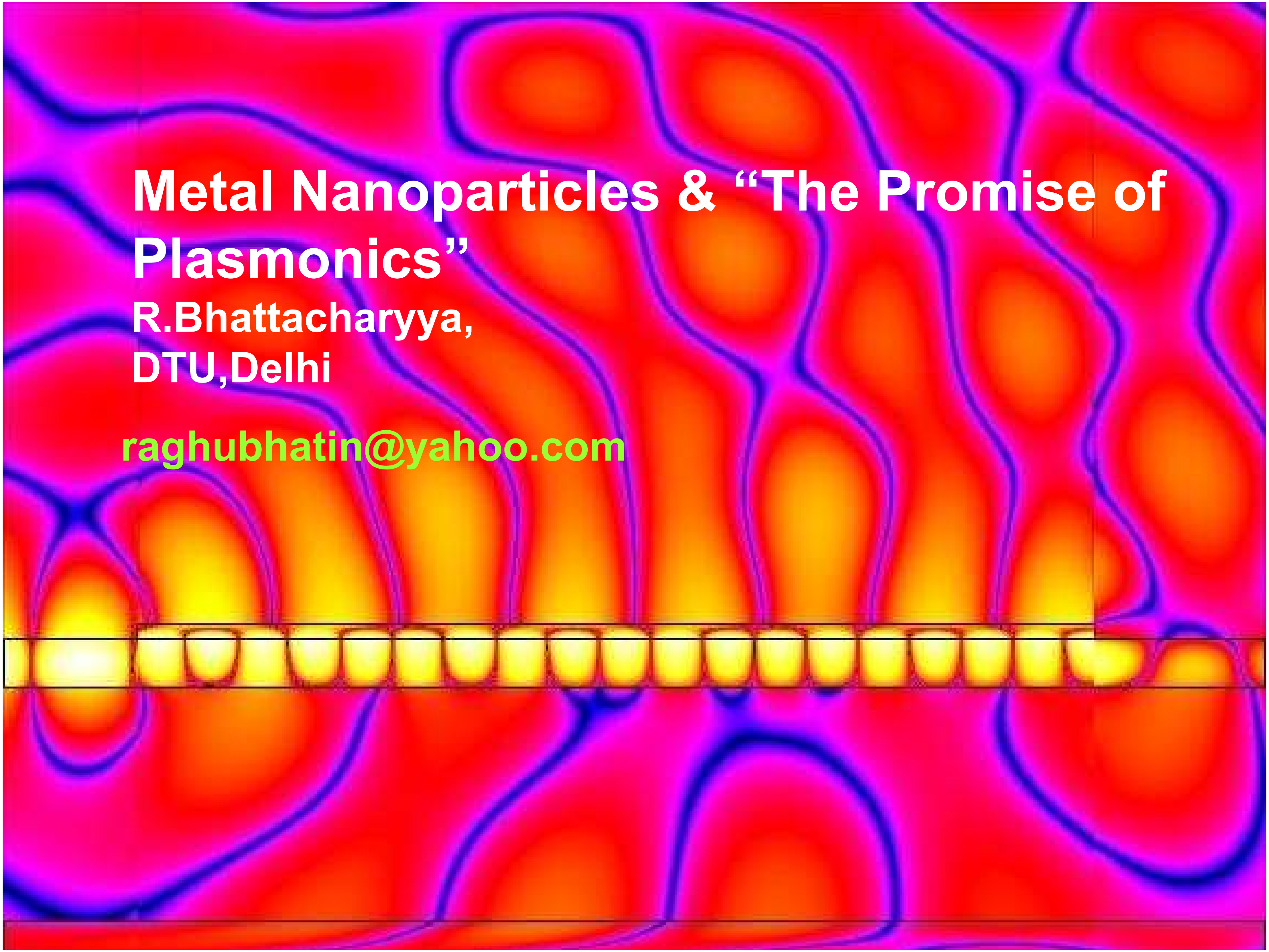


Metal Nanoparticles & “The Promise of Plasmonics”

R.Bhattacharyya,
DTU,Delhi

raghubhatin@yahoo.com

Also at

BESU Solar PV HUB

Centre of Excellence for Green Energy and Sensor Systems

Bengal Engineering and Science University , Shibpur,Howrah-7111 103

Prof.T.R.Antharaman

"Ancient Marvels of Metallurgy in India"

- **Persians considered Indian swords to be the best, and the phrase, " Jawabi hind, literally meaning " Indian answer," meant "a cut with the sword made of Indian steel."**
- **That the art of metarllurgy was highly developed in ancient India is further reaffirmed by the fact that the Gypsies, who originated in India, are highly skilled craftsmen, and it has been suggested that the art of the forge may have been transmitted to Europe through Gypsies.**
- **Steel was manufactured in ancient India, and it was being exported to China at least by the fifth century A.D. That the Arabs also imported steel from India is testified to by Al Kindi, who wrote in the ninth century.**

Nanotubes in Damascus Sword!!

- Delivering a talk on 'The contributions of elemental carbon to the development of nano science and technology' at the Indian Institute of Chemical Technology (IICT) Nobel laureate Robert F. Curl said that carbon nanotechnology was much older than carbon nano science. For the Damascus sword, Indians produced the raw material -- mined iron ore and exported it. He said that up to the middle of 18th century, the steel swords depended on this particular material and when the mines in India stopped, "they lost the technology."
- The Damascus sword when subjected to scrutiny by an electron microscope in 2006 had shown to contain large amounts of nanotubes.

(source: Nanotechnology not new to India , says Nobel laureate - the hindu.com)

- **Materials researcher Peter Paufler and his colleagues at Dresden University, Germany, have taken electron-microscope pictures of the swords and found that wootz has a microstructure of nano-metre-sized tubes, just like carbon nanotubes used in modern technologies for their lightweight strength.**

  The tubes were only revealed after a piece of sword was dissolved in hydrochloric acid to remove another microstructure in the swords: nanowires of the mineral cementite.

  Wootz's ingredients include iron ores from India that contain transition-metal impurities. It was thought that these impurities helped cementite wires to form, but it wasn't clear how. **Paufler thinks carbon nanotubes could be the missing piece of the puzzle**

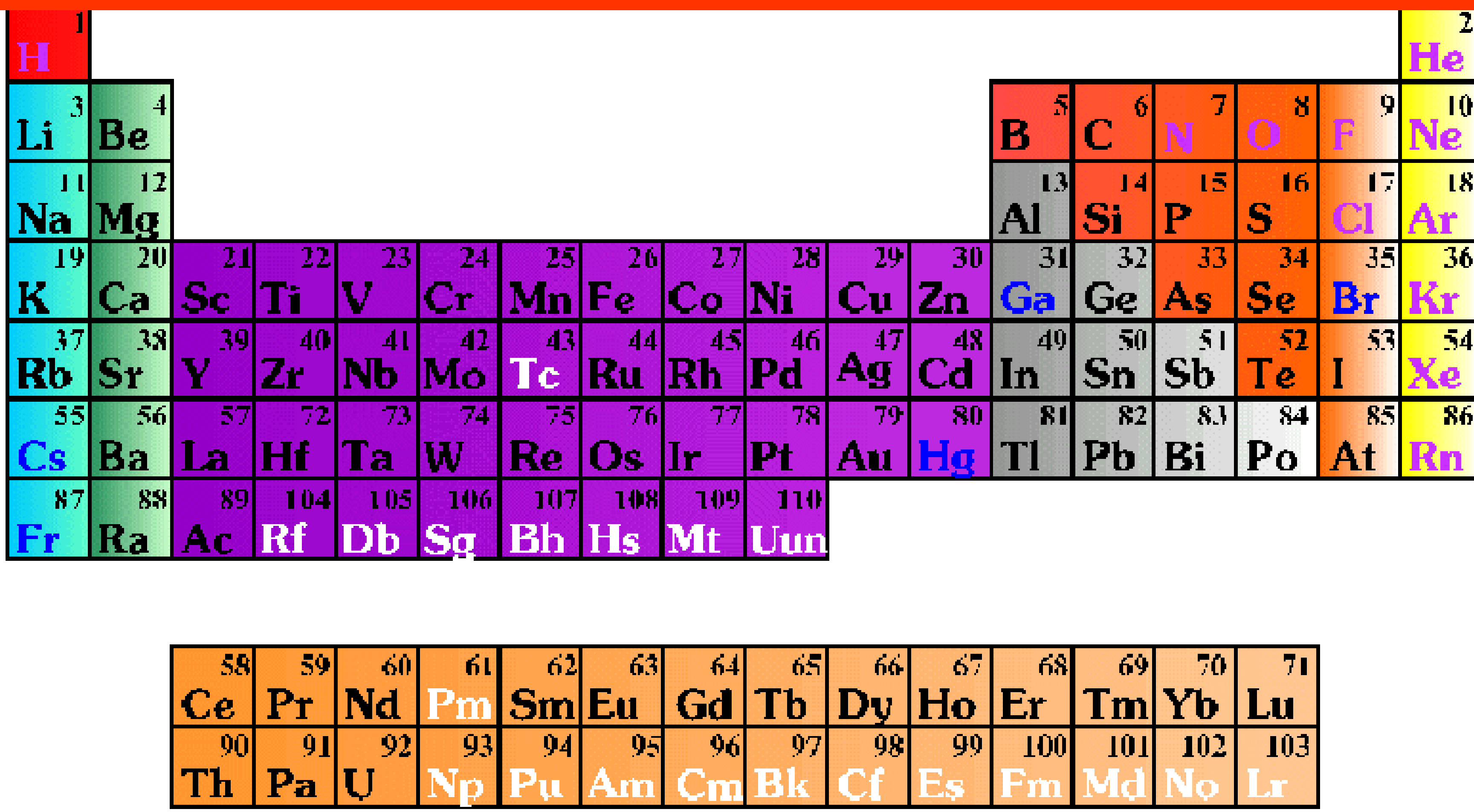
V33628 From the Orient Once Came the Finest Blades—a Sword Maker of Damascus, Syria.

Mrs. Charlotte Manning says: “The superior quality of Hindu steel has long been known, and it is worthy of record .

- **Mrs. Charlotte Manning says: "The superior quality of Hindu steel has long been known, and it is worthy of record that the celebrated Damascus blades, have been traced to the workshops of Western India."**
- **She adds: "Steel manufactured in Kutch enjoys at the present day a reputation not inferior to that of the steel made in Glasgow and Sheffield." "It is probable that ancient India possessed iron more than sufficient for her wants, and that the Phoenicians fetched iron with other merchandise from India."**

(source: Hindu Superiority - By Har Bilas Sarda p. 400-404)

About 2/3 of the Chemical Elements are Metals in periodic table .However , People in Industry think it is Si all over !



Si

14

Silicon makes up 25.7% of the earth's crust by weight, and is the second most abundant element. Because of wide use of silicon in integrated circuits, the basis of most computers, a great deal of modern technology depends on it

Silicon
28.085

PHOTONIC MATERIALS

Teaching silicon new tricks

Atomic-scale engineering turns silicon into a material in which electronics and photonics can be merged, thus leading to microphotonic integrated circuits.

ALBERT POLMAN is at the FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ, Amsterdam, The Netherlands. e-mail:polman@amolf.nl

material for photonic applications because it is an inefficient light emitter. But in a modern optical communications network, in which data is encoded and transported in streams of coloured bits of light, light must

Teaching silicon new tricks

BAHRAM JALALI

is at the University of California, Los Angeles, Department of Electrical Engineering, Los Angeles, California 90095-1594, USA.
e-mail: Jalali@ucla.edu

Arguably the most important element for the electronics industry, silicon is now being given a new lease of life in the world of photonics.

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) R1169–R1196 PII: S0953-8984(03)39709-7

TOPICAL REVIEW

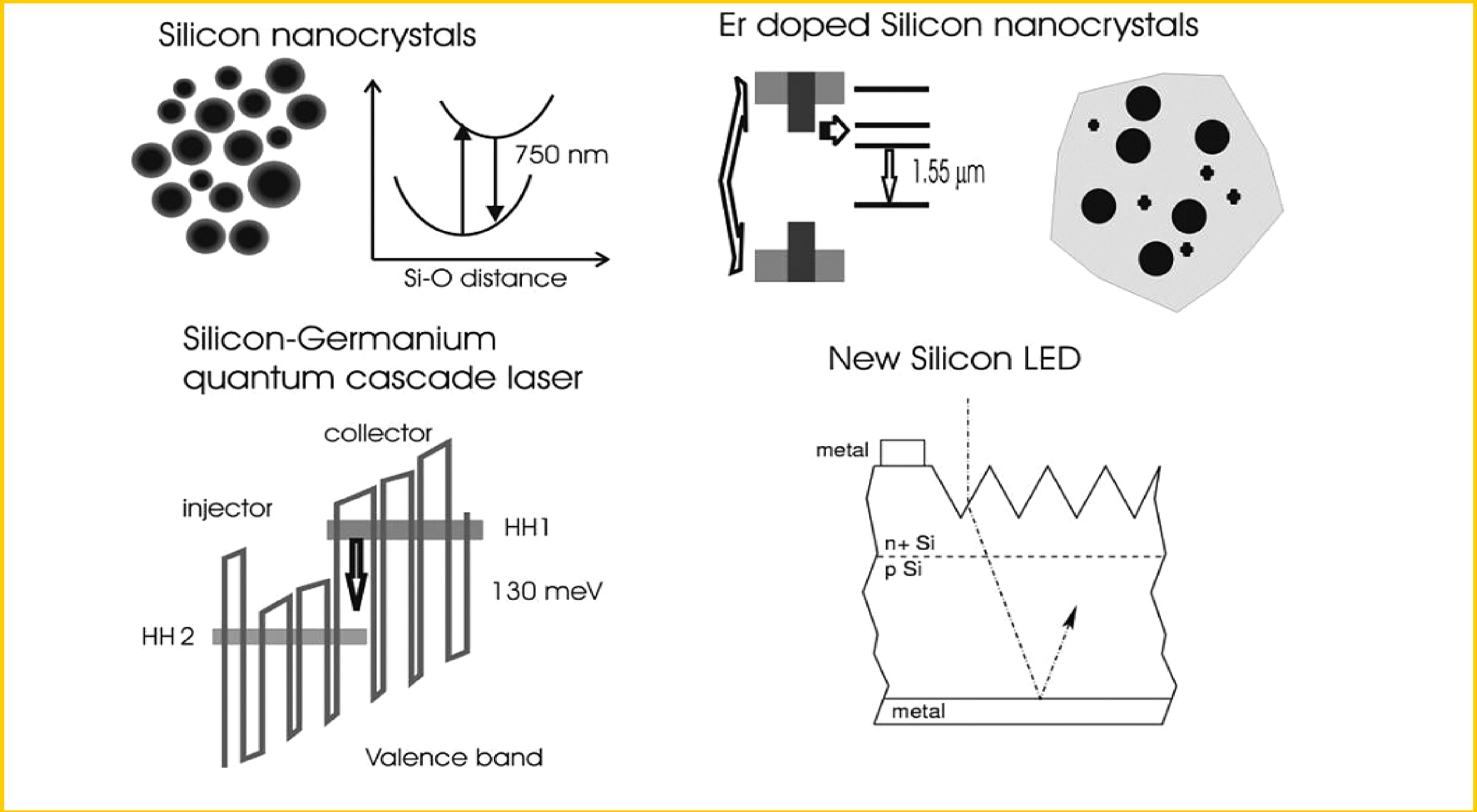
Will silicon be the photonic material of the third millenium?*

L Pavesi

INFM and Dipartimento di Fisica, Universita' di Trento, Via Sommarive 14, 38050-Povo Trento, Italy

E-mail: pavesi@science.unitn.it

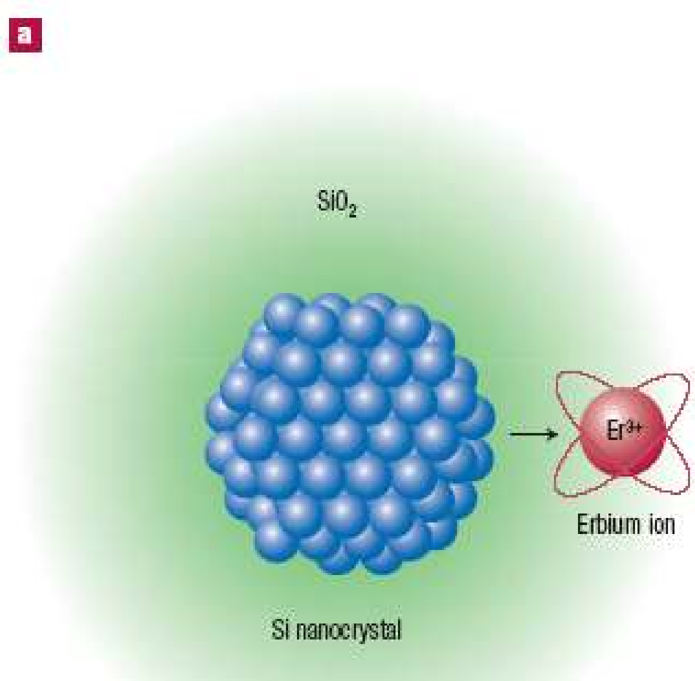
Nano silicon for LED

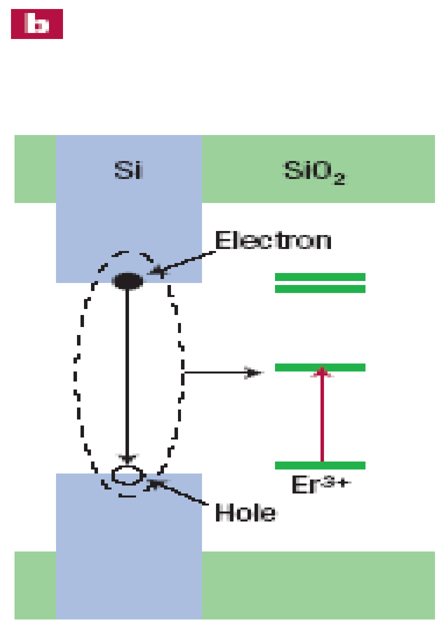


Silicon nanocrystals as an antenna for erbium.

a,The wavefunction of an electron–hole pair (‘exciton’) in a silicon nanocrystal can couple to a nearby Er ion in the silica matrix.

b,Energy bands are shown for silicon nanocrystals and erbium ions embedded in a SiO2 matrix.An optically excited electron–hole pair in the nanocrystal can recombine by transferring energy to an Er ion. The latter is then excited from the ground state to the first excited state as indicated by the red arrow. Here atomic-scale engineering in combination with nanoscale energy transfer can lead to the development of a new class of miniature optical amplifiers



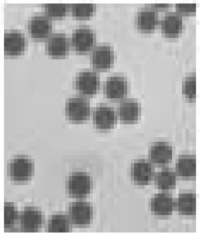


- **World record for silicon light-emission**
- Nov 5, 2002
- **Silicon is ideal for electronic applications, but its inability to emit light has limited its potential for optical processing.**
- **Now researchers at STMicroelectronics in Italy have increased silicon's light-emitting efficiency by a factor of a hundred, making silicon competitive with conventional light-emitting semiconductors such as gallium arsenide.**
- **This advance, achieved by adding rare-earth metals to silicon, will allow optical and electrical functions** to be combined on a single silicon chip.

- **The ability to combine optical and electronic processing on the same chip presents enormous opportunities for ST to be the first to develop many new types of semiconductor products,”**
- says GianGuido Rizzotto, director of Corporate Technology R&D. Rizzotto adds that the company should soon be commercialising its technology as it is compatible with existing production methods and equipment.

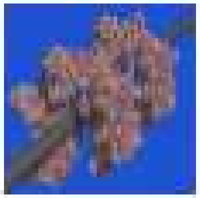
What is Nanotechnology?

Understanding — Imaging, Measuring



Control — Modeling, Manipulating

1 nm  100 nm



Unique Phenomena — **Novel applications**

Nanotechnology is the purposeful engineering of matter at scales between 1-100 nm to achieve size-dependent properties and functions.

Nanotechnology is not about simply shrinking the dimensions to 1- 100 nm level nor is the routine top-down miniaturization as we do in silicon CMOS fabrication. If that is the case, we do not need new terminologies and funding to continue the old stuff.

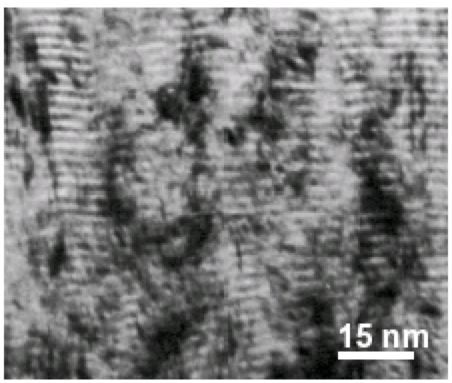
Instead, it is about exploring novel properties that arise because of the nanoscale - properties that differ from their bulk counterparts.

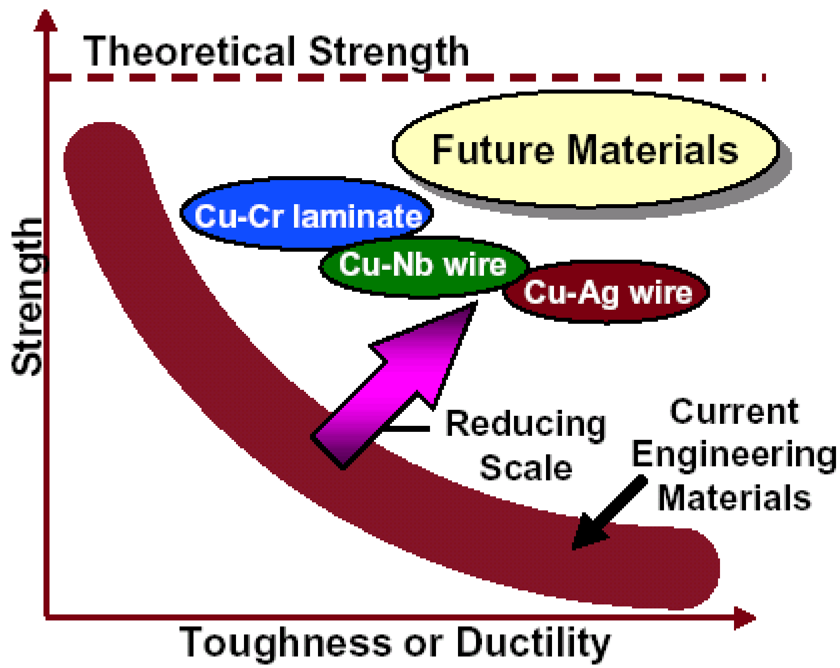
Once we identify such properties, the next big question is: What useful things can we do with that?

There are several areas in which researchers have been able to answer positively to this question, leading to the evolution of the field,PLASMONICS being one such.

“New” Materials from “Old” Materials

Cu/Cr Nanolayers





- The changes in the properties of nanoparticles are driven mainly by three factors:

  1. The increase in the surface to volume ratio:

     -Atoms and molecules on surface and interface have different environment, hence exhibit different properties

     -As size reduced, relative number of atoms on surface increases inversely as particle size and appreciable in nm range.

  2. Quantum size effect:

     -When the size of the particle is comparable to phase coherent length of electrons, the energy spectrum is quantised into discrete levels with a energy spacing E_f/N.

  3. Lattice contraction:

     -At very small sizes there are structural phase changes and decrease in lattice parameters

A fundamental limitation is the phase coherent length,the distance over which an electron retains its phase information

Factors Affected by Size Reduction: Bulk vs. Nano

Melting Points
Optical properties
Colors
Surface Reactivity
Magnetic properties
Conductivity
Specific heats

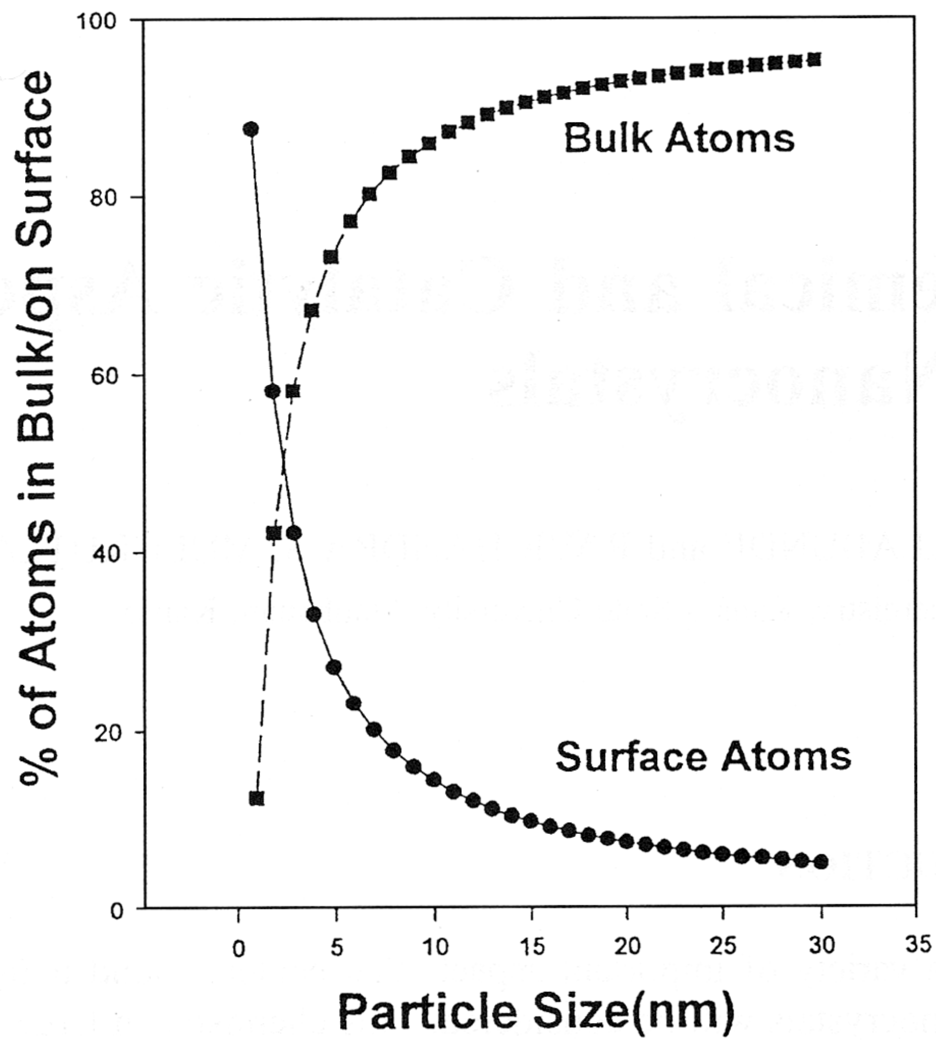
Surface to Bulk Atom Ratio

- Spherical iron nanocrystals

- J. Phys. Chem. 1996, Vol. 100, p. 12142

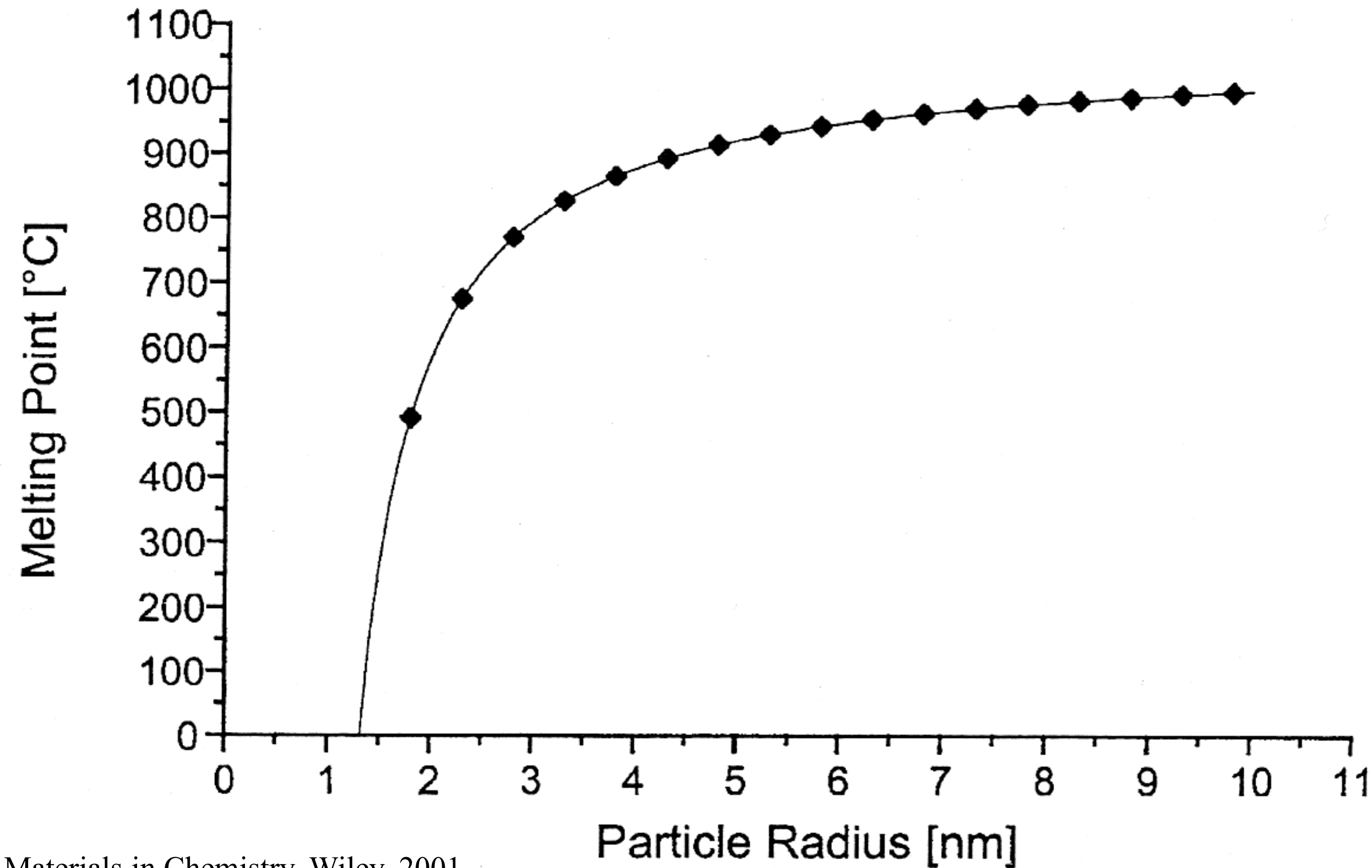
Introduction to Nanotechnology:

M. Meyyappan



Melting Point of Gold Particles

The melting point decreases dramatically as the particle size gets below 5 nm



Source: Nanoscale Materials in Chemistry, Wiley, 2001

Melting Points

Property is a consequence of the averaged coordination number of the participating atoms

Typically, for bulk materials, surface atoms form a negligible part of the total number of atoms

The smaller a particle becomes, the more the proportion of surface atoms increases

Full shell clusters are constructed by successively packing layers – or shells – of metal atoms around a single metal atom

The number of atoms per shell is

(Sum of atoms + $10n^2$ + 2)

where n = number of shell

Melting Point Dependence on Particle Size

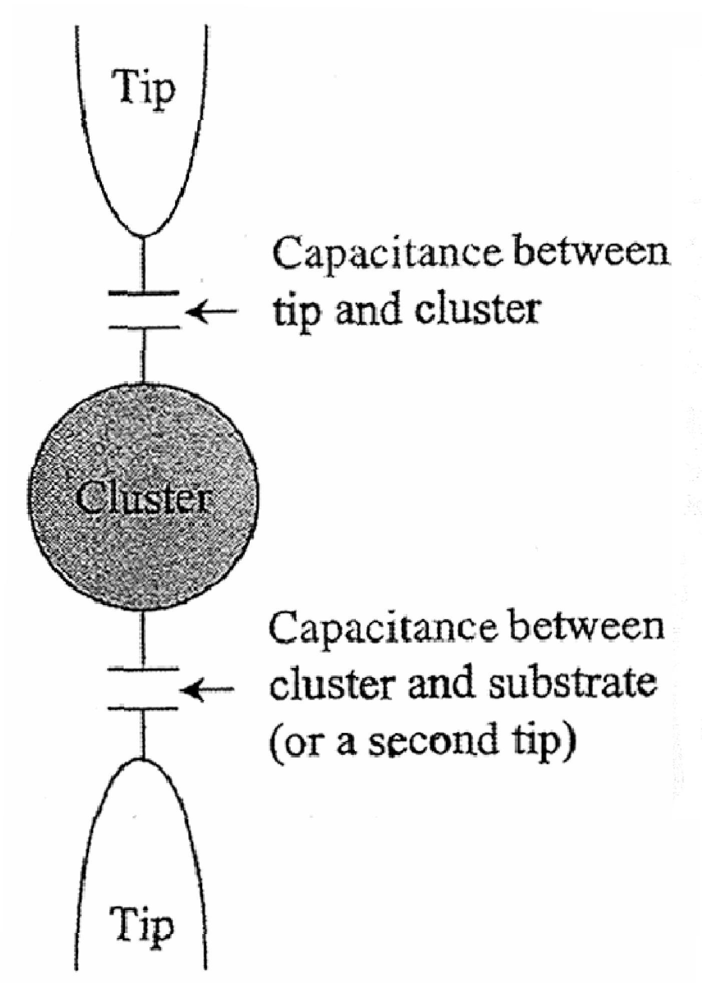
- Lowering of the melting point is proportional to 1/r

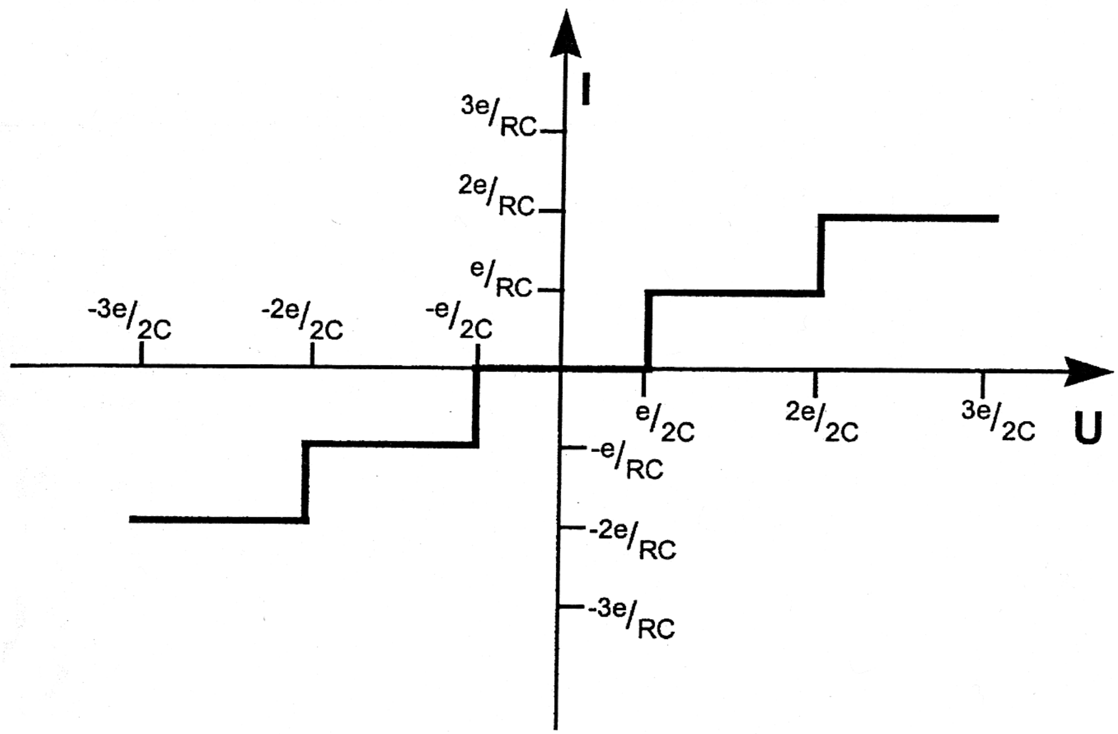
- $\Delta\theta$ can be as large as couple of hundred degrees when the particle size gets below 10 nm!

- Most of the time, σ the surface tension coefficient is unknown; by measuring the melting point as a function of radius, σ can be estimated.

- Note: For nanoparticles embedded in a matrix, melting point may be lower or higher, depending on the strength of the interaction between the particle and matrix.

I-V of a Single Nanoparticle





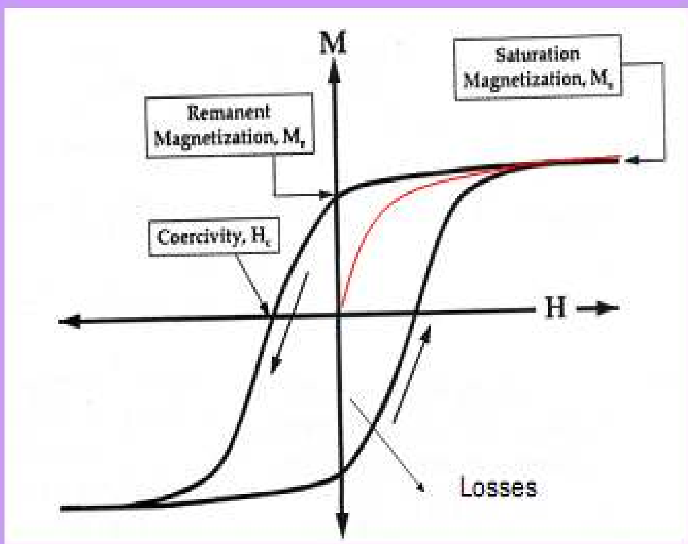
Source: Nanoscale Materials in Chemistry, Wiley, 2001

Nanomagnetism

Magnetism in nanostructured materials

A. Sundaresan

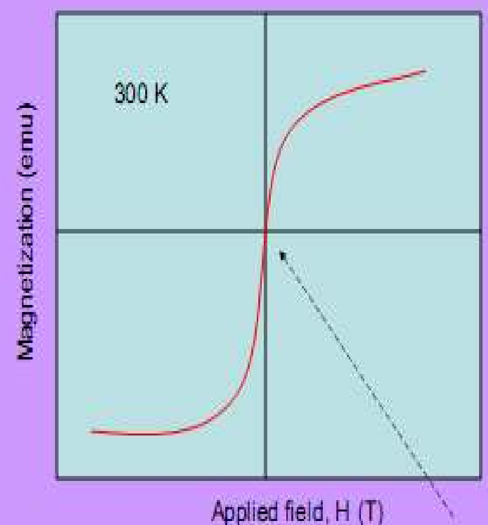
Parameters from Hysteresis loop



Parameters are **not solely intrinsic** but dependent on **grain size**, **domain state**, stresses and temperature

Superparamagnetism

in nanoparticles

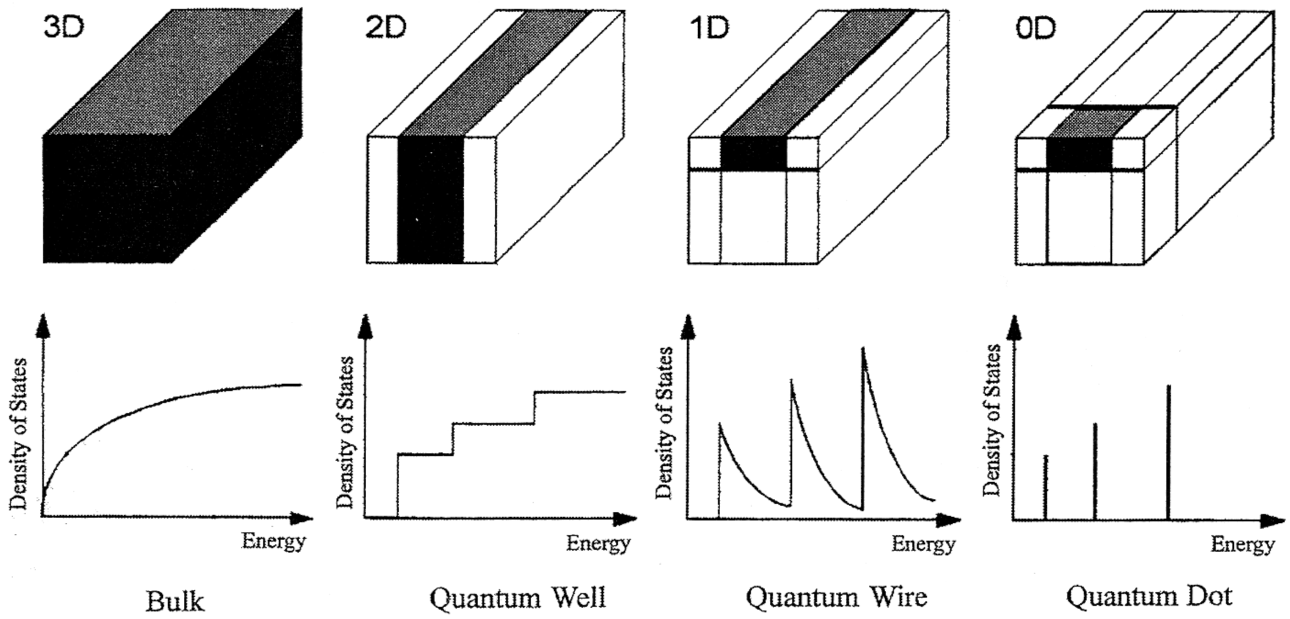


Applications:

- Magnetic Inks
- Magnetic separation
- Vacuum sealing
- Magnetic marking
- Magnetic refrigeration
- MRI

No remanent magnetism upon field removal

3D → 2D → 1D → 0D

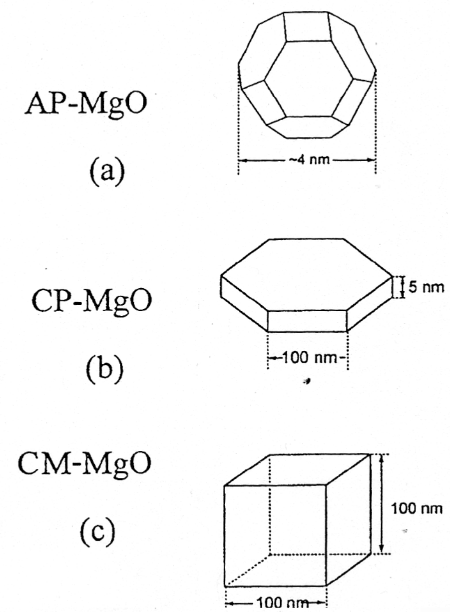


Source: Nanoscale Materials in Chemistry, Wiley, 2001

- If a bulk metal is made thinner and thinner, until the electrons can move only in two dimensions (instead of 3), then it is "2D quantum confinement."
- Next level is 'quantum wire
- Ultimately 'quantum dot'

Nanomaterials in Catalysis

- Surface chemistry is important in catalysis. Nanostructured materials have some advantages:
  - Huge surface area, high proportion of atoms on the surface
  - Enhanced intrinsic chemical activity as size gets smaller which is likely due to changes in crystal shape
  - Ex: When the shape changes from cubic to polyhedral, the number of edges and corner sites goes up significantly
  - As crystal size gets smaller, anion/cation vacancies can increase, thus affecting surface energy; also surface atoms can be distorted in their bonding patterns
  - Enhanced solubility, sintering at lower T, more adsorptive capacity



Models of (a) nanocrystalline (AP-MgO); (b) microcrystalline (CP-MgO); (c) normal commercially available (CM-MgO) magnesium oxide crystals. Reprinted with permission from *Clusters & Nanostructure Interfaces*, **1999**, p. 578, World Scientific Publishing Co Pte Ltd.[1b]

In the range 2-15 nanometer performance barrier can be overcome because

*

Quantum Mechanics begins to dictate

*Stable nanocomposites of organic and inorganic material

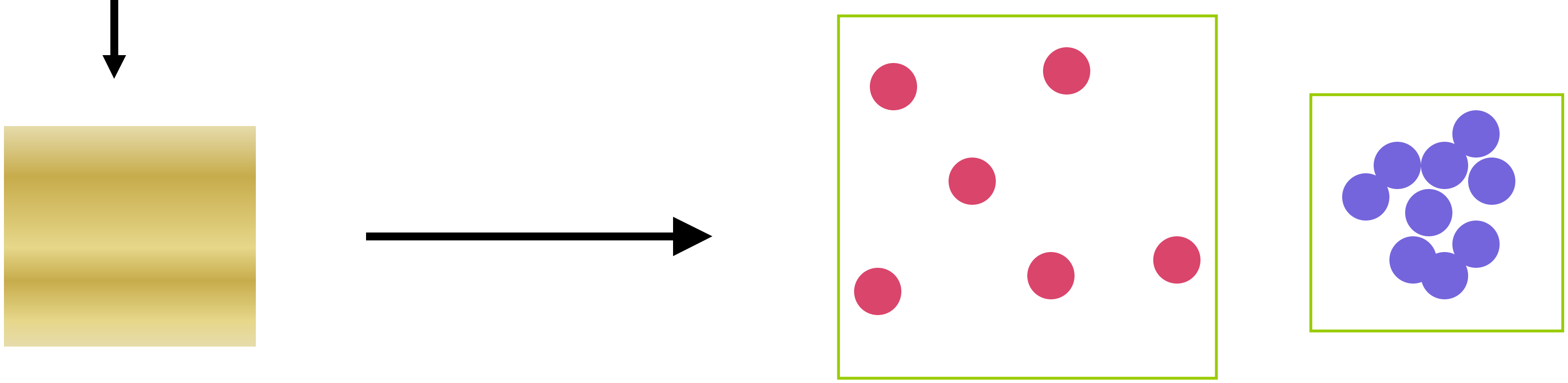
*integration of nano particles with biological components becomes feasible for the first time

*In the nano limit ,materials behave non-linearly,i.e. for a small change in input ,a large change in output is observed. This results in high Efficiency- Dr.R.Bhargava

Matter has Unusual Properties on the nm Scale

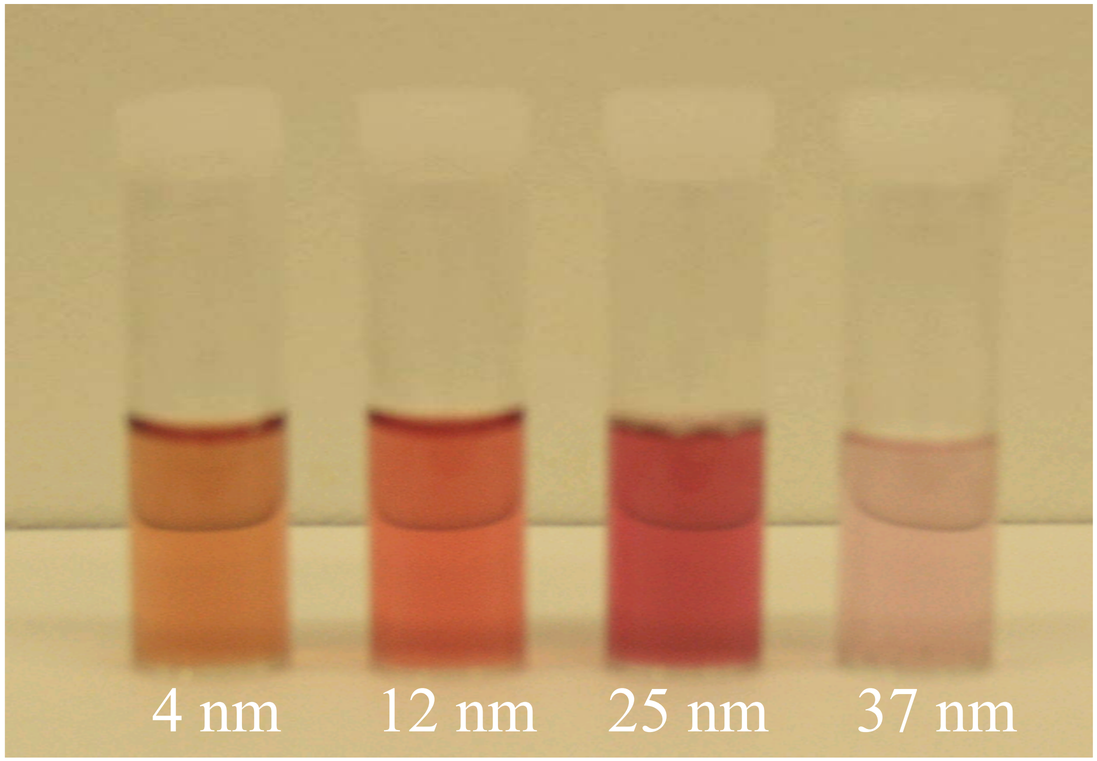
If you take gold and make particles about 10 nm in diameter, it looks wine-red or blue-gray, depending on how close the

ruby-red stained glass from gold nanoparticles



Gold Nanospheres with Increasing Diameter Size

Bulk Au



- **Optical properties of metal nanoparticles depend on their shape and size**
- **Particle functionalization can be done on the surface**
- **Visible optical changes occur**

Size dependence

Mulvaney, MRS Bulletin 26, 1009 (1996)

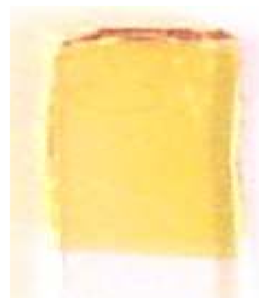
- The changes gold–blue–purple–red are largely geometric ones that can be explained with Mie theory, which describes light-scattering by a sphere.
- When the metal nanoparticle is larger than the ~30 nm, the electrons oscillating with the light is not perfectly in phase. Some electrons get behind; this phenomenon is called retardation effect or phase retardation.
- The subsequent changes, reddish - brown to orange to colorless, are due to quantum size effects.

Silver Nanoparticles with Increasing Aspect Ratio

Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80

Nanoparticles in solution

Au colloids in water
(M. Faraday ~1856)



glass containing
Ag clusters

Au colloids in water

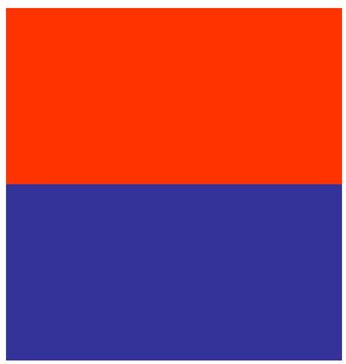
Au shell colloids in water
(larger, also scattering)

Origin of the Properties

Bulk Metal

Unoccupied states

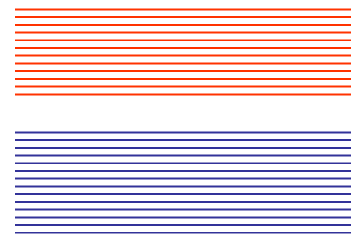
occupied states



Close lying bands

Decreasing the size…

Nanoscale metal



Separation between the valence and conduction bands

Unbound electrons have motion that is <u>not</u> confined

Electron motion becomes confined, and <u>quantization</u> sets in

Particle size < mean free path of electrons

Band Structure in Metals

E_F (Fermi Level)

E_F depends on the density

Density $\rho = N/V$ (where N = Number of electrons, V = volume)

Assuming all energy levels have the same number of electrons,

$\delta = E_F / N$

Since $N \propto V$

Therefore, $\delta \propto 1/V$

$V = L^3$ (where L = side length of the particle)

Hence,

$\delta \propto \mathbf{E_F/L^3}$

As the side length of the particle decreases the energy level spacing increase

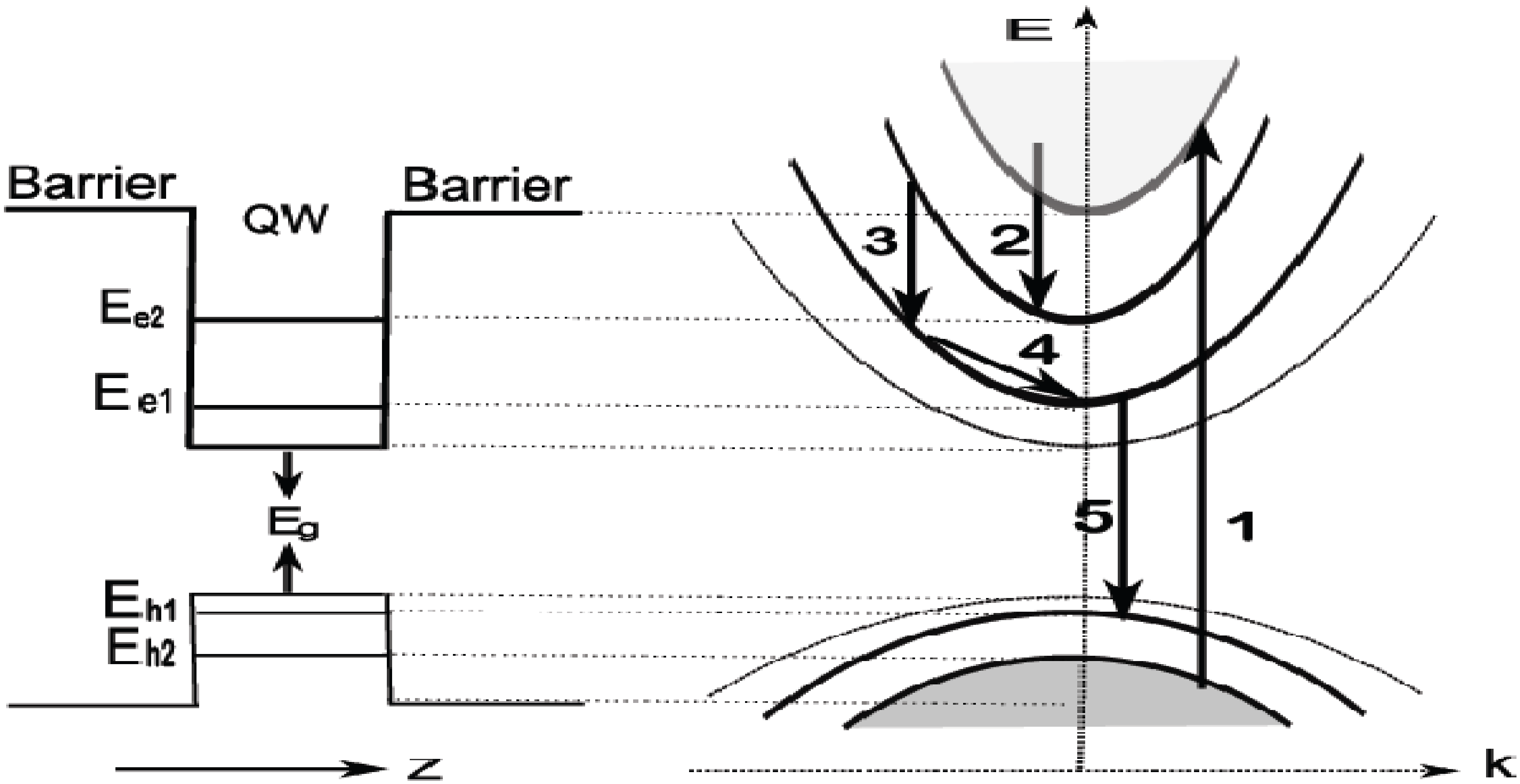
Quantum confinement

In any material, substantial variation of fundamental electrical and optical properties with reduced size will be observed when the energy spacing between the electronic levels exceeds the thermal energy (kT).

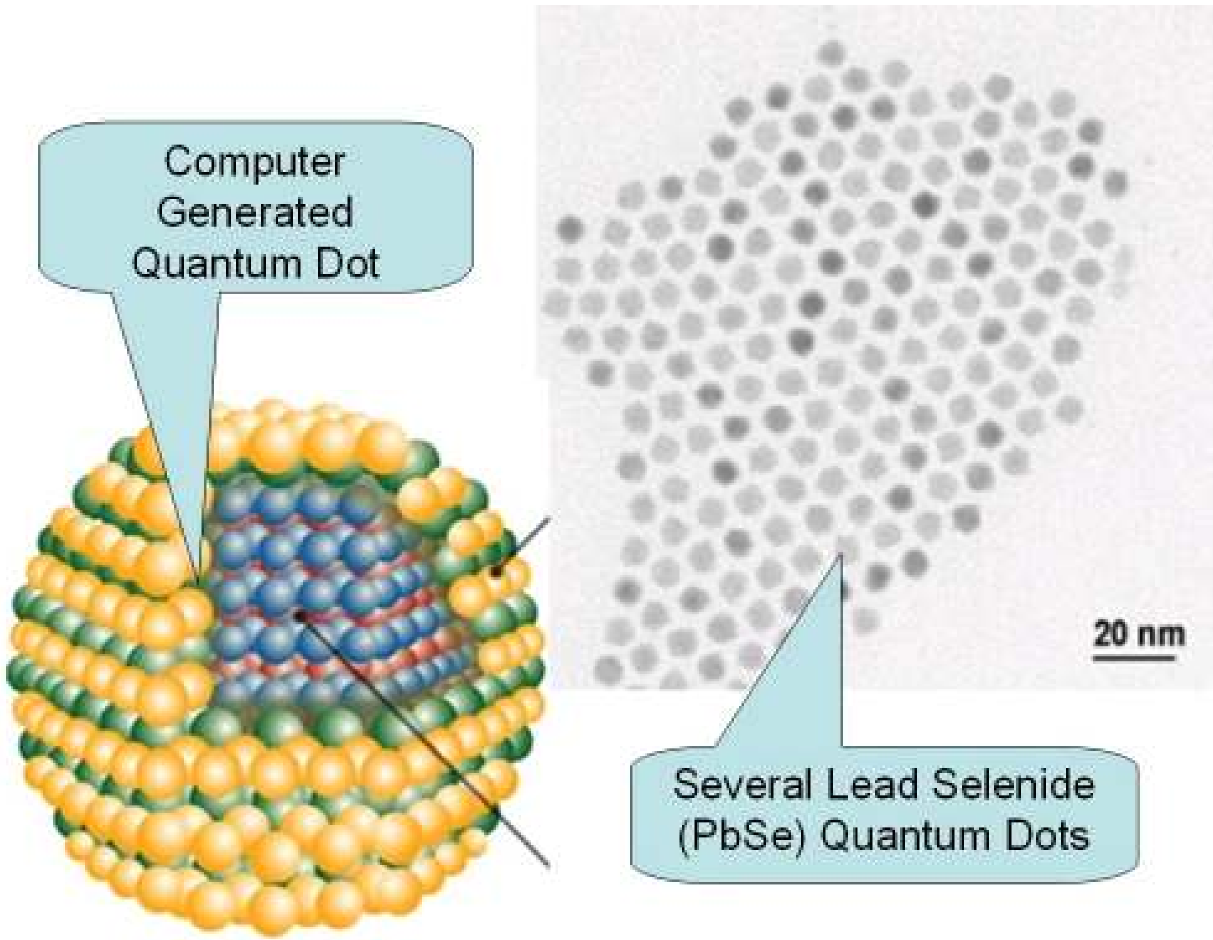
In small nanocrystals, the electronic energy levels are not continuous as in the bulk but are discrete (finite density of states), because of the confinement of the electronic wavefunction to the physical dimensions of the particles. This phenomenon is called *quantum confinement* and therefore nanocrystals are also referred to as **quantum dots (QDs)**.

Moreover, nanocrystals possess a high surface are and a large fraction of the atoms in a nanocrystal are on its surface. Since this fraction depends largely on the size of the particle (30% for a 1-nm crystal, 15% for a 10-nm crystal), it can give rise to size effects in chemical and physical properties of the nanocrystal.

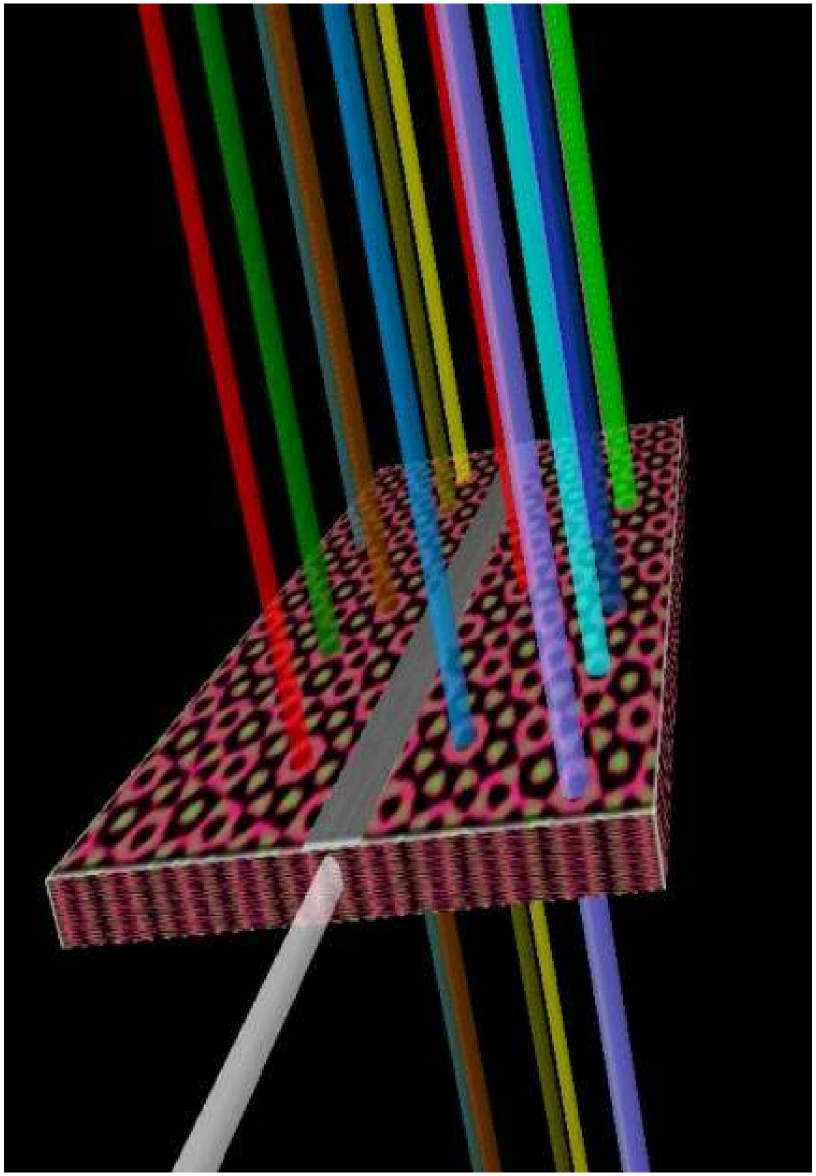
Quantum Confinement Effect



Quantum Dots

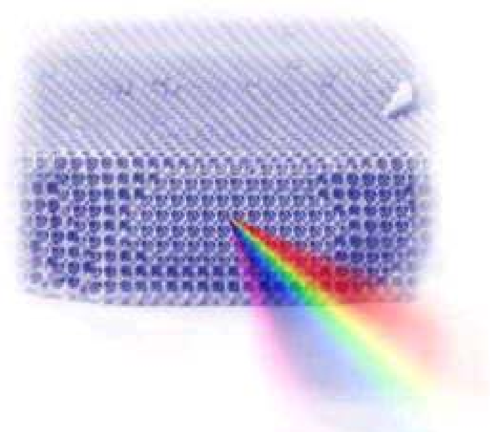


Photonic Crystals being researched actively at DTU



Photonic crystals are materials with a periodic variation in the refractive index with a lattice constant that is half the wavelength of the light used.

They offer a selectable band gap for the propagation of a certain wavelength, thus they resemble a semiconductor, but for light or photons instead of electrons.



Why Surface Modification?

1. The shell can alter the charge, functionality, and reactivity of the surface

2. The shell can enhance the stability and dispersibility of the colloidal core

3. Magnetic, optical, or catalytic functions may be readily imparted to the dispersed colloidal core

4. Encasing colloids in a shell of different composition may also protect the core from extraneous chemical and physical changes

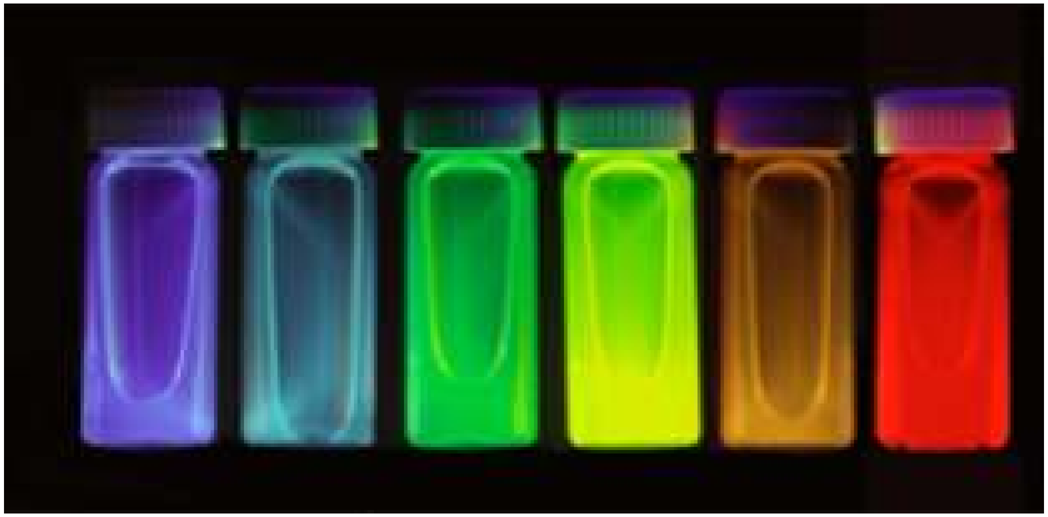
Semiconductor Nanoparticles

Group 14 (old group IV) Si, Ge

III-V Materials: GaN, GaP, GaAs, InP, InAs

II-VI Materials: ZnO, ZnS, ZnSe, CdS, CdSe, CdTe

Quantum dots are semiconductors particles that has all three dimensions confined to the 1-100 nm length scale



Colloidal CdSe quantum dots dispersed in hexane

Quantum Confinement in Semiconductor Nanoparticles

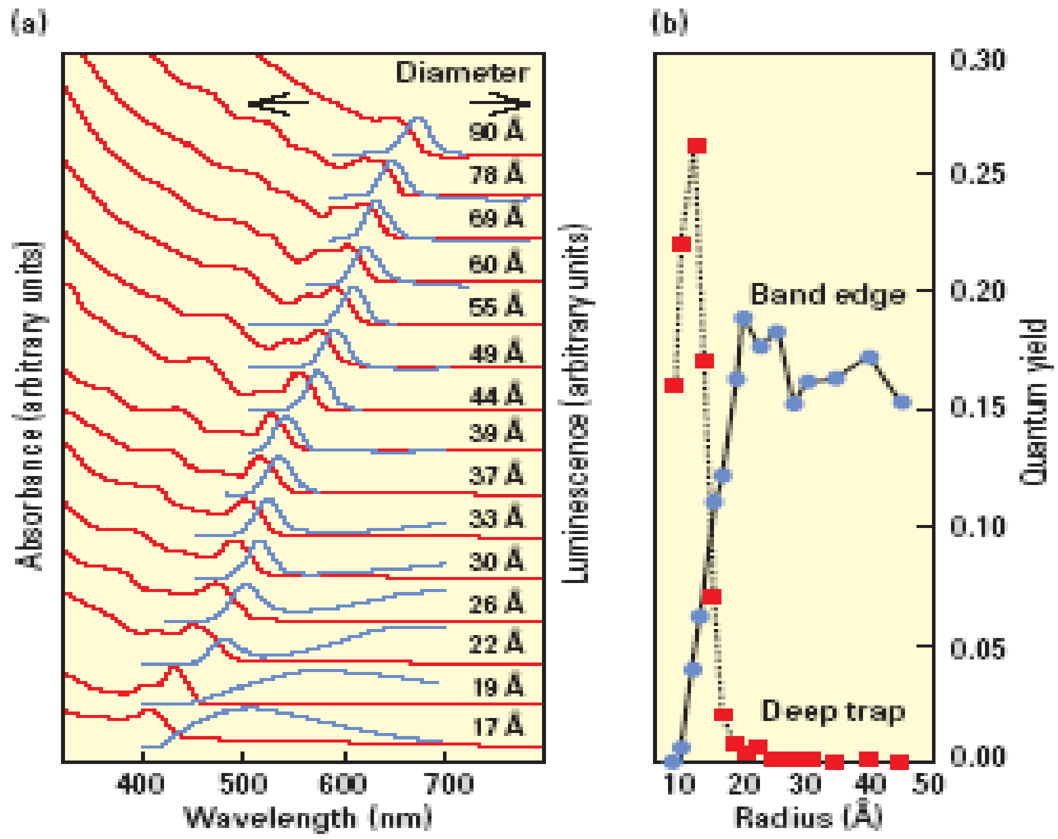
$$\mathbf{E_g\ (quantum\ dot) = E_g(bulk) + (\ h^2/8R^2)\ (1/\mathit{m_e} + 1/\mathit{m_h}) - 1.8e^2/4\pi\varepsilon_0\varepsilon \mathit{R}}$$

E_g = bandgap energy of a quantum dot or bulk solid
R = quantum dot radius
m_c = effective mass of the electron in the solid
m_h = effective mass of the hole in the solid
ε = dielectric constant of the solid
ε_0 = permittivity of a vacuum

Room-Temperature Spectra of CdSe Quantum Dots

(a) Absorption and photoluminescence spectra as a function of diameter

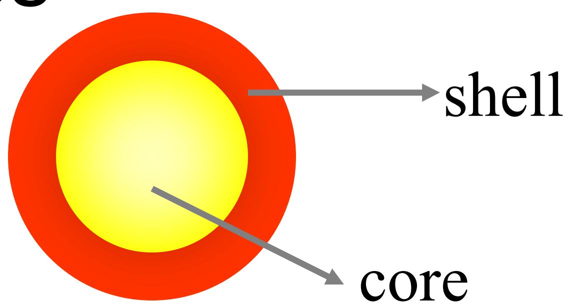
(b) Quantum yield of photoluminescence as a function of size. Squares represents deep-trap emission, and circles represent band-edge emission



Murray, C. B. Synthesis and characterization of II-VI quantum dots and their assembly into 3D quantum ot superlattices. Ph.D Thesis, MIT, Cambridge , MA 1995

What is Nanoparticle Engineering/Surface Modification

Tailored synthesis of core-shell nanoparticles with defined morphologies and properties



Types of Core-Shell Nanoparticles

- Metal-Polymer
- Metal-Metal
- Semiconductor- Semiconductor
- Semiconductor-Metal
- Metal - Semiconductor

Chemistry of Nanoscale Materials

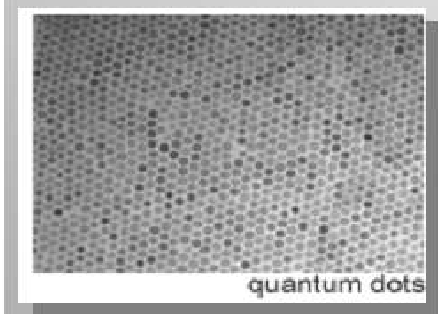
Synthesis, Properties and Applications

Potential Impacts of Nanoscale Materials

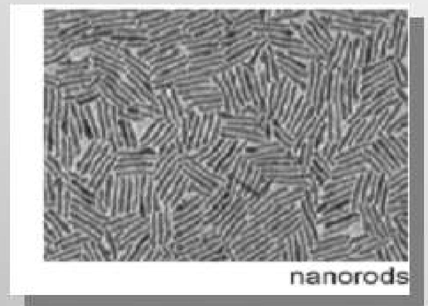
Pharmacy
Therapeutic drugs
Tagging DNA and DNA chips
Information Storage
Chemical/Optical components
Environmental/Green Chemistry
Solar Cells

Water purification
Catalysts
Sensors
Nanostructured Electrodes
Improved polymers
Smart magnetic fluids
Improved National Security

Environmental remediation

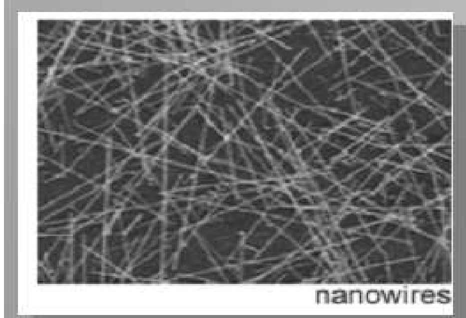


Nanoparticles

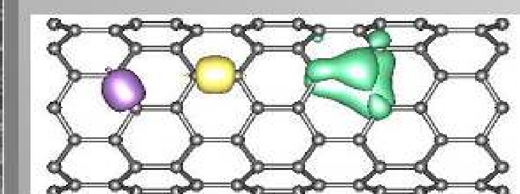


Nanorods

0 dimensional nanomaterials:
unique properties due to
quantum confinement
and very high surface/volume ratio



Nanowires



Nanotubes

1 dimensional nanomaterials:
extremely efficient
classical properties

New Silver Bandages May Help Heal Wounds

Silver reduces the growth of hundreds of types of bacteria responsible for wound infection

The new silver nanoparticle Fresh Box super airtight food storage containers can reduce bacteria by as much as 99.9%. It's not a miracle, it's the silver. Your food stay fresher longer so you throw away less. **The naturally anti-fungal, anti-bacterial and anti-microbial properties of the finely dispersed nanosilver particles permanently imbedded in the containers will save you money while helping insure you and your family enjoy safer, fresher, healthier, tastier food.**

Ku et al. Malaria Journal 2011, 10:118
http://www.malariajournal.com/content/10/1/118

MALARIA JOURNAL

METHODOLOGY **Open Access**

Quantum dots: a new tool for anti-malarial drug assays

Min-Je Ku[1†], Fernando M Dossin[1†], Youngseon Choi[2†], Carolina B Moraes[1], Jiyoung Ryu[2], Rita Song[2*] and Lucio H Freitas-Junior[1*]

Thin Solid Films 517 (2009) 6441–6478

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ELSEVIER

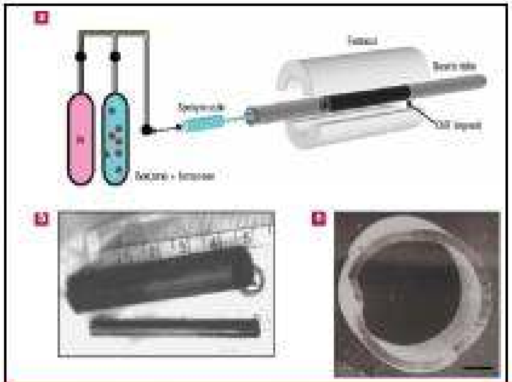
Special Feature

Noble metal nanoparticles for water purification: A critical review

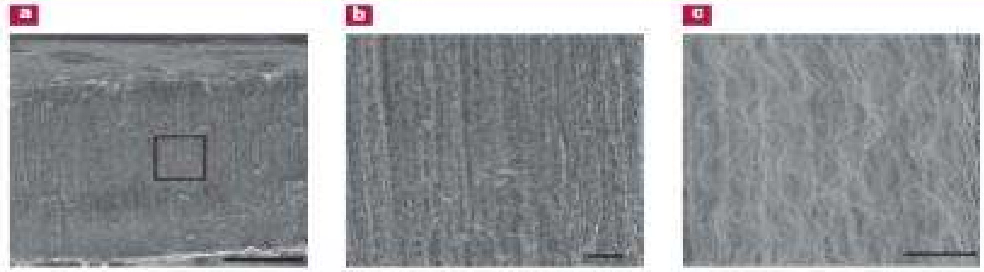
T. Pradeep *, Anshup

Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai 600 036, India

Water: Nano tube filter – water purification

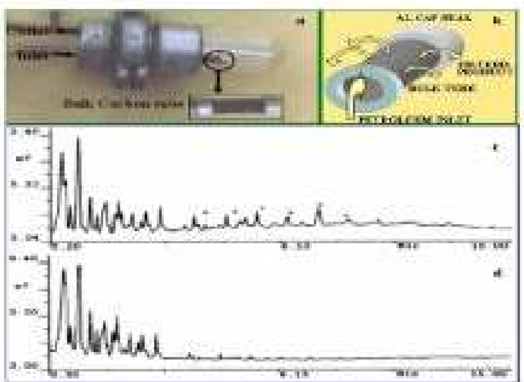


Synthesis Methods



Structural characterization of macro tubes made from MWNT

Removal of bacteria using nano tube filter.



Petroleum filtration set-up using the Nano tube filter

They can remove 25-nanometer-sized polio viruses from water, as well as larger pathogens, such as E. coli and Staphylococcus aurous bacteria.

Filters adaptable to micro fluidics applications that separate chemicals in drug discovery.

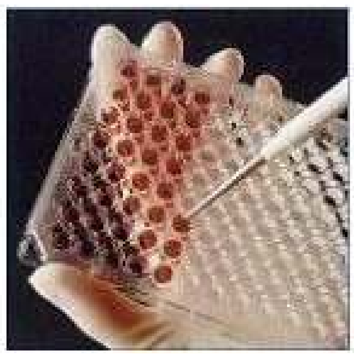
Prof. A. SRIVASTAVA & team, Banaras Hindu University

Typhoid Detection Kit

A Latex agglutination based test

1. Typhoid Detection Kit has been developed by DRDE, Gwalior using the nano sensor developed by Prof. A.K. Sood, and his team from IISc, Bangalore.
2. It is using recombinant DNA technology and immunological technique for rapid diagnosis of typhoid infection.
3. The test detects S. typhi antigen directly in patient's serum within 1-3 minutes which is very important for initiating early treatment and saving human life.

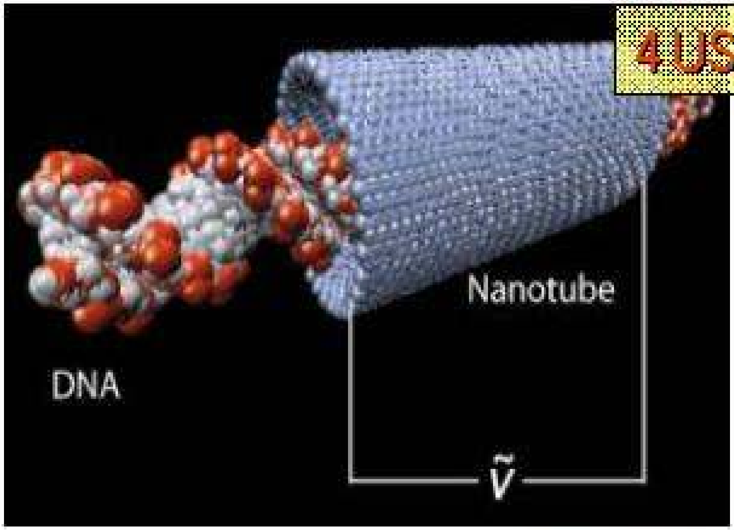
Very small quantity of clinical sample as low as 2-3 µl is required to perform the above test as compared to 10-15 µl sample required for latex agglutination test.



DRDE, GWALIOR and Prof. AK SOOD, IISc

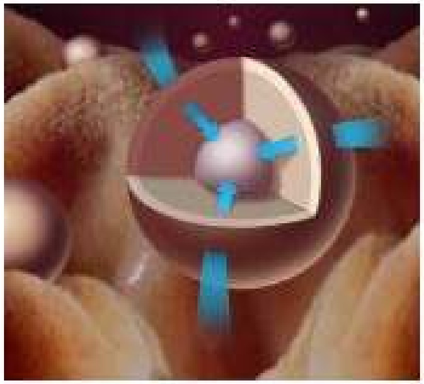
Drug Delivery system

- Development of a reverse micelles based process for the synthesis of hydrogel and 'smart' hydrogel nanoparticles for encapsulating water-soluble drugs.
- This method enabled one to synthesize hydrogel nanoparticles of size less than 100nm diameter.
- This technology has been sold to Dabur Research Foundation in 1999.
- Nanoparticle drug delivery for eye diseases. "This process improves the bioavailability of the drug on the surface of the cornea". The technology has been transferred to Chandigarh-based Panacea Biotech Ltd.



4 US Patents

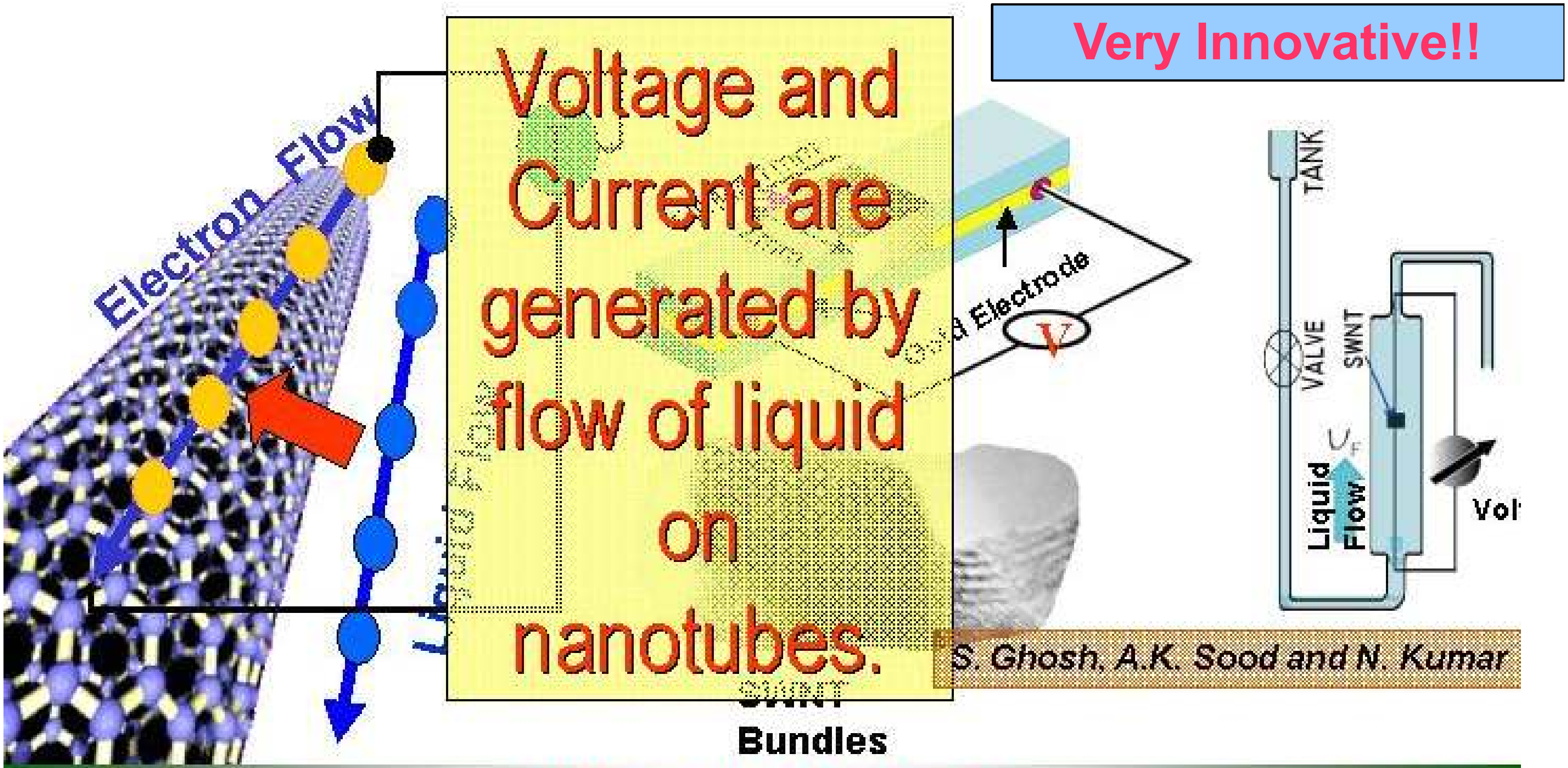
Technology transferred to Dabur & Panacea Biotech



Prof. Amarnath Maitra
Delhi University

Power: Gas flow induced generation of voltage from solids

- SWNT are 1D systems: Narrow lanes for carriers.
- Momentum transfer to the carriers either by direct or indirect processes causes electrons (holes) to scatter only in forward or backward directions along the tube.



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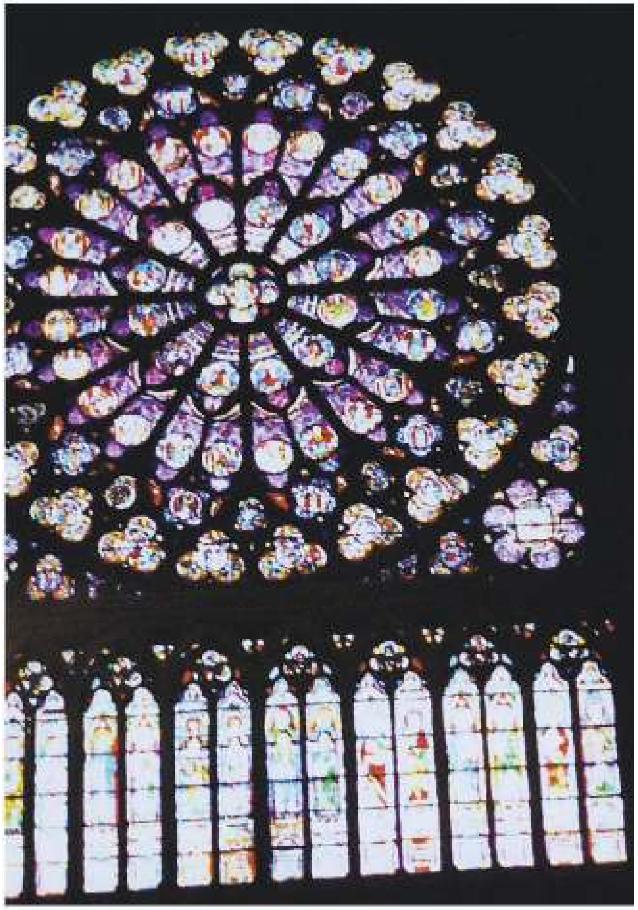
Plasmonics

Stained-Glass as Ancient Nanotechnology

Stained-glass windows have been around for centuries, but they rely on the same scattering properties of light that modern nano-based colorimetric indicators do.



1) Gold nanoparticles were used as a pigment of ruby-colored stained glass dating back to the 17th century. Figure.1 shows a picture of the Rose Window of the Cathedral of Notre Dame. The bright red and purple colors are due to gold nanoparticles.

2) Lycurgus cup: It appears green in reflected light, but appears red when light is shone from inside, and is transmitted through the glass.

•**In the fourth century AD**, Roman glssmakers were fabricating glasses containing nanosized metals. The ***Lycurgus cup*** (in London), is made from soda lime glass containing silver and gold nanoparticles. The color of the cup changes from green to a deep red when a light source is placed insided it.

What is a Plasmon ?

A plasmon is a density wave in an electron gas. It is analogous to a sound wave, which is a density wave in a gas consisting of molecules.

Plasmons exist mainly in metals, where electrons are weakly bound to the atoms and free to roam. The free electron gas model provides a good approximation (also known as jellium model).

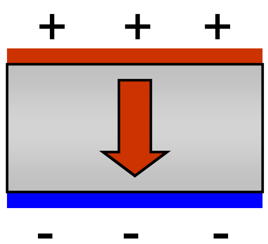
The electrons in a metal can wobble like a piece of jelly, pulled back by the attraction of the positive metal ions that they leave behind.

In contrast to the single electron wave function that we encounter, a plasmon is a collective wave where billions of electrons oscillate in sync.

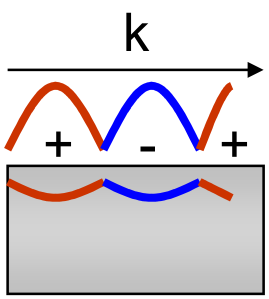
What is a plasmon?

"plasma-oscillation": density fluctuation of free electrons

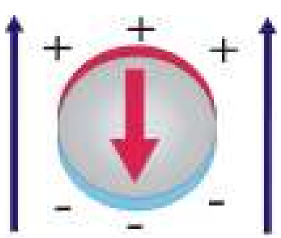
$$\omega_p^{drude} = \sqrt{\frac{Ne^2}{m\varepsilon_0}}$$



Plasmons in the bulk oscillate at ω_p determined by the free electron density and effective mass



Plasmons confined to surfaces that can interact with light to form propagating "surface plasmon polaritons (SPP)"

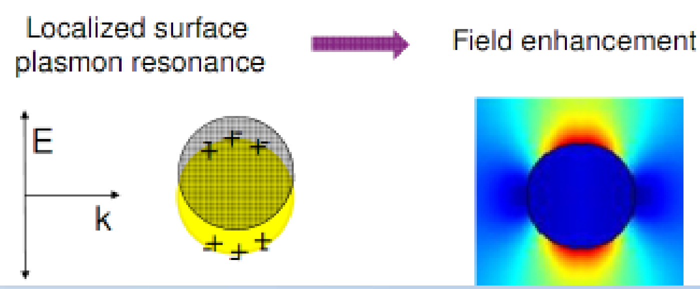


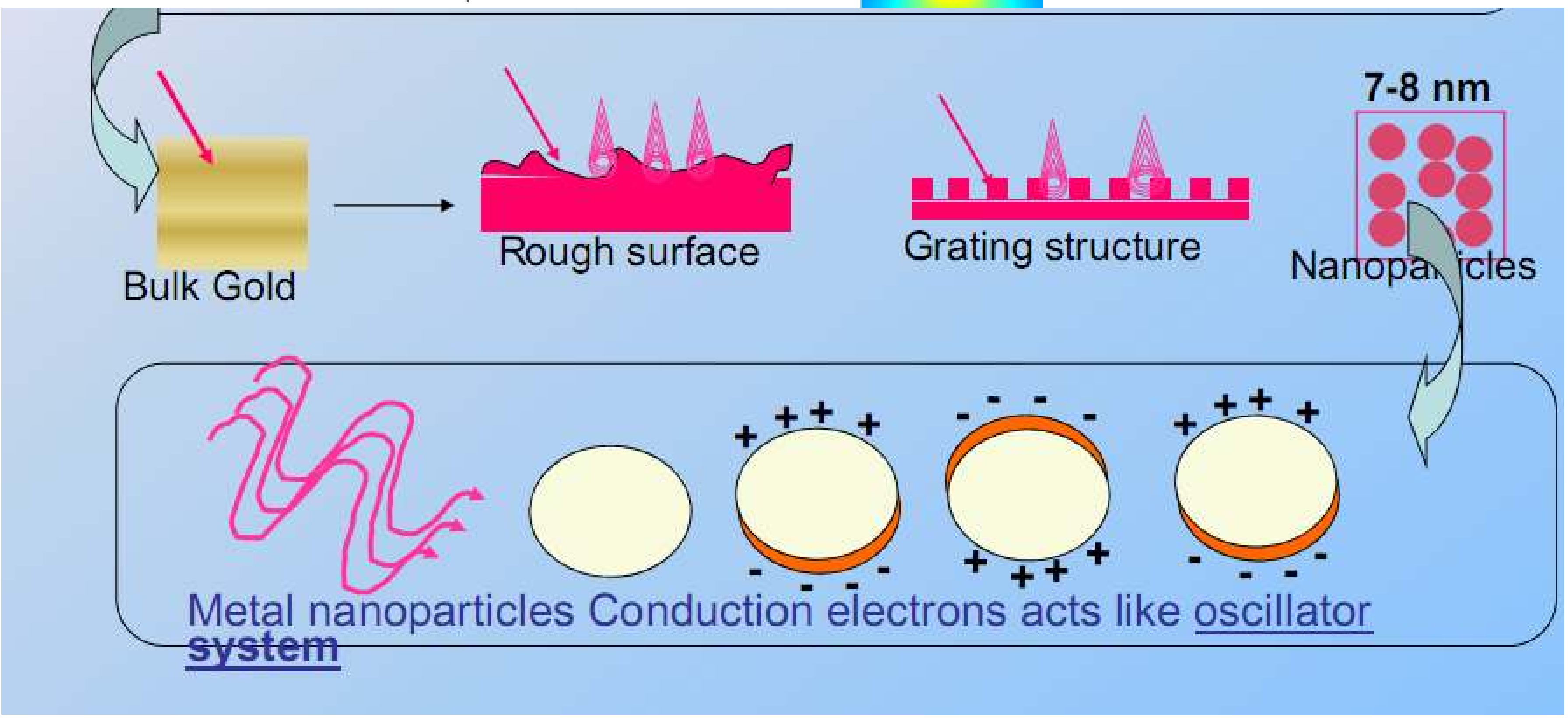
Confinement effects result in resonant SPP modes in nanoparticles

$$\omega_{particle}^{drude} = \sqrt{\frac{1}{3}\frac{Ne^2}{m\varepsilon_0}}$$

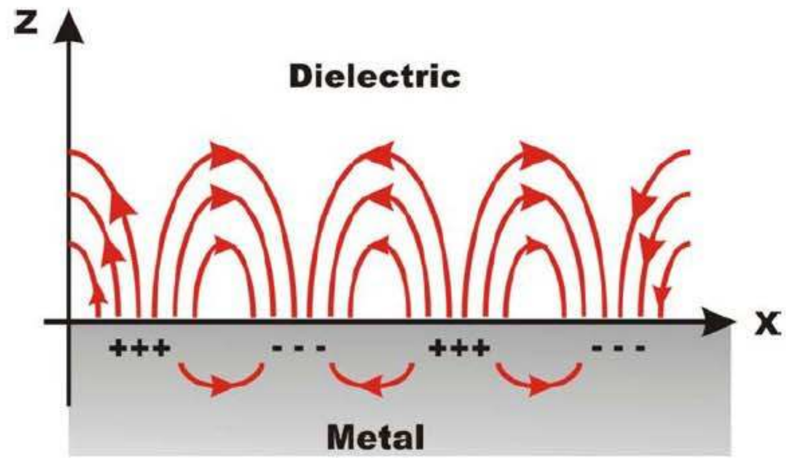
WHAT IS A PLASMON?

Plasmon – a collective oscillation of free electrons,
in this case a dipolar resonance



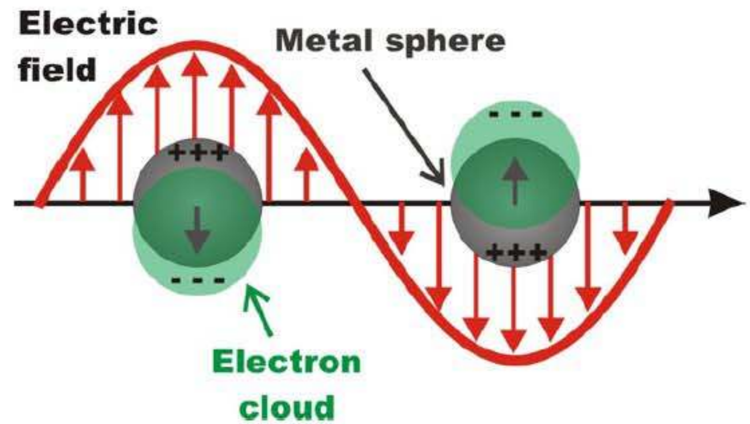


Propagating surface plasmons (surface plasmon polaritons)



- Thin metal films (~50 nm)
- Propagate 10-100 μm along x-y
- $l_d \sim 200$ nm

Localized surface plasmons

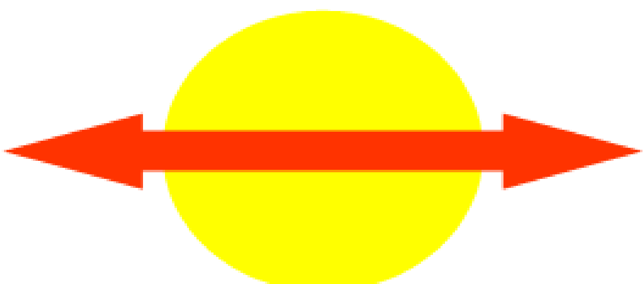


- Particle size << λ
- Plasmon is localized
- $l_d \sim 5$ nm

Types of plasmons

Localized plasmons

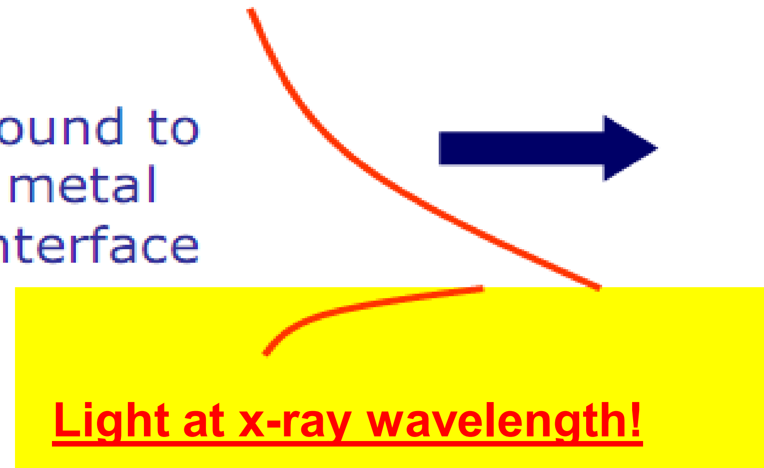
Dipole (and multipole) oscillations of electrons

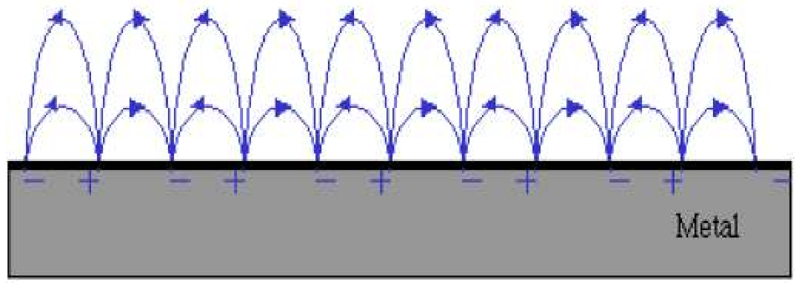


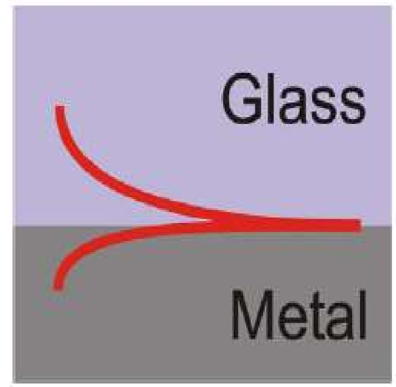
Both types of plasmons can be used to enhance absorption in solar cells.

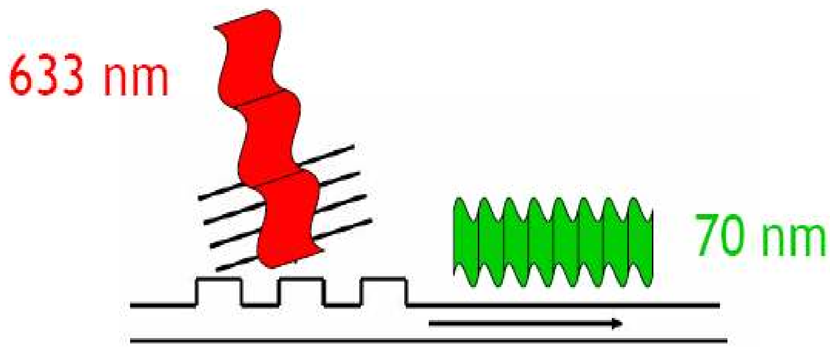
Propagating plasmons (surface plasmon polaritons)

bound to metal interface









Plasmon wavelength
is smaller than light wavelength

Surface plasmon resonance

When a nanoparticle is much smaller than the wave length of light, coherent oscillation of the conduction band electrons induced by interaction with an electromagnetic field. This resonance is called Surface Plasmon Resonance (SPR).

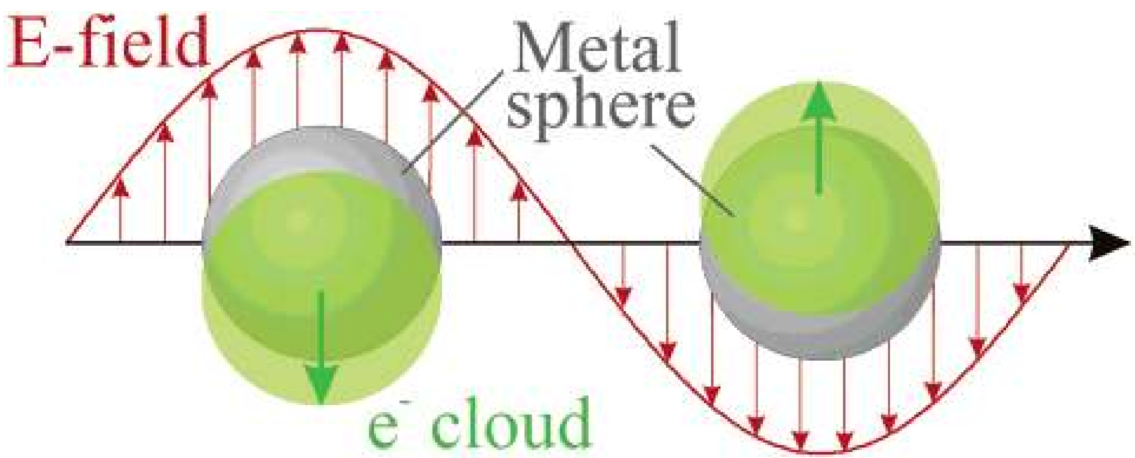
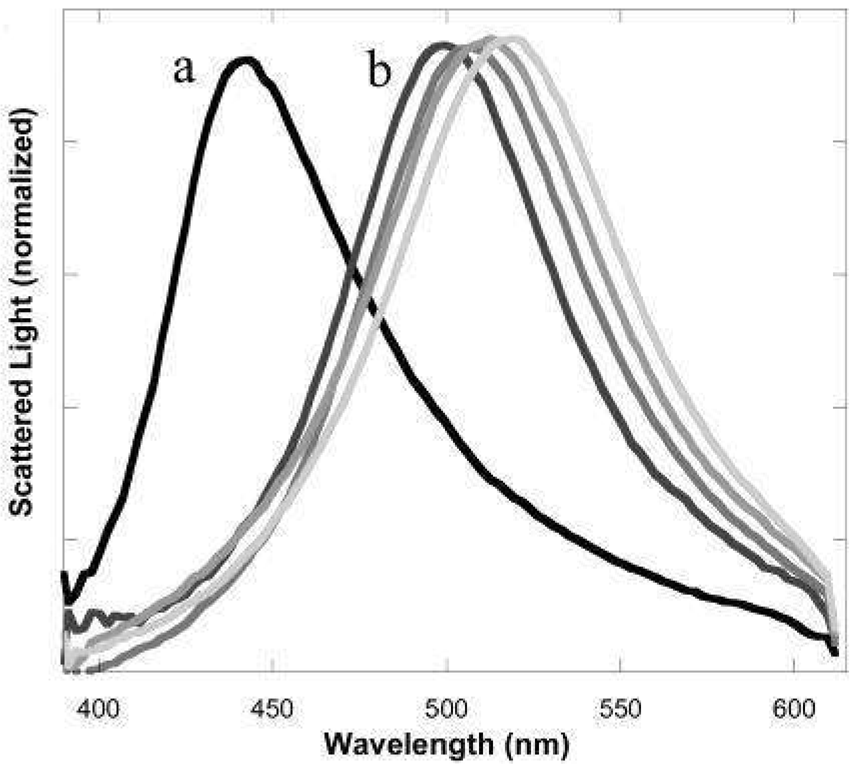


Figure: Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.

Surrounding medium



- **The surface plasmon resonance peak changes with its own dielectric properties and those of its local environment including the substrate, solvent, and adsorbates.**
- **This principle that the high sensitivity of the surface plasmon resonance spectrum of noble metal nanoparticles to adsorbate-induced changes in the dielectric constant of the surrounding nanoenvironment used in chemosensing and biosensing.**

Spectral shift for individual blue (roughly spherical) silver nanoparticles. Typical blue particle spectrum as it is shifted from (a) air to (b) 1.44 index oil, and successive oil treatments in 0.04 index incremental increases.

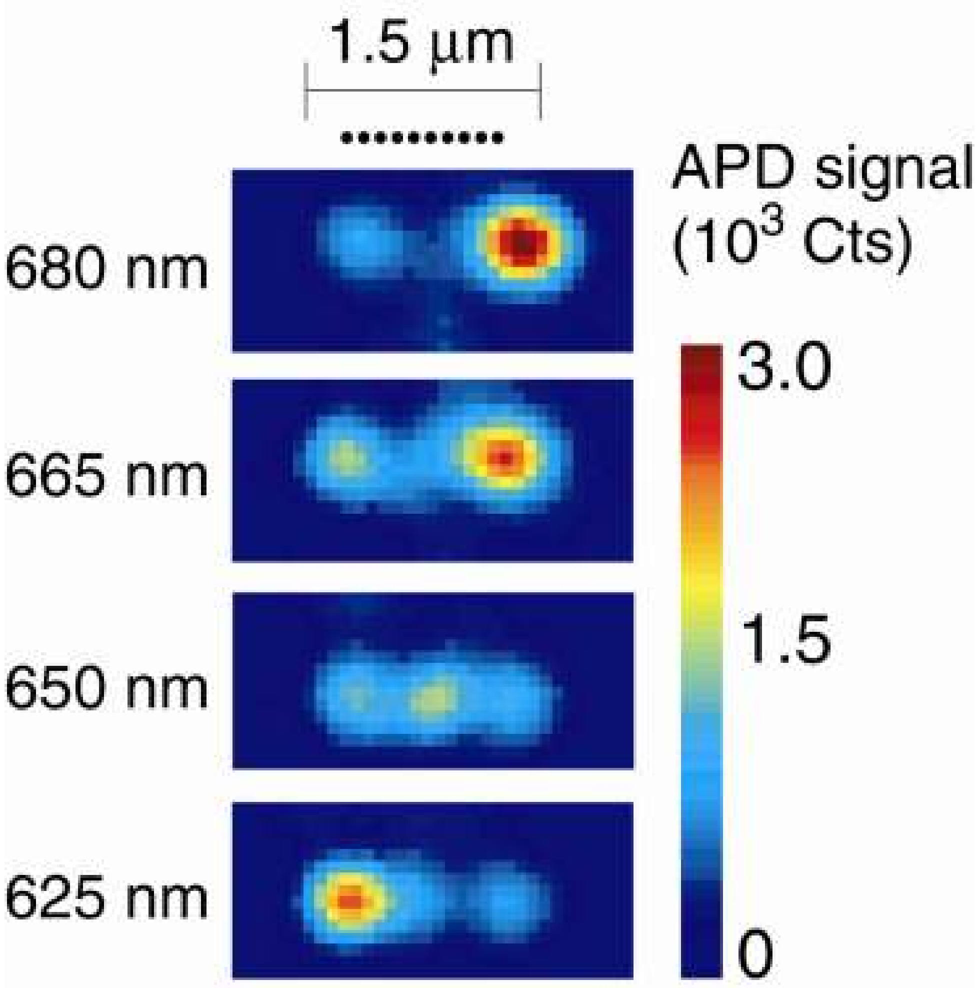
Jack J. Mock, David R. Smith, and Sheldon Schultz, Local Refractive Index Dependence of Plasmon Resonance Spectra from Individual Nanoparticles, Nano letters 2003 Vol. 3 No. 4 485-491.

- **Michael Faraday was first to report the study of the synthesis and colors of colloidal gold.**
- **In 1908, Mie explained this phenomenon by solving Maxwell's equation.**
- **Mie theory predicted optical extinction of homogenous spherical particles 2R<<λ for very small particles as (extinction = scattering + absorption)**

$$\sigma_{ext} = \frac{9 . V . \varepsilon_m^{3/2}}{c} \left(\frac{\omega . \varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2} \right)$$

Where as *V* is the particle volume, ω is the angular frequency of the exciting light, and *c* is the speed of light. ε_m and ε (ω) = ε_1 (ω)+ ε_2 (ω) are the dielectric functions of the surrounding medium and the metal, respectively

Local plasmon array response

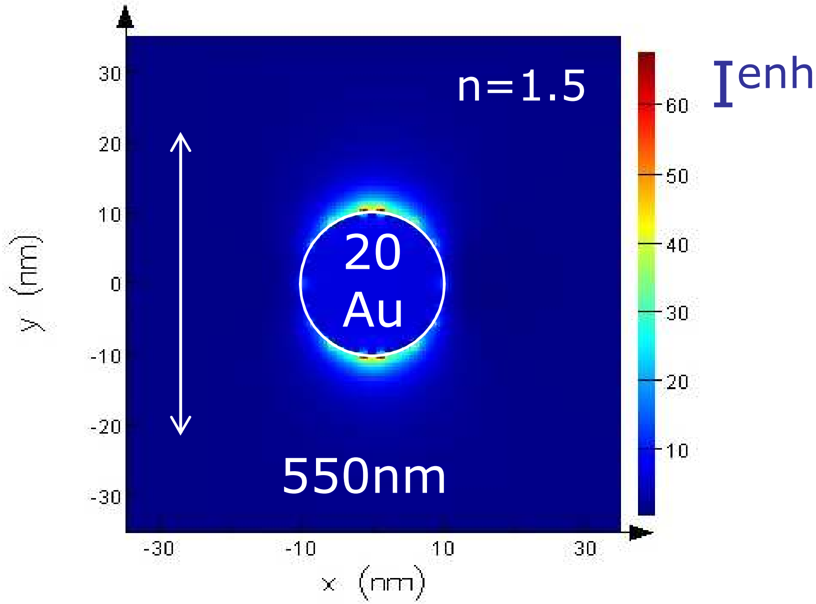


- Energy localization on front or back side of the array
- Nanoscale concentration tunable with wavelength
- NANOANTENNA

Nano Lett. 7, 2004 (2007)

René de Waele, Femius Koenderink

Metal nanoparticles: extinction = scattering + absorption



At resonance, both scattering and absorption are large

albedo = scattering / extinction = $\sigma_{sca}/(\sigma_{abs}+\sigma_{sca})$

Introduction – a Brief History

A centenary of Plasmonics!

1902 — Robert Wood observes power loss in a spectroscopy experiment for light reflected off metal grating surfaces

1907 — Jonathan Zenneck unknowingly introduces mathematical description of surface plasma waves, while studying radio waves.

1947 — Ugo Fano produces the first consistent explanation of Wood's observed power loss: surface plasma waves are properly introduced.

1956-1958

-1956: David Pines introduces quantized plasma oscillations in bulk metals, calling them "plasmons".
-1957: Rufus Ritchie studies electron energy losses in thin films: first theoretical description of surface plasmons.
-1958: John Hopfield introduces the term "polariton" for the coupled oscillation of bound electrons and light in transparent media.

1968 — Andreas Otto, Erich Kretschmann and Heinz Raether present methods for the optical excitation of surface plasmon polaritons on metal films.

This is a ***major advancement***, making experiments on surface plasmon polaritons easily accessible to many researchers (see bar chart).

2002 — The quantum optics and quantum information communities begin to develop a keen interest in using surface plasmon polaritons for QIP purposes…

Now

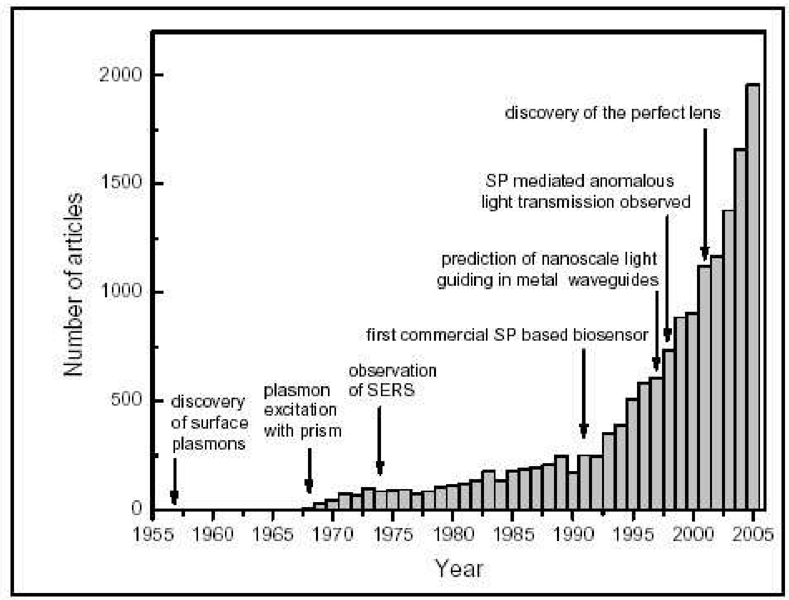
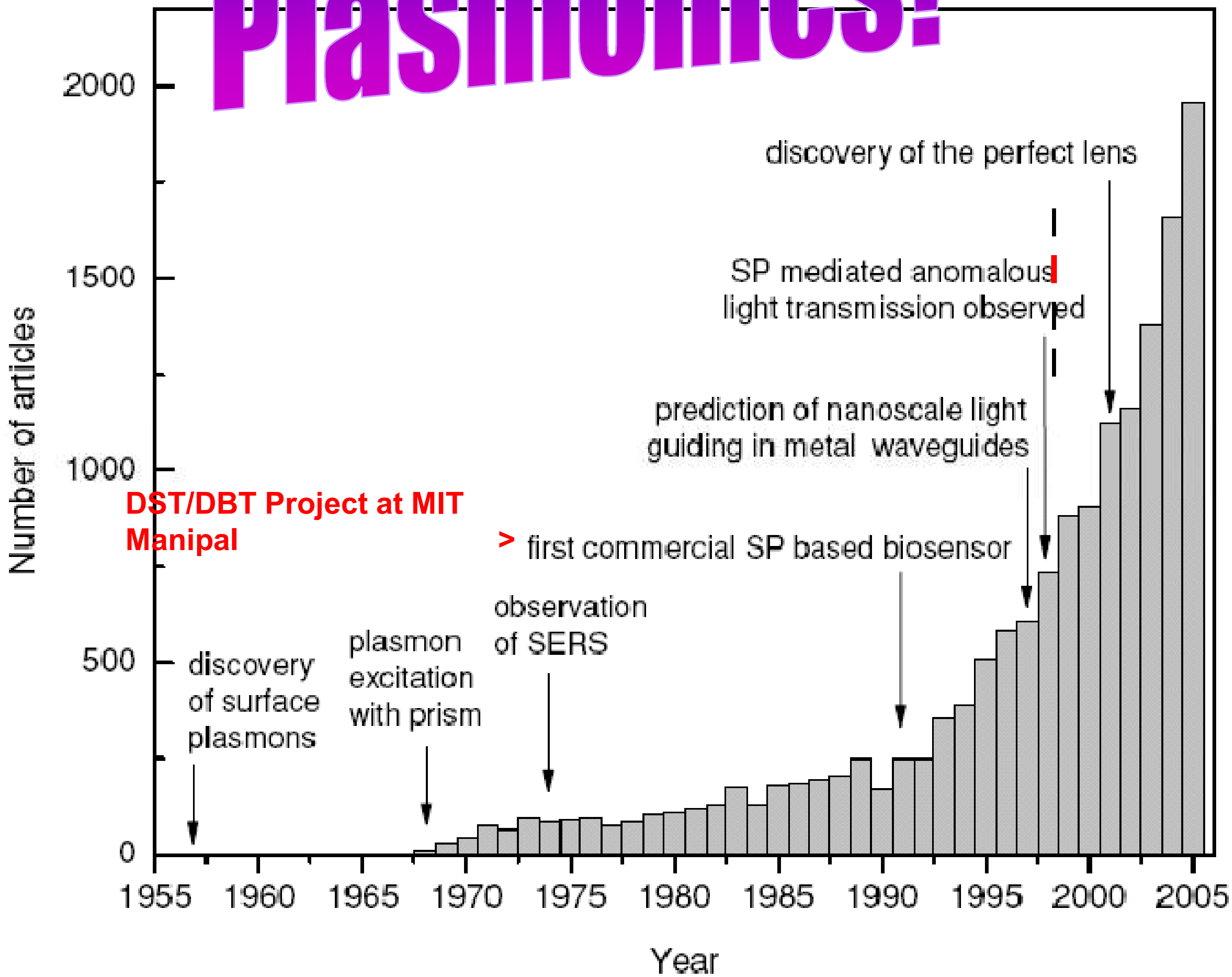


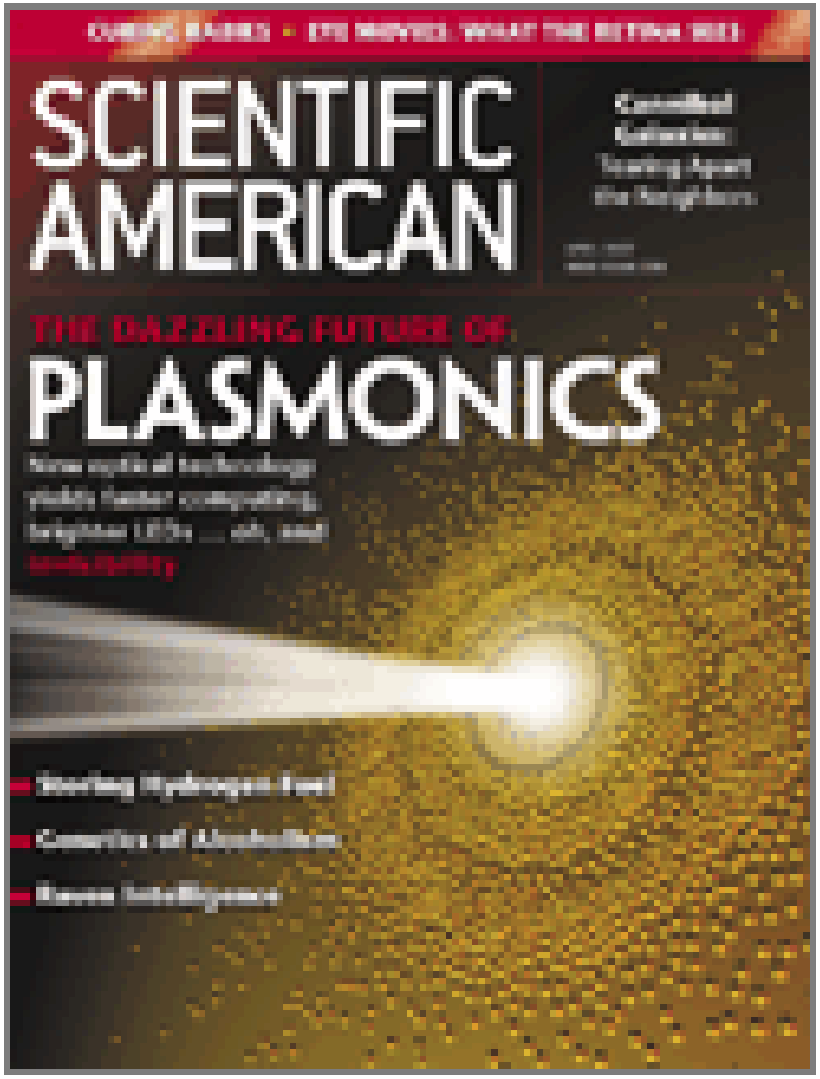
Figure 1-1. The growth of the field of metal nanophotonics is illustrated by the number of scientific articles published annually containing the phrase "surface plasmon" in either the title or abstract (based on data provided on www.sciencedirect.com)

Plasmonics!

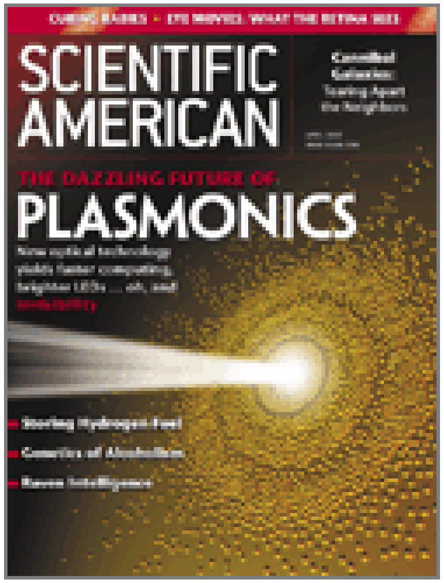


DST/DBT Project at MIT Manipal

SCINETIFIC AMERICAN-APRIL 2007



Harry Atwater, Howard Hughes Professor and Professor of Applied Physics and Materials Science, has authored the cover article of Scientific American (April 2007) with his article "The Promise of Plasmonics." He describes the potential of technologies that use electron density waves called plasmons. Among many potential applications, plasmonic circuits could help the designers of computer chips build fast interconnects that could move large amounts of data across a chip. Read more...



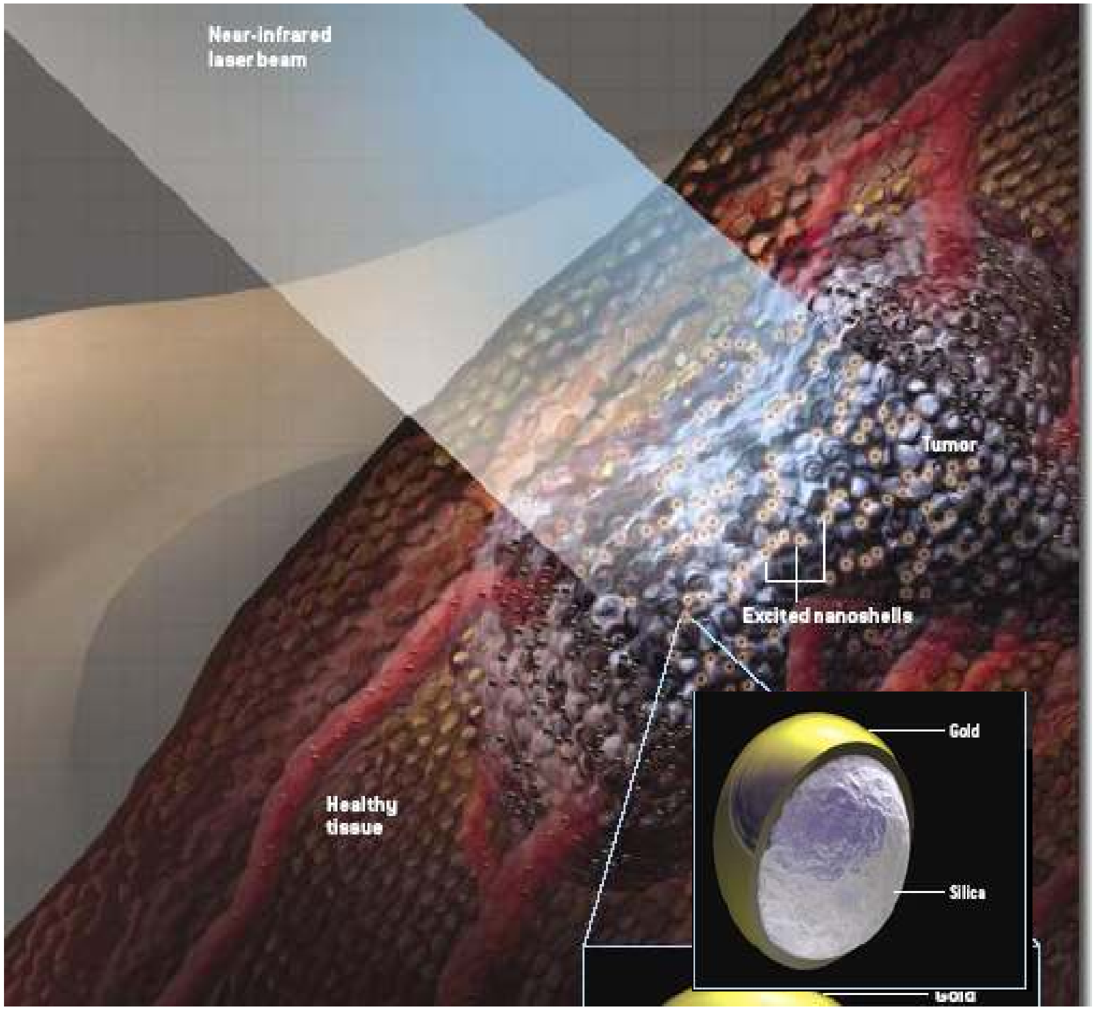
April-07

Image: PHIL SAUNDERS
Space Channel Ltd.

LIGHT BEAM striking a metal surface can generate plasmons, **electron density waves that can carry huge amounts of data.** If focused on a surface etched with a circular groove, as in this artist's rendering, the beam produces concentric waves, organizing the electrons into high- and low-density rings.

Overview/*Plasmonics*

- Researchers have discovered that they can squeeze optical signals into minuscule wires by using light to produce electron density waves called plasmons.
- Plasmonic circuits could help the designers of computer chips build fast interconnects that could move large amounts of data across a chip. Plasmonic components might also improve the resolution of microscopes, the efficiency of light-emitting diodes, and the sensitivity of chemical and biological detectors.
- Some scientists have even speculated that plasmonic materials could alter the electromagnetic field around an object to such an extent that it would become invisible.



A proposed cancer treatment would employ plasmonic effects to destroy tumors. Doctors would inject nanoshells—100-nanometer-wide silica particles with an outer layer of gold (inset)—into the bloodstream. The nanoshells would embed themselves in a fast-growing tumor. If near-infrared laser light is pointed at the area, it would travel through the skin and induce resonant electron oscillations in the nanoshells, heating and killing tumor cells without harming the surrounding healthy tissue.

JEFFREY N. ANKER, W. PAIGE HALL,
OLGA LYANDRES, NILAM C. SHAH, JING ZHAO
AND RICHARD P. VAN DUYNE*
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REVIEW ARTICLE

Biosensing with plasmonic nanosensors

Recent developments have greatly improved the sensitivity of optical sensors based on metal nanoparticle arrays and single nanoparticles. We introduce the localized surface plasmon resonance (LSPR) sensor and describe how its exquisite sensitivity to size, shape and environment can be harnessed to detect molecular binding events and changes in molecular conformation. We then describe recent progress in three areas representing the most significant challenges: pushing sensitivity towards the single-molecule detection limit, combining LSPR with complementary molecular identification techniques such as surface-enhanced Raman spectroscopy, and practical development of sensors and instrumentation for routine use and high-throughput detection. This review highlights several exceptionally promising research directions and discusses how diverse applications of plasmonic nanoparticles can be integrated in the near future.

FEATURE ARTICLE

Nanosphere Lithography: A Versatile Nanofabrication Tool for Studies of Size-Dependent Nanoparticle Optics

Christy L. Haynes and Richard P. Van Duyne*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received: February 19, 2001

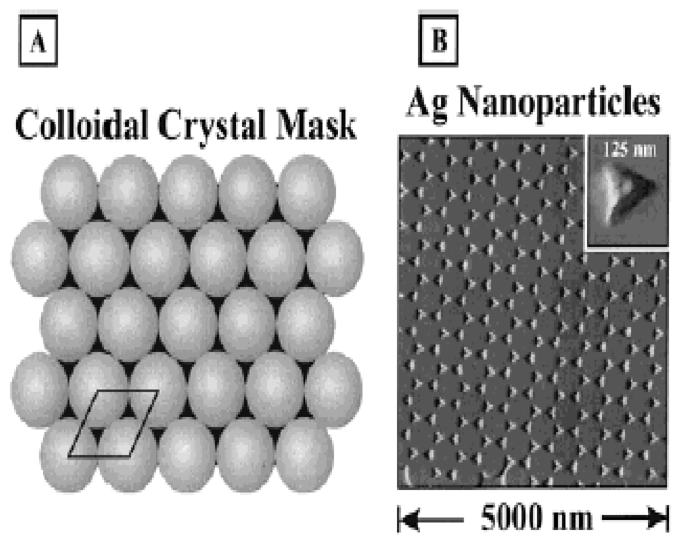


Figure 1. Schematic illustration (A) and representative AFM image (B) of SL PPA. The ambient contact mode AFM image was captured from a SL PPA fabricated with $D = 542$ nm nanospheres and $d_m = 48$ nm thermally evaporated Ag metal after 3 min sonication in methylene chloride.

Self-assembly of the hexagonal closed-packed (hcp) monolayer of latex spheres, is the basis of the nanosphere lithography (NSL).Also Polysterene sphere are used for this purpose .

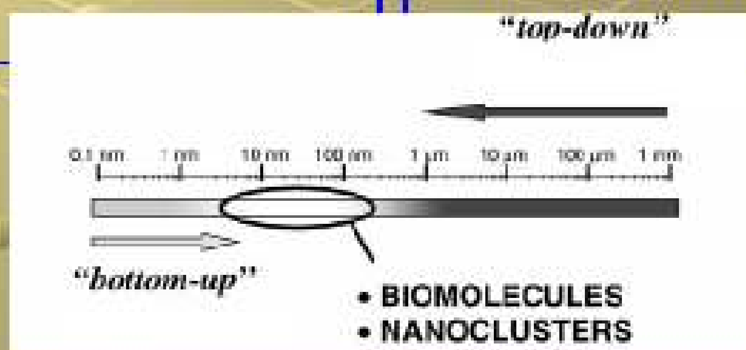
This technique is used for creation of masks for deposition of various materials, typically by evaporation or sputtering.* *It is known that NSL can be used to make honeycomb lattices of triangularly shaped islands on various substrates. Using spheres with different diameters, one can change the spacing and size of the periodically arranged islands.

By annealing the samples at the temperature of about 70% of the melting point of the bulk material and adjusting the time of the thermal treatment, spherical particles can be obtained. Van Duyne et al. shown that nanooverlaps, nanogaps, and nanochains can be obtained by multiple silver depositions at different deposition angles. **They called this technique angle-resolved NSL.**

Controlling size, shape, spacing, organization and environment of noble-metal nanoparticles and nanostructures

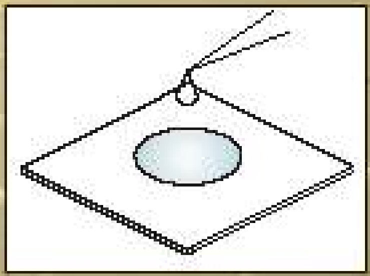
- Standard methods
- Electron-beam nanolithography
- X-ray nanolithography
- STM and AFM techniques

- Alternative methods
- Nanosphere lithography
- Self-assembling nanoparticles
- Controlled chemical synthesis of metallic clusters
- Diffusion-controlled aggregation

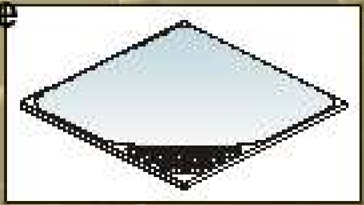


(A) Starting with the self-assembling process

1. Drop ~100 μL colloid solution onto hydrophillic substrate



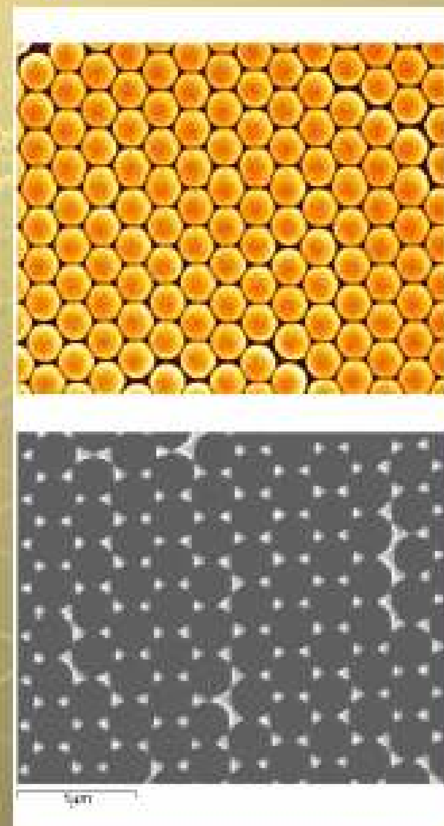
2. Dry in oven, spheres self-assemble at meniscus edge



(B) Metal deposition

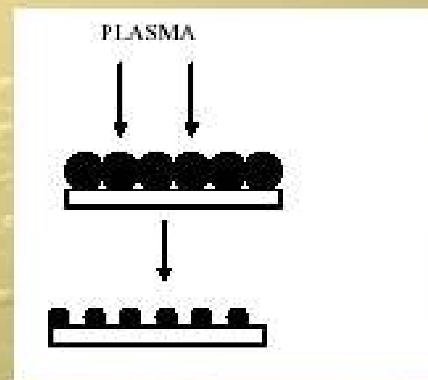
1. Thermally evaporate film of silver or gold onto the polystyrene nanosphere array.

2. Remove nanospheres leaving a hexagonal array of nanoparticles

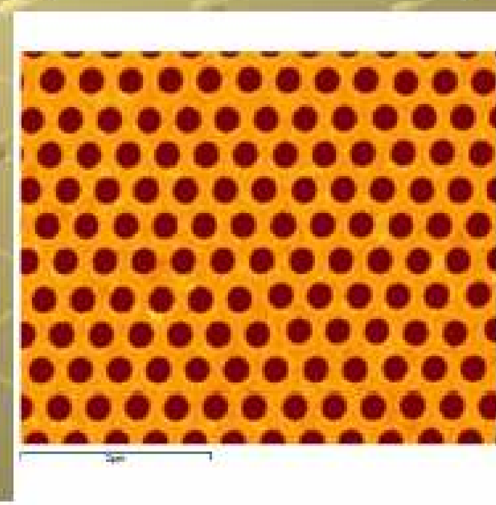


(C) Reactive Ion Etching (RIE)

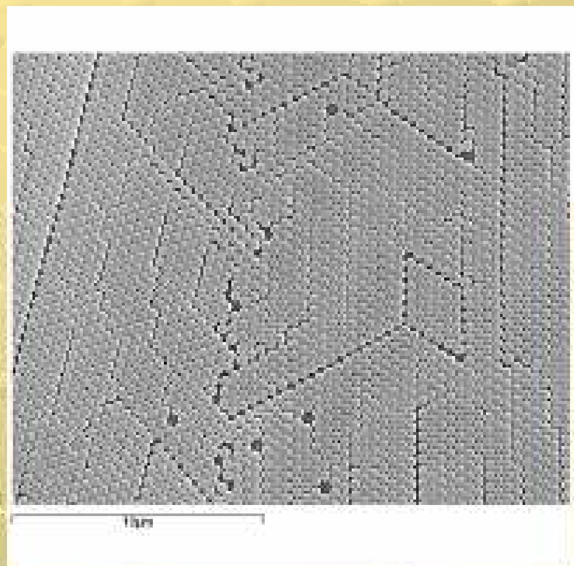
1. Etch nanosphere array in an oxygen plasma

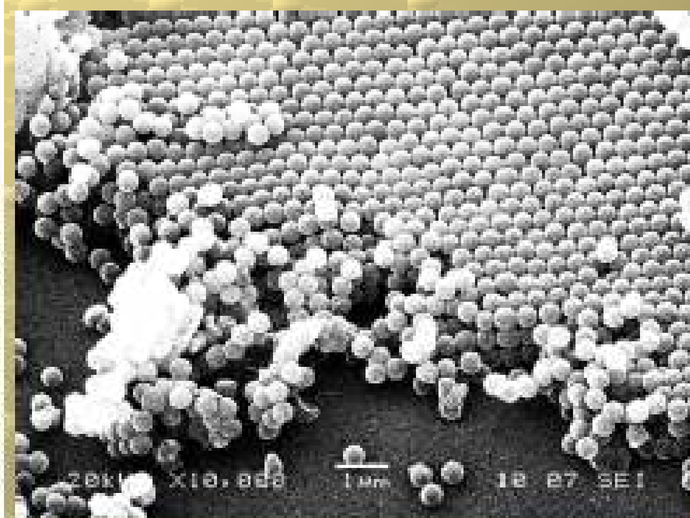


2. Remove nanospheres leaving hexagonal array of holes in a metal film



Exemples of self-assembled polystyrene nanospheres





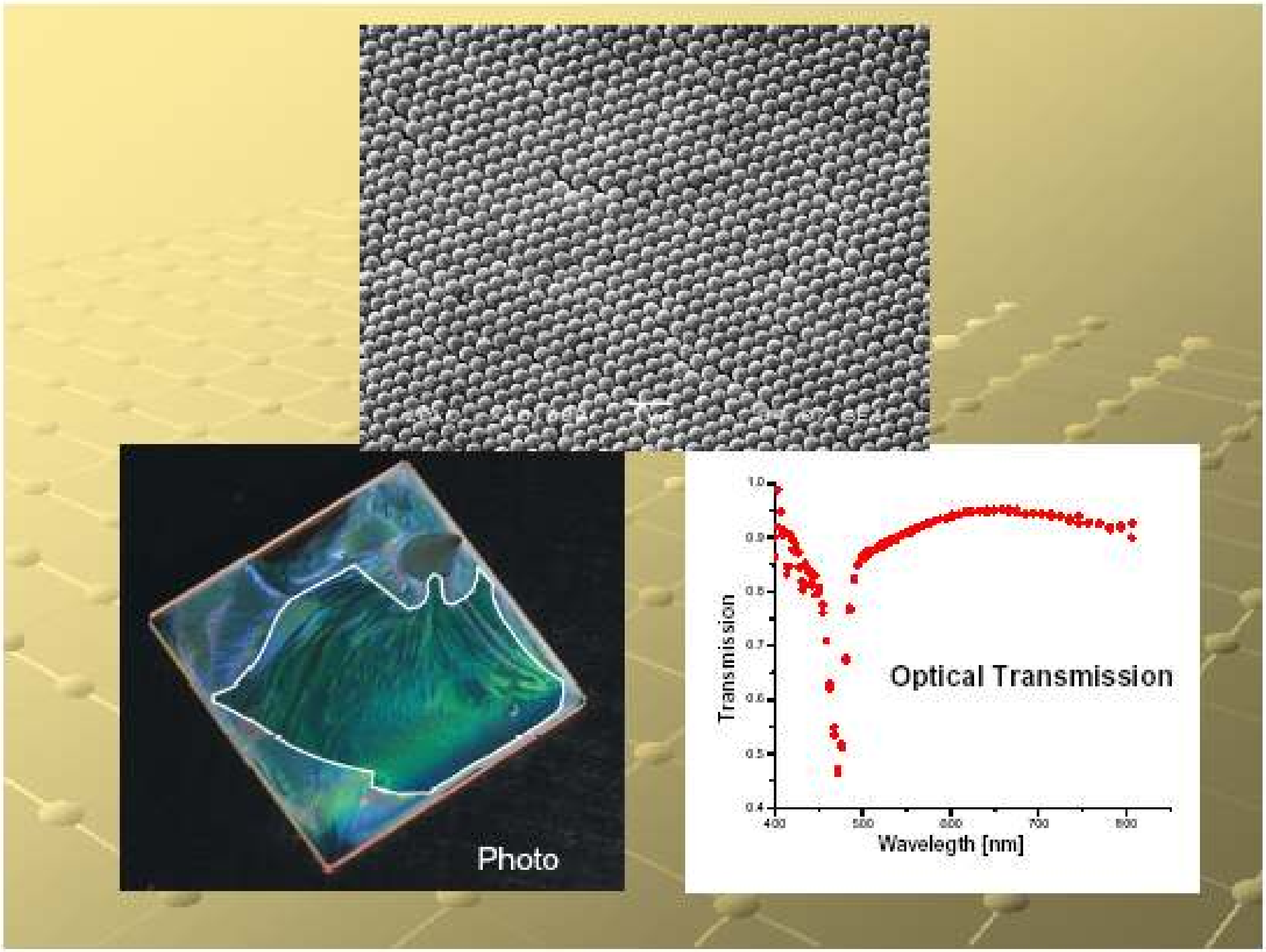
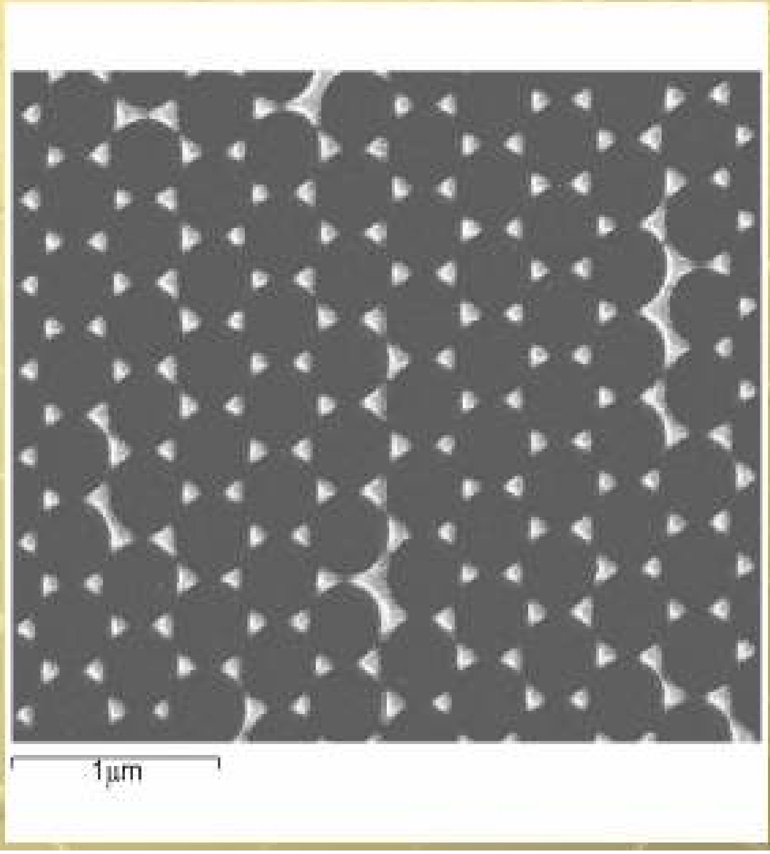


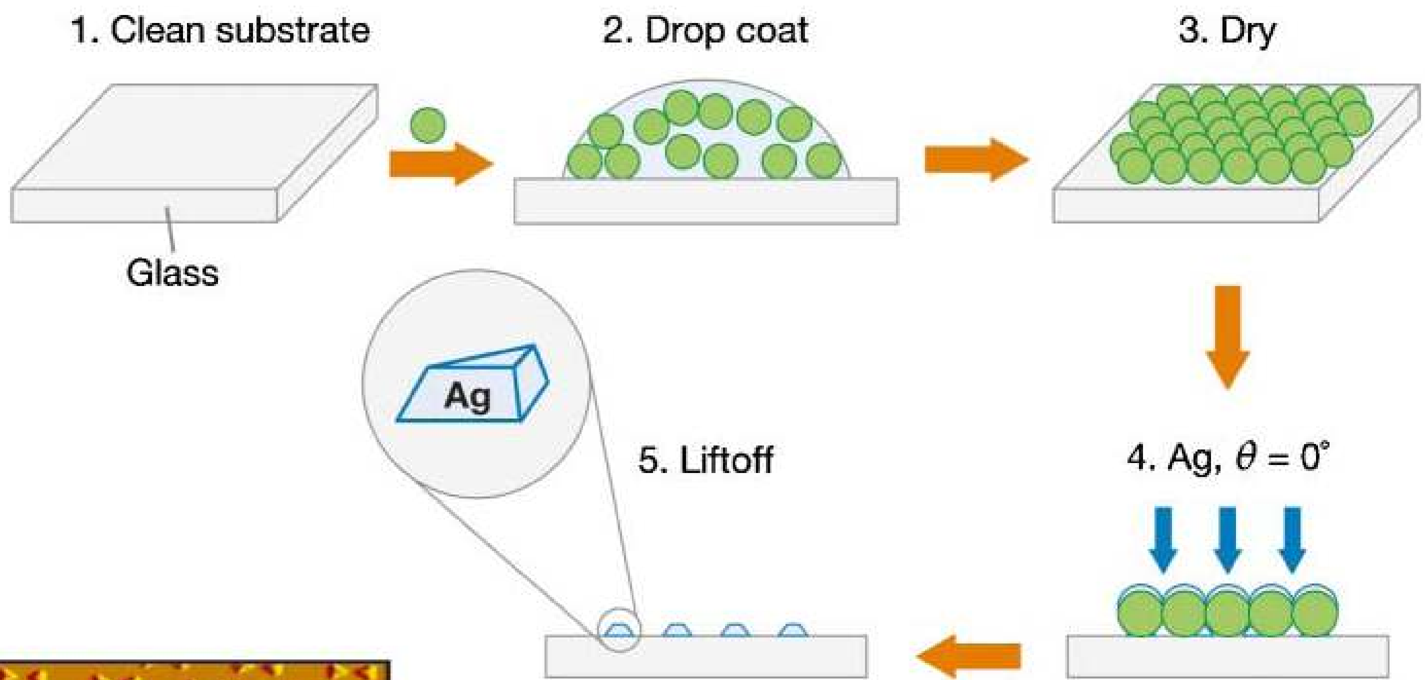
Photo
Optical Transmission
Transmission
Wavelegth [nm]

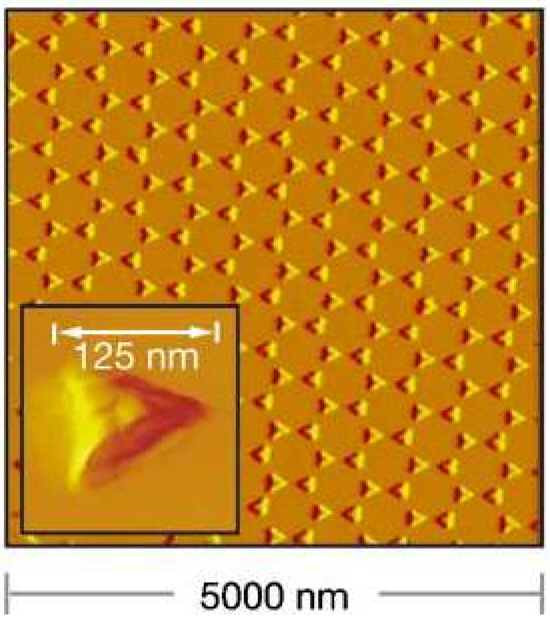
Optical Properties of Regular Arrays of Metallic Nanoparticles



- Optical Response of noble metal nanoparticles is dominated by the Localized **Surface Plasmon Resonance** (LSPR).
- Large **near-field enhancement** relative to incident field.
- **Tunable Optical Response** by altering particle size, shape, environment and proximity.

Large-area fabrication of plasmonic solar-cell structures

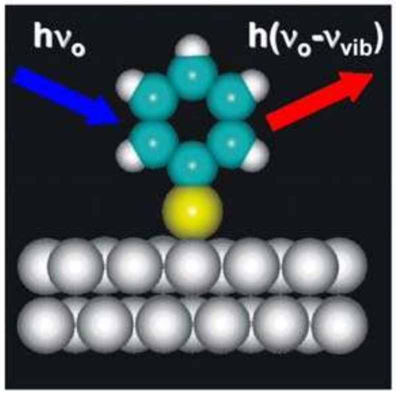


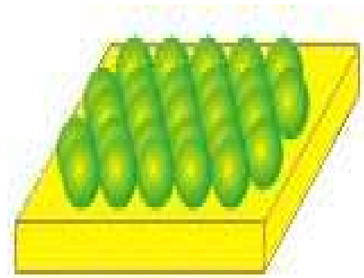


(*a) Illustration of the process of* ***nanosphere lithography (NSL)*** *in which nanospheres are drop* coated onto a surface and allowed to self-assemble into a hexagonally close-packed array (*steps 1–3), followed by metal deposition (step 4), and (optional) removal of the nanosphere mask. (b)* Atomic-force-microscope image of an NSL-fabricated nanoparticle array in which the nanosphere mask has been removed.

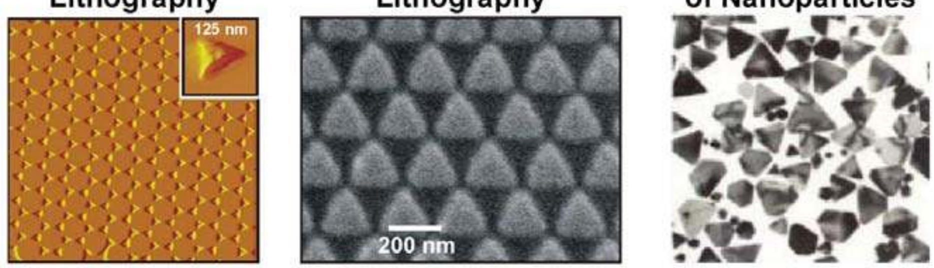
Our initiative at MIT-Manipal

Nanosphere Lithography



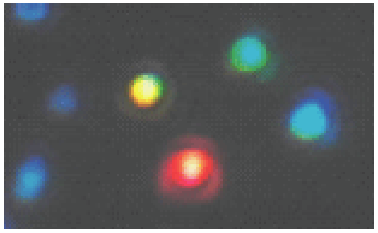


Nanosphere Lithography | Electron Beam Lithography | Chemical Synthesis of Nanoparticles

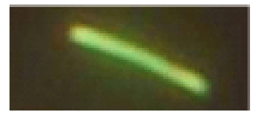


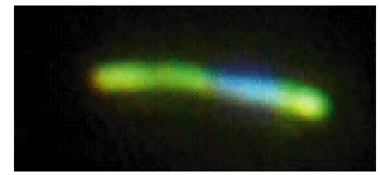
What are Plasmon Resonant Nanoparticles?

PRPs are metallic (silver or gold) nanoparticles, typically 40–100 nm in diameter, which scatter optical light elastically with remarkable efficiency because of a collective resonance of the conduction electrons in the metal (i.e., the surface plasmon resonance). The magnitude, peak wavelength, and spectral bandwidth of the plasmon resonance associated with a nanoparticle are dependent on the particle's size, shape, and material composition, as well as the local environment. A number of unique plasmon resonant nanoparticles are shown below.

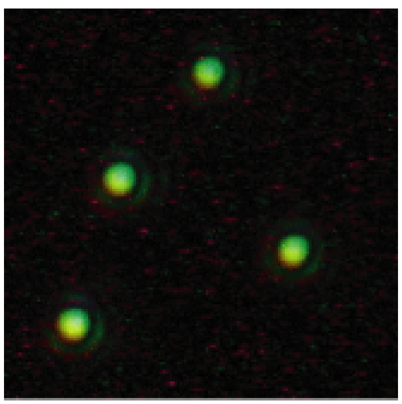


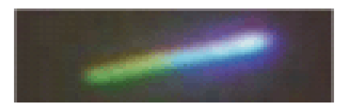
Colloidal Ag Nano particles

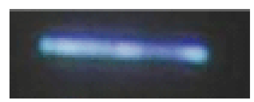


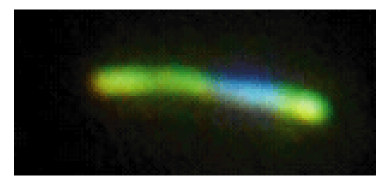


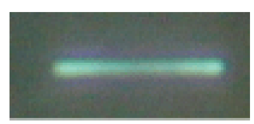
Metal Nano rods,Ag,Au.Ni





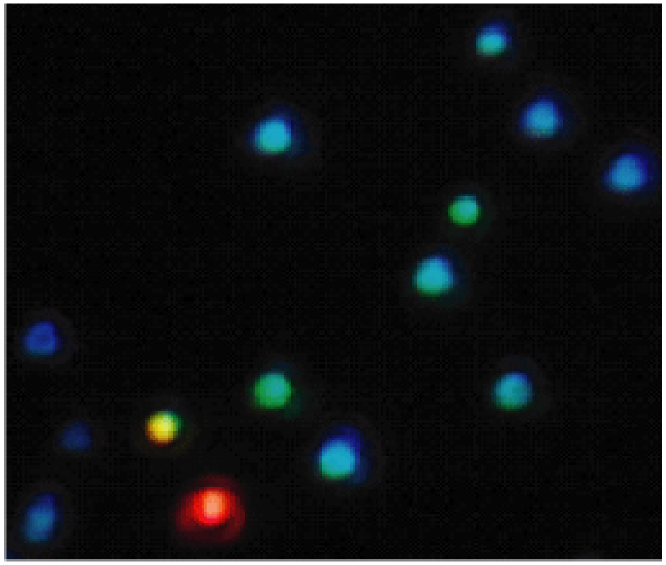


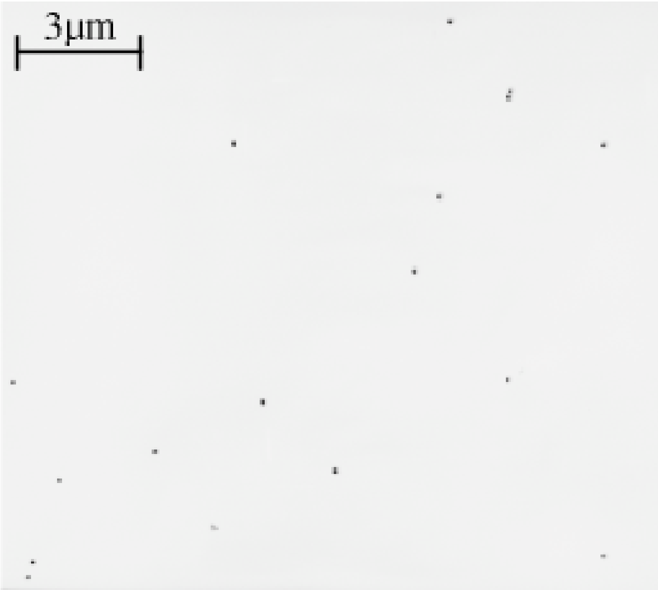




Colloidal Au Nano particles

Composite metal Nano rods





Dark field &
TEM images of
PRPS

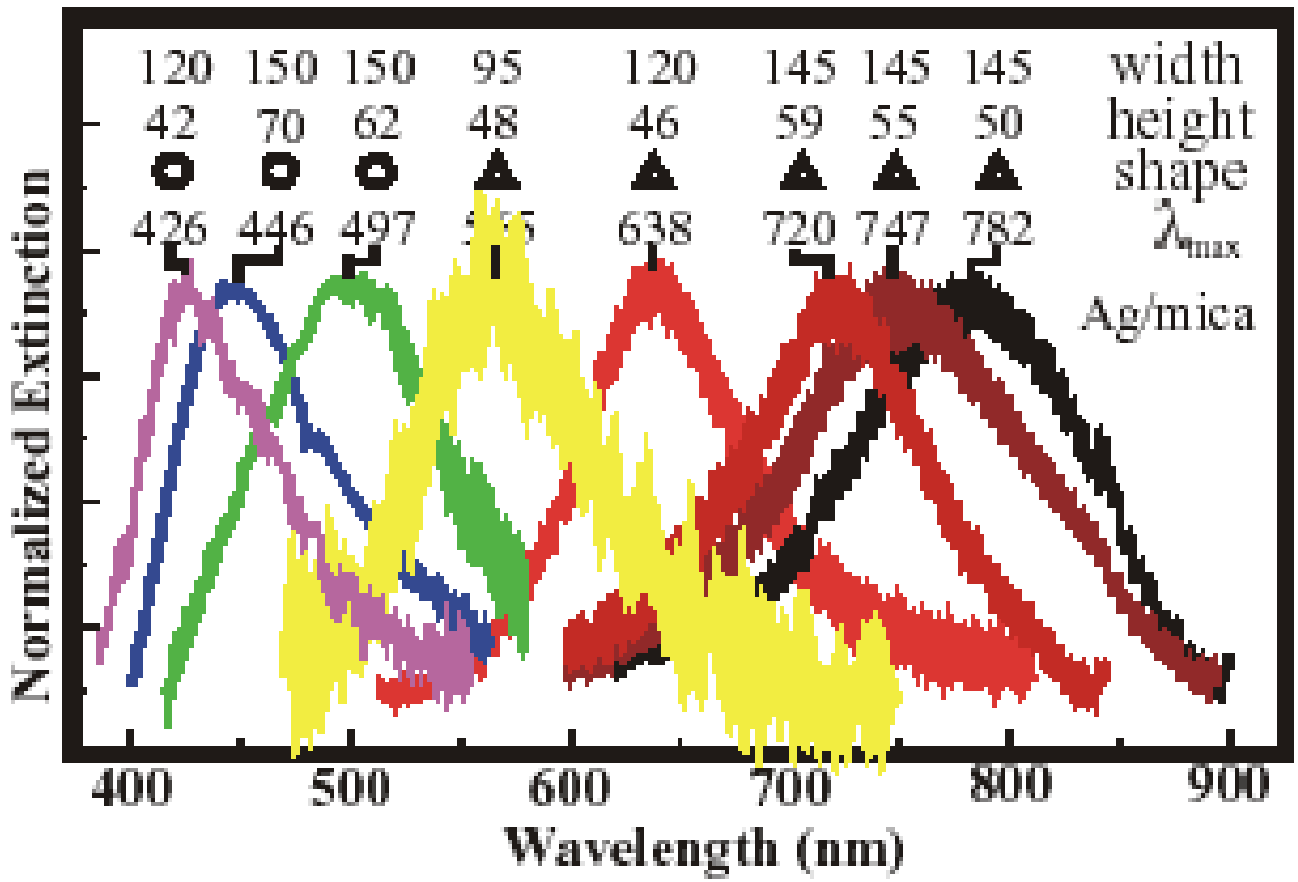


Figure 1. UV-vis extinction spectra of Ag nanoparticle arrays on mica substrates.

Van Dune

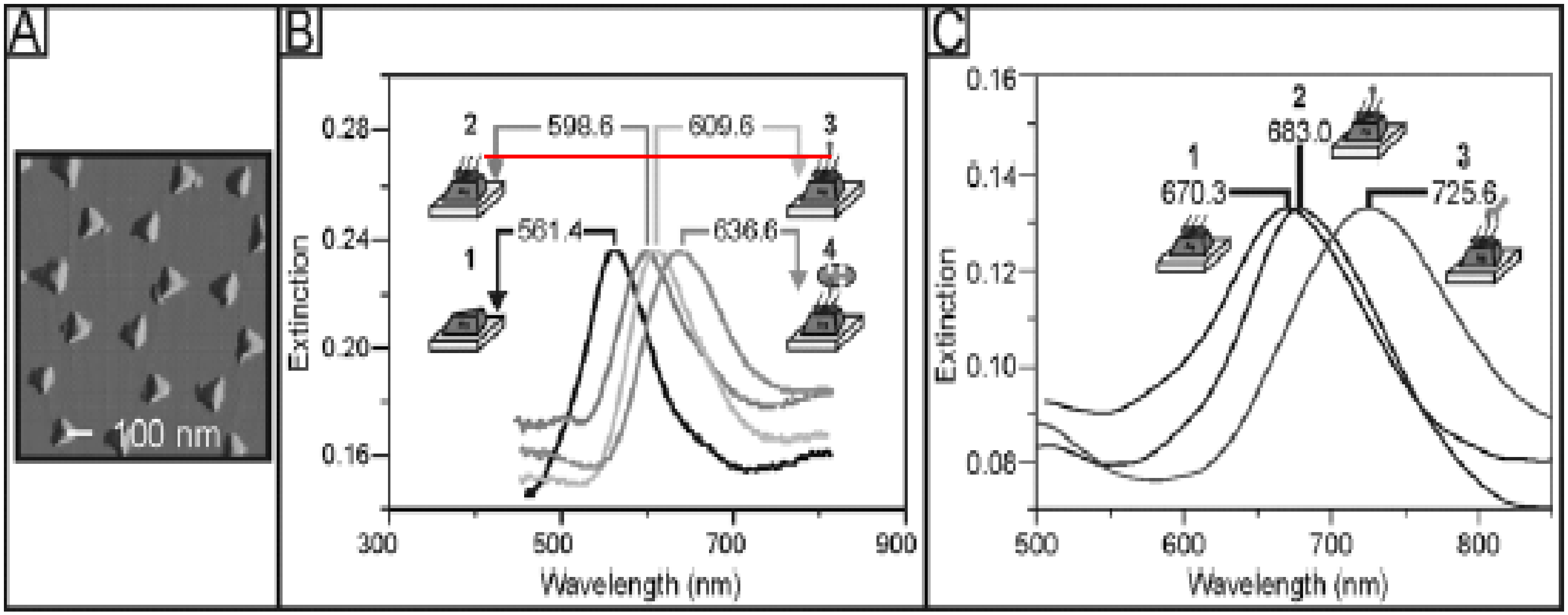
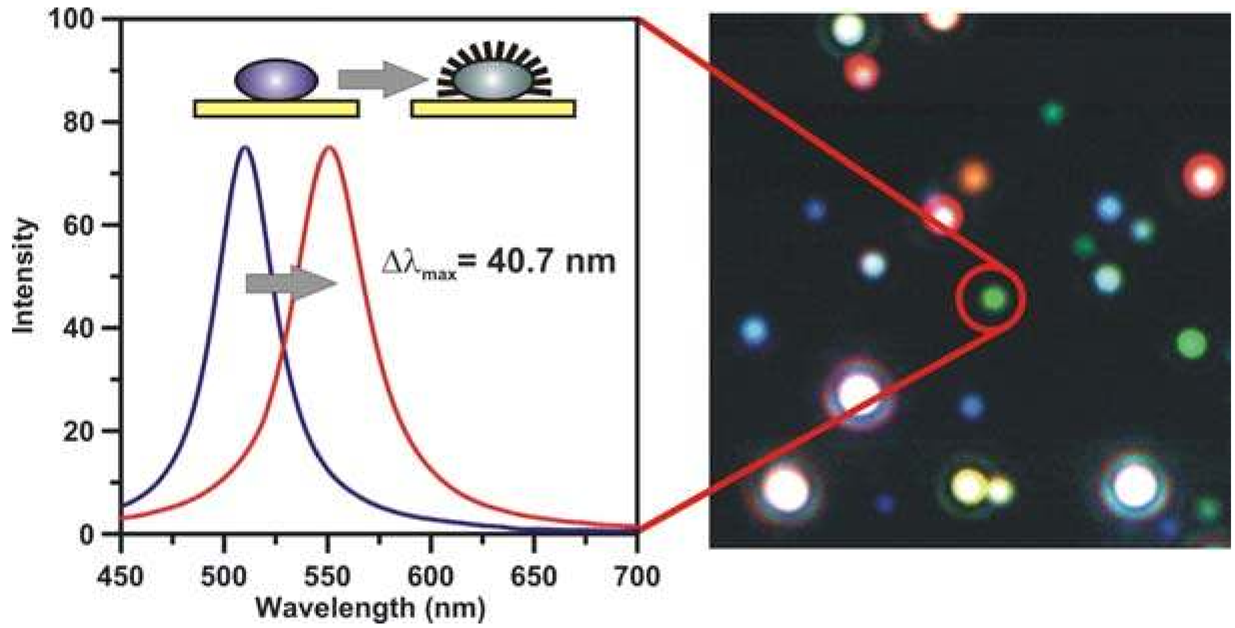


Figure 2. (A) Tapping mode AFM image of Ag nanoparticles (in-plane width~90 nm, out-of-plane widths~50 nm Ag on a mica substrate). Scan area, 1.0 μm^2. (B) LSPR spectra of each step in the surface modification of NSL-derived Ag nanoparticles to form a biotinylated Ag nanobiosensor and the specific binding of streptavidin. (1) Ag nanoparticles before chemical modification, λ_{max} = 561.4 nm. (2) Ag nanoparticles after modification with 1 mM 1:3 11-MUA:1-OT, λ_{max} = 598.6 nm. (3) Ag nanoparticles after modification with 1 mM biotin, λ_{max} = 609.6 nm. (4) Ag nanoparticles after modification with 100 nM streptavidin, λ_{max} = 636.6 nm. All extinction measurements were collected in a N_2 environment. (C) Smoothed LSPR spectra for each step of the preparation of the Ag nanobiosensor, and the specific binding of anti-biotin to biotin. (1) Ag nanoparticles after modification with 1 mM 3:1 1-OT/11-MUA, λ_{max} = 670.3 nm, (2) Ag nanoparticles after modification with 1 mM biotin, λ_{max} = 683.0 nm, and (3) Ag nanoparticles after modification with 700 nM anti-biotin, λ_{max} = 725.6 nm. All spectra were collected in a N_2 environment.

DBT Project at MIT-Manipal (PI.Dr.V.H.S.Moorthy).

Use the templates of nanostructured material developed using NSL, to identify signature spectra for Encephalitis viruses namely Herpes Simplex Viruses, Japanese encephalitis virus, Mumps virus and Enterovirus 71 using SERS. Once established, develop an assay for the rapid diagnosis of viral encephalitis using Cerebrospinal fluid (clinical specimen



Bright new world

New Scientist vol 178 issue 2392 - 26 April 2003, page 30

A strange discovery could spark a nanotechnology revolution, bringing perfect lenses, rapid medical tests and superfast computers.

THOMAS EBBESEN holds a piece of gold foil up to the light and looks through it. Made 14 years ago by technicians at the NEC Research Institute in Princeton, New Jersey - where Ebbesen was working at the time - at first glance the foil looks unremarkable. Peer at it under an electron microscope, though, and you would see that it is peppered with 100 million identical holes, each 200 times narrower than a human hair. But there's something much more extraordinary about the thin gold film: more light passes through the holes than strikes them.

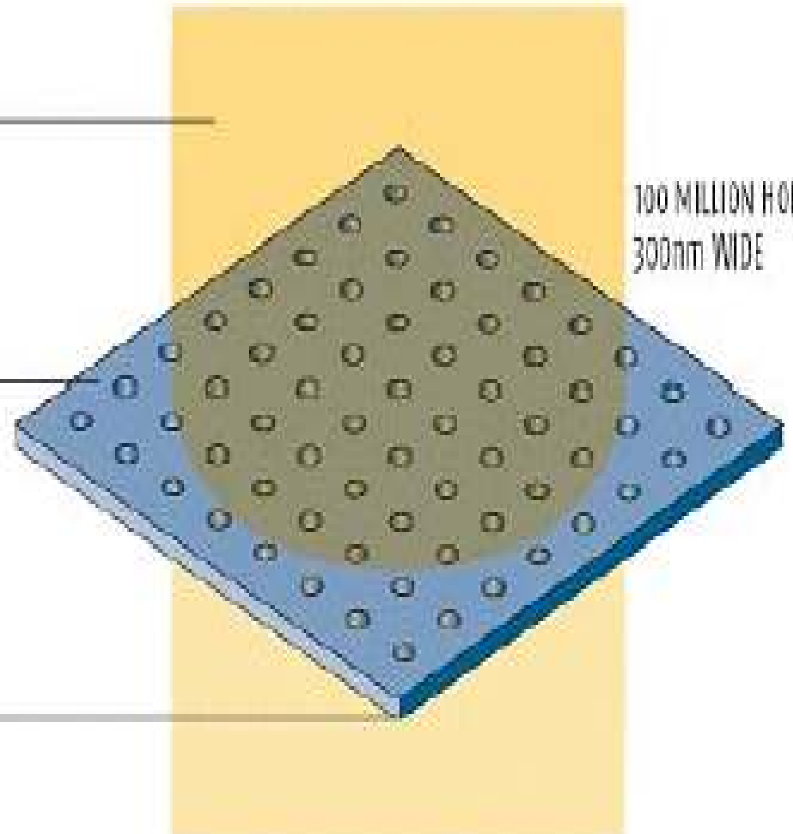
It is a finding that challenges our entire understanding of light. According to optical theory, at 300 nanometres across the holes are so small they should only let through 0.01 per cent of the visible light that falls directly on them. But Ebbesen's

experiment suggested they were transmitting more than 100 per cent. Somehow the metal was acting like a funnel,channelling all the light that hit the film through the nanoscale pores.

The phenomenon not only has theorists rethinking their approach to optics. It has sparked a new research effort called plasmonics that is revolutionising what we can do with light.

USING SURFACE PLASMONS TO CHANNEL LIGHT

Surface plasmons channel light towards the holes, so more is transmitted than expected



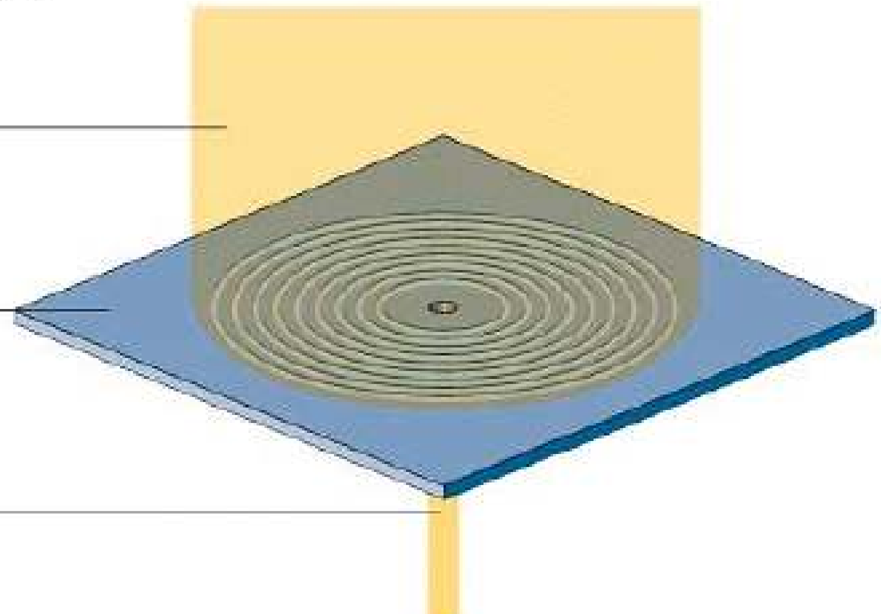
Light falls onto a thin metal film and excites surface plasmons on the metal foil

The surface plasmons accumulate so much energy around the holes that the resulting electric field penetrates the metal

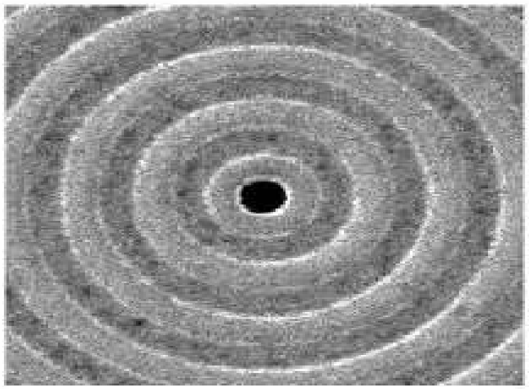
Surface plasmons on the underside of the metal foil convert the energy back into light

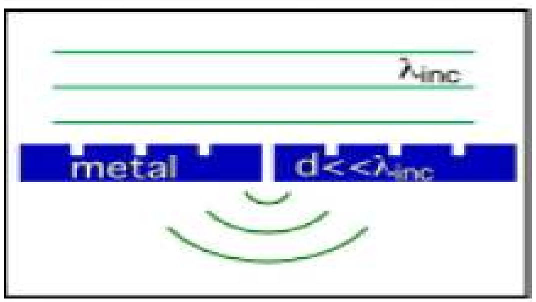
PLASMONIC BULLSEYE FIRES LIGHT BEAM

A pattern of concentric circles focuses light into a tight beam



Enhanced Transmission through Sub-λ Apertures





- Ag film with a 440 nm diameter hole surrounded by circular grooves
- Transmission enhancement of 10 x compared to a bare hole
- 3x more light than directly impingent on hole !
- Reason: Excitation of plasmon-polaritons

T. Thio et al., Optics Letters ***26,*** *1972-1974 (2001).*

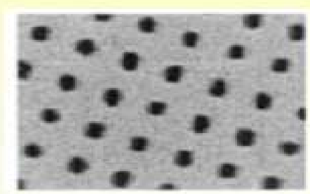
Can EOT be used to enhance Optical transmission though Ag films —replacement of ITO?

- **Extraordinary optical transmission** (**EOT**) is the phenomenon of greatly enhanced transmission of light through a subwavelength aperture in an otherwise opaque metallic film which has been patterned with a regularly repeating periodic structure.
- Generally when light of a certain wavelength falls on a subwavelength aperture, it is diffracted isotropically in all directions evenly, with minimal far-field transmission. This is the understanding from classical aperture theory as described by Bethe.
- **In EOT however, the regularly repeating structure enables much higher transmission efficiency to occur, up to several orders of magnitude greater than that predicted by classical aperture theory.**

- **This phenomenon is attributed to the presence of surface plasmon resonances and constructive interference. A surface plasmon (SP) is a collective excitation of the electrons at the junction between a conductor and an insulator and is one of a series of interactions between light and a metal surface called Plasmonics**

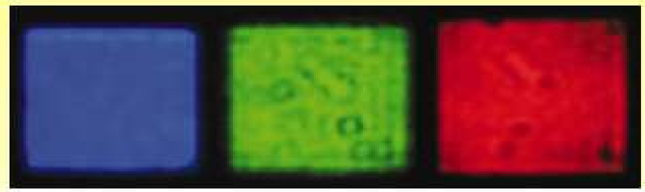
Extraordinary optical transmission through sub-wavelength hole arrays

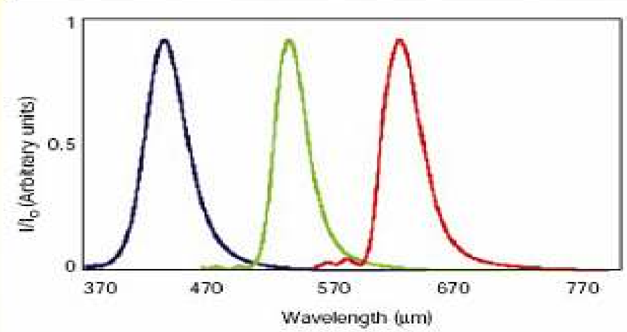
For a hole in a metal film, it is well known that the transmission of the normal incidence is in the order of $(r/\lambda)^4$, where r is the hole radius. Therefore, the transmission is very weak through a subwavelength hole.



For a subwavelength hole array, extraordinary optical transmission is observed. This is usually attributed to the **surface plasmon resonance**.

Nature, 391, 667, 1998
Thomas Ebbesen

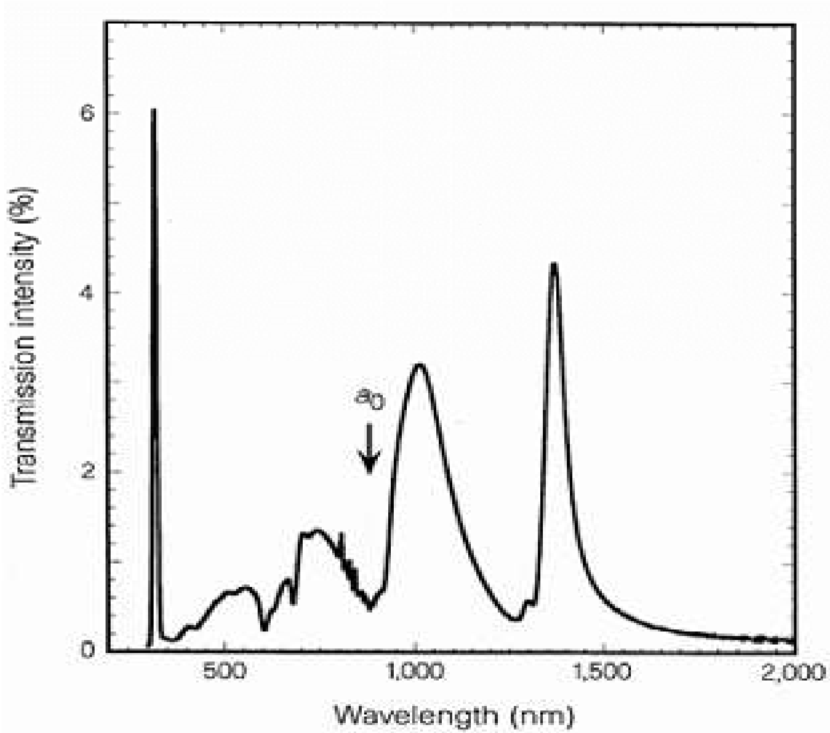




Wavelength of the peak transmission is usually the same as the lattice constant (distance between holes).

Potential applications for LED, PV, Detector, etc

Ebbesen, T.L., H.J. Lezec, H.F. Ghaemi, T. Thio, and P.A. Wolff. 1998. Extraordinary optical transmission through sub-wavelength hole arrays. *Nature* 391:667–669, doi:10.1038/35570.



3. Zero-order transmission spectrum for a square array of 150 nm holes with a period of 900 nm in a 200 nm thick Ag film. The maximum transmitted intensity occurs at 1370 nm, nearly ten times the diameter of an individual hole in the array (Ebbesen 1998).

- **Success Stories**
- **A Promising Alternative to Traditional Photovoltaic Materials**

- **NREL finds that random nanohole arrays become transparent conductors**
- Transparent conductors are essential to many thin-film photovoltaic (PV) applications but also to liquid-crystal display (LCD) and touch-sensitive displays that we use daily on mobile phones, computer tablet pads, and other touch screens. NREL researchers demonstrated a new conductor that uses arrays of nanosized holes in thin films of silver. While normally highly reflective, the thin films are perforated with nanosized holes, which provides them with a far more extensive transparency than merely the area of the holes.
- **Why it Matters**
- Scientists have been searching for an alternative transparent conductor for thin-film PVs and LCD screen applications. Although several candidates such as carbon nanotubes and graphene layers have been identified, NREL researchers have discovered another option. The new conductors show a transmission over 2.5 times larger than the physical area of the nanoholes and orders of magnitude larger than what is expected from classical diffraction of light on the holes.
- **Methods**
- The new transparent conductors are fabricated using a nanosphere lithography method that deposits latex nanoparticles (a low-cost component of paints), with sizes varying from 50 nm diameter to 100s of nanometers, from solution on a substrate such as glass. The density of the particles is easily controlled using the concentration of sodium chloride salt in the deposition solution. The particles then distribute by quickly dipping the samples in boiling pure water, which redistributes the particles to be equidistant from each other. Finally, a metal such as silver is deposited over these spheres, which are removed with a solvent that yields an array of holes in a metal electrode. Similar to ITO electrodes, these nanohole substrates can then be used to fabricate a solar cell without any changes to subsequent processing.
- The technology's extraordinary transmission capability is attributed to surface plasmons, which provide an antenna that pulls in more light than the area of the holes on one side and re-emits it on the other. These plasmons also enhance the interaction of light with the optical absorber in a solar cell, providing another way to increase the PV efficiency of such a cell.
- **What's Next**
- NREL has applied for a patent and also discussed the technology with interested partners. Additionally, researchers are studying plasmon activity of the nanohole electrodes in novel third-generation solar cell concepts. Results of these interactions could show great promise in breaking traditional limits of solar cell efficiency.

- **Appl. Phys. Lett. 92, 243304 (2008);**
- **Surface-plasmon enhanced transparent electrodes in organic photovoltaics**
- **Thomas H. Reilly, III1, Jao van de Lagemaat1, Robert C. Tenent2, Anthony J. Morfa2, and Kathy L. Rowlen2**
- **1National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393, USA**
  2Department of Chemistry and Biochemistry, University of Colorado, Boulder, 80309-0215, USA

- Random silver nanohole films were created through colloidal lithography techniques and metal vapor deposition. The transparent electrodes were characterized by uv-visible spectroscopy and incorporated into an organic solar cell. The test cells were evaluated for solar power-conversion efficiency and incident photon-to-current conversion efficiency. The incident photon-to-current conversion efficiency spectra displayed evidence that a nanohole film with 92 nm diameter holes induces surface-plasmon-enhanced photoconversion. The nanohole silver films demonstrate a promising route to removing the indium tin oxide transparent electrode that is ubiquitous in organic optoelectronics

- **Abstract**
- **Disordered nanohole arrays were formed in silver films by colloidal lithography techniques and characterized for their surface-plasmon activity.**
- **Careful control of the reagent concentration, deposition solution ionic strength, and assembly time allowed generation of a wide variety of nanohole densities.**
- **The fractional coverage of the nanospheres across the surface was varied from 0.05-0.36. Electrical sheet resistance measurements as a function of nanohole coverage fit well to percolation theory indicating that the electrical behavior of the films is determined by bulk silver characteristics.**
- **The transmission and reflection spectra were measured as a function of coverage and the results indicate that the optical behavior of the films is dominated by surface plasmon phenomena.**
- **Angle-resolved transmission and reflection spectra were measured, yielding insight into the nature of the excitations taking place on the metal films. The tunability of the colloidal lithography assembly method holds much promise as a means to generate customized transparent electrodes with high surface plasmon activity throughout the visible and NIR spectrum over large surface areas.**

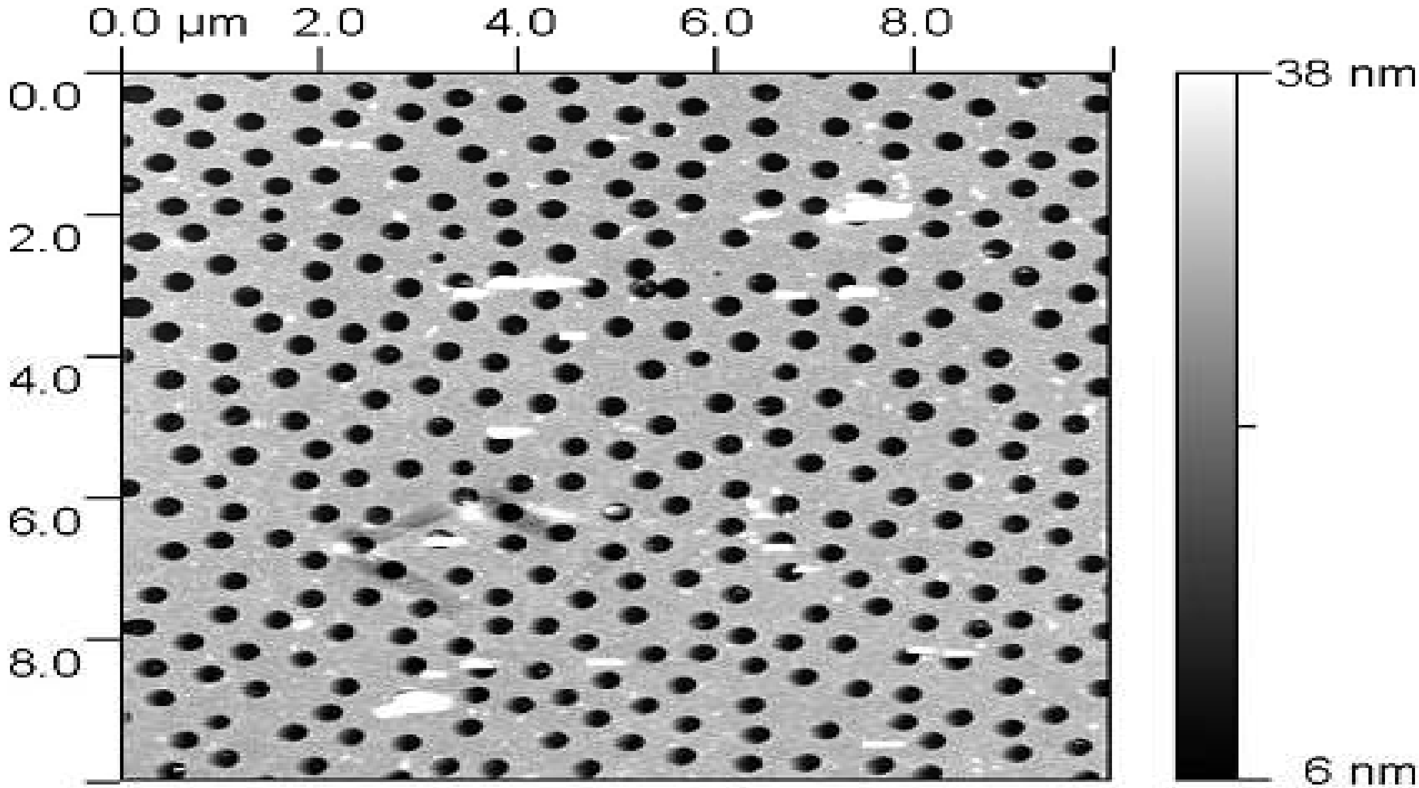


FIG. 1. Atomic force micrograph of 30-nm silver nanohole film fabricated by the colloidal lithography method using 350-nm latex spheres.

By Nanoshere Lithography

APPLIED PHYSICS LETTERS **99**, 103306 (2011)

Self-assembled plasmonic electrodes for high-performance organic photovoltaic cells

Wade A. Luhman,[1] Si Hoon Lee,[2] Timothy W. Johnson,[2] Russell J. Holmes,[1,a)] and Sang-Hyun Oh[2,b)]

[1]*Department Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA*

[2]*Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota 55455, USA*

(Received 11 May 2011; accepted 6 August 2011; published online 9 September 2011)

We investigate thin Ag films incorporating plasmonic nanohole arrays as transparent conducting electrodes for organic photovoltaic cells. Plasmonic electrodes are fabricated using nanosphere lithography to create hexagonal nanohole arrays over centimeter-sized areas. Devices constructed using a nanopatterned Ag anode show power conversion efficiencies that exceed those of devices constructed on conventional indium-tin-oxide, independent of light polarization. In comparison to cells constructed on unpatterned Ag, the power conversion efficiency is noted to double with patterning. © *2011 American Institute of Physics*. [doi:10.1063/1.3635385]

- **Appl. Phys. Lett. 93, 123308 (2008);**

- **Plasmonic nanocavity arrays for enhanced efficiency in organic photovoltaic cells**

- Nathan C. Lindquist1, Wade A. Luhman2, Sang-Hyun Oh1, and Russell J. Holmes2
- *1Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota 55455, USA*
  2Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA

- **We demonstrate enhanced power conversion efficiency in organic photovoltaic (OPV) cells incorporated into a plasmonic nanocavity array. The nanocavity array is formed between a patterned Ag anode and an unpatterned Al cathode.**
- **This structure leads to the confinement of optical energy and enhanced absorption in the OPV. Devices characterized under simulated solar illumination show a 3.2-fold increase in power conversion efficiency compared to OPVs with unpatterned Ag anodes. The observed enhancement is also reflected in the external quantum efficiency, and the spectral response is consistent with optical finite-difference time-domain simulations of the structure.**

Self-Assembled Plasmonic Nanohole Arrays

Si Hoon Lee,†, Kyle C. Bantz,, Nathan C. Lindquist,§ Sang-Hyun Oh,*, and Christy L. Haynes*,

Langmuir 2009, 25(23), 13685–13693

- The work presented herein **capitalizes on the nanosphere lithography (NSL) technique conceived of (as "natural lithography") by Deckman et al.and popularized by Van Duyne and co-workers**.
- Instead of employing an as-assembled 2D colloidal array as a shadow mask for nanostructure deposition, this work employs a reactive ion etching (RIE) step to shrink the nanospheres before metal deposition, facilitating the formation of nanohole arrays after removal of the nanospheres.
- By controlling the original nanosphere size, etching time, metal deposition thickness, and metal deposition angle, it is possible to tune the nanohole spacing, size and aspect ratio, and, accordingly, the plasmonic properties .

HOLEY Electrode Grids

US008039292B2

(12) **United States Patent**
Guha et al.

(10) **Patent No.: US 8,039,292 B2**
(45) **Date of Patent: Oct. 18, 2011**

(54) **HOLEY ELECTRODE GRIDS FOR PHOTOVOLTAIC CELLS WITH SUBWAVELENGTH AND SUPERWAVELENGTH FEATURE SIZES**

(75) Inventors: **Supratik Guha**, Yorktown Heights, NY (US); **Oki Gunawan**, Yorktown Heights, NY (US)

(73) Assignee: **International Business Machines Corporation**, Armonk, NY (US)

7,033,936	B1 *	4/2006	Green	438/669
7,087,833	B2	8/2006	Scher et al.	
7,110,154	B2 *	9/2006	Ballato et al.	359/245
7,179,988	B2 *	2/2007	Spivack et al.	136/263
7,385,231	B2 *	6/2008	Fujimoto et al.	257/121

(Continued)

FOREIGN PATENT DOCUMENTS

JP 2010157681 A * 7/2010

(Continued)

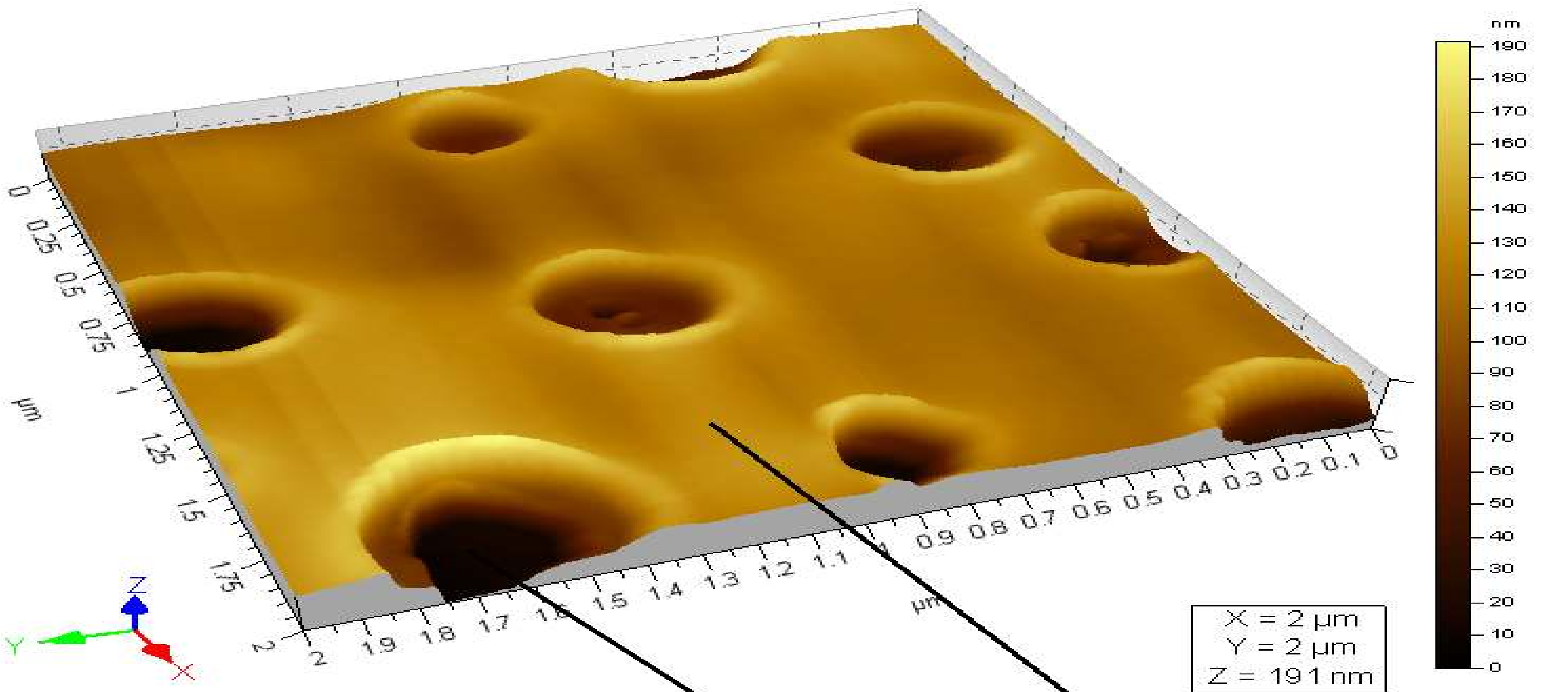
OTHER PUBLICATIONS

By Nanoshere Lithography

(57) **ABSTRACT**

A photovoltaic cell and a method of forming an electrode grid on a photovoltaic semiconductor substrate of a photovoltaic cell are disclosed. In one embodiment, the photovoltaic cell comprises a photovoltaic semiconductor substrate; a back electrode electrically connected to a back surface of the substrate; and a front electrode electrically connected to a front surface of the substrate. The substrate, back electrode, and front electrode form an electric circuit for generating an electric current when said substrate absorbs light. The front electrode is comprised of a metal grid defining a multitude of holes. These holes may be periodic, aperiodic, or partially periodic. The front electrode may be formed by depositing nanospheres on the substrate; forming a metallic layer on the substrate, around the nanospheres; and removing the nanospheres, leaving an electrode grid defining a multitude of holes on the substrate.

Courtesy,
Dr. Rabibrata Mukjerjee IIT-Kgp

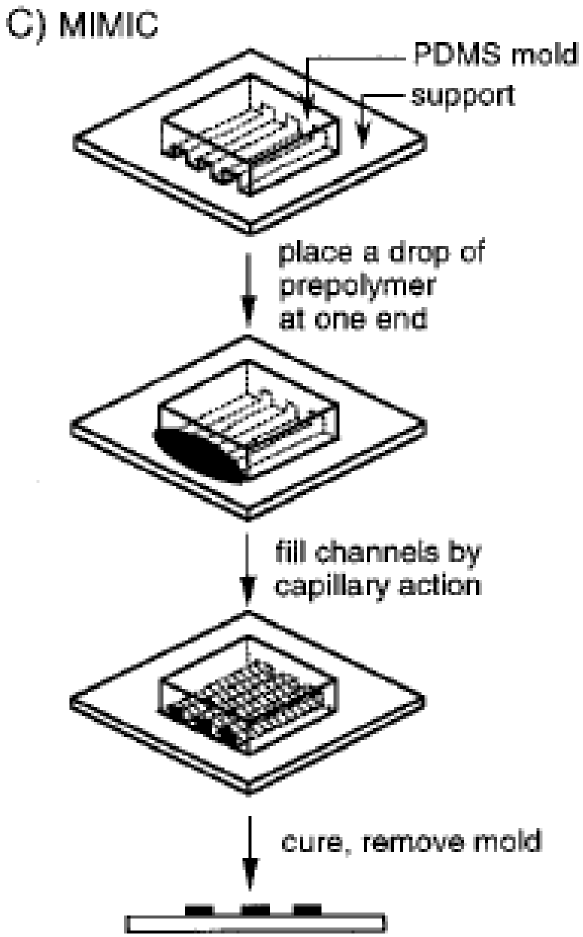


Holes created giving direct access to the silicon wafer substrate over areas where PMMA columns was

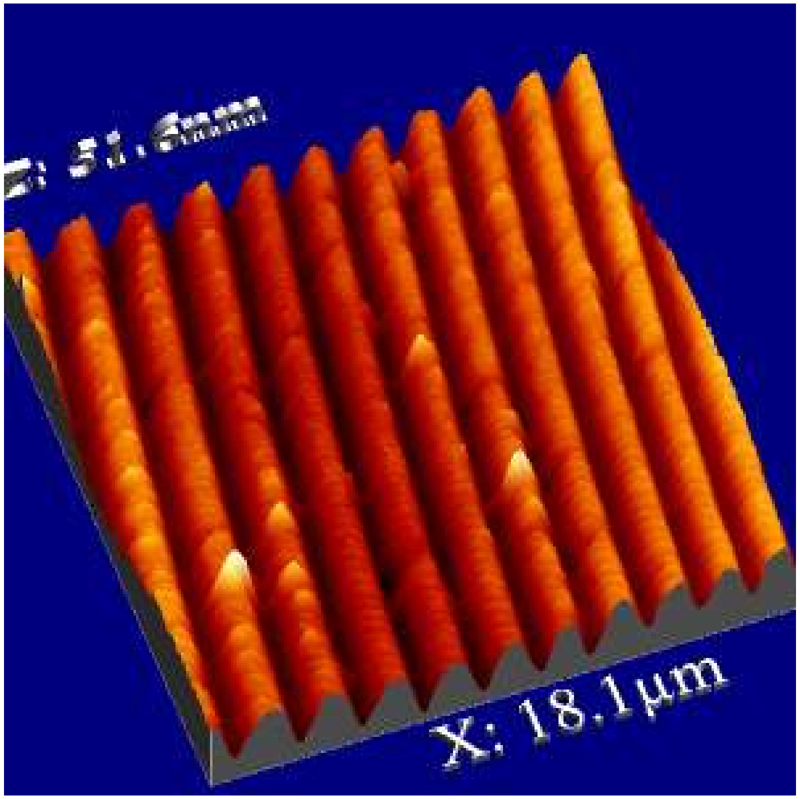
Dia roughly 300 nm

Intact Polystyrene Film

Patterning Technique: Micro Molding In Capillaries



Modified to meet the requirement of Sol – Gel Techniques.



Rabibrata /iitkgp

nature materials

REVIEW ARTICLE

PUBLISHED ONLINE: 19 FEBRUARY 2010 | DOI: 10.1038/NMAT2630

Plasmonics for extreme light concentration and manipulation

Jon A. Schuller, Edward S. Barnard, Wenshan Cai, Young Chul Jun, Justin S. White and Mark L. Brongersma*

The unprecedented ability of nanometallic (that is, plasmonic) structures to concentrate light into deep-subwavelength volumes has propelled their use in a vast array of nanophotonics technologies and research endeavours. Plasmonic light concentrators can elegantly interface diffraction-limited dielectric optical components with nanophotonic structures. Passive and active plasmonic devices provide new pathways to generate, guide, modulate and detect light with structures that are similar in size to state-of-the-art electronic devices. With the ability to produce highly confined optical fields, the conventional rules for light-matter interactions need to be re-examined, and researchers are venturing into new regimes of optical physics. In this review we will discuss the basic concepts behind plasmonics-enabled light concentration and manipulation, make an attempt to capture the wide range of activities and excitement in this area, and speculate on possible future directions.

nature materials

REVIEW ARTICLE

PUBLISHED ONLINE: 19 FEBRUARY 2010 | DOI: 10.1038/NMAT2629

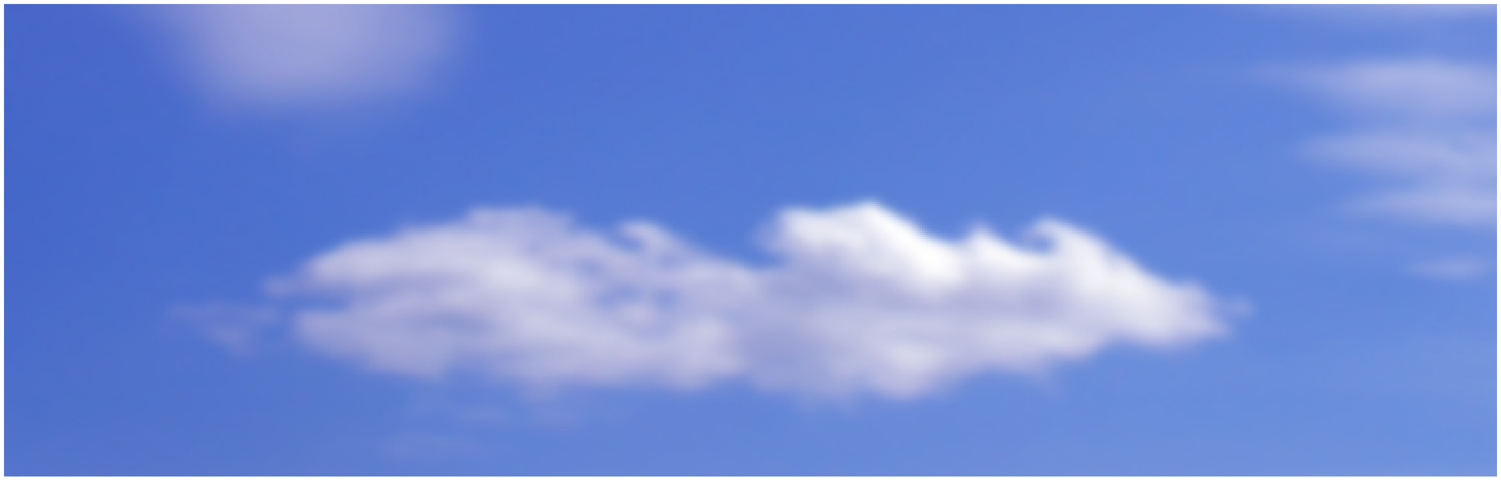
Plasmonics for improved photovoltaic devices

Harry A. Atwater[1]* and Albert Polman[2]*

The emerging field of plasmonics has yielded methods for guiding and localizing light at the nanoscale, well below the scale of the wavelength of light in free space. Now plasmonics researchers are turning their attention to photovoltaics, where design approaches based on plasmonics can be used to improve absorption in photovoltaic devices, permitting a considerable reduction in the physical thickness of solar photovoltaic absorber layers, and yielding new options for solar-cell design. In this review, we survey recent advances at the intersection of plasmonics and photovoltaics and offer an outlook on the future of solar cells based on these principles.

- **Scattering and Absorption**
- **The basic principles for the functioning of plasmonic solar cells include scattering and absorption of light due to the deposition of metal nanoparticles. Silicon does not absorb light very well**.
- For this reason, more light needs to be scattered across the surface in order to increase the absorption. It has been found that metal nanoparticles help to scatter the incoming light across the surface of the silicon substrate under very specific conditions.

Blue light is scattered more than red light



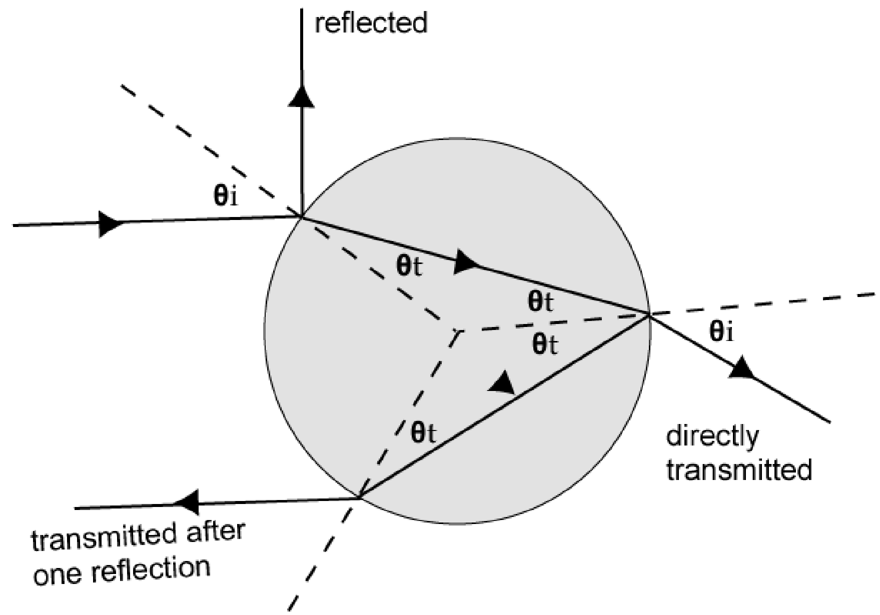
Scattering by small gas molecules in the atmosphere:

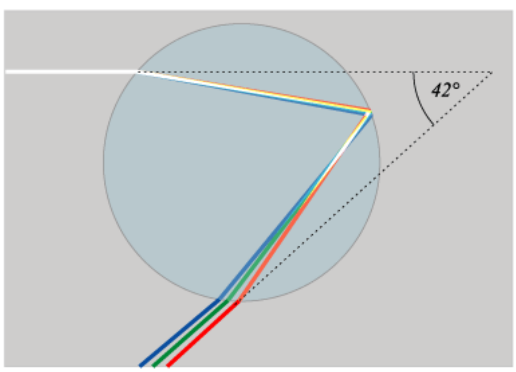
d<< λ: Rayleigh scattering

Geometrical scattering (d>>λ)

For particles very large compared to λ, the incident plane wave can be subdivided into a large number of rays which obey Snell's law and Fresnel Equations.

For complex ε, the energy W_{abs} absorbed in the sphere depends on the absorption of the dielectric and the time the light spends in the particle (the optical path length)





Rainbow formation

This has been demonstrated in OPV

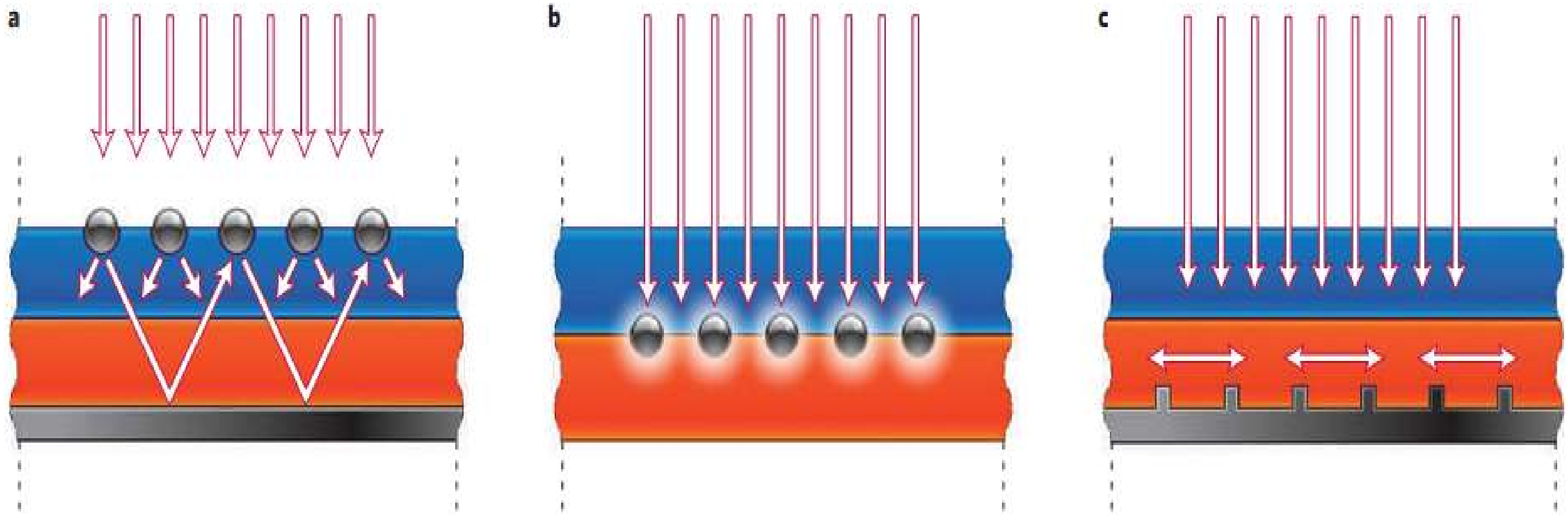


Figure 2 | Plasmonic light-trapping geometries for thin-film solar cells. a, Light trapping by scattering from metal nanoparticles at the surface of the solar cell. Light is preferentially scattered and trapped into the semiconductor thin film by multiple and high-angle scattering, causing an increase in the effective optical path length in the cell. **b**, Light trapping by the excitation of localized surface plasmons in metal nanoparticles embedded in the semiconductor. The excited particles' near-field causes the creation of electron–hole pairs in the semiconductor. **c**, Light trapping by the excitation of surface plasmon polaritons at the metal/semiconductor interface. A corrugated metal back surface couples light to surface plasmon polariton or photonic modes that propagate in the plane of the semiconductor layer.

Brief History

•**Stuart and Hall**: Photocurrent enhancement by 18x with 165nm SOI photodetector with wavelength of 800nm using silver nanoparticles used for scattering and absorption of light.

Schaadt: Gold nanoparticles used for scattering and absorption of light on doped silicon obtaining 80% enhancements with 500nm wavelength.

Derkacs: Gold nanoparticles on thin-film silicon gaining 8% on conversion efficiency.

Pillai: Silver particles on SOI obtaining 33% photocurrent increase.
Stenzel: Enhancements in photocurrent by a factor of 2.7 for ITO-copper phthalocyanine-indium structures.

Westphalen: Enhancement for silver clusters incorporated into ITO and zinc phthalocyanine solar cells.

Rand: Enhanced efficiencies for ultra thin film organic solar cells due to 5nm diameter silver nanoparticles.

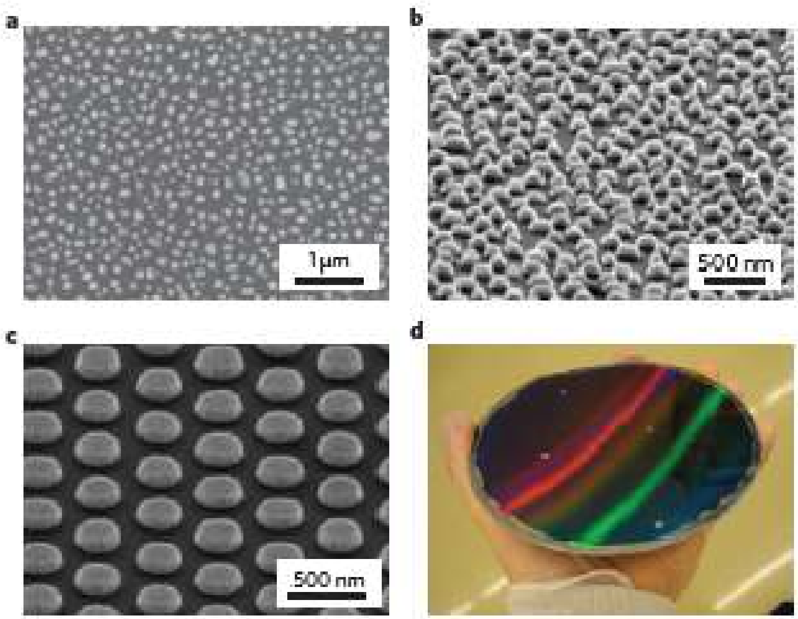
nature materials

REVIEW ARTICLE

PUBLISHED ONLINE: 19 FEBRUARY 2010 | DOI: 10.1038/NMAT2629

Plasmonics for improved photovoltaic devices

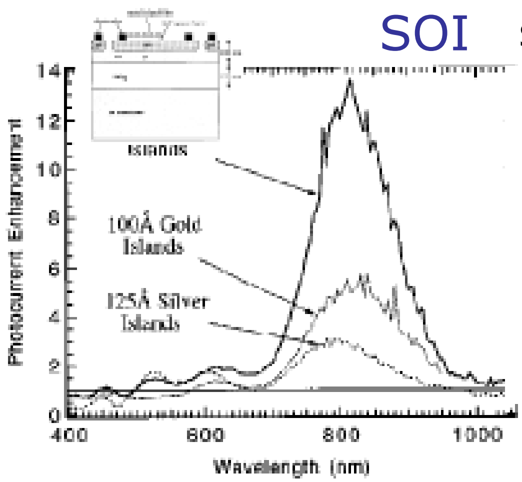
Harry A. Atwater[1*] and Albert Polman[2*]



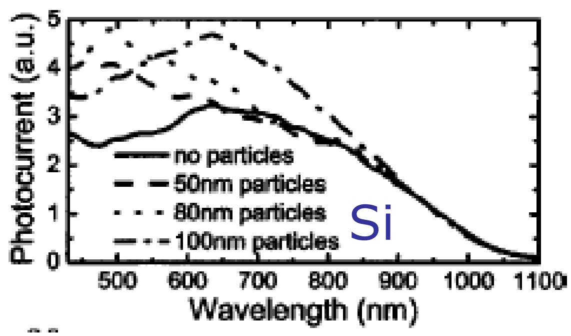
- **K. R. Catchpole and A. Polman**
  We develop fundamental design principles for increasing the efficiency of solar cells using light trapping by scattering from metal nanoparticles.
- We show that cylindrical and hemispherical particles lead to much higher path length enhancements than spherical particles, due to enhanced near-field co ... [Appl. Phys. Lett. 93, 191113 (2008)]

Plasmon-enhanced photocurrent: 5 examples

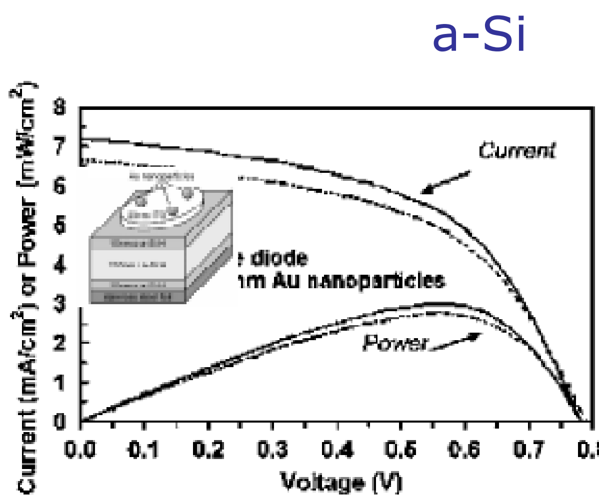
Stuart and Hall, APL **69**, 2327 (1996)



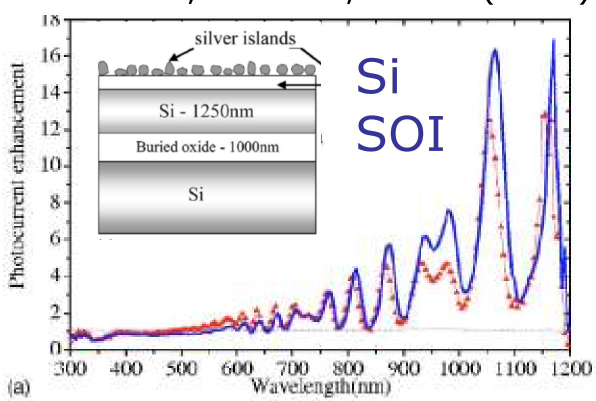
Schaadt *et al.*, APL **86**, 63106 (2005)



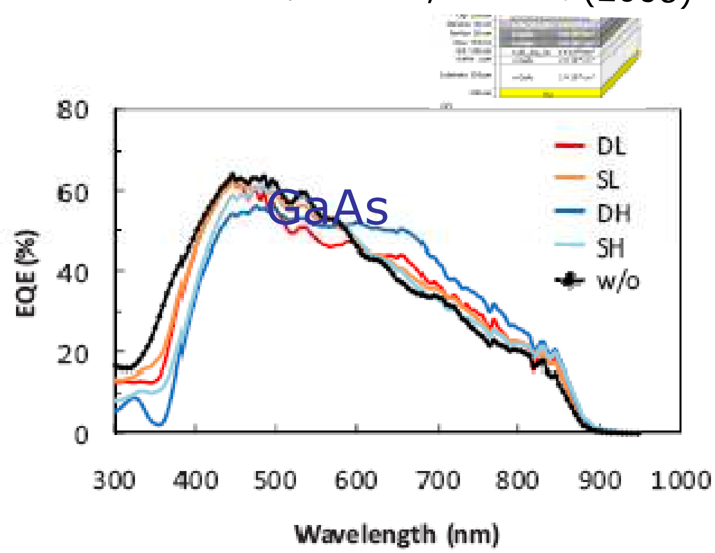
Derkacs *et al.*, APL **89**, 93103 (2006)



Pillai *et al.*, JAP **101**, 93105 (2007)



Nakayama *et al.*, APL **93**, 121904 (2008)



Metal Nanoparticles, Sterioids for Solar Cells

- **"I think we are about three years from seeing plasmons in photovoltaic generation," says Catchpole**, who has now started a new group studying surface plasmons at the Australian National University. **"An important point about plasmonic solar cells is that they are applicable to any kind of solar cell." This includes the standard silicon or newer thin-film types.**

Plasmonic Polymer Tandem Solar cell, Jun Yang et al. ,ACS Nano, 2011,5 (8), pp 6210-6217

Plasmonic Polymer Tandem Solar Cell

Jun Yang,[†,⊥] Jingbi You,[†,⊥] Chun-Chao Chen,[†] Wan-Ching Hsu,[†] Hai-ren Tan,[‡] Xing Wang Zhang,[‡] Ziruo Hong,[§] and Yang Yang[†,*]

[†]Department of Materials Science and Engineering and California NanoSystems Institute, University of California Los Angeles, Los Angeles, California 90095, United States, [‡]Key Lab of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Science, Beijing, 100083, People's Republic of China, and [§]Graduate School of Science and Enginnering, Yamagata University, Yonezawa, Yamagata, 9928510, Japan. [⊥]These authors contributed equally to this work.

Figure 1. (a) Schematic of plasmonic polymer tandem solar cell, ITO/TiO_2:Cs/P3HT:$IC_{60}BA$/PEDOT:Au/TiO_2:Cs/PSBTBT:$PC_{70}BM$/MoO_3/Al, (b) AFM images of monolayer Au NPs adsorbed on ITO substrate, (c) TEM images of Au NPs, (inset) magnified TEM image of Au NPs, and (d) TEM image of PEDOT:Au.

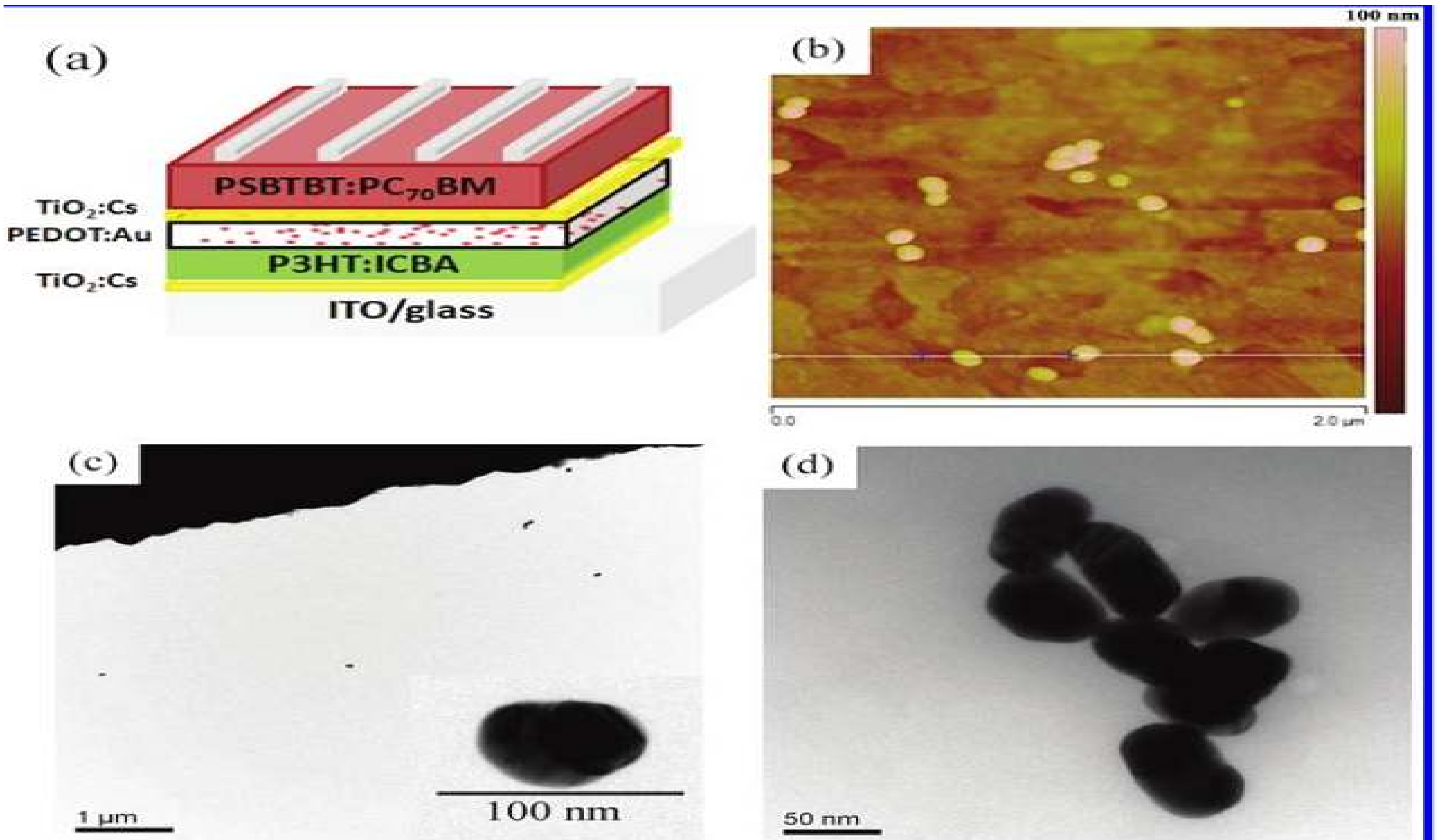


TABLE 1. Tandem and Single-Cell Performance with and without Au NPs

device	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
w/o Au (tandem)	1.455	6.06	59.22	5.22
with Au (tandem)	1.457	6.92	61.91	6.24
w/o Au (front cell)	0.830	6.81	61.81	3.49
with Au (front cell)	0.829	7.95	64.52	4.25
w/o Au (rear cell)	0.630	11.54	39.82	2.89
with Au (rear cell)	0.635	12.65	40.01	3.21

Solar energy

Seeing red

To make solar cells more efficient, sprinkle them with silver

MAKERS of solar cells face a dilemma. Purified silicon, the basic material of such cells, is expensive. The temptation, therefore, is to use less of it. As a result, the makers have developed a generation of cells whose silicon layers are only a micron or two deep, as opposed to the usual thickness of 200-300 microns. The thinner the cell, however, the less efficient it is. In particular, thin cells fail to capture much light at the red end of the spectrum. That means they produce up to 20% less electricity than standard cells of equivalent area. And that negates some of the advantage of their initial cheapness.

To remedy this problem, Kylie Catchpole of the Australian National University in Canberra and Albert Polman of the Institute for Atomic and Molecular Physics in Amsterdam have been trying to redirect the light that falls onto the surface of a cell in such a way that all colours are efficiently absorbed. Their chosen tools for this task are tiny particles of silver.

When struck by light, the electrons in an atom of silver vibrate in a way that causes them to radiate small amounts of light themselves. If the atom in question is in a small particle on the surface of a piece of silicon, the result is what is known as a surface plasmon. This is a type of electromagnetic wave (ie, the same type of wave as a light wave). However, as its name suggests, it runs parallel to the surface of the material that is propagating it, rather than penetrating this material.

By travelling horizontally in this way, a plasmon passes through more of the solar cell's silicon than any incident beam from the sun could. In effect, the cell has been turned on its side and made much thicker. That gives it the opportunity to absorb, and thus convert into electricity, most of the red light falling on it, as well as the blue. Indeed, Dr Catchpole and Dr Polman report in *Optics Express* that their system increases the absorption of red light tenfold—bringing the efficiency of thin cells much closer to that of the traditional sort.

Of course, silver is expensive. But so little is used that the new technique would add only a few cents to the price of a solar panel. And it would bring the day closer when solar electricity is as cheap as that generated from coal. ■

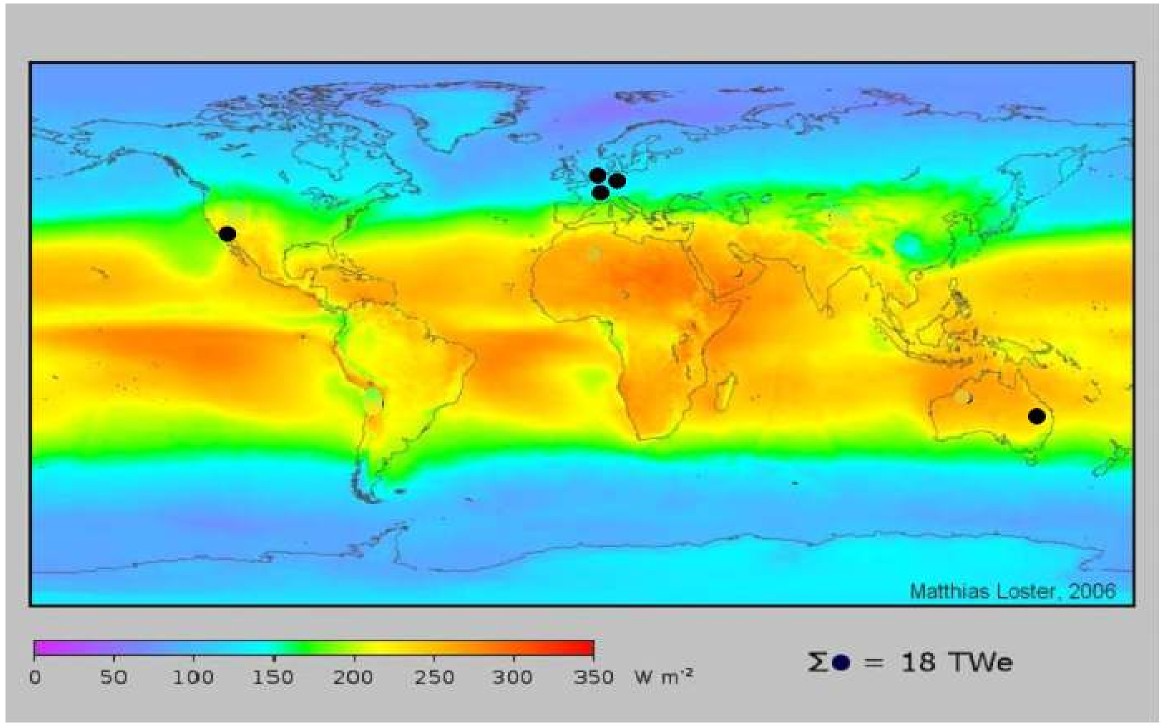
A little magic dust

The Economist
January 20, 2009

Black dots:

area of solar panels needed to generate all of the worlds energy

assuming 8% efficient photovoltaics



FOM Institute
AMOLF

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Plasmonics in Communication

Plasmonics: the next chip-scale technology

The development of chip-scale electronics and photonics has led to remarkable data processing and transport capabilities that permeate almost every facet of our lives. Plasmonics is an exciting new device technology that has recently emerged. It exploits the unique optical properties of metallic nanostructures to enable routing and manipulation of light at the nanoscale. A tremendous synergy can be attained by integrating plasmonic, electronic, and conventional dielectric photonic devices on the same chip and taking advantage of the strengths of each technology.

“Materials Today" JULY-AUGUST 2006 | VOLUME 9 | NUMBER 7-8

Appl. Phys. A 89, 221–223 (2007)
DOI: 10.1007/s00339-007-4151-1

Applied Physics A
Materials Science & Processing

M.L. BRONGERSMA[✉]
R. ZIA[*]
J.A. SCHULLER

Plasmonics – the missing link between nanoelectronics and microphotonics

Geballe Laboratory for Advanced Materials, Stanford University, Stanford, CA, 94305 USA

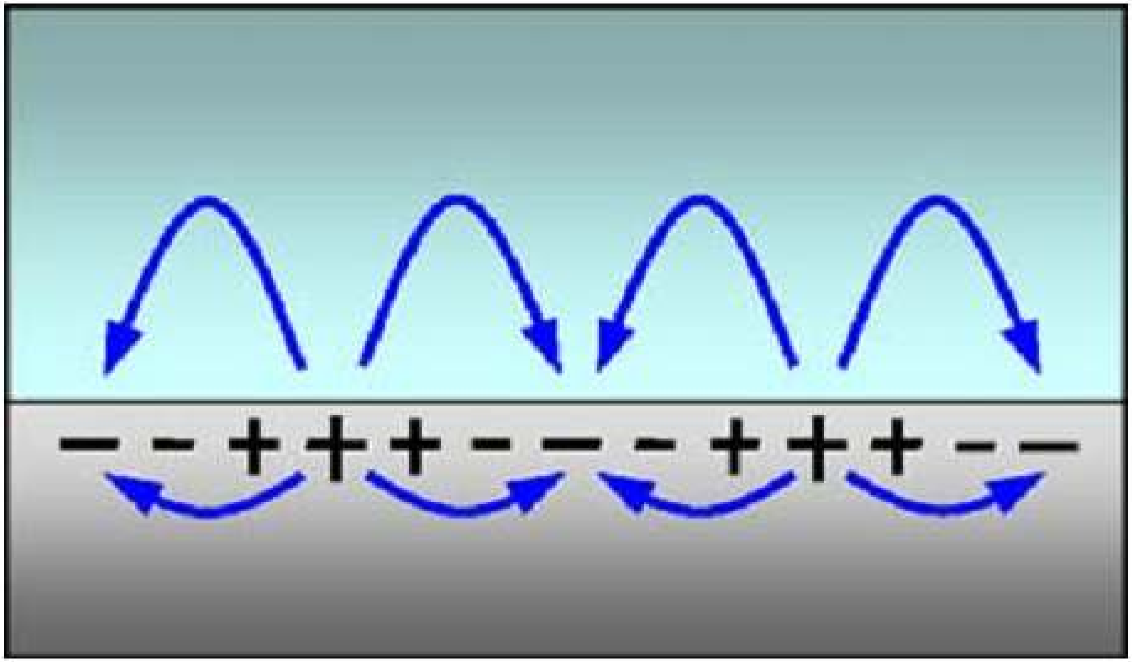
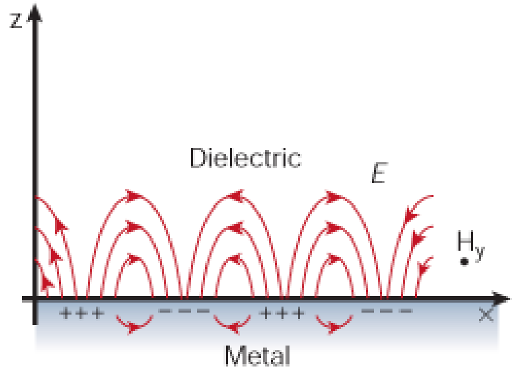


FIGURE 1 Surface plasmon–polariton (SPP) propagating along a metal–dielectric interface. These waves are transverse magnetic (TM) in nature. Their electromagnetic field intensity is highest at the surface and decays exponentially away from the interface

MOTIVATION

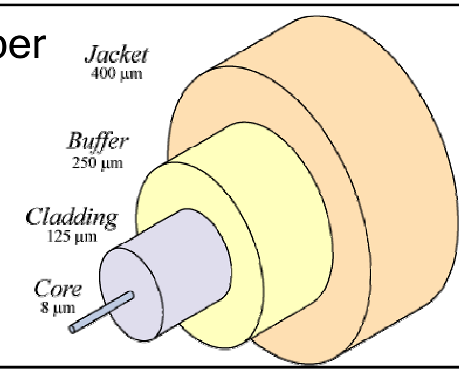


Surface plasmons have a combined electromagnetic wave and surface charge character

They reside at the interface between a metal and a dielectric material.

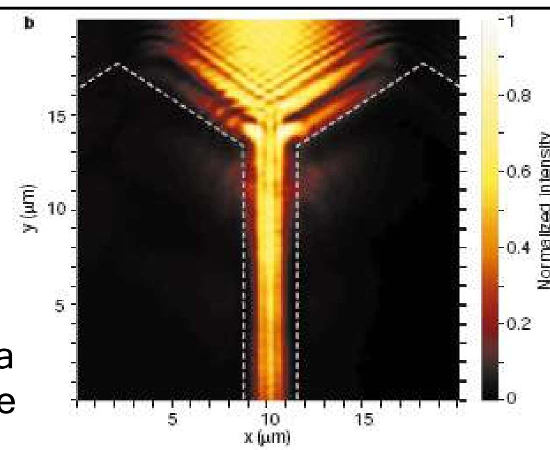
The miniaturization of conventional photonic circuits is limited by the diffraction limit, such that the minimum feature size is of the order of wavelength.

optical fiber



Using the surface plasmons one can overcome the diffraction limit, which can lead to miniaturization of photonics circuits with length scales much smaller than those currently achieved

light propagation in a plasmonic waveguide



PHYSICAL REVIEW B **73**, 035407 2006

- **Plasmon slot waveguides: Towards chip-scale propagation with subwavelength-scale localization**

J. A. Dionne,* L. A. Sweatlock, and H. A. Atwater

- *Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, MC 128-95, Pasadena, California 91125, USA*

A. Polman

- *The Center for Nanophotonics, FOM-Institute AMOLF, Kruislaan 407, 1098 SJ Amsterdam, The Netherland*

The ever-increasing demand for faster information transport and processing capabilities is undeniable. Our data-hungry society has driven enormous progress in the Si electronics industry and we have witnessed a continuous progression towards smaller, faster, and more efficient electronic devices over the last five decades.

The scaling of these devices has also brought about a myriad of challenges. Currently, two of the most daunting problems preventing significant increases in processor speed are thermal and signal delay issues associated with electronic interconnection.

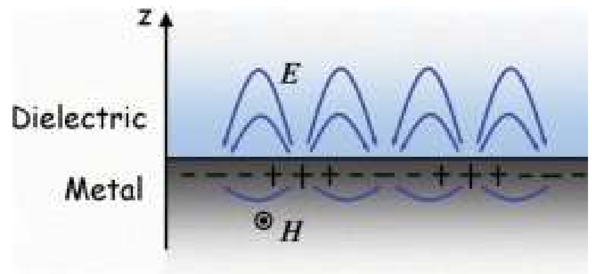
Optical interconnects, on the other hand, possess an almost unimaginably large data carrying capacity, and may offer interesting new solutions for circumventing these problems. Optical alternatives may be particularly attractive for future chips with more distributed architectures in which a multitude of fast electronic computing units (cores) need to be connected by high-speed links. Unfortunately, their implementation is hampered by the large size mismatch between electronic and dielectric photonic components.

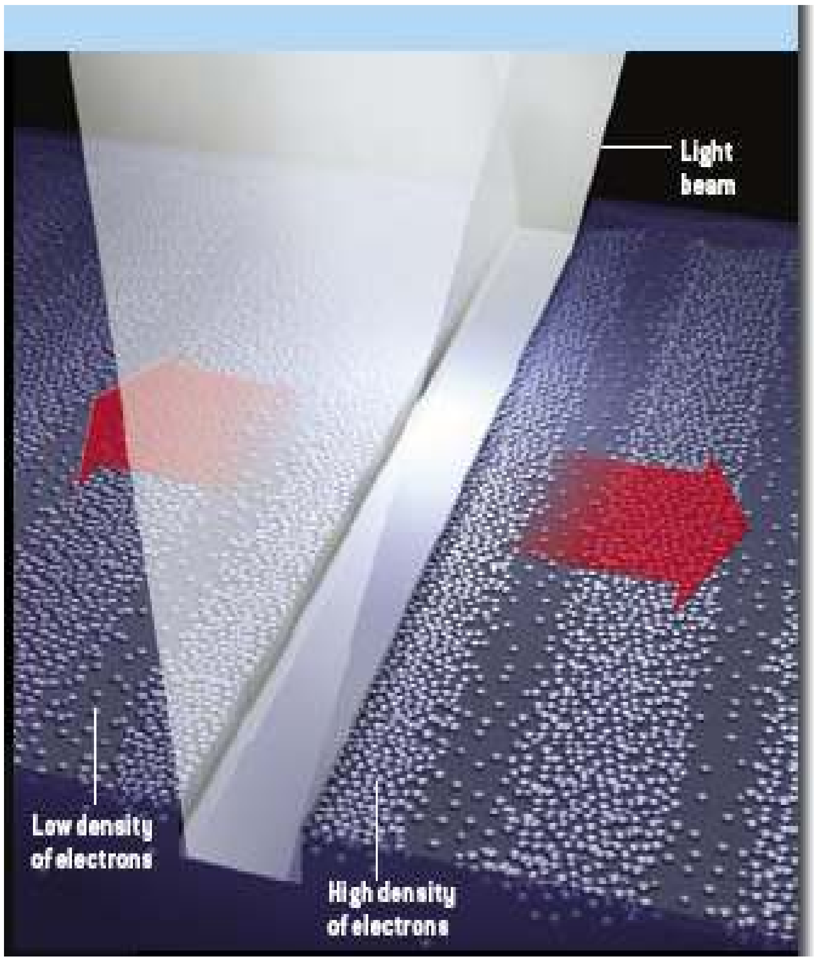
Dielectric photonic devices

are limited in size by the fundamental laws of diffraction to about half a wavelength of light and tend to be at least one or two orders of magnitude larger than their nanoscale electronic Counter parts.

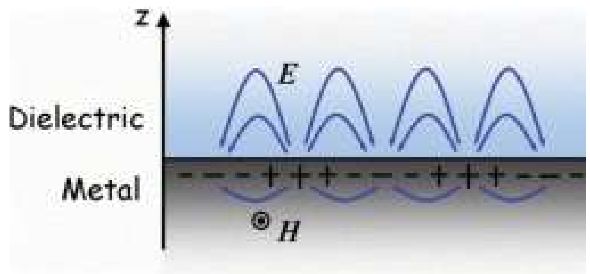
This obvious size mismatch between electronic and photonic components presents a major challenge for interfacing these technologies.

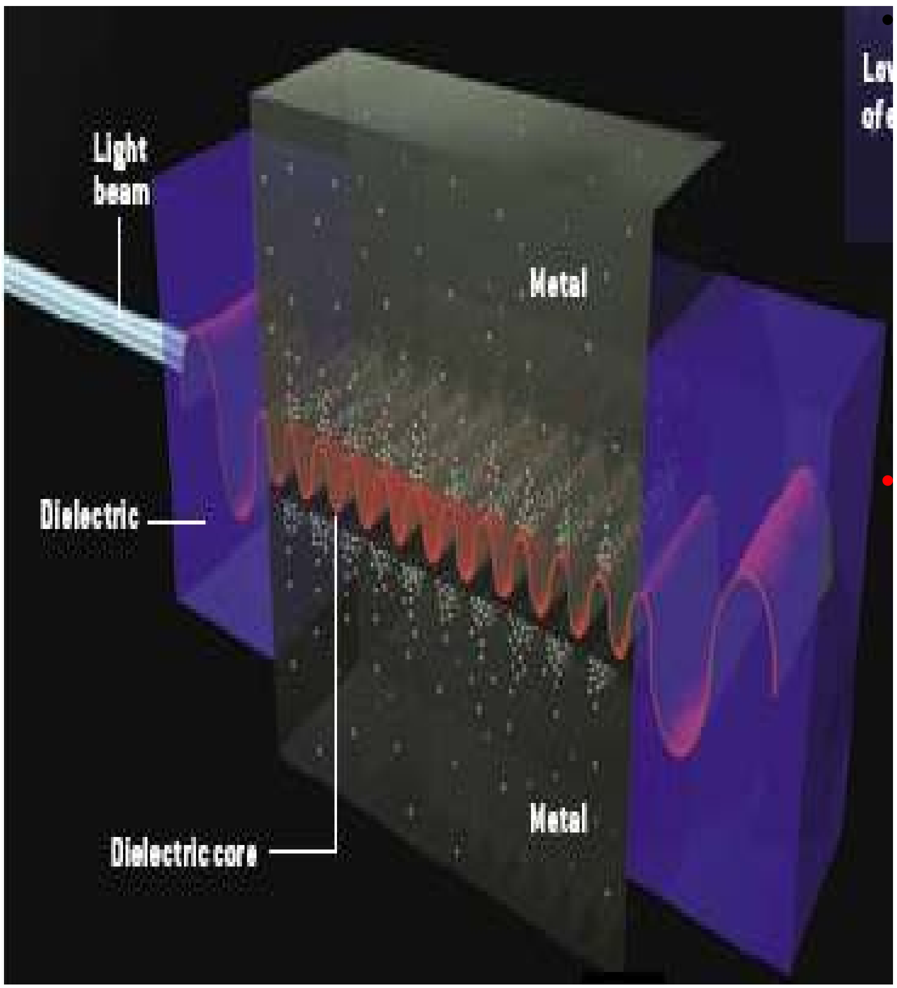
Further progress will require the development of a radically new chip-scale device technology that can facilitate information transport between-nanoscale devices at optical frequencies and bridge the gap between the world of nanoscale electronics and microscale photonics.





- **PLANAR WAVEGUIDE** Plasmons always flow along the boundary between a metal and a dielectric (. For example, light focused on a straight groove in a metal will generate plasmons that propagate in the thin plane at the metal's surface.
- A plasmon could travel as far as several centimeters in this planar waveguide—far enough to convey a signal from one part of a chip to another—but the relatively large wave would interfere with other signals in the nanoscale innards of a processor.





- **PLASMON SLOT WAVEGUIDE**
- Scientists have built much smaller plasmonic circuits by putting the dielectric at the core and surrounding it with metal. The plasmon slot waveguide squeezes the optical signal, shrinking its wavelength by a factor of 10 or more. Researchers have constructed slot waveguides with widths as small as 50 nanometers—about the same size as the smallest electronic circuits.
- The plasmonic structure can carry much more data than an electronic wire, but it cannot transmit a signal farther than 100 microns.The study of plasmonics is relatively new, but researchers have already developed prototype devices that demonstrate the promise of the technology.

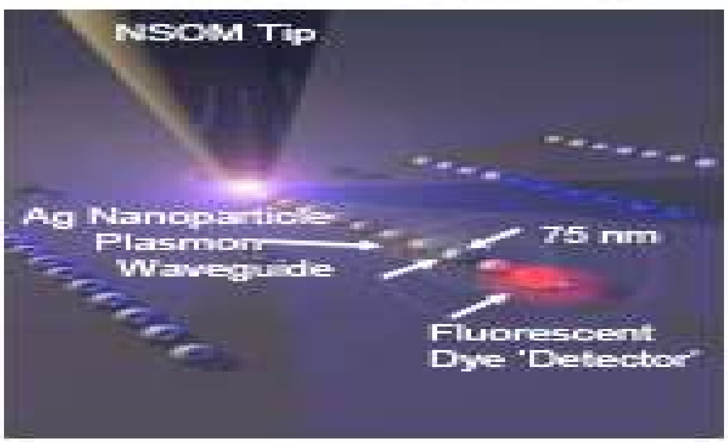
Ultra-Small (~λ/10) Plasmon Waveguides Below Diffraction Limit

Force manipulation positioning of detectors:

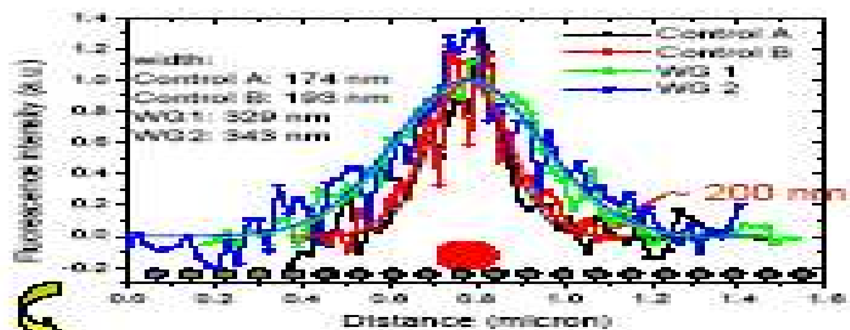
Topography:

Fluorescence:

Schematic View:

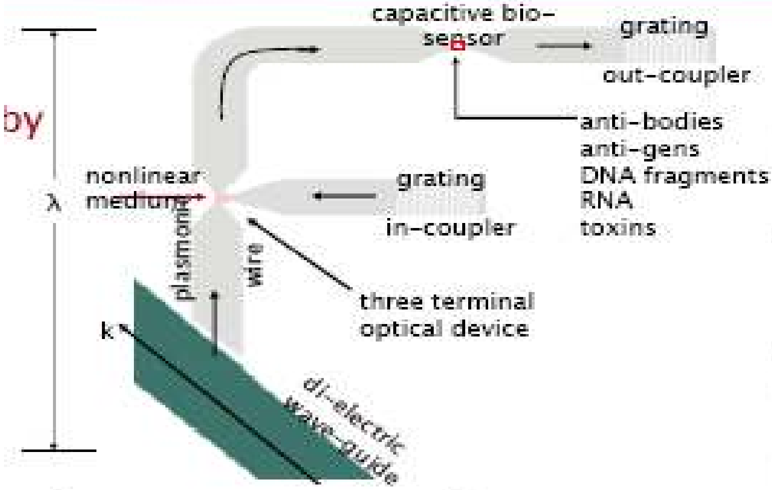


Waveguide Excitation:



Dyes on waveguide excited over a waveguide distance ~1 μm

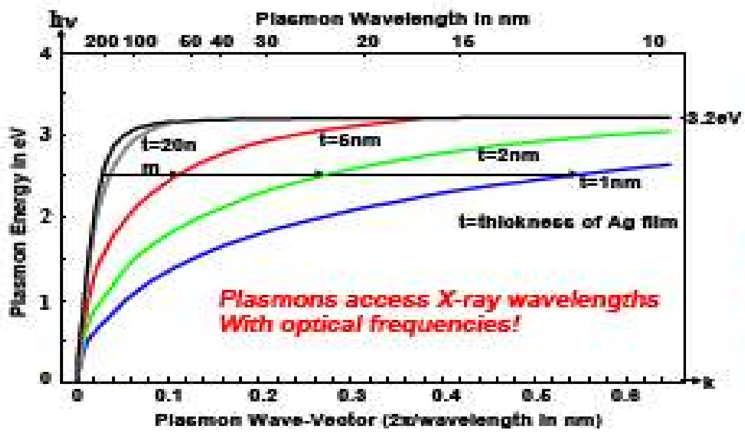
Maier, et. al. Nature Materials, April 2003

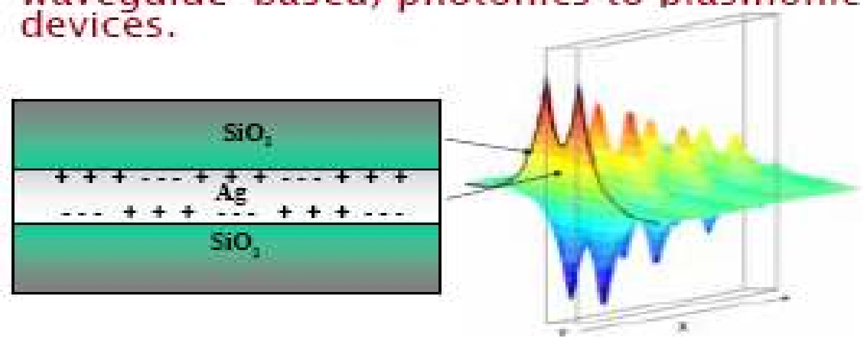


Plasmonics is Opening a New Domain for Integrated Photonics

based on:

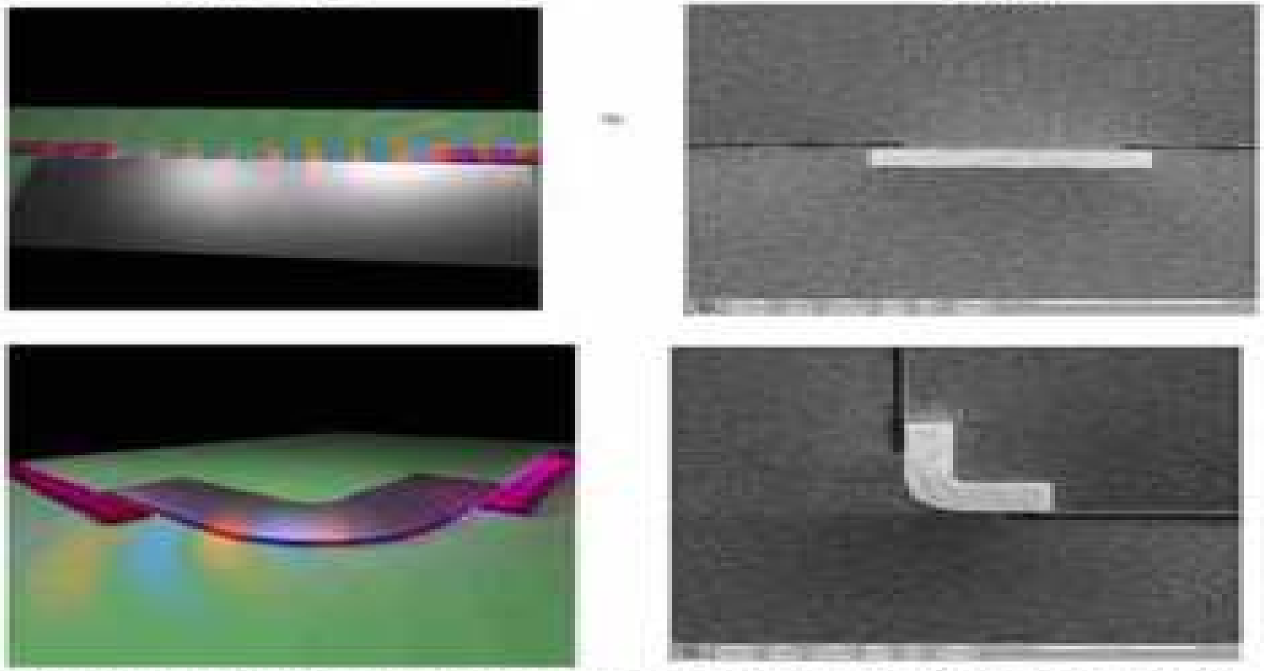
- Extreme light localization: nonlinear excitations in ultrasmall volumes → compact low-power all-optical devices
- Very high spatial frequencies: opportunity for optical imaging systems with nm-scale resolution
- Enhanced light-emission from active photonic devices via coupling to surface plasmons
- Coupling from dielectric (fiber and SOI waveguide-based) photonics to plasmonic devices.





Coupling to/from Dielectric and Plasmon Waveguides

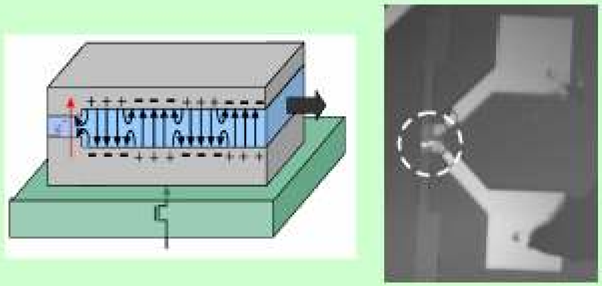
FDTD | SEM



1550nm surface plasmon mode, coupled to and from SOI waveguide:

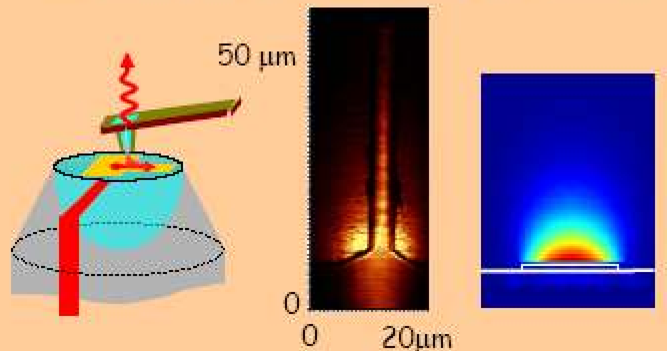
- No diffraction limit to modal volume
- ~1.2 dB/μm loss achieved (limited by roughness of silver film)
- ~2.8 dB insertion loss from SOI to plasmon waveguide

Tunnel-junction Plasmon Sources



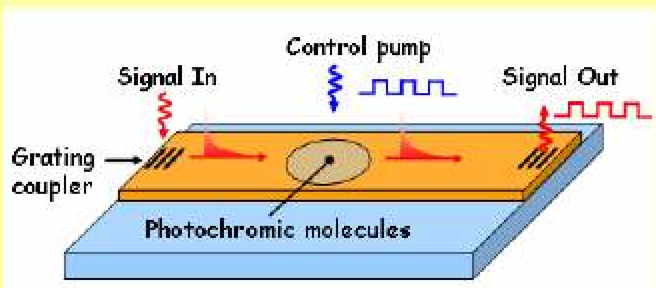
Anu Chandran, Pol van Dorpe (IMEC)

Plasmonic Waveguides\Interconnects



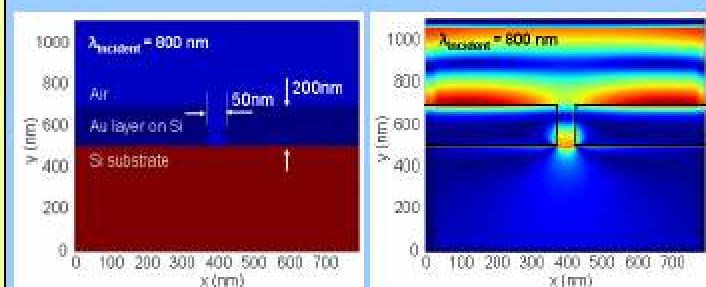
Rashid Zia, John Schuller, Mark Selker

Plasmonic Modulators



Ragip Pala, Ken Shimizu, N Melosh

Plasmonic Detectors



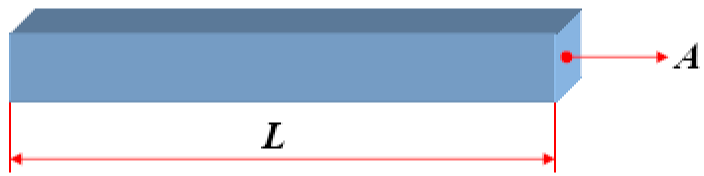
Justin White, Zhongfu Yu, Shanhui Fan

- manipulate light at the nanoscale
- By integrating plasmonic, electronic, and conventional photonic devices on the same chip, it would be possible to take advantage of the strengths of each technology.

In photonics, metals are not usually thought of as being very useful, except perhaps as mirrors. In most cases, metals are strong absorbers of light, a consequence of their large free-electron density. <u>However, in the miniaturization of photonic circuits, it is now being realized that metallic structures can provide unique ways of manipulating light at length scales smaller than the wavelength.</u>

Why not electronics?

As **data rates** AND component packing **densities** INCREASE, electrical interconnects become progressively limited by ***RC***-delay:



$$R \propto L/A \quad \oplus \quad C \propto L \quad \Rightarrow \quad B_{\max} \propto \frac{1}{RC} \propto \frac{A}{L^2}$$

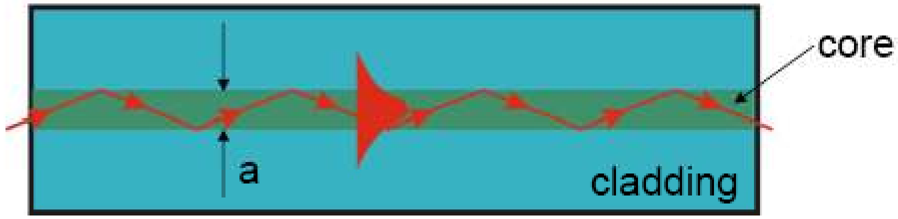
$$\Rightarrow B_{\max} \leq 10^{15} \times \frac{A}{L^2} \ \text{(bit/s)}\,(A << L^2\,!)$$

Electronics is aspect-ratio *limited in speed*!

Why not photonics?

The bit **rate** in optical communications is fundamentally limited **only** by the carrier frequency: $B_{max} < f \sim 100$ Tbit/s (!),

but **light propagation is subjected to diffraction:**

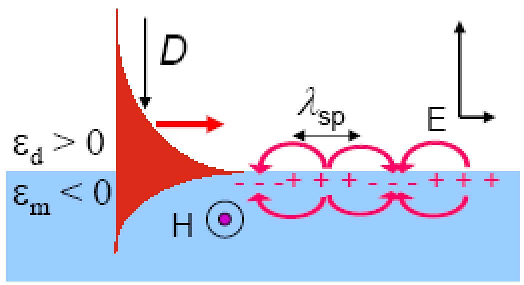


$$n_{core} = n_{clad} + \delta n = n + \delta n \Rightarrow V = \frac{2\pi}{\lambda} a \sqrt{n_{core}^2 - n_{clad}^2} \cong \frac{2\pi}{\lambda} a \sqrt{2n\delta n}$$

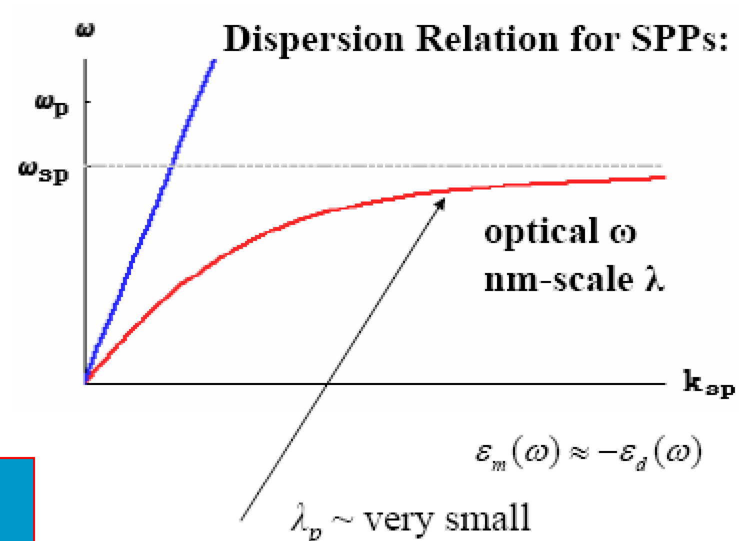
$$\text{well-guided mode}: V \propto \pi \Rightarrow a \cong \lambda / 2\sqrt{2n\delta n} - \text{mode size}: \delta n << 1 (!)$$

Photonics is diffraction- *limited in size*!

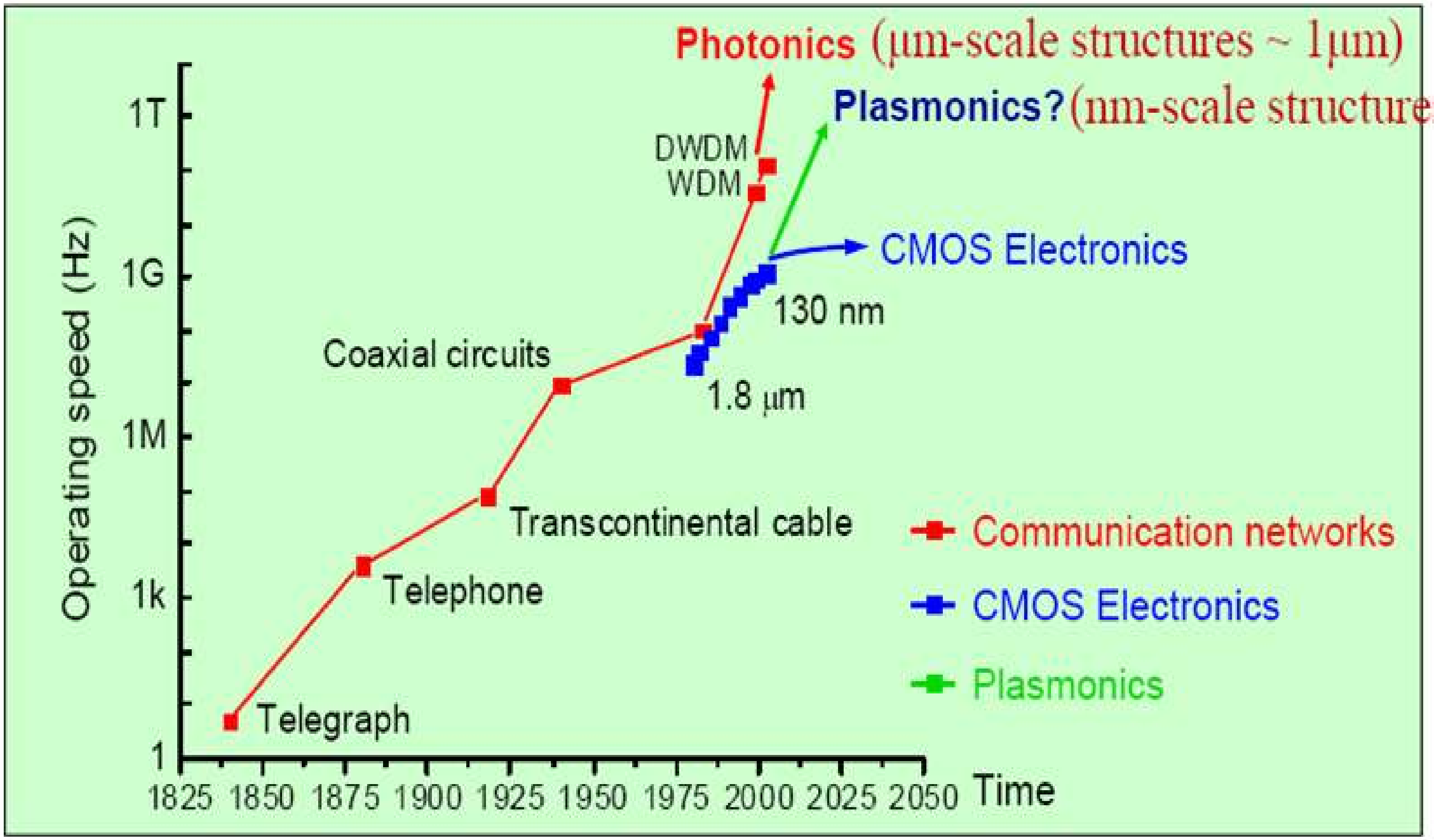
Why Plasmonics?



$$k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$



SP wavelengths can reach nanoscale at optical frequencies!
SPPs are "x-ray waves" with optical frequencies

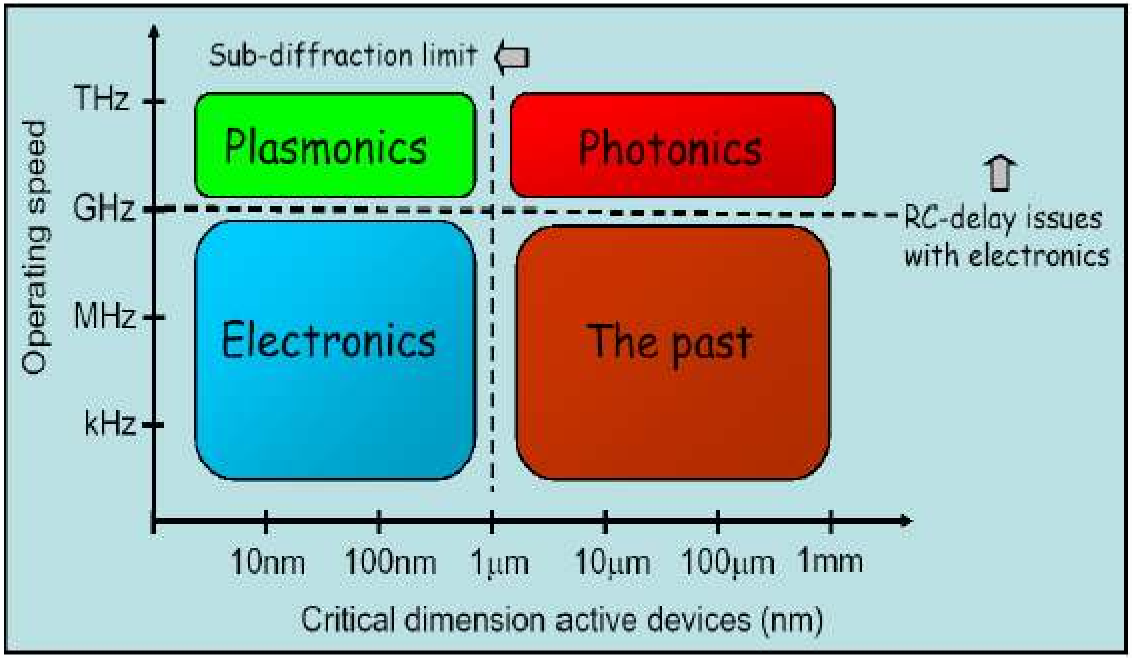


- The ever-increasing need for faster information processing and transport is undeniable

- Electronic components are running out of steam due to issues with RC-delay times

Why nanophotonics needs plasmons?

- Graph of the operating regimes of different technologies

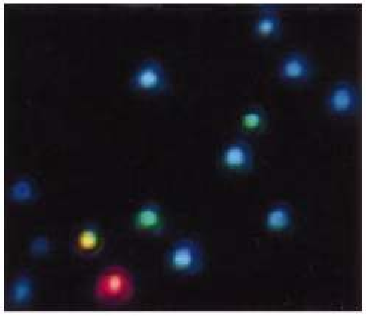


- Plasmonics will enable an improved synergy between electronic and photonic devices
  - ➡ Plasmonics naturally interfaces with similar size electronic components
  - ➡ Plasmonics naturally interfaces with similar operating speed photonic networks

Courtesy of M. Brongersma

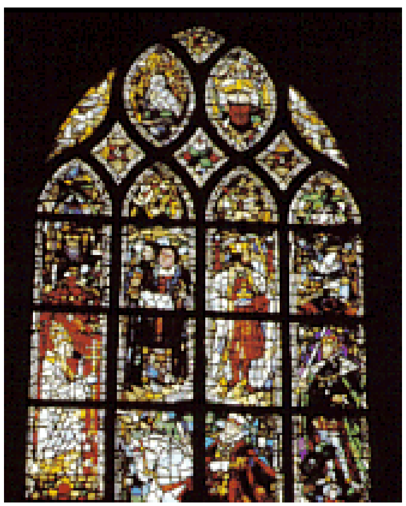
Other applications of nanoparticles

Old:

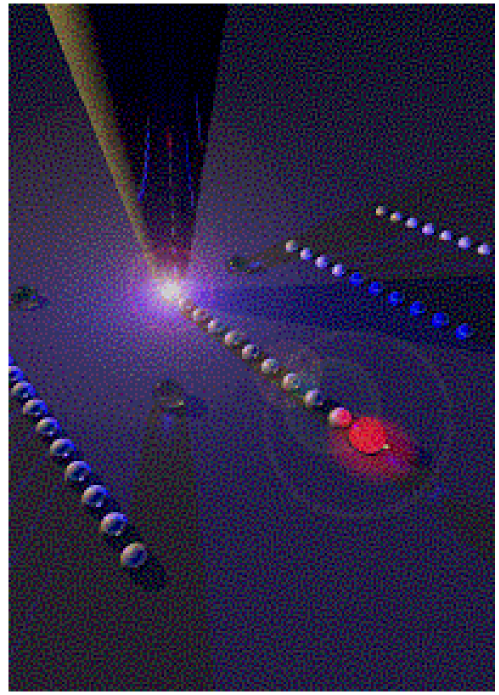


Different materials/shapes: distinct colors

Stained glass



New:
(but the same principle)



Focusing and guidance of light at nanometer length scales

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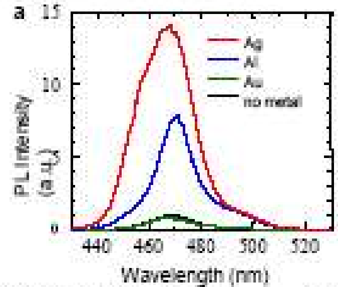
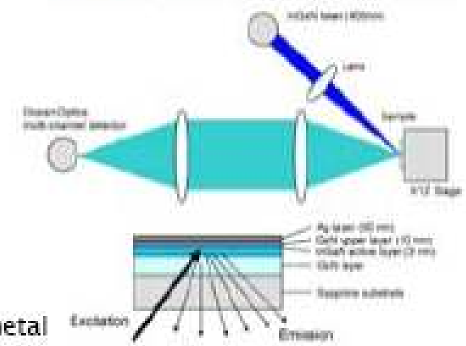
- Other devices improved incorporating Plasmonics based ideas

Plasmon-Enhanced LED Light Emission

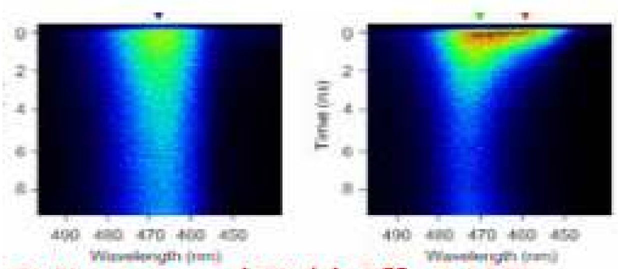
InGaN Quantum Wells:

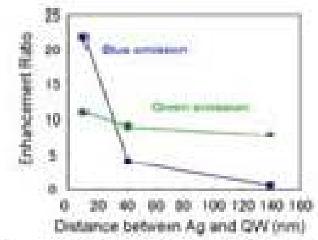


Experimental Setup and Samples



Without metal With metal





Si Nanocrystal Field-Effect LED:

- New light emission phenomenon in Si MOS transistor
- Sequential field effect carrier injection into Si quantum dots: program electrons in inversion, program holes in accumulation
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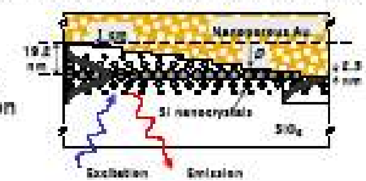
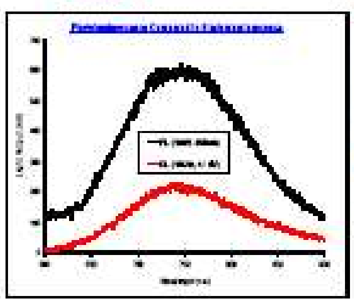
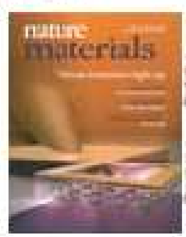
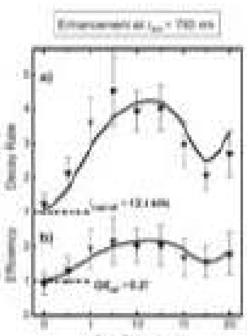
Plasmon-Enhanced Emission:

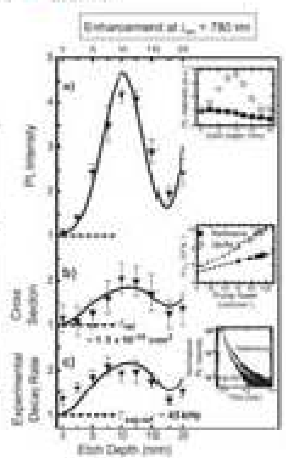


CMOS LED:



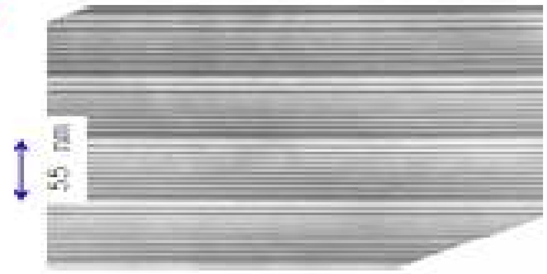






Quantum Cascade Lasers with Plasmon Waveguide Cavities

Unprecedented wavelength coverage (mid-ir, lw-ir, far-ir) by changing active region thickness: from 3 μm to 150 μm !!



AlInAs/GaInAs

Laser polarization is *normal to layers* (TM mode): has *enabled first surface plasmon laser*, and allows innovative *plasmonic resonator designs* suited *for chem/bio sensing applications*

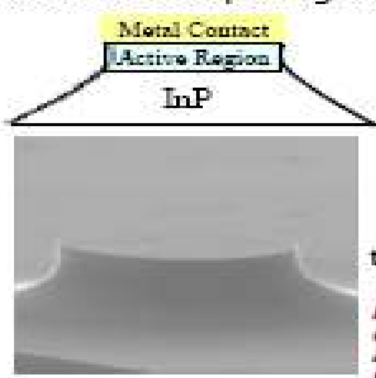
Capture agents attached to gold surface via alkyl thiol linker.

TM polarized light travels along the metal/active region interface

Surface plasmon field used to sense analytes adsorbed on top metal contact by monitoring changes in laser characteristics (threshold, power, λ).

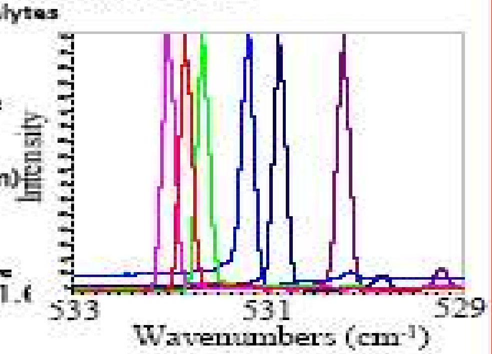
Self-assembled monolayers (SAM) deposited on thin Au contact can be functionalized with capture agents for specific analytes

Plasmon Whispering Gallery Mode Lasers



- Stripes: J_{th}=3.2 kA/cm²
- Circular disks (r=40 μm) has J_{th}=1.5 kA/cm²
- Deformed microdisks (ε from 0 to 0.3): J_{th} from 1.6 to 1.8 kA/ cm²

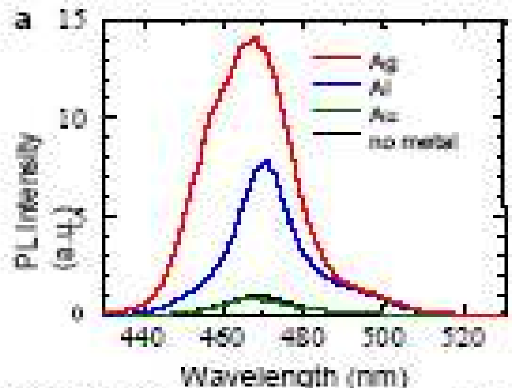
Decrease in threshold compared with stripe laser at same λ due to increase in Q



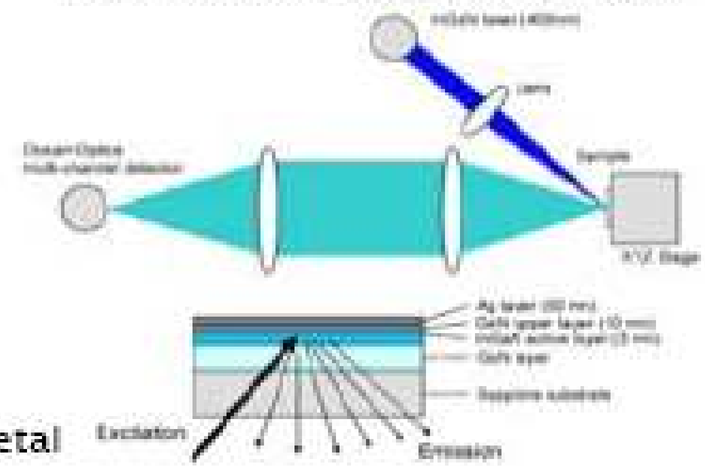
Spectral tuning of nearly circular (ε =0.027) laser for increasing current.
ε = ratio of minor to major axis

Plasmon-Enhanced LED Light Emission

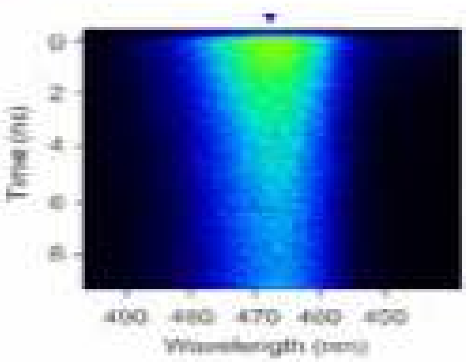
InGaN Quantum Wells:



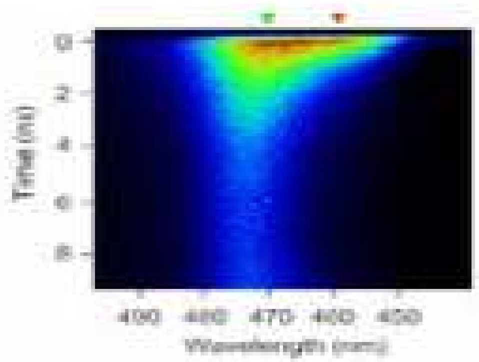
Experimental Setup and Samples

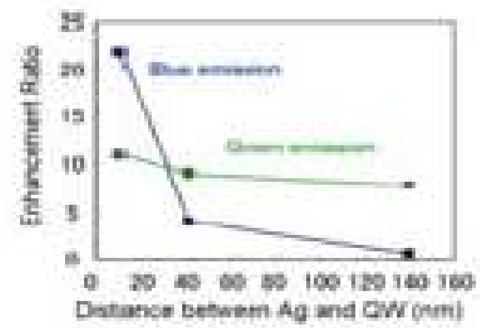


Without metal



With metal





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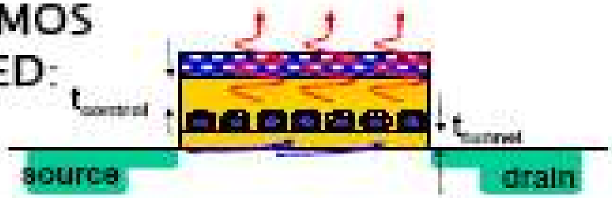
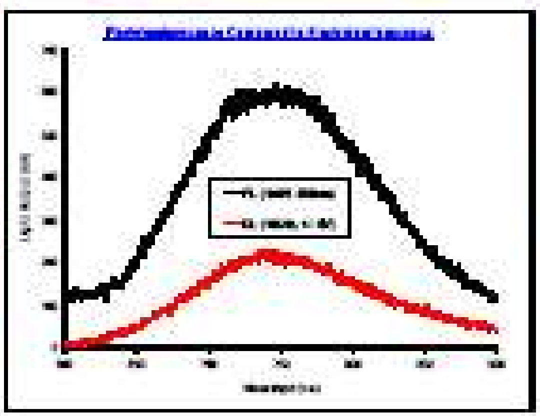
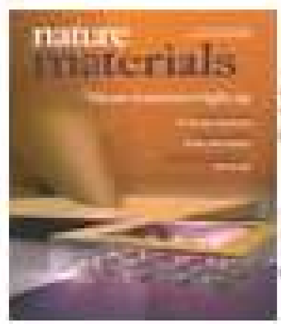
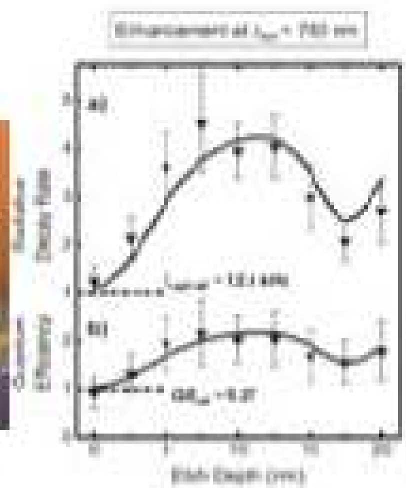
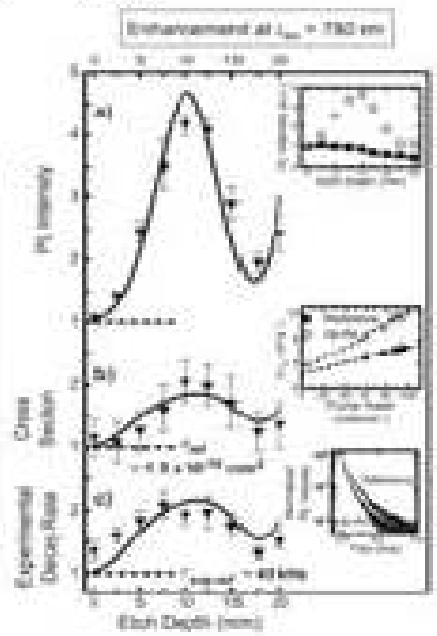


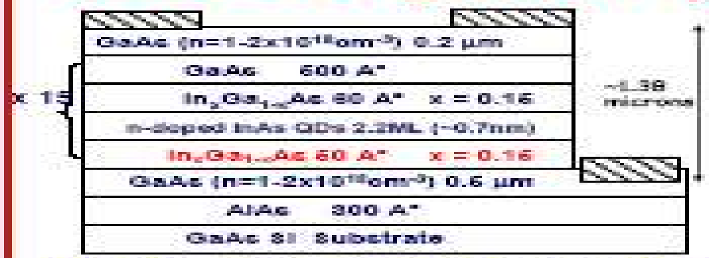








Plasmon-Enhanced Detection in Long Wave-Length IR Hyperspectral Arrays

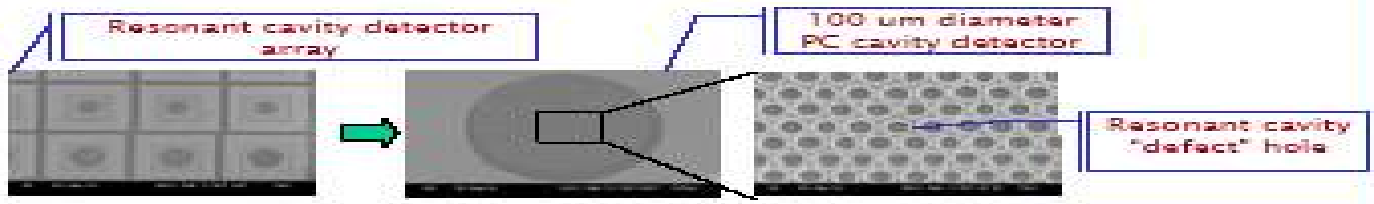


LWIR Atmospheric Window DWELL Design

Mid-infrared photodetectors in 50-400 meV (3-25 µm) range:

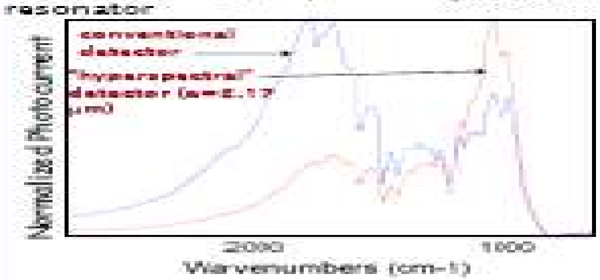
- medical diagnostics,
- thermal imaging,
- night vision for battlefield recognition systems
- chip-based detection of chemical warfare agents

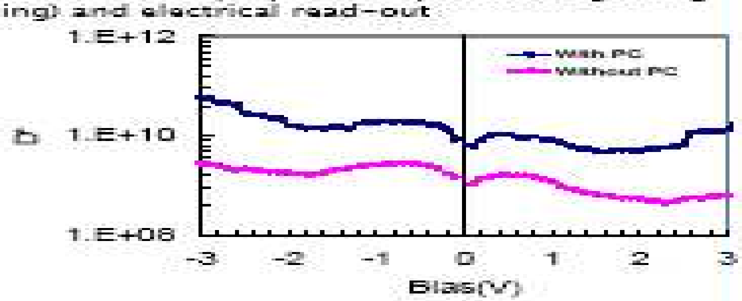
Intersubband quantum dot detectors: promising technology → normal incidence excitation and lower dark currents. InAs quantum dots in an InGaAs well (DWELL) for mid-IR detection (Krishna at UNM)… *but presently suffer from low quantum efficiency and responsivity due to small absorption volume.*



- Resonant enhanced detection using in-plane resonator

- Metal contact serves dual purpose of optical waveguiding (mode-matching) and electrical read-out





- Spectral response of an enhanced "hyperpectral" versus a conventional detector. (spectra normalized to peak detected wavelength to compare wavelength sensitivity)
- Enhanced detection efficiency for longer (9 µm) wavelengths; shorter wavelength (6 µm) suppressed

- The generation-recombination limited D* at 77K a factor of 20 higher than that of the conventional detector
- BLIP temperature raised by 20%

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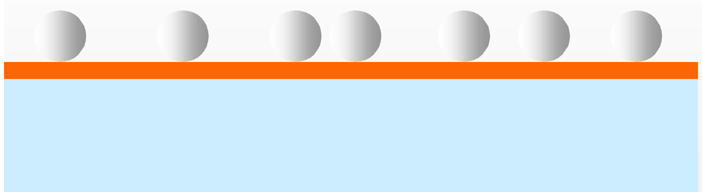
Plasmon Printing

Initial experiments

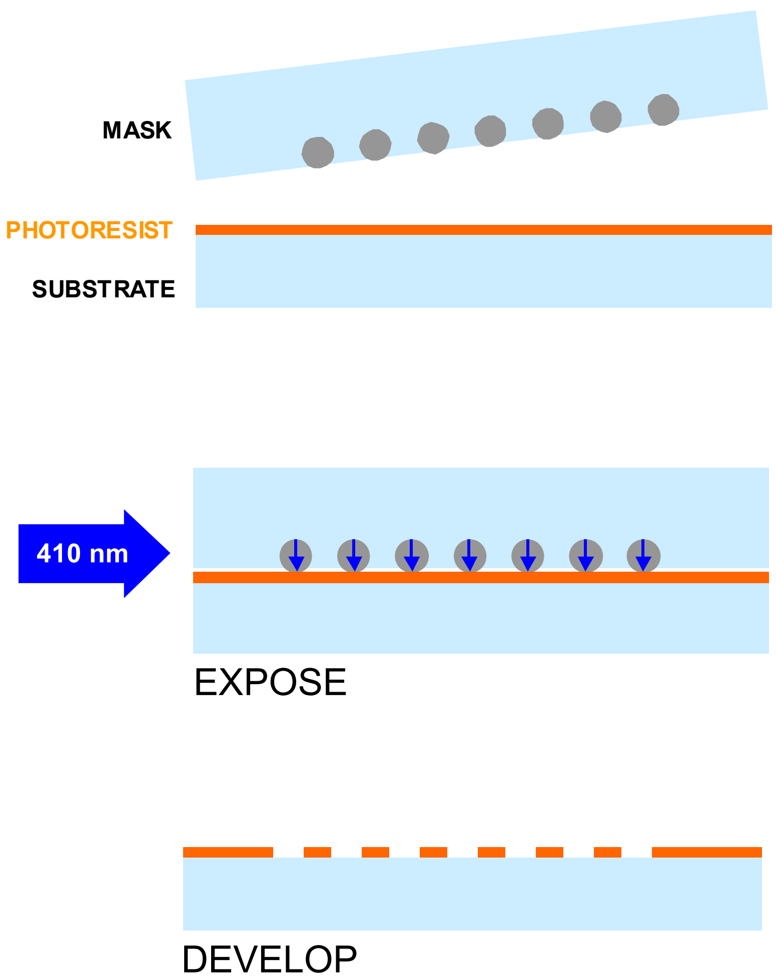


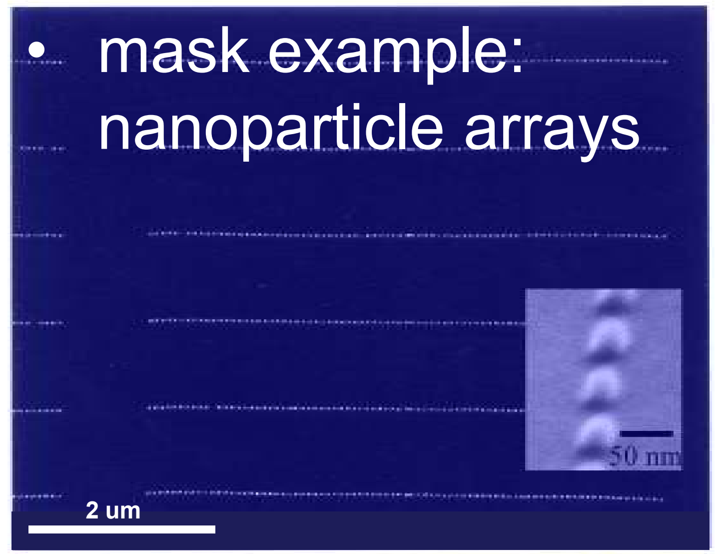
- **Nanoparticles**
- colloidal Ag (∅ 41 nm) in aqueous solution
- deposit on resist (nebulize)

- **Resist**
- AZ1813 resist, diluted to 1:4 with EBR
- spin 5000 rpm 60s ⇒ 75 nm thick layer
- developing tested OK

1. Expose — broad beam, Xe arc lamp at 410 nm; intensity ~1 mW/cm^2 (TM); exposure 15 / 30 / 45 / 60 s
2. Develop — diluted 1:1 – dev. time ~20 s
3. Analyze — Use AFM to image printed features

Printing scheme





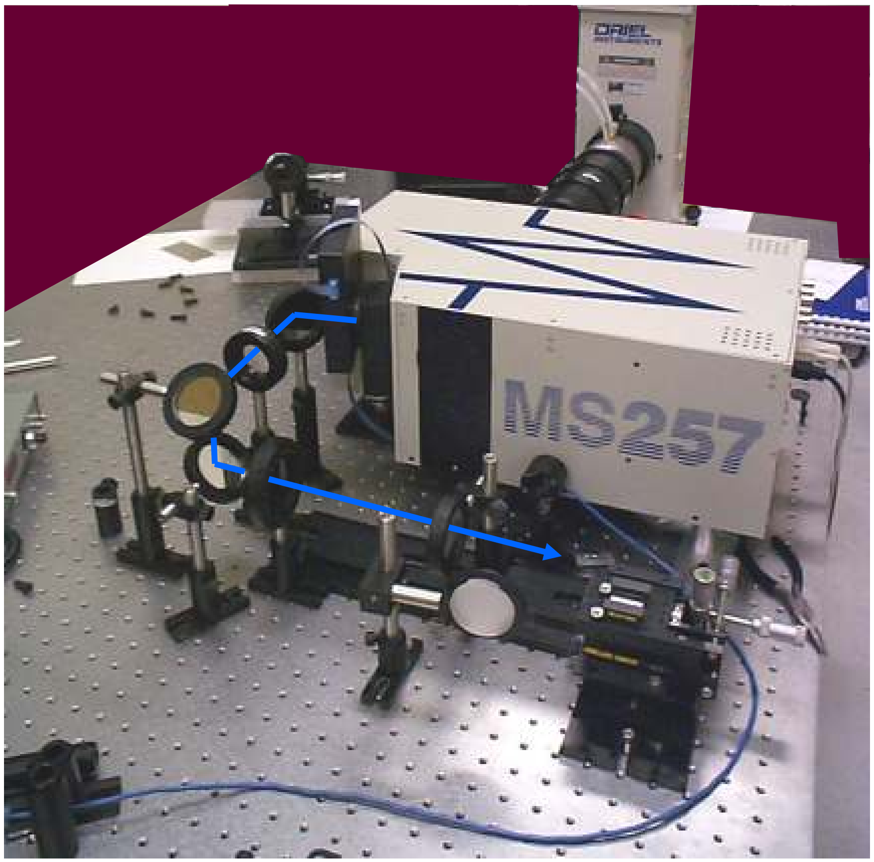
Mask fabricated with JPL, Pasadena, CA

✓high resolution mask ($$)

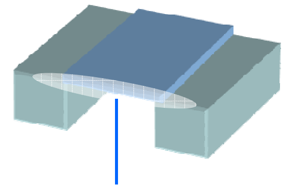
✓standard resist

✓simple light

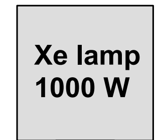
Illumination setup

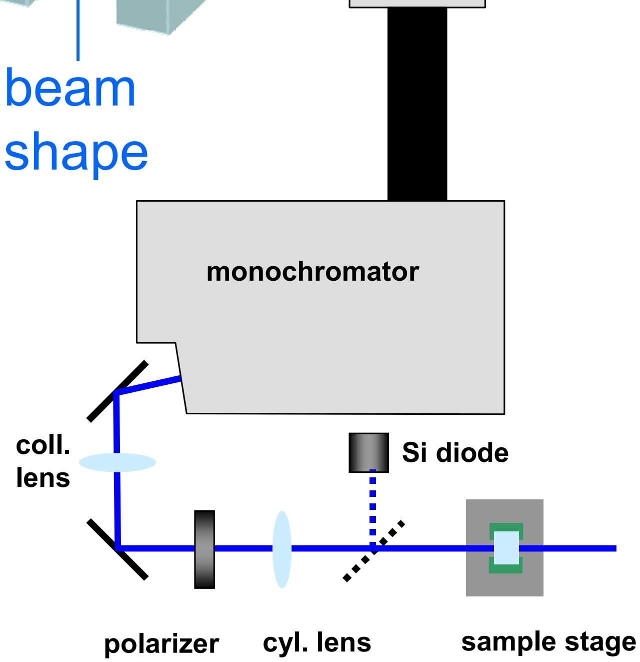


- sample holder

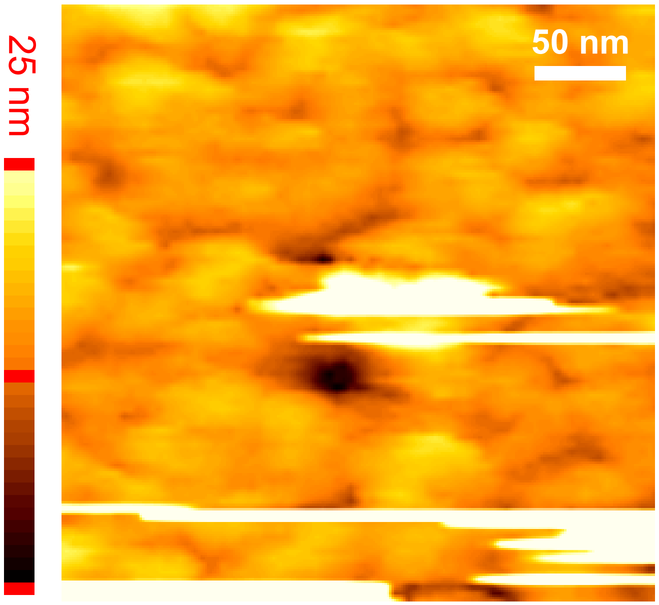


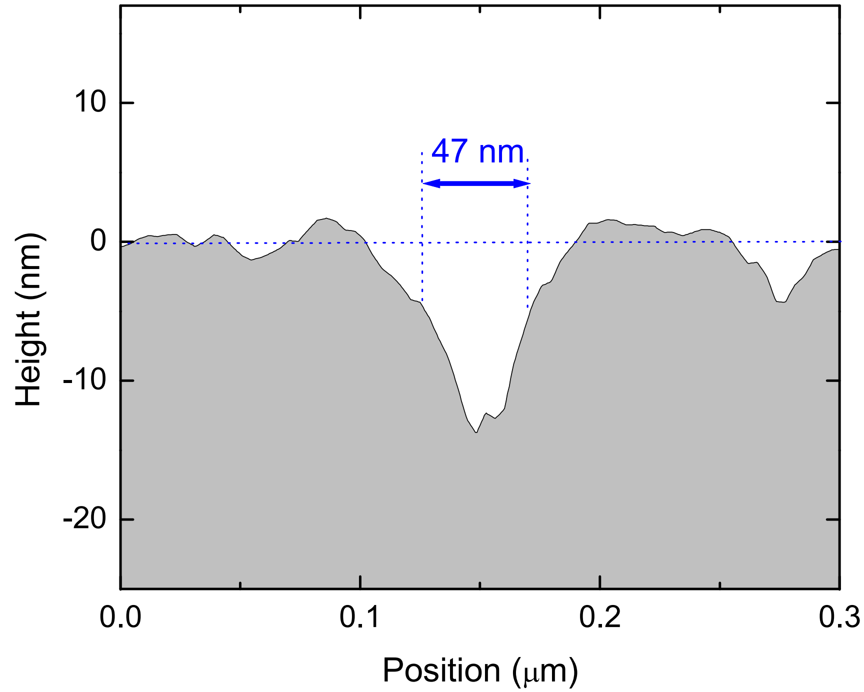
- beam shape





Contact mode AFM





- **sample: Ag 40 nm AZ resist 75 nm exp. 15s (410 nm) dev. 20s**

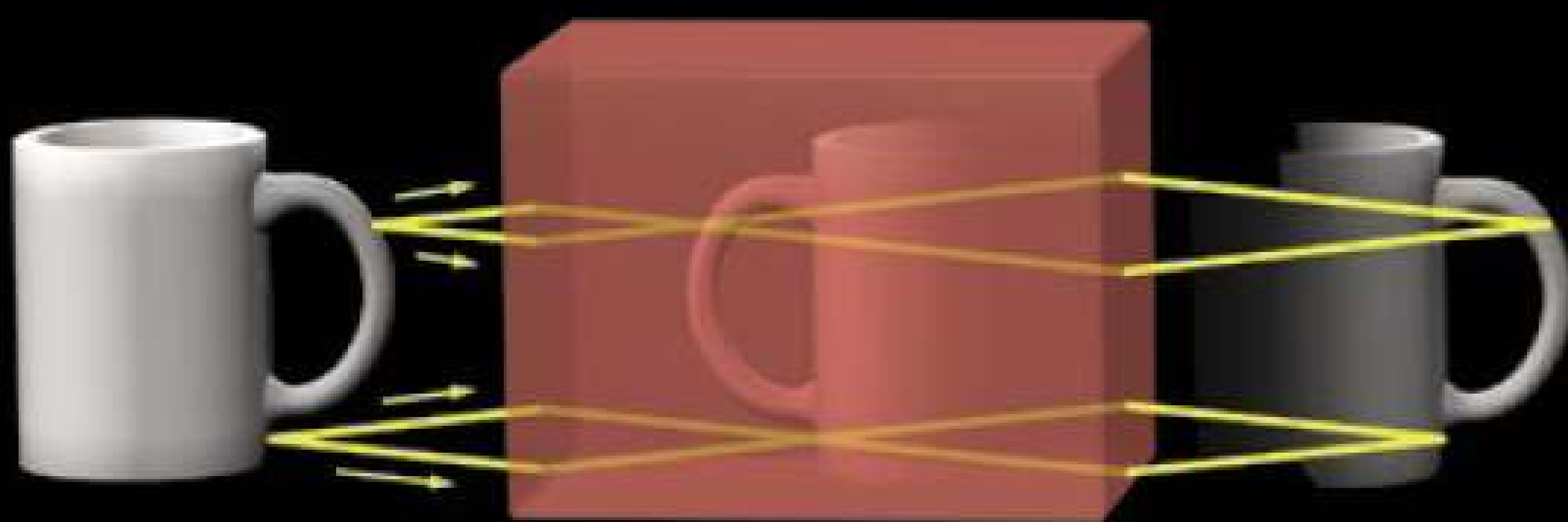
- **see - remaining Ag particles (swept by AFM tip) and**
  - sub-wavelength size dips width 30-60 nm, depth 10-15 nm

****

Metamaterial & super lenses

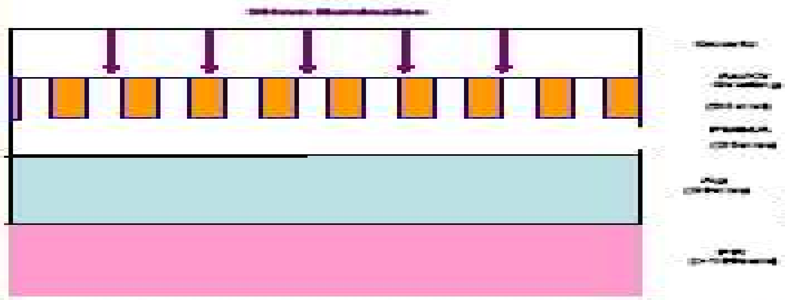
THE SUPERLENS

A rectangular slab of negative-index material forms a superlens. Light (*yellow lines*) from an object (*at left*) is refracted at the surface of the lens and comes together again to form a reversed image inside the slab. The light is refracted again on leaving the slab, producing a second image (*at right*). For some metamaterials, the image even includes details finer than the wavelength of light used, which is impossible with positive-index lenses.

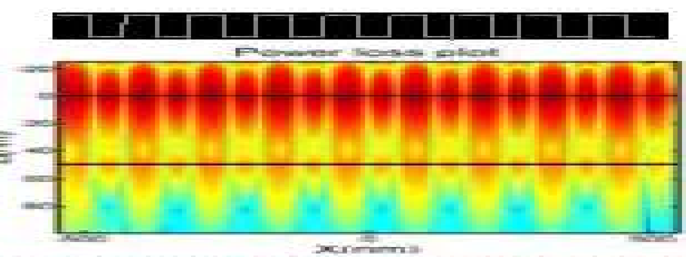


Superlenses: Imaging Below the Diffraction Limit

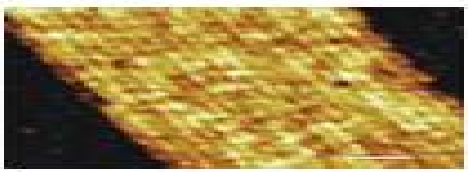
Design



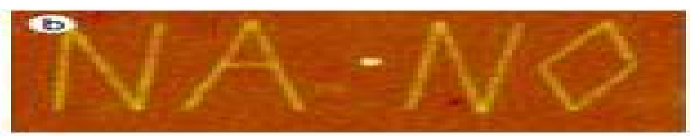
Simulated Intensity



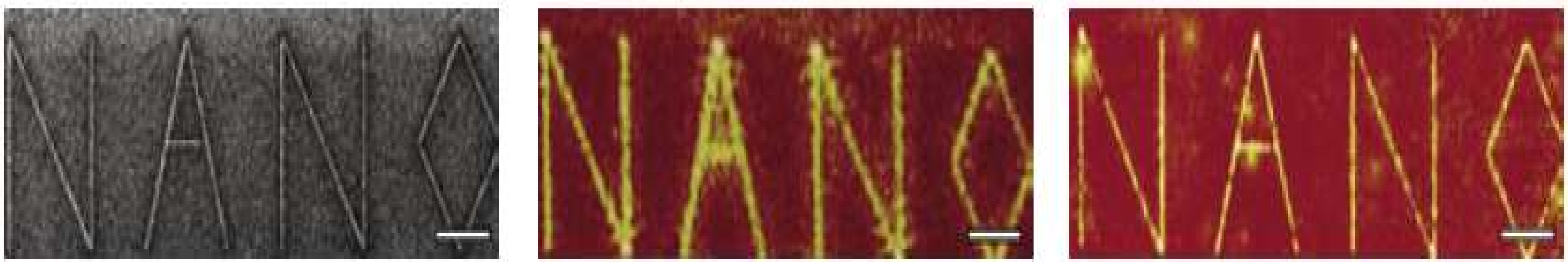
Array of 60 nm wires



Arbitrary object "NANO" (100 nm lines)



1. At grating, propagating field converts to an evanescent wave
2. At the silver surface, the evanescent waves experiences weak scattering from surface, but major component maintain the original grating wavevector;
3. Exiting from silver surface, evanescent field components recombine to form near field images



THIN LAYER OF SILVER acts like a superlens over very short distances. Here the word "NANO" is imaged with a focused ion beam (*left*), optically without a superlens (*middle*) and optically with a 35-nanometer layer of silver in place (*right*). Scale bar is 2,000 nanometers long. With the superlens, the resolution is finer than the 365-nanometer wavelength of the light used.

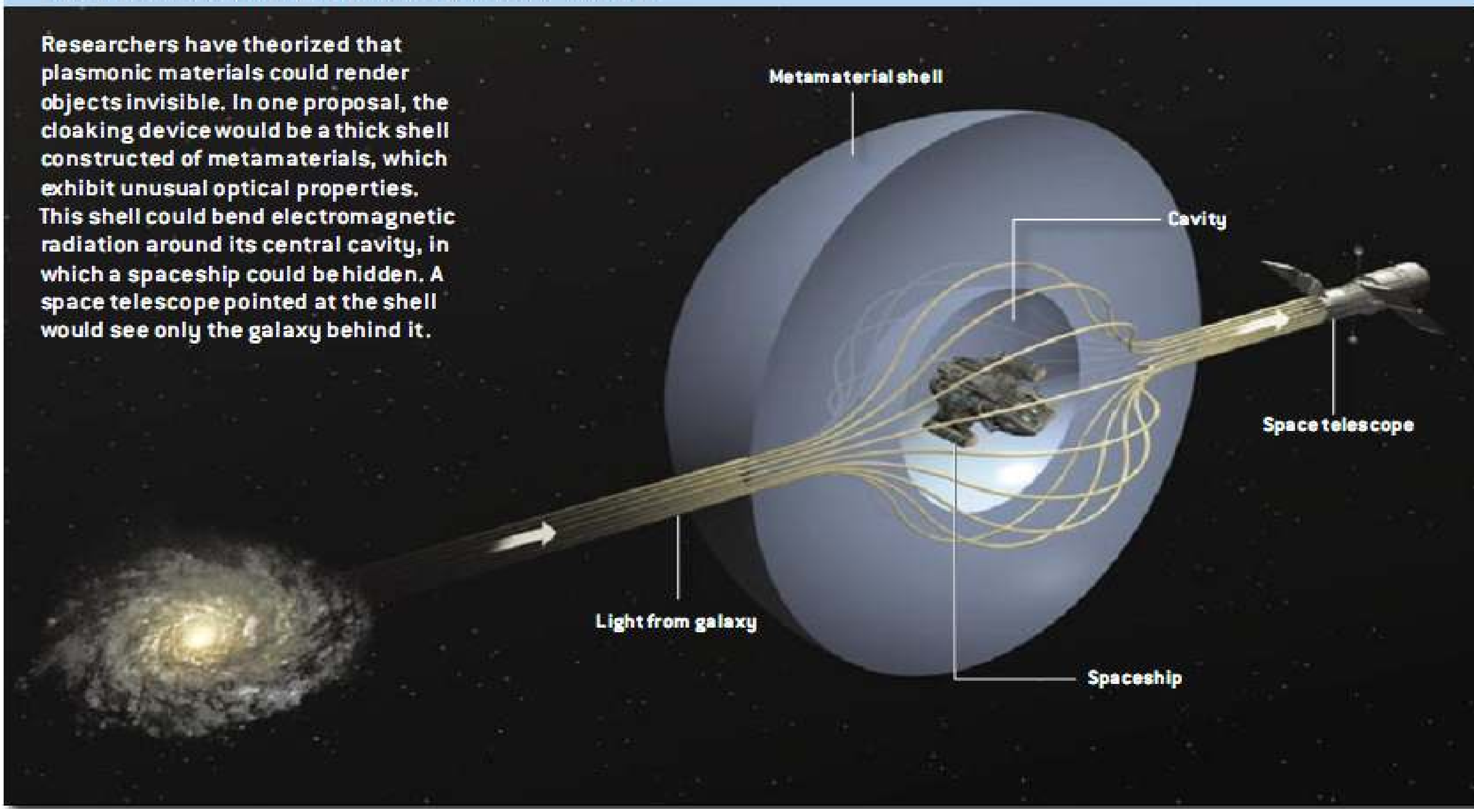
Overview/*Metamaterials*

- Materials made out of carefully fashioned microscopic structures can have electromagnetic properties unlike any naturally occurring substance. In particular, these metamaterials can have a negative index of refraction, which means they refract light in a totally new way.
- A slab of negative-index material could act as a superlens, able to outperform today's lenses, which have a positive index. Such a superlens could create images that include detail finer than that allowed by the diffraction limit, which constrains the performance of all positive-index optical elements.
- Although most experiments with metamaterials are performed with microwaves, they might use shorter infrared and optical wavelengths in the future.

*****

Invisibility Cloak

HOW A CLOAKING DEVICE MIGHT WORK

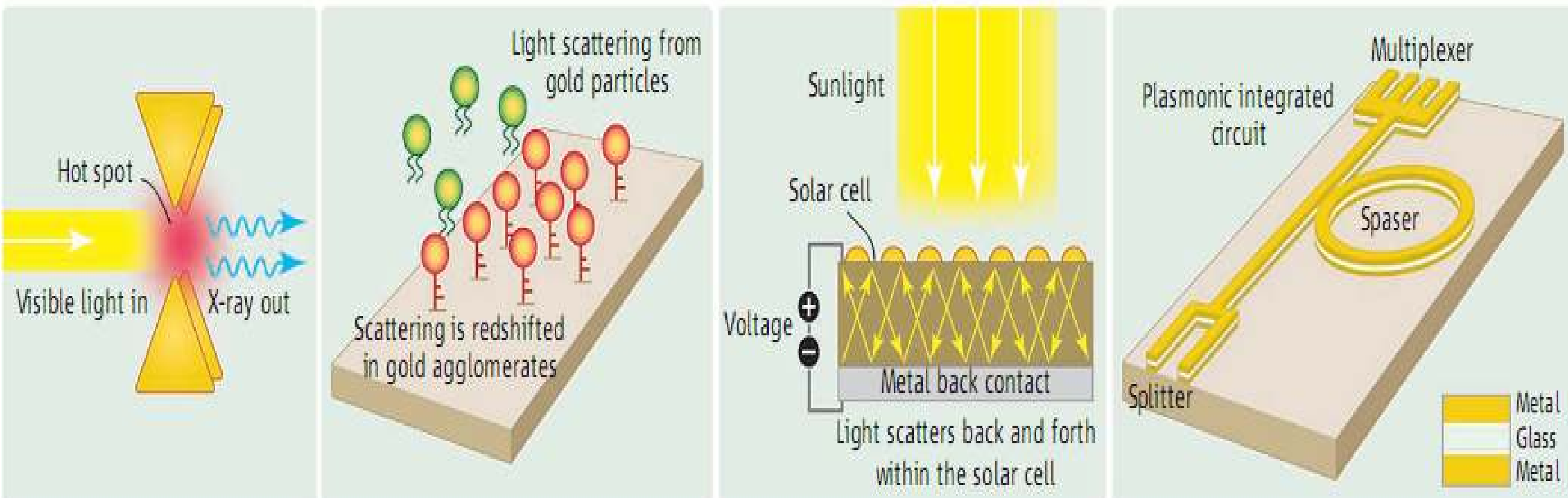


APPLIED PHYSICS

Plasmonics Applied

Albert Polman

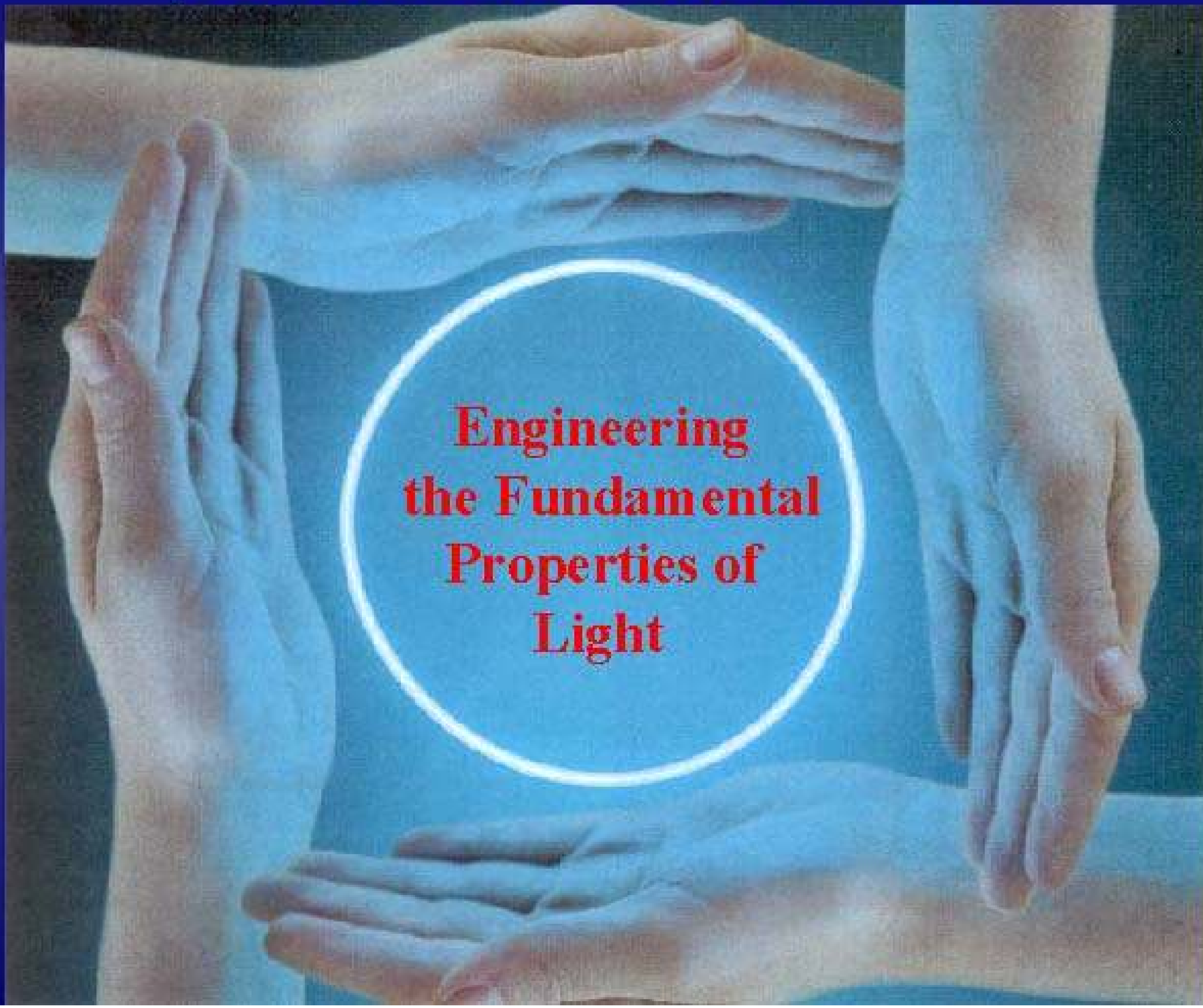
Surface plasmons, light-induced excitations of electrons on metal surfaces, may provide integration of electronics and optics on the nanoscale.



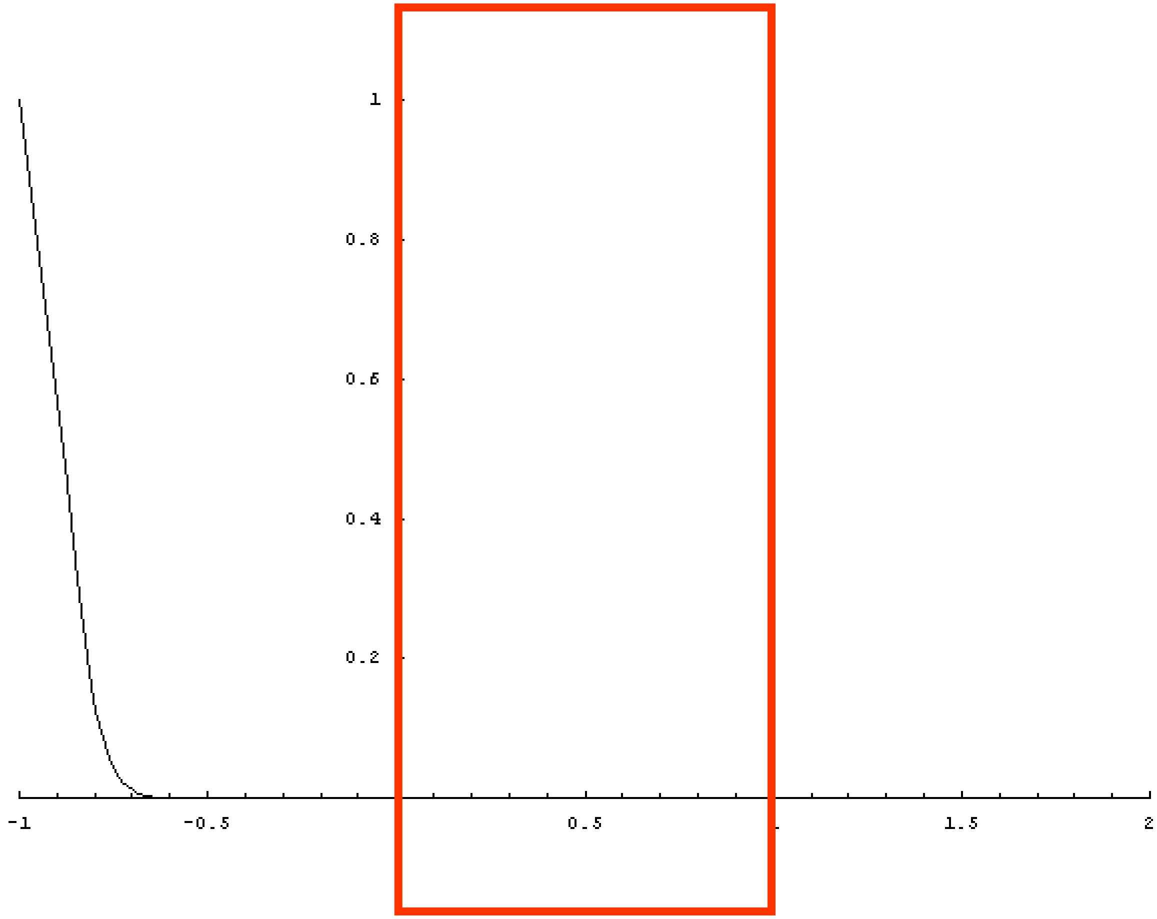
Applied plasmonics. (**Left**) A plasmonic hot spot between metal nanoparticles creates soft x-rays. (**Middle left**) Measuring the resonance shift in coupled metal nanoparticles leads to efficient sensing. (**Middle right**) Scattering from metal nanoparticles enhances light trapping in a solar cell. (**Right**) Plasmonic integrated circuit with subwavelength dimensions. A plasmonic ring laser is integrated with 50-nm-wide waveguides.

References

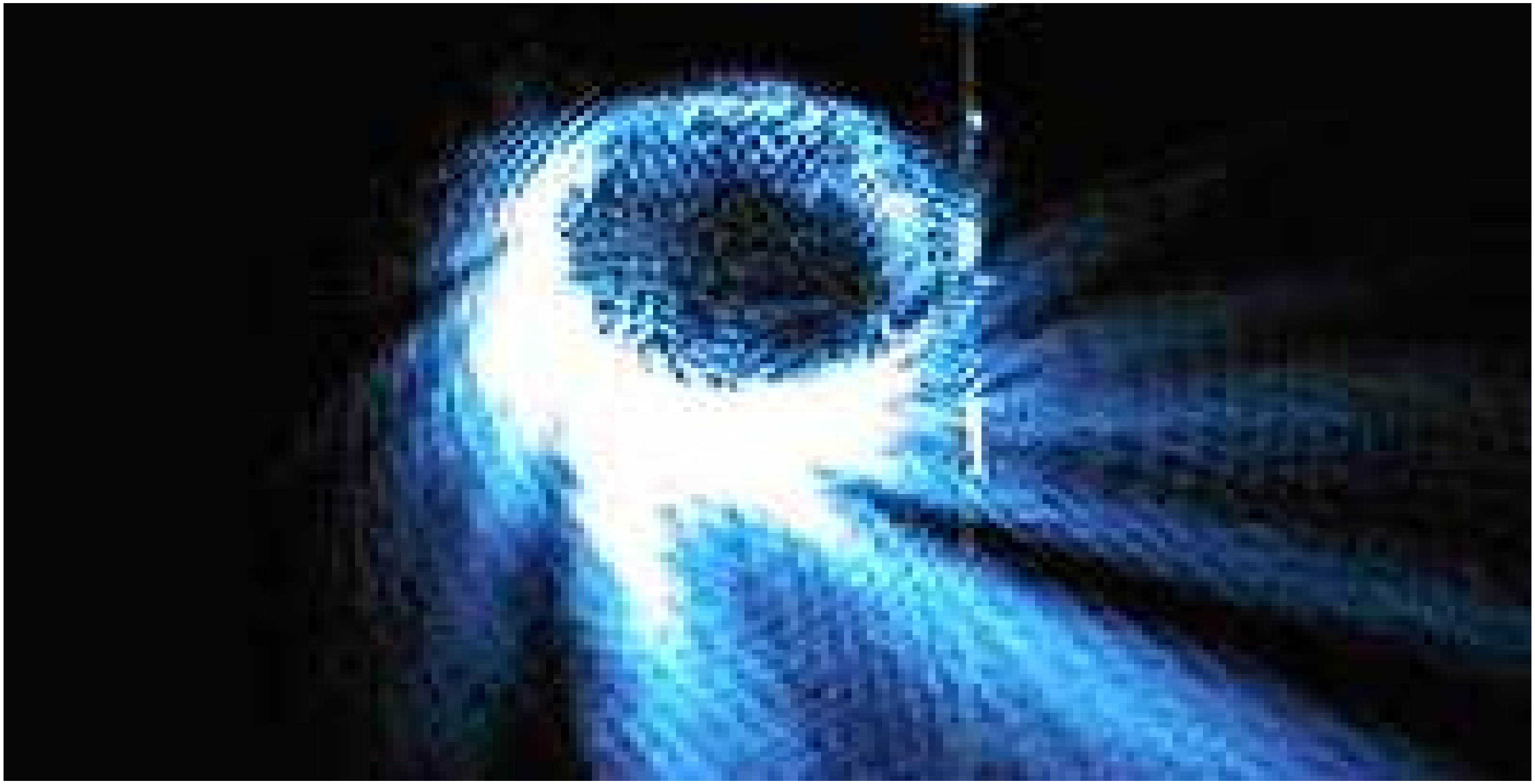
Photonic Band Gap Materials



Pulse Propagation: Slow Light (Group velocity approximation)



This is not the first time that scientists have tweaked the speed of a light signal. Even light passing through a window or water is slowed down a fraction as it travels through the medium. In fact, in the right conditions, scientists have been able to slow light down to the speed of a bicycle, or even stop it altogether. A team of researchers from the Ecole Polytechnique Federale de Lausanne (EPFL) has successfully demonstrated, for the first time, that it is possible to control the speed of light



Folding Photons!

SOLAR CELLS

Folding photons

Scientists have shown that wrinkles and folds can be used to maximize the absorption of low-energy photons by efficiently redirecting them into a thin absorbing film. This inexpensive technique for structuring photonic substrates could be used to increase the efficiency of many organic photovoltaic cells.

Brian A. Gregg and Jao van de Lagemaat

The process of photon absorption in a photovoltaic cell sounds simple. In reality, however, photovoltaic solar-energy conversion involves dissociating excitons, separating electron–hole pairs and collecting the charge carriers at electrodes with minimum recombination losses. Each of these coupled processes must proceed with the highest possible efficiency in order to provide a viable low-cost organic photovoltaic (OPV) cell. Managing photon absorption is particularly challenging because the active layer of an OPV cell must be kept thin to prevent resistance and recombination losses, and because absorption coefficients are small in the low-energy tail of an organic absorber. Finding a semiconductor-independent, low-cost way of enhancing long-wavelength absorption could potentially be used to improve the efficiency of all OPV cells.

Kim *et al.* have now developed a photonic substrate-structuring technique that could provide a solution to this problem[1]. Writing in *Nature Photonics* the researchers report

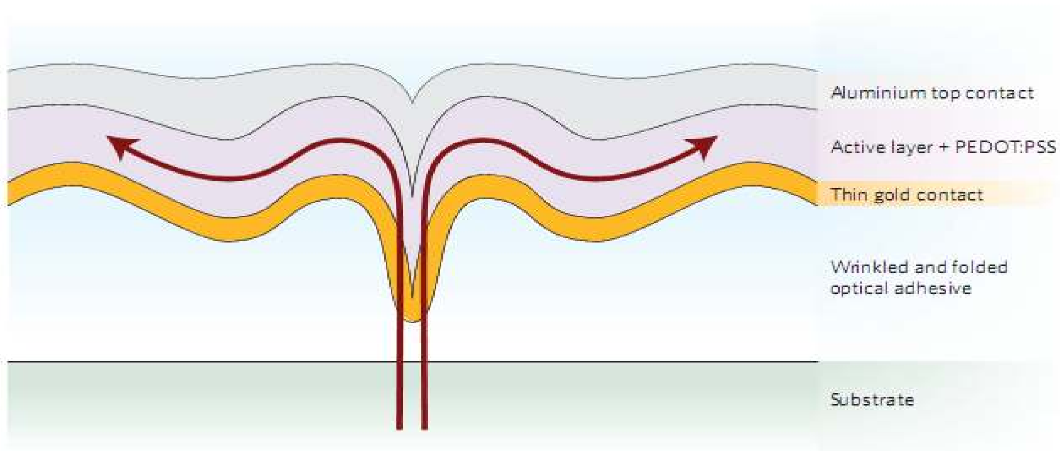


Figure 1 | Long-wavelength photons propagating across a wrinkled and folded substrate. Photons incident on the substrate side get 'folded' into the active layer of the cell by the folds in the polymer adhesive. The wrinkles further localize the light inside the layer through waveguiding effects. PEDOT:PSS, poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate).

Being studied at DTU-Delhi

Absorbing photonic crystals for thin film photovoltaics

O. El Daif[a,b], E. Drouard[a], G. Gomard[a,b], X. Meng[a,b], A. Kaminski[b], A. Fave[b], M. Lemiti[b], E. Garcia Caurel[c], P. Roca i Cabarrocas[c], S. Ahn[d], H. Jeon[d], C. Seassal[a]

[a] Université de Lyon, Institut des Nanotechnologies de Lyon-INL, UMR CNRS 5270 Ecole Centrale de Lyon, F-69134 Ecully, France;

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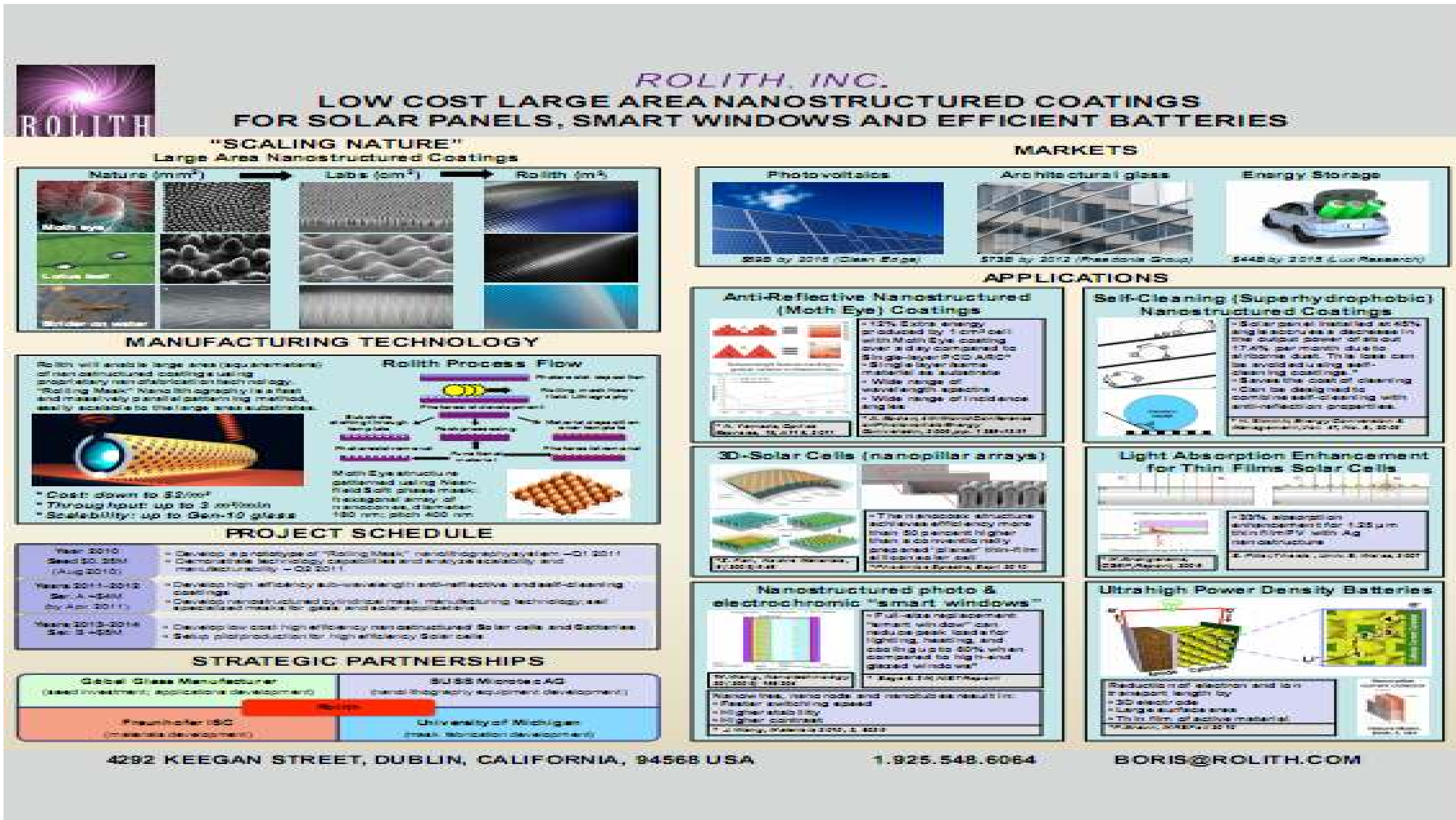
[c] LPICM, CNRS UMR 7647, Ecole Polytechnique, Palaiseau, France

[d] Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea

ABSTRACT

The absorption of thin hydrogenated amorphous silicon layers can be efficiently enhanced through a controlled periodic patterning. Light is trapped through coupling with photonic Bloch modes of the periodic structures, which act as an absorbing planar photonic crystal. We theoretically demonstrate this absorption enhancement through one or two dimensional patterning, and show the experimental feasibility through large area holographic patterning. Numerical simulations show over 50% absorption enhancement over the part of the solar spectrum comprised between 380 and 750nm. It is experimentally confirmed by optical measurements performed on planar photonic crystals fabricated by laser holography and reactive ion etching.

Industry readying to take up large area patterning challenges



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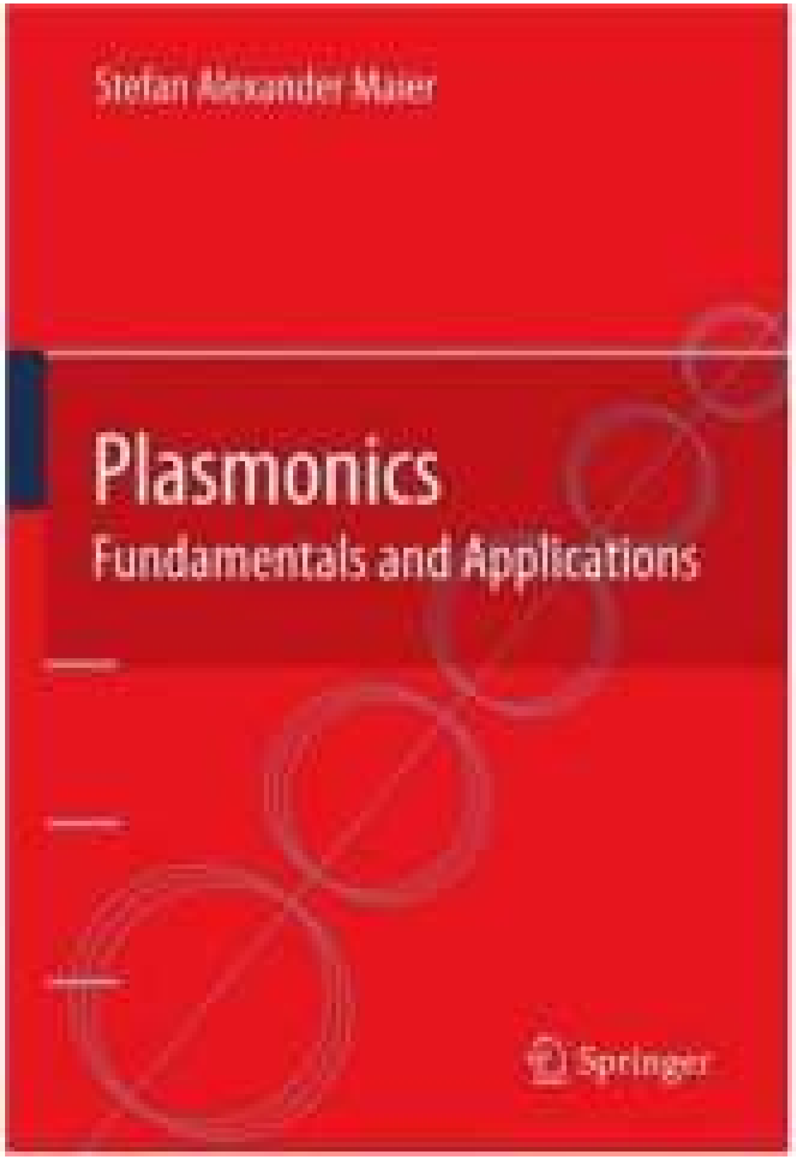

- Metals can be used in unexpected ways.......

Let us see How?

- **"During the first two years of my service at RIKEN, I prohibited those under me from publishing their findings, telling them not to write papers and refrain from giving presentations. I said that we should take our time doing our work. Even if they make a groundbreaking discovery, they should keep the fact a secret for a while. Being busy writing papers and filing patent applications are of no pleasure to researchers. The point of evaluating papers should be in their content rather than their number. I instructed them to store energy before embodying their work. Then, after two years, they all began getting desirable results."**

- Kawata says that he wants to do two things at RIKEN.

- "One of my own goals is to advance research into nanoscale science by means of the photon; this is my lifework. The other is to pioneer a new discipline we call plasmonics."

"Light is, in short, the most refined form of matter."

Louis de Broglie

- **Thank you for the opportunity provided & your Patience**