughs that will revolutionize the way we detect and treat disease, monitor and protect the environment, produce and store energy, and build complex structures as small as electronic circuit or as large as an airplane.
Nano-devices typically include nanowires (NWs), carbon nanotubes (CNTs), and nanoparticles (NPs) which are fabricated on an atomic, molecular, or macromolecular range of approximately 1-100 nanometers. Nanowires, such as semiconductor, metal, and conducting polymer nanowires, and carbon nanotubes have been the subject of intense interest as sensors [8-11] and electronic devices for high density circuits [12-15]. The techniques used to fabricate these devices have included using an atomic force microscope to manipulate individual carbon nanotubes onto prepatterned electrodes [12], random dispersion of suspended carbon nanotubes in solution onto a substrate with prepatterned electrodes [13-15], and using catalysts, such as carbon nanotube nucleation sites, lithographically patterned on electrodes [10,12]. While these methods have been adequate for demonstrating the operational characteristics of individual devices, they have intrinsic drawbacks of low throughput and limited controllability which make them unattractive for large scale circuits and remain a significant challenge.

We have demonstrated the electrochemical growth of a metal and a conducting polymer single nanowire with a width smaller than 100 nm [16, 17]. The fabrication method can be found elsewhere [16]. Our method of single nanowire growth is a promising and versatile method for fabricating nanowire sensor arrays, with a wide range of sensing materials available which can be electrodeposited. These materials include metals, alloys, metal oxides, semiconductors, and conducting polymers. Further, the equipment is simple, easily scaled-down to fabricate in nano-scale dimensions, and low cost. In this work, fabricated Palladium metal and Polypyrrole polymer nanowires were successfully used as a hydrogen sensor and DNA sensor.

2. Experiment

![Figure 1](image_url)

Figure 1. (A) electrochemically grown single Pd nanowire with 100 nm diameter, (B) hydrogen sensing circuit diagram using single Pd nanowire (100 nm), and (C) 0.1%, 1.0%, 5.0 and 10% hydrogen concentration as a function of output voltage variation and time to confirm reproducibility.
For Hydrogen sensor, we have grown single and double wires of Pd from 75nm to 1-μm diameters with up to 7-μm lengths. Using a single electrodeposited Pd wire with 100 nm diameter and 4 μm length, sensing of different concentrations of hydrogen gas (between 0.02% and 10% in N2 gas) has been demonstrated. Using single Pd nanowire, we are able to identify each peak of 0.1%, 1%, 5%, and 10% of hydrogen concentration in nitrogen which has never been demonstrated. Additionally, we have simulated hydrogen sensor using nanowire for the depth understanding of the H/Pd material system. We developed a unified model describing the absorption and diffusion process, which reproduces experimental concentration/pressure phase diagram and the H absorption kinetics for planar surfaces. The model was applied to numerically study the sensitivity of H sensors using Pd nanowires. From the simulation results, we have obtained two innovative results of this work. These are 1) development of a comprehensive model of hydrogen absorption and diffusion in palladium and 2) determination of the effect of nanowire diameter on hydrogen sensitivity and response time.

We also report the electrochemical growth of single polyaniline and polypyrrole (Fig. 1) nanowires with widths of 100 nm and 200 nm, and demonstrated their use as a pH and DNA sensor [18]. In this work, avidin, streptavidin decorated CdSe quantum dots and biotin decorated quantum dots with functionalized PPy nanowires were synthesized and fabricated so that the nanowires are between 100-nm and 200-nm wide by 3-μm long channels where formed between gold electrodes on a prefabricated silicon substrate to confine the nanowires as they grow. As previously found for nanowires without biomolecules, well-confined, dendrite-free and high aspect ratio nanowires were realized by our methodology as shown Fig 2.

Figure 2. (A) Single Polypyrrol (PPY) nanowire of 200nm wide and 3 micron long, ref. (17) and (B) electrical responses of Avidin embedded polypyrrole (200 nm) to additions of 1 μL of (i) buffered solution, (ii) 1 nM, and (iii) 100 nM biotin-DNA (single stranded). Polypyrrole nanowire containing entrapped Avidin were grown using 25 nM pyrrole in 10 mM NaCl and 2 nM of Avidin, ref. (18).

As shown Fig 2 (B), resistance ratio (ΔR/R) did not change with the addition of buffered solution (i). However, resistance ratio of the 200 nm wide avidin-functionalized nanowires increased rapidly to a constant value upon addition of 1 nM (ii) of the biotin-DNA conjugate and the resistance increased with increasing concentrations up to 100 nM (iii).

3. Conclusion
In summary, we report sensing results of single metal (Pd) and conducting polymer nanowires of controlled dimension. Our nanowires can be produced in an array of individually addressable nanowire sensors, with site-specific positioning, alignment and chemical compositions. Using Pd single wire, hydrogen gas was detected with 350 nW of power consumption and 300 mS of response time. Sensing ranges were between 200 ppm and 10.0% H. In addition, reproducible detections were observed among 0.1%, 1.0%, 5.0%, and 10% H. We also demonstrated the feasibility of fabricating single polypyrrole and polyaniline nanowires and their application as DNA sensor (1 nM) in this work.

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