

## Nature and Nanotechnology: Use of Contact Angle for the Calculation of Surface Energy

### Abstract

Very often we say the human body is much more complex than even a pioneer researcher can think of that. Many of our milestone discoveries were first originated from observation of the natural phenomena. For example, if there was no apple fell in front of Sir Isaac Newton, it might take another 50 years to discover the concept of gravitation. With the discovery of more and more sophisticated tools one by one it was realised that nature has been resembled with many sophisticated systems developed so far. In this article one of such natural effect has been studied in depth. This effect called "Lotus effect", which has changed the concept of hydrophobicity and coating industry. In this consequence the concept of the surface energy which happens to be one of the key factors related to concept of nanoscience and technology has been discussed in detail.

Here it has been shown that how a simple contact angle data can be used to determine the surface energy of any flat surface. Not only that this project also has shown that the surface energy has two components and that can be calculated separately. This polar and dispersive part of the surface energy has its different parts in determining the surface properties and thus should be taken care of separately.

In this consequence the basic concepts of nanoscience and technology and how a nanomaterial becomes novel in comparison with the bulk form has also been revisited. The article will enable one to have mastery over the structure property relation of any material in planer form.

**Keywords:** Nanoscience; Material; Surface energy; Contact angle; Aromatic compounds.

### Introduction

Nanotechnology is an interdisciplinary science in which material scientists, mechanical and electronic engineers, biologists, chemists & physicists work together to extend the nanoscale boundaries. Nano is a Greek word, which means micro or small. Every particle, whose size is 100 nm or smaller is considered a nanoparticle.

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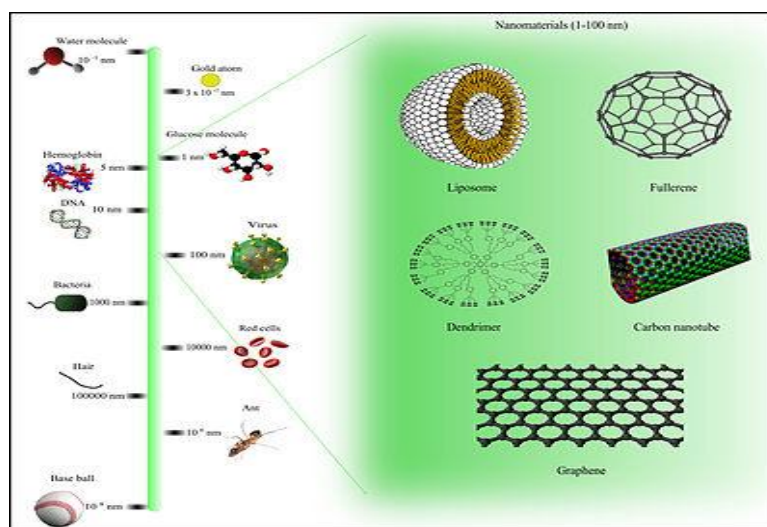
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**Received on 12.10.2022**

**Accepted on 23.12.2022**

Nanoscience is the study of the fundamental principles of molecule and structure with at least one dimension roughly between 1 & 100nm.

In 1959, Richard Feynman, an American physicist at the California Institute of Technology said during one of his lectures “There’s plenty of room at the bottom”. These lines later give the foundation of nanotechnology that’s why the father of nanotechnology is known as Richard Feynman. To indicate the object is how much small then we compare it with human hair. We know that the average diameter of human hair is about fifty thousand nanometres. In comparison the smallest features that one commonly etched on a commercial microchip is less than 100nm. The smallest things the human eye can resolve are 10,000 nm across. **Fig.1** shows the size dependence of different object in universe.



**Fig.1:** Size dependence of different object in universe.

The topic of Nanoscience deals with small things and the use of nanotechnology in various places. The chemical and physical characteristics of nanoparticle change due to the extremely microscopic shape. For example, the cubes of sugar are less sweet than the castor sugar because the surface area of the castor sugar is larger surface area than the cubes of sugar. With the help of the nanotechnology, we have ability to see the control of atoms and molecules. The materials which we use in nanotechnology are called nanomaterial. Reason for different properties in nanomaterials than their bulk materials are as under:

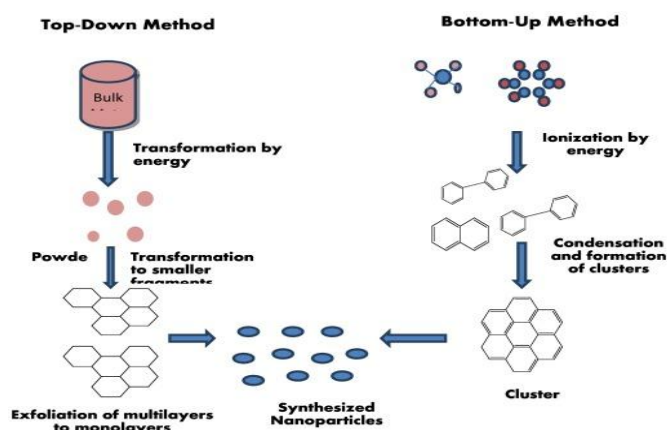
**Higher ratio between surface and volume:** The very high surface to volume ratio gives rise to higher numbers of dangling bond. This higher numbers of dangling bonds in turn develops very high chemical activities within the nanomaterial making them different from its bulk form.

**Quantum effect:** From the very basic particle in a box, problem one faces in quantum mechanics, it is seen that the energy gap between the two successive energy levels or rather any two energy levels depends inversely on the square of the box dimension thus enhancing the optical gap of the material. This optical gap governs the optical properties of the nanomaterial.

**Density of states:** Density of state i.e the numbers of states per unit energy interval per unit volume is highly dimension dependent and thus shows marked difference for 0, 1, 2 and 3 dimensional structure of same material. There are two techniques to synthesize nanomaterials as given below:

**Top-Down Approach:** It is a physical process. In this approach, a large-scale object is progressively decrease in dimension. We take a bulk material which is broken into fragments and then to nanoscale particles. It consists of ultra-fine micro machining of material using lithography, epitaxy and etching. This method required too much time and also costly. There are some top-down methods to synthesize nanomaterials and these are all physical methods: Ball Milling, Physical Vapour Deposition, Lithography, Thermal Evaporation.

**Bottom-Up Approach:** It is chemical process. In this process atom come together to form the clusters and clusters material come together to form nanoscale particles. In this approach different materials and devices are synthesized from molecular components on their own which do not require any external agent to assemble them. This method is relatively cheaper than the top-down approach. There are some bottom-up approaches to synthesize nanomaterials, these are chemical methods: Sol- Gel, Chemical Vapour Deposition, Co-Precipitation, Micro Emulsions, Hydrothermal, Sonochemical, and Microwave. **Fig.2** shows both the approaches schematically.



**Fig.2:** Schematics of top-down and bottom up approaches

There are many evidences by which it is observed that nanotechnology is used from ancient time.

**Table 1** summarizes some important point from the history of nanotechnology according to their timeline: In today's world the use of nanotechnology in the field of medicine, nano fertilizer, nano weed, etc. to save our main crop in agriculture areas. With the help of nanotechnology today's electronic item is smaller than earlier electronic items. Nanomaterials are those with particle sizes measurable in nanometres. Most common examples are activated carbon, aerogel, graphene. In nature, colours of insects are often not pigmenting at all, but very tiny structures which scatter light selectively to give an effect of colour. Titanium dioxide nanoparticles have found to have peculiar property of killing germs when walls are painted with it and thus can be very useful in hospitals. There are many examples of nanomaterials, and new ones are being discovered, which will bring

about a revolution in engineering, medicines and many walks of life. For comparison, a full stop, or a period, in print could be about 1 million nanometres.

**Table 1:** Some milestones in the history of nanotechnology according to their timeline

<b>2000 years ago</b>	Nano crystal of Sulphide used by Greeks and romans to dye hair.
<b>1000 years ago</b>	Gold nanoparticles of various sizes used to fabricate many colours in stained glass windows.
<b>1959</b>	Physicists Richard Feynman gives sentence “There’s plenty of room at the bottom.”
<b>1974</b>	The word “Nanotechnology” first time used by the professor Norio Taniguchi.
<b>1981</b>	IBM develops Scanning Tunnelling Microscope.
<b>1986</b>	The first book on nanotechnology named “Engines of creation” which was written by the K.E. Drexler.
<b>1991</b>	S. Ijima discovered Carbon nanotubes.
<b>1999</b>	R. Freitas written first book on nano medicine named “Nano Medicine”.
<b>2000</b>	National Nanotechnology Initiative was launched by US

Most objects we come across in daily life have particle size bigger than these unimaginable material dimensions, and are bulk materials. We are making extensive use of nanomaterials today- cosmetics, sunscreen lotions, super-capacitors, some new batteries, robotics, and now they are invading computers, and many more things.

### Classification of Nanomaterials

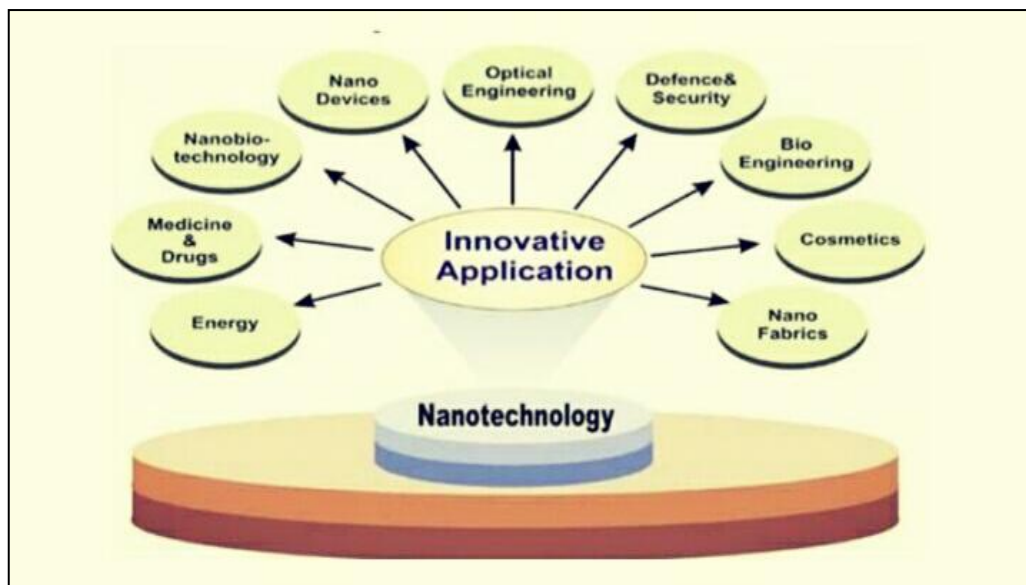
Nanomaterials can be classified dimension wise into following categories shown in **Table 2**

**Table 2:** Classification of Nanomaterials

<b>Classification</b>	<b>Examples</b>
<b>Zero dimension &lt; 10nm</b>	Particles, quantum dots, hollow Spheres, etc.
<b>One dimension &lt; 100nm in any two dimension</b>	Nanorods, nanowires, nanotubes etc.
<b>Two dimensions &lt; 100nm in any one dimension</b>	Flakes, sheets etc.

## Applications of Nanotechnology

Nanotechnology has various applications in the area of science and technology as shown in Fig.3.



**Fig.3:** Applications of Nano technology

Few specific fields are as under:

### a) Energy:

Nanotechnology has brought a revolution in the energy sector which is one of the most serious concerns in the present day. For instance nanomaterial based illumination technology can reduced the power significantly, while using LED compared to the ordinary bulb. The later can use only 5% of the electricity fed to it. In another example if we talk about present solar driven cars the best one can covert the 40 % of the solar energy whereas for ordinary commercial car, it cannot exceeds 15 – 20 %. Use of Nanomaterials with proper band gap can help conversion of the energy in much higher extend.

### b) Defence and Security:

Application of nanotechnology has enough prospects to redesign the present defence and security system. This is possible by miniaturizing the deadly weapons or developing unmanned vehicles for combat. Also there are plenty of scopes to develop different sensors, display, satellite component and others all of which may prove their importance in different part of defence and security system.

### c) Information & Communication:

The conventional silicon based electronics is now getting bit obsoleted due to its very high cost and other related issues. The nanomaterial based development of transistor, capacitors and other components are so far the hope for the new era of electronics. Also researchers are now being able to develop molecular

transistors which show the hope in this sector in the coming years.

#### **d) Medicine:**

The effectiveness of nanomaterial in the field of medicine and drug delivery came to the mind of the researchers from the fact that the size of nanomaterials is almost similar to the most of the biological molecules. It thus readily suggests that that nanomaterial based technology can effectively be used in-vivo and in-vitro medical applications. There is a remarkable success of nanomaterial based treatment that offers targeted drug delivery to a particular position of the body, say where cancer cell evolves. The other application is development of contrast agent, or different analytical tools, tools that needed for physical therapy and many others.

### **Literature Review**

There are several reports of developing hydrophobic surfaces that may be based on carbon nanotubes, graphene or other. Here the literature review regarding the development on silicon nanowire (SiNWs) based on hydrophobic surfaces have been given.

Superhydrophobic surfaces were prepared by fabricating SiNWs to enhance the surface roughness and then the chemical nature of the surface was modified with a self-assembled octadecyltrichlorosilane monolayer to lower the surface energy. The dynamic contact angle data revealed that the water droplet on those surfaces of nanowires could exhibit a transition from the Wenzel state to the Cassie state by simply controlling the etching time and the contact angle hysteresis was less than  $10^\circ$  [Shao Mingwang et.al..2009]. The contact angles depend on the surface roughness and the structure possesses stronger mechanical strength and could reach the Cassie state because of the shorter etching time [Shao Mingwang et.al..2009, Wei-Fan Kuan and Li-Jen Chen.2009]. Fluorine carbon coatings were used to convert the surfaces from superhydrophilic to superhydrophobic to maintain the Cassie-Baxter state stability by reducing the surface free energy to a quarter compared with intrinsic silicon. The morphology of the SiNWs demonstrated that their critical height exceeds several hundred nanometers for superhydrophilicity, and surpasses a micrometer for superhydrophobicity.

As stated before the superhydrophobic and superhydrophilic surfaces are differentiated in terms of the contact angle, water droplet makes with the solid surface at equilibrium. If the angle is over  $150^\circ$  It is called superhydrophobic, if it is less than  $90^\circ$  the surface is super-hydrophilic [Wei-Fan Kuan and Li-Jen Chen.2009, Kim Beom Seok , Shin Sangwoo, Shin Seung Jae, Kim Kyung Min, Cho Hyung Hee . 2011]. The superhydrophobic surface has further advantages of having self-cleaning properties which allows to clear dirt particle during rolling of a water droplet through the surface at a very small rolling angle without wetting the surface. On the contrary sometimes we want water to wet the surface i.e. the surface to be hydrophilic. This simply can be done by giving the hydrophobic surfaces to the UV light. This surface containing nanoholes can simultaneously repel oil and water or for other surfaces it can partially allow water over oil thus can be used as partial oil water separator [Togonal AS,He Lining,Cabarrocas PR, Rusli.2014]. These have other applications like water harvest, anti-biofouling, paint, coating, cosmetic industry and other [Togonal AS,He Lining,Cabarrocas PR, Rusli.2014].

SiNW has been found to be very easy to synthesize with very high uniformity and high yield. The modulation of its hydrophobic behaviour is also very easy and thus it is a very promising candidate for developing hydrophobic electronic device [ Wei-Fan Kuan and Li-Jen Chen.2009, Kim Beom Seok , Shin Sangwoo, Shin Seung Jae, Kim Kyung Min, Cho Hyung Hee.2011, Togonal AS, He Lining, Cabarrocas PR, Rusli.2014].

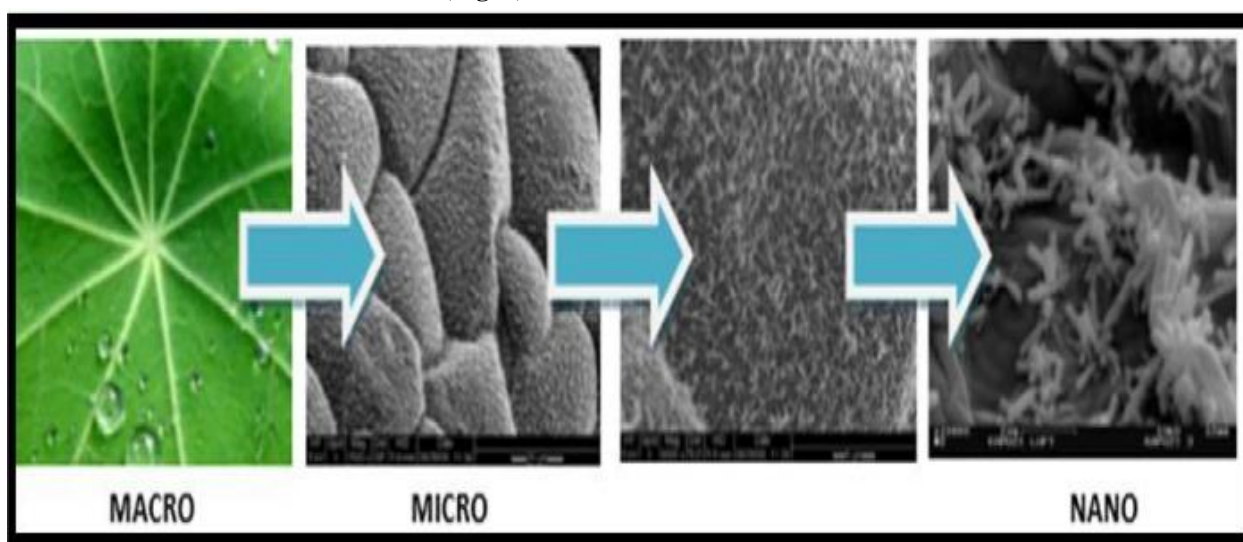
There are reports of synthesizing SiNWs by chemical vapour deposition, which during growth process, attain a critical roughness value, give water contact angle nearly  $0^\circ$ , thus exhibiting superhydrophilicity. These super hydrophilic properties may be converted again to hydrophobicity by a vacuum treatment with the exposure to it by polymer like polydimethylsiloxane (PDMS) material. In turn, this material again be converted to hydrophilic by simple nitrogen treatment at an elevated temperature as high as 873 K [Tae-il Kim, Dongha Tahk, and Hong H. Lee. 2009]. Thus, in this way, a constant swinging between hydro-phobicity and hydro-philicity may be done by simple and cheap method.

There are reports of multi-structured pyramid/nanowire network on silicon substrate by a complex NaOH and silver catalysed etching process. A superhydrophobic property with contact angle as high as  $162^\circ$  and very small rolling angle (less than  $28^\circ$ ) has been achieved for SiNW by octadecyltrichlorosilane (ODTS) induced modification. These kinds of surfaces have found their applications in silicon based solar cell and in many other applications as mentioned before [Cheng Yung Kuo and Chie Gauz.2010].

## Discussion

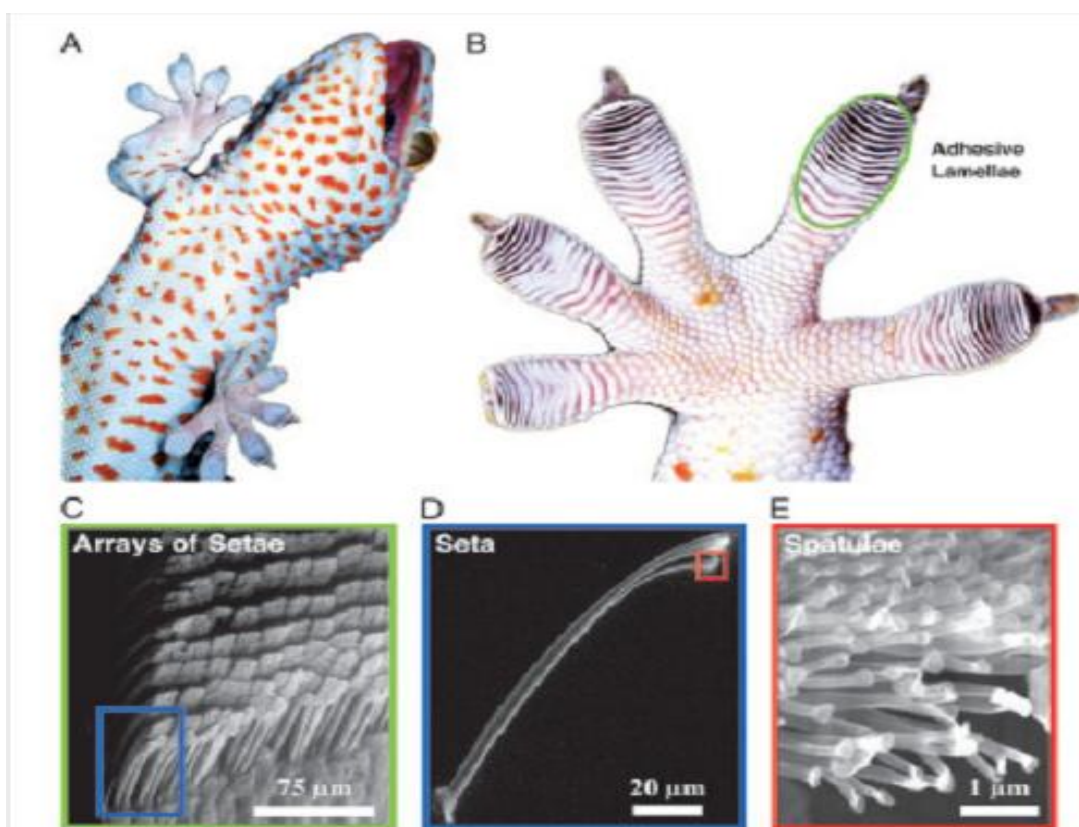
### Nature and Nanotechnology

Although nanoscience is often comprehended as a science of the future, in true sense it is the basis for all systems that are present in our living and mineral world. Natural nanomaterials proffer a great starting point to bring nanoscience among masses. Images from microscopes are great resources to understand basic structure of nanomaterial. Starting from a macro object (such as a plant leaf) and showing by zooming in with subsequent factors reveal finer and finer structures, (Fig.4).



**Fig.4:** Close-up views at progressive magnification of a Nasturtium leaf revealing the presence of surface nanocrystals.

Another example of natural “Nano” effect is seen in Gecko who can walk on almost any substrate along any direction vertically upward or with a certain angle. It can hang upside down on a smooth surface like cleaned glass. Walking on a dirty or wet surface is also not a problem for them. They in principle do not have any suction like features and or do not produce any sticky substance. Here it is to be noted that Gecko has a series of structures called scensors containing a numerous projections called setae. Each setae has dimension of  $5\ \mu\text{m}$  in diameter and  $100\ \mu\text{m}$  in length and consisting of numbers of tiny projections called spatulae of dimension  $200\ \text{nm}$ . This helps the surface area of the Gecko’s feet increased enormously. Also the spatulae are very flexible and thus they are capable of being mold into molecular structure into any substrate increasing the adhesion which is completely Van der Waals force. Also as the surface energy of such structures are such that the particles, dirt or mud will prefer to stay on the substrate rather than to stick on the feet. Thus the feet of the Gecko remained clean. The structure can clearly be seen in the below figure (Fig.5)



**Fig.5:** (A-E) The macroscopic and nanoscopic structures of Gecko’s feet with different magnifications

### What distinguishes nanomaterial from bulk?

It is to be noted that though the micro-form of the material shows almost the same properties as that of the bulk material, its nano-form shows significantly different properties and this is mainly because of the following reasons:



1. In nano-dimension the numbers of atoms at the surface increases significantly
2. It has a surface area much higher compared to its bulk form
3. It shows confinement effect and thus very different optical properties.
4. It has different density of state for 0, 1, 2, 3 dimensional material and thus fascinating electrical properties

The advantages of using nano-materials firstly involve the miniaturization of the system. In this present era when we all want entire world within our arm. This supports the Moore's law speculating numbers of transistor gets increased exponentially obviously forcing the dimension of the electronic component to be reduced.

The second advantages or rather the second characteristics of nanomaterial is the enhanced surface area and thus many more numbers of dangling bonds present in the surfaces exposed to the environment. This enhanced dangling bonds are basically chemically unstable and are always in a need of interaction with other material in order to make the bond and thus to get the minimum energy configuration. This helps nanomaterial to be exceptionally chemically active and performance in any surface induced properties like catalysis, adsorption etc is exceptional. As mentioned before, result of the changes that occur in particles with reduced particle size, nanomaterials can have extremely high biological and chemical reactivity. For example, catalytically active nanomaterials enhance either chemical or biochemical reactions by tens of thousands, and even a million times. This attribute explains, even 1 g of nanomaterial can be more effective than 1 ton of a similar but macro substance.

Another aspect we must be taken account is that the free surface is a place of accumulation (sink) of crystallographic defects. At small particles sizes, the surface concentration of such defects increases considerably. It was calculated classically and showed that the largest changes of proportions between facets, edges, corners, and micro defects at the surface occur between 1 and 5 nm. As a result, strong lattice distortion and even a change of lattice type can take place on the surface layer. In fact, due to accumulation of structural defects and chemical impurities on the surface, we can observe purification of the bulk area of the nanoparticles.

An important specific characteristic of nanomaterial properties (we mean here polycrystalline materials with grain size less than 40 nm) is an increase of the role of interfaces with decrease of the size of grains or crystallites in nanomaterials. Experimental research has shown that the state of grain boundaries has a non-equilibrium character, conditioned by the presence of the high concentration of grain boundary defects. This non-equilibrium is characterized by extra energy of the grain boundaries and by the presence of long-range elastic stress. At the same time, the grains have ordered crystallographic structure, while the grain boundary defects act as a source of elastic strains. Non-equilibrium of the grain boundaries initiates the occurrence of the lattice distortion, the change of interatomic distances, and the appearance of sufficient displacement of atoms, right up to loss of an ordered state. Another important factor peculiar to nanoparticles is their tendency to aggregation. The possibility of migration (diffusion) of either atoms or groups of atoms along the surface and the boundaries, as well as the presence of attractive forces between them, often leads to processes of self-organization into various cluster structures. This effect has already been used for creation of ordered nanostructures in optics and electronics.

One more important aspect of nanomaterial properties is connected with the fact that, during transport processes (diffusion, electro- and thermal conductivity, etc.), there are certain effective lengths of free path of a carrier of

this transport ( $L_e$ ), such as phonon and electron mean free paths, the Debye length, and the exciton diffusion length for certain polymers. While proceeding to sizes smaller than  $L_e$ , transport speed starts to depend on both the size and the shape of the nanomaterial; generally, the transport speed increases sharply.

The principal characteristics of nanomaterials are conditioned not only by their small the size, but also by the appearance of new quantum mechanical effects in a dominating role at the interface (Esaki 1991; Serena and Garcia 1997). Those quantum size effects occur at a critical size, which is proportionate with the so-called correlative radius of one or another physical phenomena, for example, with the length of the free path of electrons or photons, the length of coherence in a superconductor, sizes of magnetic domains, and so on. As a rule, quantum size effects appear in materials with crystallite sizes in the nano range  $D < 10$  nm. As a result, in nanomaterials with characteristic size, one can expect the appearance of effects which cannot be observed in bulk materials.

## Surface Energy

The surface energy ( $\sigma$ ), is one of the main parameter that characterize a surface and its activity. It is mainly related to the numbers of dangling bonds or uncompensated bonds. It is easy to understand that when a material goes from bulk to nano more numbers of surfaces get exposed to the environment and thus due to the inherent tendency of any natural system to be in minimum energy state they try to interact with environment and make bonds. Thus in other word its chemical activities get very high. Surface energy is also defined as energy associated with the energy required breaking a bond.

Intermolecular bond or bond strengths in the middle of a liquid with molecules cause surface tension. If the water comes into contact with another substance, there is an attractive force between them. The coupling forces between the water and the second one is effective on the coupling of the forces acting on the fluid. Liquids with low correlation to bonds and a strong adhesion to the other materials will tend to lay out over the material. Liquid with a strong, cohesive bonds, and weak adhesive forces, get ready to create a droplet in contact with other materials.  $\sigma$  Influences the surface properties and the associated interaction, such as adsorption, wetting, adhesion etc.

## Wetting

The property of a liquid to keep in touch with a solid surface arising from the interaction between molecules of both solid and liquids at their actual points of contact. Degree of wetting is measured by the energy balance between the grip and the bonding force. The bonding force between the liquid and the solid causes the liquid to drop to a higher degree.

The cohesive force within the liquid causes a rise in elevation and avoids contact with the surface.

To check the wet condition, take a drop of water on a solid specimen. When the surface strength of a specimen differs to the addition of a drop, the specimen is known as a wetting. The distribution variable can be used to measure this statistically:

$$S = Y_s - Y_l - Y_{s,l} \quad (1)$$

where  $S$  is the distribution variable ,

$Y_s$  is the Eof the specimen,

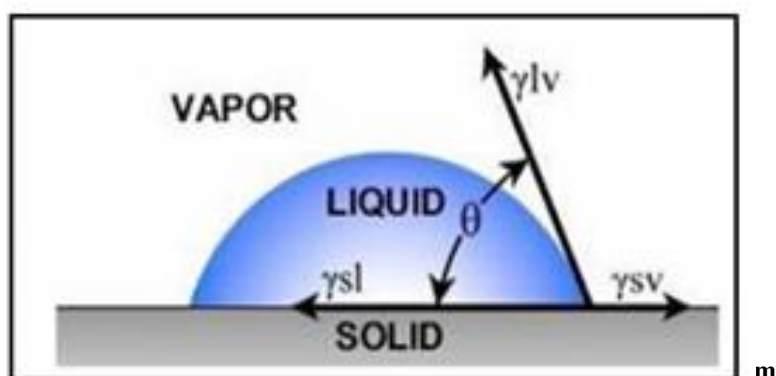
$\gamma_1$  is the E of the water, and

If,  $S < 0$  the specimen gets partly wet by the liquid and if  $S > 0$  specimen gets completely wet.

### Contact angle:





It can be explained as the angle formed at the joint of the liquid / solid contact and the liquid / air contact.

It can also be defined as the angle b/w the face of the solid sample, and the tangent of the egg-shaped droplet and droplets edge. As shown in **Fig.6**



A high value of  $\theta$  depicts a small energy of the solid, and a small amount of wetting. A small value of  $\theta$  indicates a high energy of solids and for high-and sometimes the full extent of the wetting. Several of the factors influencing the contact angle are harshness, functional group present on the surface, contamination, porosity and surface energy. Another method of measuring the liquid surface wetting element is to measure  $\theta$  of the liquid drop on the surface of the object. Water wet areas where  $\theta$  is less than 90 degrees. For an input to generate,  $\theta$  must be as low as possible. In fact, the  $\theta$  of most liquids is very close to zero degrees. In liquid penetration tests, there are commonly three visible combinations, a solid-gas contact, a liquid-gas contact, and a solid-liquid contact. In order for the liquid to set more than a certain fraction, two conditions should be met. First, the surface strength of the solid-gas contact should be larger than the total strength of the liquid gas and the solid liquid interface. Second, the surface power of the solid- gas contact must surpass the surface power of the solid-liquid contact. The wetting factor also plays a key role in its capability to fill the gap. Penetrant materials are pulled in surface breaking defects by action of capillary. The capillary force that guides a penetrant into a crack is a function of the complexity of the liquid-gas interface, the angle of contact, and element opening size( **Table 3**).

**Table 3: Values of contact angle and associated inference**

Contact angle	Degree of wetting	Strength of		Pictorial Representation
		Solid/liquid interaction	Liquid/liquid interaction	
$\theta = 0^\circ$	Perfect wetting	strong	weak	
$0 < \theta < 90^\circ$	high wettability	strong	Strong	
		weak	weak	
$90^\circ \leq \theta < 180^\circ$	low wettability	weak	Strong	
$\theta = 180^\circ$	Perfectly non-wetting	weak	Strong	

### Surfaces with high energy and low energy

Solid surfaces are categorized into high-energy solid-and low-energy types. Solid materials, such as metal, glass, are well-known as a "hard solids" as for the chemical bonds that connect them to each other, such as covalent, ionic, or metallic) are very strong. Thus, the distribution of these structures, it requires a large amount of energy, and that is the reason why they are called "high-energy". Nearly all of the molecular liquids are designed to be a complete wetting with high-energy surfaces.

Next is weak molecular crystals (e.g., ammonia, hydrocarbons, etc.) what are the molecules are connected to each other, mainly as a result of physical forces (like van der Waals, and hydrogen bonds). Because of this, the bodies are connected to one another by weak forces, very little energy is needed to split them, and so they are called the "low-energy". Depending on the nature of the fluid has been selected, low- energy surfaces can be assumed to be either completely wet or partially wet.

### Hydrophobicity, Hydrophilicity and Lotus Effect

Hydrophobicity ("it's a fear of water"), is a physical property of a substance which appears to have been derived from the weight of the water. A polar molecule or part of a molecule is a molecule that is able to communicate with, or dissolve in water and other polar substances. Hydrophobic particles have the ability to repel water, and, therefore, prefer other neutral molecules and non-polar solvents. Superhydrophobic surfaces with a  $\theta$  greater than  $150^\circ$  c, which indicates that there has been almost no connection between the drop and the surfaces of the earth. It is also sometimes referred to as the "Lotus-effect"

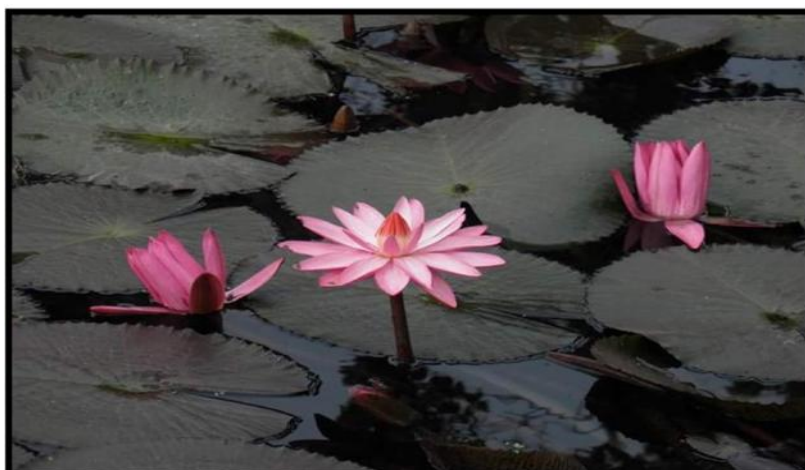
Because of the amorphous carbon films have been, it is easy to film it on various substrates, that is why, when you are in control of their hydrophobic characteristics, they will be useful to create water-and stain-resistant surfaces.

On the other hand hydrophilicity stands for loving water and thus in such surface water gets attracted and show low contact angle. Hydrophilic compounds take the water from the air. The sugar and salt, are absorbent, and can be used to remove water from the foods. This is thermodynamically favourable and is soluble in water as well as in other polar solvents. Soap, which has a hydrophilic head and a hydrophobic tail, which allows it to disintegrate in both water and oil is also another example.

A hydrophilic molecule or part of a molecule is a common charge and is able to combine hydrogen, allowing it to disintegrate more easily in water rather than oil or other hydrophobic solvent. Polar molecules and weak molecules are also referred to hydrophilic and Hydrophobic molecules, respectively. Some polar substances do not disintegrate. This type of compound is called colloid. Hydrophilic membrane filters are used in some industries to filter various beverages. These hydrophilic filters are used in the medical, industrial, and chemical fields to filter out bacteria, viruses, proteins, particles, drugs, and other pollutants.

### **The Lotus-effect**

The lotus effect (shown in **Fig.7**) tends to properties of self-cleaning that are a consequence of very high water repellency (superhydrophobicity), as shown on lotus leaf. The dirt builds up on the drop of water due to the microscopic -and nanoscopic architecture on the surface, so the sticking of the droplets in the plane was brought down. Superhydrophobicity and self -leaning features are also discovered in other plants, such as tropeolus, (West Indian cherry), prickly pear (opuntia), and on certain insects wings. In 1997, the self-cleaning properties of superhydrophobic (microstructural) surfaces have been studied by Barthlott , that is, for the first time explained their self-cleaning and superhydrophobic properties, such as the "lotus effect" [ Barthlott, W. and Neinhuis, C., 1997].



**Fig.7:** Lotus effect

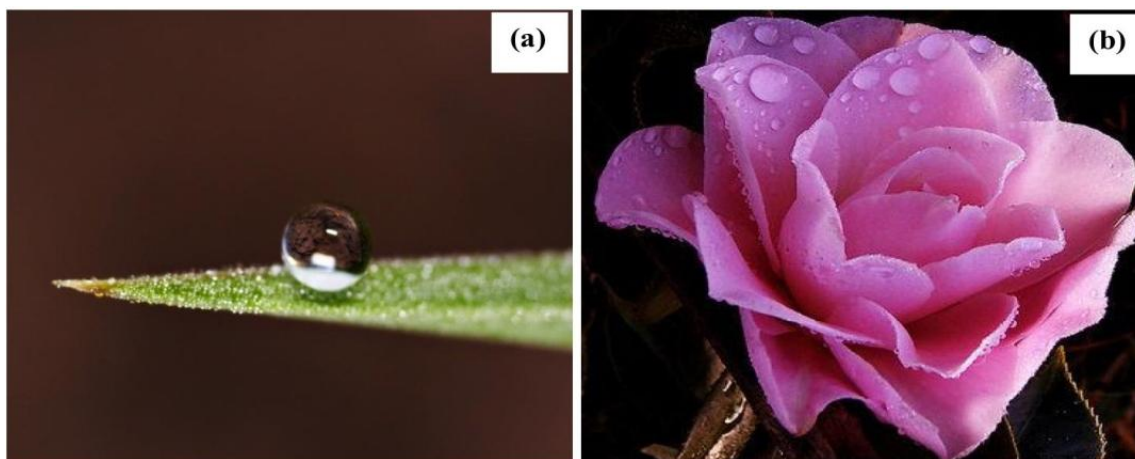
The natural hydrophobicity of the plain area be increased by adding textures with a variety of hardness scale lengths. The red roses makes use of it by considering a hierarchical structure of microstructure and

nano-structures on each petal) to ensure enough rigidity for the super-hydrophobicity. In particular, every group has a group of micropapillaries on the surface, and each of these, on its part, offers a lot of nanofolds.

The phrase "petal effect" to explain the fact that the drops of water on the face of the rose and have a circular shape, but that will not fall out, even turned down. Water droplets retain its spherical shape nature due to the superhydrophobicity of the petals of a flower (the contact angle was about  $152.4^\circ$  c), but do not fall off, due to the fact that some of the deeper subsurface is characterized by a high adhesion force of water.

The differentiation of the "petal effect" with the "lotus effect", there are some significant differences between them. The lotus petal has an uneven, rough surface, and a low hysteresis of the  $\theta$ , which means that a drop of water does not wet the micro-structure of the space between the rods. This means air can remain in space to the interior of the grains, which makes the structure of the surface is made up of air and solid. As a result, the adhesion force between the liquid and a solid plane is very low, so the water can easily fall (that is, the self- clean phenomenon).

However, the microstructure and nano-structures of the petals are, the higher in the scale than that of the lotus leaves, by which a liquid layer go all the way to the texture. The fluid can be given in larger slots, but can't get into the lower spikes. This is known as the Cassie wetting mode. Because the liquid can wet the major groove, and the adhesion force b/w the water and the solids are very strong. This is why a drop of water does not run down the hill, even as the petals of a flower, put at an angle or turned upside down. However, this effect is likely to be destroyed if the drop has a large capacity, such as the balance between the weight and the surface tension is exceeded (**Fig.8**).



**Fig.8: Petal Effect**

The hydrophobicity of a surface can be determined on basis of the  $\theta$ . The greater the  $\theta$  values the greater the hydrophobicity of the surfaces. Surfaces with a  $\theta$  of  $< 90^\circ$  and are called hydrophilic, while those with  $\theta > 90^\circ$ , hydrophobic called. Some of the plants show  $\theta$  up to  $160^\circ$  c, and are called superhydrophobic, which means that it is only 2 to 3% of the droplet- contact. Plants have a double structure of the surface, such as the lotus, can be extended to the  $\theta$  of up to  $170^\circ$ . All of this tends to a self-clean effect. This effect is more important to plants, such as defense from bacteria, such as algae, fungi and animals, such as butterflies, dragonflies, and many other insects that are not in a position to have to clean all of the parts of the body.

## The application of the hydrophilic and hydrophobic surfaces/ particles

If the self-cleaning feature, it was observed that the nature of this discovery opens up the possibility of the use of this result in the man-made surfaces. Few nanotechnology scientists have made, treatments, coatings, films, paints, tiles other surface which can remain dry and clean to make their own, to duplicate a scientific approach to the self-clean features of plants such as the lotus plant. This can also be accomplished with the help of a fluoro-chemical or silicone treatments on a clean surface or in the compositions of micro-particles. Superhydrophobic coatings with Teflon micro-particles have been used in the field of medical diagnostic slides for more than 30 years of age. This result is achieved by the use of a mixture of polyethylene glycol, glucose, and sucrose, in a combination with a hydrophobic compound. Additional applications, such as self-cleaning mirrors mounted on German motor control unit sensors and sprayers have been produced to create self-cleaning films in different parts. Superhydrophobic coverage installed in microwave radiation antennas can notably reduce rainwater runoff and snow and ice formation. products that are easy to clean in advertising are usually mistaken for hydrophobic or superhydrophobic self-cleaning products. Well-designed superhydrophobic properties also deliver the promise of microfluidic lab on a chip devices can notably improve further bioanalysis. Also superhydrophobic or hydrophobic features are used for dew harvesting, or for liquid mixing in the borehole for irrigation. **Fig.9** explains the phenomena.



**Fig.9: Application of hydrophobicity and hysteresis effect**

### Relationship between energy and $\theta$

The surface free energy is the amount of increase of free energy when the area increases, per unit of A. The surface free energy of the samples, it is usually accomplished by calculating the  $\theta$  to liquid and the sample surface. The relationship between the E of the samples (Y) the  $\theta$  usually, it is described by the equation of Youngs equation

$$Y_{s-g} = Y_{s-l} + Y_{l-g} \cos\theta \quad (2)$$

Surface energy can be sub characterized due to the different connections that root them, like surface energy because of van-der-Waals forces, hydrogen bonding, polar interactions, acid/base interactions, etc. The total surface energy both for liquid and the solid is suppose conventionally to simply be the addition of the dispersive and polar components. The equation explaining the further division of surface energy into the distribution of disruptive connections and polar interactions would be

$$\sigma_S = \sigma_{Sd} + \sigma_{Sp} \quad (3)$$

$$\sigma_L = \sigma_{Ld} + \sigma_{Lp} \quad (4)$$

### Cassie and Wenzel State

If a surface is the same in every shape or character like shape, size, weight, height distribution, then it is called a uniform surface otherwise it is known as a non-uniform surface. The uniform wetting is when the liquid fills the barriers of local hardness grooves. On opposite side, a non-uniform wetting is when the surface is covered with 2 varieties of patches. A prime case of such a compound environment is air and solid dots patches. Such areas have a different effect on the  $\theta$  of a liquid. Cassie - Baxter and Wenzel gave two key models that try to define wetting.

The Wenzel model explains the uniform wetting reign, as shown in **Fig.10 (b)**, and is explained with the below equation for the  $\theta$  on a harsh area

$$\cos\theta^* = r \cos\theta \quad (5)$$

Here  $\theta^*$  is the plain contact angle that is analogous to the steady balanced condition (i.e. min. free energy phase for the system),  $r$  is the harshness ratio and  $\theta$  is the contact angle

The harshness ratio,  $r$ , is a result of how surface roughness affects uniform surface. The roughness ratio is explained as the ratio of real area of the solid surface to the apparent area.

The Cassie equilibrium states can be explained by the equation as:

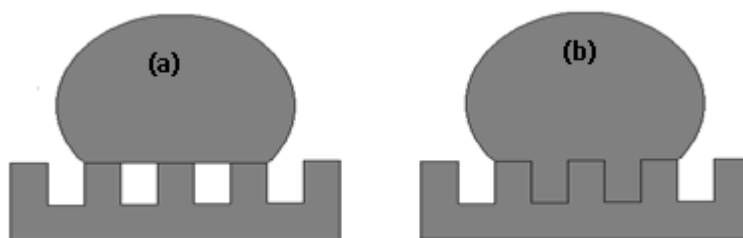
$$\cos(\theta) = \Phi \cos(\theta_1) + (1-\Phi) \cos(\theta_2) \quad (6)$$

where  $\theta$  is the contact angle,

$\theta_1$  is the contact angle of liquid on a plane area of the specimen in examination

$\theta_2$  180 is the contact angle of liquid on air

$\Phi$  is the solid fraction of A at the top of the asperities  $fp = (1 - \Phi)$  would show the surface porosity on a hydrophobic surface, liquid has a very wide angle, and it can also very simply fall, that is to say, a very, very small hysteresis. This is simply because a drop of water sits on top of an uneven surface, and the water, can't go down into the grooves as shown in **Fig.10 (a)**,.



**Fig.10:** (a) Cassie state and (b) Wenzel state

### Calculation of Surface Energy:

From the young's equation we have



$$S_{lv} \cos \theta = S_{sv} - S_{sl} - \pi_e \quad (7)$$

where,  $\theta$  contact angle between solid and liquid

$S_{lv}$  and  $S_{sv}$  are liquid and solids free energies which act against their saturated vapour pressure.

$S_{sl}$  is the interface energy between solid and liquid

$\pi_e$  is balanced pressure of adsorbed vapor of the liquid on the solid.

Surface energy can be solved into polar (SP) and disruptive component (Sd). The widespread part of the discrepancy between solids and liquids is given by the compound law of Good - Girifalco - Fowkes

$$S_{dsl} = S_{dsv} + S_{dlv} - 2 [S_{dsv} * S_{dlv}]^{1/2} \quad (8)$$

Rearranging, the Young's equation takes the final form as:

$$[1 + \cos \theta] = 2/S_{lv} [ \{S_{dsv} * S_{dlv}\}^{1/2} + \{S_{psv} * S_{plv}\}^{1/2} ] \quad (9)$$

If polar and dispersive component of surface vapour and liquid vapour components of two liquids of known polarity are known then the polar and dispersive part of solid-liquid interface can be known.

## Conclusion

The hydrophobicity phenomenon given by nature to different biological species, such as the lotus flower and the butterflies wings, has generated a great deal of interest in education and industry. Super-hydrophobicity has now been recognized as one of the top 50 technologies. Research over the past decade has shown that it is dealing with serious problems such as those related to rust and biological degradation, as evidenced by the effective use of hydrophobic facilities in engineering systems such as aircraft, automobiles, pipelines and marine vessels. In the current article I have discussed the basic concepts of low dimensional materials mainly low dimensional materials and have shown how they exhibit novel properties. I have also shown some ready resemble of natural effect with the concept of nano and how they affect our daily life.

I have reviewed an easy concept to determine the surface energies of any flat surfaces and its components. In this consequence different equilibrium state of any liquid droplets on a surface came into the discussion.

After studying a practical data set it is seen that that it is the polar part of the surface energy that probably determine the hydrophobicity of any surface provided the chemical composition, roughness, nanostructures and other parameters remains same.

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