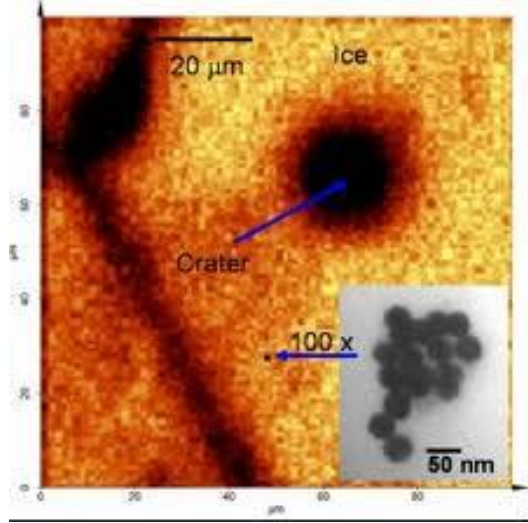


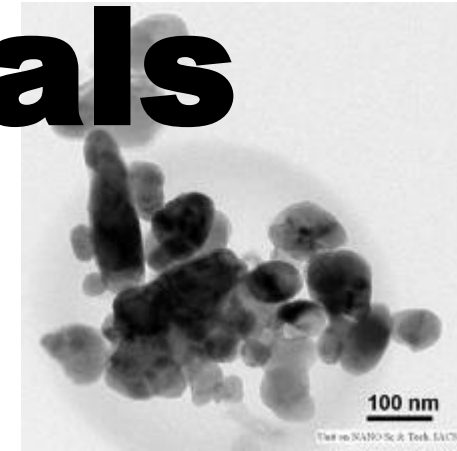
nanomaterials

introduction



nanomaterials

- Top-down Science
- Bottom-up Science

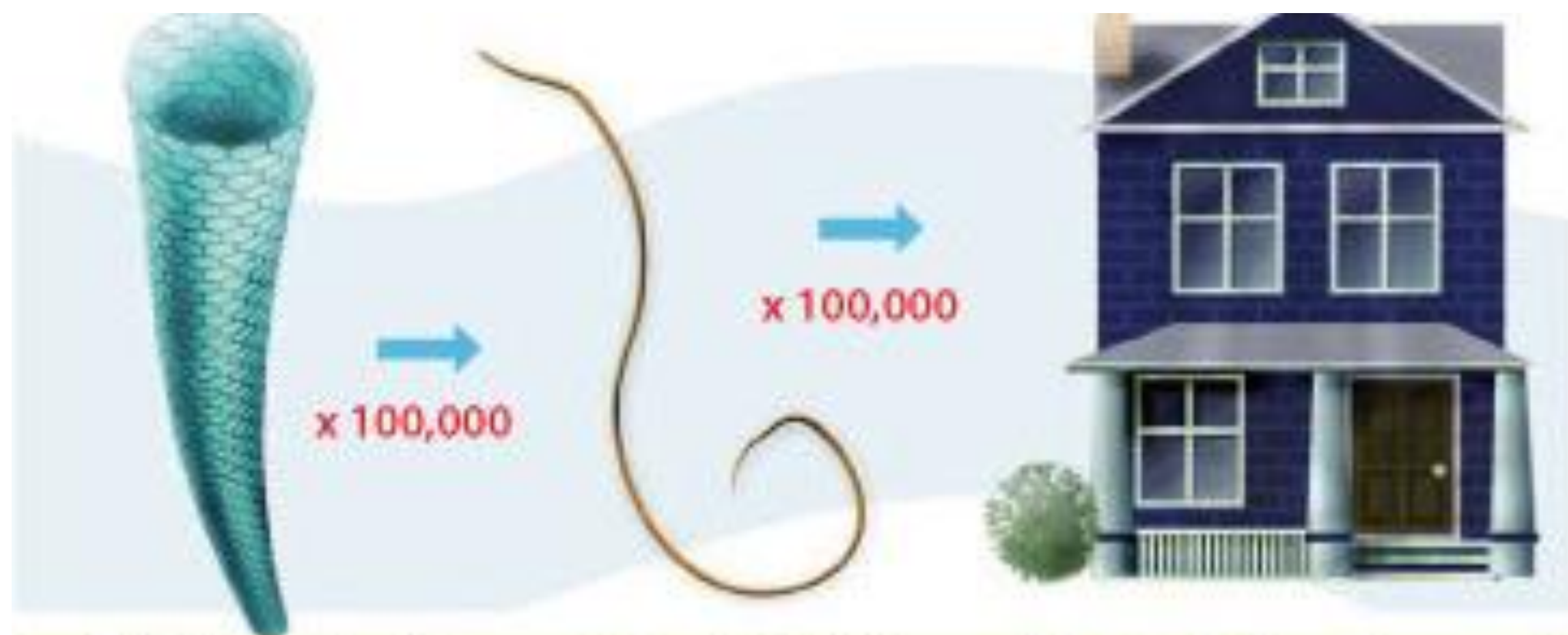


What are nanomaterials?

Nanomaterials are materials are materials possessing grain sizes on the order of a billionth of a meter. (10^{-9} M)

A material in which at least one side is between 1 and 1000 nm.

Nanomaterial research literally exploded in mid -1980's

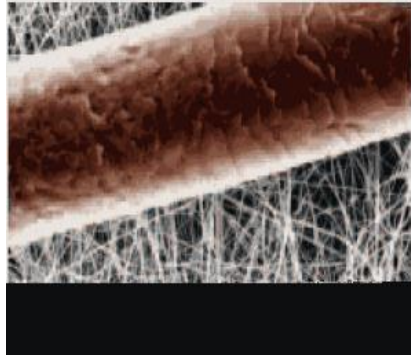


**Single-walled
Carbon Nanotube**
1 nanometer diameter

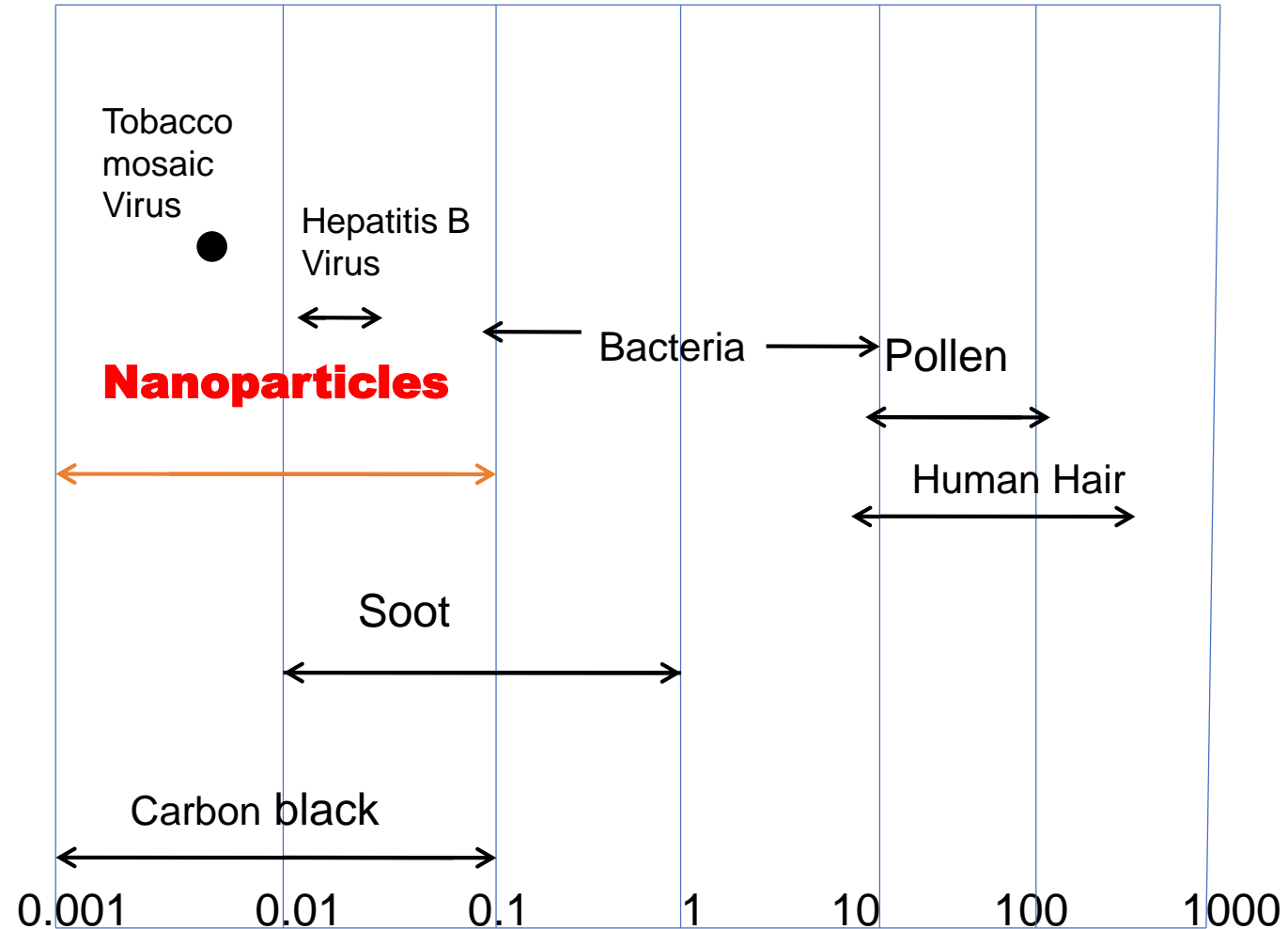
Strand of Hair
100 micrometers
diameter

House
10 meters
wide

Typical size of small particles



Particle size μm

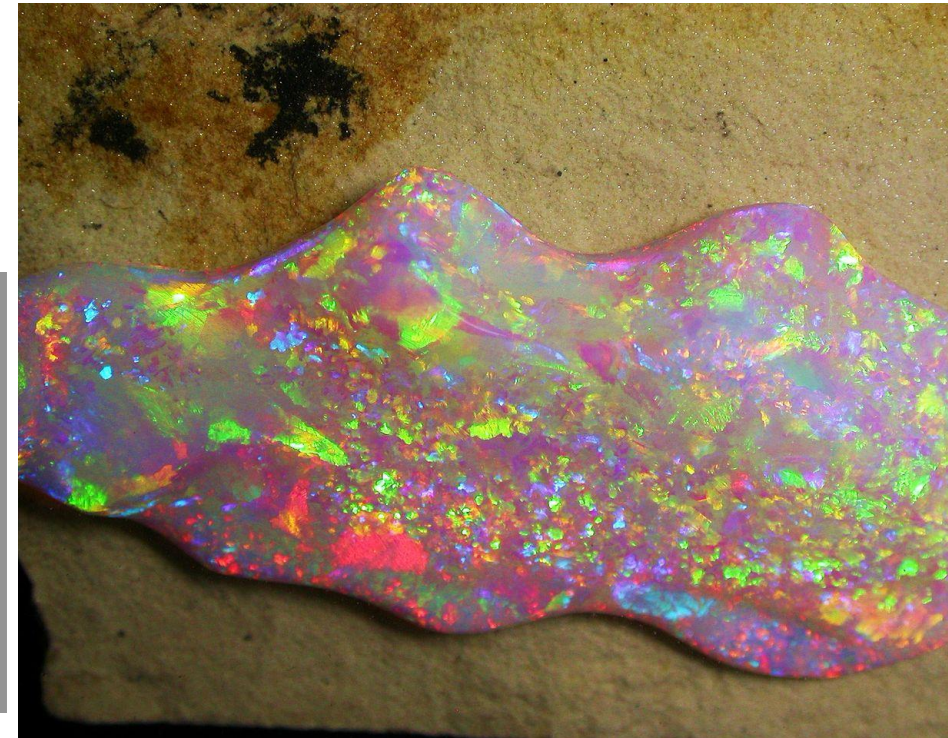
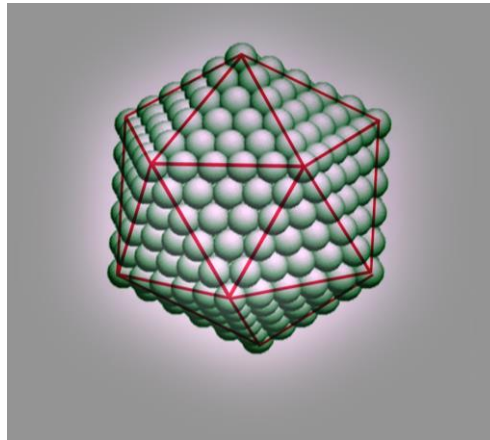


history

- Big bang
- Fires
- 1950- fused silica
- Why such a buzz word today?

Examples

- Several biological materials are nanomaterials- bone, hair, wing scales on a butterfly etc.
- Viruses are nanomaterials
- Clays
- Pigments
- Volcanic ash



Engineered nanomaterials (ENM or EN)

Materials manufactured for their properties

- Sunscreens
- Paints
- Cosmetics
- Fillers
- Catalysts

- Conventional materials have grain size anywhere from 100 μm to 1mm and more
- Particles with size between 1-100(0) nm are normally regarded as Nanomaterials
- The average size of an atom is in the order of 1-2 Angstroms in radius.
- 1 nanometer =10 Angstroms
- 1 nm there may be 3-5 atoms

Two principal factors cause the properties of nanomaterials to differ significantly from Bulk materials:

- **Increased relative surface area**
- **Quantum effects.**

These factors can change or enhance properties such as reactivity, strength and electrical characteristics.

Surface Effects

- As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of
- Size-30 nm-> 5% of its atoms on its surface
- Size-10 nm->20% of its atoms on its surface
- Size-3 nm-> 50% of its atoms on its surface
- Nanoparticles are more reactive than large particles (Catalyst)

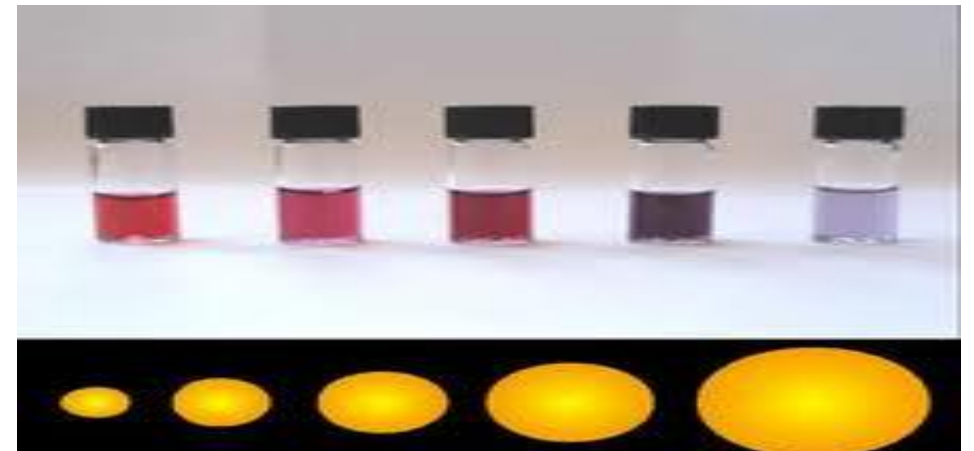
Quantum Effects

Quantum confinement

The quantum confinement effect can be observed once the diameter of the particle is of the same magnitude as the wavelength of the electron [Wave function](#).

Quantum confinement is responsible for the increase of energy difference between energy states and band gap. A phenomenon tightly related with the optical and electronic properties of the materials.

When materials are this small, their electronic, mechanical and optical properties deviate substantially from those of bulk materials. (GOLD)



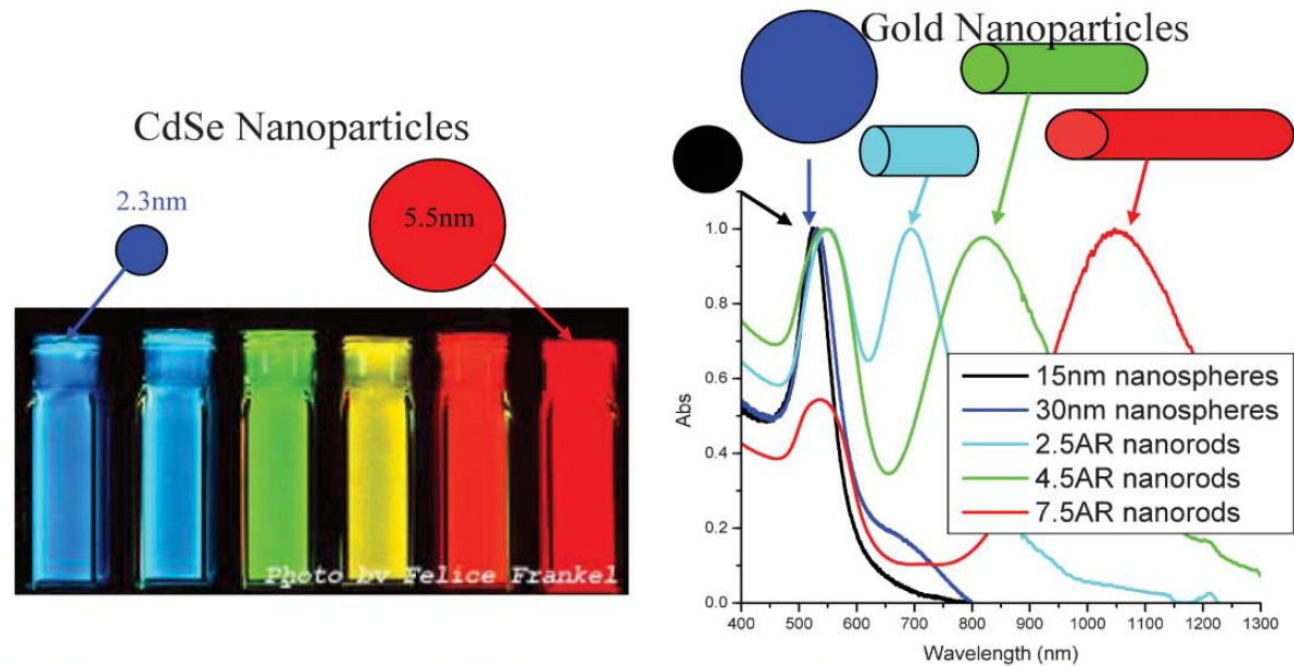
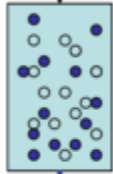


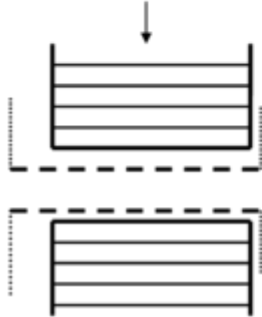
Fig. (12): Fluorescence emission of (CdSe) ZnS quantum dots of various sizes and absorption spectra of various sizes and shapes of gold nanoparticles (Chem. Soc. Rev., 2006, 35, 209–217).

Nanoparticles

λ : wavelength



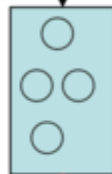
Energy level



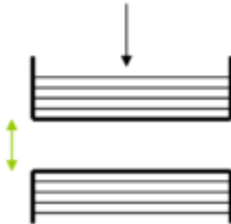
Radiation shift between the two edges of visible spectra

Bulk mode material

λ : wavelength



Energy level



ΔE_{nano}

$\Delta E_{\text{nano}} > \Delta E_{\text{bulk}}$

ΔE_{bulk}

Classification of Nanomaterials

- **Nanomaterials as those which have structured components with at least one dimension less than 100nm.**
- **One dimension in nanoscale (Other two dimensions are extended)**

Thin films

Surface Coatings

Computer chips

- **Two dimensions in nanoscale (Other one dimension is extended)**

Nanowires

Nanotubes

- **Three dimensions in nanoscale**

Nanoparticles

Precipitates

Colloids

Quantum dots (tiny particles of semiconductor material)

Nanocrystalline materials

Nanocomposites, Nanophase materials

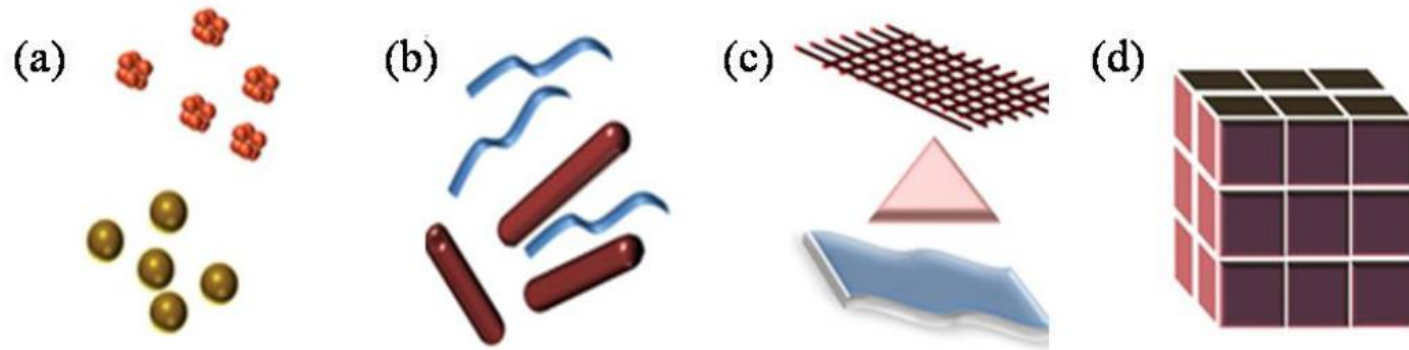
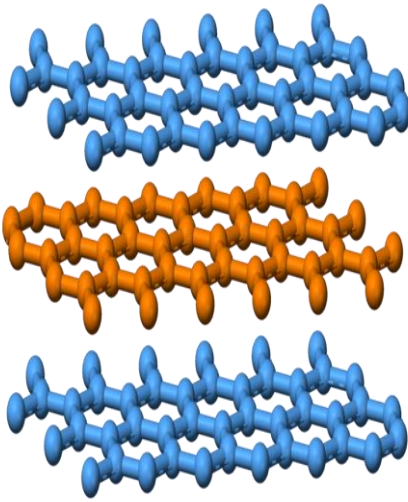


Fig (3): Classification of Nanomaterials (a) 0D spheres and clusters; (b) 1D nanofibers, nanowires, and nanorods; (c) 2D nanofilms, nanoplates, and networks; (d) 3D nanomaterials.

3D nanomaterials are also known as nanophase materials
There are also nanocomposites.



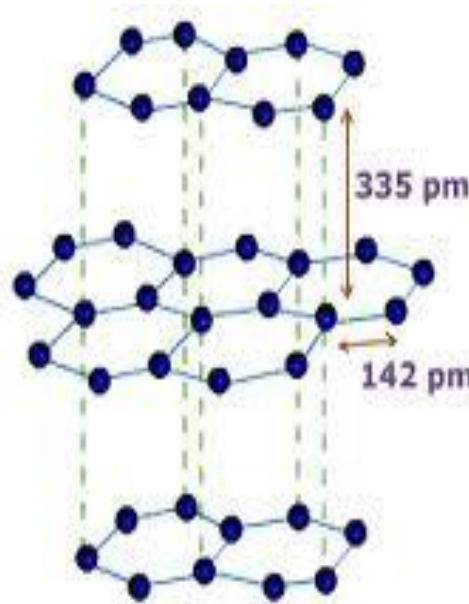
Graphite

It is also a crystalline form of carbon.

STRUCTURE OF GRAPHITE

In graphite each carbon atom is covalently bonded to three carbon atoms to give trigonal geometry. Bond angle in graphite is 120° . Each carbon atom in graphite is sp^2 hybridized. Three out of four valence electrons of each carbon atom are used in bond formation with three other carbon atoms while the fourth electron is free to move in the structure of graphite.

Basic trigonal units unite together to give basic hexagonal ring. In hexagonal ring C-C bond length is 1.42 \AA . In graphite these rings form flat layers. These layers are arranged in parallel, one above the other. These layers are 3.35 \AA apart and are held together by weak van der Waals forces only. These layers can slide over one another. Thus it is very soft. Fourth electron of each carbon atom forms delocalized p-bonds which spread uniformly over all carbon atoms. Due to this reason graphite conducts electricity parallel to the plane.



Uses

Solid lubricants
Electrodes

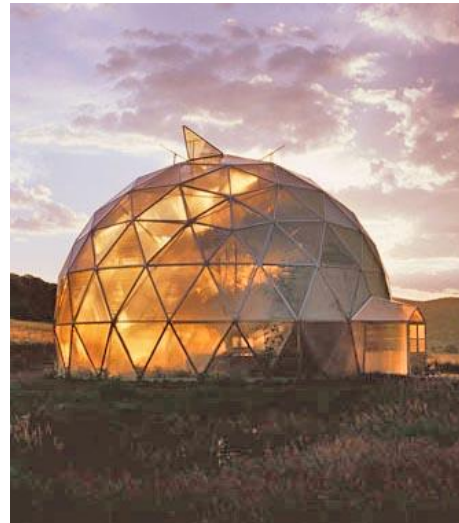
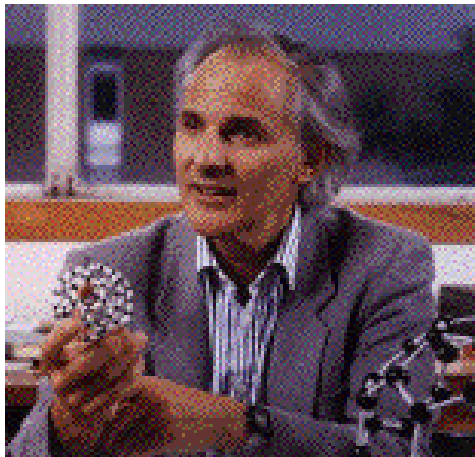
Moderator in nuclear reactors
Pencil lead

Fullerenes

The 1996 Nobel Prize for Chemistry has been won by Harold W. Kroto, Robert F. Curl and Richard E. Smalley for their discovery in 1985 of a new allotrope of carbon, in which the atoms are arranged in closed shells. The new form was found to have the structure of a truncated icosahedron, and was named Buckminster fullerene, after the architect Buckminster Fuller who designed geodesic domes in the 1960's. In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of C₆₀ by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate.

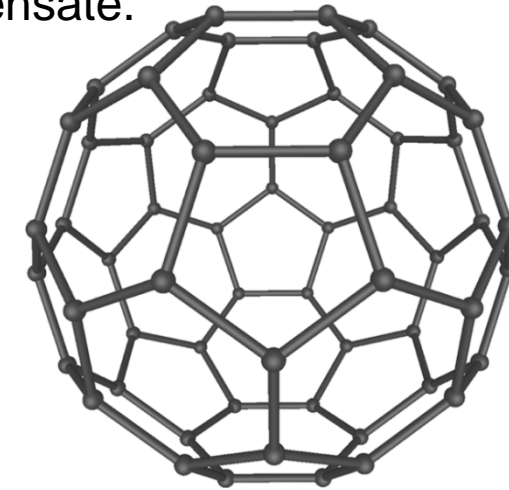


Professor Sir Harold W. Kroto



Geodesic dome

C₆₀



Football like structure
20 hexagones
12 pentagones

Applications-

The fullerenes have synthetic pharmaceutical and industrial applications.

Degenerative diseases and ordinary aging processes are caused by intracellular

Oxygen free radicals with unpaired electrons. C60 fullerenes can react with radicals

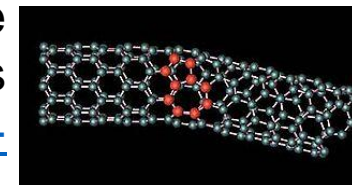
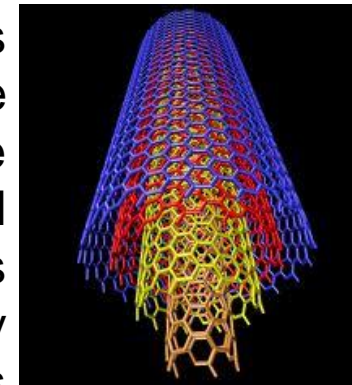
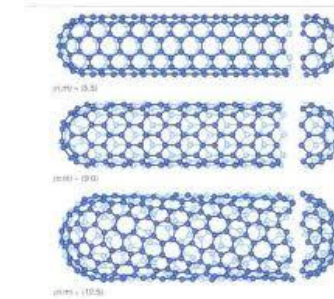
Thus halting the process of aging. It acts as a good MRI contrast agent. They can also

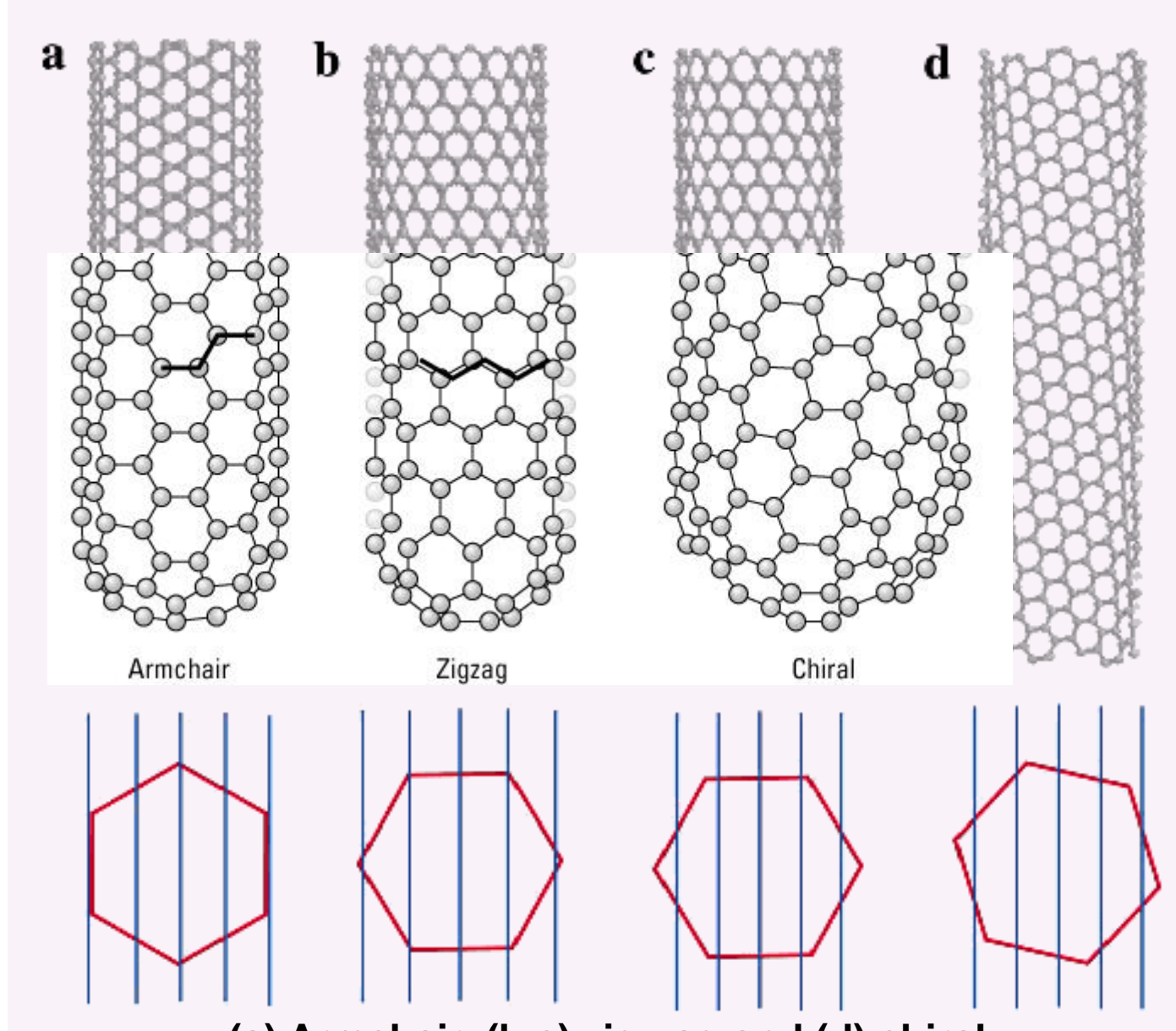
be used in light emitting diodes in different electronic equipment and computing

devices

Carbon nanotubes (CNTs) are [allotropes of carbon](#) with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material.

These cylindrical [carbon molecules](#) have unusual properties, which are valuable for nanotechnology, [electronics](#), [optics](#) and other fields of [materials science](#) and technology. In particular, owing to their extraordinary [thermal conductivity](#) and mechanical and [electrical](#) properties, carbon nanotubes may find applications as additives to various structural materials. Nanotubes are members of the [fullerene](#) structural family, which also includes the spherical [buckyballs](#), and the ends of a nanotube may be capped with a hemisphere of the buckyball structure. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called [graphene](#). These sheets are rolled at specific and discrete ("[chiral](#)") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a [metal](#) or [semiconductor](#). Nanotubes are categorized as [single-walled nanotubes](#) (SWNTs) and [multi-walled nanotubes](#) (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by [van der Waals forces](#).





(a) Armchair, (b,c) zig-zag and (d) chiral tube; (a) metallic, (b) small gap semiconductor, and (c,d) semiconductor.

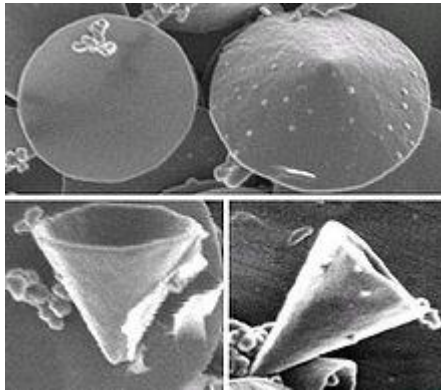
Properties and Applications:-

Nanotubes are extremely strong and stiff and relatively ductile. For single walled nanotubes tensile strengths range between 50 and 200 Gpa more than carbon fibres. This is strongest known material. Elastic modulus values are of the order of one tera (10^{12}) pascal with fracture strains between 5% to 20%. They have very low densities. Because of these properties carbon nano tube has been termed as ultimate fibre. It has been regarded as 100 times stronger Than steel at the same time six times lighter (weight wise). They find applications in filling material in composite material.

They can act as either conductors or semiconductors depending on their chirality so they find their applications in molecular electronics and Computers they are used as ultra sensitive electrochemical sensors. They are used in batteries and fuel cells.

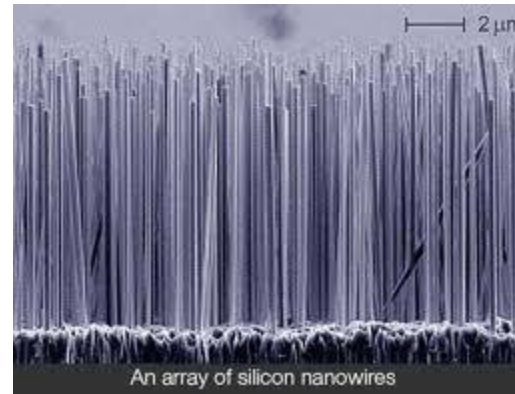
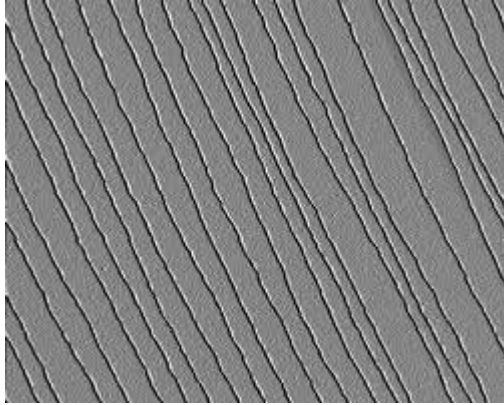
Field emission results from the tunnelling of electrons from a metal tip into Vacuum under application of strong electric field. Small diameter and high aspect ratio (lower loading of CNTs is needed compare to other conductive additives to achieve same electrical conductivity .CNTs are very favourable for field emission.) Even for moderate voltages a strong electric field develops at free end of supported CNTs because of their sharpness. The large surface area and high absorbency of CNTs make them ideal candidates for use in air gas and water filtration

Carbon nanocones



The open carbon cone can be modeled as a wrapped [graphene](#) sheet. In order to have strain-free, seamless wrapping, a sector has to be cut out of the sheet. That sector should have an angle of $n \times 60^\circ$, where $n = 1, \dots, 5$. The nanocones are produced by carbon condensation on a Graphite substrates and pyrolysis of heavy oil. The essence of the method is heating the graphite surface with intensive short laser pulse, which evaporates some number of atoms from role as the cut and glue procedure. On the graphene sheet, and other atoms rearrange into the conical surface described above. There is also one special class of nanocones, called **nanohorns** with exact five defects. These structures with good electron emission properties are easy to get and stable enough. Nano horns show metallic behaviour.

Nanowires



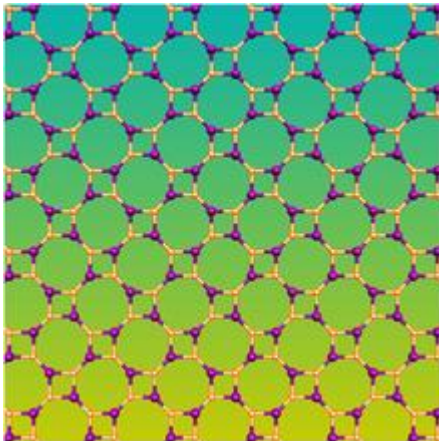
A **nanowire** is a nanostructure, with the diameter of the order of a nanometer (10^{-9} meters). Alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of [nanometers](#) or less and an unconstrained length. At these scales, quantum mechanical effects are important — which coined the term "[quantum wires](#)". Many different types of nanowires exist, including metallic (e.g., [Ni](#), [Pt](#), [Au](#)), semiconducting (e.g., [Si](#), [InP](#), [GaN](#), etc.), and insulating (e.g., [SiO₂](#), [TiO₂](#)). [Molecular nanowires](#) are composed of repeating molecular units either organic (e.g. [DNA](#)) or inorganic (e.g. $\text{Mo}_6\text{S}_9\text{I}_x$). The nanowires could be used, in the near future, to link tiny [components](#) into extremely small [circuits](#). using [nanotechnology](#), such components could be created out of [chemical compounds](#).

Typical nanowires exhibit aspect ratios (length-to-width ratio) of 1000 or more. As such they are often referred to as one-dimensional (1-D) materials. Nanowires have many interesting properties that are not seen in bulk or 3-D materials. This is because [electrons](#) in nanowires are [quantum](#) confined laterally and thus occupy energy levels that are different from the traditional continuum of energy levels or bands found in bulk materials.

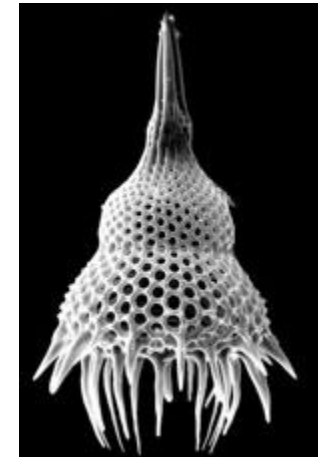
Nano wires are synthesized in laboratory from elements. There are many applications where nanowires may become important in electronic, opto-electronic and nanoelectromechanical devices, as additives in advanced composites, for metallic interconnects in nanoscale quantum devices, as field-emitters and as leads for biomolecular nanosensors.

Haeckelites

If we try to bend graphene sheet it will straighten up. A new hypothetical type of graphene sheet which admits pentagons heptagons and hexagons. It has been proposed, noting that the no. of heptagons and pentagons should be same, In order to compensate for the negative curvature of the heptagons and positive curvature of pentagon. These arrangements are now called **haeckelites** in honour of **Emst Haeckel** a German zoologist who produced a beautiful drawing of radiolaria, (Organism) in which heptagonal hexagonal and pentagonal rings are observed. Carbon haekalite structures are metallic. It is possible to roll up the haekelite sheets to form nanotubes which will be conductors independent of diameter and chirality.



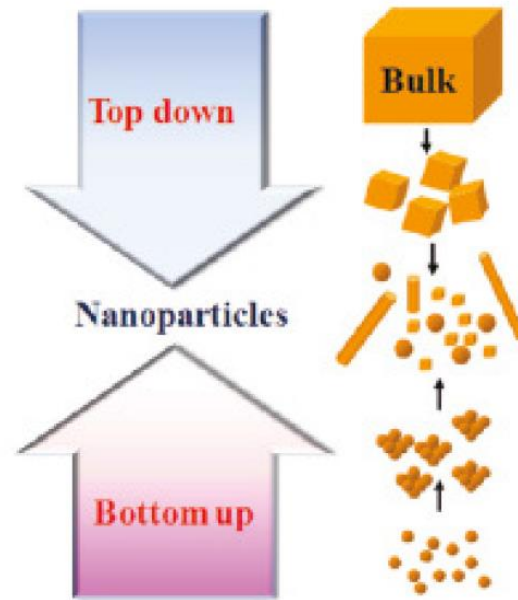
Haeckelites are three-fold coordinated networks of carbon atoms generated by a periodic arrangement of pentagons, hexagons and heptagons. They were first proposed by Humberto and Mauricio Terrones and their colleagues in 2000.^[2] They were named in honour of [Ernst Haeckel](#), whose diagrams of [radiolaria](#) contained similar structural features. They have not yet been synthesised in the laboratory, but have been the subject of a considerable amount of theoretical work.



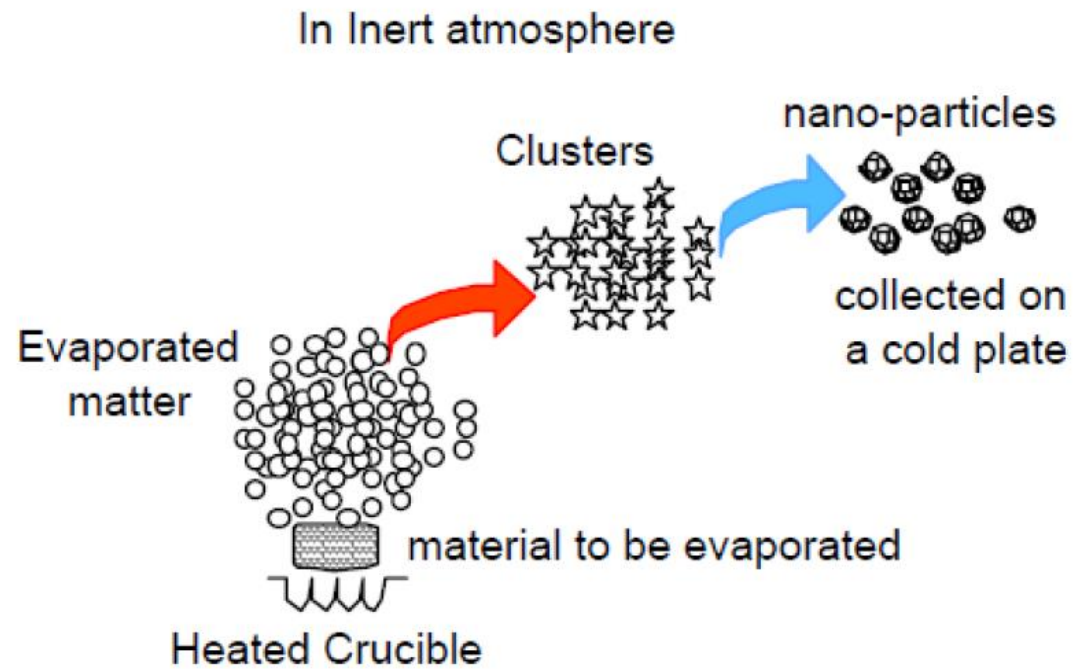
Applications of nanocarbon

- Production is several 1000 tons/year
- Motor brushes
- Water filters
- Sport goods
- Boat hulls
- Automotive parts
- Nanotubes can improve the mechanical performance of biomedical polymers, but their toxicity is a concern.

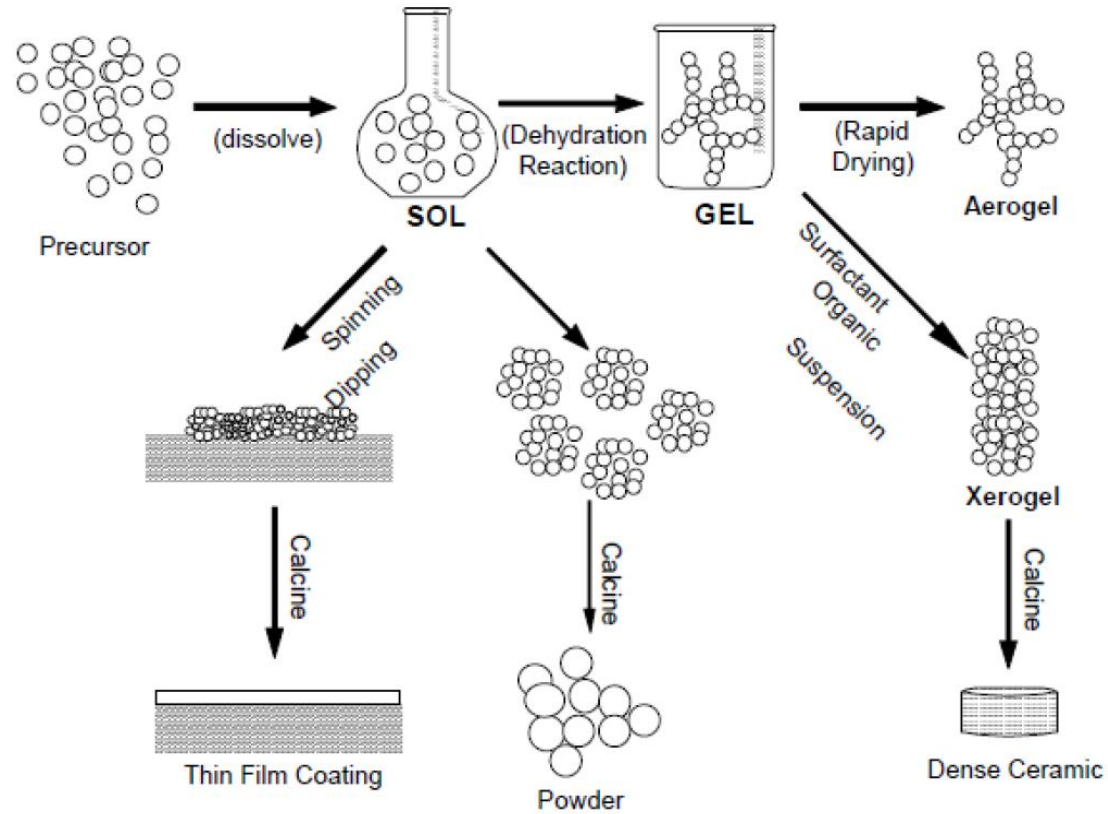
Nanoparticle synthesis



Gas phase synthesis



Sol gel



Sol: colloid, molecules suspended in a liquid
Gel: the molecules form a cross linked polymer
Aerogel: gas phase
Eg. metal chlorides , silica

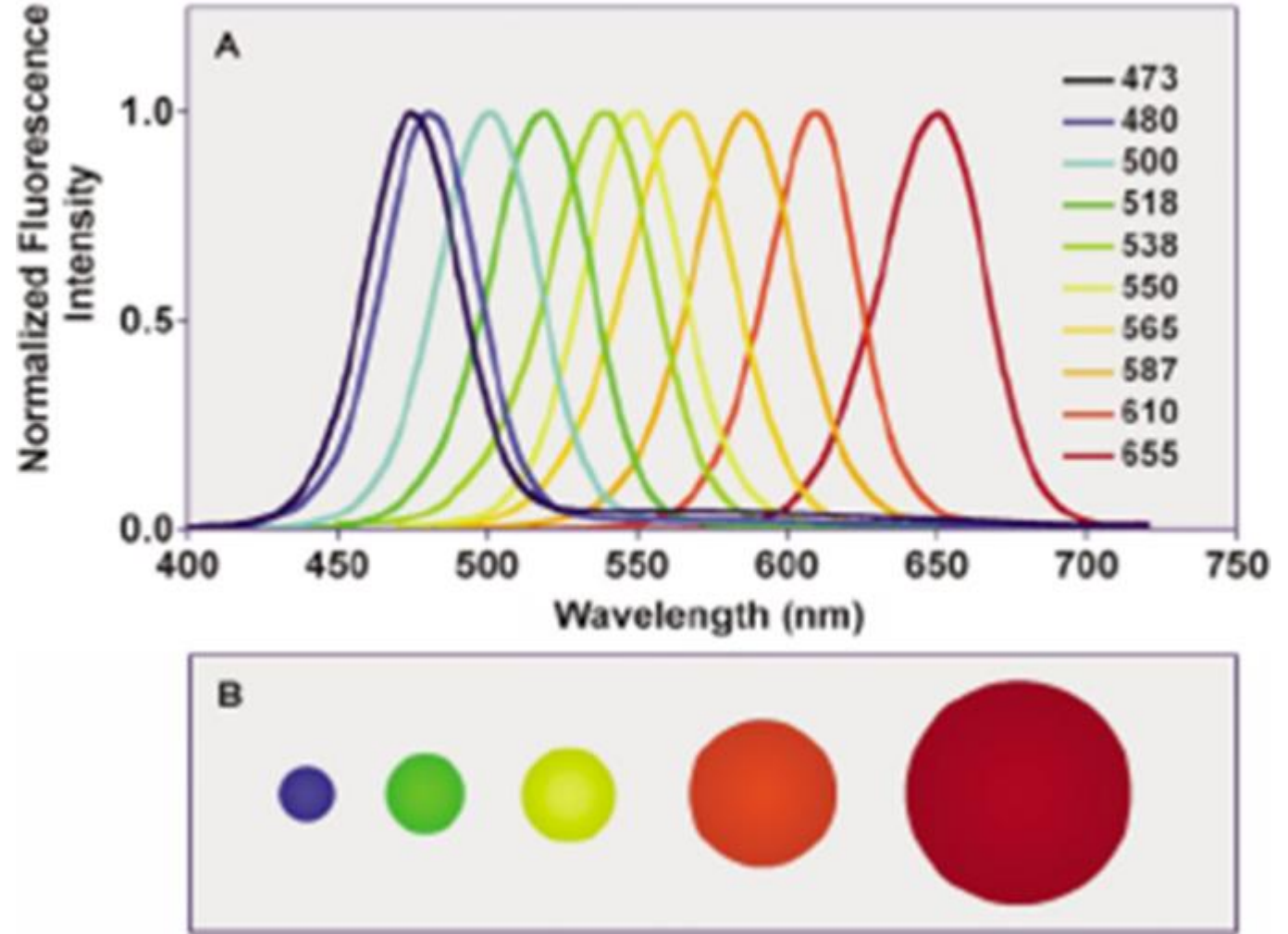
Fig. (6): Schematic representation of sol-gel process of synthesis of nanomaterials.

Quantum dots

- Quantum dots (QD) are very small semiconductor particles, only several nanometres in size, so small that their optical and electronic properties differ from those of larger particles
- In semiconductors, light absorption generally leads to an electron being excited from the valence to the conduction band, leaving behind a hole. The electron and the hole can bind to each other to form an exciton. When this exciton recombines (i.e. the electron resumes its ground state), the exciton's energy can be emitted as light (fluorescence). In a simplified model, the energy of the emitted photon can be understood as the sum of the band gap energy between the highest occupied level and the lowest unoccupied energy level, the confinement energies of the hole and the excited electron, and the bound energy of the exciton (the electron-hole pair)
- In QDs the gap changes with QD size

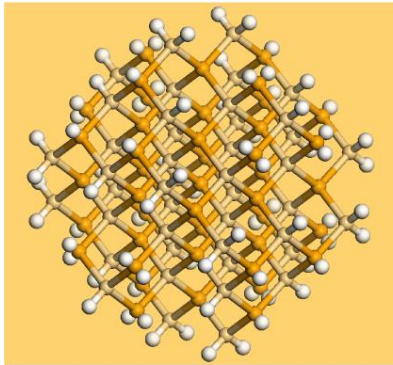
QDs: CdSe

- As the confinement energy depends on the quantum dot's size, both absorption onset and fluorescence emission can be tuned by changing the size of the quantum dot during its synthesis. The larger the dot, the redder (lower energy) its absorption onset and fluorescence spectrum. Conversely, smaller dots absorb and emit bluer (higher energy) light

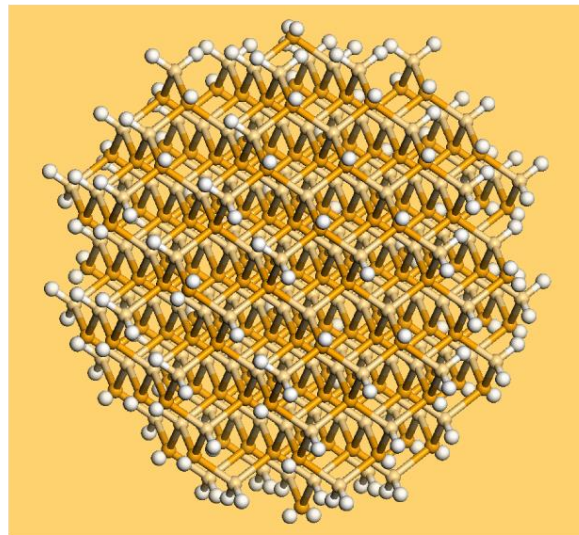


Can be purchased

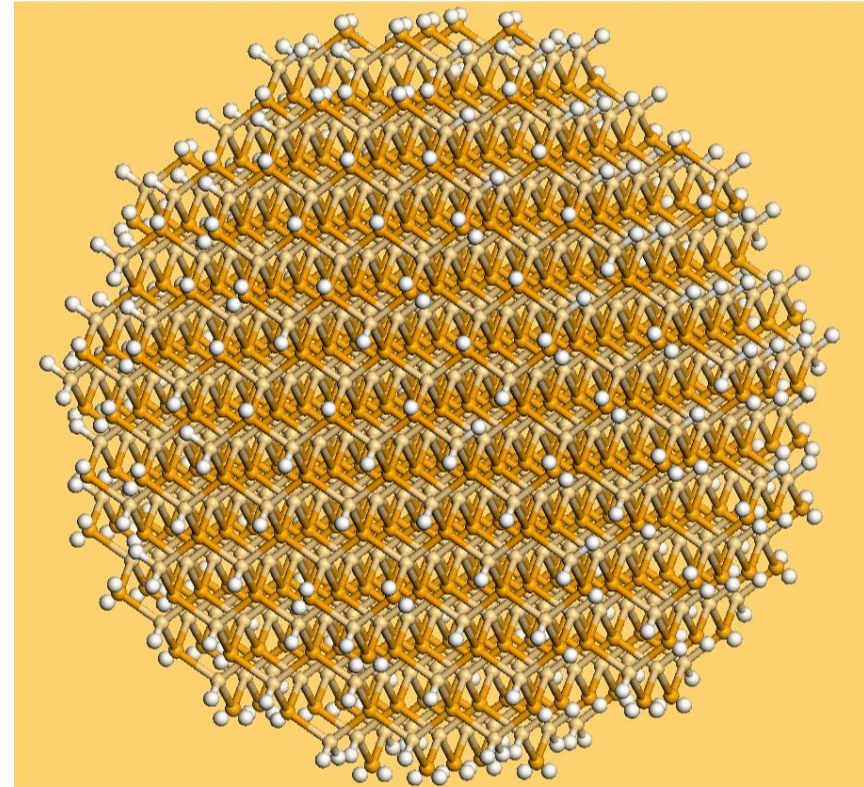
CdSe Quantum Dots



Cd₄₃Se₄₄

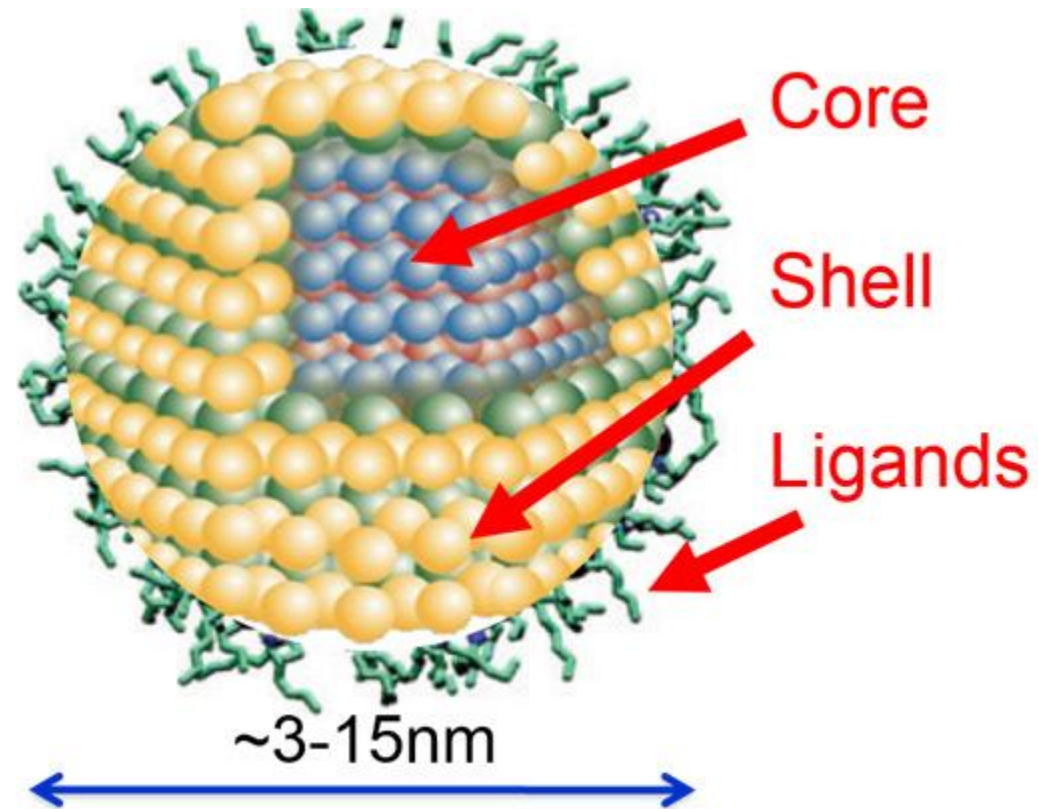


Cd₁₅₂Se₁₄₁



Cd₄₈₄Se₄₉₅

Core shell nanomaterials and nanosensors



Nanotechnology 00 (2017) 000000 (8pp)

Synthesis of magnetic cytosine-imprinted chitosan nanoparticles

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2.2. Formation of magnetic CIPs

The preparation of magnetic molecularly imprinted and non-imprinted chitosan nanoparticles (respectively CIPs and NIPs) is shown in scheme 1. MNPs [30] were added to the chitosan solution (chitosan/acetic acid solution = 0.0001–0.1 wt%) to a concentration of 0.2 mg ml^{-1} . The interactions between chitosan segments and MNPs were the hydrogen bonds of hydroxyl groups, hydrophobic and carboxylic acid and amine with the oleic acid [30], which were used to enhanced the suspension of MNPs. The chitosan/magnetic particle solution was then mixed with $0\text{--}1.0 \text{ g ml}^{-1}$ of cytosine. The chitosan/cytosine template/magnetic particle suspension was dispersed in 10 ml deionized water at 4°C followed by removal of the cytosine template from magnetic chitosan nanoparticles by washing with 1 ml deionized (DI) water for 10 min and separating a magnetic plate for three times. All composite nanoparticles were equilibrated with deionized water overnight before use. The magnetic NIPs were prepared identically, except that the cytosine template was omitted.

Cytosine
Guanine
Adenine
Thymine

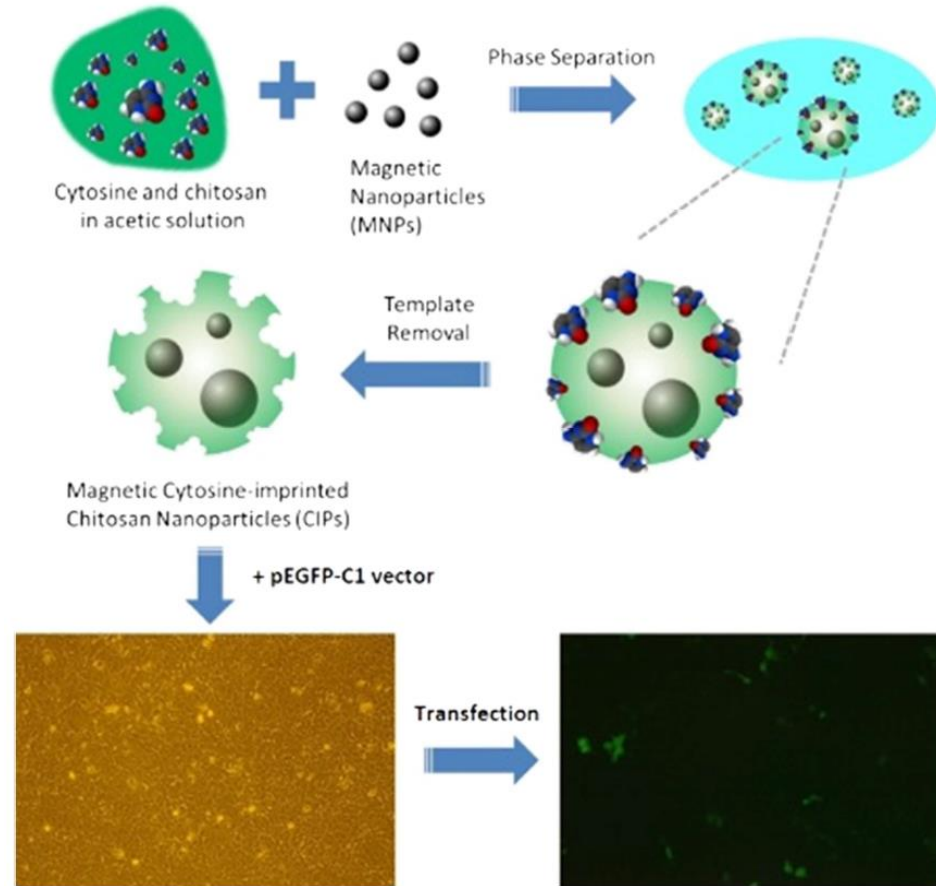


Figure 1. Synthesis and application of Magnetic Cytosine-imprinted Chitosan Nanoparticles (CIPs).

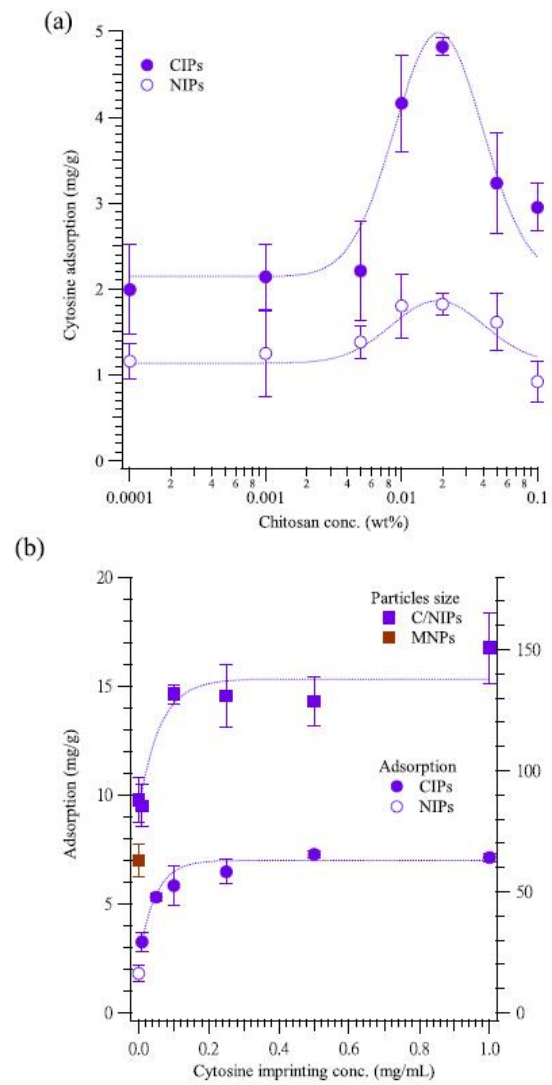


Figure 1. Optimization of the preparation of magnetic cytosine-imprinted chitosan nanoparticles. The cytosine adsorption of particles prepared with (a) various chitosan concentrations; (b) various cytosine imprinting concentrations and their mean particles size. The cytosine imprinting concentration in (a) and the chitosan concentration in (b) are 0.1 mg ml^{-1} and 0.01 wt\% , respectively, and rebound with 0.1 mg ml^{-1} of cytosine for 30 min ($n = 3$ for each determination).

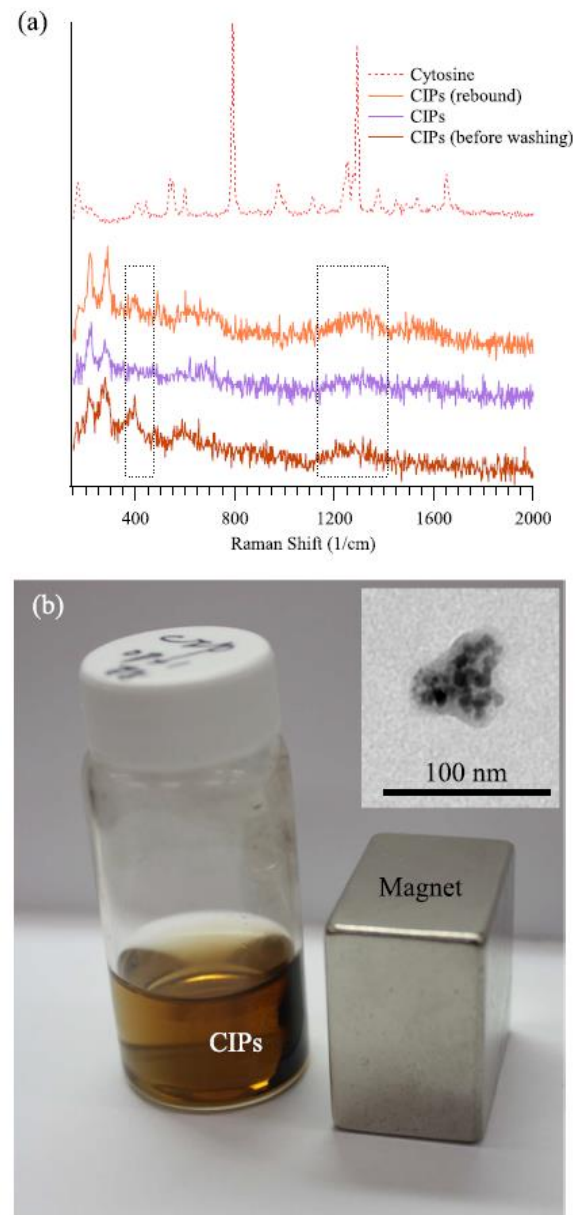


Figure 2. (a) Raman scattering of cytosine and magnetic cytosine-imprinted chitosan nanoparticles before and after template cytosine

Nanosensors:site specific sensing at the nanoscale

frontiers in
PHYSIOLOGY

METHODS ARTICLE

published: 16 January 2014
doi: 10.3389/fphys.2013.00401

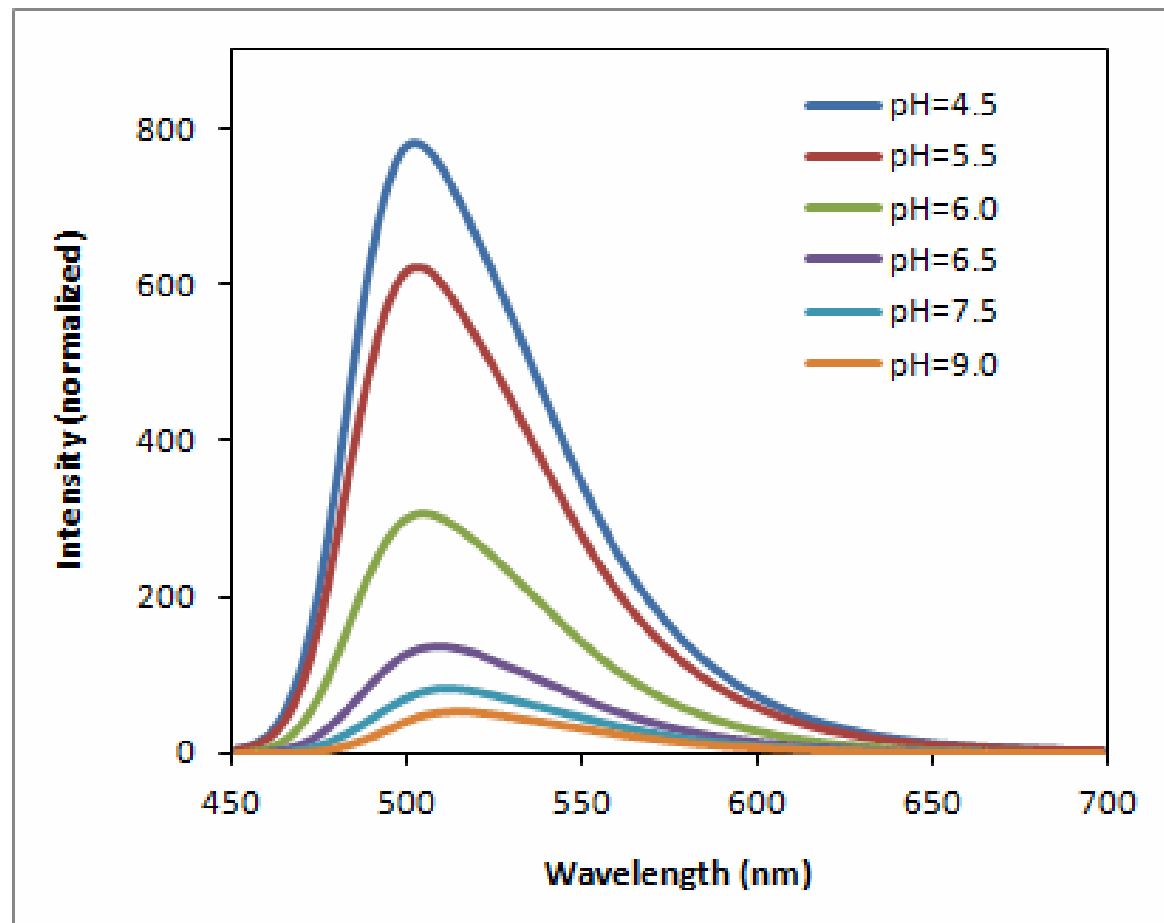


Fluorescent nanosensors for intracellular measurements: synthesis, characterization, calibration, and measurement

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FITC and pH

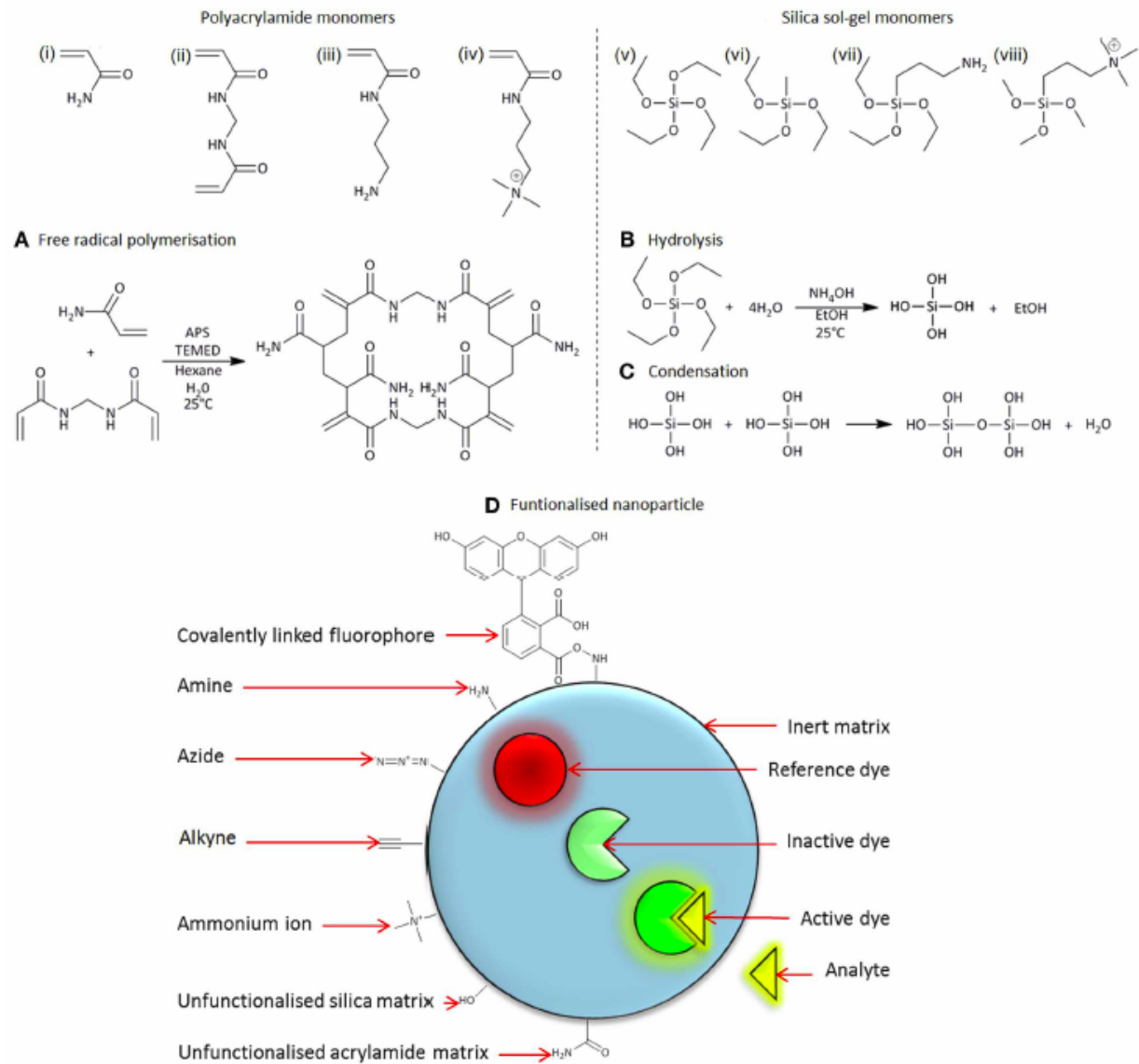


FIGURE 1 | Monomers (i–iv) and (v–viii) are used to synthesize polyacrylamide and silica sol-gel nanoparticles, respectively: (i) acrylamide, (ii) N,N'-methylenebis(acrylamide), (iii) N-(3-aminopropyl) methacrylamide (APMA), (iv) (3-acryamidopropyl)trimethylammonium (ACTA), (v) tetraethoxysilane (TEOS), (vi) methyltriethoxysilane

(MTEOS), (vii) (3-aminopropyl) triethoxysilane, and (viii)-trimethoxy silylpropyl-N,N,N'-trimethyl-ammonium (TMAC). (A) Free radical polymerization of polyacrylamide monomers. (B) Hydrolysis and (C) condensation of silica sol-gel monomers. (D) Diagrammatic representation of a functionalized nanoparticle.

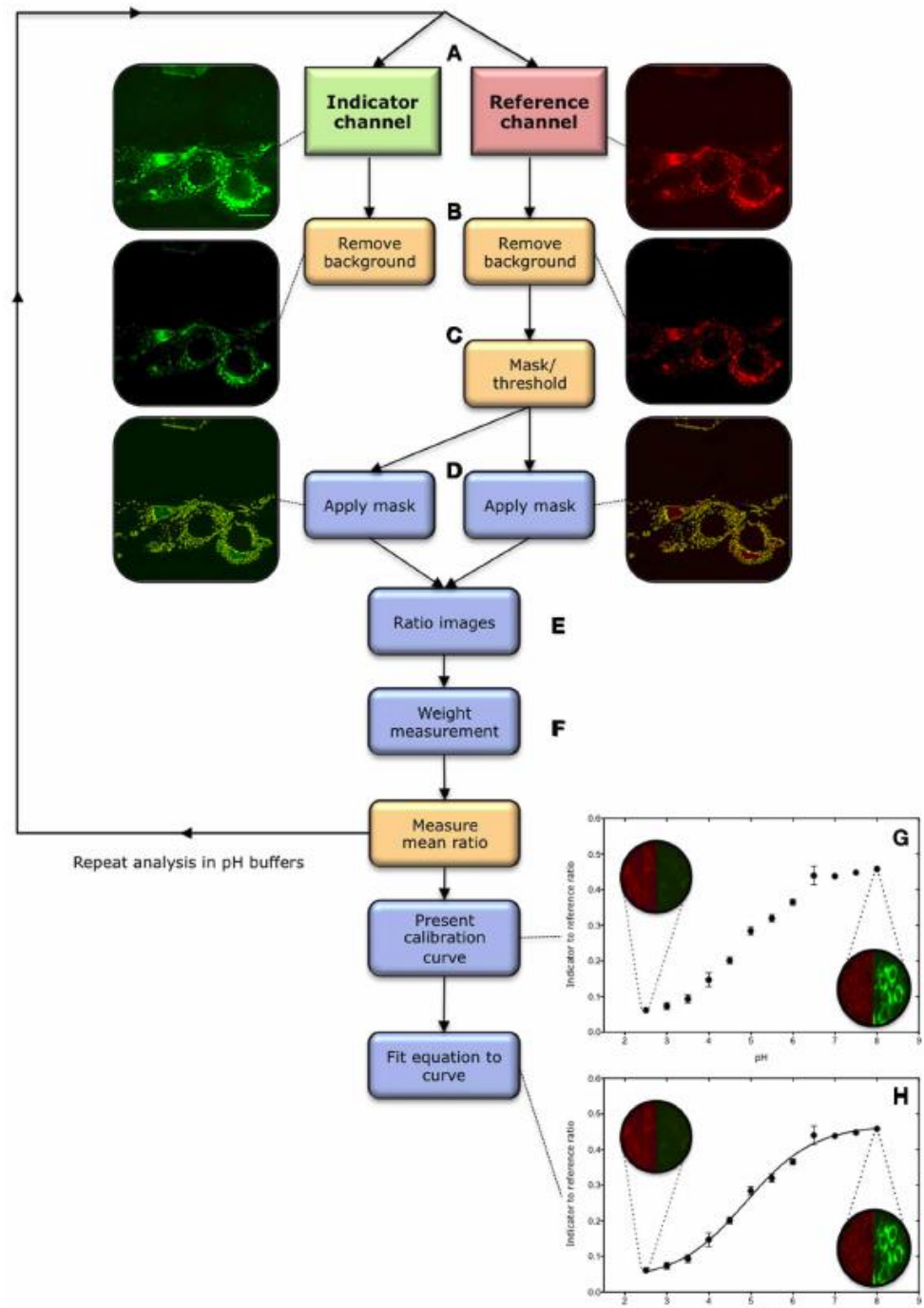
Table 1 | Selected commercially available indicator and reference fluorophores.

Analyte	Fluorophore	$\lambda_{\text{max,abs}}$ (nm)	$\lambda_{\text{max,em}}$ (nm)
pH (near neutral)	BCECF	503	525
	BCPCF	505	527
	Carboxyfluorescein	492	516
	CarboxySNARF-1	544	575
pH (acidic)	Oregon green 488	490	514
	CDCF	503	525
	HPTS	405	514
	Acridine orange	495	530
Oxygen	Ru(II)-tris(4,7-diphenyl-1,10-phenanthroline) chloride	455	615
Reference	Alexa 488	495	519
	TAMRA	555	580

The majority of fluorophores are available in an amine reactive form.

Abbreviations: BCECF, 2',7'-Bis-(2-carboxyethyl)-5-(and-6)-carboxyfluorescein; BCPCF, 20,70-bis-(2-carboxypropyl)-5-(and 6)carboxyfluorescein; CDCF, 5(6)-carboxydichlorofluorescein; HPTS, 8-hydroxypyrene-1,3,6-trisulfonic acid; TAMRA, 6-carboxytetramethylrhodamine.

Image analysis for calibration





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Nano-in-Micro Self-Reporting Hydrogel Constructs

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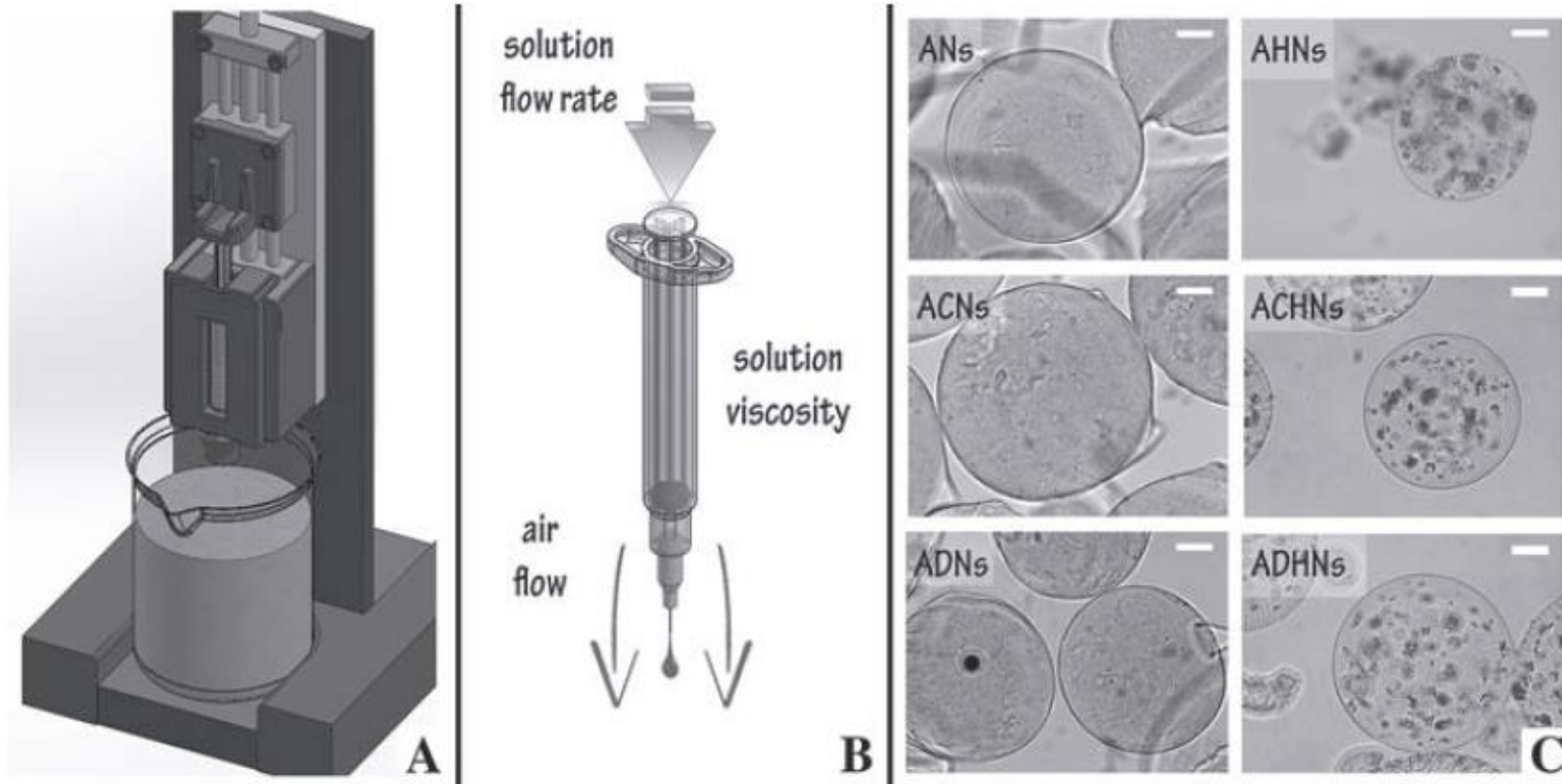


Figure 1. Microbead fabrication: (A) The Sphyga layout; (B) The working principle, whereby multiple parameters are controlled to obtain microspheres with well-defined and controlled shape and size; (C) Brightfield microscope images of microbeads (scale bar 100 μm).

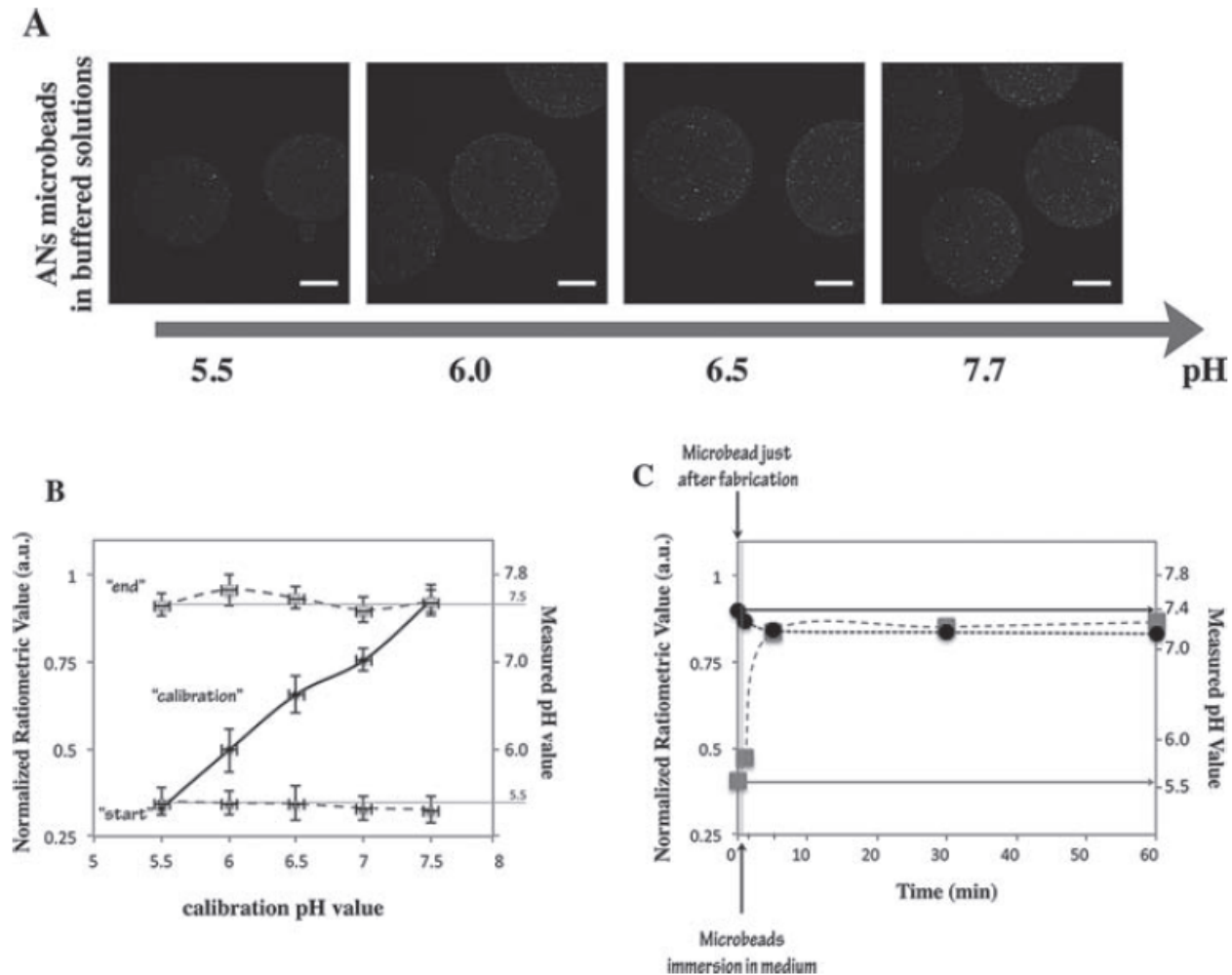


Figure 2. Calibration and time response of self-reporting Nano-in-Micro hydrogel beads. (A) Nano-in-Micro beads from ink ANs immersed in different pH buffers, showing maximum projections from confocal acquisitions. Scale bar 100 μm . (B) Reversibility of pH-sensitive microbeads with spectrofluorimetric tests: at the “start” samples were immersed in pH = 5.5 buffer solution, then different samples were exposed to “calibration” buffers [pH 5.5:0.5:7.5], finally they were placed in pH = 7.5 buffer (“end”). (C) Confocal analysis of microbeads immersed in cell culture medium: acquisitions were performed: immediately after fabrication ($t = 0$) and after 1, 5, 30 and 60 minutes of immersion in cell culture medium, reporting the measured pH value in the graph for both ACNs (gray squares) and ADNs (black circles). Reported values are obtained averaging several confocal sections of at least $n = 5$ beads.

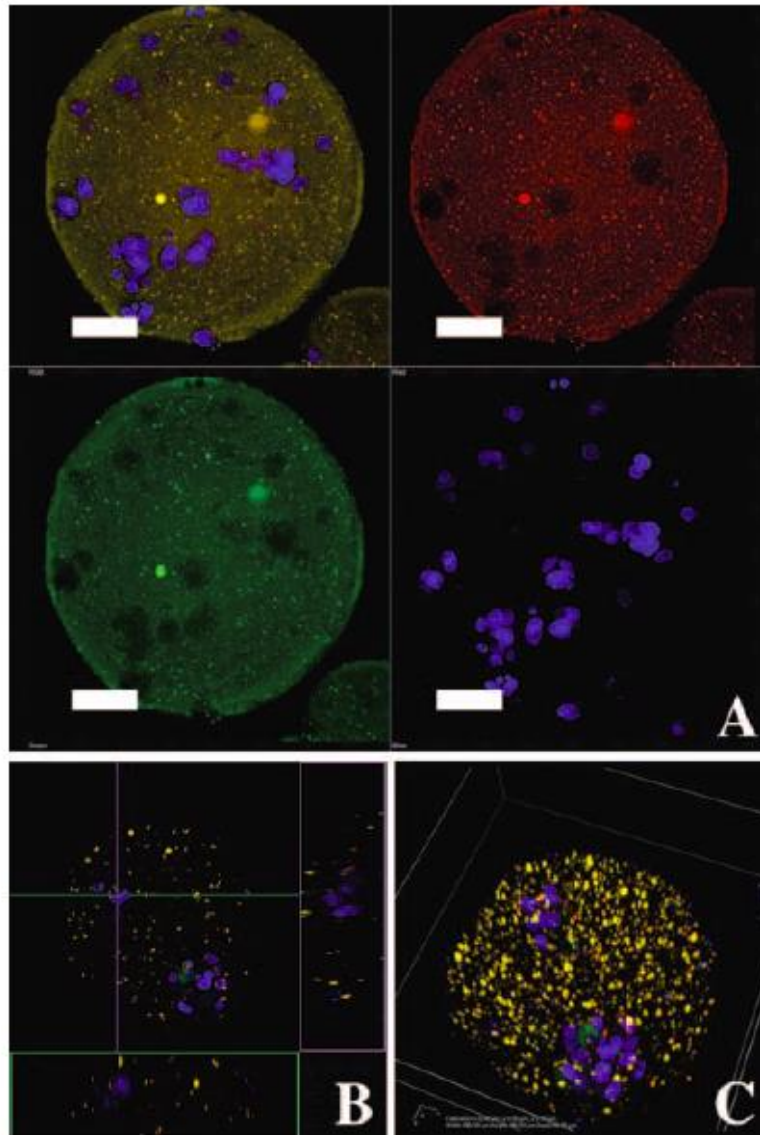


Figure 5. Confocal acquisitions of DAPI stained HepG2 in alginate/protein/pH-Ns microbead (ACHNs, day 10): (A) Sequence of z-projections showing (clockwise from top left) the bead with respectively merged, TAMRA (red), DAPI (blue) and FAM (green) acquisition channels; (B) orthogonal views and (C) volume view. Scale bars 100 μm .