TAIWAN PHOTON SOURCE

Novel Nano materials and applications

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National Synchrotron Radiation Research Center

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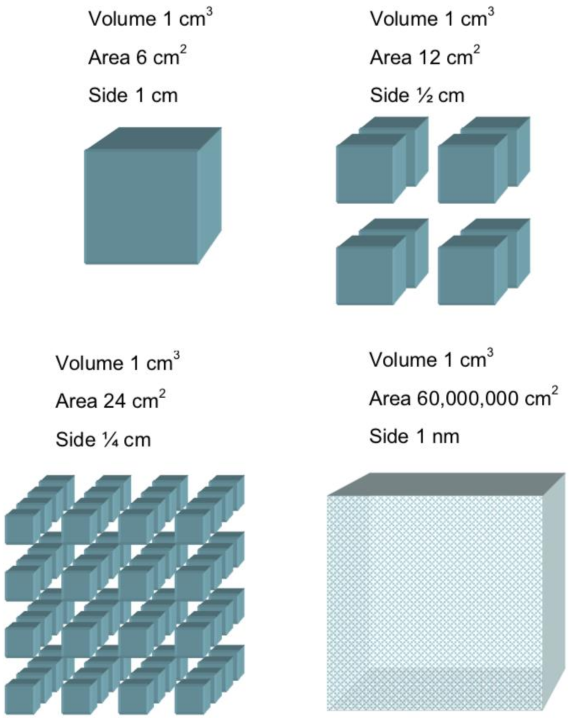
Outline

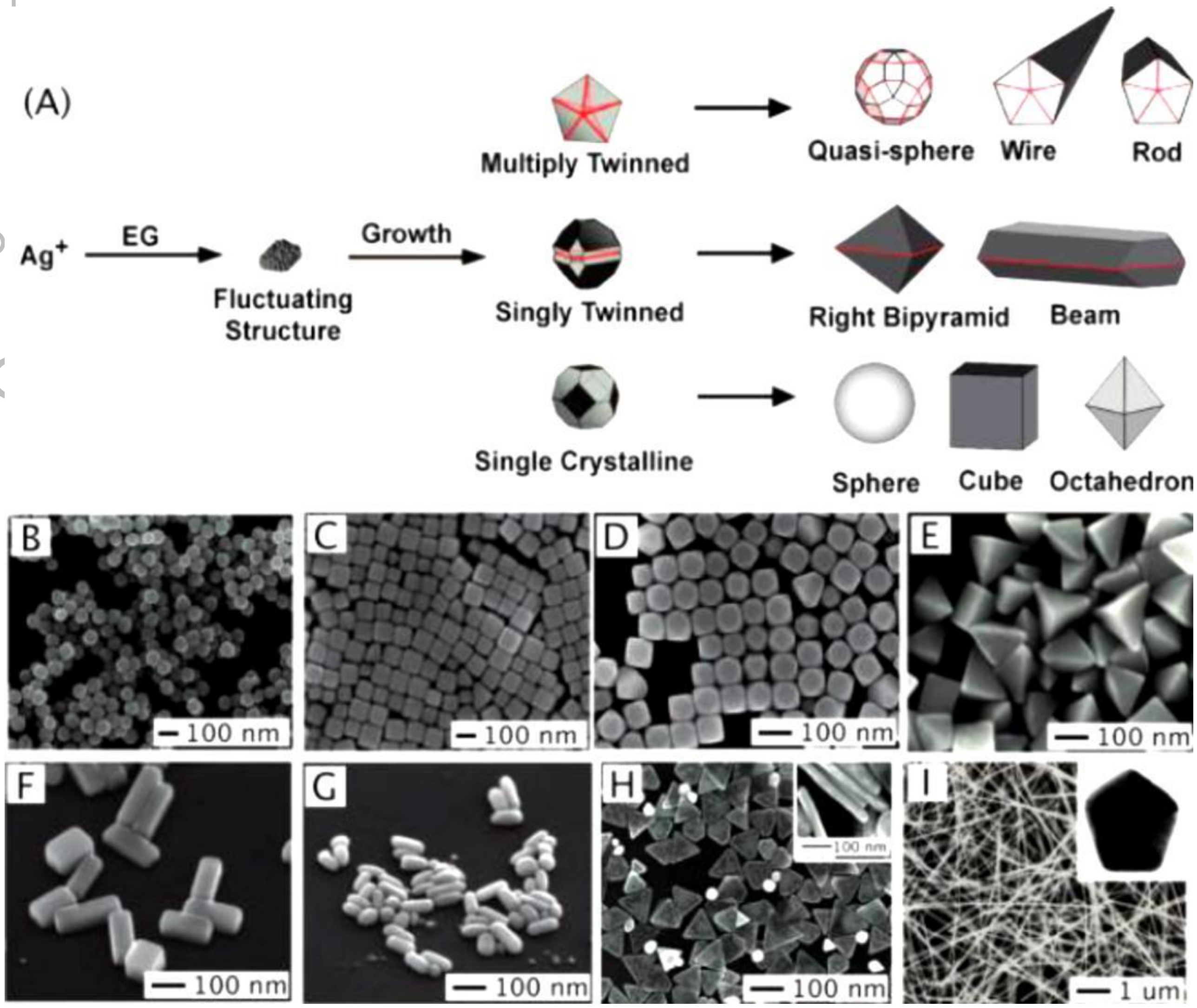
- Advantage of materials in nanometer dimensions
- Nanomaterial analysis technology



What is the nanotechnology? The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, with at least dimension in the nanometer range (1 nm = 10^{-9} m).

There are many uses and applications available using nanotechnology that are not possible using conventional materials which make it unique. For applications that use a substance's chemical properties, substantially less nanomaterial may be required to do the job of a conventional material. The chemical reactivity of a material is related to its surface area compared to its volume and the surface area for a nanoparticle is enormous per unit volume. The diagram below illustrates how surface area increases when a material is dissected into nano-sized particles.

Methods of controlling the NPs size



Since NPs exhibit special properties and these properties vary with the size of NPs, controlling the NPs sizes becomes an important issue. Changing the size of NPs in chemical synthesis methods is usually carried out by precisely controlling the synthesis process and concentration of reactants.

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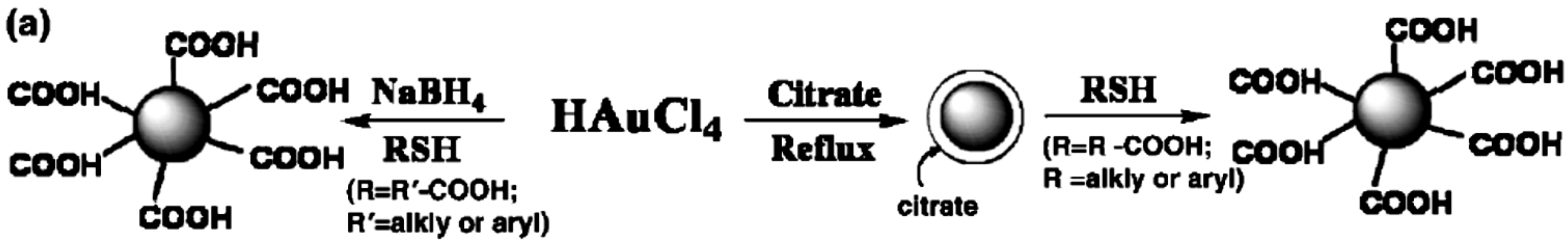
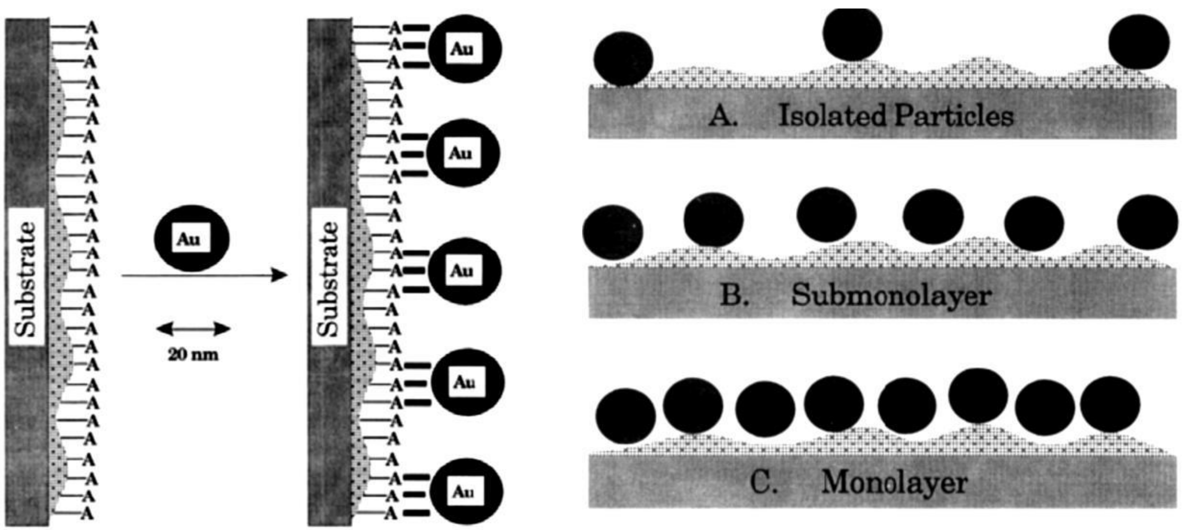
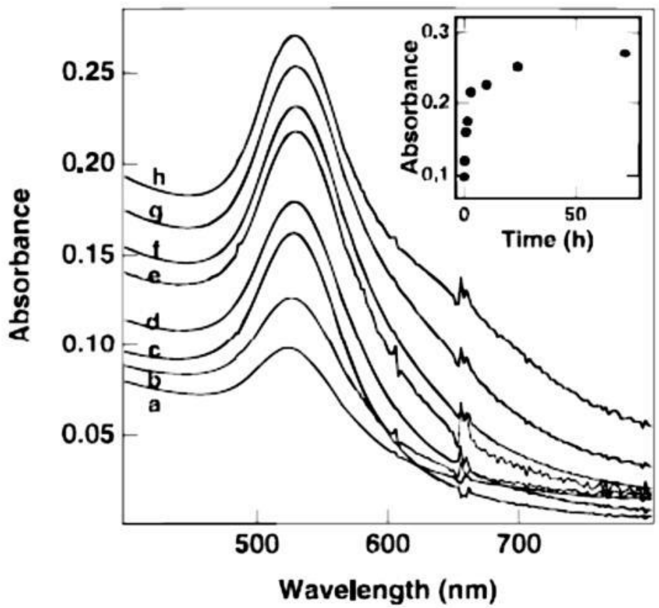
NC arrays fabricated by Chemical self-assembly

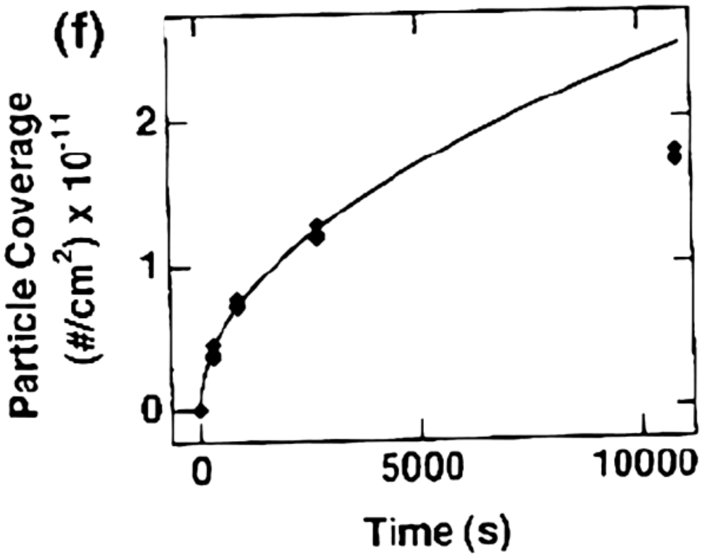


NCs of different sizes have been synthesized from $AuCl_4^-$, predominantly, using either citrate or sodium borohydride as reducing agents.



Hydroxyl/oxide groups on the substrate (e.g., glass, quartz, Si) surface provide active sites for the attachment of an alkoxysilane possessing functional group A, where A has a high affinity for gold.





The absorbance spectra and particle coverages for glass slides immersed in 15-nm-diameter colloidal Au solution as a function of time.

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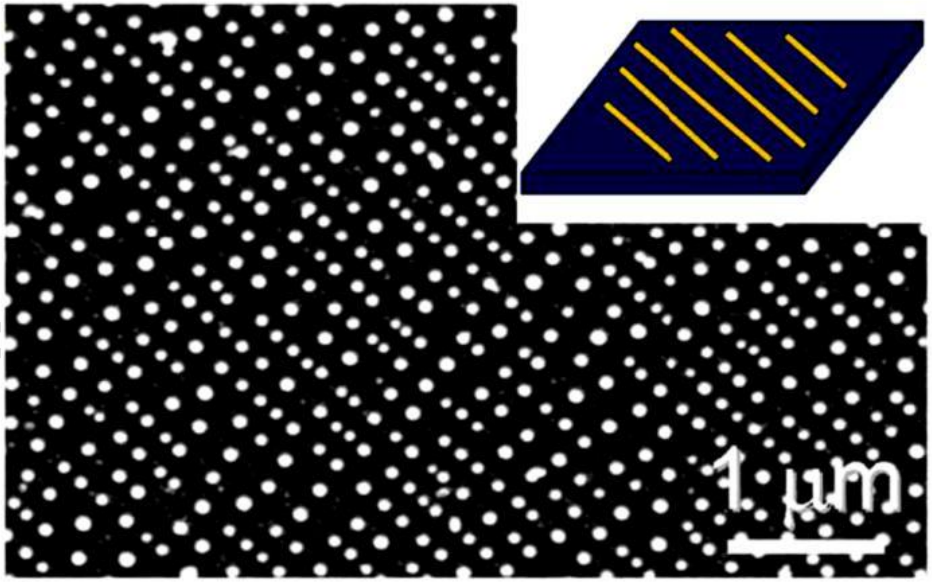
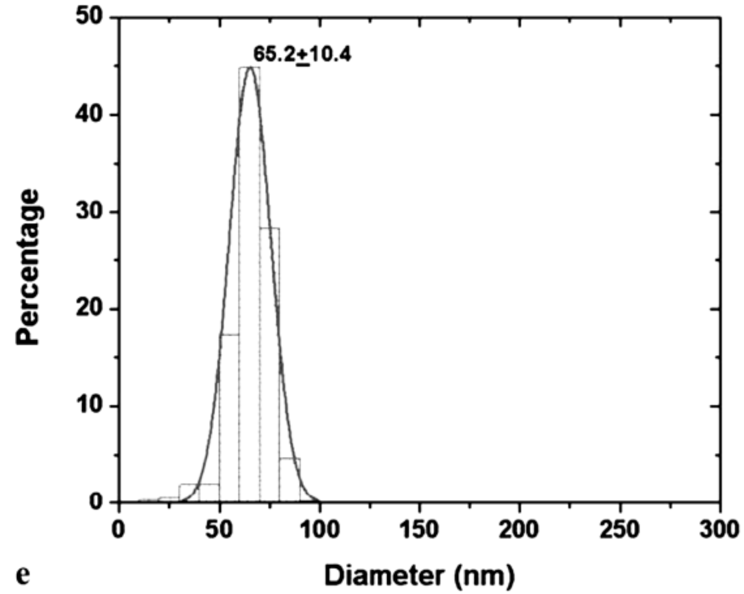
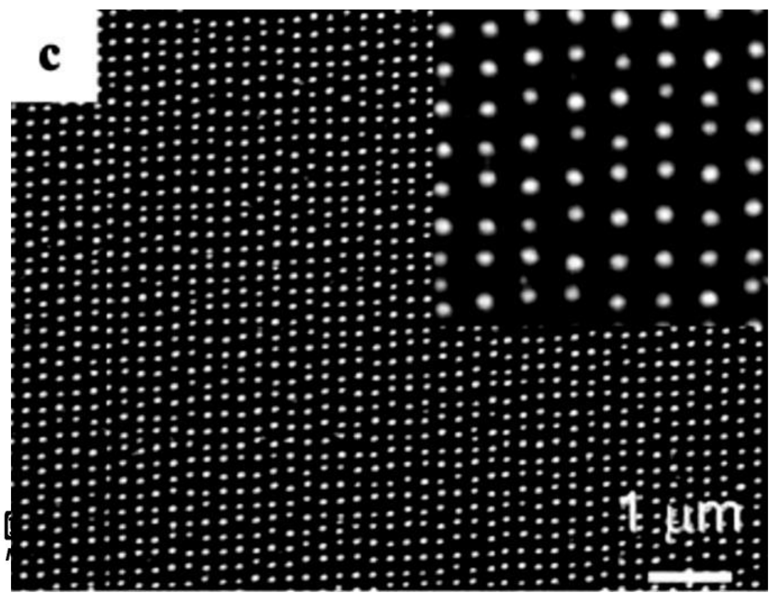
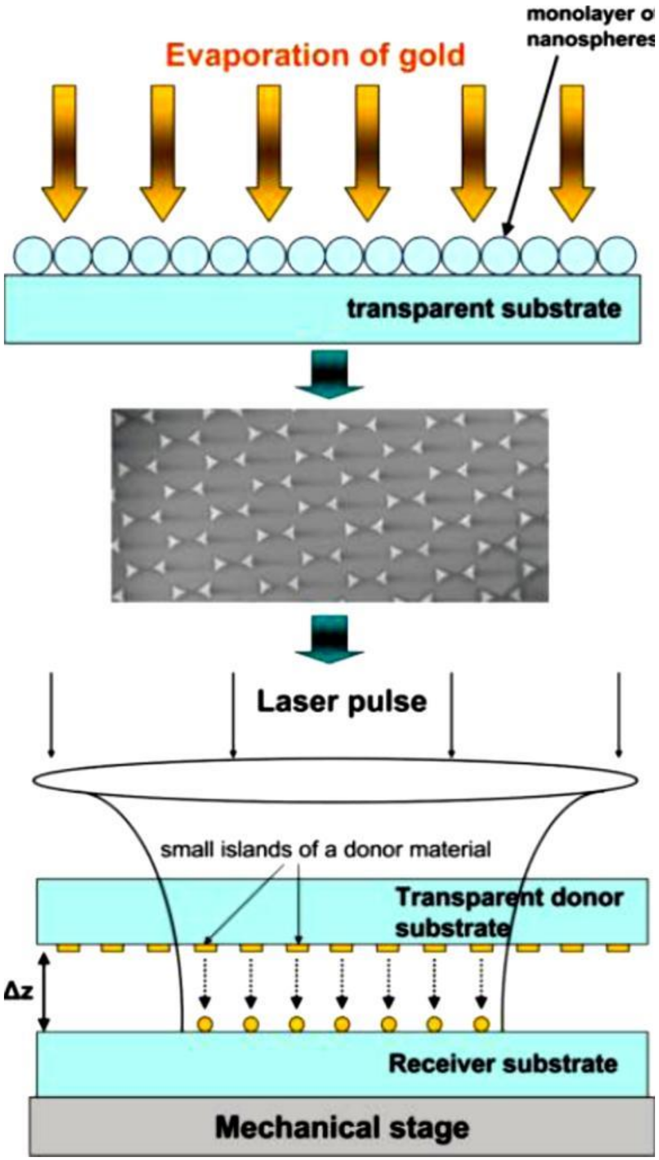
Nanocluster arrays fabricated by laser annealing

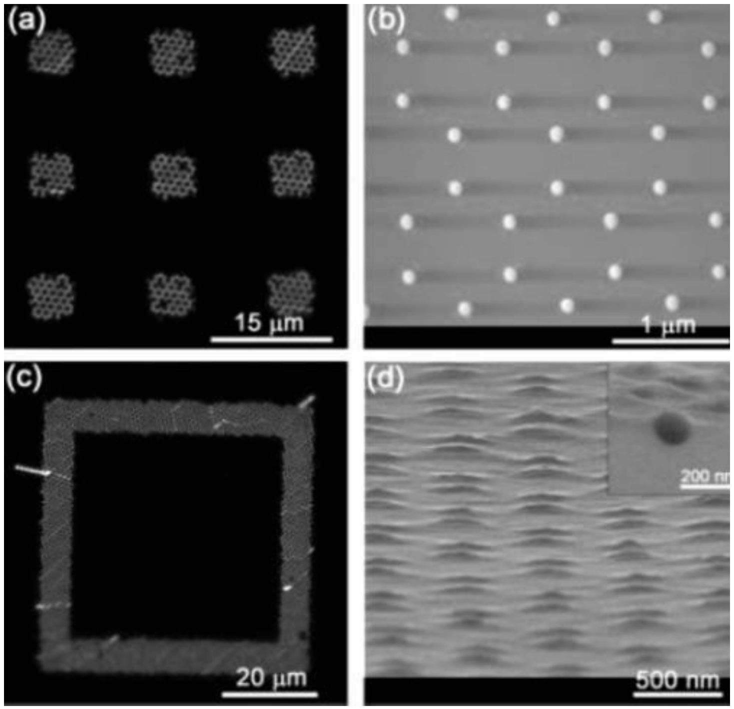




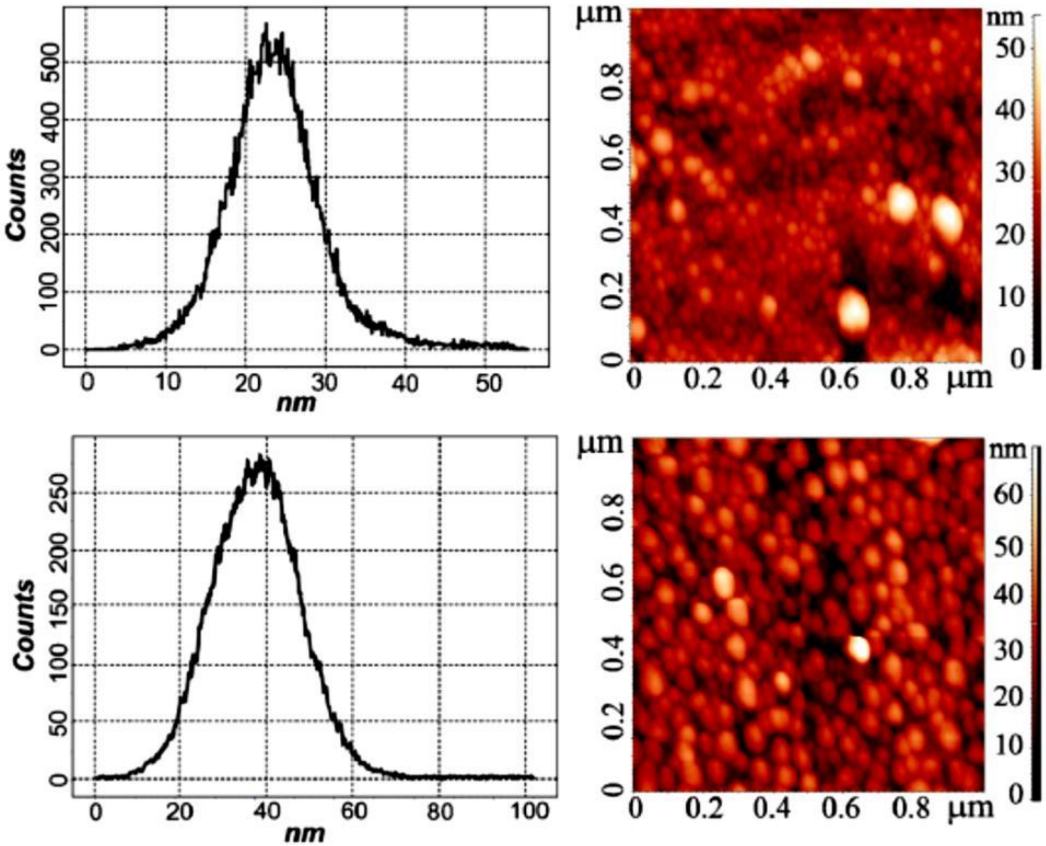


The method starts with a thin metal lines deposited on a substrate, followed by melting using a single excimer laser pulse.

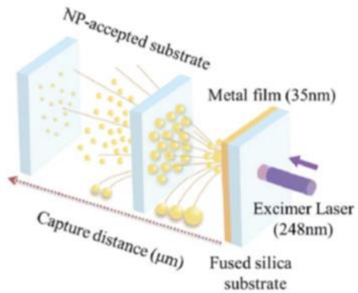


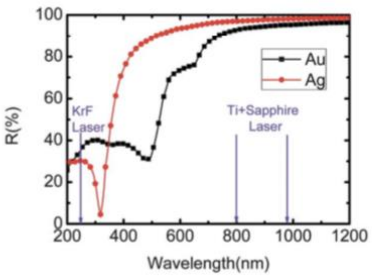


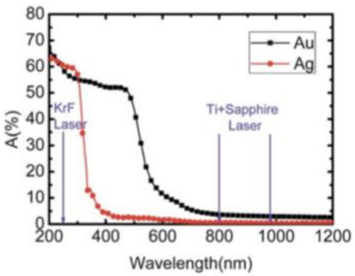
(a) NP structure fabrication by a combination of the nanosphere lithography and laser-induced transfer. (b) Dark-field microscope image and SEM of gold NPs fabricated by single laser pulses on a receiver substrate.

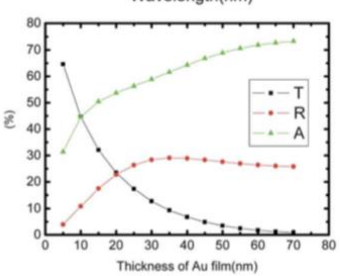


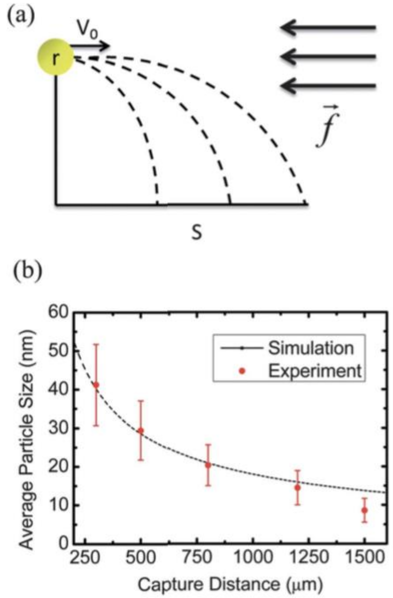
The averaged Ag NP size fabricated under the 45 fs pulse shot was about 20 to 25 nm and those fabricated by 300 ps was about 40 to 50 nm.

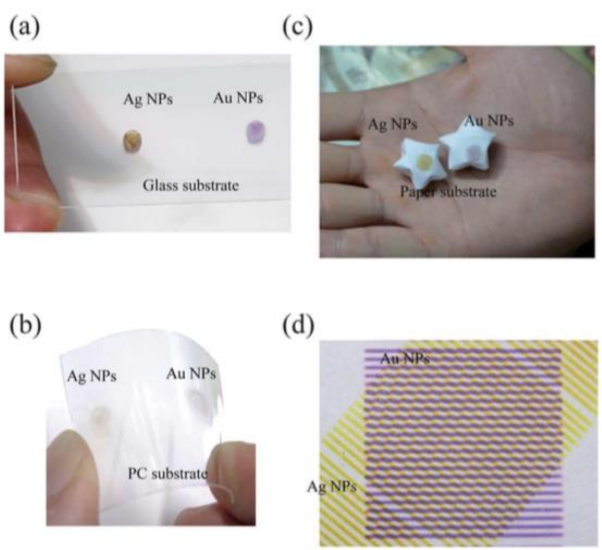












Therefore, the air drag force acting on the NPs in the ambient air was

$$f = -kr^{\alpha}v^{\beta} \tag{1}$$

where k is a constant, r is the diameter of the NPs, and v is the relative velocity of the NPs in air (760 torr).[29,30]

The air drag force on a nanoscale particle moving in a gaseous medium had been reported previously from related theoretical calculations.[31] We proposed that the air drag force was proportional to the volume and the velocity of the NPs; therefore, it was reasonable to assume values of α and β of 3 and 1, respectively. For uniformly accelerated motion,

$$s = v_0 t + \frac{1}{2}at^2 \tag{2}$$

where s is the travelling distance of the NPs. Because the motion of our NPs was a varied accelerated motion, we assumed that the acceleration in a very small velocity change in each moment was constant:

$$ds = \frac{(v - dv)^2 - v^2}{2a} = \frac{v^2 - 2v\,dv + (dv)^2 - v^2}{2a} \xrightarrow{\text{ignore}(dv)^2} ds = -\frac{v\,dv}{a}$$

furthermore, we proposed that each metal NP was a sphere having a mass density ρ and a mass m. Therefore, the kinetic energy was described as

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}\frac{4}{3}\pi r^3 \rho {v_0}^2 \tag{3}$$

substituting $F = ma$ into eqn (1), we obtain

$$s = \int_0^{v_0} \frac{4\pi\rho}{3k} dv = \frac{4\pi\rho}{3k}\int_0^{v_0} dv = \frac{4\pi\rho}{3k}v_0 = \frac{4\pi\rho}{3k}\left(\frac{3E_k}{2\pi\rho r^3}\right)^{\frac{1}{2}}$$
$$= \frac{4\pi\rho}{3k}\left(\frac{3E_k}{2\pi\rho}\right)^{\frac{1}{2}} r^{-\frac{3}{2}} \tag{4}$$

from these equations, we find that s is proportional to $r^{-(3/2)}$. Fig. 5b (dashed line) presents a plot of the calculated average particle size with respect to the jet distance. The experimental data (red dots) fitted the calculated curve quite well.

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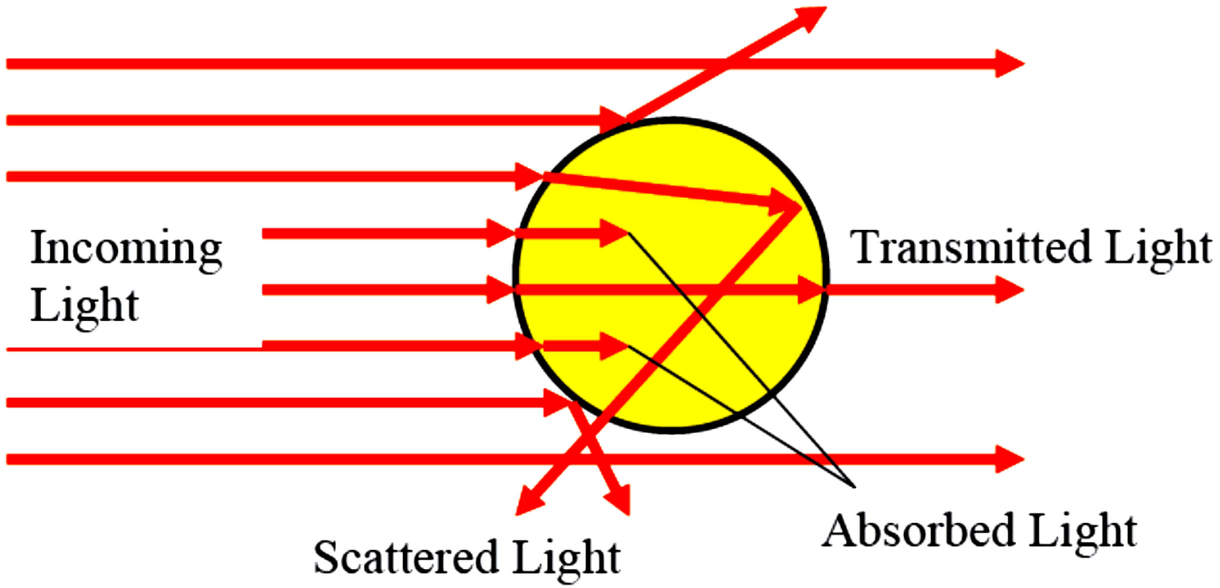
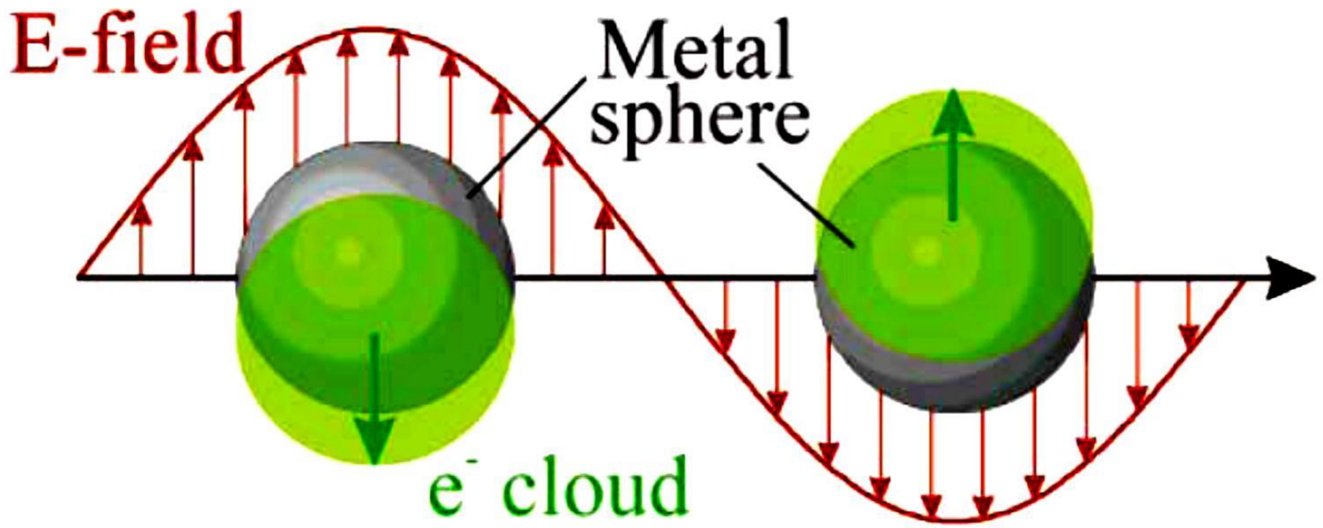


The theoretical principles that describe the metal NCs interaction with light are covered by Mie, Maxwell–Garnett and Drude models.

The extinction spectra (extinction = scattering + absorption) of spherical particles of arbitrary size.

Physical and chemical properties of metal NCs

Surface plasmon resonance (SPR)



Schematic diagram of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.

The strong interactions of metallic NCs with incident light, i.e., with the oscillating electric field, originate from the excitation of collective oscillations of conduction electrons within these particles. The collective oscillation of the electrons is called the dipole plasmon resonance of the particle.

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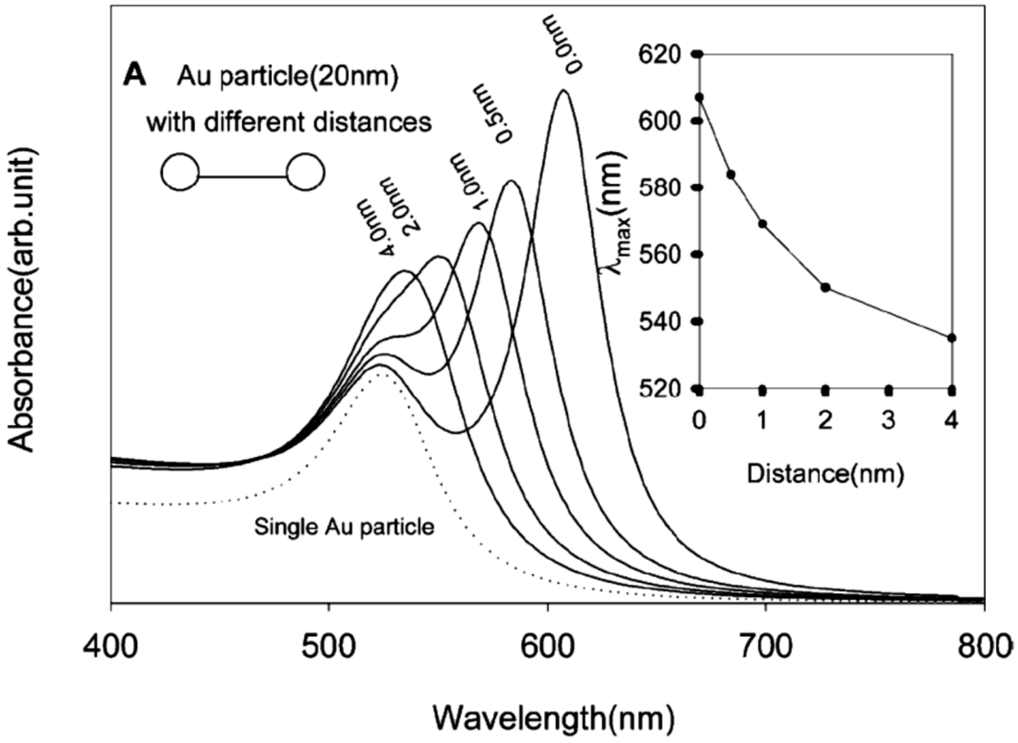
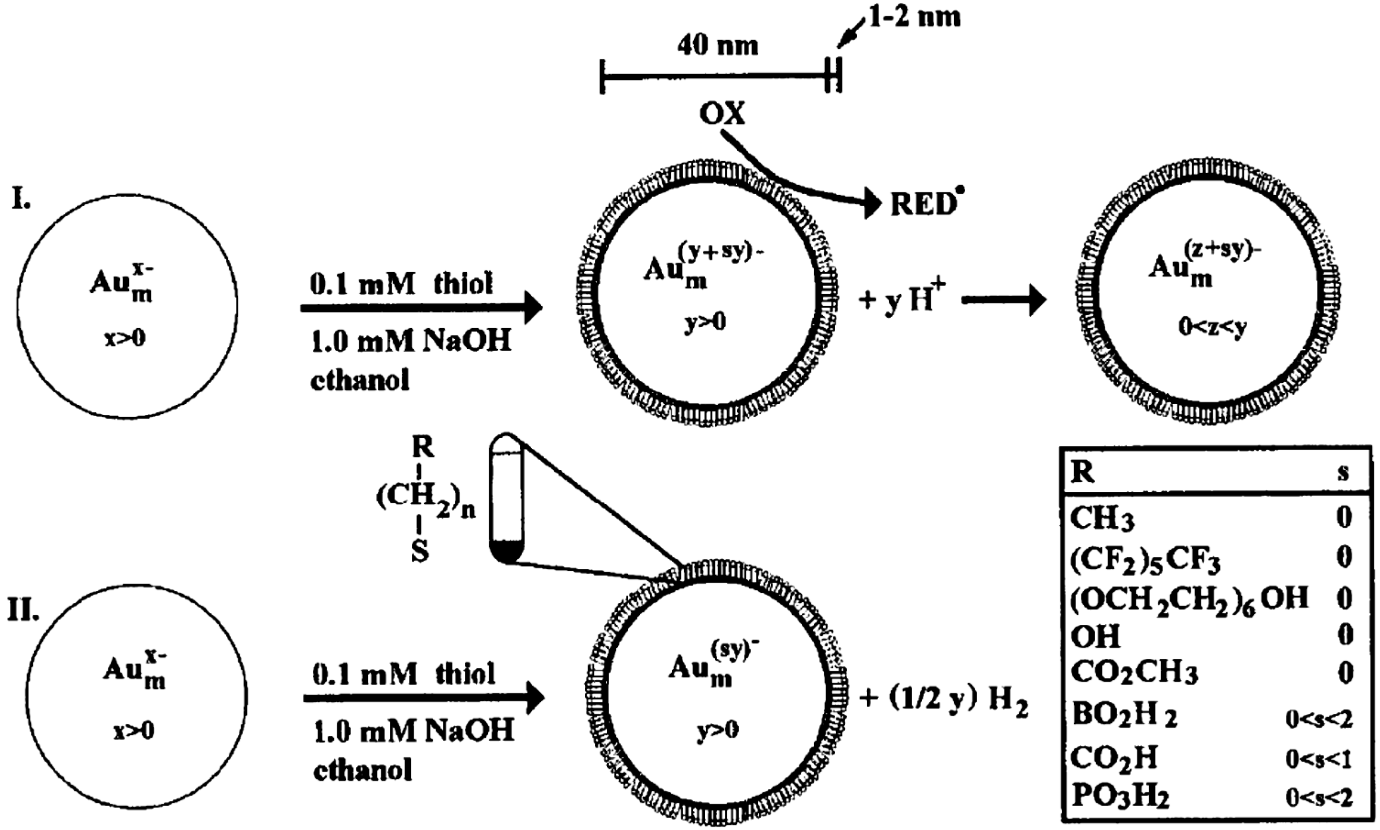
Particle-particle coupling

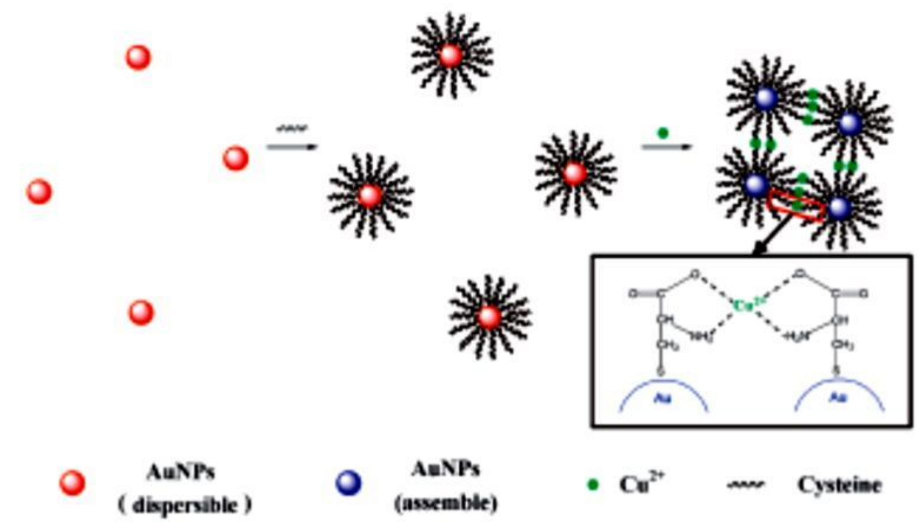


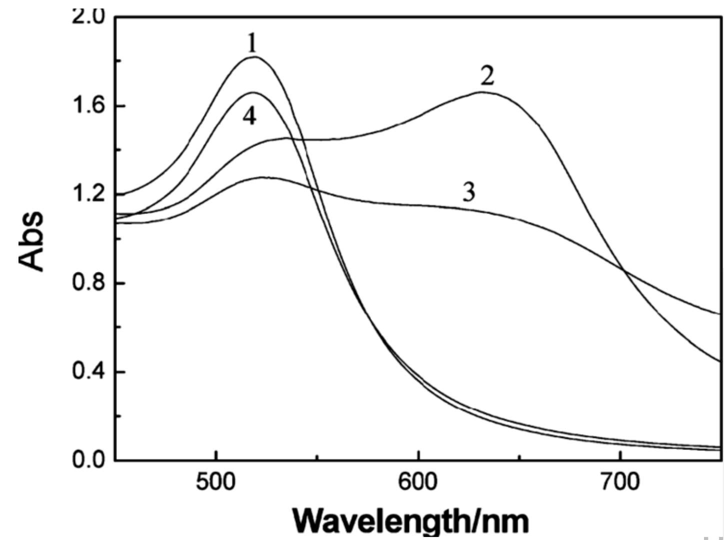
The close contact of metal NCs leads to the appearance of an SPR band attributed to the coupled plasmon absorbances of the NCs. This property has been predicted theoretically.

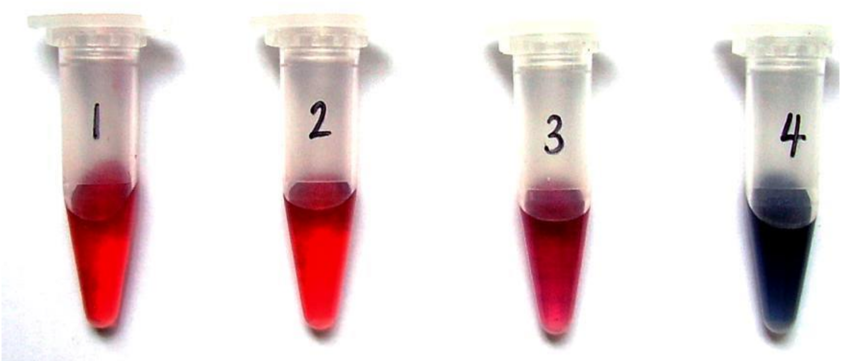
Chemical affinity



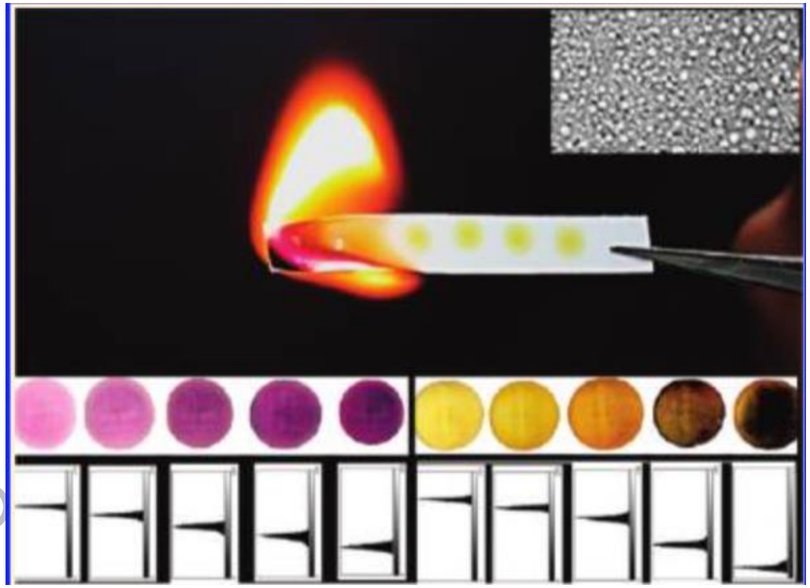
Gold-thiol chemistry: The modulation of SPR for surface-modified Au nanostructures should be dominated by the dielectric constant of the absorbed layers instead of the bulk solvent medium. As a result, Au nanostructures provide a highly sensitive means of detecting changes that occur in the region extremely close to the gold-solution interface.

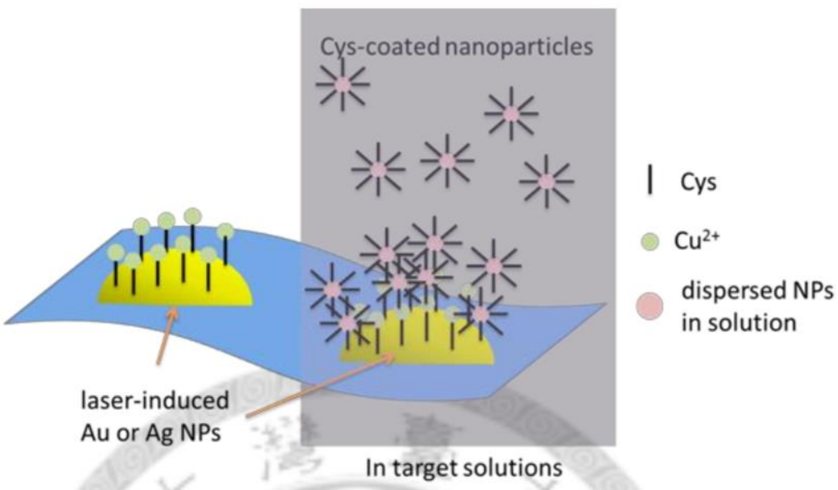


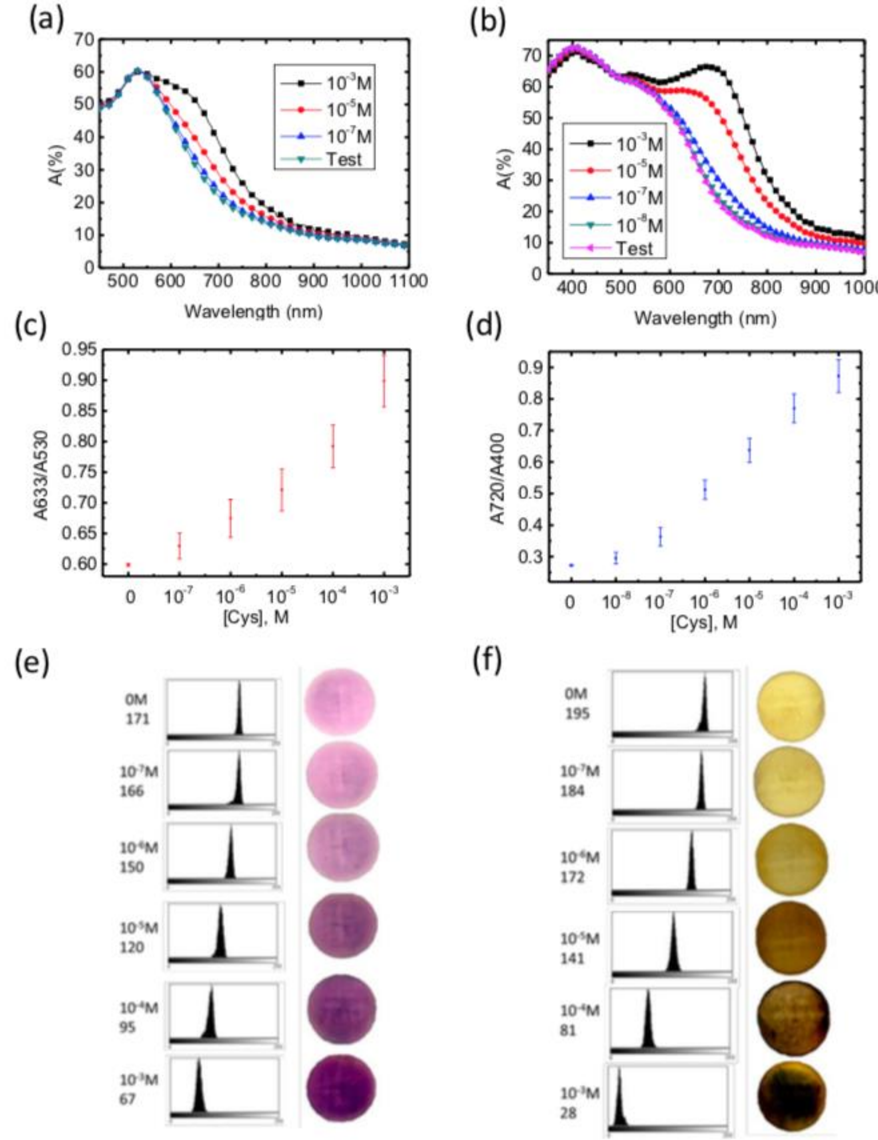




Absorption spectra of AuNPs (1) in the absence of cysteine, (2) in the presence of $1*10^{-5}$M cysteine and 1mM Cu^{2+}, (3) in the presence of $1*10^{-6}$M cysteine and 1mM Cu^{2+}, and (4) in the presence of $1*10^{-7}$M cysteine and 1mM Cu^{2+}.







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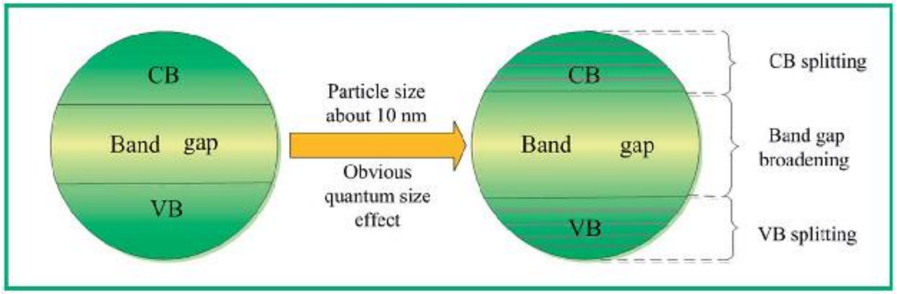
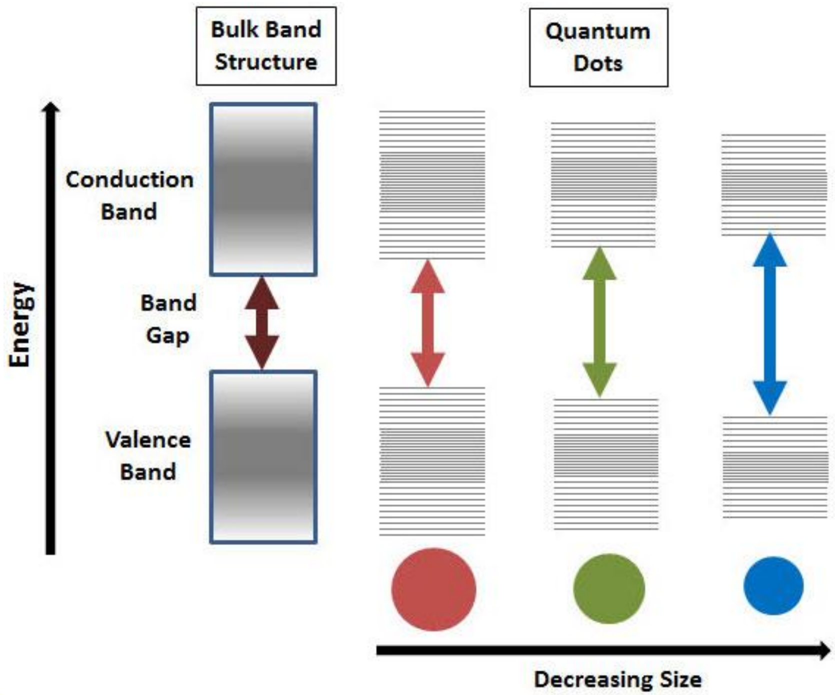
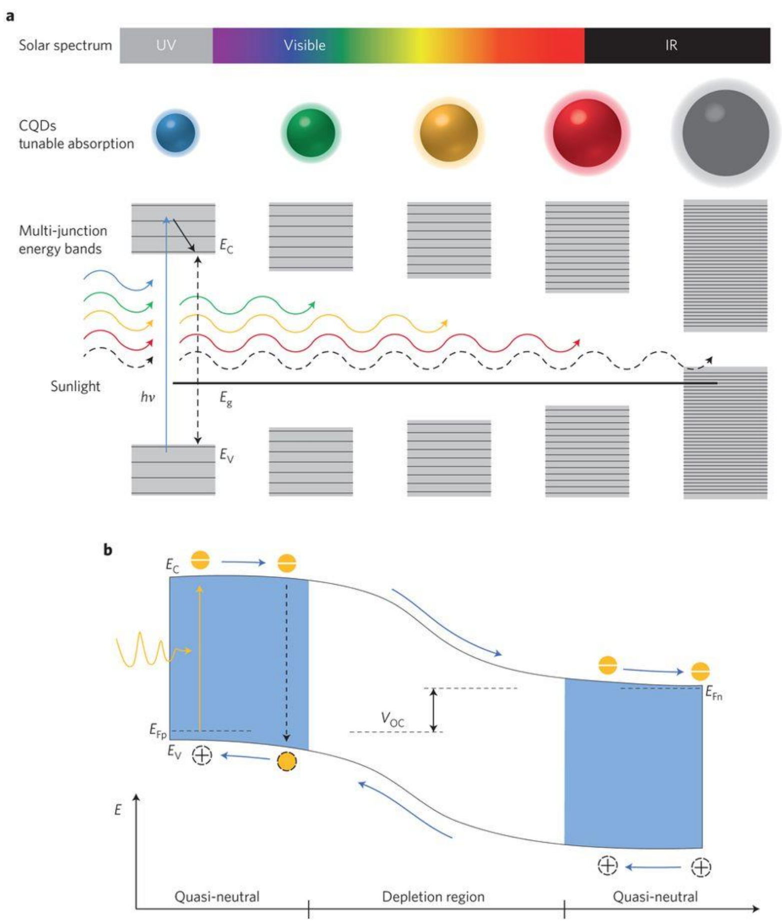
Quantum size effect







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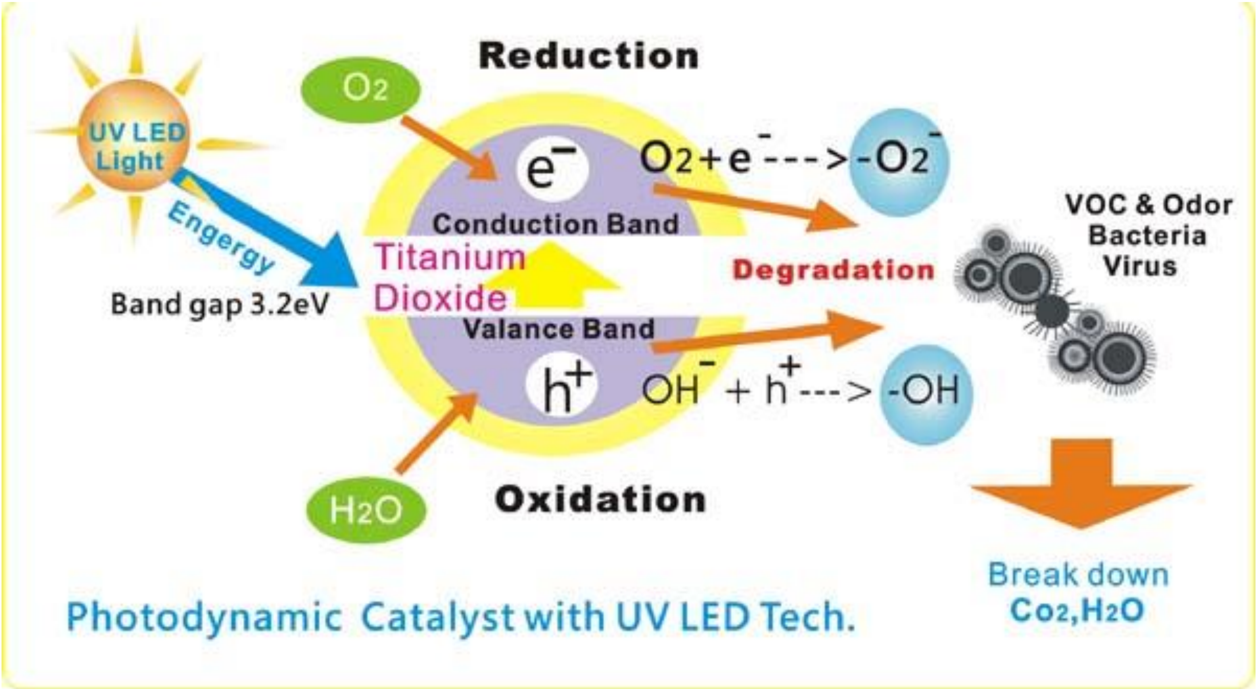
Nature Materials **volume13**, pages233–240 (2014)

Catalytic properties



Au NCs supported on Co_3O_4, Fe_2O_3, or TiO_2 were highly active catalysts, under high dispersion, for CO and H_2 oxidation, NO reduction, water-gas shift reaction, CO_2 hydrogenation, and catalytic combustion of methanol was a surprise, and was considered important by the chemical community.

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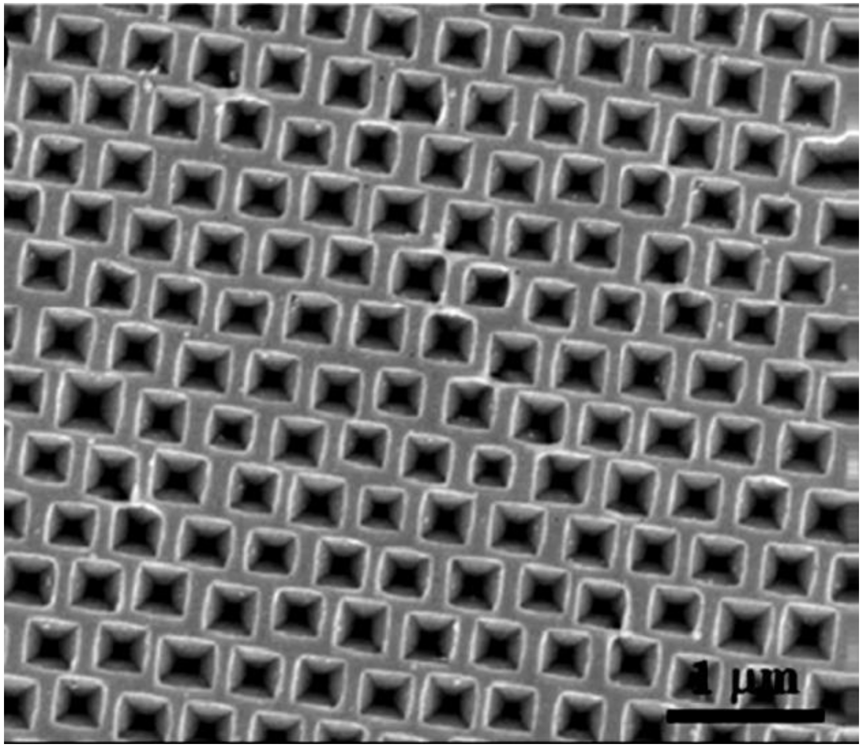
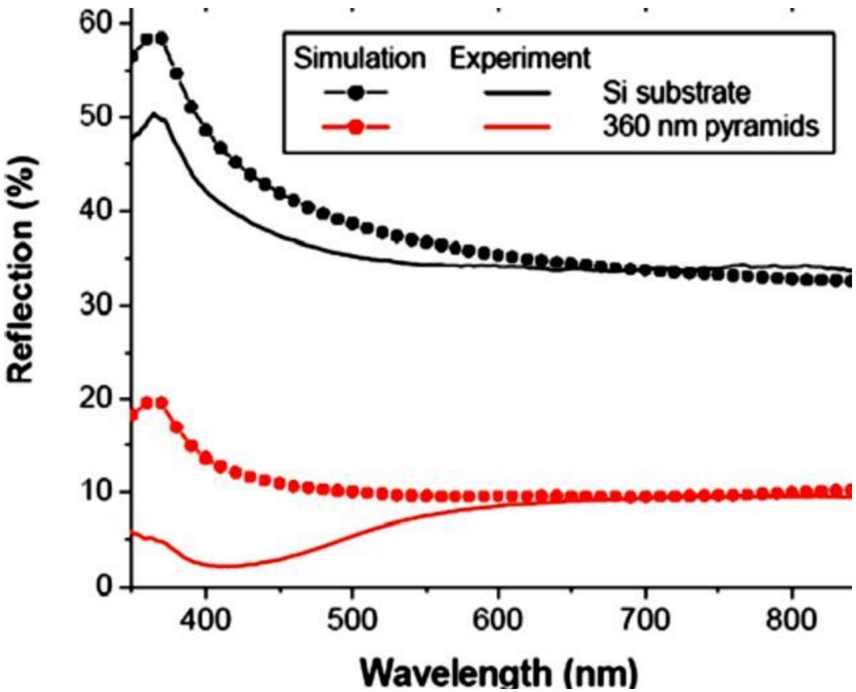
Surface Antireflection

Micro-scale texturing techniques



Replicated inverted pyramid arrays in silicon.



Experimental (solid) and simulated (dotted) optical reflectivity at normal incidence.

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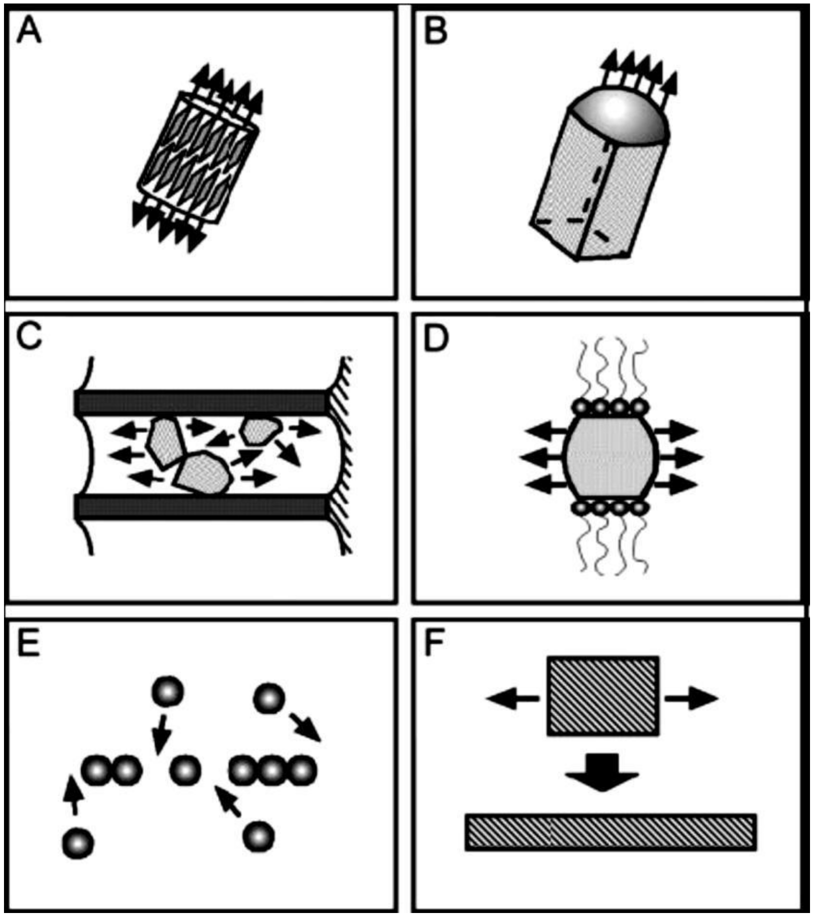
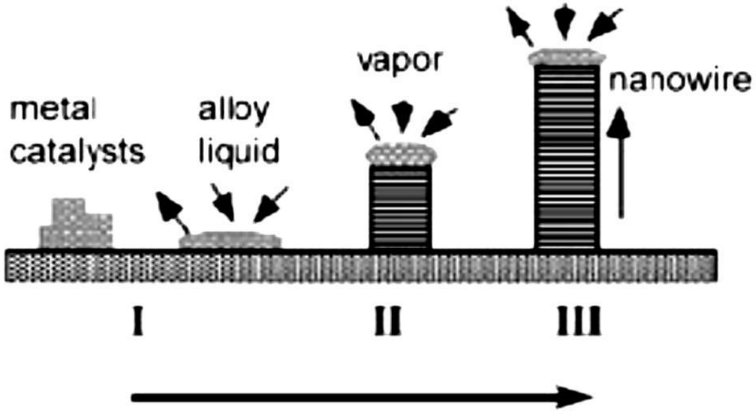
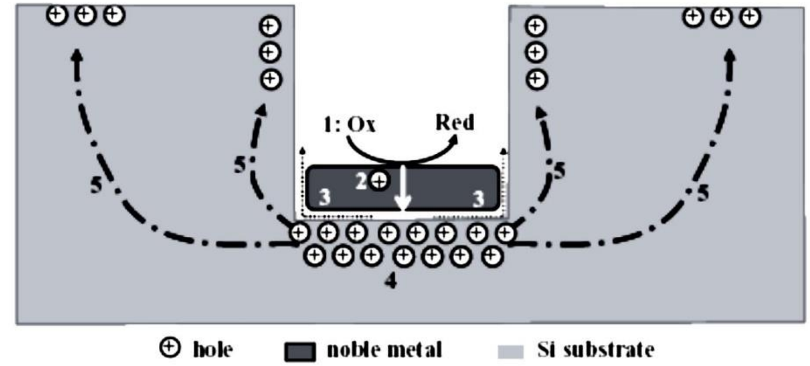
Most of optical devices on thin layer of a dielectric as a antireflective coating to reduce the reflection of light from the front surface of the cell.

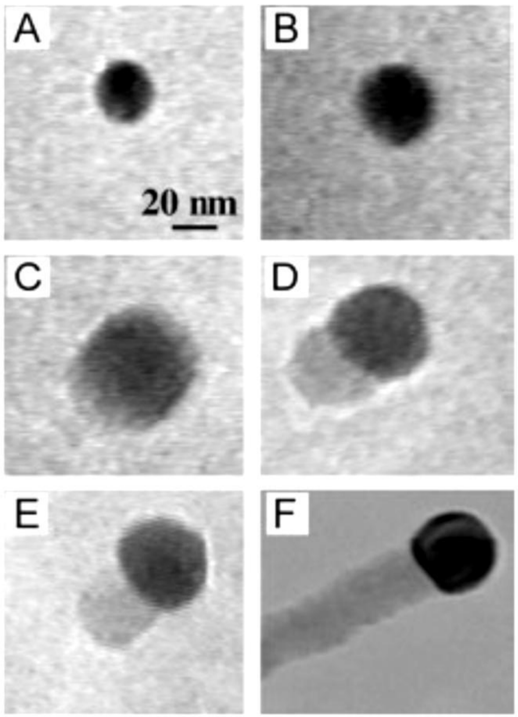
Sub-wavelength antireflective texturing techniques

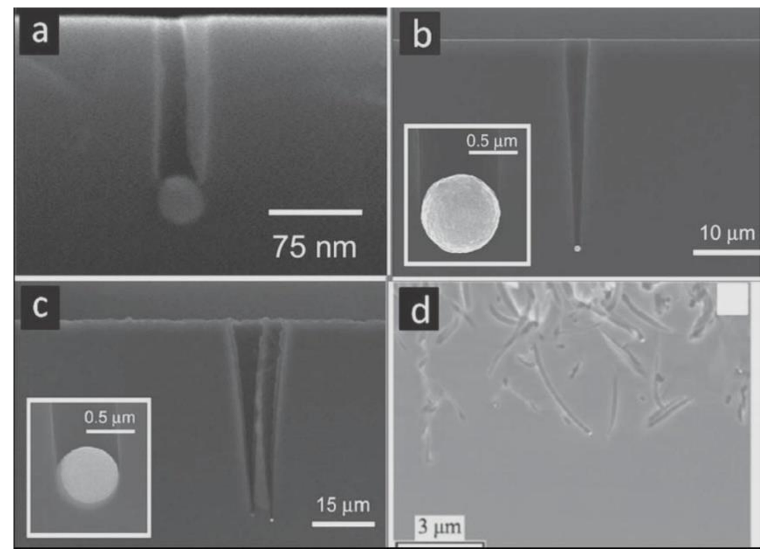


Numerous methods have been developed to fabricate Si nanostructures using top-down or bottom-up approaches



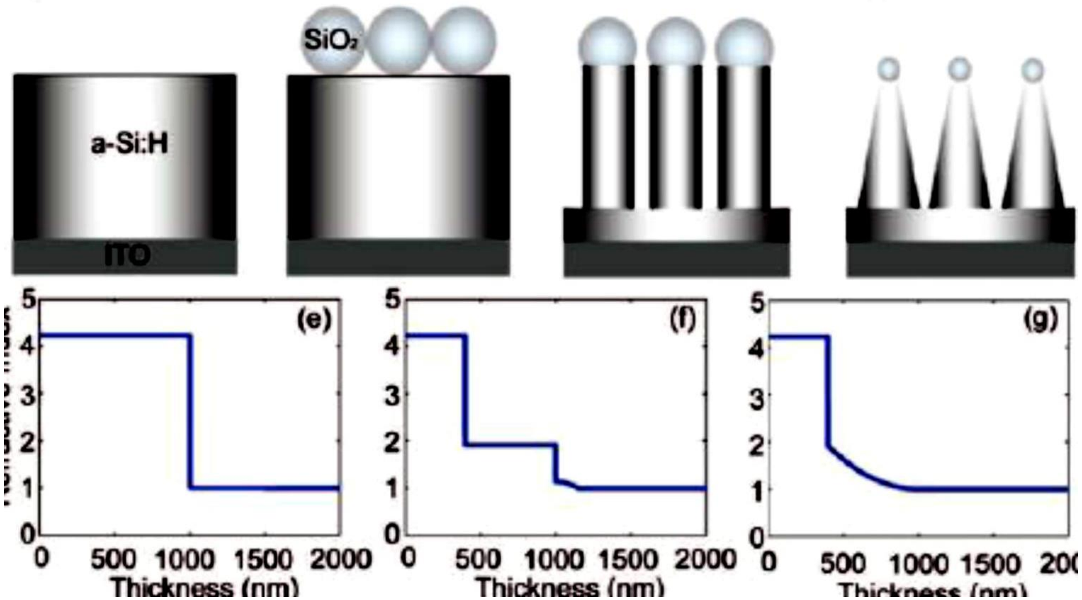


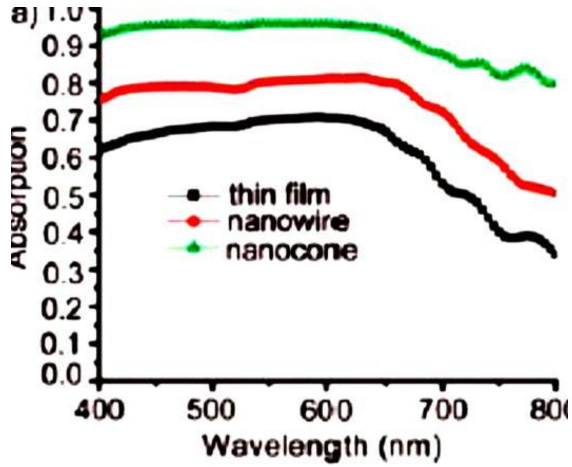




Vapor-liquid-solid (VLS) growth, reactive ion etching (RIE), electrochemical etching, or metal-assisted chemical etching, all of which aim to control various parameters of the Si structures.

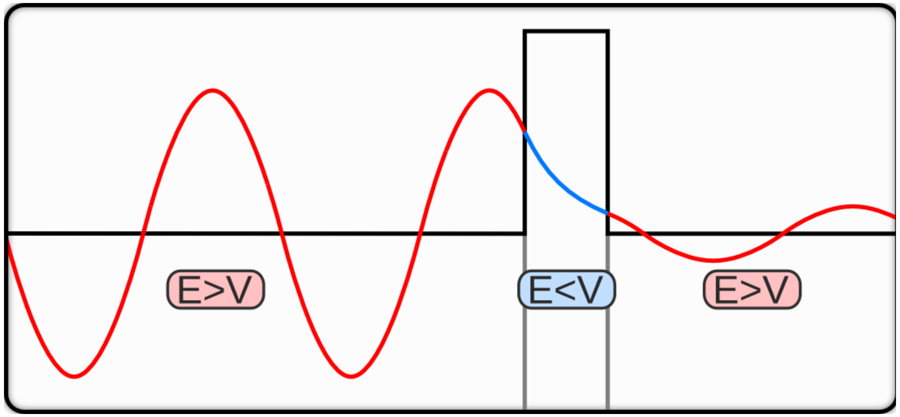
One-dimensional nanostructure optical

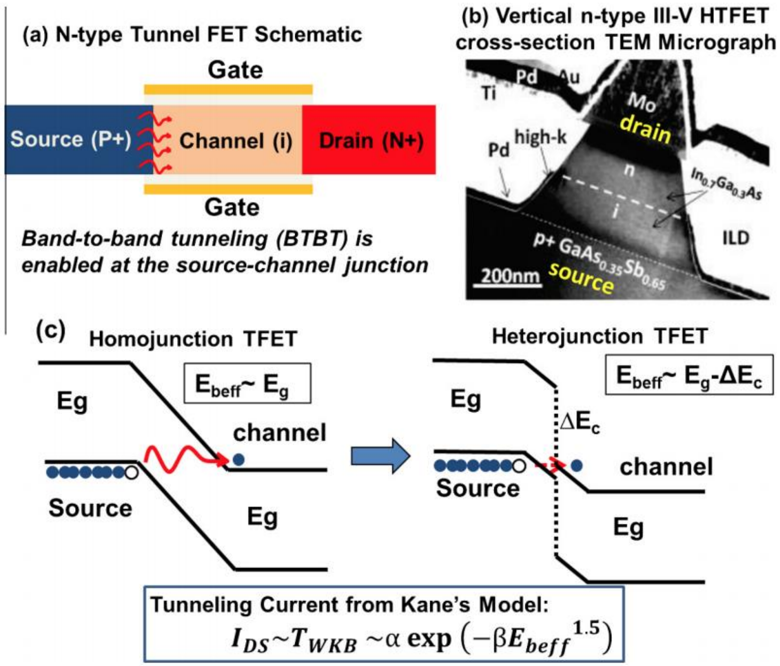


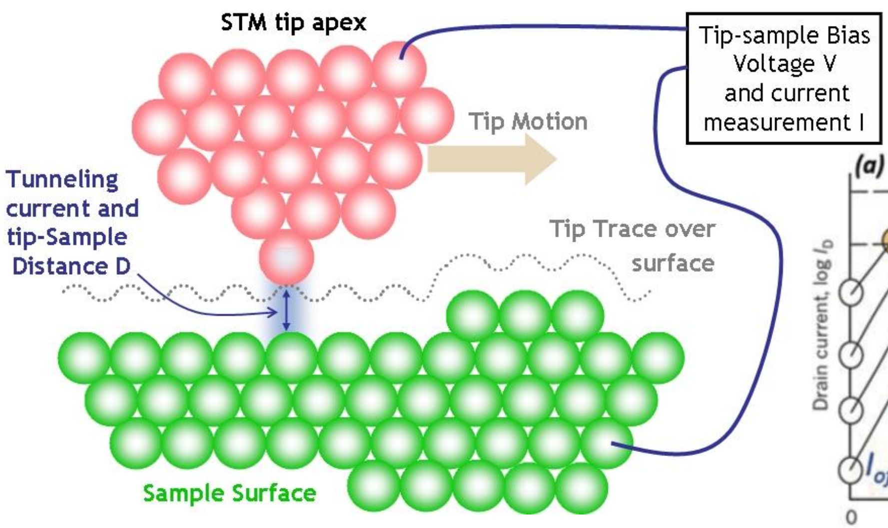


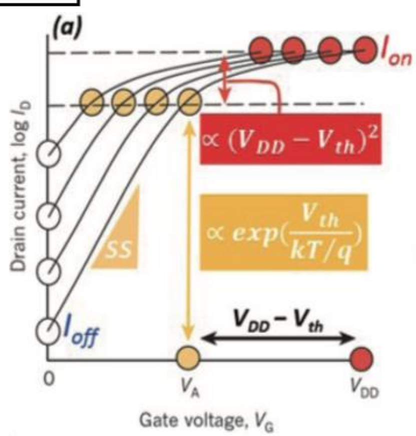
The enhancement effect is particularly strong for Si surface nanostructure arrays, which provide nearly perfect impedance matching between Si and air through a gradual reduction of the effective refractive index.

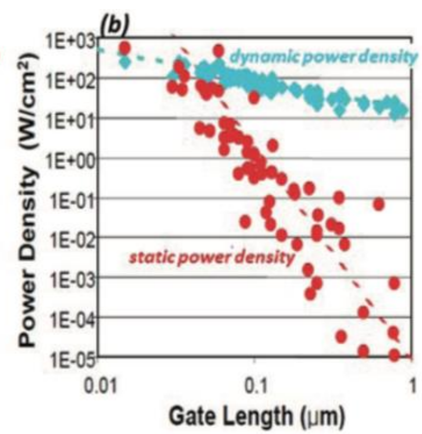
Tunneling effect











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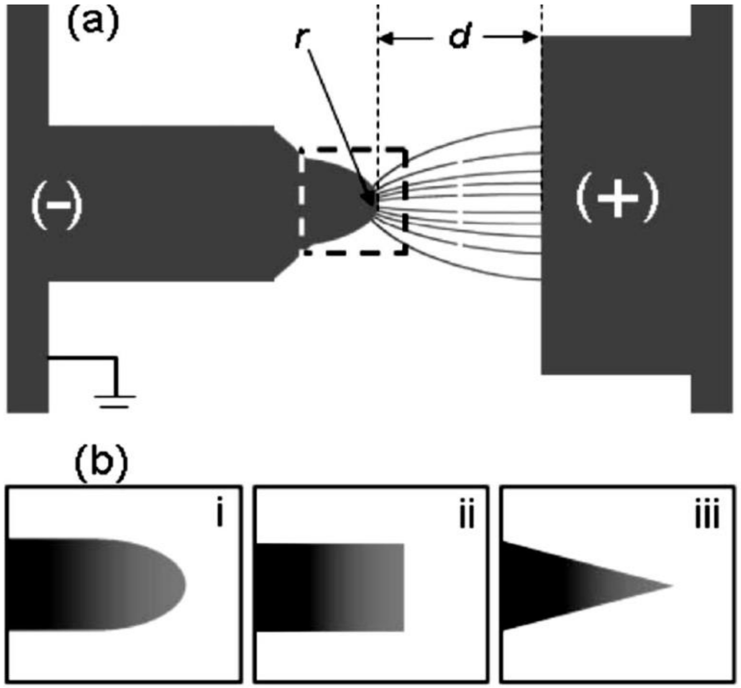
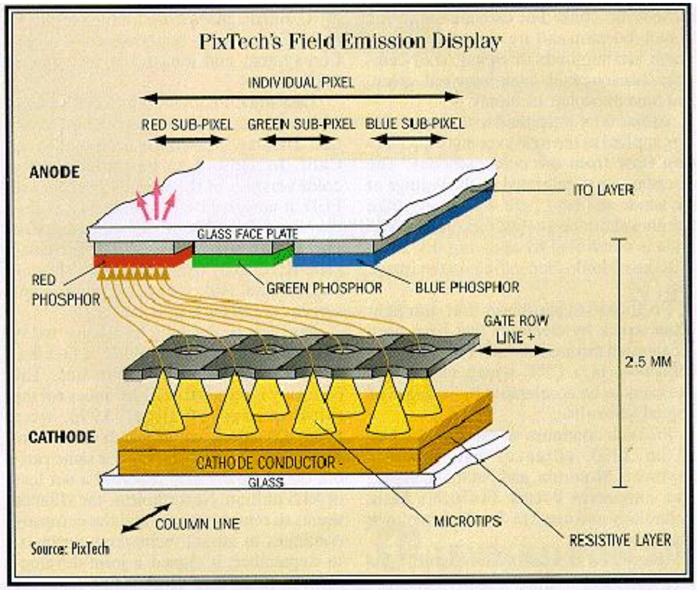
One-dimensional nanostructure field emission properties

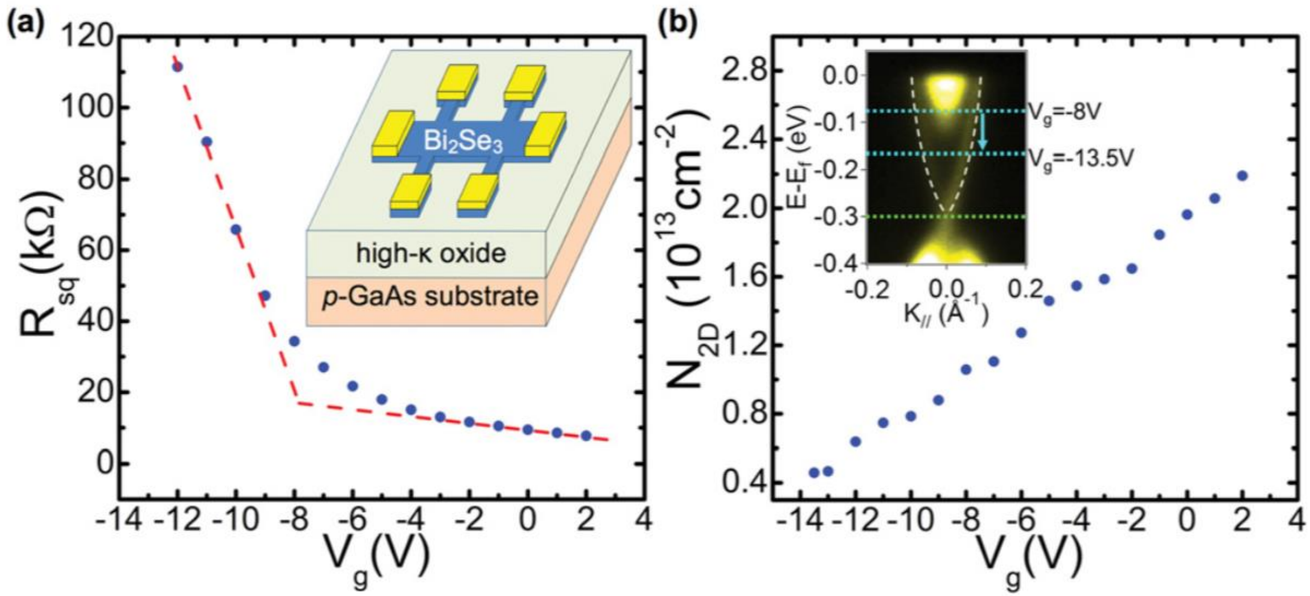


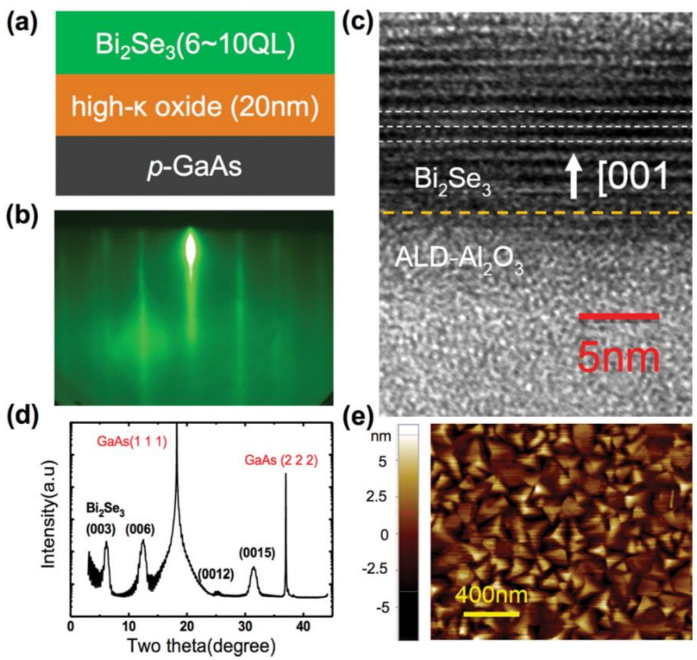


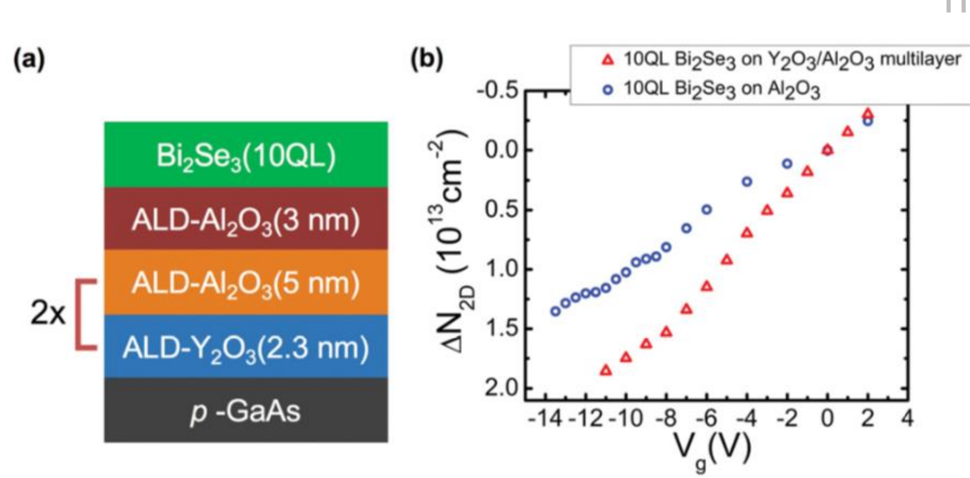
PixTech uses a Spindt-type conical cathode structure. The molybdenum cathodes are about 1.2 μm tall. There are hundreds of such cathodes for each pixel, containing red, green, and blue phosphor elements.

Field-emission, is one of the main features of nanomaterials and nanostructures, and is of great commercial interest in displays and other electronic devices.

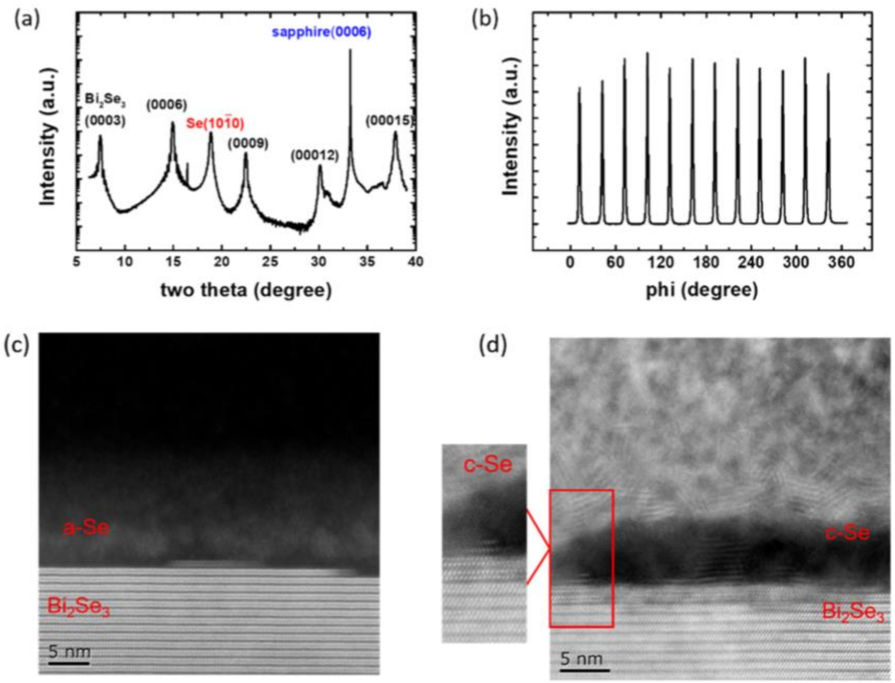
2D Materials--Device

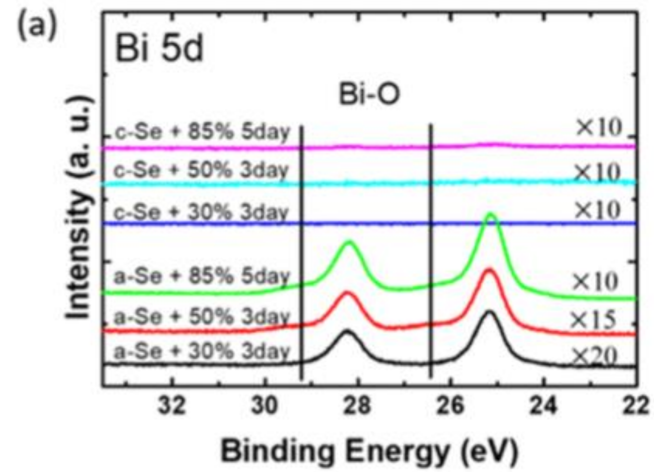


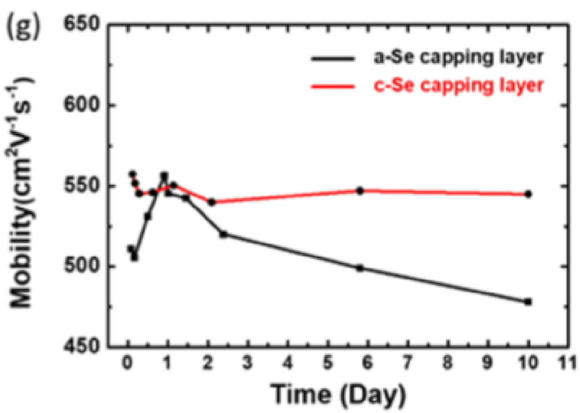


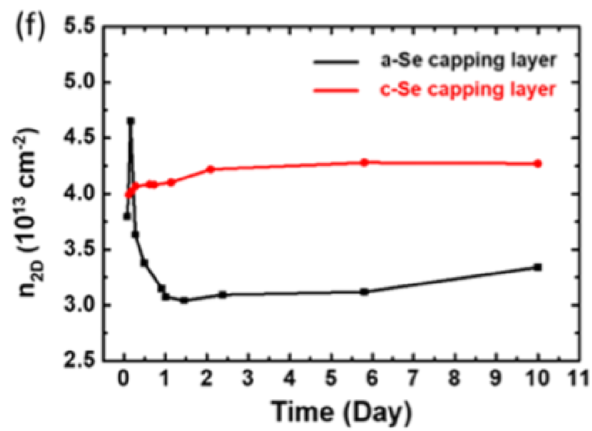


Appl. Phys. Lett. **108**, 202403 (2016)









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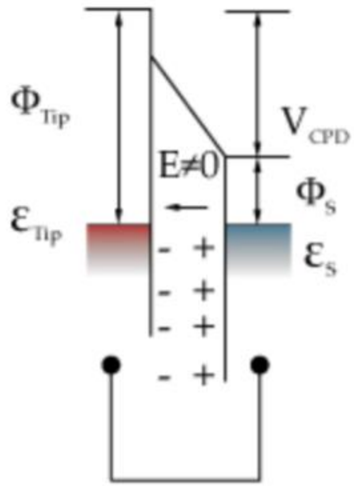
APL Mater. **6**, 066108 (2018)

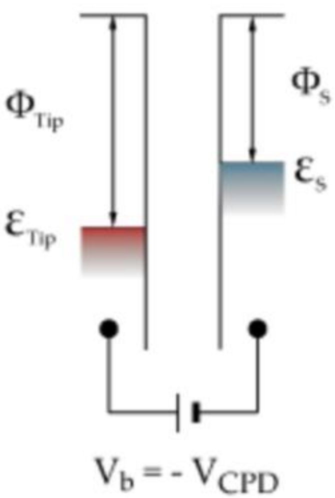
Outline

- Advantage of materials in nanometer dimensions
- Nanomaterial analysis technology

Annalysis-Workfunction

Kelvin Probe



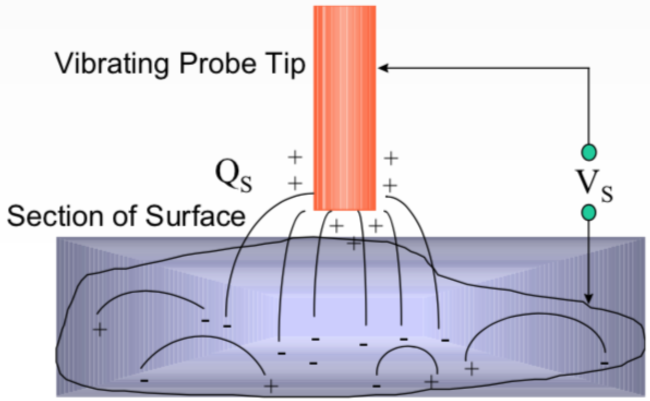


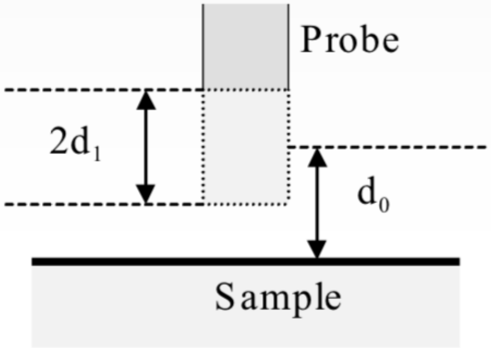
Non-contact, non-destructive vibrating *capacitor* device used to measure the *work function* of conducting materials or *surface potential* of semiconducting or insulating surfaces.

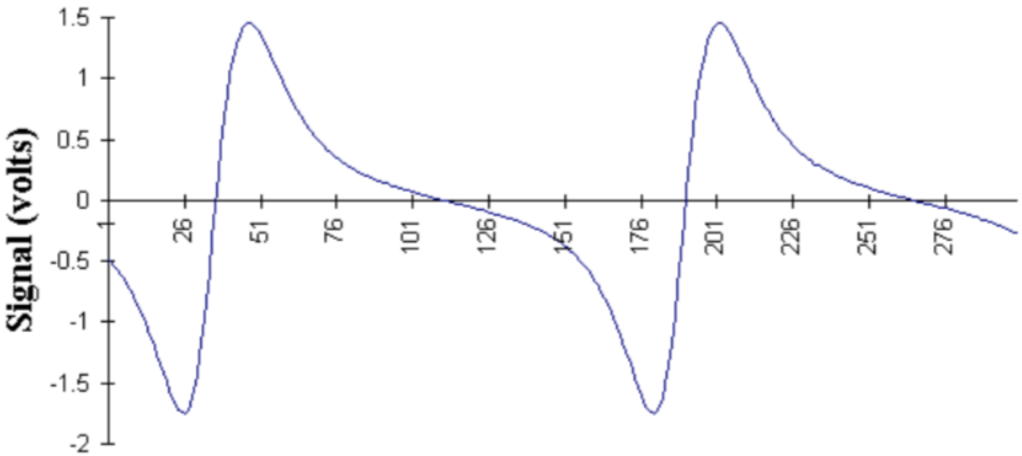
• The technique is extremely sensitive to the topmost layers of atoms or molecules, work function resolution of 1 - 3 meV.

• Unique 'off-null' measurement system also maintains average tip-sample separation to within 1 m, tip to sample tracking

Vibrate the tip, AC Signal Produced







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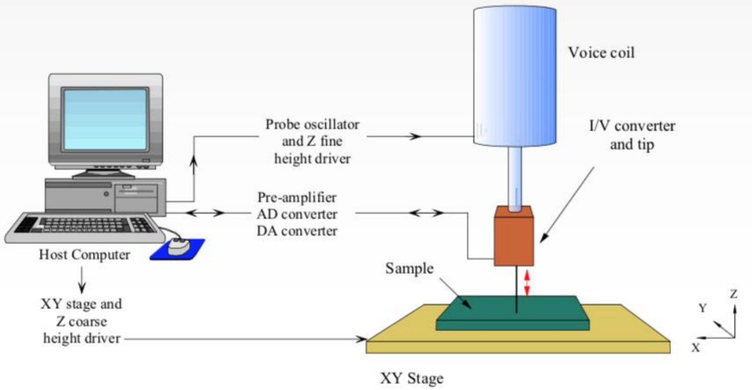
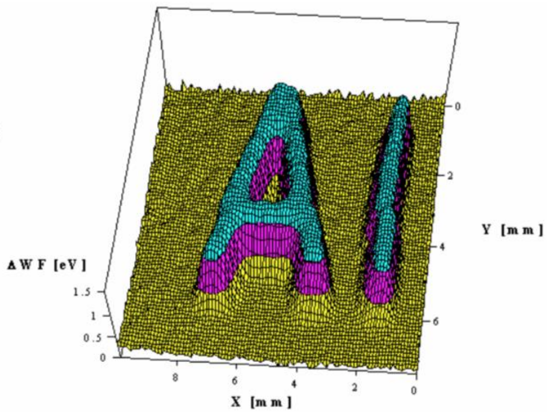
Scanning Kelvin Probe 1993



PC houses the digital oscillator (which powers the voice coil actuator), data acquisition system and motorised (x,y,z) stage controller. The signal is derived from a low-noise, high-gain current to voltage (I/V) converter mounted close to the tip.

I.D. Baikie et al Rev. Sci. Instrum. 70, 1842 (1999), Rev. Sci. Instrum 69, 3902 (1998).



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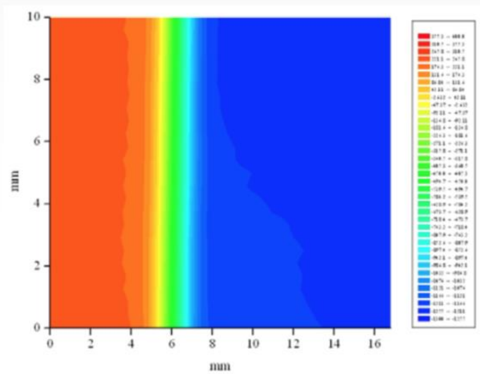
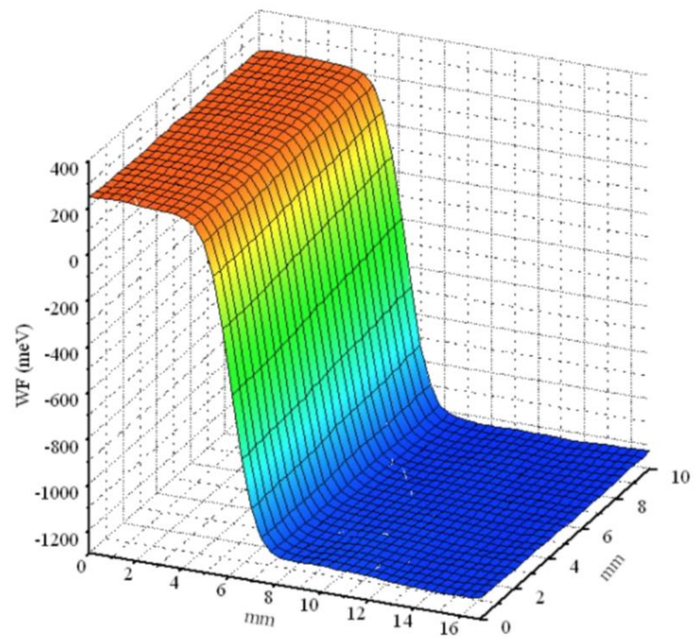
Gold / Aluminium Reference Sample

Tip Size: 2mm
Scanning Area: 10x16mm
Operator: I. Baikie





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Thanks for your attentions