Electrochemical Synthesis and Characterization of Palladium Nanostructures

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Abstract. Palladium (Pd) is a good candidate material for hydrogen gas sensing at room temperature due to its high affinity to hydrogen. Pd in the form of nanostructures has demonstrated better performance in its gas sensing property as compared to that in the form of bulk metal because of its large surface area to volume ratio. In this work, various Pd nanostructures were synthesized via electrochemical route. Pd in the form of nanowires can be produced directly via template-assisted electrodeposition while Pd nanotubes were synthesized by galvanic displacement with morphology and composition governed by electrolyte temperature and reaction time. Using similar electrodeposition conditions, Pd in the form of nanoparticles were electrochemically decorated on the surfaces of ZnO rods and Si nanowires arrays. Growth study on various Pd nanostructures produced is presented here, using microscopy, diffraction and probe-based techniques for microstructural, morphological and chemical characterizations.

1. Introduction
Nanostructures such as nanowires and nanotubes have been used as critical components in the latest sensor devices due to their capabilities in improving the sensor efficiency and charge transport property [1, 2]. In addition, due to its low dimensional nanostructures, high-density arrays of sensor elements can also be assembled for better detection accuracies and signal-to-noise ratios as compared to the conventional sensor instrumentations [3]. Palladium nanostructures for examples have been used in many of the hydrogen sensors. Palladium has been a favorite candidate for hydrogen gas sensing because it selectively absorbs hydrogen gas to form chemical palladium hydride.

This work focuses on the preparation of various palladium nanostructures using electrochemical deposition techniques. These techniques offers great advantages in preparing nanostructures, including precisely controlled operation at near-room temperature, low energy requirement, rapid deposition rates, low cost, scalable with easily maintained equipment and flexibility in geometry design. Template-assisted electrodeposition, for example, allows the deposition of high aspect ratio nanostructures such as single elemental or heterostructure nanowires [4, 5] while electrodeless deposition by galvanic displacement of the materials allows the transformation of materials to nanostructures such as nanotubes or coaxial nanowires [6, 7] to achieve the desired chemistry, morphology and microstructures.
In this work, Pd nanostructures were fabricated directly via template-assisted electrodeposition technique and by galvanic displacement of Ni nanowires. Porous anodic alumina (PAA) was used as the templates for confining the electrodeposited materials within their nanopores in order to produce nanowires with controllable dimensions. Using similar electrodeposition conditions, Pd in the form of nanoparticles can also be electrochemically decorated on the surfaces of other nanowires such as ZnO nanorods or silicon nanowire arrays. The microstructures and morphology of the nanostructures were examined using a scanning electron microscope (FEI QUANTA 400) equipped with an X-ray Energy Dispersive Spectrometer (EDS) and operating at an accelerating voltage of 30 kV. The crystallographic information was obtained using X-ray diffractions performed on an X-ray diffractometer (Panalytical X-Pert PRO MPD) operating at 40 kV and 20 mA using Cu Kα radiation.

2. Materials and Methods
Using commercially available anodized alumina (Whatman Anodisc 13) as templates, Pd nanowires with approximately 200 nm diameters were synthesized chronoamperometrically using a three-electrode system with platinum as the counter electrode, Ag/AgCl as reference electrode and alumina template as the working electrode from electrolyte consisting of 0.047 M Pd(NH₃)₂Cl₂ + 0.1 M NH₄Cl at -0.8 V and ambient temperature. Prior to electrodeposition, the templates were sputter-coated with a layer of Au on the back. After electrodeposition, the gold-sputtered layer was removed using gold etching solution constituting 2.5 g KI, 10 ml I₂ and 90 ml H₂O. The template was subsequently dissolved in a 5 M NaOH solution. The nanowires were concentrated by centrifuging and rinsing in nanopure water and the process was repeated several times to remove the NaOH solution before finally suspended in isopropyl alcohol.

Similarly, Ni nanowires were prepared potentiostatically at fixed current densities of 10 mA cm⁻² from Ni electrolyte consisting of 1 M NiSO₄.6H₂O + 0.5 M H₃BO₃. A 2 μL of the Ni nanowire suspension was dispensed on a silicon wafer to allow the solvent to evaporate followed by a dispension of Pd electrolyte onto the nanowires, to galvanically displace the nanowires with Pd. Temperature and time are varied to yield fully displaced Pd nanotubes. Using the same electrodeposition condition, Pd nanoparticles were formed on superhydrophobic surfaces containing ZnO nanorods and silicon nanowires array as working electrode.

3. Results and Discussion
Figure 1 shows the typical scanning electron micrograph of Pd nanowires fabricated by template-assisted electrodeposition and the corresponding X-ray diffractogram shows the presence of Pd with face-centered cubic (FCC) structure. Pd of sub-100 nm diameter can be similarly obtained using template of equivalent pore size fabricated by anodisation process. Figure 2 shows the formation of Pd nanotubes with ~ 20 nm thickness after galvanically displacing Ni nanowires. The inner diameter of the Pd nanotubes was controlled by the diameter of the Ni nanowires. Increasing reaction time or temperature yields rougher and grainier morphologies due to aggregation of more Pd particles along the surface of the nanowires. The driving force behind the galvanic displacement reaction comes from the difference in the reduction potential gaps between Ni^{2+}/Ni and Pd^{2+}/Pd according to the following reaction equation:

\[ \text{Ni}^{0} (s) + 2 \text{Pd}^{+} (aq) \rightarrow 2 \text{Pd}^{0} (s) + \text{Ni}^{2+} (aq) \]

The exchanged reaction is initiated from the external surfaces of the nickel nanowires with Pd ions accepting electrons from Ni to form Pd nucleus which chained up to form a coating. As the reaction proceeds, Pd evolves into a very thin nm thick shell at the edges of Ni nanowires while nickel nanowires dissolve to form a uniform channel along the nanowires axis. Longer reaction time or higher temperature tends to thicken the Pd surface with aggregation of Pd particles to form rougher Pd nanotubes.
Figure 1. Pd nanowires fabricated by template assisted electrodeposition (a) cross-sectional SEM view of Pd nanowires arrays embedded in the template (b) X-ray diffractogram of the nanowires. Scale bar is 5 µm.
Pd can also be electrochemically deposited on surfaces of semiconductor nanowire arrays such as silicon nanowires or zinc oxide rods. Figure 3 shows the SEM images of quasi-oriented ZnO rods which were electrochemically grown on indium-tin-oxide glass substrate using a three-electrode configuration with Ag/AgCl as reference electrode, platinum as counter electrode and ITO-coated glass substrate as the working electrode respectively using electrolytes consisting of ZnO$^{2+}$ ions [8], and ZnO rods which has been decorated with Pd. The thickness of Pd coating increases with deposition time at a rate of 2.8 nm/min, resulting in the increase in diameter of rod to micron size. The Pd-ZnO rods not only exhibits larger diameter compared to the bare ZnO rods, the tips of the nanorods were also become more rounded and circular as compared to the original hexagonal tips of the bare ZnO rods. It was found that these Pd modified ZnO rods exhibits improved physical properties such as better UV photoresistivity and faster response time as compared to bare ZnO rods [9]. Pd modified ZnO rods are also good candidate materials for hydrogen gas sensing.
Figure 3. SEM images of the (a) ZnO rods and (b) Pd-ZnO rods. Insets show the tips of the rods. Scale bars are (A) 2 µm and (B) 5 µm.

Unlike ZnO rods where Pd was attached on its walls, Pd was suspended on the tips of the vertically-oriented Si nanowires as nanoparticles without affecting the diameter of the Si nanowires. Silicon nanowires were grown by electroless etching [10]. The SEM images in Figure 4 compare the silicon nanowires before and after Pd deposition. As the free-ends of the Si nanowires of average diameter 70 nm tend to bundle into clusters, the Pd nanoparticles of average size 92 nm were also agglomerated to form micron sized clusters. The addition of the Pd nanoparticles was found to improve the effectiveness in catalytic dissociation of hydrogen molecules into atomic hydrogen, thereby increasing the sensitivity of the sensor device [11]. The size and density of the nanoparticles, which affects the gas sensing capability, can be tuned by the deposition time. Longer deposition time yields higher density of particle and bigger particle size.

Figure 4. SEM images of (a) silicon nanowires (b) deposition of Pd on top of the Si nanowires. Inset shows the Pd nanoparticles decorated at the free-end of the Si nanowires. Scale bars are 2 µm.
4. Conclusion
Various one dimensional Pd nanostructures ranging from nanowires to nanotubes had been synthesized using a combination of template-assisted electrodeposition and galvanic displacement techniques. We have also demonstrated that Pd in the form of nanoparticles was electrochemically decorated on the surfaces of ZnO and Si nanowires arrays. These Pd-modified surfaces should enhance the gas sensing efficiency and charge transport property of the materials.

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