Hitchhiking in the nanoworld - A spontaneous drift from Nanoscience to Nanotechnology

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Atoms made the humans, humans made the nanoparticles.

Prelude

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.Nanotechnology has evolved as a result of some inherent shortcoming of its neighbouring branches of science e.g., biology. In fact being unable to visualize bio-molecular events,as Feynman realized, one needs a science like nanotechnology. The aspirations of the fast-changing techno-world to have further miniaturization has catalysed the progress of this field at a lightning speed. The inspiration to explore nanoscale has led to numerous inventions in agriculture,environment,electronics, textile, cosmetics, drug delivery and diagnostics. However, there exists a phase lag between nanotechnology and nanoscience. The success in technology has not necessarily improved our understanding of simple facets of this strange nanoworld. We can't explain a simple event like blinking of the gold nanoclusters..The interplay between 1D and 2D materials with biomaterials remain at a less than satisfactory level.The close association of flow of electrons, spin, photons and phonons and polarization originating at the nanosurface remain largely unexplained till this day. While we can keep on enjoying the fruits of nanotechnology to understand the science in nanoscale we may state following Feynman that we must behave a little "unsmart".

Nano-Form versus content

The language of the nano-world has evolved by the close interplay between nanomaterial type and functionality. From the beginning of its evolution spanning from half a century, the nano-research has branched into two groups, one aiming at determistic nano-configurations,the other craving for Boltzman machines where determinstic plugins are embedded in a stochastic template. Nano-chip developments for example, fall mainly in the first category, whereas, the drug development,or nano-treatment in agro industries or, industries related to paper or textiles, fall in the second. The sensor development has to use essence of both the worlds as at the fabrication level it needs the the first, whereas at the sensing level it needs a staochastic adaptibility. An interesting gap area that is left out in this classification is the gas phase nanotechnology (2D materials being a known candidadte for this).This would relate to interaction of nanmaterial with the gas phase.

Some questions related to nano-basics

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

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

The resonance occurs if the extinction coefficient is maximum.This happens if:

$$-\epsilon_1 = 2\epsilon_M \tag{2}$$

Why this simple explanation fails?

The equation (2) predicts that the resonant condition will be independent of R , the particle size. But we know that the plasmon resonance changes as the partcle size becomes smaller. The yellow to red or red to blue transition of gold nanoparticles are well known. For this purpose we consider the Drude equation that overcomes the limitations of the free electron gas approximation.

$$\omega_p = \sqrt{\frac{me^2}{m_{eff}\epsilon_0}} \tag{3}$$

$$\epsilon(\omega, k) = 1 - \frac{\omega_p^2}{\omega.(\omega + i\gamma) - \beta^2 k^2} + \epsilon_{IB}(\omega) \tag{4}$$

γ is a retarding coefficeint depending on size and the complexity of response is expressed by the interband component ϵ_{IB}.

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

We also do not understand how the functional properties change when we change the shape. For a **spherical nanoparticle**:

$$E_{nl} = \frac{\hbar^2 \chi_{nl}^2}{2m_e R^2} \tag{5}$$

where, χ_{nl} in the n-th root of the i-th order spherical Bessel function. For a cube shaped nanoparticle on the other hand the energy is given by :

$$E_{nml} = \frac{\hbar^2 \pi^2}{2m_e a^2}(n^2 + m^2 + l^2) \tag{6}$$

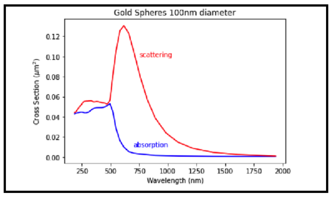
The simple particle in a box approach explains that the energy of resonance would depend on the radial size R (spherical nanoform) and dimesion a (for cubic nanoform). A detailed qunatum mechanical approach describing plasmonics is muddled with mathematical complexity on one hand and idealization on the other.

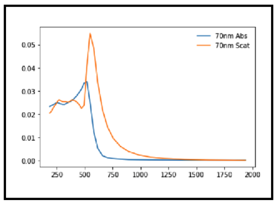
Miepython

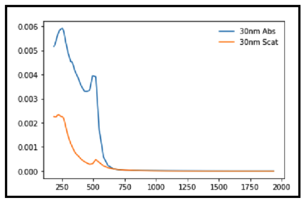
We use a simulation perspective of Mie scattering is a pure Python module to calculate light scattering by non-absorbing, partially-absorbing, or perfectly conducting spheres.

```
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()
```







A note for the "unsmarts"

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 signifiant extent,absorbance slifgtly blue shifted. - 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 fluorometer (scattering based). The design of nanosensors may be enriched if these basics of nanoscience are clearer to us.

Our random Nano-walk (2006-2020)

Nano is small but work and expeditions in the nanowold need a big and competent group (I was lucky to have one) We initiated nanoscale exploration in 2006 which also marked firstever Nanobiointerface seminar in India.

Our first work was an interaction of hemoglobin and copper nanoparticles (Bhattacharya et al. (2006)).Our work (Roy et al. (2006)) explored the potential of cadmium sulphide nanorods as an optical probe to reveal the folding state of cytochrome C. This was followed by two works related to nanotechnology based glycation sensing (GhoshMoulick et al. (2007)) and nanomaterial as antiglycation agent (Singha et al. (2009)). We exploited nanomaterials to control a protein assembly (Roy and Dasgupta (2007)). Our next goal was to explore nano-surface directed modulation of protein folding. We reported gold nanoparticles as chaperons (Singha, Datta, and Dasgupta (2010)) for the first time. The notable part was that the gold nanomaterial not only behaved as chaperons, their chaperon properties were dependent on nanoparticle size. We also designed solid state chaperons using immobilized α-Crystallin (Namrata Ray and Sarkar (2014)). Basically this was a synthetic heat-shock resistant surface. We also did some nano-characteriztion work e.g.,(Sarkar et al. (2008), (Patra, GuhaSarkar, and Dasgupta (2009)).

Our expeditions then included study of Chirality sensitive binding of tryptophan enantiomers with pristine single wall carbon nanotubes(Bhattacharyya, Roy, and Dasgupta (2014)).The chirality work was also followed up with few more perspectives e.g.,(Roy, Basak, and Dasgupta (2010)) and (Roy et al. (2013)).

We took two approaches in our work on interaction of nanoparticles and cells. The first cellular target was platelet (Deb et al. (2007)). We showed how gold nanoparticles can affect the platelet aggregation profile. The work which has got some attention is (Patra et al. (2007)) in which we highlighted for the first time in cellular specificity of the AuNP interaction. The nano-drug would remain unreal unless we consider such specificity.

We raised another important but simple question, namely whether nanoparticles can behave as drug carrier and drug and at the same time (Patra et al. (2011)). We also used gold nano as a probe for an anticataract drug (Azharuddin, Dasgupta, and Datta (2015)) .

We then did some work with carbon nanomaterial. The work that seemed to have some signifiance was a SWNT based lipid sensor (Bhattacharyya et al. (2012)).The work was followed up by two other works in which we could biomimic the liposome by using SWNT loaded lipids (Bhattacharyya and Dasgupta (2018)).

We probed into the domain of synthetic biology of nanomaterials (S. Ray, Mukherjee, et al. (2018)) and showed how magnetic nanomaterial can be expoited to synthetically induce quorum sensing like behaviour in a microbial population.

In the next phase we did some work on nano-sensing. The NO-sensor by Chl A (A. Bhattacharya, Biswas, et al. (2017)) and its continuation (A. Bhattacharya, Raja, et al. (2017)) reveal some interesting aspect of biomimicry. It showed that Hb-analogues like Chl can serve as NO sensor and canalso distinguish between different forms of NO. Our sensing work also was further enriched by the pesticide sensing work (Sahoo et al. (2018)).

A parallel research direction also included effects of static magnetic field (SMF) effects in the nano-world. We employed different classes of magnetic nanomaterial for this purpose. One work was related to determination of ferritin level using SMF (Raja et al. (2014)). The cellular effects of SMF is also described in (Shaw, Raja, and Dasgupta (2014)) in which it is shown that SMF changes are more conspicious in cancerous cells as compared to cells closer to normal. The work (Bhattacharya et al. (2014)) implied SMF can bring forth changes in the chemiosmotic circuit in the phhotosynthetic metabolism. In this context what we suggested is that the nanomaterial can be an important probe for reserach in quantum biology. Lately we have been engaged with graphene–biofilm interface (S. Ray, Sen, et al. (2018)). We reported how electrical isosbestic point can characterize frequency dependent configutaional changes in nanomaterials. The most intriguing work in this direction is (Bose et al. (2020)), showing graphene defect specificity of photosynthetic microbes. The work can be regarded as a nano-cognition model of a bioform.

Comments on the future of nanotechnology

Every tour should have (and has) an end. At thid point I would like to highlight a few additional perspectives that may lead to some interesting development of nanotechnology. 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). Here is the list:

- 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 sensors.

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