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NANOSTRUCTURED METALS AND METAL ALLOYS FOR HYDROGEN SENSORS

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OUTLINE

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    b. Nanogap based Pd nanostructure resistor
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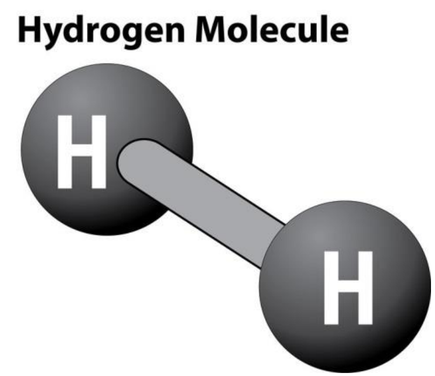
1. Motivation

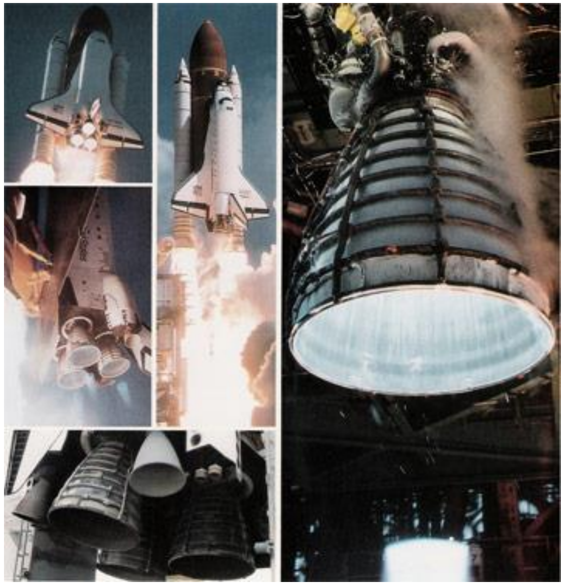
Hydrogen

- very low density (0.0899 kg/m^3)
- low boiling point (20.39 K)
- high diffusion coefficient (0.61 cm^2/s in air)
- high burning velocity
- ignition temperature of 500 °C,
- low minimum ignition energy (0.017 mJ)
- high heat of combustion (142 kJ/g H_2)
- wide flammable range from 4% (i.e., lower explosive limit) up to 75% (i.e., upper explosive limit)



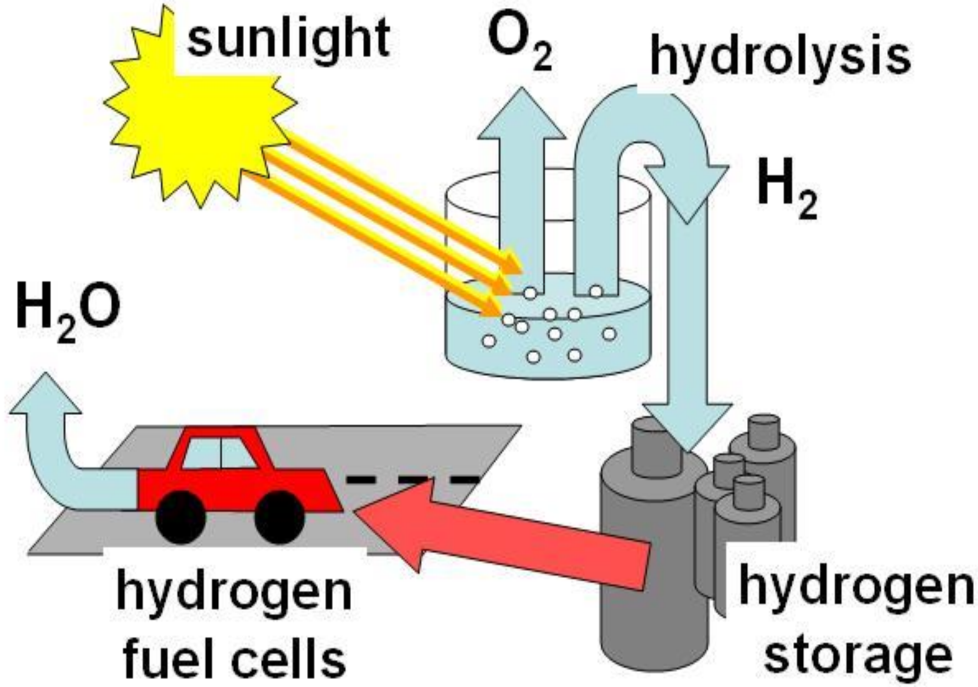
Application of Hydrogen

- Transportation (as fuel in fuel cells, rockets for space vehicles)
- Chemical industries (refining crude oil, plastics, reducing environment in float glass)
- Food industry (hydrogenation of oils and fats)
- Semiconductor industry (as processing gas in thin film deposition and in annealing atmosphere)



The hydrogen detection is so important

- *in safety issue due to the flammable and explosive properties of hydrogen*
- *in hydrogen source for leak detection*
- *in hydrogen production process for real-time quantitative analysis of production.*



Comparison of Commercially Available Hydrogen Sensor

Comparison of performance specifications of commercially available sensors.

Sensor type	Principle/Device	Performance*					
		Measuring range/vol%	Accuracy/% of indication	Response time (t_{90})/s	Power consumption/mW	Gas environment	Lifetime/years
Catalytic	Pellistor	Up to 4	<±5	<30	1000	−20–70 °C 5–95% RH 70–130 kPa	5
Thermal conductivity	Calorimetric	1–100	±0.2	<10	<500	0–50 °C 0–95% RH 80–120 kPa	5
Electrochemical	Amperometric	Up to 4	≤±4	<90	2–700	−20–55 °C 5–95% RH 80–110 kPa	2
Resistance based	Semiconducting metal–oxide	Up to 2	±10–30	<20	<800	−20–70 °C 10–95% RH 80–120 kPa	>2
	Metallic resistor	0.1–100	≤ ±5	<15	>25	0–45 °C 0–95% RH Up to 700 kPa	<10
Work function based	Capacitor	Up to 5	<±7	<60	4000	−20–40 °C 0–95% RH 80–120 kPa	10
	MOS field effect transistor	Up to 4.4	<±7	<2	700	−40–110 °C 5–95% RH 70–130 kPa	10
Optical	Optrode	0.1–100	±0.1	<60	1000	−15–50 °C 0–95% RH 75–175 kPa	>2

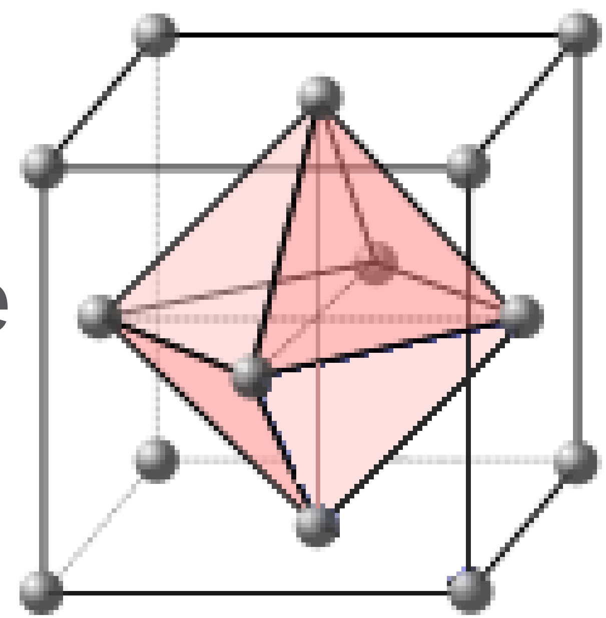
T. Hübert et al. Hydrogen sensors – A review, Sensors and Actuators B 157 (2011) 329– 352

2. Sensing Principle of Metalic Resistor

- In general, Palladium and/or palladium alloys are used as sensitive materials.

$Pd + H2 \rightarrow PdHx$

During PdHx formation, the lattice parameter inceases



2. Sensing Principle of Metalic Resistor

•Two phases of PdHx depending on concentration of hydrogen atoms in Pd

•At low H_2 concentration (α phase PdHx) x< 1%

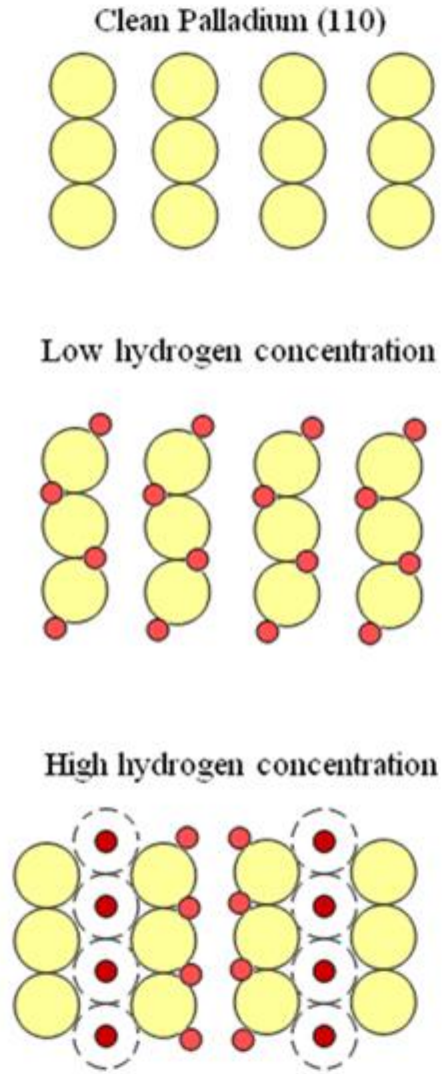
a_0 = 0.3890 nm for pure Pd $a_{\alpha,\ max}$ = 0.3895 nm

•At high H_2 concentration (β phase PdHx) x> 4%

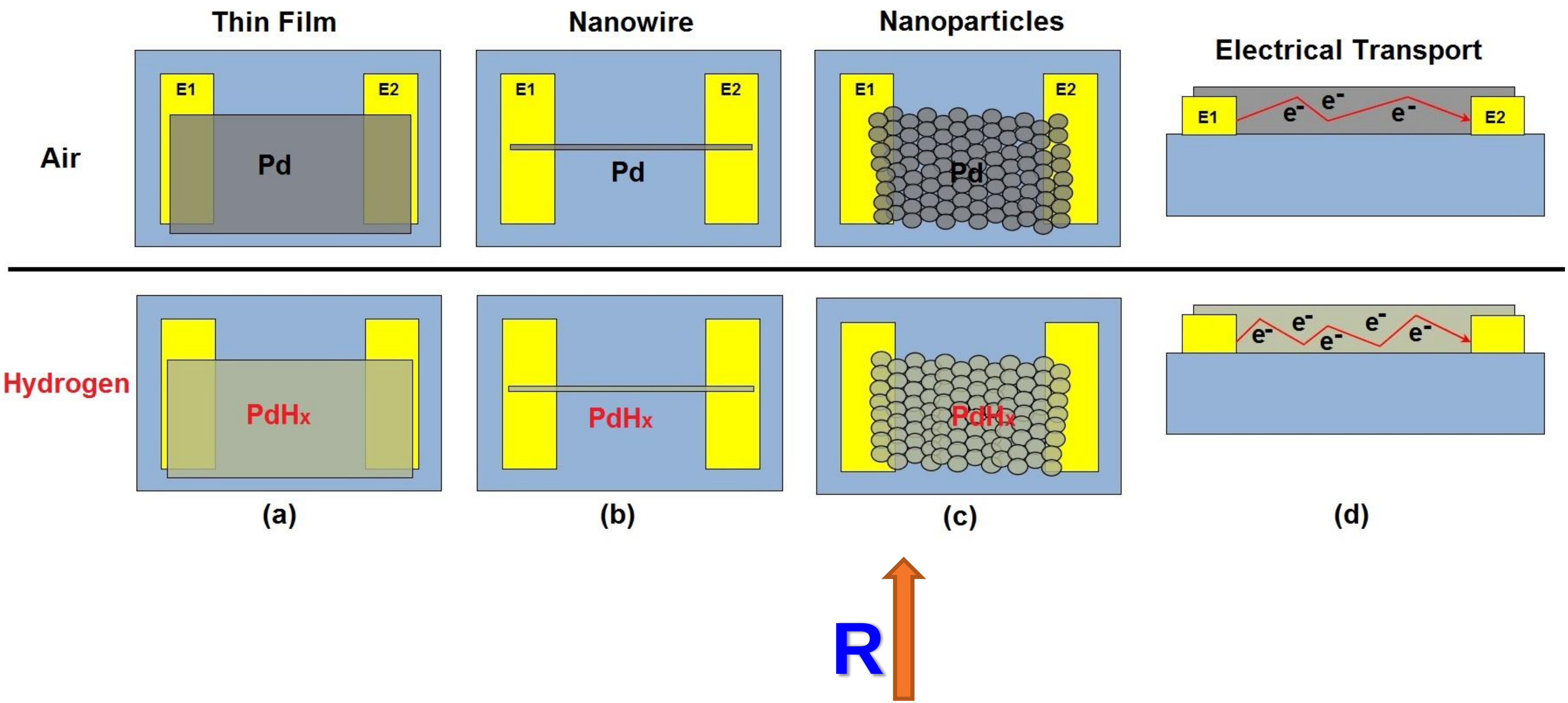
a_0 = 0.3890 nm for pure Pd $a_{\beta,\ max}$ = 0.4025 nm

The sensing mechanism could be explained in two categories:

1. Continuous Pd nanostructure based resistor
2. Nanogap based Pd nanostructure resistor

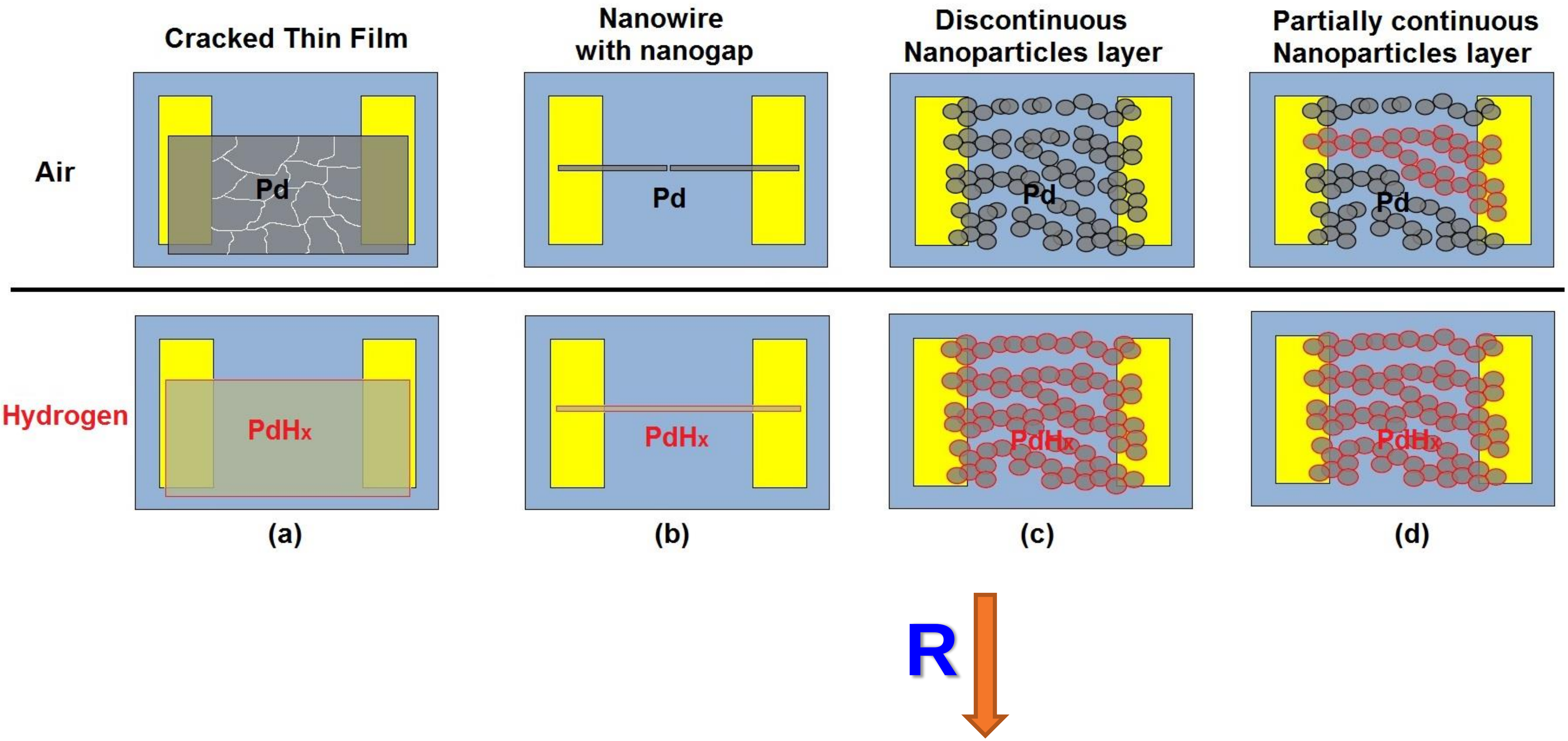


a. Continuous Pd nanostructure resistor



N. Kılınç, Nanoscience and Nanotechnology Letters 5 (2013) 825-841

b. Nano-gap based Pd hydrogen sensors



N. Kılınç, Nanoscience and Nanotechnology Letters 5 (2013) 825-841

3. Key Examples

Continuous Nanoporous Pd and Pd alloy Films

AAO fabrication process

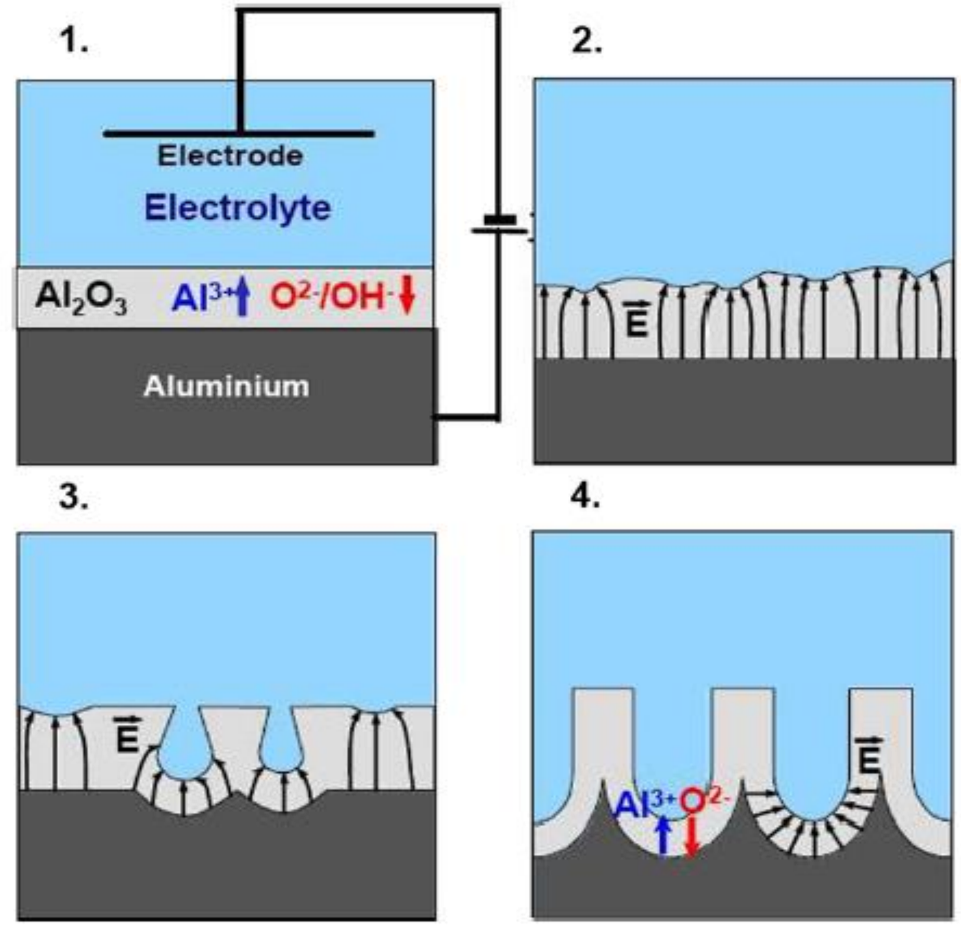
Solution: 0.3 M oxalic acid

Temperature: 10C

Voltage: 40V

Nanoporous film:

Pd and Pd alloy films coated on AAO template with evaporation method and Nanoporous films observed



D.Y. Ding, Z. Chen, Sensor Letters 4 (2006) 331-333.

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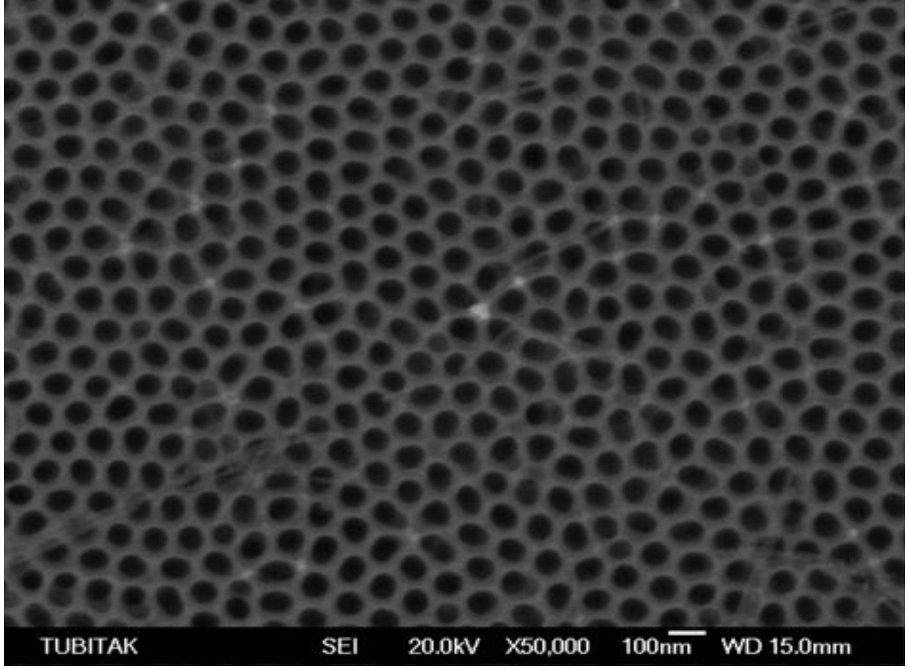
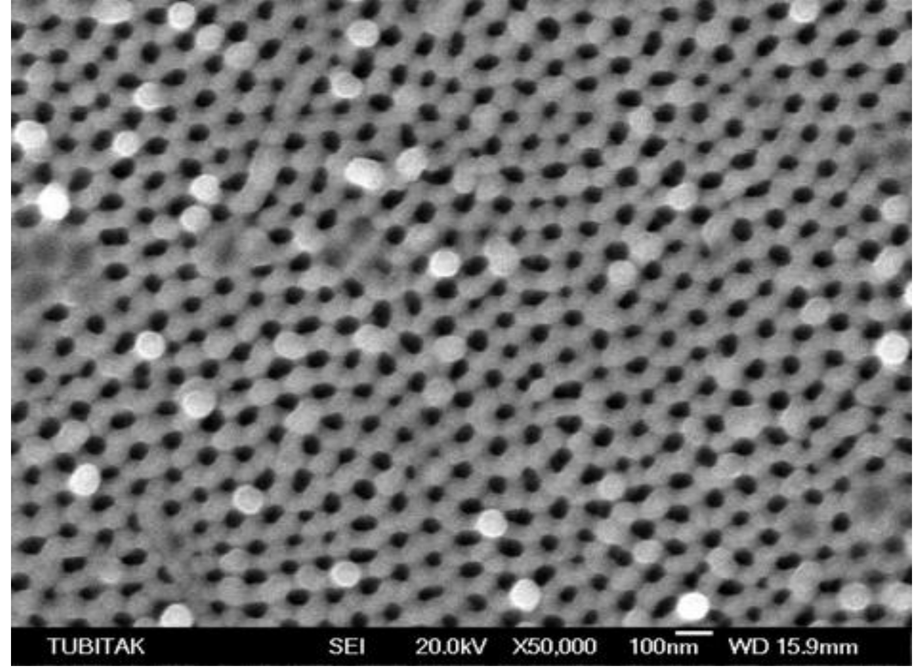
N. Taşaltın et al., Appl Phys A 97 (2009) 745–750

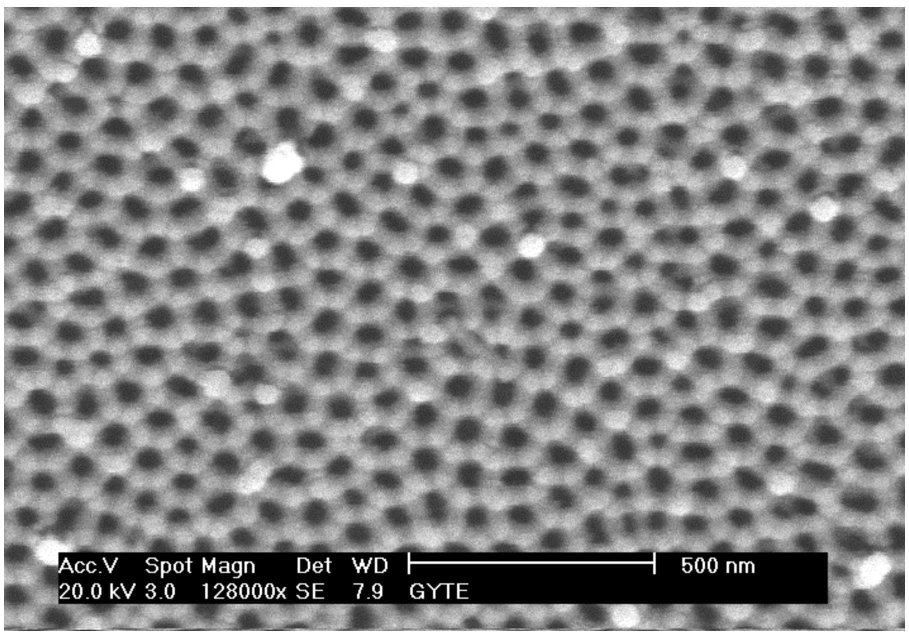
N. Taşaltın et al., Journal of Alloys and Compounds 509 (2011) 4701–4706



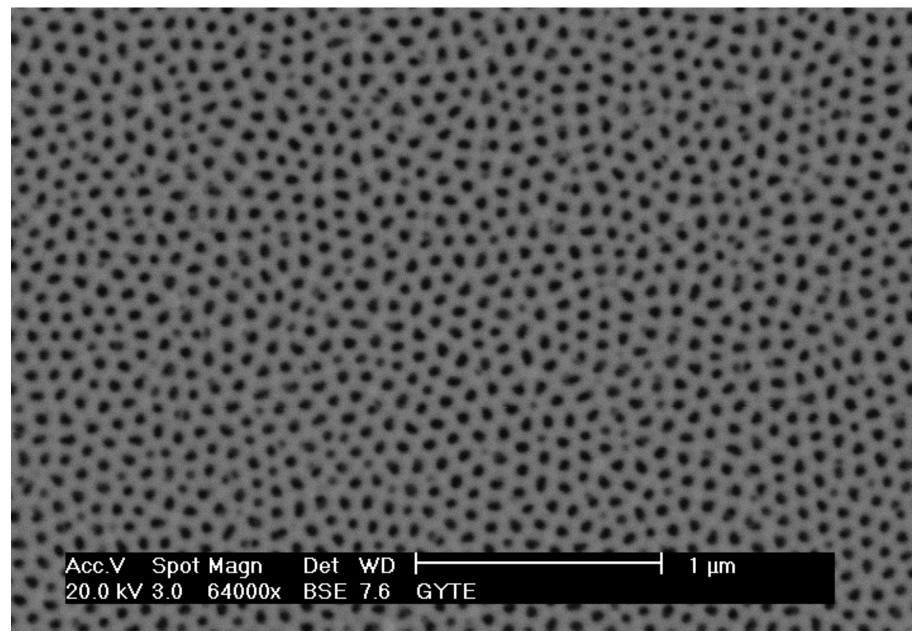
AAO template



Pd film

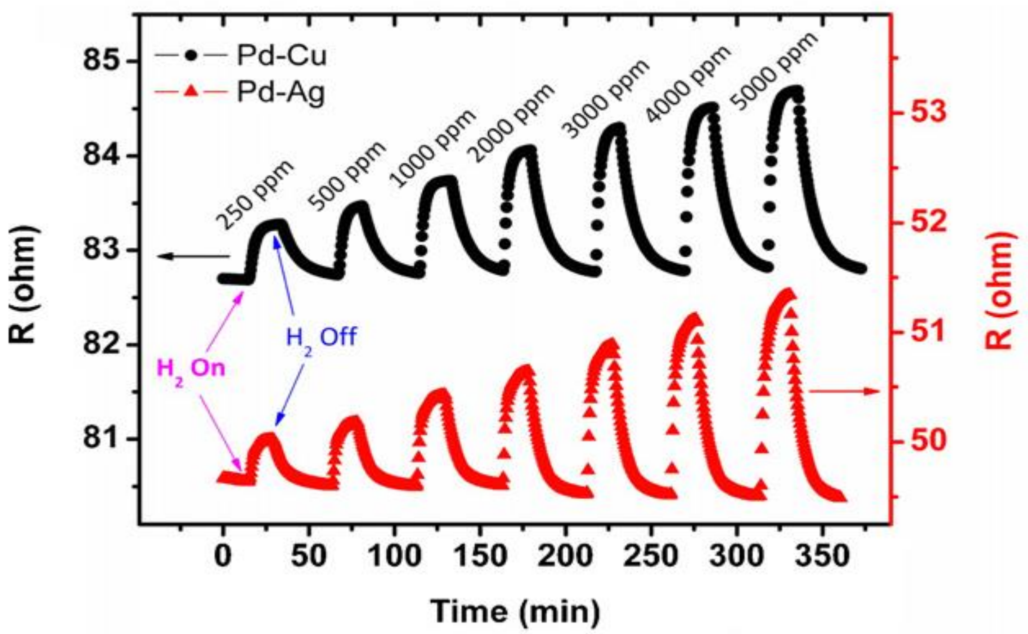


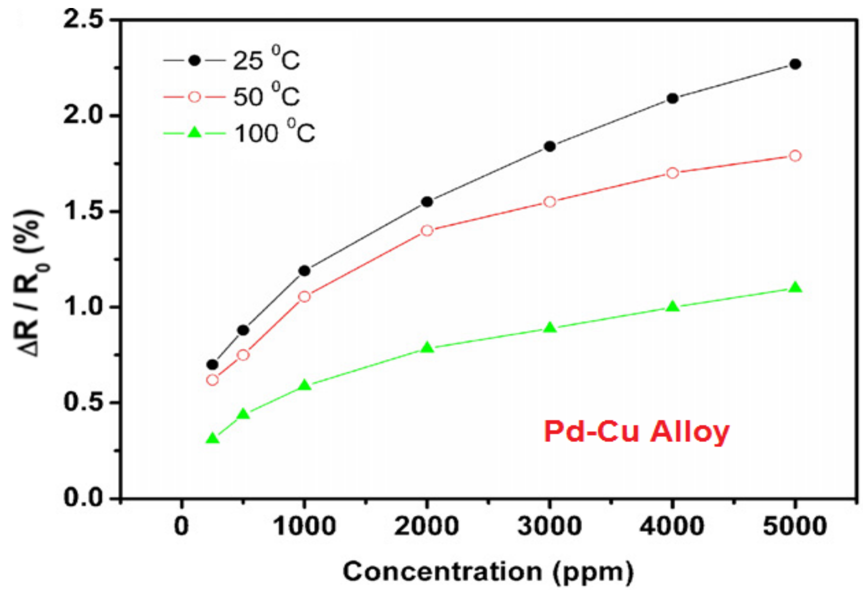
Pd-Ag alloy

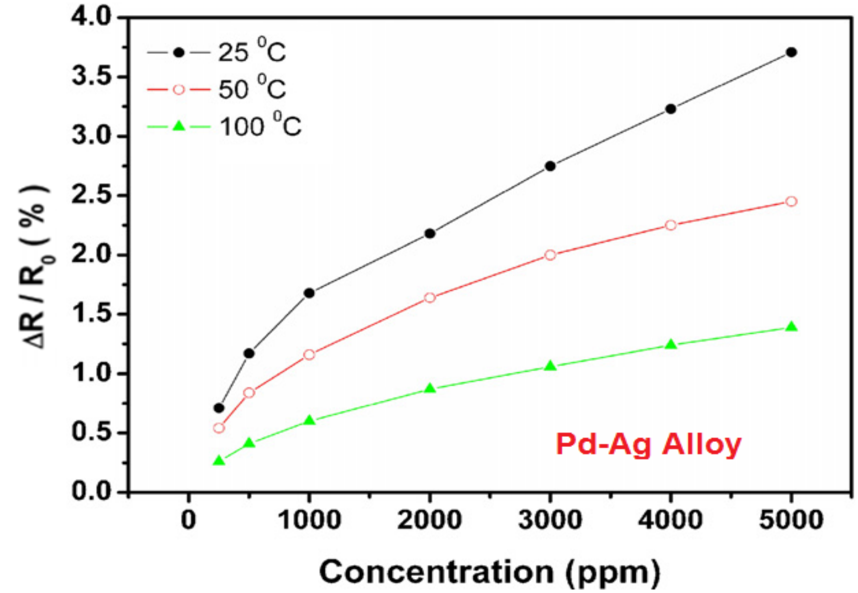


Pd-Cu alloy

Nanoporous Pd Alloy

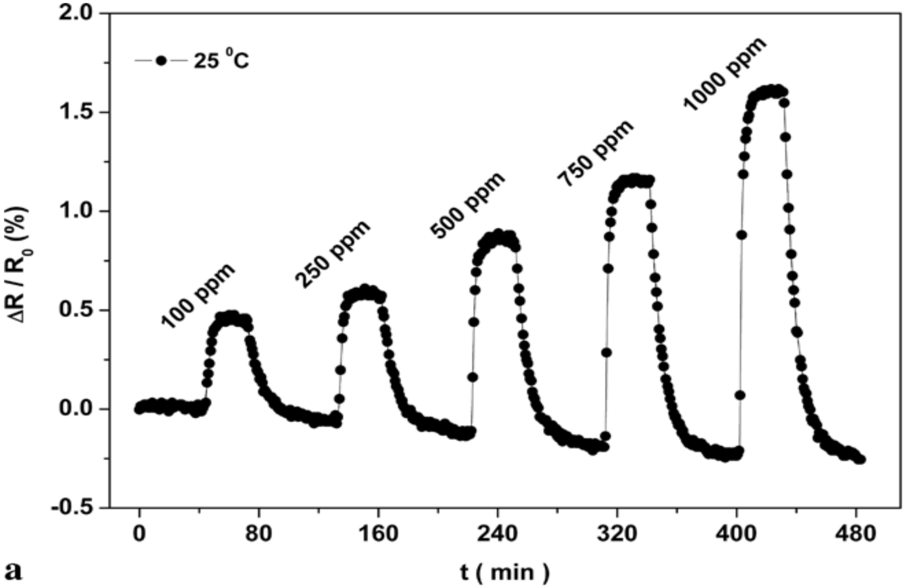




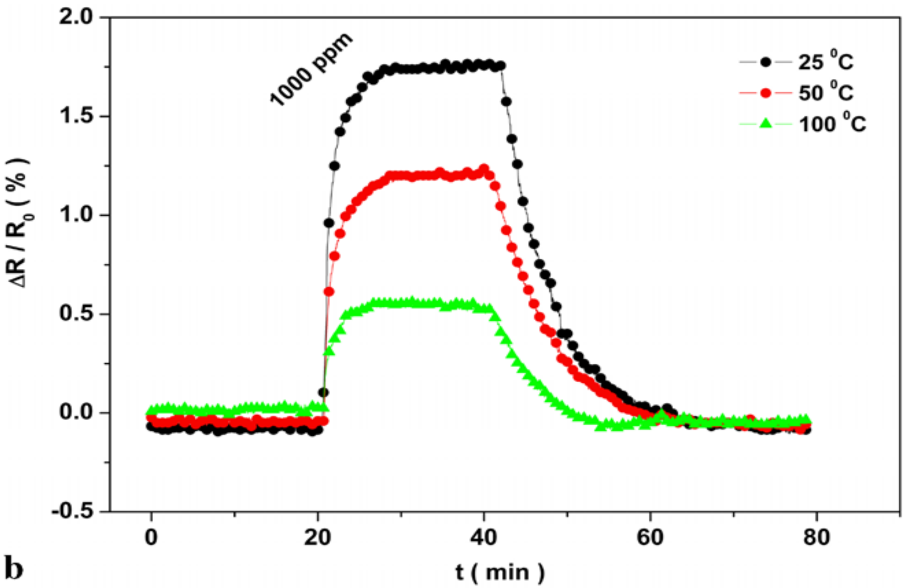


N. Taşaltın et al., Journal of Alloys and Compounds 509 (2011) 4701–4706

Nanoporous Pd film



a



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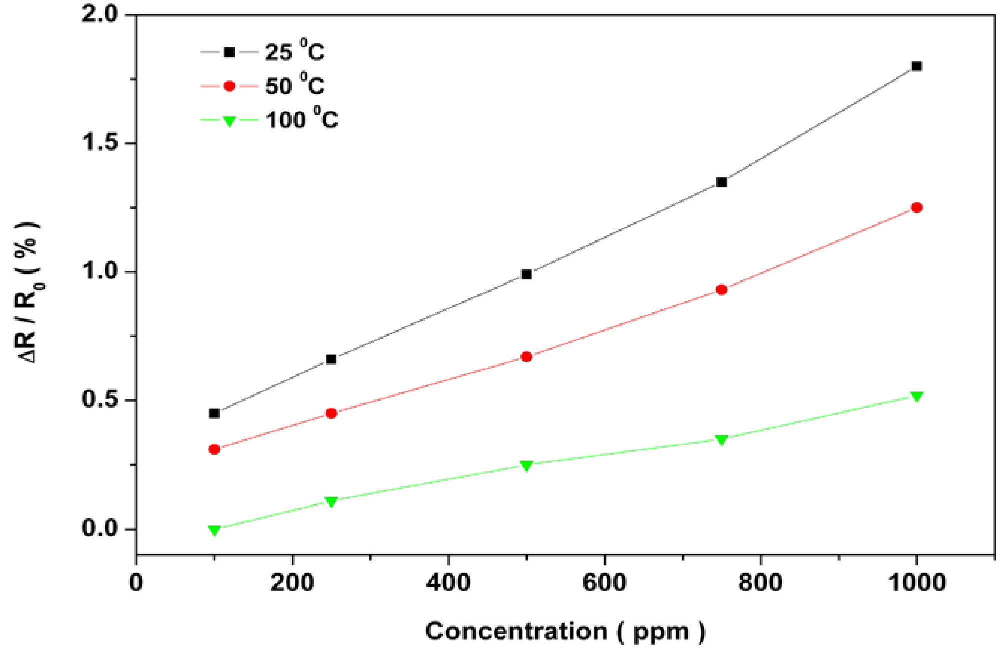

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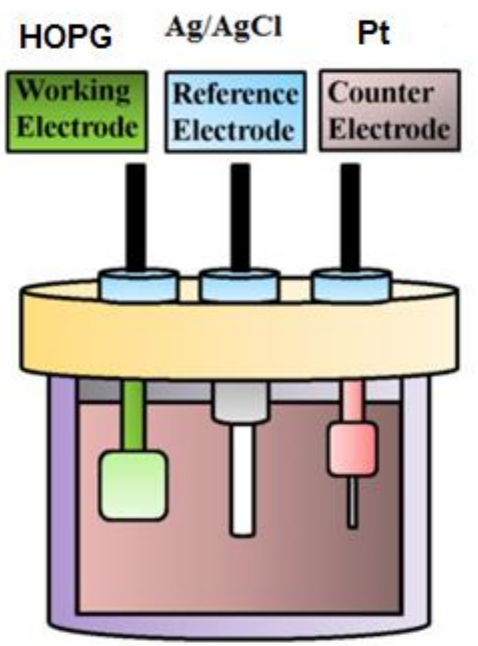
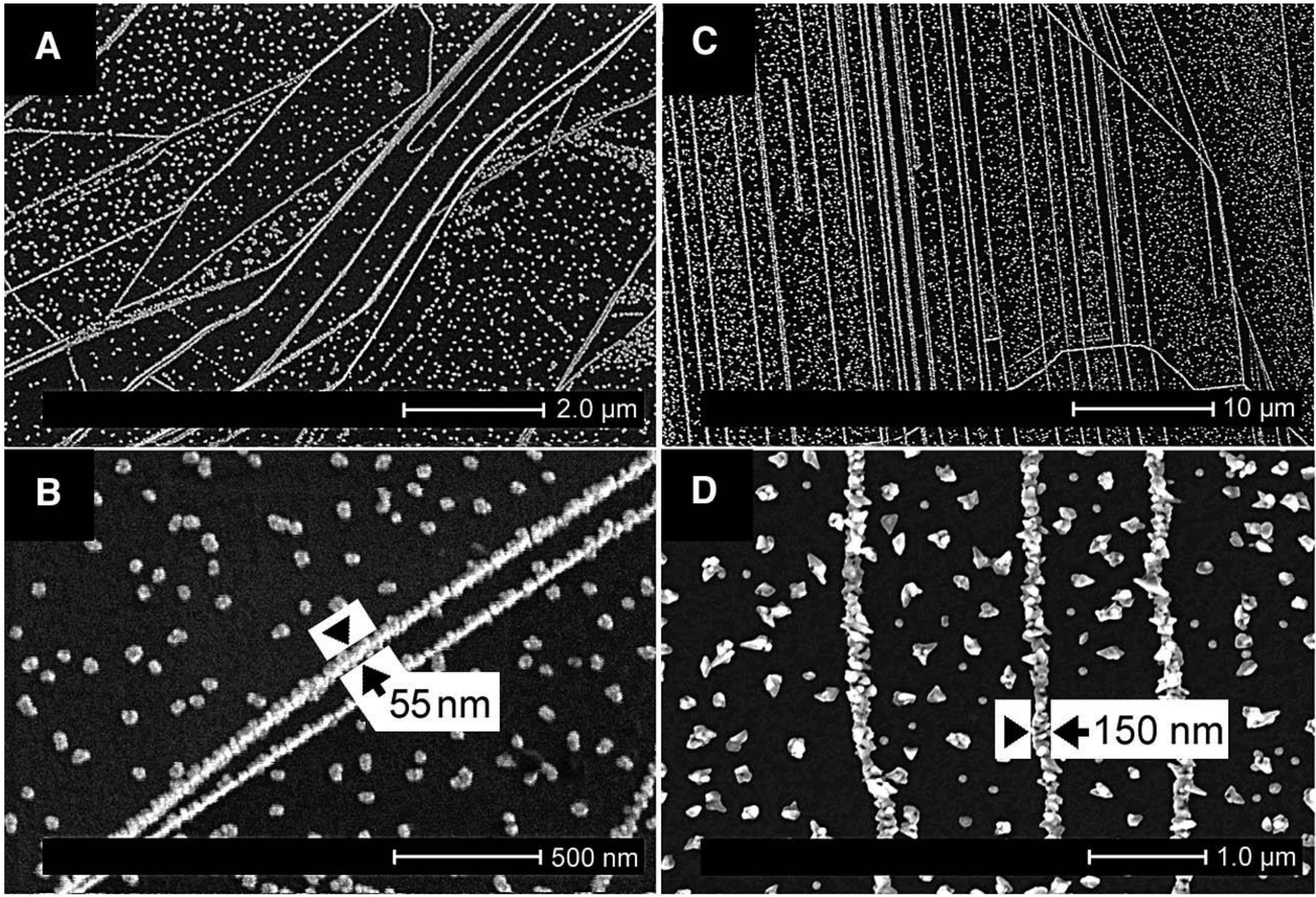
Nano-gap based Pd hydrogen sensors

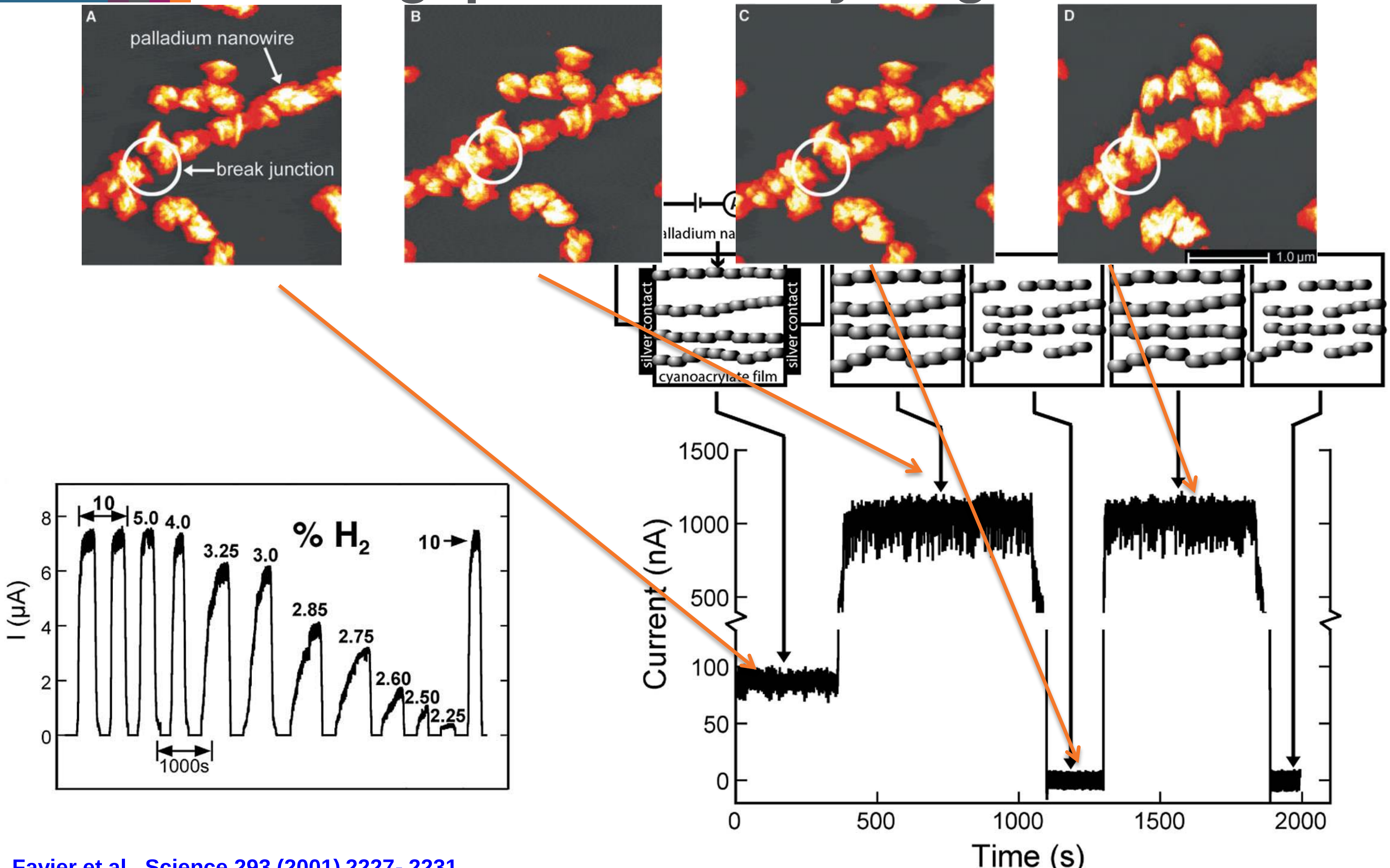




Solution: Pd(NO2)3 and PdCl2 in various concentration
Temperature: RT
Cathodic voltage:
the oxidation potential, Eox: 0.8V
the nucleation potential, Enucl: -0.8V
the growth potential, Egrow: 0.3V

Favier et al., Science 293 (2001) 2227- 2231

Nano-gap based Pd hydrogen sensors



Favier et al., Science 293 (2001) 2227- 2231

Summary

- Pd and Pd alloy nanostructures are a good candidate for hydrogen sensor.
- The sensing mechanism could be explained in two categories:
  - Continuous Pd nanostructure based resistor
  - Nanogap based Pd nanostructure resistor
- Nanostructured Pd and Pd alloys could be syhthesized with various methods such as hydrothermal, electrochemical deposition, e-beam lithography … etc

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Thank you