Self-assembly and Nanotechnology 10.524

Lecture 7.
Nanocomposites and Nanoporous Materials

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Lecture 7

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Section I: Nanocomposite Materials

Nanocomposite Materials

Nanocomposites are materials that are created by introducing nanoparticulates into a microscopic sample material.

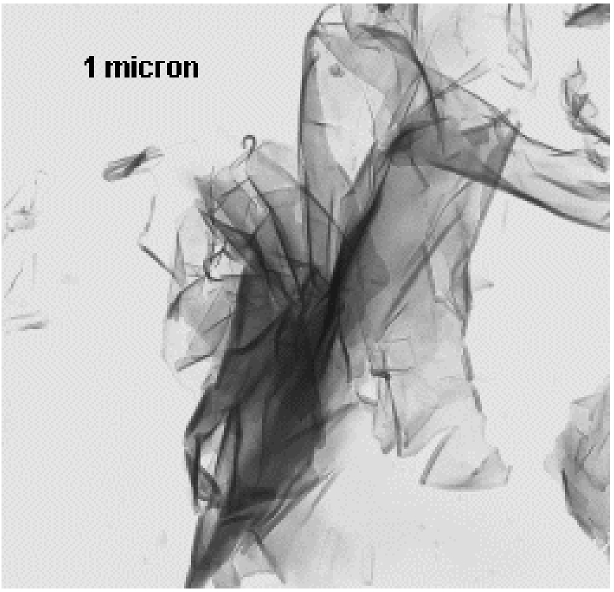
In general, the nano substance used are carbon nanotubes, nanoparticles and they are dispersed into the other composite materials during processing. The percentage by weight of the nanomaterials introduced is able to remain very low (on the order of .5% - 5%) due to the incredibly high surface area to volume ratio of the particles. Much research is going in to developing more efficient combinations of materials and to impart multifunctionalities to the nanocomposites.

Wiki

Polymer Nanocomposites

Clay-based polymer nanocomposites

Polymer nanocomposites are a class of reinforced polymers with low quantities (<5%) Of nanometer-sized clay particles. These minerals considerably increase the mechanical and thermal properties of standard polymers, notably by:
Improving fire resistance and barrier properties
Improving the performance of materials without significantly increasing the density of the polymer, changing its optical properties or its recycling



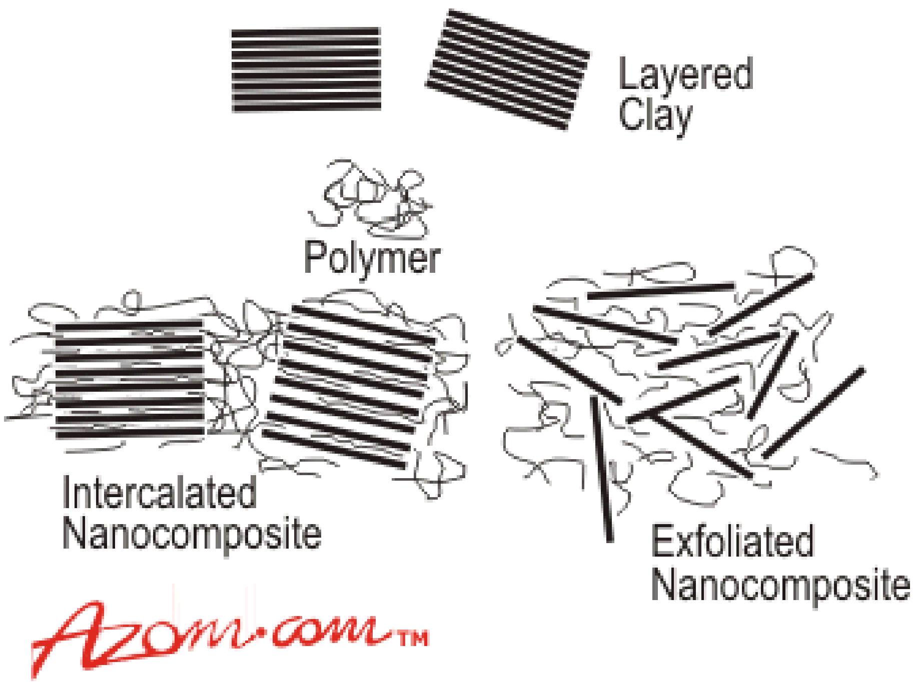
TEM image of morphology of Montmorrillonite (clay)

http://www.imi.cnrc-nrc.gc.ca/english/HTML/Carrefour_d_informations/Factsheets/nanocomposites_polymeres.htm

Polymer Nanocomposites

Nanocomposite formation
Injection molding
Blow molding
Form extrusion
Film blowing

Industrial applications:
Automobile (gasoline tanks, bumpers, interior and exterior panels, etc
Construction (shaped extrusions, panels)
Electronics and electrical (printed circuits, electrical components)
Food packaging (containers, films)

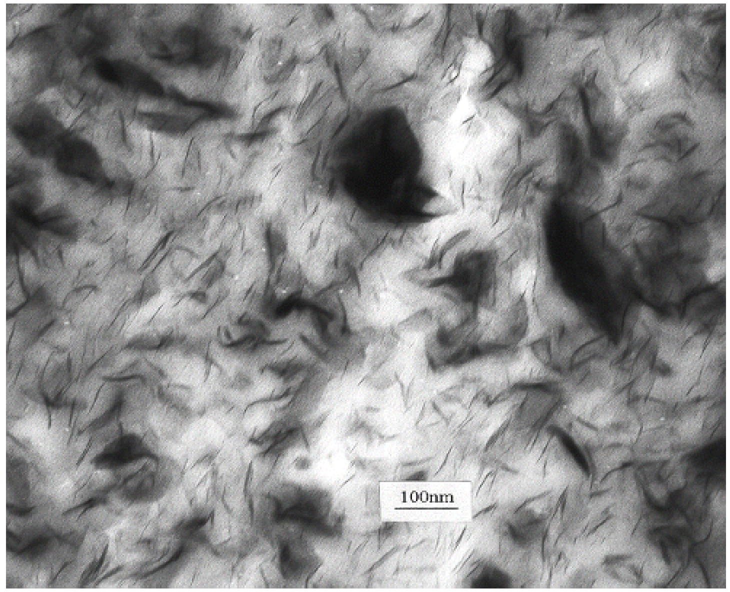


Nanocomposites formation

http://www.azom.com/details.asp?ArticleID=936

http://www.imi.cnrc-nrc.gc.ca/english/HTML/Carrefour_d_informations/Factsheets/nanocomposites_polymeres.htm

Polymer Nanocomposites



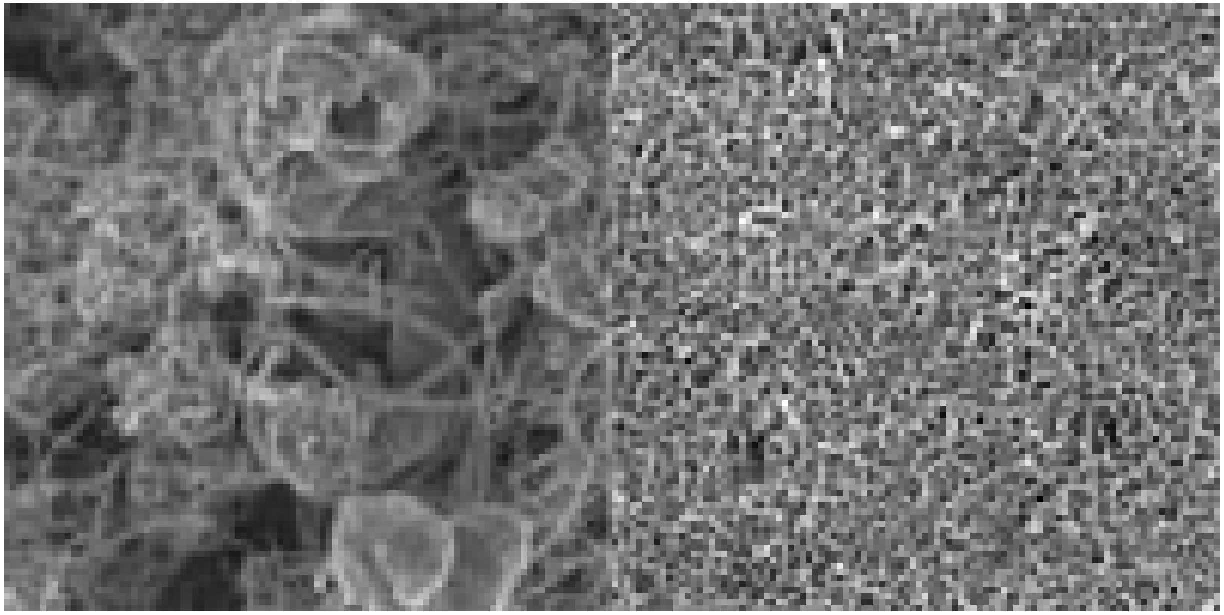
Morphology of nanocomposites

Property characterization

• Rheological
• Thermal (enthalpy, thermal capacity, crystallization kinetics, etc)
• Thermodynamics (PVT behavior, equation of state, gas permeability)
• Short- and long-term mechanical behavior (stress-deformation, fatigue life, fatigue-propogation, low-speed impact, durability, fracture behavior)
• Characterization of the effects of the time-temperature-pressure processing conditions on the microstructure development (orientation, distribution and interaction of nanoclays)

http://www.imi.cnrc-nrc.gc.ca/english/HTML/Carrefour_d_informations/Factsheets/nanocomposites_polymeres.htm

Carbon Nanotube Nanocomposites



Source: Zyvex
Nanotube dispersion comparison: The scanning electron micrographs (SEMs) illustrate untreated multi-wall nanotubes vs. Zyvex functionalized tubes. The pictures were taken with 50Kx magnification at 300 nm resolution (samples were prepared with equal concentrations).

http://www.compositesworld.com/ct/issues/2005/April/809/2

Nanocomposites: Wide Applications and Potential

Source: Easton Bicycles
Easton Bicycle's top-of-the-line triathlon handlebar, the DeltaForce with Aeroforce Clip-ons, incorporates nanotubes in the bar and the clip-ons for a total weight of only 535g/18.9 oz.

http://www.compositesworld.com/ct/issues/2005/April/809

Nanocomposites: Wide Applications and Potential

Source: GM
The composite cargo bed trim, center bridge, sail panels and box rail protectors of this GM *Hummer* use a molded-in-color, nanoclay-filled thermoplastic olefin (TPO).

http://www.compositesworld.com/ct/issues/2005/April/809

Section II: Nanoporous Materials

Nanoporous Materials

Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. Pores are by definition roughly in the nanometre range, that is between 1x10-7 and 0.2x10-9 m.

Subdivisions:
Nanoporous materials can be subdivided into 3 categories, set out by IUPAC:

- Microporous materials: Such as Zeolites, 0.2–2nm
- Mesoporous materials: 2–50nm
- Macroporous materials: 50–1000nm

Wiki

Nanoporous Materials

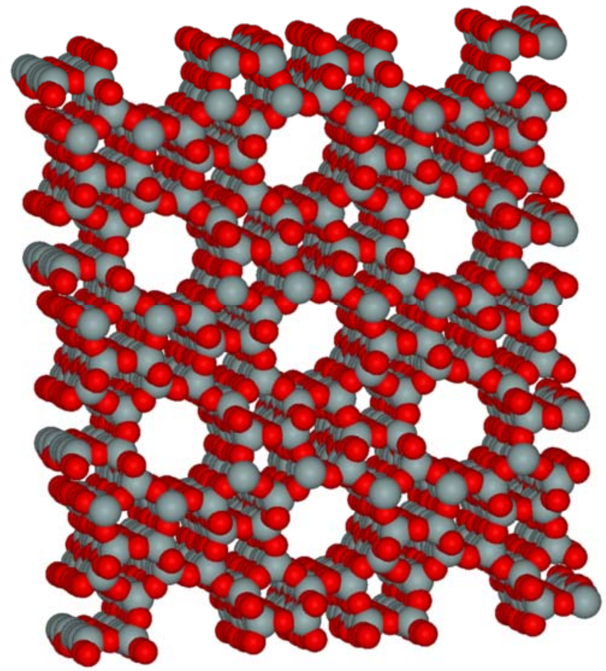
Table 1. Classification of nanoporous materials

	Polymeric	Carbon	Glass	Alumino-silicate	Oxides	Metal
Pore size	Meso-macro	Micro-meso	Meso-macro	Micro-meso	Micro-meso	Meso-macro
Surface area / Porosity	Low >0.6	High 0.3-0.6	Low 0.3-0.6	High 0.3-0.7	Medium 0.3-0.6	Low 0.1-0.7
Permeability	Low-medium	Low-medium	High	Low	Low-medium	High
Strength	Medium	Low	Strong	Weak	Weak-medium	Strong
Thermal stability	Low	High	Good	Medium-high	Medium-high	High
Chemical stability	Low-medium	High	High	High	Very high	High
Costs	Low	High	High	Low-medium	Medium	Medium
Life	Short	Long	Long	Medium-long	Long	Long

Lu and Zhao.

Nanoporous Materials: Zeolites

Zeolites are minerals that have a micro-porous structure.



The micro-porous molecular structure of a zeolite, ZSM-5

More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. They are basically hydrated alumino-silicate minerals with an "open" structure that can accommodate a wide variety of cations, such as Na+, K+, Ca2+, Mg2+ and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are: analcime, chabazite, heulandite, natrolite, phillipsite, and stilbite.

Wiki

Nanoporous Gold

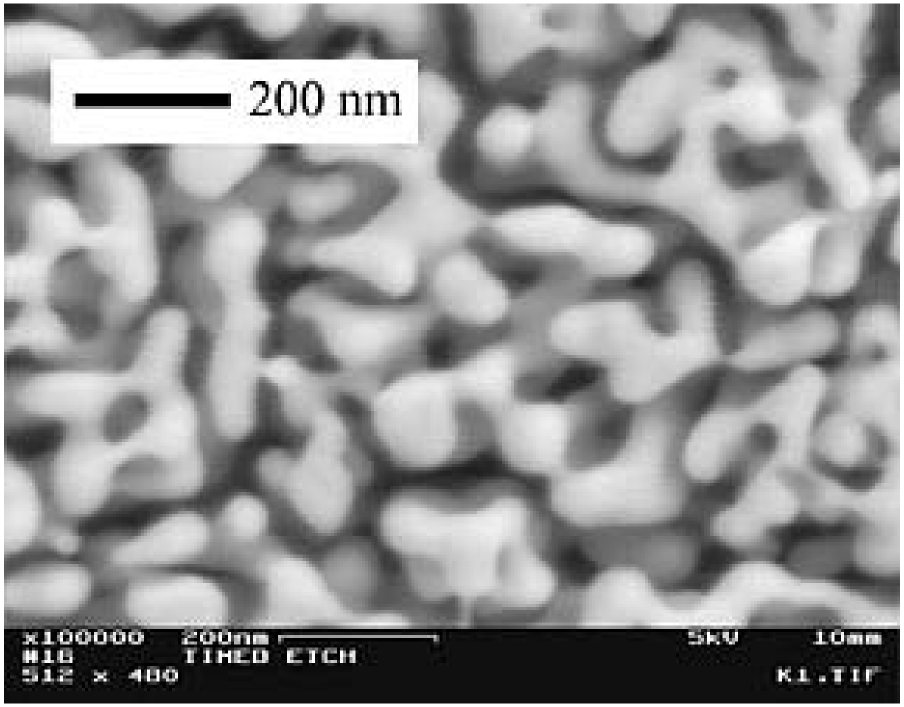
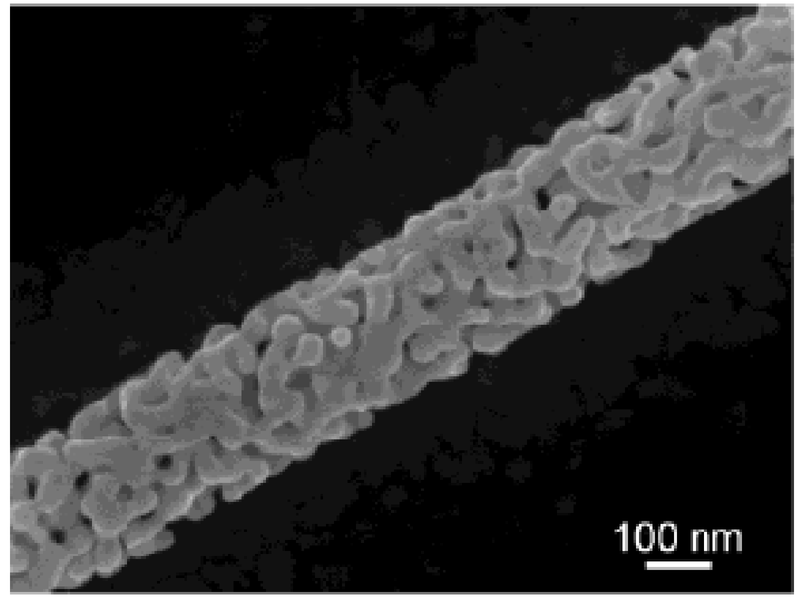


Image of nanoporous gold at 100,000 times magnification, taken with a scanning electron microscope.

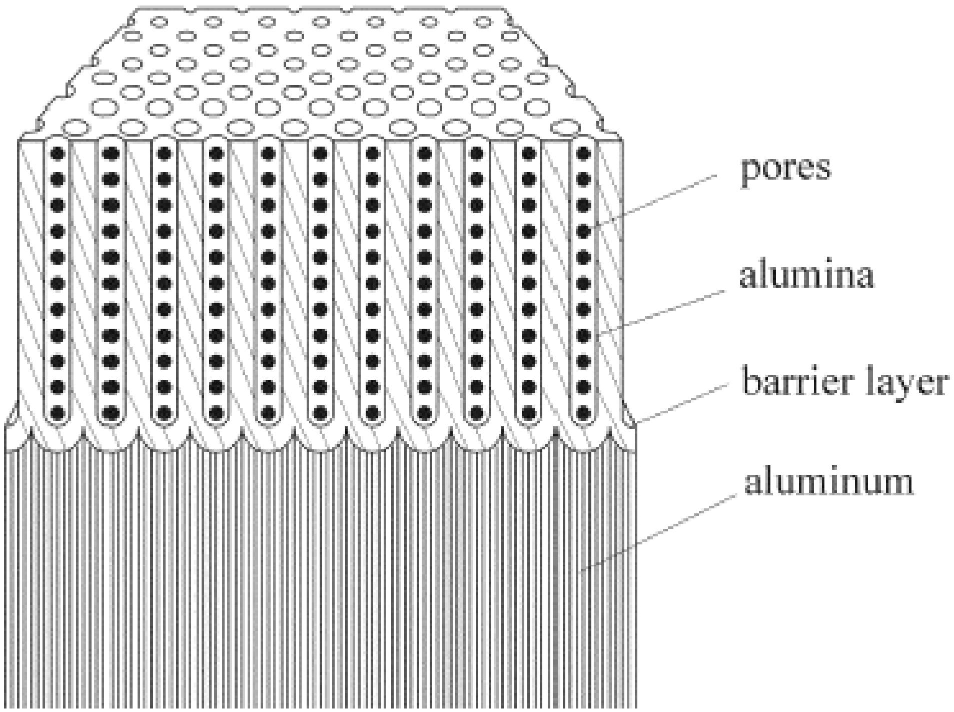
Jonah Erlebacher group, Johns Hopkins University

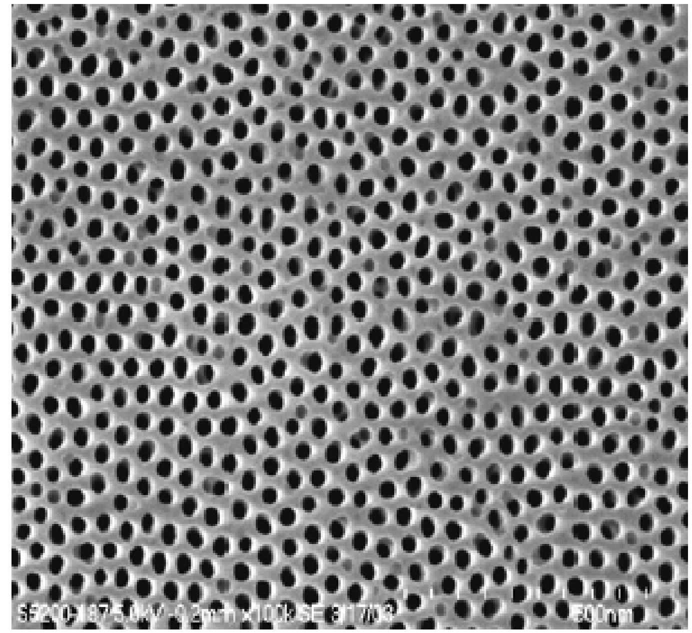


Nanoporous gold nanowires

J. Phys. Chem. B **2003,** *107,* 4494-4499

Case study I: Anodized Aluminum Oxide (AAO)

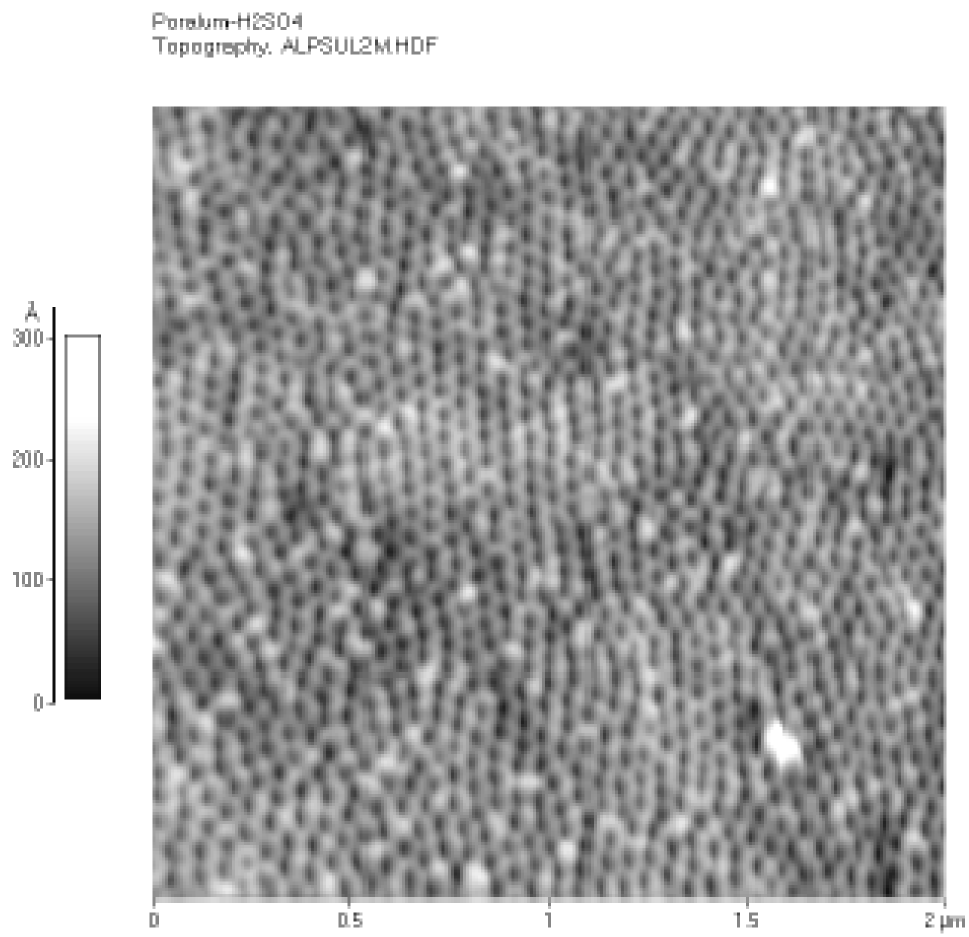




Sketch of an alumina membrane on aluminium filled with nanoparticles including the barrier layer.

J. Mater. Chem., 2002, 12, 1231–1238

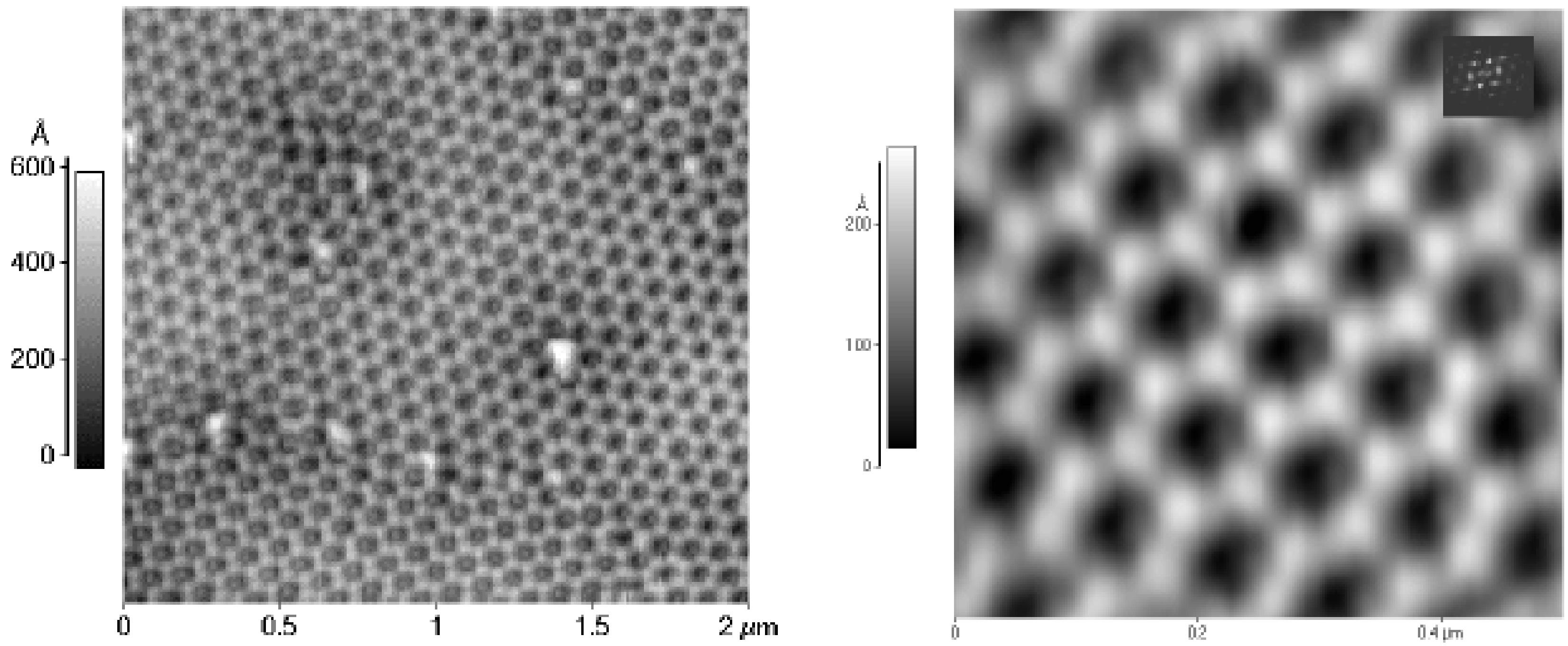
Case study I: AAO



AFM topographic image (2x2µm) of a single step AAO film anodized with 10% aqueous H2SO4 solution.

Sui et al., *Mat. Res. Soc. Symp. Proc.* **2001**

Case study I: AAO



AFM topographic images of a two-step AAO film anodized with 0.16M aqueous (COOH)2 solution. 2(a) 2x2µm ; 2(b) 500x500 nm. Inset in figure 2(b) shows the Fourier transformed image.

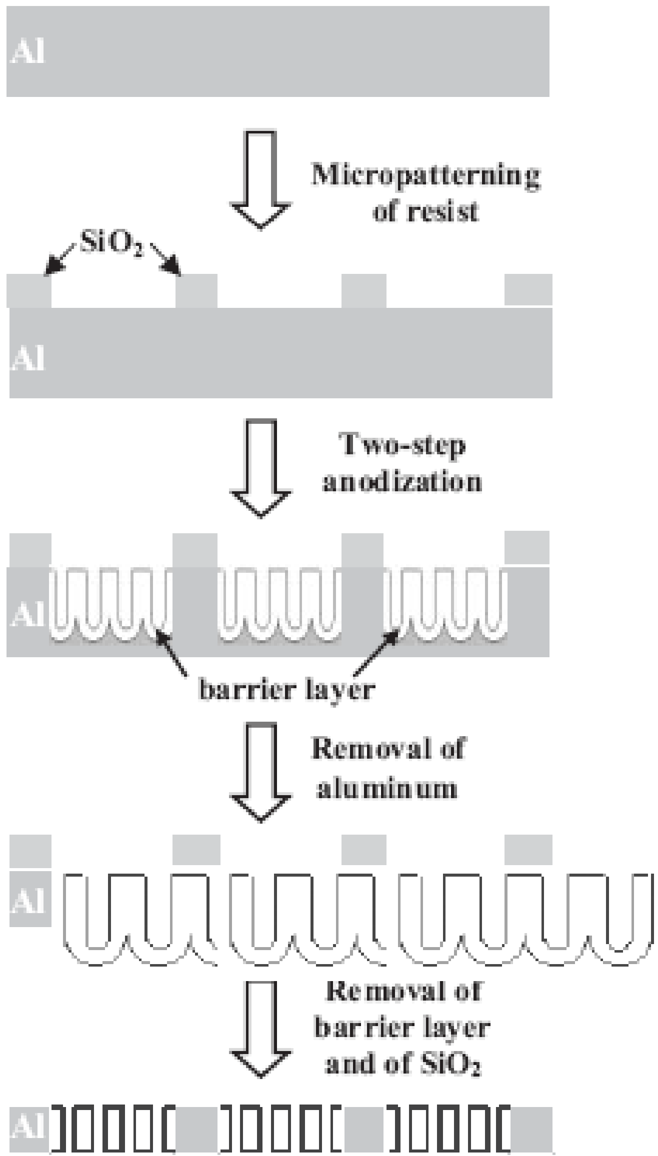
Sui et al., *Mat. Res. Soc. Symp. Proc.* **2001**

Case study I: AAO Procedures

AAO membranes are prepared with high purity aluminum sheets (99.998%) through anodization in aqueous solutions. Typical steps involve the following: 1. Cleaning, degreasing, and mechanical polishing; 2. Annealing at 500 °C under argon atmosphere for 4 hours to enhance the grain size; 3. Electropolishing in a solution of HClO4 (60 wt%) and EtOH (1:8 in **Mat. Res. Soc. Symp. Proc. Vol. 775 © 2003 Materials Research Society P4.8.1** volume) at a current density of 100 mA/cm2 and a temperature of 0 °C for 10 min;

4. **A two-step anodization** to prepare highly ordered nanopores (see below); 5. Removal of unreacted aluminum through chemical etching utilizing a saturated HgCl2 solution or amixture of 0.1MCuCl2 and HCl (37 wt%) in 4:1 by volume; 6. Opening of the barrier layer through etching (5 wt% phosphoric acid at 30 °C). This procedure provides AAO membranes with both ends open for additional processing. The concept for the two-step anodization is to first generate aligned nanopores, followed by removal of the initial surface alumina layer [5]. This process generates highly ordered dents on the fresh aluminum surface. The second anodization leads to deep nanopores that were initiated from the surface dents. Typical anodization conditions are listed in the following Table 1.

Case study I: AAO Procedures

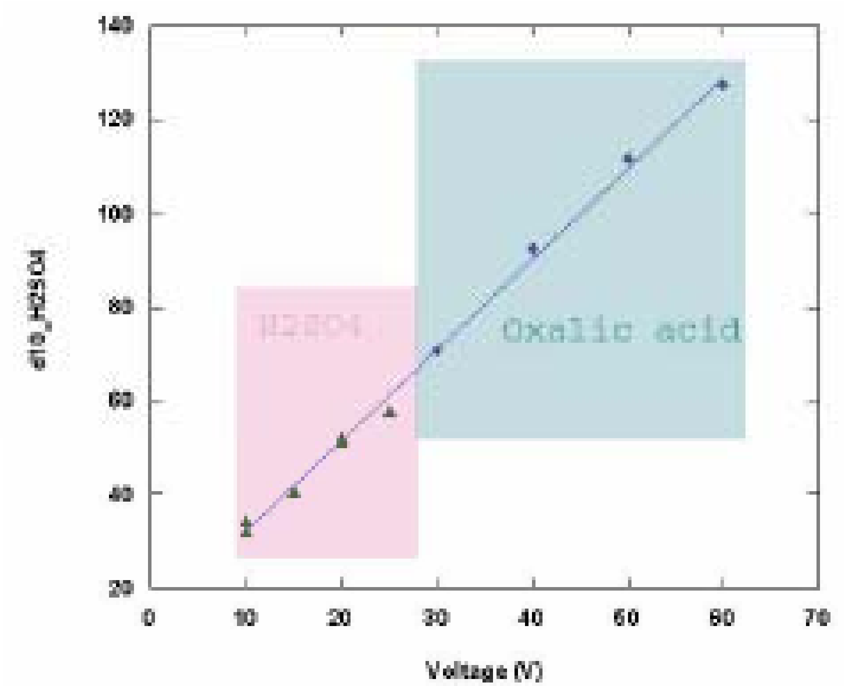


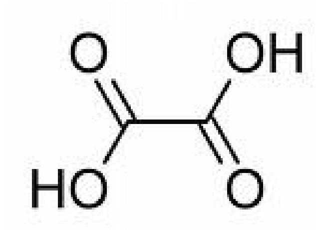
nano
manufacturing center at UML

Case study I: AAO

Table 1. Anodization conditions to prepare AAO membranes with ordered nanopores

Anodization Solution	Temperature	Etching time	Anodization Potential	Potential Range For Ordered Arrays
0.3 M Oxalic acid	3 °C	8 to 24 hrs	30-60 V	40-50 V
0.3 M Sulfuric acid	3 °C	8 to 24 hrs	10-30 V	25-27 V



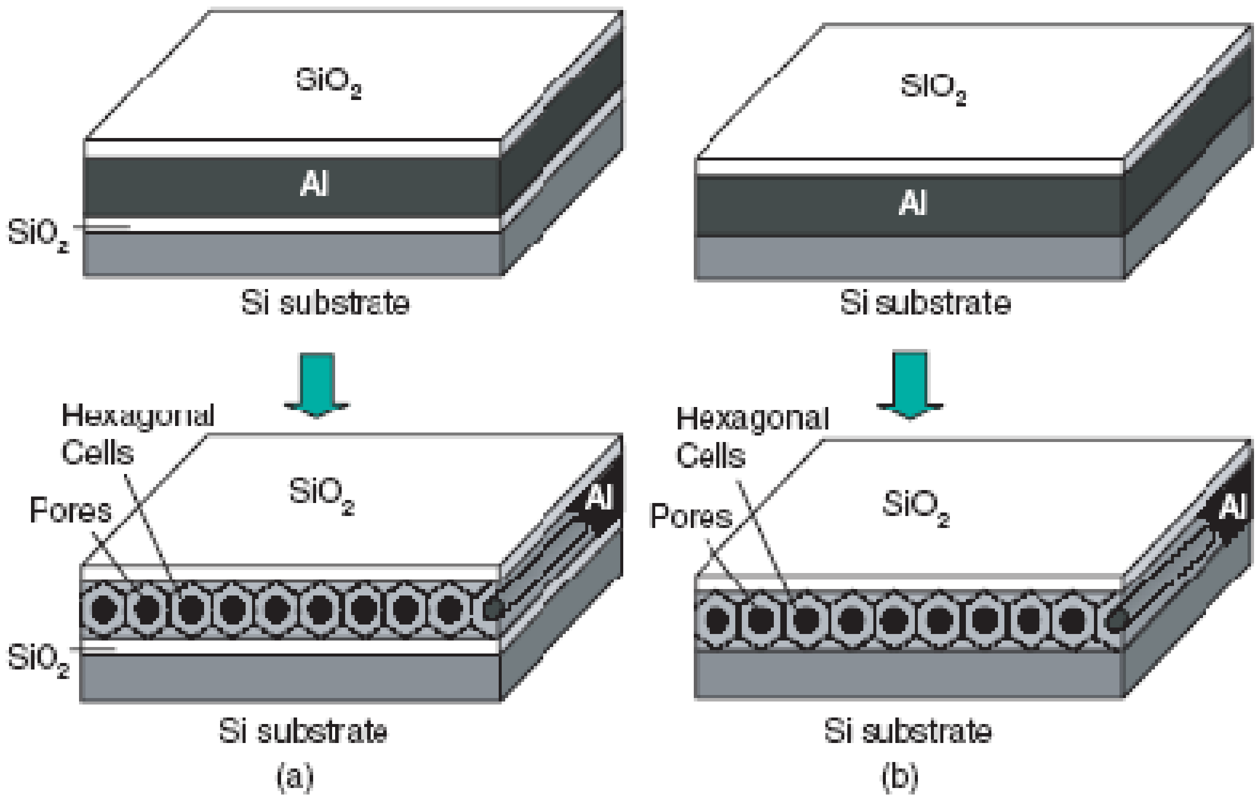


Oxalic acid

Plot of distances (d10) between two arrays of nanopores vs. the anodization potentials including both ordered and disordered arrays.

Wang et al., Mat. Res. Soc. Symp. Proc. 2003

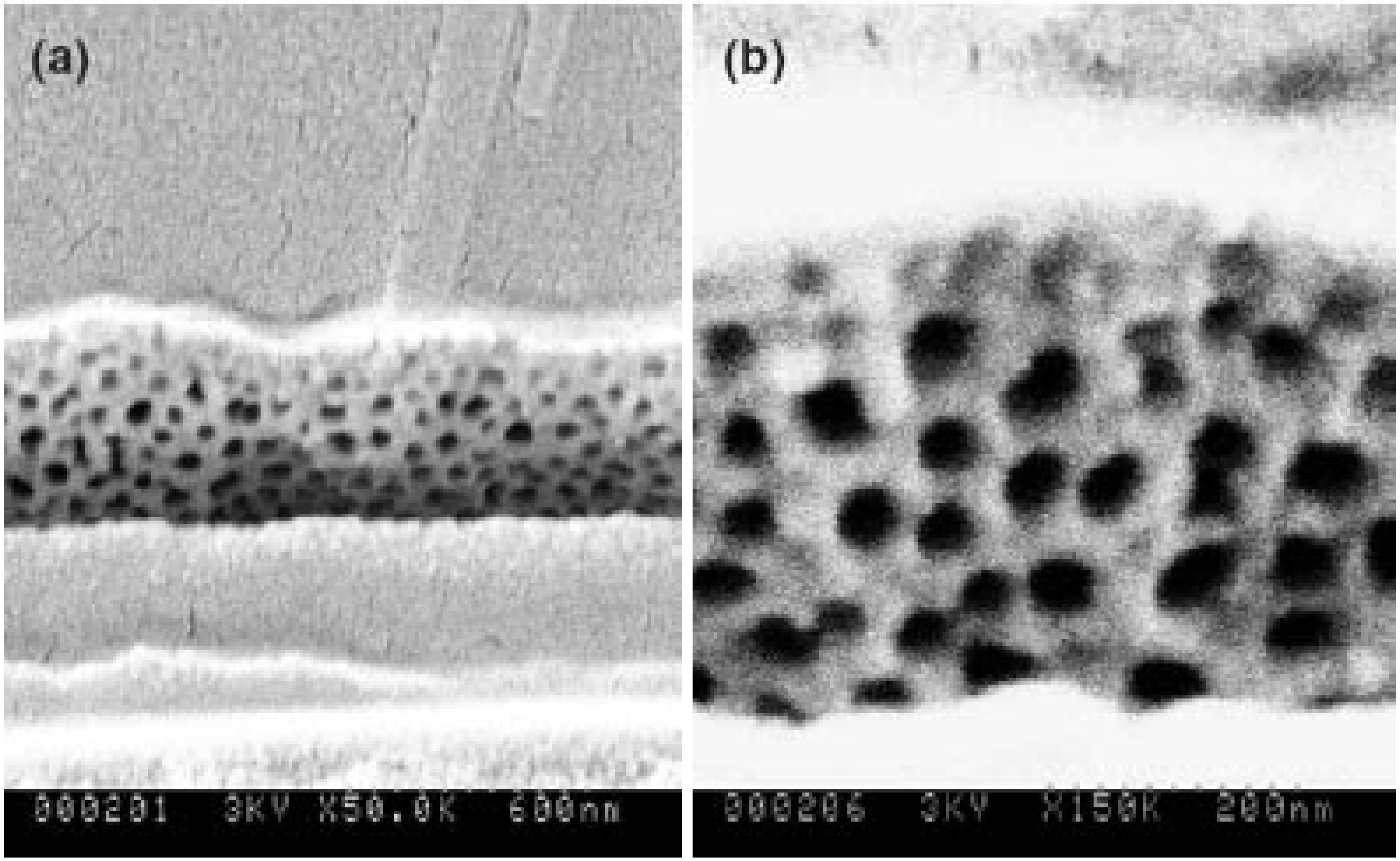
Case study I: Horizontal AAO



Fabrication procedures of one-dimensional horizontal nanopore arrays based on two types of structures: (a) SiO2/Al/SiO2/Si and (b) SiO2/Al/Si.

J. Nanosci. Nanotech. 5, 1745–1748, 2005

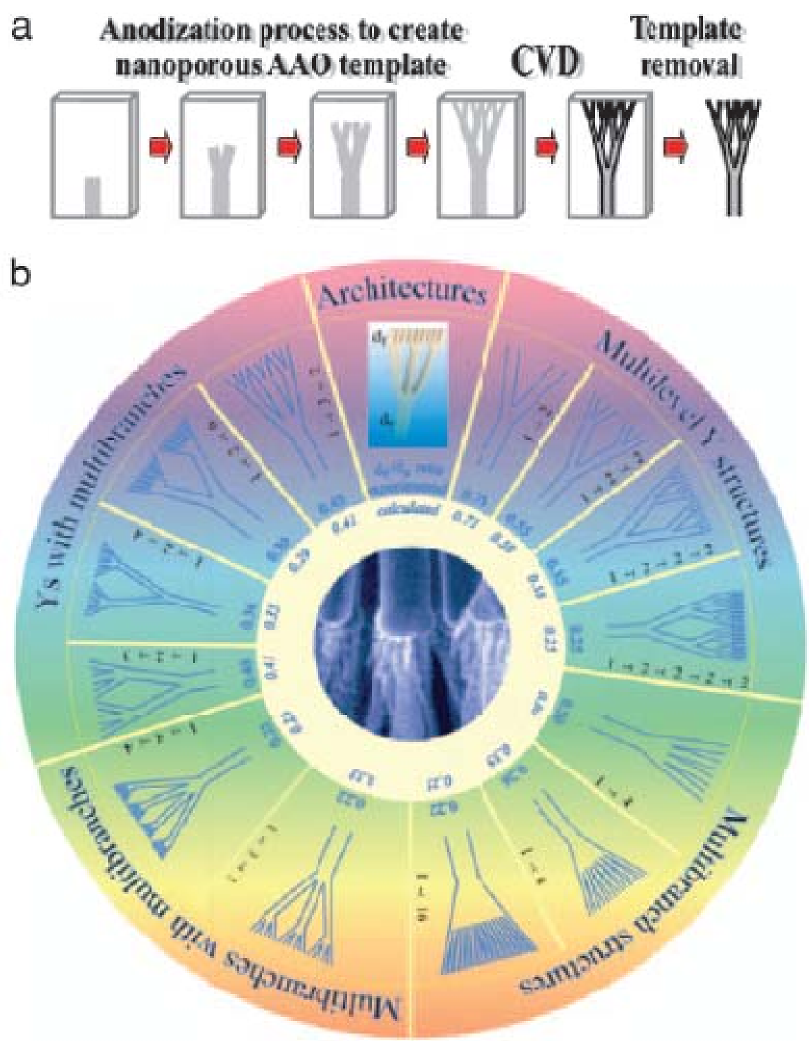
Case study I: Horizontal AAO



Scanning electron microscope (SEM) images of AAO arrays based on SiO2/Al/SiO2/Si structure with perfect interfaces for 600-nm thick aluminum film (a) (b) and 140 nm thick aluminum film

J. Nanosci. Nanotech. 5, 1745–1748, 2005

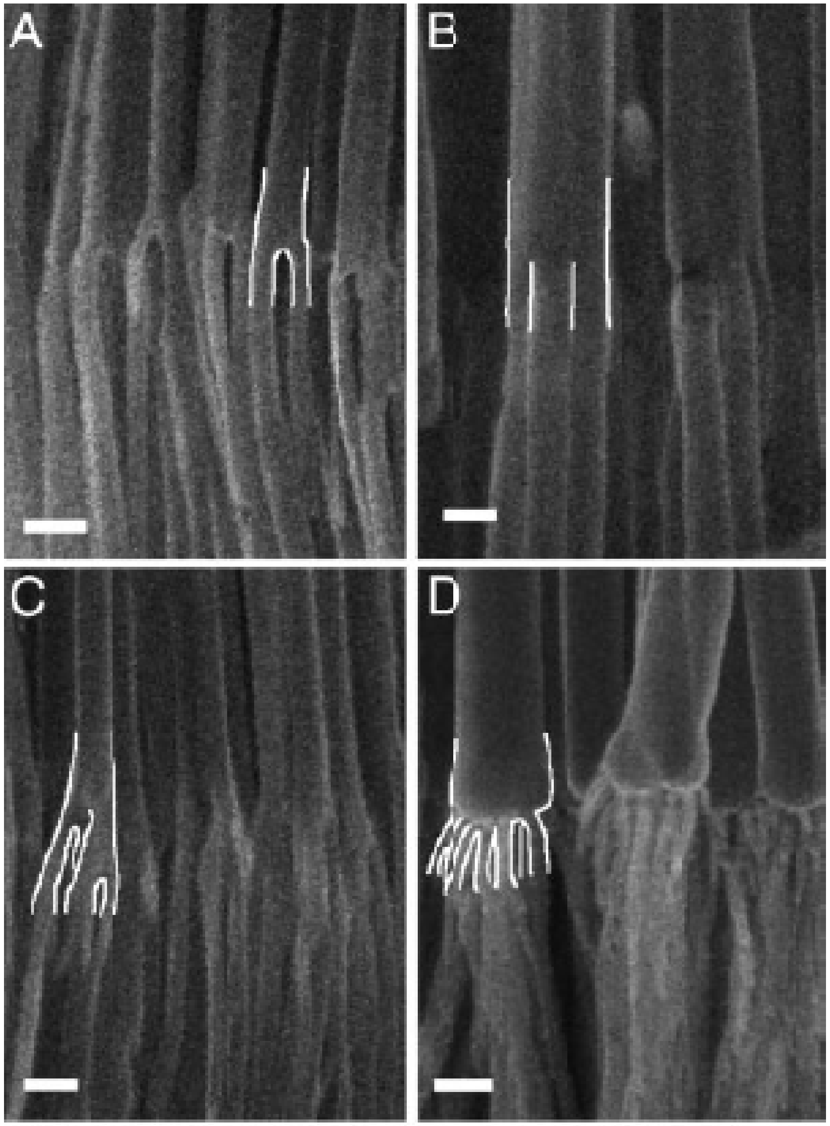
Case study I: Branched AAO

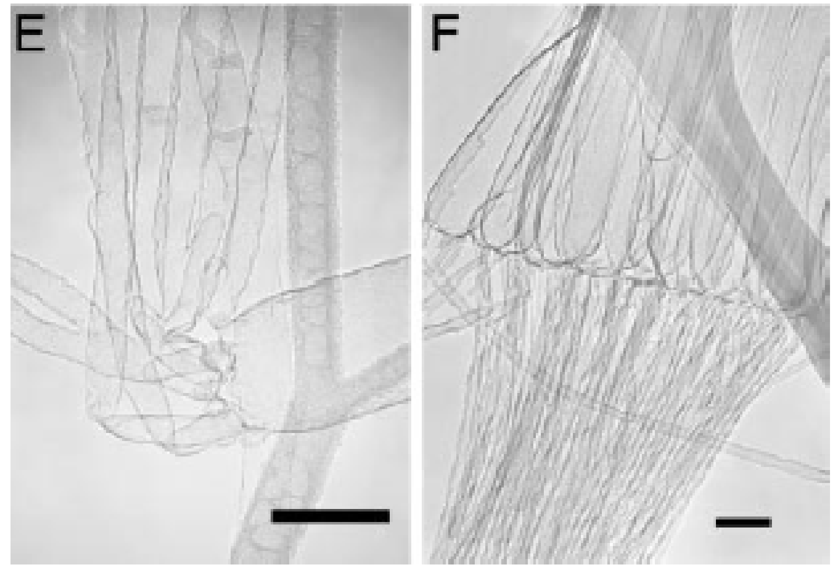


Schematics of fabrication process and the resulting branched nanowire structures.

PNAS, 2005

Case study I: Branched AAO





CNT architectures showing multiple branching.

PNAS, 2005