

# Hitchhiking in the nanoworld

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Sept 2020

# Prelude

Hitchhiking in the  
nanoworld

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Hitchhiking is an unstructured but primitive pivot for human quests. We have hitchhiking traits in our genes. Genetic hitchhiking (or genetic drift) is allele frequency change, caused by neighbouring genes.



# Quote

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"Tiny hitchhikers attack cancer cells: Gold nanostars first to deliver drug" - *Is it like requesting a UFO for a ride?*



# Failed in Bio - Created nano

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- ▶ Nanotechnology has evolved as a result of some inherent shortcoming of related branches of science e.g., biology.
- ▶ Feynman realized, one needs a science like nanotechnology only after he was frustrated with his biology PostDoc.

# Definitions

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- ▶ **Nanoscience** is the study of structures and materials on an ultra-small scale (A nanometre is one billionth of a metre).The physical and chemical properties of matter change at the nano level.
- ▶ **Nanotechnology** has the potential to revolutionise a diverse range of fields, from health care to manufacturing,agriculture to environment, textile to sensing.

# Nanomaterials Database

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If 50% or more of the constituent particles of a material in the number size distribution have one or more external dimensions in the size range 1 nm to 100 nm, then the material is a nanomaterial.

- ▶ <http://www.pubvinas.com>
- ▶ <https://cananolab.nci.nih.gov/caNanoLab/#/>

# Classification

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The classification of nanomaterials is based on the

- ▶ *number of dimensions of a material, which are outside the nanoscale (<100 nm) range.*

# Examples of Dimensionality variations

## 0D

Accordingly, in zero-dimensional (0D) nanomaterials all the dimensions are measured within the nanoscale (they are essentially tiny 3D materials). **Qdots** are often termed as 0D material.

## 1D

In one-dimensional nanomaterials (1D), one dimension is outside the nanoscale. **Borophene, Graphene, SAM**

## 2D

In two-dimensional nanomaterials (2D), two dimensions are outside the nanoscale.

**Nanofibres, Nanorod, Nanotube, Nanowire, Quantum wire**

## 3D

Three-dimensional nanomaterials (3D) are materials that are not confined to the nanoscale in any dimension. This class can contain **bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers**.

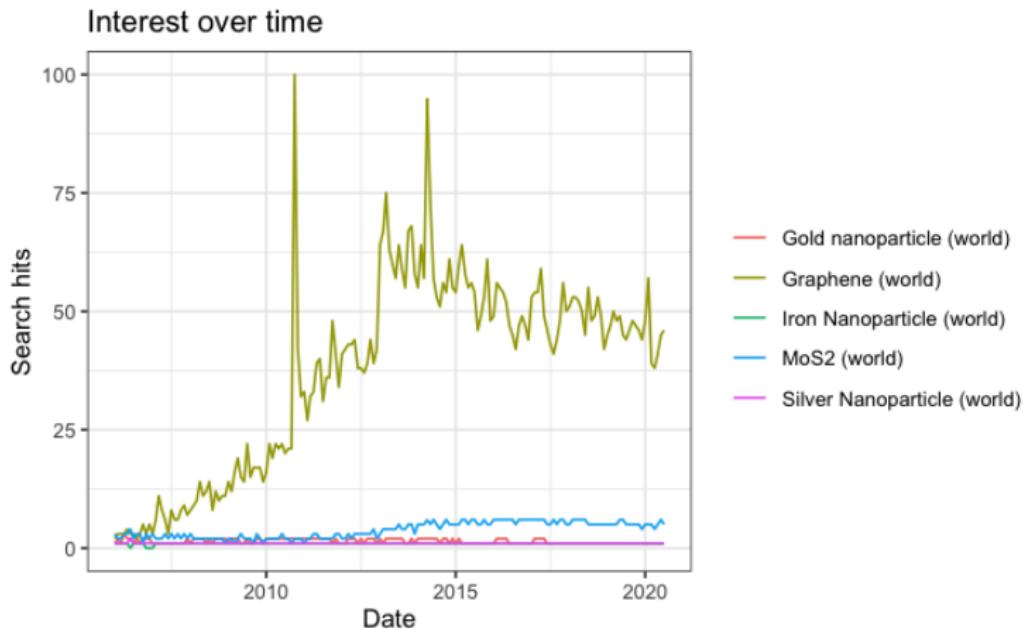
# Nano-Trends

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**Figure 1:** Nanotrend

# Our Nanotour began in the year 2006

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## **ATIP SCOOP™**

*Country: India  
Technology: Advanced Materials, Biology,  
Bio-Nano, Biotechnology, Conferences,  
Environmental Remediation,  
Government Funding*

### **Nano-Bio Interface 2006 Kolkata, India, 1–3 March 2006**

10 June 2006

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This document is formatted for US letter-size paper

#### **Contents:**

1. Overview of Nano-Bio Interface 2006
2. Important Lectures and Presentations
  - A. International Guest Speakers
  - B. Domestic Guest Speakers
  - C. Oral and Poster Presentations
3. ATIP Evaluation
4. References & Contacts

# First ever nanobio meet ever held

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# The Nanocentre proposal

The proposal for the nanocentre came out in the next year - A significant portion of the proposal contained the small progress that we achieved in our lab at that time.

The image consists of two main parts. On the left is a poster for an "International Conference Nano-Bio Interface 2006" held at Calcutta University. The poster features a blue-toned photograph of laboratory equipment, a logo with a hand holding a DNA helix, and text detailing the conference date (March 1-3, 2006), location (SINP Auditorium, Kolkata), and organizers (Dr. B.C. Guha Centre for Genetic Engineering & Biotechnology). On the right is the logo for the "Centre for Research in Nanoscience and Nanotechnology" (CRNN), which includes a circular emblem and the acronym CRNN in large letters.

The proposal for the nanocentre  
came out in the next year -  
proposal contained the small progress that we achieved in our lab at that time.

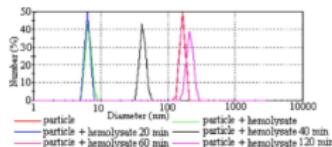
- ▶ We started our almost random nanowalk in the year 2006
- ▶ Jaydeep was working on folding of a protein which most of the protein scientists avoid, but many medical biologists love
- ▶ It was hemoglobin
- ▶ The clinical angle came out from the fact that the hemoglobin structure varies considerably in a disease called thalassemia
- ▶ With the help of Dr. P.Sen who was in possession of copper nanoparticles (using top down ball mill methods) we attempted to study Hb folding using CuNP

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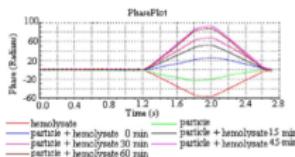
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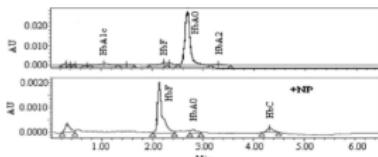
## Interaction of hemoglobin and copper nanoparticles: implications in hemoglobinopathy



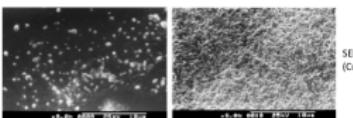
Size distribution of nanoparticles, nanoparticle-hemolysate complex, and their respective size changes with indicative colors.



Zeta potential-dependent phase of copper nanoparticles (CuNPs), CuNPs plus hemoglobin, and their changes with time, represented in different colors.



Comparison of soluble fraction of hemolysate before (upper panel) and after (lower panel) addition of copper nanoparticles (CuNPs). The soluble fraction was prepared after pre-incubation with 1.5 ppm of CuNPs for 1 hour and then centrifuging at 4000g to remove aggregates. High-pressure liquid chromatography was run using the Chromsystems kit under identical flow conditions.



SEM image of copper nanoparticles (CuNPs) and CuNPs + HbAO

**Interaction of Hemoglobin and Copper Nanoparticle: Implications in Hemoglobinopathy;**  
Jaydeep Bhattacharya, Upal Choudhuri, Omprakash Swarach, Prasenjit Sen, Anjan K Dasgupta\*;  
*Nanomedicine:nanotechnology, biology, and medicine* 2[3](2006)191-199

Patent: NOBEL METAL NANOPARTICLE SPECIFIC INTERACTIONS IN CLOSELY HOMOLOGOUS HEMOGLOBIN. 39/DEI/2006



Jaydeep Bhattacharya  
Assistant Professor  
School of Biotechnology, JNU

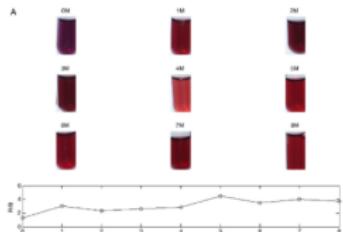
- ▶ In the mean time a new student Tapan (late Tapan Das) synthesized AuNP in our lab.
- ▶ Jaydeep thought it worth trying to probe hemoglobin folding using AuNP
- ▶ Here is what we got

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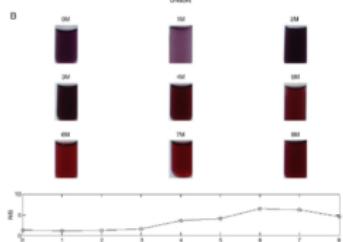
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## Gold nanoparticle-based tool to study Hemoglobin conformational variants



Unfolding of haemoglobin and BSA were compared in presence of 0-8 M urea by synthesizing the gold nanoparticles from the unfolded template. The different folded states resulted in different size and plasmonics of GNPs and enabled to define the folding states.

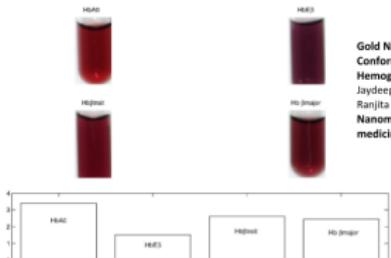


GNPs synthesized from Unfolded (4M urea) haemoglobin variants were compared. The E beta variant was more bluish, as revealed from the diagram, and this was followed by the beta major and beta trait. The normal had the maximal red colour. So the plasmonic based folding sensor can differentiate between protein variants too and can be used as carrier detection

Jaydeep Bhattacharya  
Assistant Professor  
School of Biotechnology, JNU



Gold Nano Particle Based Tool to Study Protein Conformational Variants: Implications in Hemoglobinopathy;  
Jaydeep Bhattacharya, Sinu Jasrapuria, Tapan Sarkar, Ranjita GhoshMoulick, Anjan Kr. Dasgupta\*  
*Nanomedicine: nanotechnology, biology, and medicine* 3 (2007) 14-19



- ▶ Ranjita was contemporary to Jaydeep and was gaining experience in a MD simulation project.
- ▶ She joined in my newly funded DST project on protein Glycation

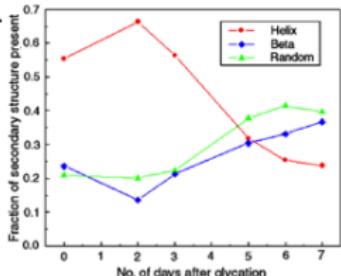
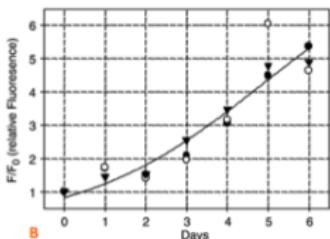
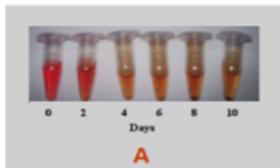
- ▶ Ranjita came out with an interesting observation that there is a **systematic but compensatory unfolding of protein** it is subjected to synthetic glycation.
- ▶ She published a comprehensive paper on this topic in the BBA.
- ▶ We thought it worth trying to probe the glycation level using Au seeding
- ▶ The result was that different level of glycation led to different sizes of AuNP formation (showing different colors).
- ▶ A primitive glycation sensor was reported

Dr. Ranjita Ghosh Moulick

Assistant Professor

Amity Institute of Integrative Sciences and Health &amp; Amity Institute of Biotechnology

- In Vitro glycation of Hemoglobin and quantification of AGE products-** A. The time dependent changes in physical appearances of hemoglobin B. The increase in characteristic fluorescence emission showing AGE formation. c. Compensatory loss of alpha helix with the corresponding increase in beta and random structure.



- A
- 2. Gold nanoparticles as sensors of AGE products –** Using protein templates with different degrees of glycation, an assay technique was designed to determine the propensity of glycation, based on gold nanoparticle formation



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FEBS Letters 581 (2007) 5533–5542

## Controllable self-assembly from fibrinogen–gold (fibrinogen–Au) and thrombin–silver (thrombin–Ag) nanoparticle interaction



**Shibsekhar Roy, Anjan Kumar Dasgupta\***

*biochemistry, University of Calcutta, 35 Ballygunge Circular Road, Kolkata 700 019, India*

Dr. Shibsekhar Roy Received 12 September 2007; revised 20 October 2007; accepted 25 October 2007  
 UGC Assistant Prof.  
 Osmania Univ.

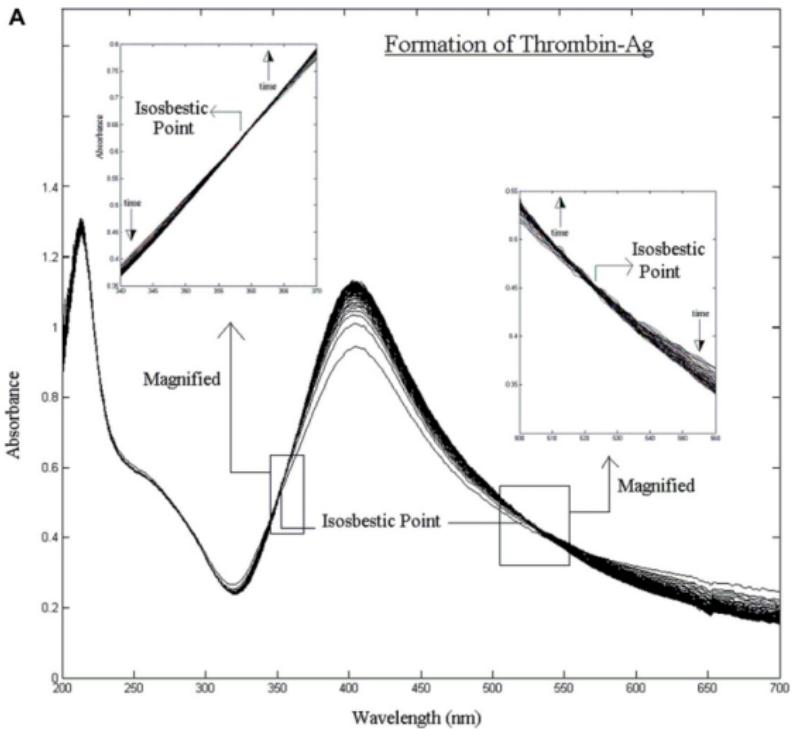
Available online 5 November 2007

Edited by Veli-Pekka Lehto

**Abstract** **Fibrinogen conjugated gold nanoparticles** (fibrinogen–Au) and **thrombin conjugated silver nanoparticles** (thrombin–Ag) were synthesized by heating (90 °C) the proteins (50 µg protein/ml) with 1 mM AgNO<sub>3</sub> or AuCl<sub>3</sub>. The resultant particles were harvested and examined by flow cytometry, scanning electron microscopy (SEM), transmission emission microscopy (TEM), optical microscopy and dynamic light scattering. SEM and TEM images revealed that the fibrinogen–Au and thrombin–Ag particles interacted. The emergent bio-nanoconjugate population could be controlled by addition of thrombin–Ag. The method may be exploited in parametrizing coagulation factors and other clinically important protein–protein interac-

of near micron level structures the population of nanoclusters is conveniently detected by flow cytometry from the scattering behavior of interacting molecules and their proteolysis product.

The fibrinogen–thrombin interaction is a part of the physiological process of blood clotting. The reaction cascade leading to the final step comprises the chemical reaction between the serine protease thrombin and the precursor protein fibrinogen (with subunit Aα2Bβ2γ2) to form fibrin clots. The reaction involves the proteolytic cleavage of fibrinogen by thrombin. The cleavage takes place between Arg16 and Gly17 of subunit Aα and between Arg101 and Glu15 of subunit Bβ to form fibri-



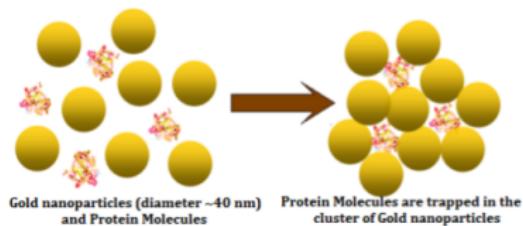
- ▶ Just when Jaydeep Ranjita and Shibsekhar were experimenting on sensing some clinically important protein phenomena, Santi joined.
- ▶ When nothing interesting was happening to him for a year long spell, he thought of exploring the possibility of chaperons properties of AuNP.

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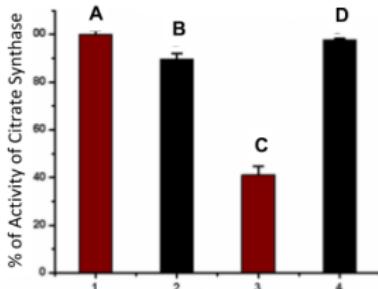
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## Size dependent chaperone-like activity of gold nanoparticle



- A**: Citrate Synthase (without heat treatment)
- B**: Citrate Synthase in presence of gold nanoparticle (without heat treatment)
- C**: Citrate Synthase (after heat treatment for 1 hr)
- D**: Citrate Synthase in presence of gold nanoparticle (after heat treatment for 1 hr)



Santiswarup Singha, Ph.D.  
Staff Scientist IV  
National Institute of Immunology  
Aruna Asaf Ali Marg, New Delhi-110067  
email: santiswarup@niit.ac.in | santiswaroop@gmail.com

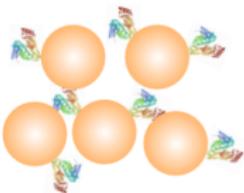
- ▶ But this was not all. He looked into protein glycation from another perspective.
- ▶ Not as glycation sensor
- ▶ But as antiglycating agent

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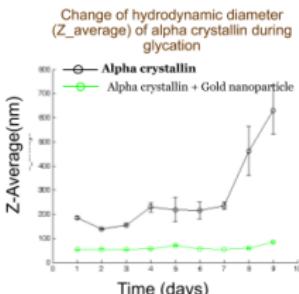
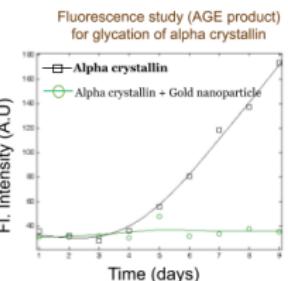
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### Anti-glycation activity of gold nanoparticle



Gold nanoparticle blocks the primary amine of proteins and prevents the glycosylation

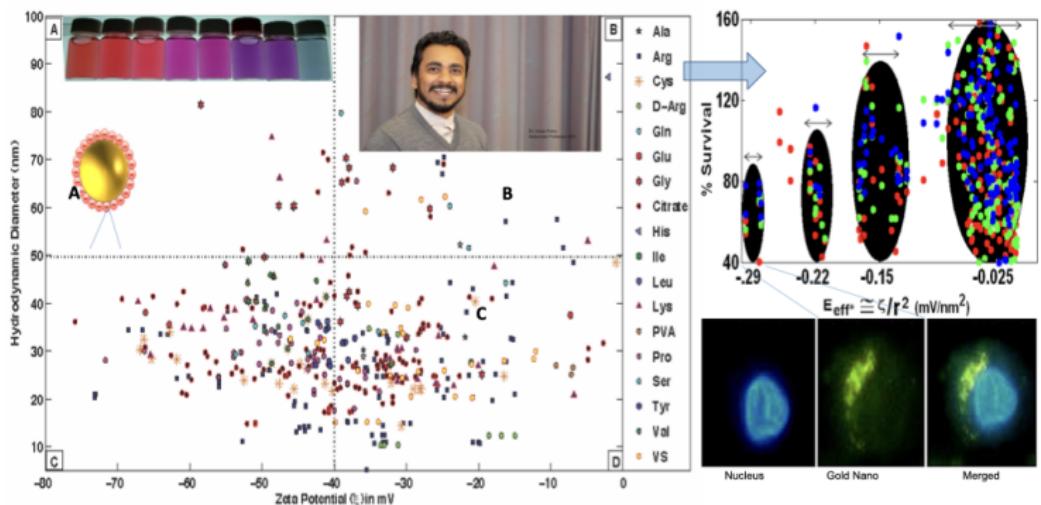


- ▶ Our first tryst with cancel cell nanoparticle interaction started with Hirak.
- ▶ What became a solid new finding by Hirak was the cell specificity of the nanoparticle interaction.
- ▶ The other new finding was selectivity of the size distribution - some nano-sizes were more probable than others.

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Patra et al., Nanomedicine 2007; Patra et al., Analytica Chimica Acta 2009; Patra et al., Nanomedicine 2012

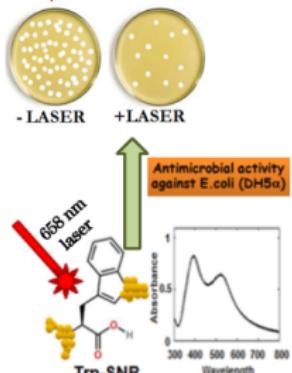
- ▶ Then came Sarita
- ▶ Sarita wanted to try silver nanoparticle
- ▶ The rule of the thumb was that she wanted to do something totally different - Being from chemistry she was fascinated by the chirality concept.
- ▶ She started studying chirality of AgNPs.

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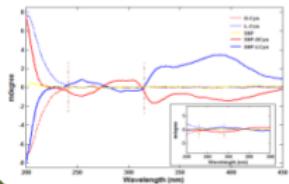
adgcal@gmail.com

Chemically designed double plasmonic silver nanoparticles as a smart antimicrobial agent

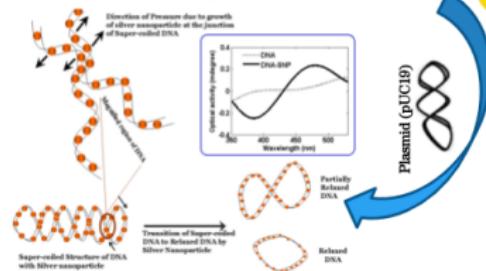


Post-doctorant(e) at Department of Physical Chemistry, University of Geneva

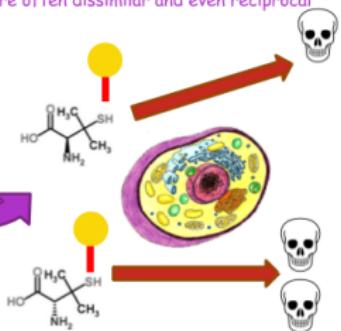
Amplification and emergence of nanoscale chirality upon preadsorption of nanoparticle with biomolecules mainly amino acids



DNA template silver nanocluster and appearance of chirality at nanoscale



Chirality and the amplified chirality induced reciprocal responses are often dissimilar and even reciprocal



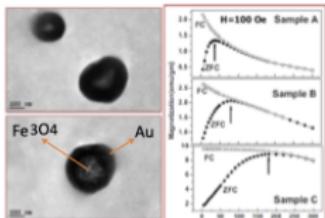
- ▶ It was a memorable moment in the lab when Raja joined
- ▶ like everyone else in the lab he wanted to do something new and totally different.
- ▶ I asked him to probe into a challenging problem in biology
- ▶ Role of static magnetic field.

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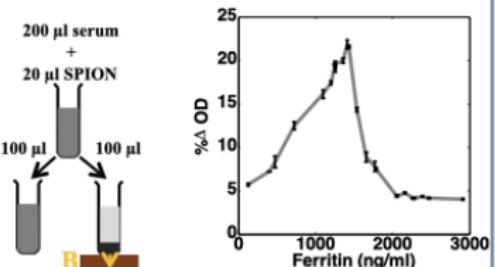
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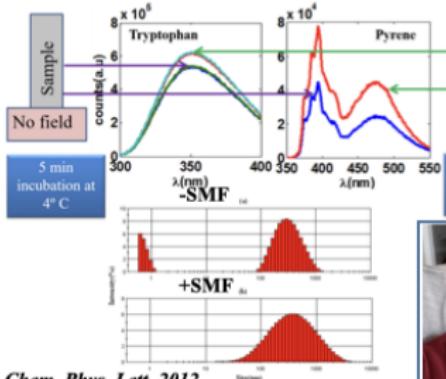
Emergent properties due to interfacial effects-gold coating induced increase in magnetic moment of iron oxide nanoparticle (*J. Appl. Phys. 2011*).



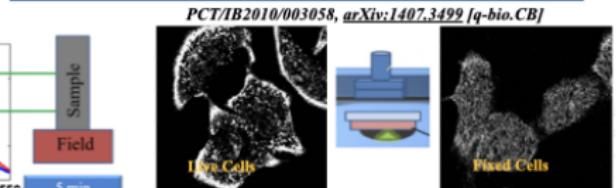
Crosstalk between synthetic and natural iron oxide nanoparticle-an approach towards antibody free serum ferritin detection assay (*WO 2011/141766 A1, bioRxiv 10.1101/211102*)



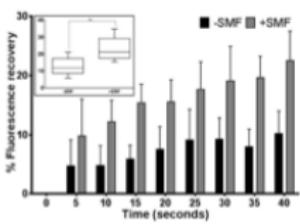
Magnetic memory of biological systems-key to quantum biology



*Chem. Phys. Lett. 2012*



Dr. Sufi O Raja  
Postdoc  
Associate  
Duke University,  
USA



- ▶ Tamoghna was the first person in the lab to try carbon nanomaterial
- ▶ He got himself trained in IIT Kanpur to an expert in carbon nanomaterial
- ▶ After some efforts he came up with the idea of studying interaction of SWNT and lipids.

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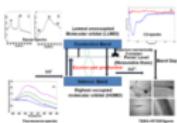
adgcal@gmail.com



Schematic representation of solid state capillary reaction

- A new insight in characterization of solid state functionalized carbon nanotubes in terms of intrinsic properties of semiconducting singlewall carbon nanotubes and interplay in-between topological and geometrical chirality at nanoscale.  
*J. of Mater. Chem. A* 2 (2014) 3759-3765.

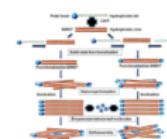
**Patent number:** 9817093, **Type:** Granted,  
**Date of Patent:** November 14, 2017, **Publication date:** July 2, 2015, **Filed:** August 6, 2012, **Inventors:** Anjan, Kr. Dasgupta, Tamogna Bhattacharyya



- A novel carbon nanotube self-assembly based supramolecular molecular machine for making versatile molecular trap for making viable bio-sensors (glucose sensor)

*Nanoscale* 5 (2013)  
9231-9237.

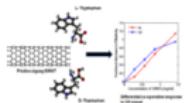
**Patent number:** 9322012, **Type:** Granted,  
**Date of Patent:** April 26, 2016, **Publication date:** March 19, 2015, **Filed:** August 8, 2014, **Inventors:** Anjan Kr. Dasgupta, Tamogna Bhattacharyya, Arka Mukhopadhyay, Nalok Datta, Krishana Chakraborty



- Chirality Sensitive Binding Property of Pristine Singlewall Carbon Nanotubes: An Approach to Differentiate Geometrical Chiral Molecules

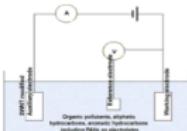
*Phys. Chem. Chem. Phys.* 16 (2014)  
14651-14655.

**Patent number:** 9726596, **Type:** Granted,  
**Date of Patent:** August 8, 2017, **Publication date:** May 14, 2015, **Filed:** November 12, 2014, **Inventors:** Anjan Kr. Dasgupta, Tamogna Bhattacharyya, Sarita Roy



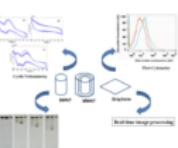
- Carbon nanotube based supercapacitor design for making a hydrocarbon sensor

*J. Electroanal. Chem.* 706 (2013)  
133-139.



- Soft gel based differential electrical diffusion for carbon nanomaterial characterization and purification in large scale

*Electrophoresis* 36 (2015)  
3009-3013



Tamogna Bhattacharyya

Carnegie Mellon University  
Research Associate



- ▶ Azhar used nanotechnology of eye disease.
- ▶ He is still doing something related to nanotechnology of the cornea.
- ▶ But here is what he did during his PhD

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**Mohammad Azharuddin, PhD**  
*Postdoctoral fellow*  
*Department of Biomedical and*  
*Clinical Sciences (BKV)*  
*Linköping University, Sweden*

### Thesis title: Nanoscale Interactions in Mammalian Eye

- Penetration of gold nanoparticles (20 nm) into different layers of the cornea
- Synthesis of aqueous soluble curcumin nanoparticles and its anti-glycation activity
- Human tear proteins as template for gold nanoparticles with subsequent dry eye disease diagnosis.

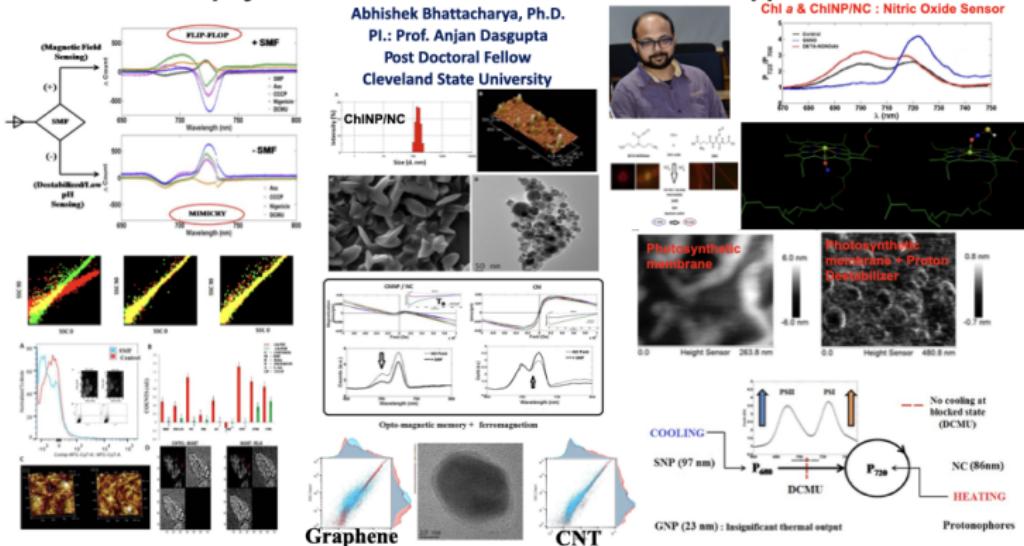
- ▶ Abhishek was one student who made me nervous as he was a plant science student, a background unfamiliar to me.
- ▶ Abhishek started working on the spectroscopic studies on plant photosynthetic system
- ▶ In the process he came up with an interesting sensing behaviour of Chl A Nanoparticle.

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## Chlorophyll a - Membrane Bound / Nano Scale - Applications



- ▶ I am now describing the concluding part of my nanotour.
- ▶ It was Sanhita who started looking in nanointerface of biofilm
- ▶ She started with conceptualizing a oxygen sensor
- ▶ She then came up with the idea of introducing a nano-inspired synthetic biology. By conjugating the microbial surface with magnetic NP, and then using SMF.
- ▶ She also made some interesting observation on interaction with biofilms with a 2D Dirac material (graphene) .



# Microbial community inspired nanotechnology

Sanhita Ray

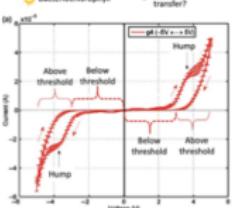
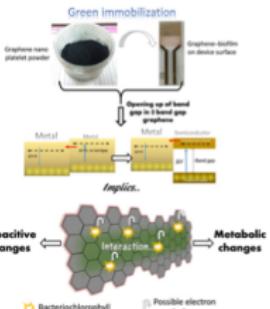
Postdoctoral Scholar

University of California Santa Cruz

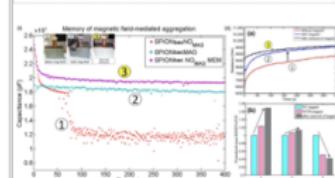
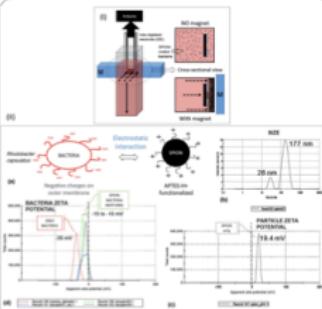
Jack Baskin School of Engineering

Department of Electrical and Computer Engineering

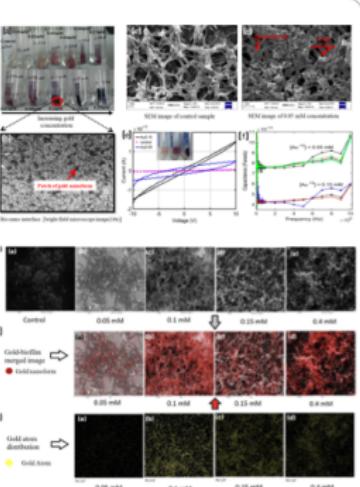
## Graphene + bacteria



## SPION + bacteria

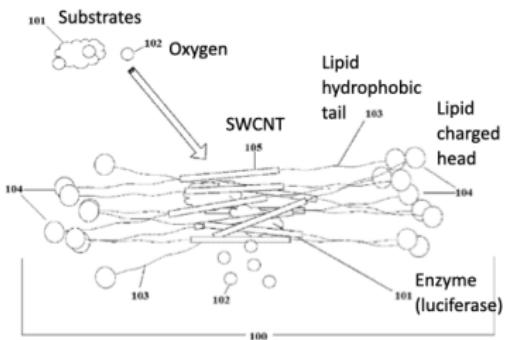


## Gold nanonetworks + bacteria



Microbial community inspired nanotechnology

## Oxygen sensor



# Back to basics

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The equation expressing the extinction cross section of a spherical nanoparticle within the quasistatic approximation is given by:

$$C_{ext} = 24\pi^2 R^3 \frac{\epsilon_m^{1.5}}{\lambda} \cdot \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_M)^2 + \epsilon_2^2} \quad (1)$$

# Why this simple explanation fails?

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- ▶ The equation predicts that the resonant condition will be independent of the particle size i.e.,  $\epsilon_1 = -2\epsilon_M$  is independent of R.
- ▶ But we know that the plasmon resonance changes as the particle size becomes smaller
- ▶ Drude equation that overcomes the limitations of the free electron gas approximation.

# Modified Drude

If  $\gamma$  is a medium dependent damping factor,

$$\omega_p = \sqrt{\frac{me^2}{m_{eff}\epsilon_0}} \quad (2)$$

$$\epsilon(\omega, k) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma) - \beta^2 k^2} + \epsilon_{IB}(\omega) \quad (3)$$

The resonance then becomes size dependent.

# A particle in a box approach - The size & shape effect

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**Spherical nanoparticle:**

$$E_{nl} = \frac{\hbar^2 \chi_{nl}^2}{2m_e R^2} \quad (4)$$

where,  $\chi_{nl}$  in the n-th root of the i-th order spherical Bessel function.

**Cubic nanoparticle:**

$$E_{nml} = \frac{\hbar^2 \pi^2}{2m_e a^2} (n^2 + m^2 + l^2) \quad (5)$$

# Miepython

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We use a simulation perspective of Mie scattering is a pure Python module to calculate light scattering by non-absorbing, partially-absorbing, or perfectly conducting spheres.

```
import numpy as np
import matplotlib.pyplot as plt
import miepython

# wavelength in microns

radius = 0.1          # in microns
num = len(ref_lam)
m = ref_n-1.0j*ref_k
x = 2*np.pi*radius/ref_lam

qqabs = np.zeros(num)
qqsca = np.zeros(num)

for i in range(num) :
    qext, qsca, qback, g = miepython.mie(m[i],x[i])
    qabs = qext - qsca
    qqabs[i]=qabs*np.pi*radius**2
    qqsca[i]=qsca*np.pi*radius**2

plt.plot(ref_lam*1000, qqabs, color='blue')
plt.plot(ref_lam*1000, qqsca, color='red')

plt.title(r"Gold Spheres 100nm diameter")
plt.xlabel("Wavelength (nm)")
plt.ylabel(r"Cross Section ($\mu m^2$)")
plt.annotate("absorption", xy=(700,0.01), color='blue')
plt.annotate("scattering", xy=(750,0.1), color='red')
plt.show()
```

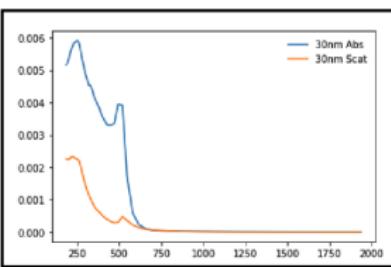
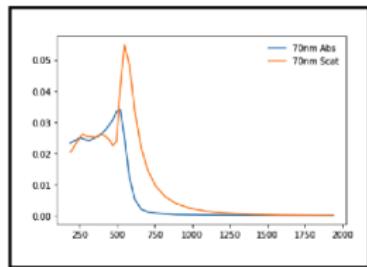
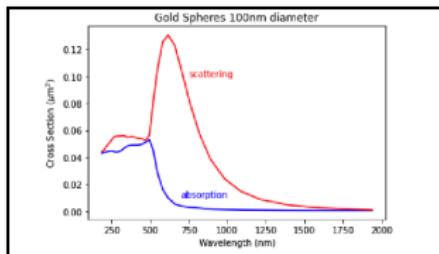
# Plasmon simulation

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## A note for the “unsmarts”

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When size of the NP is reduced from 100 nm to 30 nm -  
Scattering intensity is lowered relative to the absorbance -  
The intensity of both scattering and absorbance lowers - With  
higher wavelength scattering is red-shifted to a significant  
extent,absorbance slifgly blue shifted. # The Sensing lies in  
the eye of the detector

- ▶ Why there is Difference of the Absrobance and Fluoresence detections system?
- ▶ Those who have tried to measure plasmon resonance using different detection system will relaize that we often get significant variations in the plasmonic frequency when we use spectrophotometer (abs based) as compared a fluorimeter (scattering based).
- ▶ The design of nanosensors may be enriched if these basics of nanoscience are clearer to us.

# Future Directions

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- ▶ The main challenges in nanotechnology are the following:
- ▶ Existential; Will the technology will merge with other sister disciplines or it will retain an independent existence
- ▶ How nanotechnology can merge with other trending disciplines like chip development and/or big data
- ▶ How nanoscience can contribute to the emerging disciplines of quantum biology/quantum computation.
- ▶ It is however important for us to realize that we will never have a technology that is sub-nano, but would retain the identity of molecules constituting a given material.
- ▶ Below nanoscale the atoms are no more atoms , and the science therein belongs to a different world of physics (subatomic).

# Deep learning the Nanoworld

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- ▶ We are poor in **nano-aerosol** interaction. It will be interesting to probe how nanoforms can be exploited in sanitizing the air quality or removing the undesirable toxicants from air.
- ▶ Nanotechnology may be used in the **pulp and paper** industry
- ▶ **Medical textiles** for Nanofiber-based 'smart' dressings.
- ▶ Printed papers using **nanoparticle based electronic component** (inks of graphene, gold and silver being already available)
- ▶ We may use **nanomaterials for developing effective sanitations** (important post-covid step).
- ▶ Deeper understanding of biomaterials nanmaterial interaction interaction would enable us to make smarter

# Nanosnart to NanoGate

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<https://phys.org/news/2020-09-nanoparticle-based-architecture-nanoparticle-neural-networks.html>

# Their story

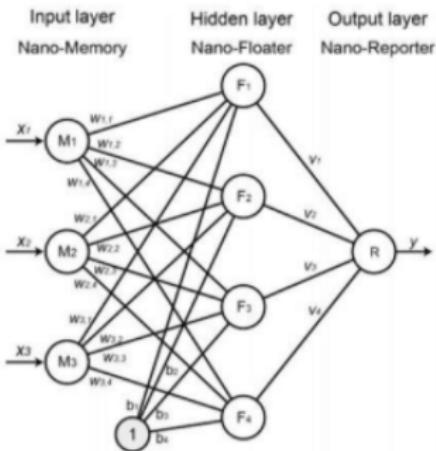
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- ▶ Then they calculated the number of nanoparticle nodes needed to functionally complete Boolean logic operators on the neural network.
- ▶ The hardware relied on covalently modified nanostructures on a lipid chip for multiple executions.
- ▶ They tested the reset function of the system for reusability by dehybridizing all DNA assemblies after exchanging the buffer solution in the setup.
- ▶ The reset allowed thiolated DNAs alone to remain on the nanoparticles, thereby returning to the initial state for the next function.



$$x_i = \{0, 1\} \quad w_{i,j} = \{1, 0, -1\}$$

$$b_j = -h \quad (h \text{ is the number of } w_{i,j} \text{ equal to 1})$$

$$v_j = \begin{cases} 1 & \sum_{i=1}^n w_{i,j} \cdot x_i + b_j \geq 0 \\ 0 & \text{otherwise} \end{cases}$$

$$y = \begin{cases} 1 & \sum_{j=1}^m v_j > 0 \\ 0 & \text{otherwise} \end{cases}$$

Nanoparticle neural network (NNN) for a functionally complete 3-input system. ...

# At the END

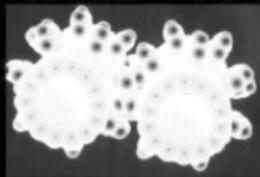
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# THANK YOU

AMITY

FOR GIVING ME A CHANCE TO DESCRIBE THE  
NANO-EXPERIENCES



From Nano  
Rajesh, to Dhr  
Sept 2010