Size Matters: Tiny Dots and Their Potential

Swarna Basu
Susquehanna University

Follow this and additional works at: http://scholarlycommons.susqu.edu/chem_fac_pubs
Part of the Chemistry Commons

Recommended Citation
http://scholarlycommons.susqu.edu/chem_fac_pubs/1

This Article is brought to you for free and open access by Scholarly Commons. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of Scholarly Commons. For more information, please contact sieczkiewicz@susqu.edu.
Size Matters: Tiny Dots and Their Potential

Dr. Swarna Basu
Department of Chemistry
2016 John C. Horn Lecture
February 23, 2016
“There is plenty of room at the bottom” – Cal Tech, 1959

He argued that is was possible, using an electron beam, to write all 25,000 pages of the 1959 edition of the Encyclopedia Britannica on the head of a pin.

He said that people were forced to accept “some atomic arrangement that nature gives us” and argued that “when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have…”

He added, “we are not doing it simply because we haven’t yet gotten around to it.”

Father of Modern Nanotechnology
In the beginning...

1981: Invention of the Scanning Electron Microscope

1985: Discovery of the fullerene (C\textsubscript{60}, buckyball) by Richard Smalley et al


Private Sector investment (IBM)

Government funding (1990s)
Nano?
Nanoscience/Nanotechnology

• Synthesis, characterization, exploration, interrogation, exploitation and utilization of materials that have at least one dimension in the nanometer range.

• Bridge between single molecules and bulk systems.

• Biological systems
  • nanoscale of proteins and other bio-macromolecules
  • micron scale of cells and cellular components.

Nanometer = 1 x 10^{-9} m or 0.000000001 m
Comparative Size Scale

~ 1 nm: 10 H atoms span 1 nm. DNA molecules are ~ 2.5 nm wide

6-8 μm: red blood cells

Pinhead sized patch: 1 m nm in diameter

< 1 nm: individual atoms are up to a few Å in diameter
~0.0000000001 m

Zlatan Ibrahimovich (Sweden): 6 ft 5 in or 195 cm tall. That's almost 2bn nm!
Why are nanomaterials unique?

The chemical and physical properties are different than their bulk counterparts.

They have tunable properties.

They can be functionalized (coatings, tags, etc.)

They have high surface-to-volume and high strength-to-weight ratios.

Most nanoparticles are easy to manufacture in the lab.
Typical nanomaterials

Nanoparticles
- Gold
- Silver
- Titanium dioxide
- Zinc Oxide
- Copper

Quantum Dots
- Semiconducting materials
- 2 - 10 nm, corresponding to 10 - 50 atoms in diameter
- Cadmium selenide (CdSe)
- Graphene
Magnetic Nanoparticles

*Magnetotactic bacteria* – chain of 20 magnetic crystals (each 35-120 nm in diameter) act like a mini-compass so that the bacteria knows where to go.

Material: magnetite ($\text{Fe}_3\text{O}_4$) or greigite ($\text{Fe}_3\text{S}_4$)
Early days...
What it used to be like...

ENIAC - Electronic Numerical Integrator and Computer

The first electronic, digital computer. It was unveiled at U.Penn in 1946.

It weighed 27 tons and occupied 1800 sq.ft.

Price tag: $500,000
17,468 vacuum tubes,
7,200 crystal diodes,
1,500 relays,
70,000 resistors,
10,000 capacitors,
~ 5 million soldered joints
Moore’s Law

“The number of transistors on a chip roughly doubles every two years” – Intel website
Moore’s Law

If the transistors in a microprocessor were represented by people, the following timeline gives an idea of the pace of Moore’s Law.

1970: Intel 4004
2,300 Average music hall capacity

1980: Intel 286
134,000 Large stadium capacity

1990: Pentium III
32 Million Population of Tokyo

2000: Core i7 Extreme Edition
1.3 Billion Population of China

Now imagine that those 1.3 billion people could fit onstage in the original music hall. That’s the scale of Moore’s Law.
Moore’s Law

IF FUEL EFFICIENCY IMPROVED AT THE SAME RATE AS MOORE’S LAW, YOU COULD EASILY DRIVE A CAR FOR YOUR ENTIRE LIFE ON A SINGLE TANK OF GAS.

IF CARS SHRUNK AT THE RATE OF TRANSISTORS, TODAY THEY’D BE THE SIZE OF AN ANT.
Recent advances

Some advances in recent years:

- Nanoparticles for purifying water in flood-hit regions
- Scientists mimic fireflies to make brighter LEDs
- Nanoparticles Loaded With Bee Venom Kill HIV
- Nanogenerators for large-scale energy harvesting
- Nanowire-Paper Offers Strength, Flexibility
- New Approaches Target Nanoparticles to Cancer Cells
- Smartphone-based nano-biosensors for early detection of tuberculosis
Nano-sports
Nano-sports

Tennis balls – use nanocomposite clay (vermiculite) to keep them bouncing longer (Wilson, 2001-2002)

Also, tennis racket frames contain SiO$_2$ nanoparticles.

Re-engineered golf ball from a molecular level such that the weight within the ball shifts less while it is spinning (2004).

“Best shot” spray: $37/bottle (2012)

- This spray penetrates the surface of a golf ball with its special nano encoded particles.
- Reduce wind resistance

http://www.nanotechsports.com
Biomedical Applications

Almost 250 nanomedicine products approved or in clinical study

- European Medicines Evaluation Agency

Majority of current commercial applications of nanotechnology to medicine is geared towards drug delivery to enable new modes of action

- Better targeting and bioavailability of existing medicinal substances.

Novel applications of nanotechnology

- nanostructure scaffolds for tissue replacement
- nanostructures that allow transport across biological barriers
- remote control of nanoprobe
- integrated implantable sensory nanoelectronic systems
- multifunctional chemical structures for drug delivery and targeting of disease.
Security Applications

“Nanotechnology and the fight against terrorism” – Kevin Coleman (2003)

Nanotechnology will provide a foundation on which real-world applications can be based.

Improved power sources, new materials for armor and fabrics, sensors (detect chemical and biological agents), surveillance equipment.

Protect infrastructure

http://www.nanoid.co.uk/nanotechnology_economy.html
Funding

  • "Some of our research goals may take twenty or more years to achieve, but that is precisely why there is an important role for the federal government."


• Early “visions”- entire Library of Congress on a device the size of a sugar cube? Stronger steel?

• $1.5 bn budget for FY 2016 (down from $1.8 bn in FY 2013)
  • Cumulative NNI investment since fiscal year 2001, including the 2016 request, now totals almost $22 billion.

• Early days: Funding in other countries jumped 164% from 1997 to 2001.
Concerns

Fate of nanomaterials

Toxicity concerns

Security/Privacy

Environmental concerns

Unrealistic? Hype?
- Fantastic Voyage (1966)

Doomsday Scenarios
- Gray Goo
- Outer Limits (1995), Revolution (NBC, 2012-2014)
Nano in food

Nanotechnology found in popular foods, despite repeated denials by regulator (Sydney Morning Herald, 9/17/15)

- Nanoparticles of titanium dioxide and silica in 14 popular products
- The Food Standards code (Australia) does not require nanoparticles to be declared on labelling.
  - Nano-titanium dioxide (E171) can be simply described as the conventional-sized type and as "Colour (171)".
  - Nano-silica (E551) can be listed as the conventional version and as "Anti-caking agent (551)".

http://www.smh.com.au/business/retail/nanotechnology-found...
Nano in food

EU: All ingredients present in the form of engineered nanomaterials shall be clearly indicated in the list of ingredients. The names of such ingredients shall be followed by the word ‘nano’ in brackets.

US FDA: “FDA regulators want companies to consult with the government before launching nanotechnology products, though the decision will essentially rest with manufacturers.” (2014)
Nano in Food

TiO$_2$ NPs in Mentos

Silica NPs in gravy
Nano in Food

Titanium dioxide has been used widely in foods for decades as a whitener and a base for other colors.

**Inert and Safe**

US FDA: up to 1% titanium dioxide without the need to include it on the ingredient label
- Substance must conform to **stringent levels of purity**.

TiO$_2$ NPs in Mentos
What do nanostructures look like?

“atom” in Japanese script, written with atoms

Nanoscale pyramid of germanium atoms, one type of quantum dot – on top of silicon.

Application? New generations of tinier electronic devices that are governed by quantum phenomena.
35 atoms to make the IBM logo

Nanograins or nanoscale grains of palladium metal. ~12 nanograins = nanostructured metal.

Application? The smaller grains with more internal boundaries will lead to a stronger metal.
What do nanostructures look like?

- Collaboration between a materials scientist and an art/media professor at U.Ga.

- “NanoArt” - a new art discipline in the intersection of art, science and technology.

- The materials scientist:
  - Heated metals and metal oxide powders (Zn, Ga) at low pressure.
  - Powder vaporized and accreted into different forms depending on the substrate, temperature and other factors.

- The artist:
  - Used electron microscopy to scan structure and find a “view to die for”.

Zinc oxide shrub on top of zinc foil at 500-600 °C
What do nanostructures look like?

Nanoapocalypse now: melted top layer of Zn foil oxidizes into nanorods (50-150 nm diameter). Twisted geometries form.

Inorganic prairie: highly aligned ZnO nanorods assembled inside a tube furnace from ZnO vapor.
What do nanostructures look like?

- Pattern of microscopic iron “seeds” onto a plate (7-8 nm thick).
- A blast of heated gas causes a miniature forest of carbon nanotubes to spring up.
Lead sulfide (PbS) nanocrystals and hair dyes.

Ancient Egypt (>4000 years ago).

Control of PbS nanocrystal growth inside a hair!

Hair dye: PbO + Ca(OH)$_2$ + H$_2$O $\rightarrow$ paste (source of Pb)

Source of S: amino acids of hair keratins (fibrous structural proteins).

Blackening is caused by precipitation of galena (PbS)
The dyeing process

Non-treated

6 hours

72 hours

Smaller PbS particles accumulate inside the microfibrils.
Nanomedicine

Goals laid out by the NNI – improvement in detection, diagnosis and treatment of diseases.

- Improved imaging – tumors (red)
- Localized drug delivery
- Implants – durable and biocompatible
History of Nanomedicine

1993: literature review of robotics did not include a single reference to nanotechnology or nanomedicine.

1996: The first nanomedical device-design technical paper by Freitas: Respirocyte – an Artificial Red Cell.
The size scale and other considerations

- For medical applications, nanoparticles should
  - recognize a disease cell
  - attach to the membrane or pass through it
  - release drugs or heat up in response to external stimuli.

- Identified as intruders by RES (reticuloendothelial system)

- Too small to block capillaries (d = 5μm)

(a) White blood cell
(b) Red blood cell
(c) 100 nm NP (liposome, magnetic NP for drug delivery)
(d) 5 nm NP (dendrimer, QD, magnetic NP for hyperthermia)
Modifying NPs

Polyethylene glycol (PEG)

Prevent recognition by leukocytes

Heat-triggered 'grenades' hit cancer

- Nanomedicine Lab in Manchester, UK
- Liposomes release drugs when heated
  - “water tight” at 37 °C
  - “leaky” at 42 °C
  - Heat pads (surface), UV

Polymer based

- Ester bonds in the shell
  - Kidneys hydrolyze ester bonds: drug delivery to kidneys
- Inject into veins
  - Target tumor tissues (irregular cell linings)

If specific antibody-antigen combination is known, NP-antibody conjugate can be developed

- They will target tumor cells and not healthy cells
Imaging with Gold Nanoparticles

- Cervical epithelial cancer cells.
- Gold NPs conjugated with anti-EGFR antibodies, which target EGFR receptors that are overexpressed in cancer cell membranes.
- Au NPs are covering the cell membrane of the cancer cells.

Healthy cell
Gold Nanoparticles

Discovered in 1996.

13 nm Au nanoparticles – color changes upon aggregation.

DNA detection: exploit these optical properties – a polymeric network of nanoparticles forms.

Earlier Detection limit = 10 nM
More recently: 2.1 nM (Crouse, 2012)
Aggregation

Citrate shield is disrupted by the environment

Solution changes color due to altered optical properties
  ◦ Longer absorbance wavelength
Au nanoparticles (shapes)
Gold nanorods

Aspect ratios:
(a) 4.6
(b) 13
(c) 18
Magnetic Nanoparticles

Fix magnetic particles as labels to selected antibody molecules

Apply strong magnetic field to determine whether or not the antibodies have latched onto their target.

- free antibodies “tumble” rapidly in solution: no magnetic signal
- bound antibodies are unable to rotate: signal!
Carbon Nanotubes

An ideal nanotube can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a cylinder.

Pentagonal rings cause graphene sheets to curl

Hexagonal rings lead to stable carbon nanotubes

SWNT: single wall carbon nanotube

MWNT: multiple-wall carbon nanotube
DNA sequencing with CNTs

Nanotube fits into the major groove of the DNA strand

Apply bias voltage across CNT, different DNA base-pairs give rise to different current signals

With multiple CNT, it is possible to do parallel fast DNA sequencing

Top view and side view of the assembled CNT-DNA system
Silver Nanospheres

12 ± 2 nm particles

Plasmon absorbance 400 nm

Antimicrobial/antibacterial properties

Signal enhancement

Different shapes possible.
Silver Nanospheres

Absorbance (a.u.)

Wavelength (nm)

130nm
SERS

Surface Enhanced Raman Scattering

![Graph showing Raman shift vs. intensity with a peak at 1000 cm⁻¹ and another at 500 cm⁻¹ labeled 'Without Ag NPs']

Megan Wright (summer '14)
Andrew Clarkson (2015-16)
SERS

Surface Enhanced Raman Scattering

[Graph showing Raman shift vs. intensity with and without Ag NPs]

Megan Wright (summer ‘14)
Andrew Clarkson (2015-16)
Slightly larger “tiny dots”

- Micron-scale protein cross-linking.

- Model for modern tissue engineering: micron and submicron size scales

- Photochemistry is very flexible and works in aqueous environments.
  - Chemical reactions using photons from lasers

- The photochemistry must involve minimal photon flux to avoid damaging fragile biological systems.
  - Challenging when using a low-cost system

- Going smaller: nanoparticles
Doing this at SU

- Biggest challenge: working with a Nd$^{3+}$:YAG laser with nanosecond pulses
  - Higher photon flux
    - $10^{14} - 10^{15}$ photons per pulse
  - Microscope: manual stage limits design capabilities

Gus Reynolds (2015-16)

Lafferty et al, J Photochem Photobiol (2014)
Protein “dots”

Potential applications:
- Artificial Tissues
- Repair
- Drug delivery

Generates **Singlet Oxygen**

Work in progress: Use gold nanoparticles

Protein: Bovine Serum Albumin
Photoactivator: Rose Bengal
10 seconds, 10 Hz

Lafferty et al, J Photochem Photobiol (2014)
Gus Reynolds (2015-16)
Work in Progress

Zinc oxide nanoparticles

Goal: DNA detection

Brian Etz (2014-15)
Mariana Bianchini Silva and Joann Butkus (2015-16)
The 2015-16 team

Mariana Bianchini Silva (2016)
Al Montoya (2017)
Joann Butkus (2018)
Andrew Clarkson (2016)
Gus Reynolds (2018)
Matt Sawka (2016)
Former Research Students

Peter Kerns (2016), Joe Lafferty (2014)
James Strande (2012)
Greg Trout (2010)
Heather Crouse (2012)
Shelby O’Riley (2015)
Brian Etz (2015)
Megan Wright (2017)
Acknowledgments

Susquehanna University
- Department of Chemistry
- Committee on Faculty Scholarship
- Summer Research Partners Program
- George I. Alden Trust

II-VI Foundation Undergraduate Research Grant 2013-2014


Bucknell University
- Dr. Molly McGuire (AFM)
- Dr. Brian Williams

- Dr. Jason Shear (UT Austin)