Chemistry of Tomorrow Today: Nanotechnology
An Introduction to Nanotechnology through Chemistry

Everywhere in the manifest universe, (except at the heart of stars and black holes), atoms and molecules are the smallest stable units of matter. So what if we could manipulate matter on the atomic scale using atoms and molecules like Lego bricks? This was essentially the musings of Nobel Prize winning physicist Richard Feynman in 1959 when he gave a talk entitled ‘There’s Plenty of Room at the Bottom’.

In that talk he speculated about writing the entire Encyclopedia Brittanica (pre Wikipedia) on the head of a pin. He demonstrated that each letter would have to be written in an area of 32 x 32 atoms across. He mused over being able to individually move atoms, he speculated about miniaturizing electronic circuits so that were wires only 10 atoms wide, and electronic circuits a few thousand atoms across. If we could do that – he speculated - computers would not only be smaller (in those days a computer filled a room) but they could also thousands times of times more complicated and potentially could be much more capable of handling complex tasks like say face recognition! In 1959 it would have taken a computer the size of the pentagon recognize your face and we can do that today with a device as small as a smartphone (see table 1 below)!

In that talk he laid out the field that we call today Nanotechnology, and nanotechnology is the frontier of technology today. Nanotechnology lies at the frontiers of Physics, Chemistry, Biology, Engineering and Materials Science.

**Nanotechnology - What is it?**
Nanotechnology is the manipulation of matter on the scale of nanometers from 1 to 100s of nanometers (nm). A nanometer is 10 Angstroms, or one billionth of a meter ($10^{-9} \text{m}$). For a scale comparison on the molecular scale a C-C bond is 0.12 nm long while DNA has a diameter of 2 nm. The bacterium *Mycoplasma*, is around 200 nm in length. The essential functions of the cell therefore can only really be truly understood in the nanometer regime, where behavior is dominated by chemistry, molecular geometry and quantum mechanics. In fact, in this regime, quantum mechanical effects (where particles must also be considered as waves of probability) make materials behave differently from their bulk behavior, and this can be manipulated to the advantage of technology.

Succinctly we could say that nanotechnology is the engineering of functional systems at the molecular scale. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products. In a sense we could say that biology utilizes nanotechnology since it uses specialized molecules and environments to construct the
essential elements inside the cell. So we can use nature as seen from molecular biology’s perspective as an inspiration for this field of endeavor.

Nanotechnology is very diverse. It fails to fit within the auspices of a single scientific discipline, the appreciation of the subject in all of its diversity requires an appreciation of physics, chemistry, biology, as well as some of the more specialized disciplines including surface science, organic chemistry, molecular biology, semiconductor physics, microfabrication. The study and exploitation of this field requires very expensive, state-of-the-art equipment, ultra high vacuum systems as well as ultra clean environments. The field utilizes methods ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale.

The Birth of Nanotechnology
To be able to work in this regime, we have to have tools that allow us to characterize matter on the nanometer scale. Essentially nanotechnology emerged with the advent of the scanning tunneling microscope (STM), an instrument that can image surfaces on the atomic scale. This was developed at IBM in Zurich in 1981 and for the first time scientists could see the atoms that had been theorized since the time of Democritus.

With the emergence of the STM we now had a visible window into physics, chemistry and biology on the atomic scale, and the discoveries have led to the new field of nanotechnology.

Why Nanotechnology?
Why is it that today humanity is becoming so interested in nanotechnology? What are the advantages to us? First let us consider the advantages to the electronics industry. In electronics we use electrons to do work, we pass the electrons through various devices, resistors, capacitors, transistors, inductors, and all of these devices allow us to control the electrons to do useful work. For example in a microprocessor (computer chip) by passing electrons through an array of transistors we can create logic circuits that allow the electrons to perform logical tasks. The smaller each transistor is, the quicker the electrons can perform the task of interest, often, the smaller the device is the more efficient the device is. So in the electronics industry the advantage is clear, the smaller the device, the faster and more efficient the device is, and this leads to ultrafast and ultra small computing devices today. For example an iPhone today has more computing power than the Apollo spacecraft that went to the moon in the late 60s and early 70s.
Table 1: The Relentless Advance of Nanotechnology. A comparison of the on-board Apollo flight computer that put man on the moon in 1969 (very little nanotechnology) and a modern smart phone (a lot of nanotechnology) in 2014.

<table>
<thead>
<tr>
<th></th>
<th>Apollo Guidance Computer circa 1969</th>
<th>iPhone 5S</th>
<th>Nano Advantage iPhone / Apollo</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processor Speed</strong></td>
<td>0.004077 GHz</td>
<td>1.3 GHz × 2 cores</td>
<td>478 × faster</td>
</tr>
<tr>
<td><strong>Memory size</strong></td>
<td>2k</td>
<td>1,000,000k</td>
<td>50,000× more memory</td>
</tr>
<tr>
<td><strong>Mass</strong></td>
<td>40,000g</td>
<td>112g</td>
<td>357× less mass</td>
</tr>
<tr>
<td><strong>Storage</strong></td>
<td>32k</td>
<td>Up to 64,000k</td>
<td>2,000× more storage</td>
</tr>
</tbody>
</table>
| **Functions**            | Adds, subtracts, multiplies, divides| Plays music in stereo and HD video, performs math, portable color TV, makes wireless phone calls, connects to the internet, records HD video at 60 fps and audio, sound recognition (in multiple languages) access to most of human knowledge, wireless router, Detects orientation in space and position on Earth’s surface | ![Quantum Dots: What are they and why are we interested in them?](image)

Quantum Dots (QDs) are small particles that are 10–40 times the diameter of an atom. These dots are made of elements that, when combined, make semiconductors.

In a battery, ions travel between two electrodes where certain redox reactions occur. The current generated by the battery depends on the number of these reactions occurring at the electrode, and this is often limited by the time it takes ions to travel from one electrode to the other. This is what limits the rate of charging of a typical Li-ion battery in your phone or laptop. In nature however the essential distance between the ‘electrodes’ in a biological battery may be of the order of billionths of a meter so the current can be much higher. So if we can create batteries with nanotechnology these batteries will be far more efficient, and will charge faster.

In nature, chemical reactions can often be conducted at temperatures and pressures that are much lower than we can conduct them in the lab. This happens because reactions in nature are conducted in specialized nanoscale environments with catalyzing atoms that significantly increase the rate of reaction. Again nature - by designing systems that work on the nanoscale - is able to create much more efficient reaction pathways.
For dots with dimensions in the range (1-100nm) it is found that the optical properties vary with their size. This is illustrated in Figure 2, where we see fluorescence of five colloidal Quantum Dots solutions irradiated with UV light.

Generally speaking, the smaller the QD the bluer the fluorescence spectrum. By controlling the size of QD made, it is possible to make dots with very specific colors, as well as conductivities. As such QDs are finding applications in transistors, solar cells, LEDs (see Figure 3), and diode lasers. They have also investigated quantum dots as agents for medical imaging and hope to use them as qubits in quantum computing.

**Understanding Quantum Dots**
For those of you that consider yourselves chemists and have little understanding of physics there are going to be some ideas from physics that we are going to have to become familiar with. In this section a brief introduction to the essential ideas from physics are introduced

Semiconductors
Semiconductors (materials that possess a conductivity that is less than a metal but more than an insulator), along with insulators, are essentially molecular solids where the atoms are covalently bonded in extended crystalline structures.

Since in crystalline materials, there are many molecular orbitals with the same energy, they hybridize to make orbitals that extend throughout the entire crystal. These hybridized orbitals split in energy to form a continuum of energies in a small range of energy that are called bands. The band created from the Highest Occupied Molecular Orbitals is called the **valence band**, and the band created from the Lowest Unoccupied Molecular Orbitals is called the **conduction band**. In Figure 4 this concept is illustrated for ethane (ethylene) which when stacked in a cofacial configuration forms a conducting polymer.
Figure 4: Illustration of the bonding – antibonding interactions between the HOMO/LUMO levels of two ethane molecules in a co-facial configuration. Stacking two ethene HOMO orbitals you can make two linearly independent orbitals a bonding and an antibonding (the lowest two in energy in the middle), the next two in energy correspond to linear combinations of the LUMO orbitals in bonding and antibonding configurations.

On the right we see how bands are formed when a large number of stacked molecules interact, essentially one makes a continuum of energy levels, but in a semiconductor and in an insulator the LUMO related band never overlaps with the HOMO related band and the gap in energy between the highest point in energy of the HOMO band and the lowest part of the LUMO band is called the band gap.

The gap in energy between the valence and conduction bands called the band gap. A semiconductor is a solid whose valence bands do not overlap with the conduction bands, and the band gap lies in the range $3 \, \text{eV} > E_g > 0.1 \, \text{eV}$ (Conductors have no band gap while insulators have a band gaps in excess of 3 eV). So in a semiconductor at low temperature the valence band is filled and the conduction band is empty.

**Excitons**

If a photon, of sufficient energy, is absorbed by an electron in the valence band, it can be excited into the conduction band, leaving a hole where it once was. The hole and the electron are called an exciton. The exciton consists of the excited electron in the conduction band and the hole left in the valence band.

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Prior to excitation the electrons are arranged in a self-consistent low energy state. Once an electron is excited into a new state, it can appear, to the other electrons and nuclei, that an electron has left, and a new electron state created. In condensed phases like solids we simply the essential physics of this by considering the excited electron, and the 'hole' left where the electron was distributed prior to excitation. It is somewhat akin to a bubble of air in an otherwise full bottle of water. Even though holes are in fact the absence of a negatively charged particle (an electron), they can be treated theoretically as positively charged particles, whose motion gives rise to electric current.
The hole is generally much less able to move around than the electron (it is involves the concerted motion of many valence electrons so is more sluggish than one electron), so the two form a kind of pseudo hydrogen atom, and as such the exciton has H-like electron orbitals $a_0$ (average distance of the electron from the center of positive charge – see Fig. 5). However whereas there is only vacuum ($\varepsilon = 1$) within the H atom, in an exciton, the other electrons and nuclei, respond to the presence of the excited electron and the hole, electrons are polarized moving toward the hole and away from the excited electron, this effectively reduces the strength of the interaction between the electron and the hole. We account for this using the dielectric constant ($\varepsilon > 1$) of the material which effectively reduces the strength of the Coulombic attraction of the electron for the hole, making the exciton’s Bohr radius, much larger than that of H (which is a little over half an Angstrom).

$$a_0 = \frac{4\pi\varepsilon_0 \varepsilon \hbar^2}{mq^2} = \varepsilon a_0^H$$

where $\varepsilon_0$ is the permittivity of free space, $m$ is the mass of the electron and $q$ the charge of a proton. Notice that the Bohr radius of an exciton is $\varepsilon$ times the Bohr radius of Hydrogen $a_0^H$. So in the case of CdSe quantum dots the Bohr radius of the exciton is $10.2a_0^H$ or about 5Å. Since in a H atom electron density extends out beyond $5a_0$, it is prudent to assume that in bulk CdSe electron density from the exciton would extend to a radius of 25Å.
Excitons in Quantum Dots
So what happens if the radius of the quantum dot is smaller than the Bohr radius for the exciton? Basically the electron, which is significantly more stable inside the dot than outside, is confined within the dot, and the situation is analogous to a particle-in-a-box.

Particle in a 1-Dimensional Box
In the normal treatment of a particle in a box we solve the Schrödinger equation for a particle confined to an infinitely deep well of width L. Inside the well the potential $V(x) = 0$ for $0 < x < L$, and outside the well the potential is infinite $V(x) = \infty$ for $0 > x$ or $x > L$.

Solving the 1D Schrodinger equation is equivalent to solving for a free particle

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E \psi(x)$$

(2)
subject to the boundary conditions \( \psi(0) = \psi(L) = 0 \).

The solutions are

\[
\psi_n(x) = N \sin \left(\frac{n \pi x}{L}\right)
\]

\[
E_n = \frac{\hbar^2}{8mL^2} n_x^2
\]

(3)

The eigen energies \( E_n \) (\( n_x = 1, 2, 3 \ldots \)) are the possible energies of the particle. Since the particle exists within the box where it has no potential energy this energy is purely kinetic. The larger the \( n_x \) is, the larger the particle’s momentum. The energy \( E_n \) can be considered the confinement energy which gets smaller and smaller the larger \( L \) becomes. Both the electron and the hole are far more stable inside the dot than outside, the fact that the quantum dots dimensions are smaller than the exciton’s Bohr radius we can treat the electron and the hole as fully delocalized throughout the particle. Under these conditions equation (4) is valid. Notice that there is a lowest energy for the particle that is not zero. The particle in the box has a zero-point energy just like in a harmonic oscillator\(^1\). In our case, there are two particles the electron and the hole, these have effective masses that are different - to reflect the fact that the electron is a lot more mobile than the hole\(^2\). Also with the hole and the electron there is an attractive Coulomb interaction to consider, which can be done by averaging the Coulomb potential over the possible positions of the hole and the electron with the result that for a sphere of CdSe of radius \( R \)

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\(^1\) Zero point energy is central to a quantum mechanical description of phenomena, it occurs as a result of the wave-nature of matter, one can understand it also as a consequence of the Heisenberg uncertainty principle, for if there was truly a temperature at which all motion stopped (zero energy) then we would know a particle’s position exactly and matter would no longer be wave-like – which is an inherent contradiction in the true nature of phenomena – which is essentially wavelike

\(^2\) A hole is an volume of diminished electron density – like a bubble or air in water – for a hole to move requires a collective motion of all neighboring electrons, so it is more sluggish than a free electron.

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1 When the equation is solved for a sphere the radial differential equation has solutions that are spherical Bessel functions, and the imposed boundary condition is met by ensuring the energy of the wavefunction is a zero of the Bessel function.
\[
E_n = \frac{\hbar^2}{8m_e R^2} \left( n_x^2 + n_y^2 + n_z^2 \right) \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi \varepsilon_0 \varepsilon R}
\] (5)

This is the energy of the \( n \)th exciton state relative to the bottom of the conduction band. The first term is the confinement energy and the second term is called the exciton energy. Relative to the top of the valence band one has to add the energy of the band gap. This would be the excitation energy (Y. Kayanuma, Phys. Rev. B38, 9797, (1988))

\[
\Delta E_n = E_{\text{gap}} + \frac{\hbar^2}{8m_e m_h R^2} \left( n_x^2 + n_y^2 + n_z^2 \right) + \frac{\hbar^2}{8m_e m_h R^2} \left( n_x^2 + n_y^2 + n_z^2 \right) - \frac{1.8e^2}{4\pi \varepsilon_0 \varepsilon R} - \frac{e^4}{8(h\varepsilon_0^2)} \left( \frac{m_e}{m_e} + \frac{m_h}{m_h} \right)^{-1}
\]

= band gap + electron confinement energy + hole confinement energy + exciton energy (6)

Figure 7 shows the various contributions in equation (6) to the overall excitation energy. When visible and UV light is absorbed by a quantum dot, the excited state of the electron is confined to the spatial dimensions of the dot. Notice that as \( L \) gets larger \( \Delta E_n \) gets smaller. We call that a red shift. As \( L \) gets smaller \( \Delta E_n \) gets bigger and we call that a blue shift.

To give you a sense of the predicted spectrum for the exciton we now connect equation (6) to the observed optical properties of the dot.

**Connecting \( \Delta E_n \) to the Optical Properties of the QD**

In the early days of quantum mechanics when Niels Bohr pondered the line spectra exhibited by H atoms, concluded that emission lines came from transitions between quantum states. The energy of the emitted photon \( h\nu \) plus the energy of the final quantum state \( E_f \) is equal to the energy of the emitting quantum state \( E_i \). Line is related to the energy difference of the two quantum states

\[
E_i = E_f + h\nu \quad \text{for emission of a photon}
\] (7)

\[
E_i = E_f - h\nu \quad \text{for absorption of a photon}
\]

This relation is a mathematical assertion of energy conservation, i.e. the total energy of the system before the transition and the total energy after the transition are the same. We can rearrange the above equation to arrive at expressions for either the frequency or wavelength of the photon.
\[ \Delta E_i = E_i - E_f = h\nu = \frac{hc}{\lambda} \quad : \text{for emission of a photon} \ (E_i < E_f) \]

(8)

\[ \Delta E_f = E_f - E_i = h\nu = \frac{hc}{\lambda} \quad : \text{for absorption of a photon} \ (E_i > E_f) \]

Here \( h \) is Planck’s constant, \( c \) is the speed of light, \( \nu \) is the frequency of the photon and \( \lambda \) is the wavelength of the photon.

So let us connect this with the problem of the absorption of light by the QD. If we wish to calculate the longest wavelength of absorption, \( \lambda_{\text{threshold}} \), then we consider a transition from the highest energy hole state to the lowest energy electron state which occurs when \( (n_x^2 + n_y^2 + n_z^2) = 1 \). Using equations (8) and (6) we can easily obtain an expression for \( \lambda_{\text{threshold}} \) with the result that

(9)

This leads to an approximately quadratic dependence of the wavelength of dot size. Referring back to Figure 2, we see a series of test tubes containing dispersed quantum dots of different sizes. As we move from left to right we have increasingly large quantum dots see how in emission frequencies are higher as the dots get smaller.

To calculate the absorption spectrum we have to calculate the wavelengths for all accessible transitions. Because we are treating the dot as spherical, it is most natural to write the eigenstates as products of a radial wave function and the spherical harmonics, like is done with the hydrogen atom. The eigenstate energies instead of depending on \( n_x, n_y \) and \( n_z \) are replaced with \( \beta_{nl} \) which represents the \( l \)th zero of \( n \)th spherical Bessel function

(10)

Solutions to the radial equation for the QD are Spherical Bessel functions and the boundary condition that the wavefunction vanish at the edge of the dot leads to the eigen-energies depending on the zeros of the spherical Bessel function (see http://www.morris.umn.edu/academic/math/Ma4901/Sp2012/Near/Schliep-near.pdf)
The spectrum is made up from transitions to all possible exciton states. In figure 8 we show pictorially what is calculated in equation (10). Below in figure 9 we compare the results of this relatively simple theory with the cold hard fact of reality. This relatively simple theory in which the many-body problem is reduced to an exciton in a spherical well, captures the essence of what is seen optically. This is what makes this a great system to introduce into undergraduate labs.

Figure 9 Left: the measured Absorption spectrum for a CdSe dot with an estimated radius of 4.5 nm, along with a fit of this spectrum to a sum of 8 Gaussians. Right: The simulated spectrum calculated from equation (10) assuming a spherical dot of 4.5 nm