

Sensors from electrodeposited metal nanowires

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Based on their electronic conductivity behaviour, metallic nanowires may have analytical applications ranging from interconnects to sensors. We present in this paper an electrochemical method for synthesizing Mo and Pd metal nanowires ranging in diameter from a few tens of nanometres up to one micrometre, with millimetre lengths. Nanowires are prepared by the electrodeposition of metal at step edges present on a graphite surface. These nanowires can be used to connect metal nanoparticles (Ni, Au, etc.). Once transferred in a polymer cast, they can operate as sensors. We describe how these nanowires may be manipulated to make devices for analytical chemistry and, as an example of such nanodevice, a detailed overview of the characteristics of the first nanowire-based sensor of hydrogen gas (H₂) is given. Copyright © 2002 John Wiley & Sons, Ltd.

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Chemical sensing is about surface and interface interactions between the analyte molecules and the sensing material. In that sense, nano-objects with a large surface atom-bulk atom ratio, such as nanoparticles and nanowires, are potentially very efficient chemical sensors. The mechanism envisaged involves adsorption (and eventually diffusion) of the analyte molecule at the surface, which induces a change in the electrical resistance of the nano-object: sensing is the process of measuring these conductivity changes. The most convenient way to measure conductivity changes in such devices is to obtain the specific material as nanowires or as connected nanoparticles. Although chemically selective sensors operating on this principle do not yet exist, Tao and coworkers have shown changes in the conductivity of gold nanowires upon exposure to thiols or amines.¹ In the same way, single-walled carbon nanotubes exhibit resistance changes upon exposure to gaseous oxygen, water and amines.²

We describe in this paper an electrochemical method for the preparation of naked (palladium) and bimetallic beaded nanowires in which nickel, gold or palladium beads are connected by molybdenum or palladium nanowires. We also show how to manipulate these objects to build chemical sensors. As an example, the characteristics of a nanowire-based sensor for the detection of hydrogen gas are presented.

EXPERIMENTAL

Sensors described hereafter consist of up to 100 nanowires arrayed in parallel, as shown in Fig. 1(a). These arrays were prepared by electrodeposition at step edges present

on a graphite surface, as shown schematically in Fig. 1(b). For beaded nanowires, nickel, gold and palladium particles were first electrodeposited from aqueous solutions of Ni²⁺, Au³⁺ or Pd²⁺ respectively. In a second step, nanowires of molybdenum oxide (MoO_x) or palladium were grown from MoO₄²⁻ or Pd²⁺ solutions, respectively. Both particles and wires were prepared according to methods described previously.^{3,4} Briefly, starting with a freshly cleaved graphite surface, a nucleation pulse was first applied for a few milliseconds at a potential well negative of the reversible potential for metal deposition (Fig. 2). After this nucleation pulse, the growth of particles or wires was carried out for durations from a few tens of seconds to a couple of hours using lower overpotentials. Depending on the chosen potentials, particles or wires are preferentially obtained with a diameter controlled by the duration of the electrolysis. Palladium nanowires were used as prepared.

For beaded nanowires, the particles were protected by the use of hexanethiol before the electrolysis of molybdenum nanowires to prevent the deposition of an MoO_x shell on the surface of the particles. In a final step, MoO_x nanowires were reduced in H₂ at 500 °C to produce metallic Mo⁰ nanowires that connect nanoparticles along step edges.

Figure 3 shows micrographs from various samples. As estimated by these SEM measurements, for both particles and wires, diameters ranged from 50 nm up to 1 μm depending on the particular metals. This 'slow-growth' method yielded particles ranging in diameter from 50 nm to 5 μm, having a relative standard deviation ($RSD_{\text{dia.}} = \sigma_{\text{dia.}} / \langle \text{dia.} \rangle$) as low as 7%. Using the same method, metal nanowires (Mo and Pd) ranged in diameter from 50 nm up to 1 μm (dispersity of ~10%) with millimetre lengths.

Freshly prepared nanowires were transferred from the graphite electrode surface onto a glass slide coated with cyanoacrylate, as shown schematically in Fig. 1(b). When

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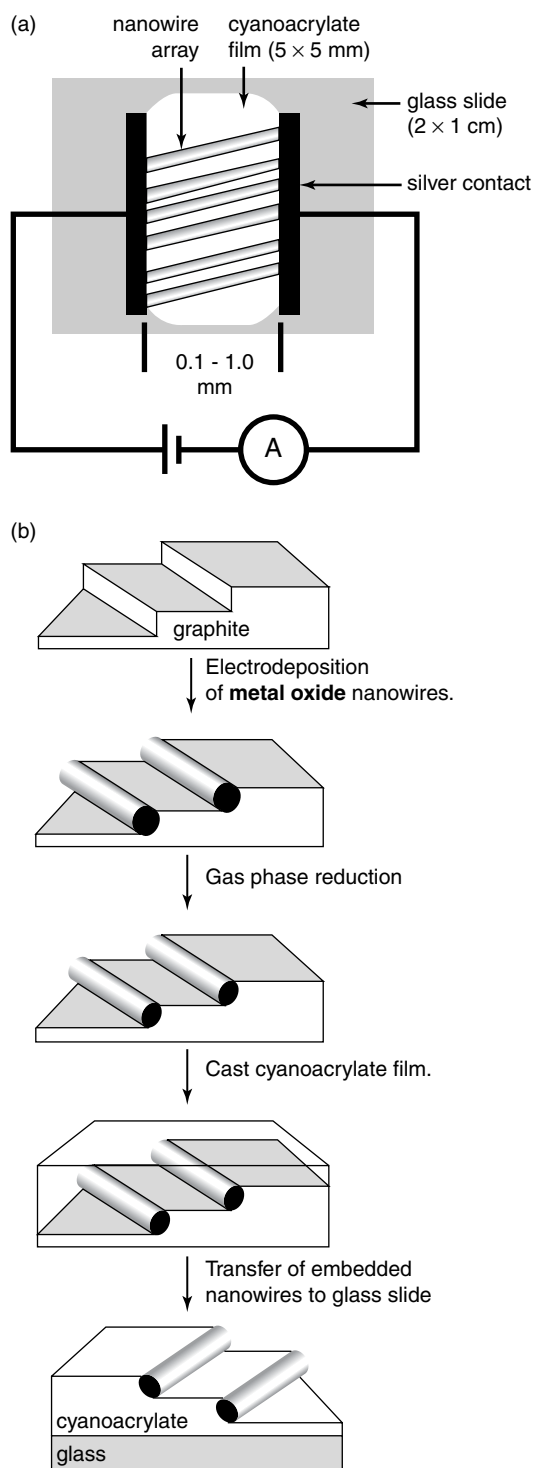


Figure 1. (a) Schematic diagram of a nanowire array-based sensor. (b) Nanowire arrays were prepared by electrochemical step-edge decoration at graphite surfaces and transferred to a cyanoacrylate film.

the cyanoacrylate film had hardened overnight, arrays of nanowires were contacted using silver epoxy. The SEM micrograph in Fig. 4 shows the active area of a sensor constituted of an array of tens of nanowires contacted on each side by silver paint. In these devices, the gap between silver contacts varied from 100 to 500 μm .

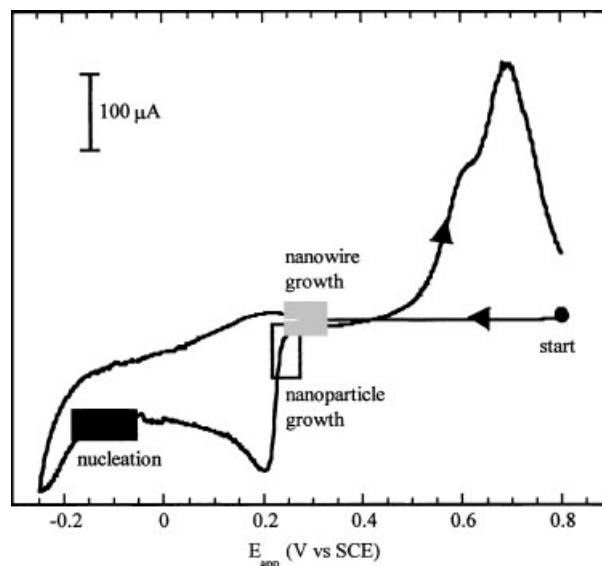


Figure 2. Cyclic voltammograms for a graphite electrode in a plating solution. The potential ranges used for nucleation (black) and nanoparticle (white) or nanowire (grey) growth are indicated.

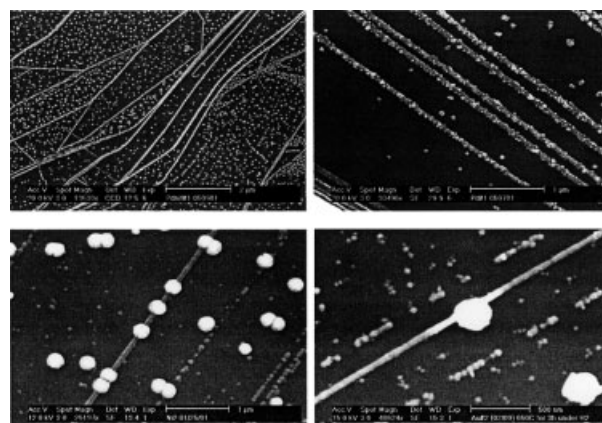


Figure 3. Scanning electron micrographs of palladium nanowires (top right and left) prepared by electrodeposition from aqueous 2.0 mM $\text{Pd}(\text{NO}_3)_2$ and 0.1 M HClO_4 ($E_{\text{dep}} = +0.3\text{V/SCE}$, $t_{\text{dep}} = 900\text{ s}$), respectively and of nickel (bottom left) and gold (bottom right)-connected nanoparticles prepared from 10 mM $\text{Ni}(\text{NO}_3)_2$, 0.2 M NaCl , 0.2 M NH_4Cl and 1 mM AuCl_3 , 0.1 M NaCl , respectively. These nanoparticles are connected by molybdenum nanowires electrodeposited from aqueous 1.0 mM MoO_4^{2-} , 1.0 M NaCl and 1.0 M NH_4Cl (pH 8.5) solution.

RESULTS AND DISCUSSION

Beaded nanowires

The general principle for the use of such a beaded nanowire-based sensor is shown in Fig. 5. The idea is that, depending on the chosen metal, the analyte molecule in solution will absorb on the nanoparticle surface (via specific recognition elements or not). This absorption process is expected to change the surface electronic density and then induce a measurable change in the conductivity of the sensor. For example, using connected gold nanoparticles, a large number

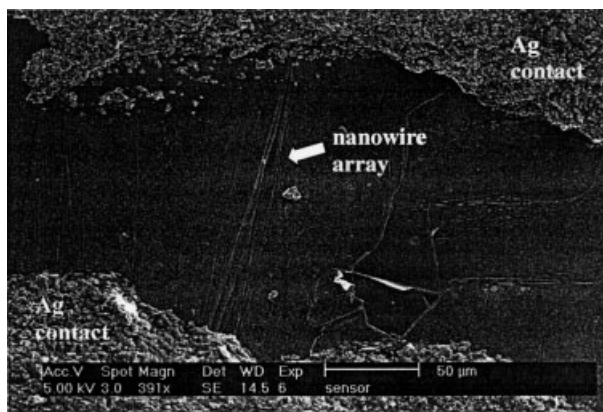


Figure 4. Scanning electron micrograph of the active area of an H₂ sensor constituted of an array of tens of palladium nanowires contacted by silver paint.

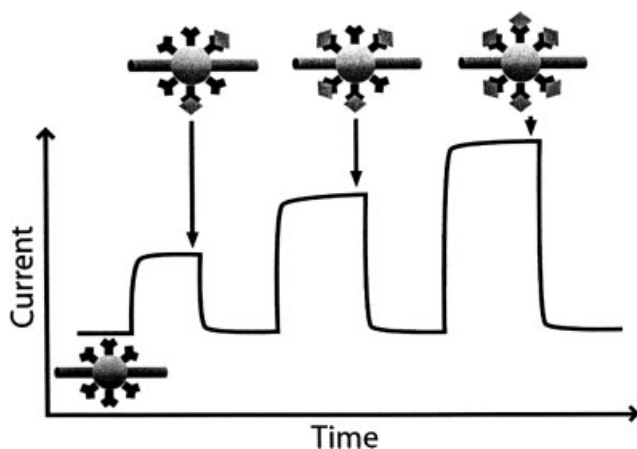


Figure 5. Schematic diagram of a beaded nanowire-based sensor. Depending on the chosen metal and/or the presence of recognition elements, the interaction of a specific analyte molecule with the surface of the particle induces a conductivity change.

of highly sensitive and highly specific biosensors can be imagined. With magnetic nanoparticles, magnetoresistance effects could also allow specific molecules or radicals of interest to be sorted or detected.

Palladium nanowires

Palladium nanowire arrays were operated as H₂ sensors by applying a constant voltage of 5 or 10 mV between the silver contacts and measuring the corresponding 1–20 μA current. As shown in Fig. 6, the resistance of the sensor *decreased* in the presence of H₂. This decrease was related to H₂ concentration, with a limit of detection at 0.5% H₂ in N₂. After a first series of exposure to hydrogen, this sensor acted as hydrogen-activated switches: in the absence of H₂, the resistance became infinite. In this 'wait state', the sensor dissipated no power and produced no noise. Under hydrogen, the switch closed and a device resistivity became measurable. Sensors were insensitive to various gases other than H₂ (or D₂), including Ar, He, N₂, H₂O or poisoning gases such as O₂, CO or CH₄. A response time of 75 ms at 5% H₂ has been observed.

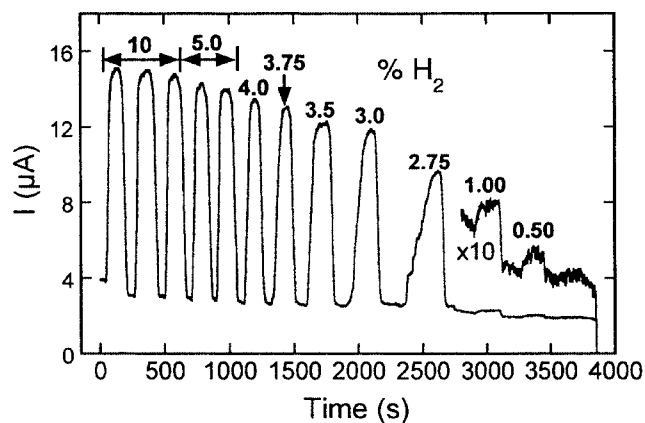


Figure 6. Current response of a palladium nanowire-based H₂ sensor under exposure to hydrogen/nitrogen mixtures (concentration of H₂ as shown).

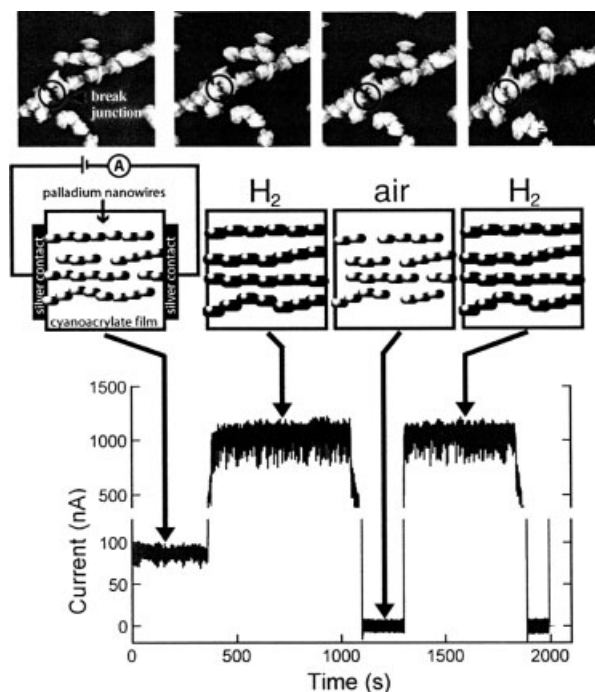


Figure 7. Current response of a sensor to successive exposures to air and hydrogen. In this case, an irreversible transition from initial mode to switcher mode occurs after the first H₂ exposure. The proposed mechanism for the operation mode is shown in the cartoon. (Top) The corresponding AFM images of a palladium nanowire on graphite, showing the opening and closing of a break junction depending on the gaseous atmosphere.

With conventional macroscopic palladium resistors, exposure to H₂ induces the formation of palladium hydride, which causes an *increase* in the resistance by a factor of up to 1.8 at 25 °C relative to pure palladium. In contrast to all existing resistance-based H₂ sensors, however, the resistance of our palladium nanowire-based sensors *decreased* in the presence of H₂. The mechanism that we propose to account for this 'inverse' response is shown in Fig. 7 and has been confirmed using AFM: before any initial exposure to H₂, the sensor showed a measurable value

for the resistance in air. At this stage, the nanowire array includes continuous as well as broken wires (top left). Under a hydrogen atmosphere, palladium metal converts into the thermodynamically stable PdH_{0.7} (β -phase). The subsequent increase in the lattice volume (3.5% at 25 °C with 1.0 atm H₂) closes some nanoscopic gaps along these wires. It is the closing of these 'break junctions' that accounts for the decreased resistance of the sensor in opposition to the increased resistivity of palladium hydride relative to palladium. Exposure back to air opens these gaps in some (initial mode) or all (switcher mode) nanowires in the sensor. Atomic force microscopy data reveal that multiple grains slide in a concerted fashion and affect the opening and closing mechanism. The motion of nanowire segments responsible for the reversible and reproducible break junctions is the direct result of the swelling of individual palladium grains in the presence of H₂.

With a fast response (even at room temperature), diminutive power requirements of <100 nW and a chemical resistance to the usual poisoning gases, the performance of these nanowire array-based sensors challenges existing H₂ sensing technologies.

CONCLUSION

Step edge decoration by electrodeposition on graphite surfaces allows the organization of metals particles and wires at the nanometric scale. By transfer into a polymer cast and contacting these nanocircuits, we developed a palladium nanowire-based sensor for hydrogen gas. By choosing the nature of the metallic compound for the nanowires and for the nanoparticles, we can now conceive specific nanosensors for a large variety of gases as well as for various species and biomolecules in solution.

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