



Adventures in the nanoworld

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Friday 9th December 2022 @ University of Nagoya, Japan

Poll 1



<https://strawpoll.com/polls/Q0Zp4BwejZM>

Which of these statements is NOT true?

Poll 2

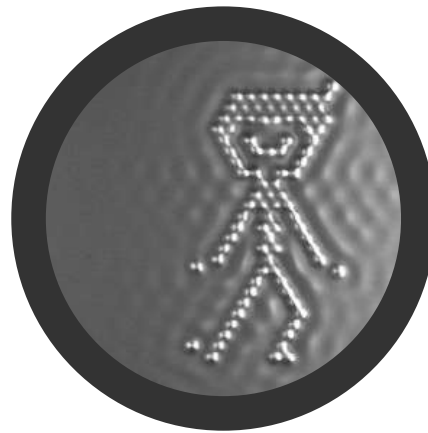


<https://strawpoll.com/polls/bVg86wk73yY>

Which of these is NOT a common function of a porous material?

Layout of talk

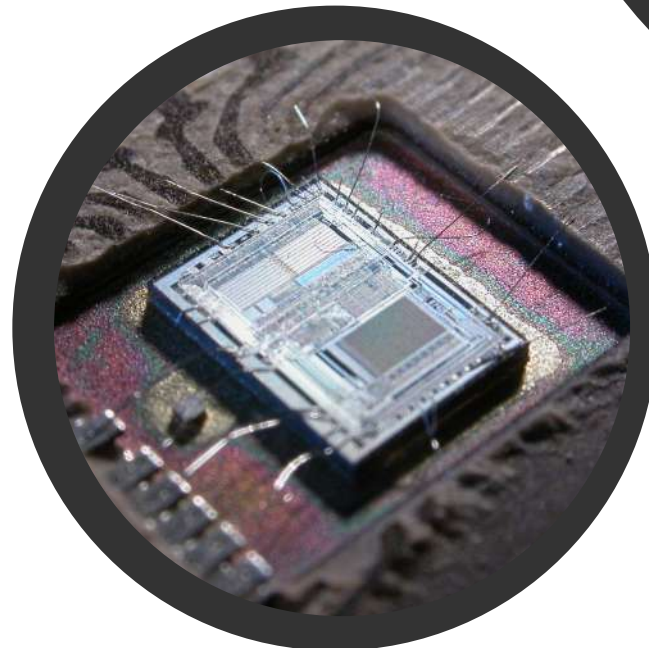
- NanoScience/NanoTechnology
- Seeing, moving and assembling atoms
- Nanoporous materials
- Silicon & Nanostructured silicon
- Tuning properties with nanomaterials
- Fighting cancer & preventing blindness
- “Green” synthesis
- New types of toothpaste, chewing gum & cosmetics
- Careers in (nano) science



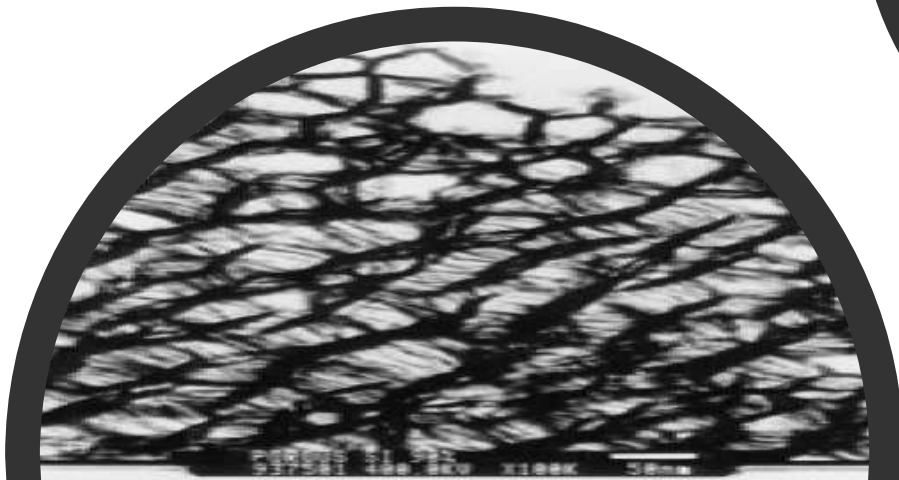
<https://youtu.be/ulk9ouHrCwM> 2022.12.16



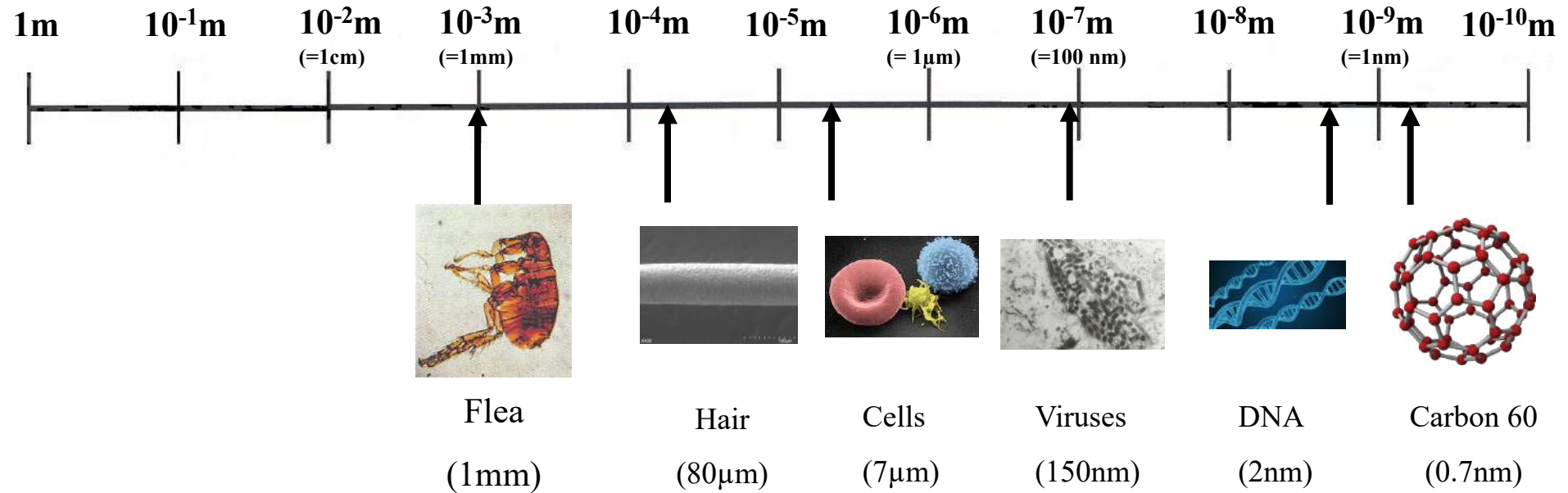
<https://www.pinterest.com/pin/261068109630060/> 2022.12.19



<https://ja.wikipedia.org/wiki/電子回路> 2022.12.16



Definition of nanotechnology

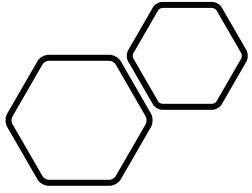


“Nanotechnology is the design, characterisation, production and application of structures, devices and systems by controlling shape and size at nanometre scale”.

The Royal Society Report, July 2004

<https://youtu.be/F7vo8hPwQtl> 2022.12.16

<https://www.lbv.jp/analysis/hairphoto.html> 2022.12.16

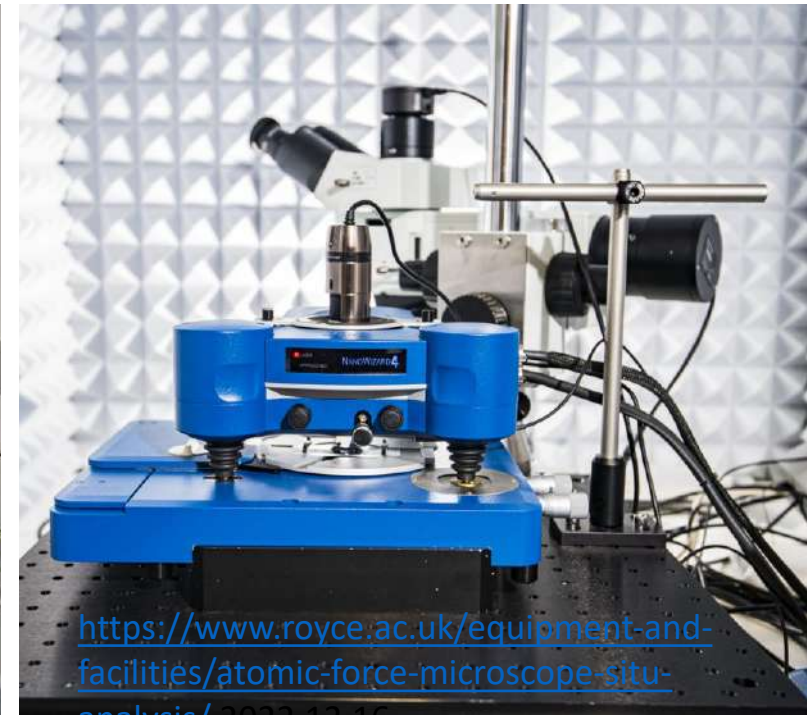
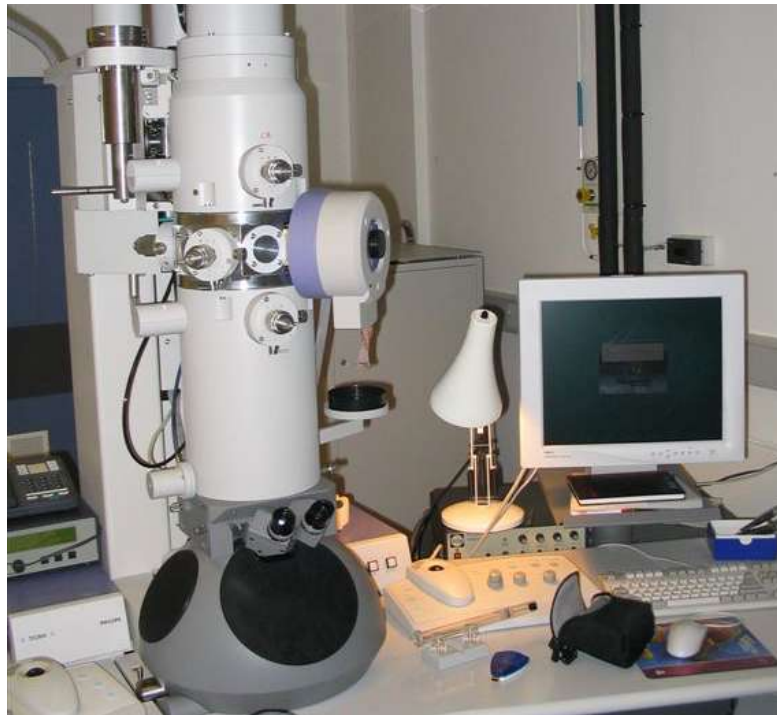


Seeing nanostructures

- Optical microscope
- (up to 2000x magnification)
- **Electron Microscopes**
- **Scanning Tunnelling Microscopes**
- **Atomic Force Microscopes**
- (eg. >1,000,000 x)



<https://www.ibm.com/ibm/history/ibm100/us/en/icons/microscope/> 2022.12.19

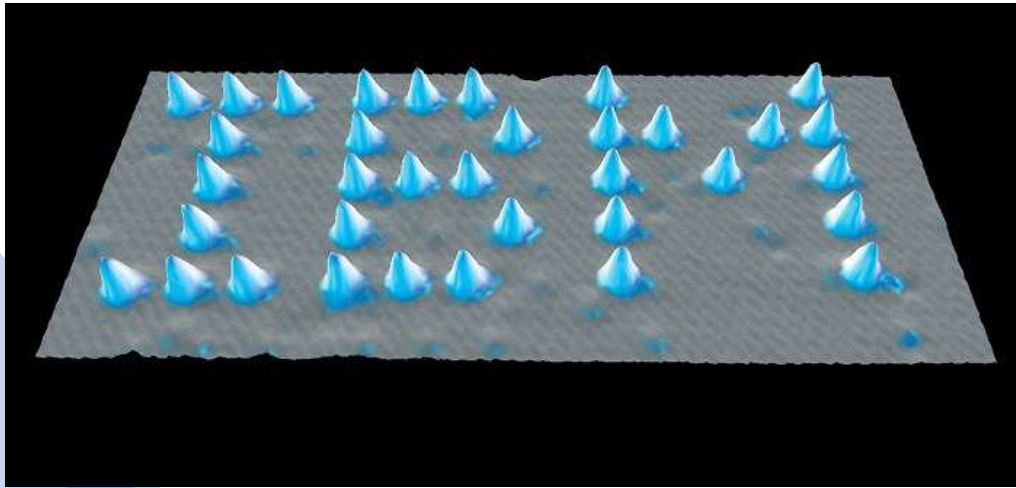


<https://www.pinterest.com/pin/533465518335725374/> 2022.12.19

<https://www.royce.ac.uk/equipment-and-facilities/atomic-force-microscope-situ-analysis/> 2022.12.19

Manipulating atoms

- [Published: 05 April 1990](#)
- **Positioning single atoms with a scanning tunnelling microscope**
- [D. M. Eigler](#) , [E. K. Schweizer](#)
- [Nature](#) volume **344**, pages 524–526 (1990)



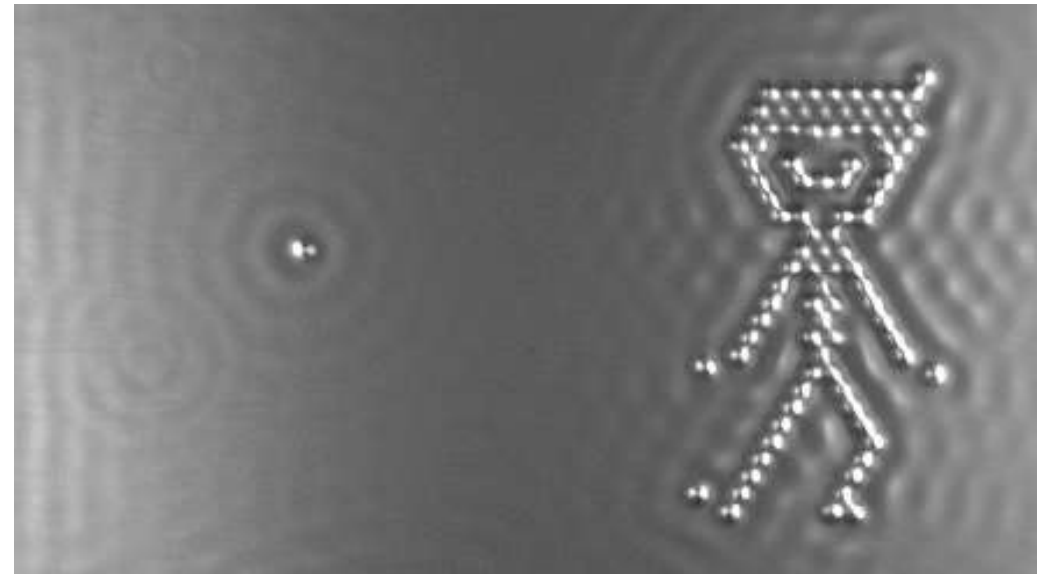
35 Xenon atoms on a cold nickel surface
Took 22 hours (November 9th – 10th 1989) !

Published : 30 April 2013

A boy and his atom : the world's smallest movie

IBM Research

Youtube 1min. 33 seconds



<https://youtu.be/ulk9ouHrCwM> 2022.12.16

Types of nanostructures

- Quantum confinement in 1,2 & 3 dimensions
- Metals, semiconductors, ceramics, organics
- Quantum “dots”, “wires”, “layers”
- **Mesoporous or microporous solids**
- Nanoparticles
- Nanocolloid
- Nanoemulsions
- Nanocomposites

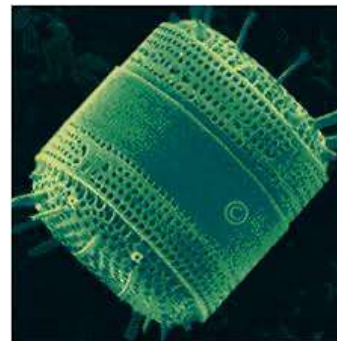
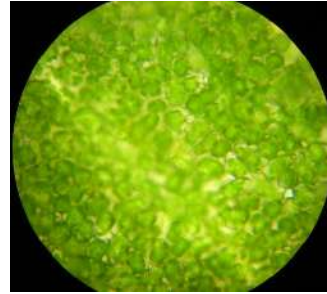
A 1nm diameter NANOPARTICLE of silicon has about 30 atoms

A 5nm NANOPARTICLE of silicon has more than 3000 atoms

Bayda S, Adeel M, Tuccinardi T, Cordani M, Rizzolio F. The History of Nanoscience and Nanotechnology: From Chemical-Physical Applications to Nanomedicine. *Molecules* (Basel, Switzerland). 2019 Dec;25(1):E112.



Quiz No 1. Naturally porous !



<https://www.facebook.com/timbercut4u/photos/a.711452155588689/3489027117831165/> 2022.12.19

<https://www.pinterest.jp/pin/432134526716183802/> 2022.12.20

<https://pl.wikipedia.org/wiki/44Pumeks> 2022.12.20

<https://mobius.world/2021/09/> 2022.12.20

<https://thepotterywheel.com/types-of-clay-for-pottery/> 2022.12.20



Quiz No.2

Well- established synthetic porous materials

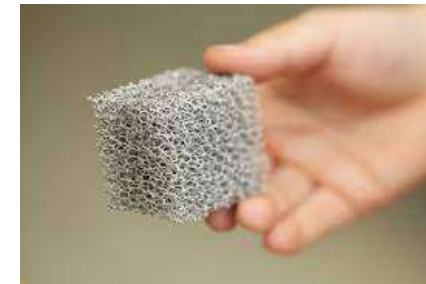


<https://businessday.ng/news/article/kog-i-dangote-cement-dispute-jubilation-as-dangote-cement-obajana-plant-reopens/> 2022.12.20

<https://ifdesign.com/en/winner-ranking/project/spongiosa-metal/27189> 2022.12.20

<https://timesofindia.indiatimes.com/life-style/health-fitness/health-news/what-happens-if-you-accidentally-eat-a-silica-gel-packet-we-tell-you/articleshow/66431539.cms> 2022.12.20

<https://www.wfb-bremen.de/en/page/bremen-invest/mac-panther-materials-metal-foams-from-bremen> 2022.12.20



Classification (IUPAC) of porous materials

BY PORE SIZE :

MACROPOROUS (pore diameter, d , $>50\text{nm}$)

MESOPOROUS ($2\text{nm} > d < 50\text{nm}$)

MICROPOROUS ($d < 2\text{nm}$)

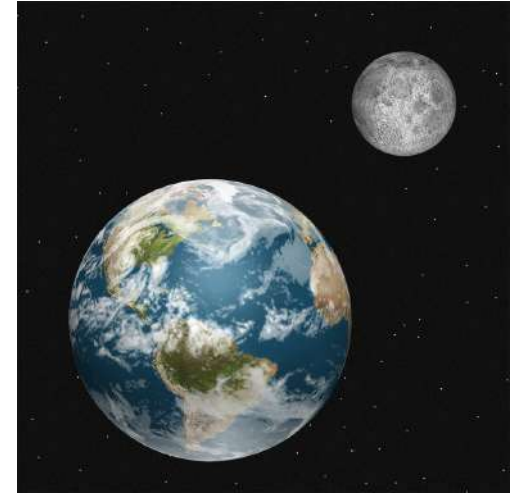
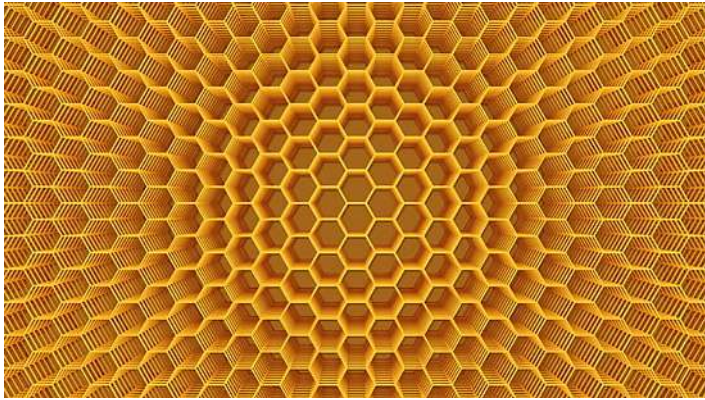
BY PORE SHAPE :

Cylindrical, conical, ink bottle, slit.....

By isotherm position & shape....class I....IV etc

Porosity and nanostructuring

- Directional, “honeycomb” porous structure
- Nanostructured : mesopores of 2-50nm diameter



1cm³ of mesoporous silicon
i.e. sugar cube

Equivalent **surface area** of
a tennis court

Combined pore length of about
10 million km
(25 times distance of earth to moon)

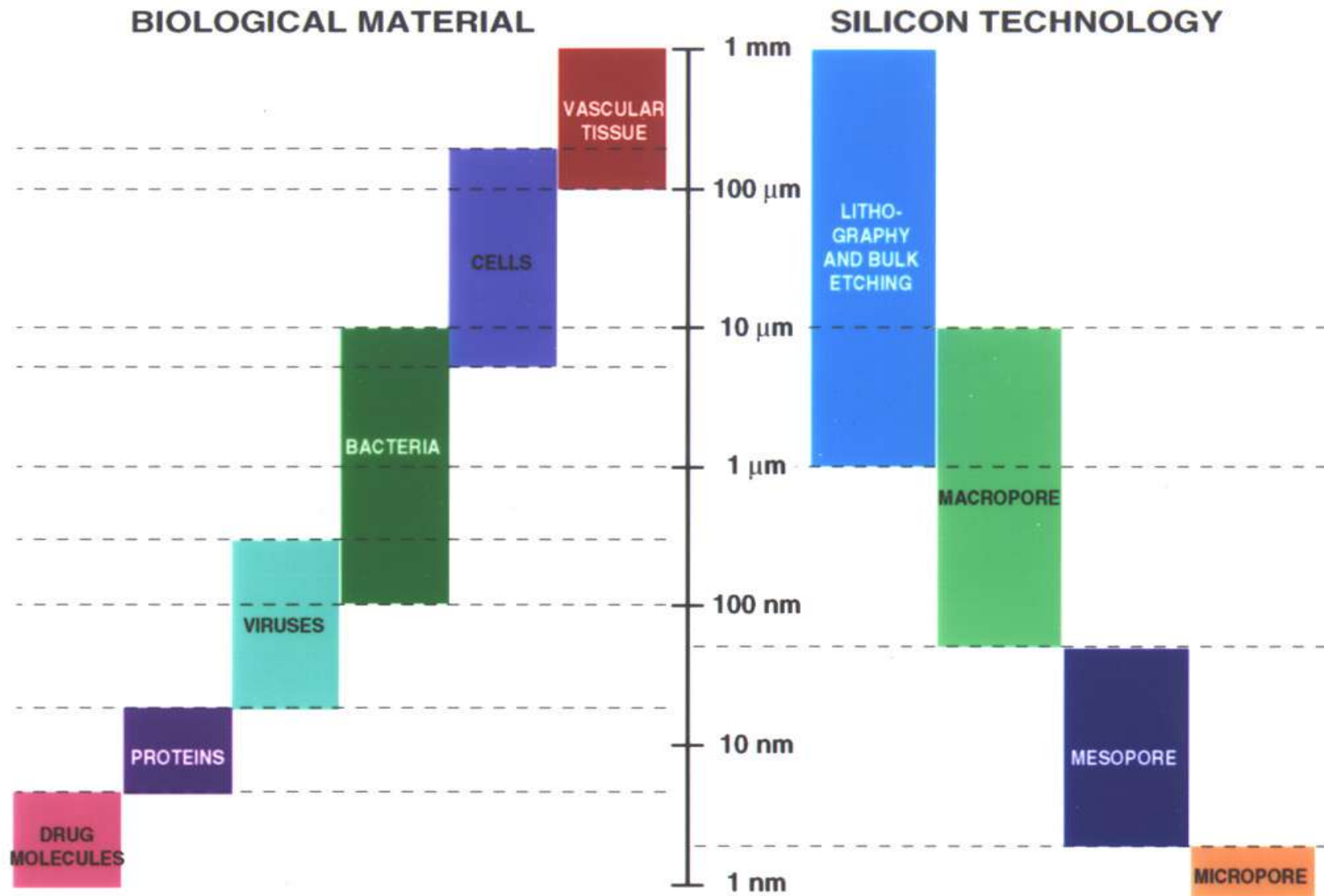


Common functions of porous materials (applications)

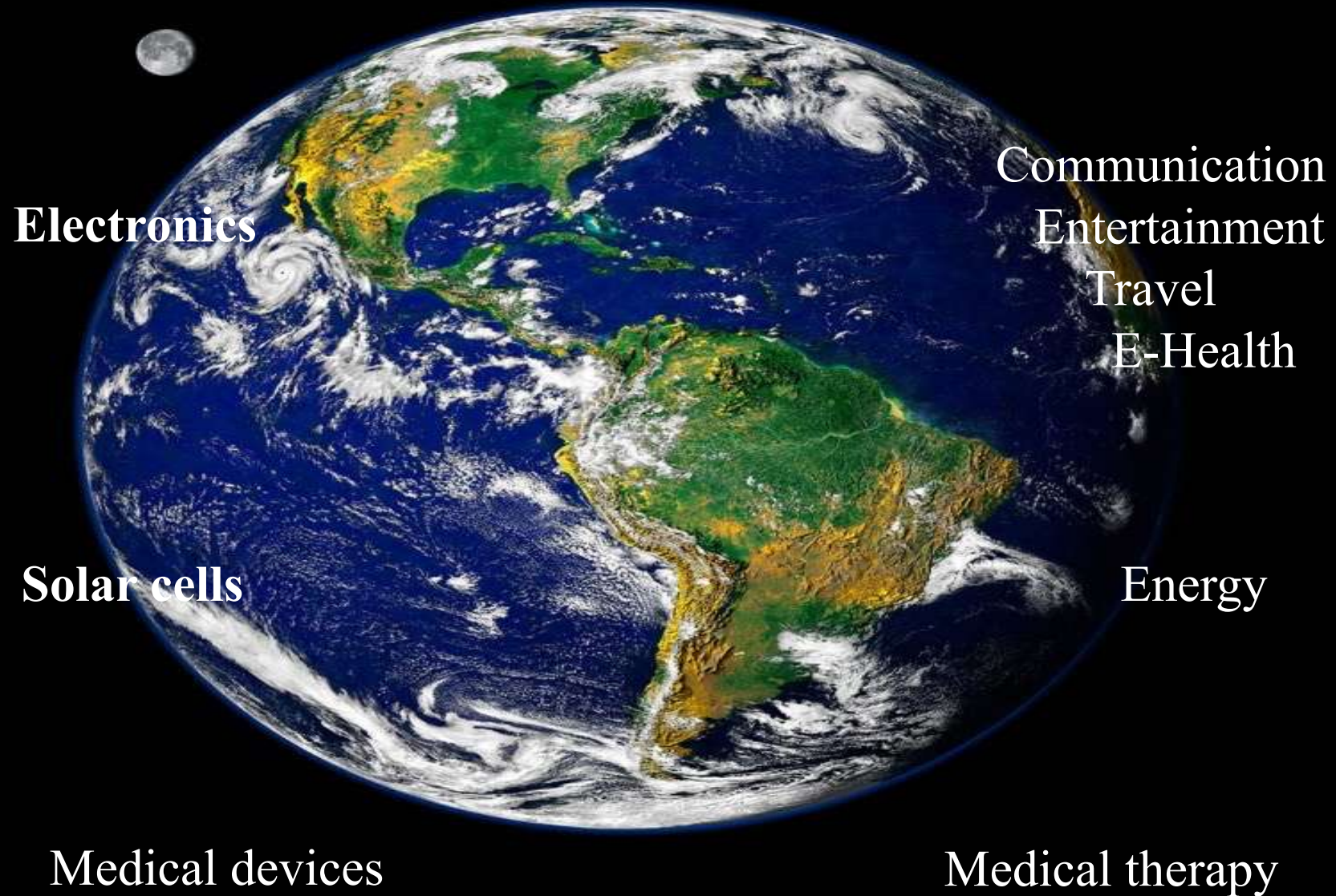
- **FILTRATION** –flow through with restricted access
- SIZE SELECTION
- **ADSORPTION** - selective interaction with skeleton
- CO₂ CAPTURE
- TOXIN CAPTURE
- SENSING
- **STORAGE** – high surface area/pore volume
- TOXINS, NUTRIENTS, HYDROGEN....
- **CONTROLLED RELEASE** – restricted diffusion
- DRUGS, VOLATILES, LITHIUM.....
- **BARRIER** – minimal transport
- THERMAL INSULATION
- ELECTRICAL INSULATION
- **SUPPORT** – high surface area for dispersed “actives”
- CATALYSTS
- BIOSCAFFOLDS



Interfacing silicon with biological building blocks



Silicon in our environment & society



Electronics

Solar cells

Medical devices

Communication

Entertainment

Travel

E-Health

Energy

Medical therapy

Electronics

- >1000 billion \$ market
- Consumer electronics
- Embedded electronics

- A decade ago there were already
- 6 billion mobile phone contracts
- 4 billion people watching television
- 640 million PCs

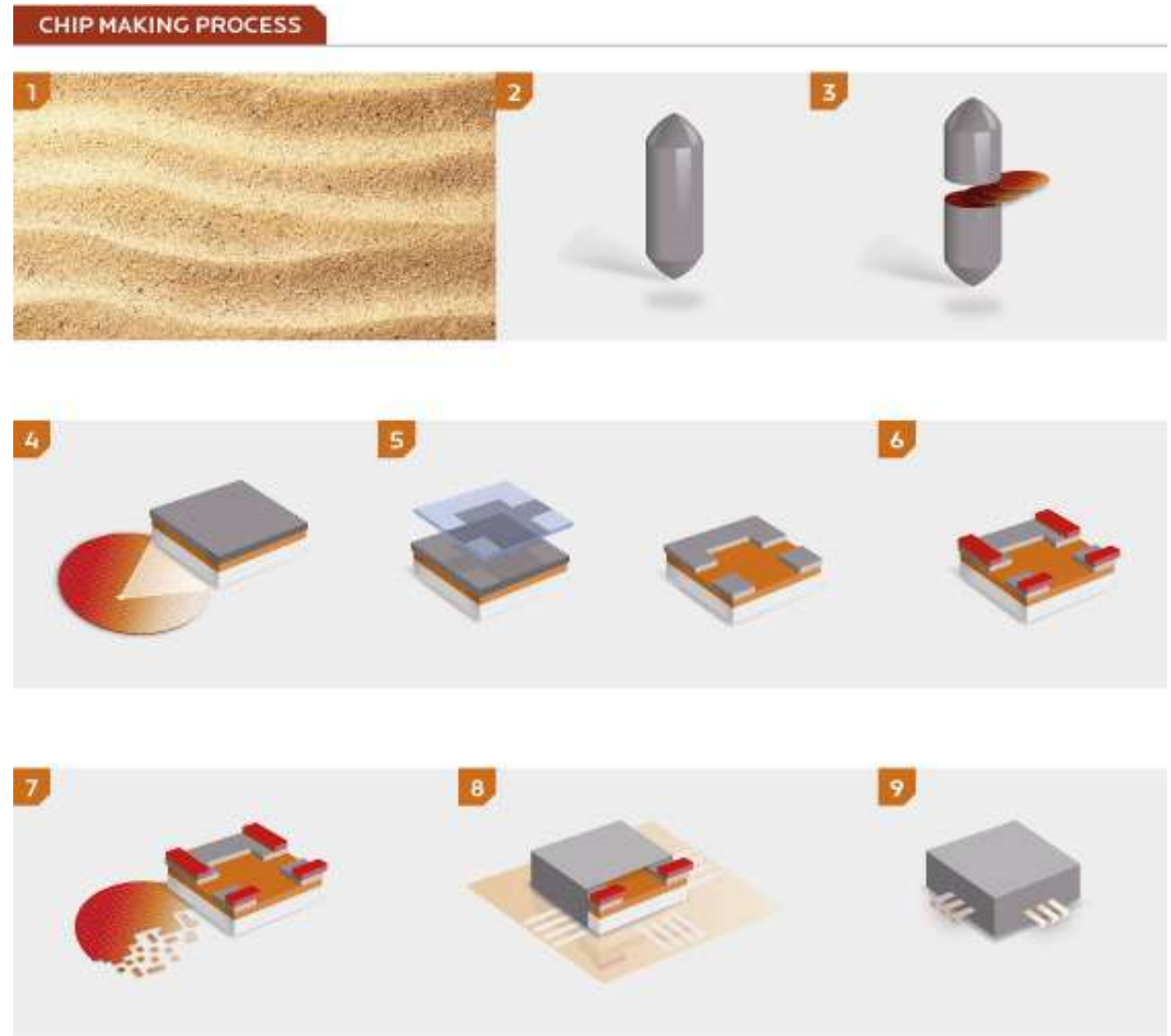


Types of solid silicon

GRADE OF SILICON	INDUSTRY	PURITY (%)	COST (\$/kg)	GLOBAL PRODUCTION (tonnes)
Wafer	Electronics	99.99999	1000	5,000
Electronic	Si crystals	99.999	10-100	19,000
Solar	Solar cells	99.99	10-50	26,000
Chemical	Silicones	99.9	10	675,000
Metallurgical	Steel	97-99	1-5	1,000,000

Electronics “from sand”

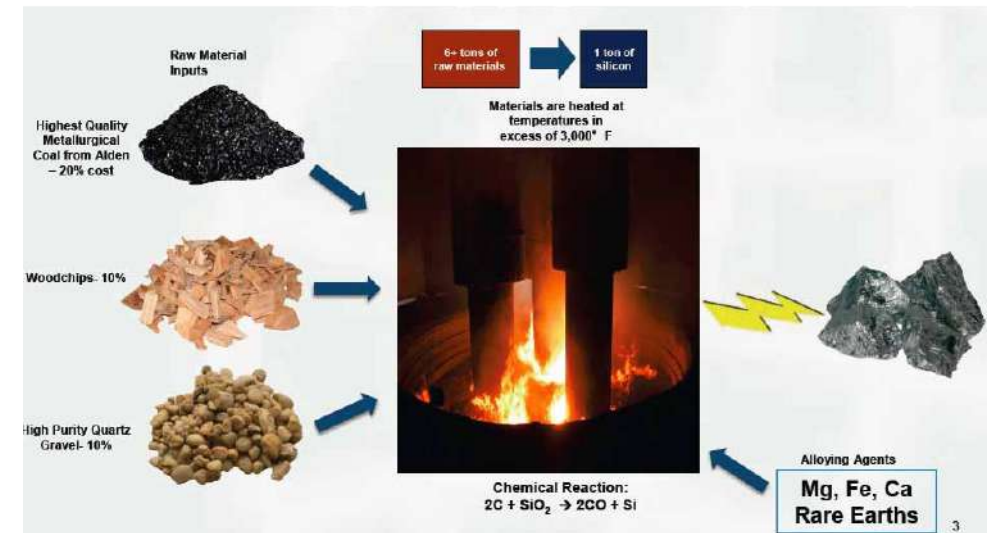
1. Sand → Impure silicon
2. C-Si ingot
3. Wafers
4. Deposition
5. Masks
6. Photolithography
7. Chips
8. Protection
9. Testing

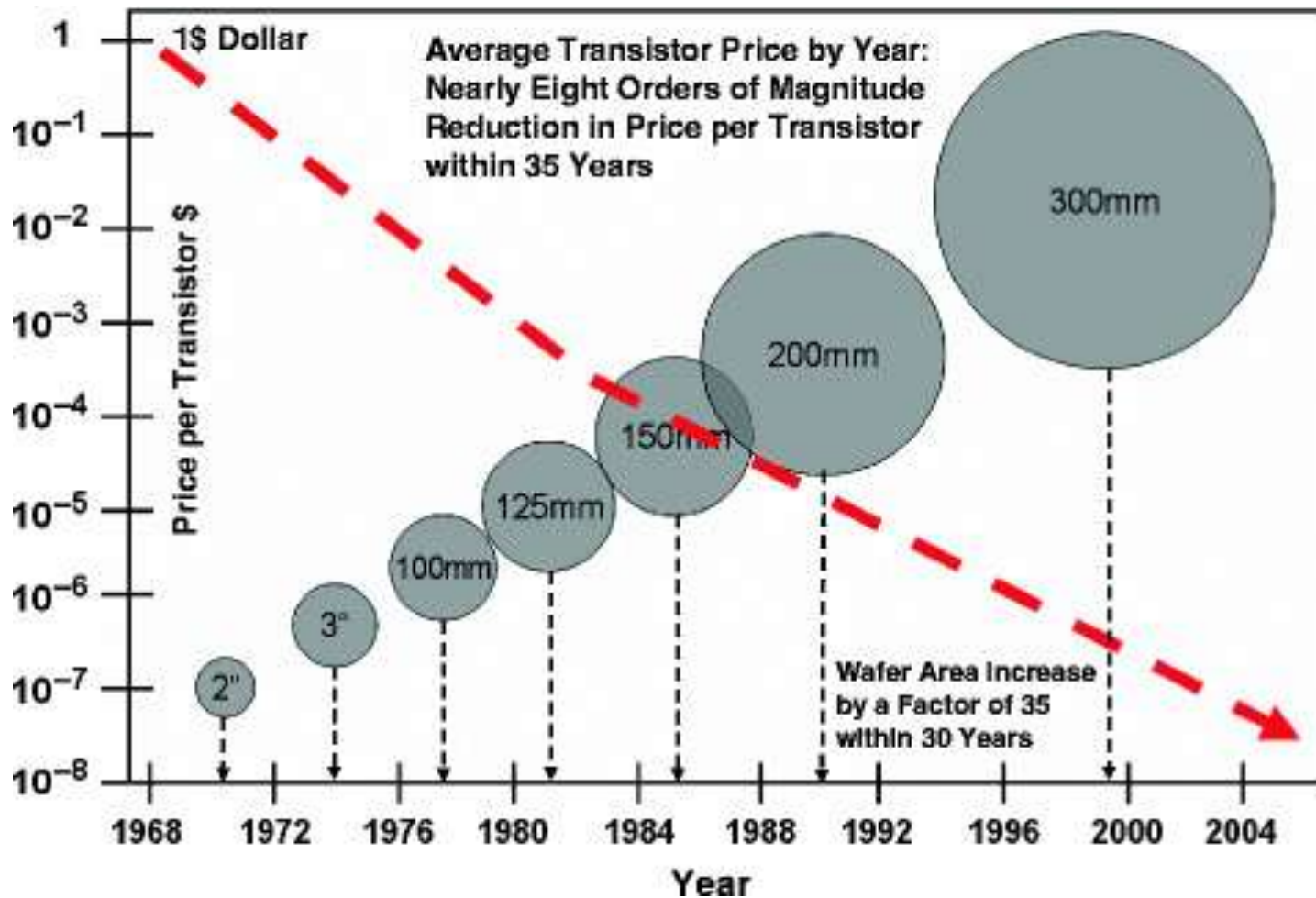


Silica to Metallurgical grade Silicon (MG Si)



- **Submerged Arc furnace** with a crucible diameter about 7 metres and fed by 3 carbon electrode columns about 15 metres high and weighing 20 tons each
- Low cost electricity is critical
- Every ton of Silicon needs 12MWh of energy





Plummeting
 cost of
 silicon-
 based
 electronics

By 2019, nearly 70% of all humans used Si based electronics

Photovoltaics

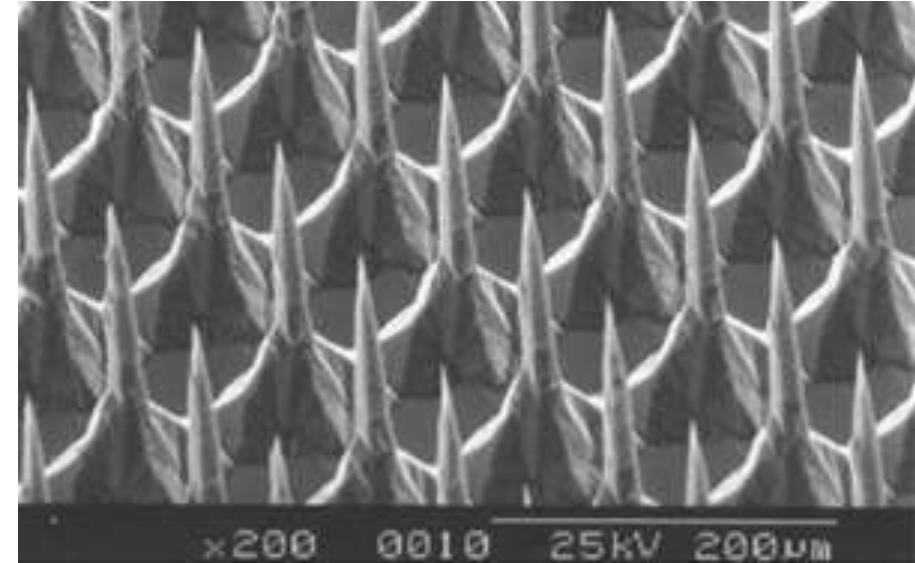
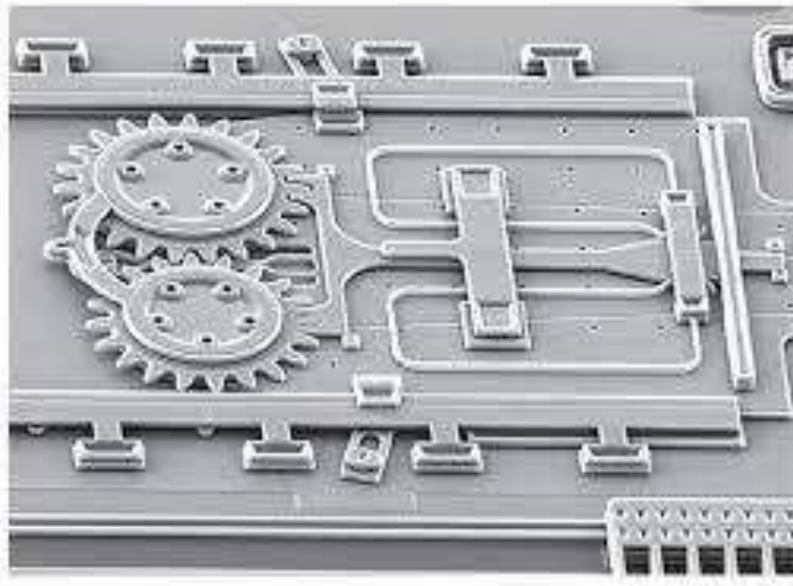


<https://project.nikkeibp.co.jp/ms/article/NEWS/20150527/420383/?ST=msb> 2022.12.21



<https://www.kankyo-business.jp/news/005138.php> 2022.12.21

“MEMS” MicroElectroMechanicalSystems



- Sandia National Labs, USA
<https://www.sandia.gov/media/NewsRel/NR2002/chain.htm> 2022.12.21

MEMS Group, Univ. Nagoya, Japan
<https://nanofab.engg.nagoya-u.ac.jp> 2022.12.21

Tiny devices, often with moving parts, fabricated via similar techniques & infrastructure developed for microelectronics.

Silicon MEMS Devices

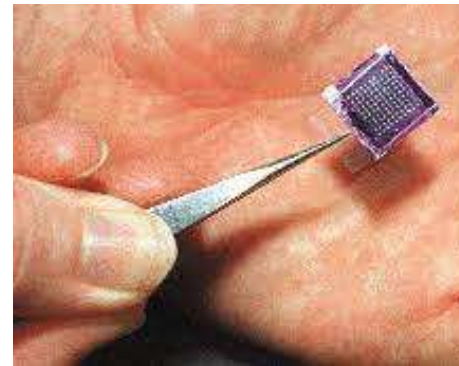
<https://cdn-brand.napaonline.com/bosch-automotive/> 2022.12.22



- There are Silicon-based.....
.....microrobots, drones
.....retinas, cochlears, noses, tongues
.....timers, pressure sensors
.....microphones, accelerometers.....



<https://www.rfmw.com/products/detail/sit95141aib00030-sitime/699874/?pid=> 2022.12.22



<https://www.eetimes.com/mems-tongue-mimics-taste-buds/> 2022.12.22

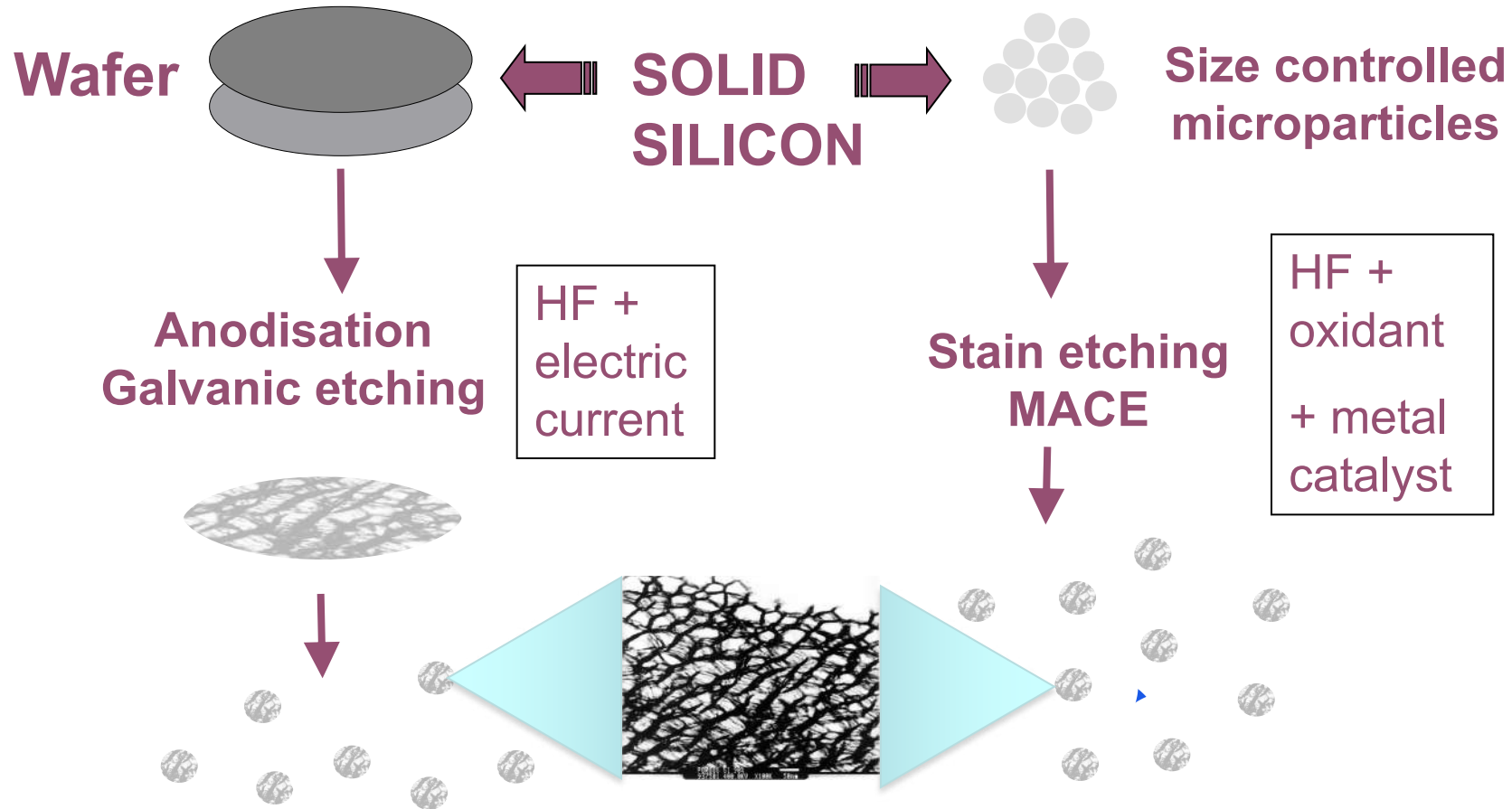


<https://youtu.be/qFmeHPVtK0o> 2022.12.22



<https://www.hearingloss.org/hearing-help/technology/cochlear-implantable-devices/> 2022.12.22

Electrochemical etching of solid silicon



Very wide size range of directional mesopores in microparticles and nanoparticles

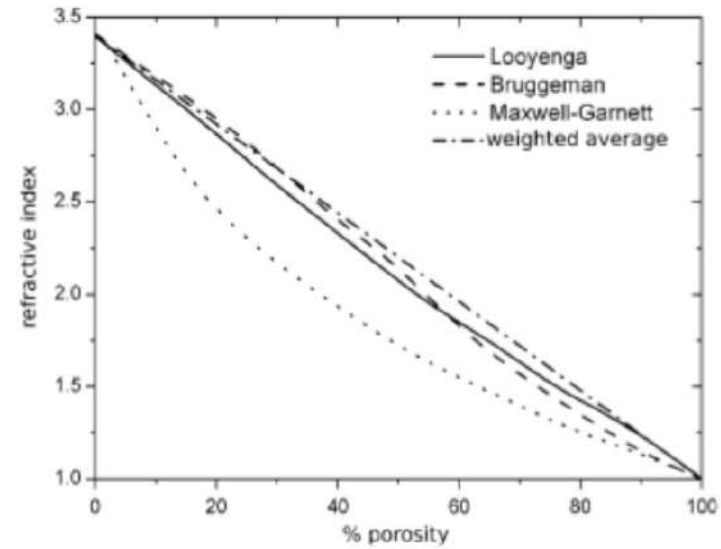
Motivation for nanostructuring :

tunable properties & **novel** properties

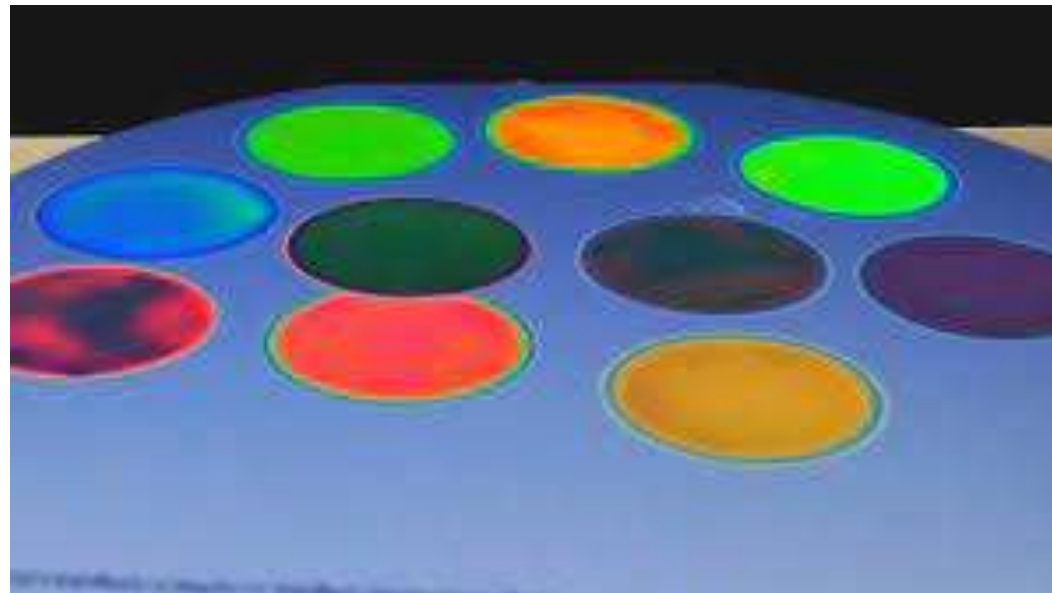
	SILICON	MESOPOROUS SILICON
Pore Size	N/A	1.5nm - 50nm
Surface Area (BET)	N/A	1 - 700 m ² /g
Bandgap	1.1eV	1.1 - 3.2 eV
Resistivity	10 ⁻³ - 10 ³ ohm cm	10 ³ - 10 ¹² ohm cm
Youngs Modulus	160 GPa	1 - 100 GPa
Thermal Conductivity	150 Wm ⁻¹ K ⁻¹	1 - 100Wm ⁻¹ K ⁻¹
Refractive Index (IR)	3.5	1.1 - 3.0

Tunable optical property :

- **Refractive index, n**
- Effective medium modelling : mixture of air, silicon, silicon oxide.
- Modulated n
- → mirrors
- → photonic crystals
- → microcavities
- → waveguides
- → optical biosensors



Surf.Sci.Reports 29, 91 (1997)



Emissive properties :

Types of luminescence

- **PHOTOLUMINESCENCE**
- **ELECTROLUMINESCENCE**
- **CATHODOLUMINESCENCE**
- **CHEMILUMINESCENCE**
- **BIOLUMINESCENCE**
- **MECHANOLUMINESCENCE**
- **LYOLUMINESCENCE**
- **THERMOLUMINESCENCE**
- **RADIOLUMINESCENCE**



<https://twitter.com/DrummerBoy2112/status/928618851151106048> 2022.12.26

Quiz No. 3

Type of luminescence ?



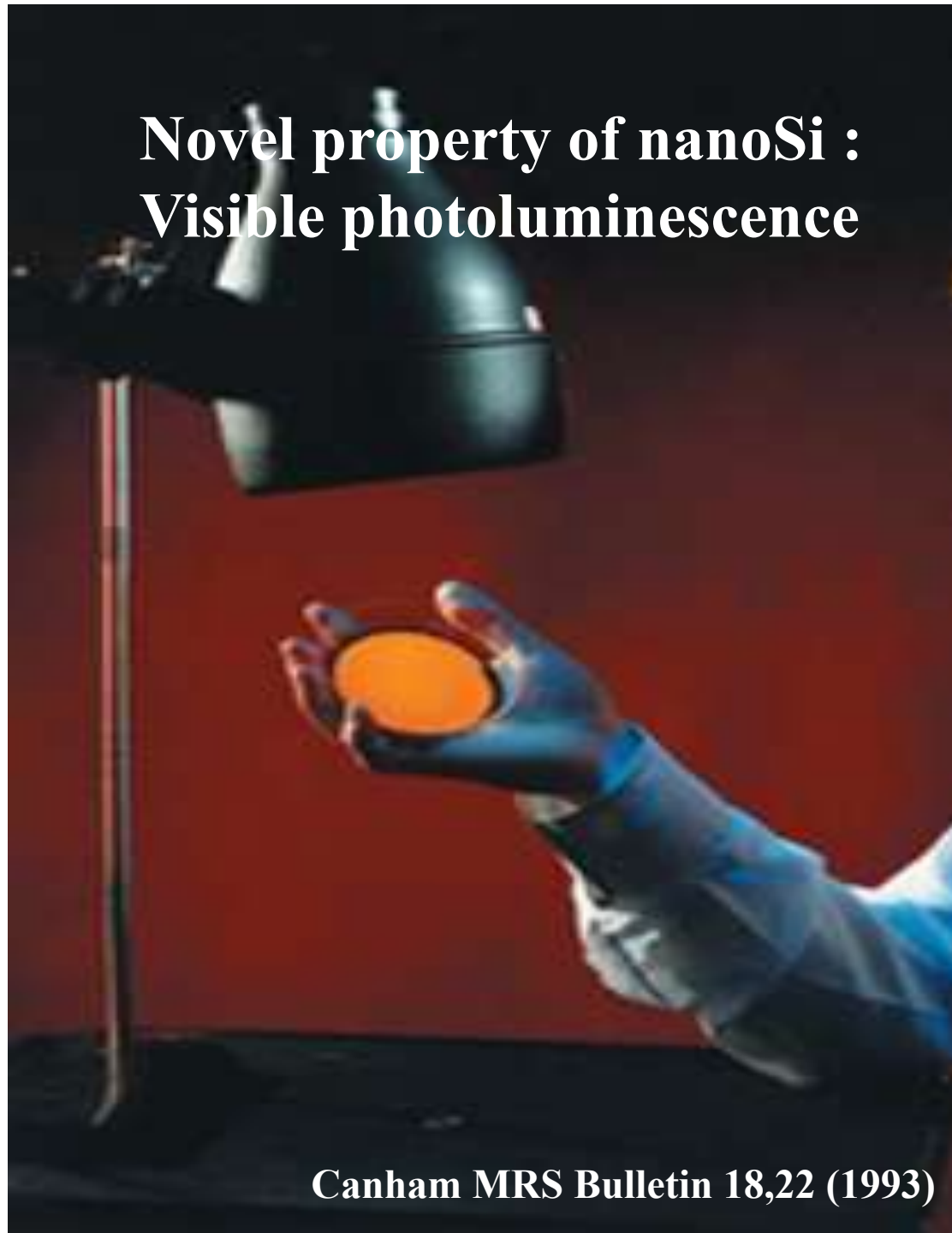
<https://www.amazon.co.jp/TURNMEON-Glow-Sticks-バルクパーティー記念品用品-暗闇で光るパーティーパック/dp/B0834TMXF2> 2022.12.26

Type of luminescence ?

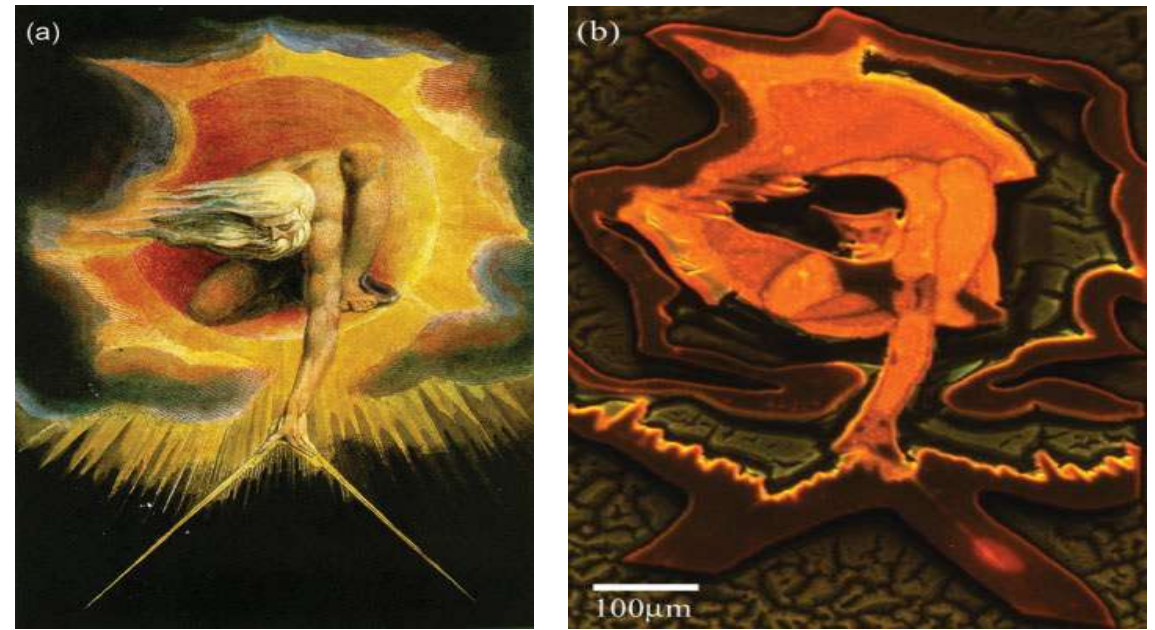


Type of luminescence?

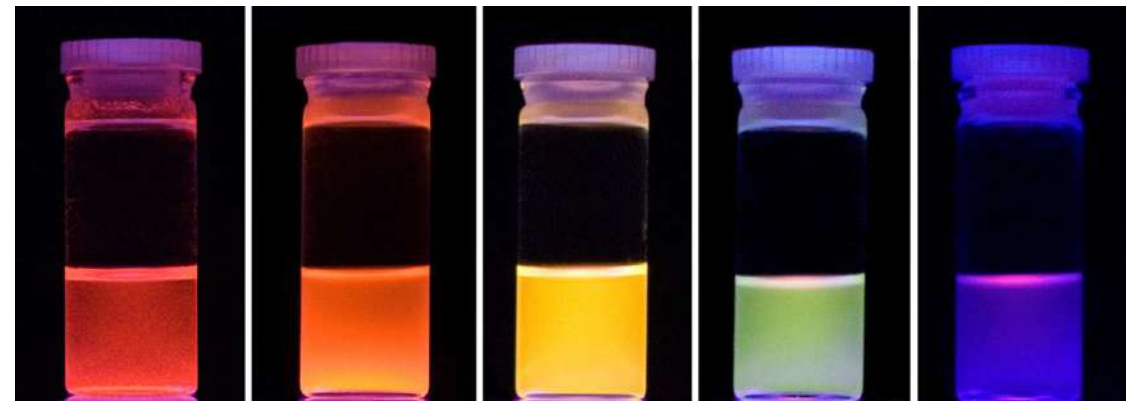
Novel property of nanoSi : Visible photoluminescence



Canham MRS Bulletin 18,22 (1993)

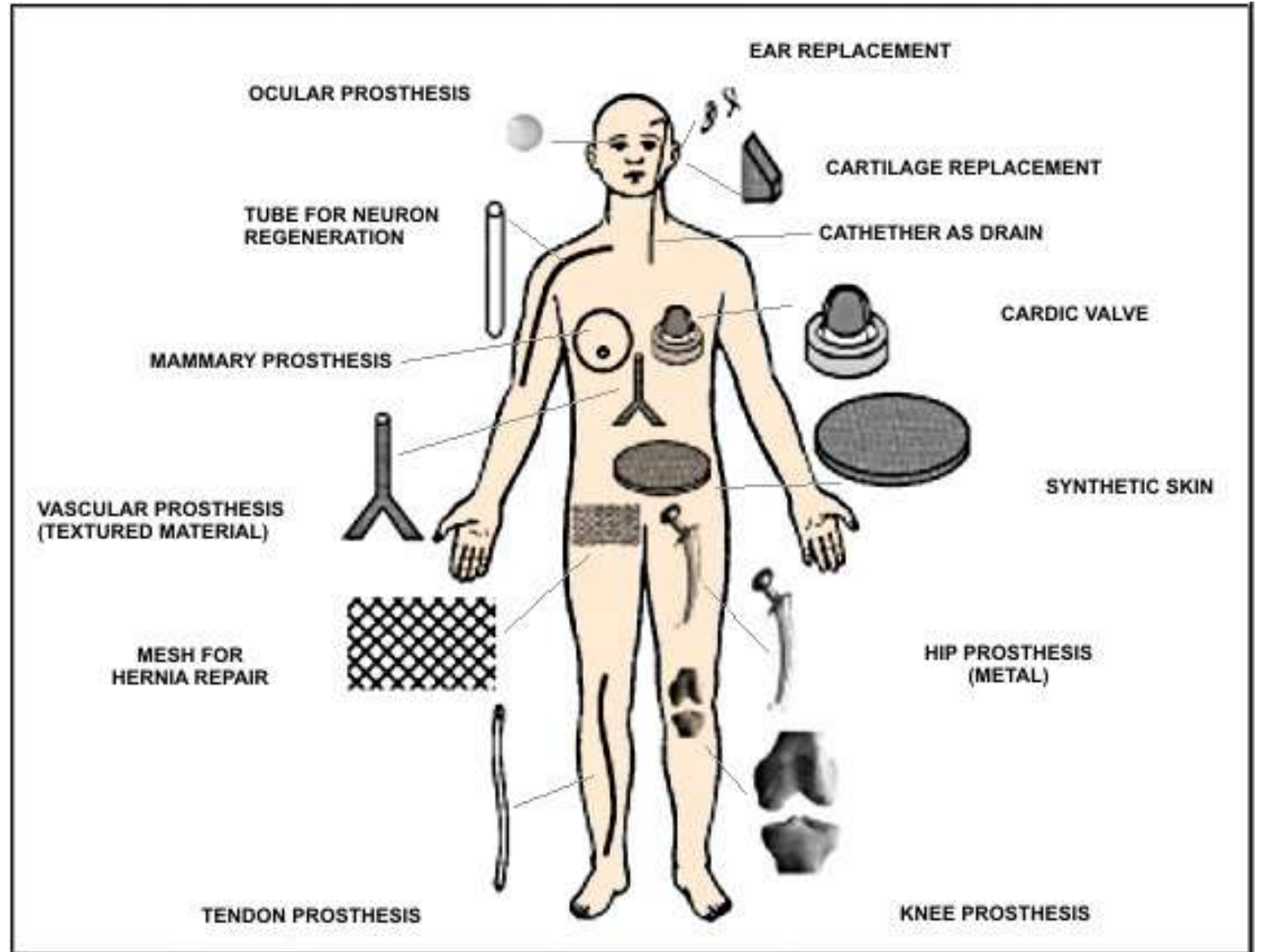


Teo et al. Adv.Mater. 18,51 (2006)



Pi et al. Nanotechn.19,245603 (2008)

Quiz No.4. What is a “biomaterial”



Asmatulu, R.. (2023). Biomaterials Course Development for Undergraduate Engineering Education.

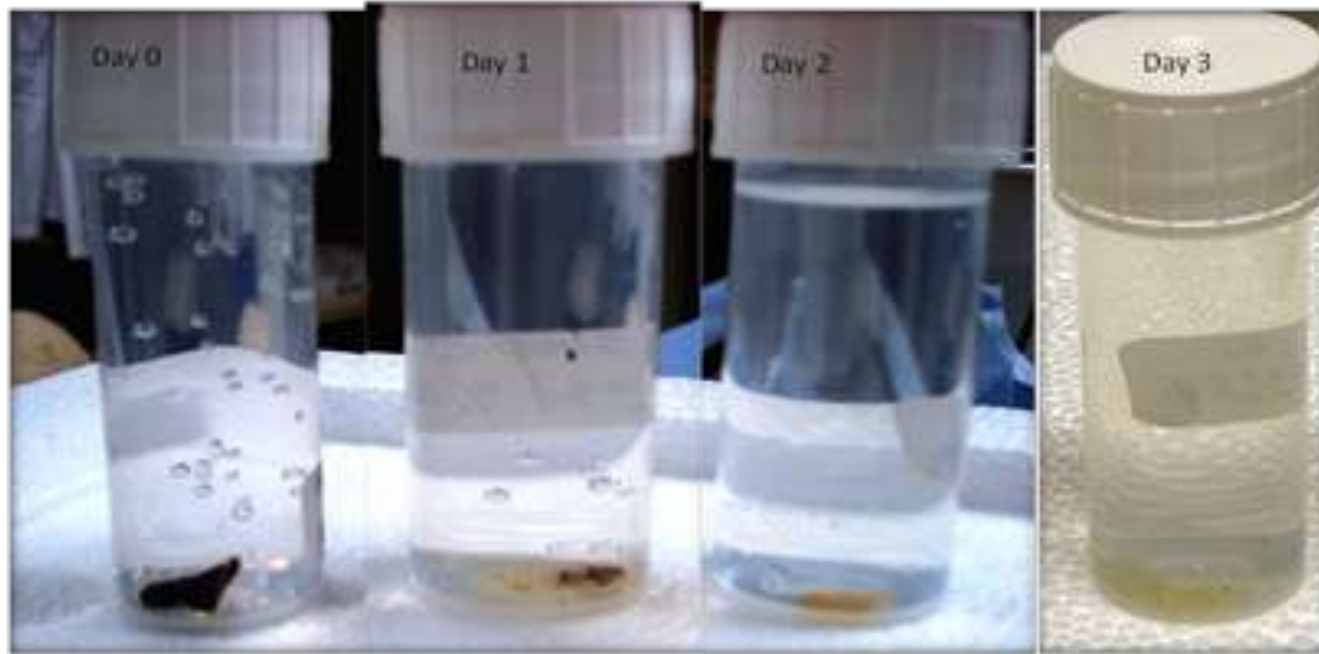
What is a “biomaterial” ?

- “A biomaterial is a nonviable material used in a medical device, intended to interact with biological systems” (Williams 1987)
- ‘any substance or combination of substances, other than drugs, synthetic or natural in origin, which can be used for any period of time, which augments or replaces partially or totally any tissue, organ or function of the body, in order to maintain or improve the quality of life of the individual” (NIH, USA)
- **“a synthetic material used to replace part of a living system or to function in intimate contact with living tissue”
(Park & Lakes 1992)**
- “any material used to make devices to replace a part or function of the body in a safe, reliable, economic and physiologically acceptable manner” (Park & Lakes 2007)

→ “biomaterial” vs “ biological material”

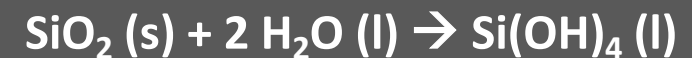
→ “in-vivo” vs “in-vitro” use

Novel property of nanoSi : medical biodegradability



- nanostructured silicon undergoes hydrolysis into orthosilicic acid Si(OH)_4 .

- It can be described as:



- Silicic Acid is the most natural form of silicon - the form we absorb from our diet and is present in our blood at about 1ug/ml
- Excretion is via kidneys

Silicon microelectronics in the body

CLINICAL AREA	MICROELECTRONIC IMPLANT
Cardiovascular	Pacemaker
Audiology	Cochlear implant
Orthopaedics	Spinal fusion stimulator
Drug delivery	Programmable pump
Urology	Bladder stimulator
Gastroenterology	Endoscopic pill
Neurology	Vagus nerve stimulator
Radiology	In-vivo dosimeter
Obstetrics	Radio pill
Pathology	Smart microneedles

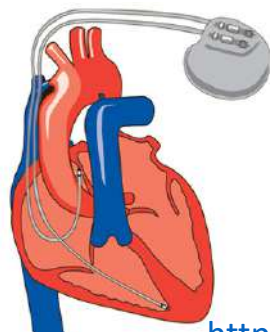
<https://seekingalpha.com/article/1604312-given-imaging-slightly-undervalued-strong-upside-potential-but-also-some-risks> 2023.1.4



<https://neupsykey.com/vagus-nerve-stimulation-therapy-2/> 2023.1.4



<https://www.ronc.ru/about/lenta-sobytiy/nevrokhirurgi-onkotsentra-lechat-khronicheskiy-bolevoy-sindrom-s-pomoshchyu-sovremennykh-implantirue/> 2023.1.4



<http://www.exeterheart.com/services/pacemakers-for-slow-heart-rates-2/> 2023.1.4

Biomedical MEMS: Clinical applications of silicon technology.
Technology Tracking Report 201pp .Canham. (IOP Publishing 2003)

Brachytherapy

Drug delivery

Imaging

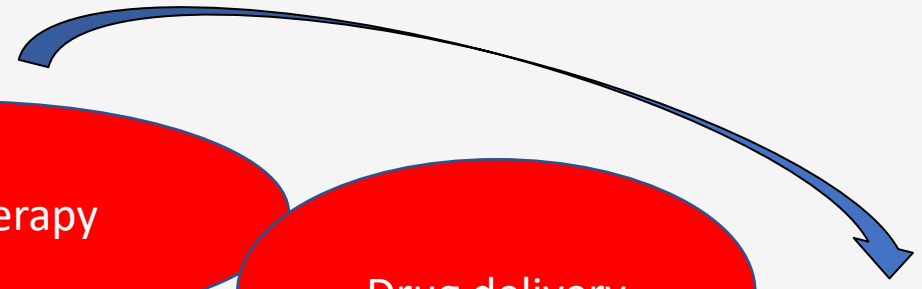
PDT

Orthopaedics

Wound repair

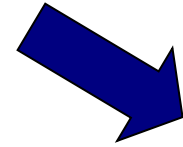
Tissue engineering

MEDICAL USES OF BIODEGRADABLE SILICON

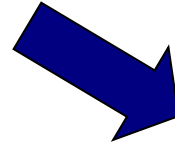


Clinical trials & the regulatory process for a medical device

Device classification



Biocompatibility tests

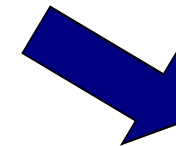


Clinical trials

Phase I Clinical Trial: screening for safety
1.5 years, 10-100 healthy volunteers, \$10M

Phase II: suitable protocol for large study
2 years, 50-500 patients with disease, \$20M

Phase III: confirmation of efficacy
3.5 years, 300-30,000 patients, \$45M

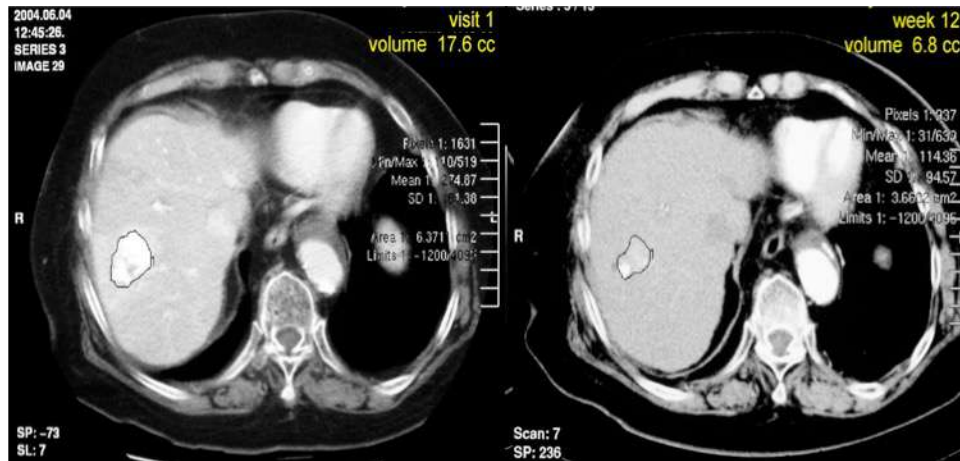


Marketing approval

Clinical Trials - Brachytherapy

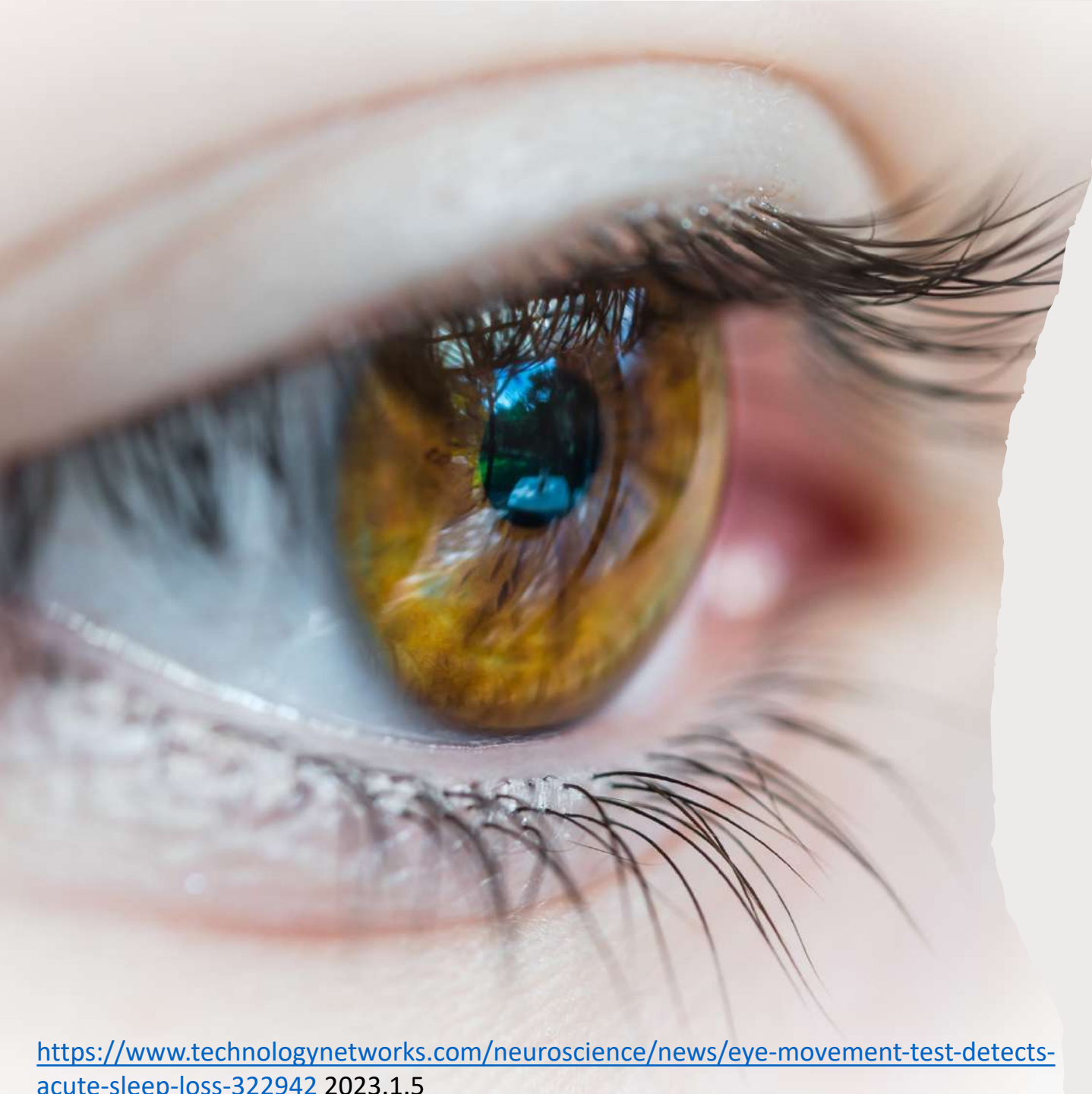


First clinical trials:
Liver cancer 2004
Pancreatic cancer 2007



Efficacy:
Tumor regression after 12 wks (CT scan).

Cf. pSiMedica Ltd, UK ; pSiOncology, Singapore



Ocular biomolecule delivery

- **Retinal diseases** are the main cause of blindness and severe vision loss in industrialized countries
- **Age related Macular Degeneration (AMD)**
- 34 million people affected in EU currently
- Nearly 1 million require treatment
- Of particular concern in countries with elderly populations eg. Japan
- IVT – monthly injections to back of eye
- In UK : Eylea £800 per 2mg injection
- Strong driver for **sustained release (6 month – 1 year) formulations**

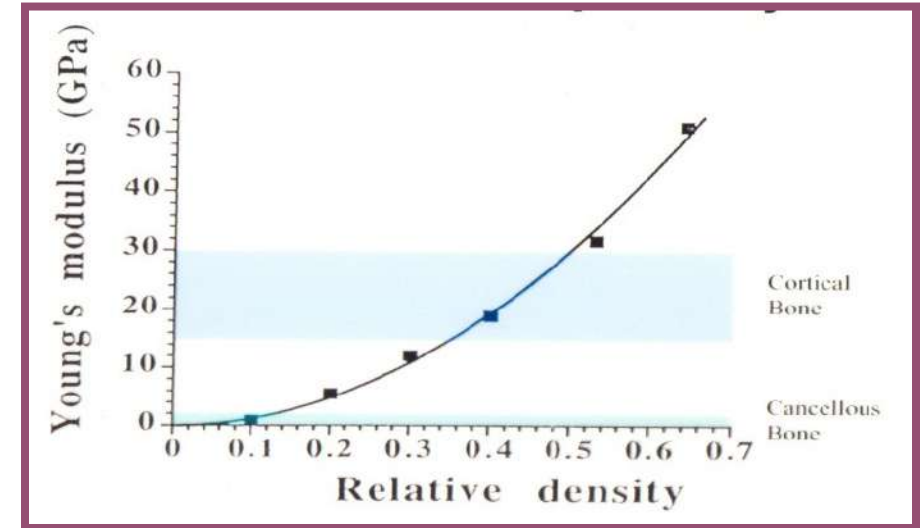
Application illustration : orthopaedics

4

Bone fixators for children's faces

- Biodegradable pins/screws for maxillofacial surgery
- Target: moldable osteo-inductive material with slow biodegradability
- pSi/PCL molded microcomposite
- In-vitro bone marker assays (osteoblasts)
- Mechanical characterization

PhD project at Nottingham Medical School.



2020+



Green synthesis

The semiconductor from **plants** !

- Botanists call some plants “silicon accumulators”
- They take up silicon-based molecules from soil
- They make silica nanostructures in their stems and leaves



<https://tabledebates.org/research-library/journal-article-increased-greenhouse-gas-intensity-rice-production-under-future> 2023.1.5

<https://www.pinterest.jp/pin/708754060082607043/?mt=login> 2023.1.5

What are the chemical reactions we can use ?



Vegetation → mesoporous silicon



Silicon accumulator plant

1. Cultivate, crop, wash, dry, grind
2. HCl-based wash
3. Calcination

Biogenic silica plant extract

1. Magnesiothermic reduction
2. HCl wash to remove Mg phases

Biogenic mesoporous silicon

<https://www.flickr.com/photos/30541846@N03/7837951872> 2023.1.5

<https://akbelkimya.com.tr/sodyum-metasilikat-143-urun> 2023.1.5



<https://www.belt-furnace.com/projects> 2023.1.5

Continuous feeding of trays with powders of biogenic silica, magnesium and salt (30g batch size)



Batchelor et al. Silicon 4: 259-266 (2012)



2010-2015 Intrinsiq Nanomaterials Ltd

Nutrition, cosmetics and
consumer care products from
nanoporous silicon

Functional foods

Chewing gum

Sunscreens

Toothpaste

Quiz No. 5

What is it in toothpaste that cleans our teeth?

Market sector	Global Market (billion \$)
Oral hygiene	24
toothpaste	14
toothbrushes	6
mouthwash	2
denture care	1.7
dental floss	0.5



Answer : **Abrasives**

Crushed bone.....crushed egg shells Powdered charcoal

Alumina.....calcium phosphate.....calcium carbonate

Silica... → porous silica → porous silicon?

Strength vs Hardness

Cleaning vs Eroding



Our target : multifunctional gentle toothpaste

<https://www.facebook.com/Coipiodonto/photos/4638782186198182> 2023.1.11

Functional foods

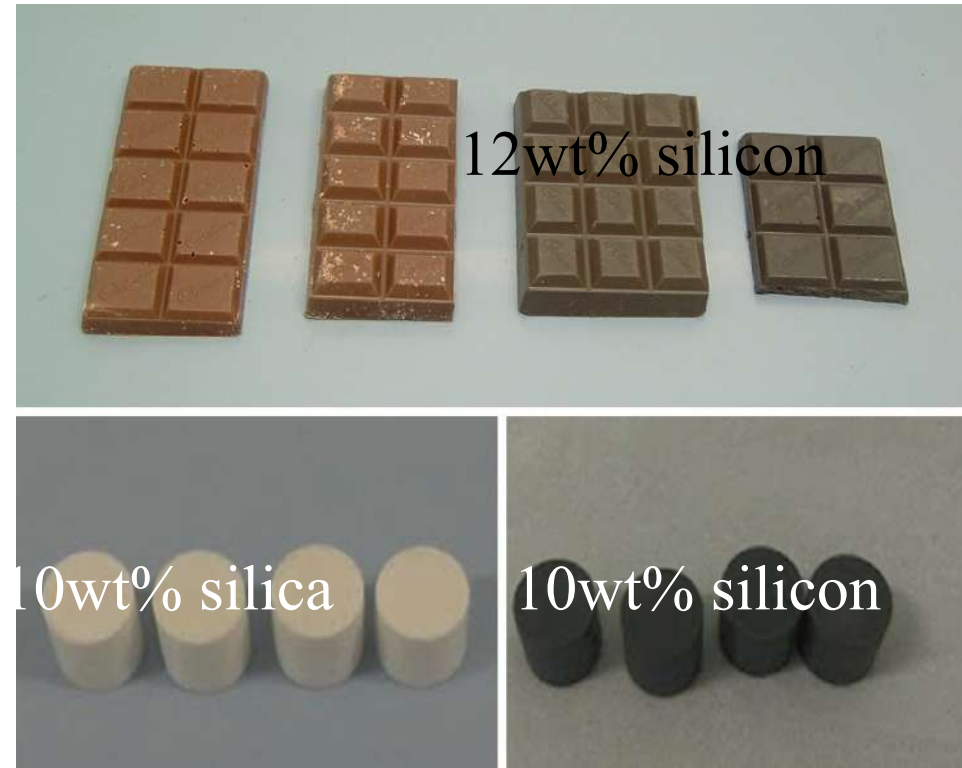


<https://youtu.be/MWYDOPtw6Fc> 2023.1.11

- Stability in saliva, stomach fluid, intestinal fluid.
- Taste & mouthfeel
- Oral toxicity
- Colour
- GRAS status

- pSiMedica Ltd
- Intrinsiq Materials Ltd

Nutrient protection
Nutrient bioavailability
Controlled release



How can we improve Chewing Gum ?



<http://napajapan-candy.blogspot.com/2016/11/japanese-chewing-gum-options-galore.html> 2023.1.11

Application illustration: foodstuff

- **Target : multifunctional gum**
- £18 billion global market>20% of population in Japan chew gum once a week (2017 survey)
- **Controlled release** of actives through modulation of particle porosity
- **Improved bioavailability** or dissolution kinetics through entrapment in mesopores
- **Improved range of actives:**
 - flavours , sweeteners & nutrients
 - antimicrobials
 - effect ingredients
- **Re-mineralization** – possibility of using it as a re-mineralizing agent in-situ for sensitive teeth
- *Stride gum – flavour switching*



<https://bigdaddysliquors.com/shop?product-id=57aa2a1269702d1fad1b0e01&option-id=4ccb2db22e09ca5cce45d637edaf04eafb3b0d954ed597ba5073c52e398f5885> 2023.1.11



<http://www.nearof.com/review-stride-spark-vitamin-chewing-gum/> 2023.1.12

Application example : cosmetics

- OPPORTUNITIES :
- **Eg. Anti-aging formulations** : optical brighteners (facial)
 - → biocompatible blue/green emitting silicon nanoparticles
- **Eg. Sunscreen** in bronzers
 - → UV absorbing brown microparticles
- **Eg. Sebum absorbent** in foundation
 - → High pore volume microparticles



https://phpspot.org/blog/archives/2008/07/photoshop_83.html 2023.1.12

Bronzers



Foundation



Facial cream

Careers in science



Opportunities: Academic research, industrial research, industrial product development, technology analysts, technology marketing, freelance consultant, entrepreneurship, teaching, patent attorney, scientific publishing, scientific journalism, TV presenter.....



What area(s) of science do I enjoy most?



Am I more interested in understanding or using science?



Am I more practical or more analytical?



Is job satisfaction or salary more important to me?

Are **you** creative or innovative or a future entrepreneur?

- Akio Morita
- Tsunetzawa Kahoko
- Albert Einstein
- Elvis Presley
- Steve Jobs
- Florence Nightingale



<https://www.britannica.com/biography/Steve-Jobs> 2023.1.12



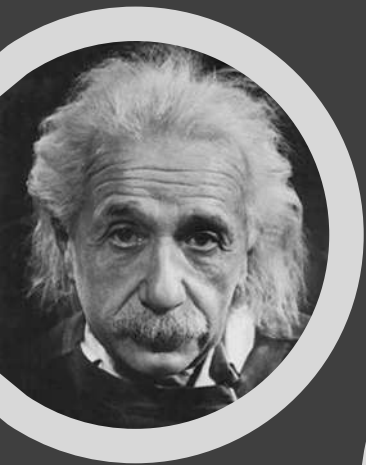
<https://musique2013.hatenablog.com/entry/2015/02/09/154355> 2023.1.12



<https://apt-women.tokyo/program/participant/participant12.html> 2023.1.12



<https://www.wikiwand.com/ja/盛田昭夫> 2023.1.12



SORAIA GUERREIRO(2016), Intelligent minds, SFGUERREIRO.

Careers in nanoscience & nanotechnology



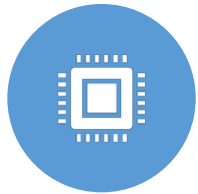
Interdisciplinary :
Physics, chemistry, biology,
medicine, engineering....



Making nanocrystals,
nanowires, superlattices



Theoretical understanding



Making, marketing, selling
nano-products



Teaching & research in
nanoscience



Explaining to the general
public



Working with viruses, cells,
animals, human patients

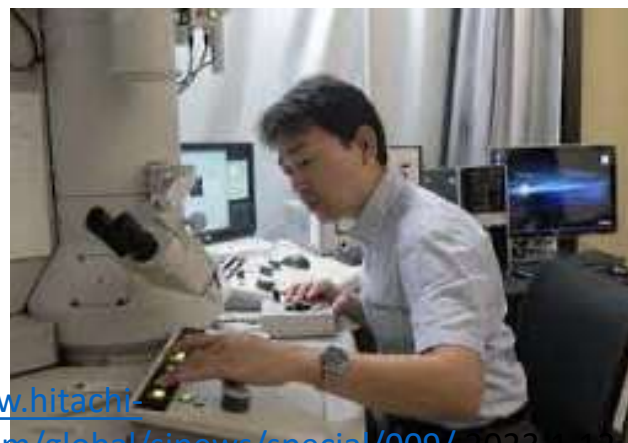
<https://www.cbc.ca/news/world/tokyo-medical-university-women-admission-discrimination-altering-exam-1.4779570> 2023.1.12

Concluding comments

- We now have the tools to study the nanoworld in detail
- Exploring & manipulating materials at the nanoscale reveals novel properties and can give size-tunable properties
- Nanoporous silicon has found varied uses outside electronics and photovoltaics
- **Nanoscience and nanotechnology are very interdisciplinary and offer a range of career options**



<https://www.wsj.com/articles/BL-JRTB-20053> 2023.1.12



<https://www.hitachi-hightech.com/global/sinews/special/000/>



Poll 1



<https://strawpoll.com/polls/Q0Zp4BwejZM>

Which of these statements is NOT true?

Poll 2



<https://strawpoll.com/polls/bVg86wk73yY>

Which of these is NOT a common function of a porous material?