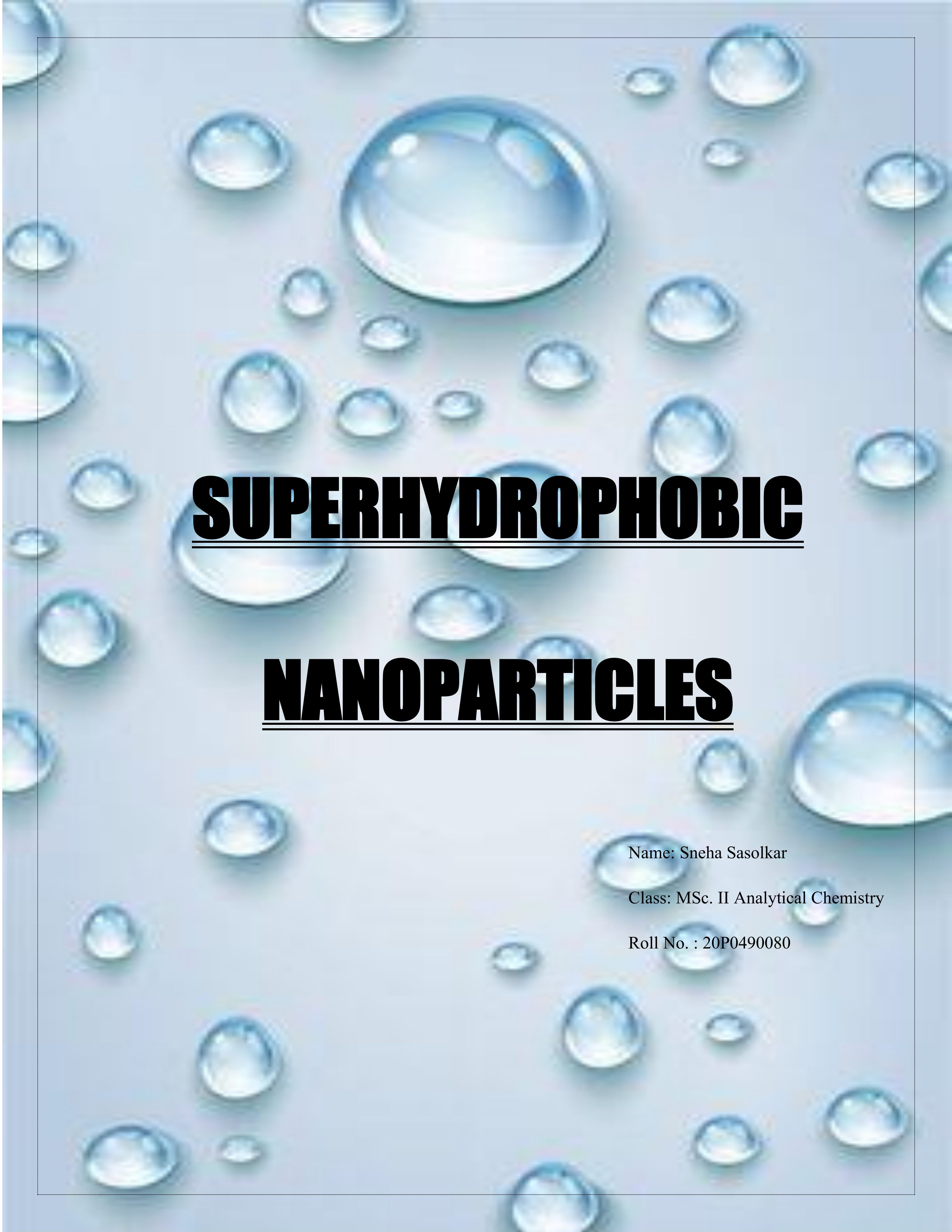

SUPERHYDROPHOBIC

NANOPARTICLES

Name: Sneha Sasolkar

Class: MSc. II Analytical Chemistry

Roll No. : 20P0490080

SUPERHYDROPHOBIC NANOPARTICLES

A DISSERTATION REPORT

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Ms. Sneha V. Sasolkar

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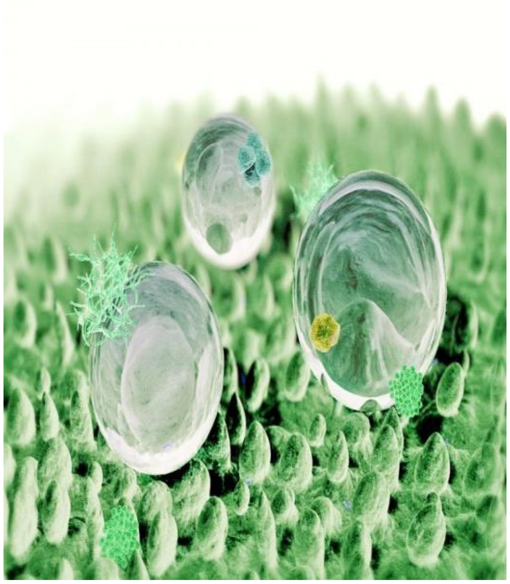
SUPERHYDROPHOBIC NANOPARTICLES

Introduction

Nanoparticles or Ultrafine particles exist in different forms. They are tiny particles having size ranging from 1-100 nm . This review specifically provides an overview of synthesis , properties and applications of superhydrophobic nanoparticles.

Superhydrophobic nanoparticles , combination of nanotechnology and superhydrophobic surfaces, have received immense attention recently. Inspired by the *lotus leaf*, the discovery of nano and micro-hierarchical structures has brought great changes in the superhydrophobic nanocoating field. The peculiar properties of superhydrophobic nanocoatings, such as self cleaning, anti bacterial, anti icing, corrosion resistance and so on are the most widely known.[1] This review briefly discusses the principle behind its phenomenon and some of the challenges faced in this field.



Theory of wettability

From a scientific standpoint, water resistance of a coating can be categorized into two different types: Hydrophobicity and Hydrophilicity. Hydrophobicity can be measured by a Tensiometer. This device measures the "contact angle" of the surface. If the contact angle is under 90°, it means liquid wets the surface (hydrophilic with zero equating to complete wetting). If it exceeds 90°, surface is non wetting with that liquid (hydrophobic). Meanwhile, if its exceeds 150°, it is considered superhydrophobic.[2]

In the absence of a liquid, a solid surface is characterized with intrinsic surface free energy. Once any liquid contacts with the solid, this excess energy drives the liquid molecules to bind to the surface (i.e. adhesion forces). However, the intermolecular forces acting within the liquid tend to compactly hold all the liquid molecules and coerce the liquid droplet to minimize it's energy and acquire a spherical shape. The competition between adhesion and cohesion forces determines whether the liquid will or will not wet the solid and the of its wettability.[3]

Thomas Young in 1805, gave a classical equation of wettability. The balance of interfacial forces at the contact line is γ_{sv}, γ_{sl} and $\gamma_{lv}\cos\theta$ as shown in the fig.1 below which shows a liquid drop is spread on a flat surface and forms a contact angle with a solid surface. At equilibrium, the contact line is static and these forces vanish. The simplified equation is given as:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad \text{........(1)}$$

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \qquad \text{.........(2)}$$

where γ_{sv}, γ_{sl} and γ_{lv} are the interfacial energy of solid-vapour, solid-liquid and liquid-vapour respectively and the contact angle was called intrinsic contact angle. However, a solid surface is often rough and uneven in reality and the real contact angle on a rough surface is different from Young's wettability model.[4]

Wenzel supported that liquid was completedly filled into the rough structure. Here, surface areas of the solid-liquid and solid-vapour interfaces associated with the advance of the contact line are increased by a roughness factor of *r* . As the contact line advances along the surface by a small distance *dx,* this leads to a change in the total surface free energy.

$$\Delta E = (\gamma_{sl} - \gamma_{sv})rdx + \gamma_{lv}\cos\theta dx \qquad \text{…………(3)}$$

At equilibrium, $\Delta E = 0$ thus,

$$\text{Cos}\theta^* = \frac{r(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \qquad \text{…………..(4)}$$

above equation is substituted with Young’s equation to obtain wenzel equation, which is given as :

$$\cos\theta^* = r\cos\theta \qquad \text{………..(5)}$$

where r is the roughness factor (denoted as the ratio of the actual liquid/solid contact area to the nominal contact area) and θ^* is the contact angle.

When the $\theta < 90°$, increasing the roughness factor r can further lower the apparent contact angle (θ^*). When $\theta > 90°$, increasing the roughness can further increase the apparent contact angle (θ^*) towards 180°. Hence Wenzel equation points out that constructing a rough surface is an effective approach to realize the non wettability of a surface with high contact angle.

An alternative contact between liquid and solid is that the liquid no longer retains complete contact with the solid at all points below the droplet. Cassie and Baxter proposed that droplet makes contact with a solid surface by composite liquid/solid and liquid/vapour contacts as shown in the figure below.[5] The relationship between the apparent contact angle and rough structures was analysed by thermodynamic equilibrium states of vapour- liquid-solid and is given as :

$$\Delta E = (\gamma_{sl} - \gamma_{sv})_1 f_1 dx + (\gamma_{sl} - \gamma_{sv})_2 f_2 dx + \gamma_{lv}\cos\theta dx \qquad \text{……….(6)}$$

Combining with the above equation 2, at equilibrium the above equation can be simplified to the following :

$$\text{Cos}\theta^* = f_1\cos\theta_1 + f_2\cos\theta_2 \qquad \text{………(7)}$$

Where θ_1 and θ_2 represent the apparent contact angle of a liquid on solid and vapour (air) respectively and f_1 and f_2 represent the fraction of the contact area of the liquid/solid and liquid/vapour ($f_1 + f_2 = 1$) respectively. Since the liquid was totally in contact with vapour $\theta_2 = 180°$. Thus, above equation is rewritten as :

$$\cos\theta^* = f_1\cos\theta_1 + f_1 - 1$$

This is the famed *Cassie-Baxter equation*. A smaller f_1 among the hydrophobic surfaces means a low interfacial fraction at the contact line. In the Cassie- Baxter state, the liquid bridges between the surface features and no longer penetrates between the species separating them. It resulted in a high apparent contact angle and lower sliding angle of liquid on a rough hydrophobic surface.[6]

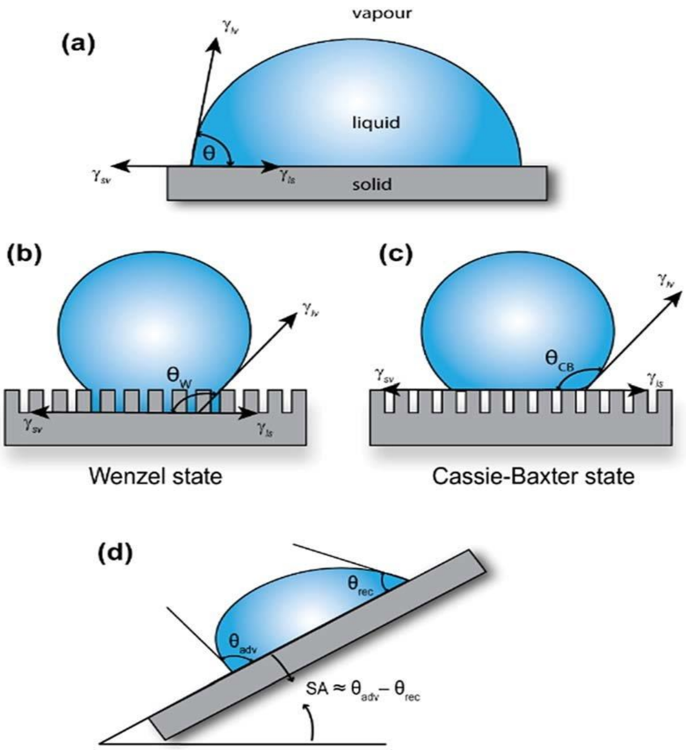


Fig.1. Schematic illustration of a) Young's model b) Wenzel's model c) Cassie-Baxter's model d) contact angle hysteris (also called as sliding angle). [2]

Current Research

Research on superhydrophobic surfaces has made huge progress, most preparation methods are complicated requiring special conditions or expensive equipments. For superhydrophobic surfaces, high transparency is a requirement in many applications. But, the transparency of coatings becomes worse when surface roughness increases [since light scattering occurs when light strikes the rough surface causing translucence]. Although many research studies were successful in obtaining the desired hydrophobicity and transparency, the robustness and wear resistance of the film were not good because of the flexibility of the polymer[6].

Xiao Gong and Shuang He developed a one step spray coating method for preparing superhydrophobic coatings on different substrates. They mixed hydrophilic SiO_2 and hydrophobic SiO_2 nanoparticles in a certain ratio and blended with PDMS [polydimethylsiloxane], to obtain a hierarchical micro- nanostructured surface where PDMS is used as both, a low surface energy modifier and an adhesive. The prepared coatings were subjected to various tests to study its durability. These included tape peeling test, UV resistance test and corrosion resistance test. Alongwith this, self cleaning ability of the coating was studied using black carbon powder. Sand and water drop abrasion impact was also measured. This research concluded that when the amount of PDMS was 0.5 and 1.0 g, and the ratio of hydrophilic and hydrophobic SiO_2 was 4:2, the contact angle was greater than 150° and sliding angle was lower than 5°. Thus showing superhydrophobicity.[6]

Mechanical durability is the key issue for application of superhydrophobic coatings and its necessary to create a rough structure on the surface. However, roughness can be easily destroyed during wear process. Based on the above research they were successful in making superhydrophobic nanocoating with water contact angle of 156.4° and a sliding angle of lower than 5° which were highly durable and transparent.

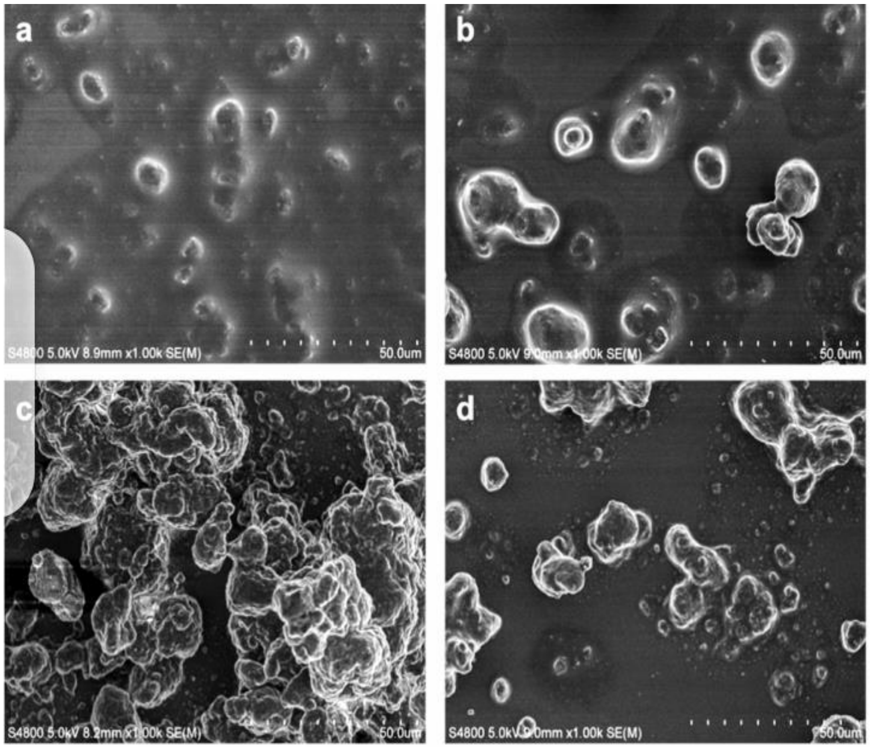


Fig.2. SEM images of hydrophilic SiO_2 / hydrophobic SiO_2 = [a] 1:5, [b] 2:4, [c] 4:2, [d] 5:1[7]

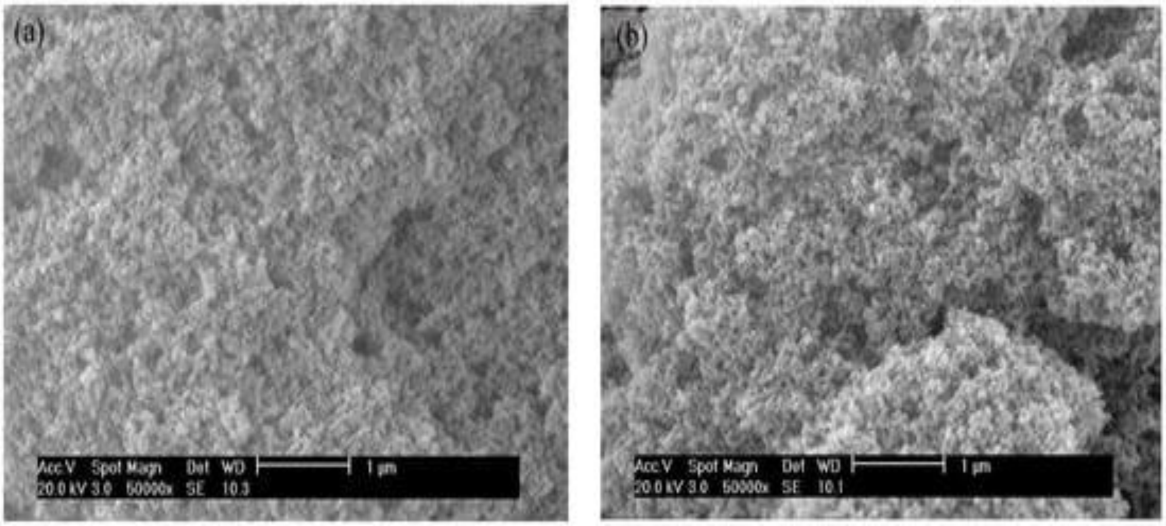
Nikhil Agarwal and group at the IIT Delhi have managed to develop a superhydrophobic nanocoating material with a static water contact angle >160° by modifying ZnO nanoparticles with room stable palmitic acid [PA]. ZnO nanoparticlesof size ~24nm were prepared by hydrothermal method with grafting of PA on ZnO surface. Superhydrophobic nature of PA-ZnO is due to palmitic acid on ZnO which was confirmed bu conducting the water contact angle measurement of PA-ZnO samples after heating at different temperatures[8]. Surface morphology and roughness were observed as a function of temperature and it was observed that superhydrophobic nature of PAN-ZnO nanoparticles reduces with heating at higher temperature and surface becomes hydrophilic [~230°C]. The decrease in water contact angle was due to thermal decomposition of PA from ZnO surface.

For aircraft, its necessary to have de-icing or anti-icing systems. However, current de-icing systems release chemicals into the environment. Therefore an environment friendly and cost effective solution is to use a durable icephobic coating on the aircraft surface. In an article proposed by Junpeng Liu, silica nanomaterials were deposited by spin coating method to form nano structured rough surface to trap small scale air pockets. Self assembled monolayers of flouroalkyl silane

1H,1H,2H,2H-perflourooctyltriethoxysilane [POTS] were grafted onto the silica nanoparticle surface by chemical vapour deposition method to obtain low surface energy. The hydrophobicity, icephobocity and durability of the coatings were investigated.[9][1]

For fabrication, the samples were heated at 550°C to fuse the silica nanoparticles together and silica coatings of 30µm thickness were obtained. The samples were grafted using POTS to reduce surface energy. Ice adhesion test was performed using a centrifuge method with a glaze ice block at -5°C. The water droplet icing tests were performed by monitoring the water droplets on 3 spots of coated samples and uncoated samples on a cold plate setting at -10°C. By observing the video of the water droplets, icing duration was obtained.[10] Durability was evaluated by erosion rig test under pressurized pneumatic water impinging with gas pressure. Pressurised water droplets were sprayed onto the coated samples for various durations and contact angle was measured on 3 spots before and after erosion test.

Uniformity and morphology of the coatings were characterized by SEM techniques.[9]



Above image shows distinguishable particles and porous structures which are similar before and after treatment. There was no obvious change in the morphology of silica particles during surface treatment as the POTS are very thin self-assembled monolayers. Confirmation of POTS successfully being deposited on silica nanoparticles was done by EDS.

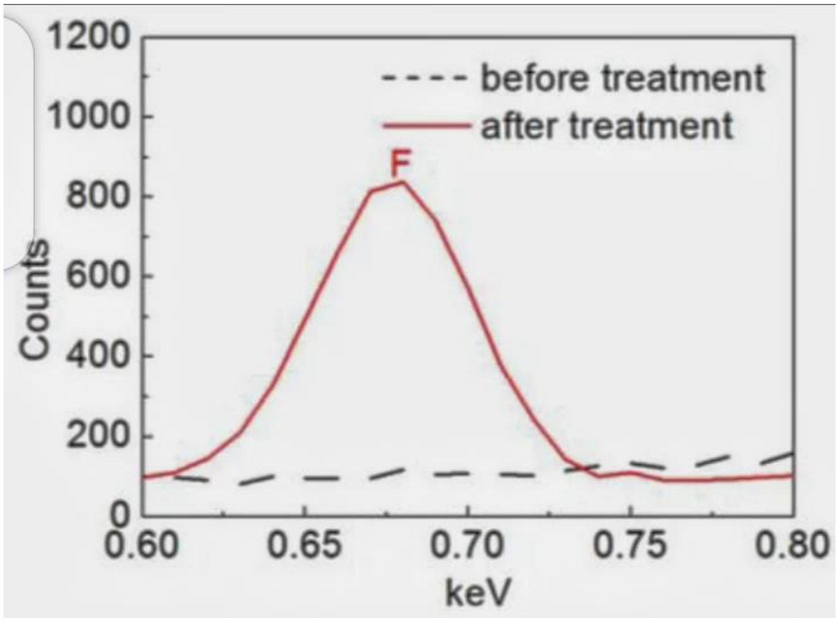


Fig.3. Energy dispersive X-ray spectroscopy [EDS] results for silica nanoparticles with POTS treatment and without treatment.[9]

Above figure depicts a clear F [fluorine] peak after POTS treatment, while there’s no F peak before treatment .For further confirmation, results of XPS were also recorded.

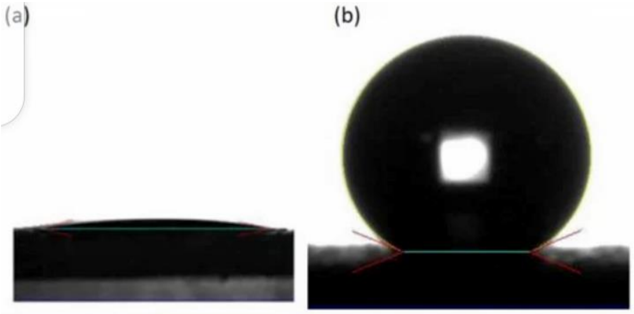


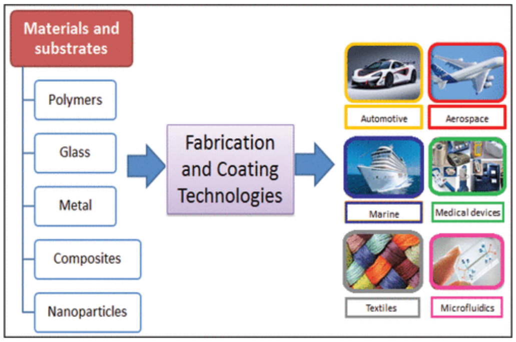
Fig.4. Water contact angle of water droplets on silica nanoparticles-based coating [a] without and [b] with POTS treatment.[9]

Above figure depicts water contact angle before and after POTS treatment. The water contact angle changes from 13°± 0.9° without treatment to 163°± 7.4°. The fractions of solid surface and air in contact with water droplets [f_1] was obtained as 5.3% which contributes to icing delay due to limited thermal exchange between solid-liquid surface. Ice adhesion is also an important parameter for icephobicity. With low adhesion strength, ice can be easily removed. The ice adhesion strength test showed that shear stress between the treated surface/ ice block were much lower than those between bare surfaced/ ice block.[9][2]

Wear resistance and transparency are important issues for the applications of superhydrophobic coatings. G.Luo et al. developed a good wear resistance PU/SiO_2 [polyurethane/silica] composite superhydrophobic coating with double step sol-gel process. The PU and SiO_2 occurs crosslinking reaction forming composite superhydrophobic coating. This coating was characterized by environmental scanning electron microscope and the results showed that PU/SiO_2 composite coating had excellent wear resistance. This was concluded by measuring the water contact angle after the abrasion resistance test. The water contact angle still remained 138.7°. The PU/SiO_2 coating also showed high transparency in visible light. The largest water contact angle of PU/SiO_2 superhydrophobic coating could reach 162.1°.

Applications

Varoius materials like metals, glass, polymers, composites and micro and nanoparticles are fabricated and chemically treated to generate products for application in various industrial and research based scenarios.



Some of the basic applications are as follows :

- Applications in the field of energy storage devices

Surface treated nanostructured silicon electrodes having superhydrophobic properties have been developed which can effectively separate active electrode components from liquid electrolyte, thus creating a very high interfacial capacitance that acts as ultrahigh storage centres. Poonam et al. discussed the use of graphene oxide extracted from coffee waste for the development of superhydrophobic electrodes for rechargable batteries.[1]

- Coatings for protection of electronic devices in humid environment

Superhydrophobic coatings are deposited using a photochemical process on a sensor surface to reduce surface conduction and improve the sensor signalling by reduction in the drift in the signal due to water absorption in the humid environment.[1][11]

- Superhydrophobic microvalves

For any microfluidic biochip, main concern is the protein fouling with the microchip and protein folding near the device surface. Lu et al. developed a fish bone shaped valve instead of the usual capillary valves to make use of the superhydrophobic property inorder to reduce the binding of proteins to the surface and lower the characteristics imposed by protein folding.

- Superhydrophobic textiles and for oil-water separation

Cotton based textiles are modified using sol-gel deposition of the silica nanoparticles, modified using fluorinated silanes as coupling agents or deposition of gold nanoclusters by chemisorptions or deposition of carbon nanotubes modified using polybutylacrylate. Such modifications improve the non wetting properties of cotton and also maintains its warmth and softness. Superhydrophobic fibres are used for the separation of various oils from water.[12][13]

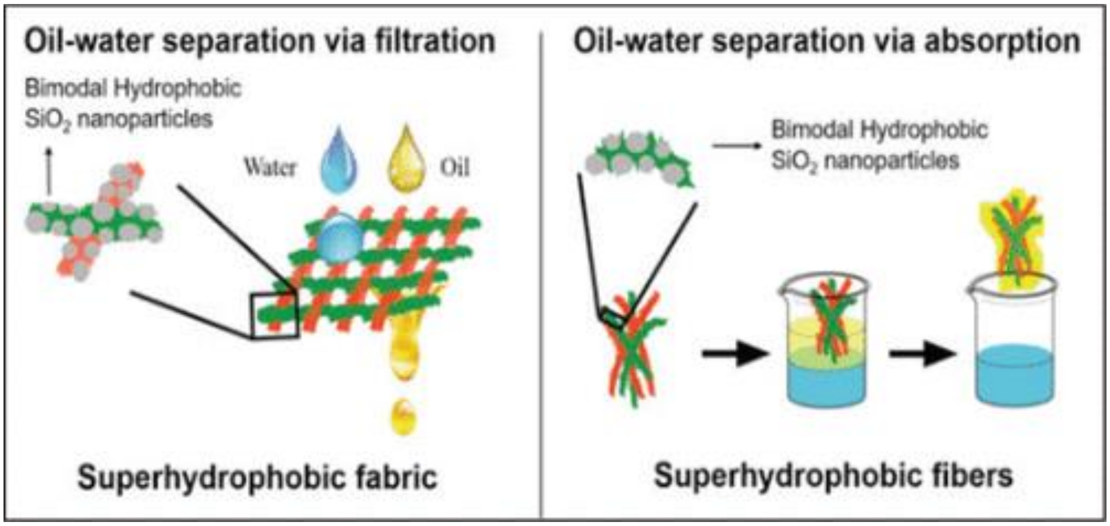


Fig.5. Oil-water separation using superhydrophobic fibres and fabrics.[1]

❖ Transparent and anti- reflective superhydrophobic coating

Such coatings are used as protective coatings for solar cells, car windshields, mirrors, window glasses etc. These coatings have shown a reduction in the effective refractive index and substantial improvement in the performance of the solar cells.[14][1]

❖ Antibiofouling

Fields belonging to marine, medical and industrial areas are prevalent of biofouling. Most microorganisms settle on the surfaces with maximum contact area. If the area of contact is low, there are only fewer points of attachment on the surface. Nanotexturing with chemical coatings and other surface treatment processes decrease the adhesion of microbes on the surface, thereby reducing their biofouling effects.[1]

- Anti icing and Desalination

Superhydrophobic coatings prevent formation of ice as shown in the figure below.

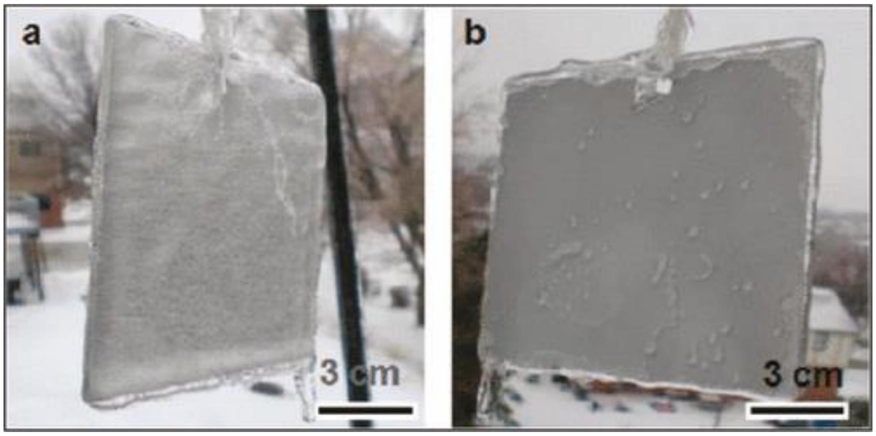


Fig.6. Testing of the anti icing properties of a superhydrophobic surface in the 'freezing rain' [a] untreated side of aluminium plate [b] aluminium plate coated with the superhydrophobic composites, after the rain.[1]

It is seen that the aluminium plate gets iced while the composite coated side of the plate remains ice free. Converting seawater into freshwater and removal of salts are usually carried out using reverse osmosis desalination process which is complicated and expensive. Evaporative desalination is a simple method but abandoned due to the corrosive effects of salts left as residue. Superhydrophobic coatings reduce or prevent any salt residue or salt-water based corrosion of surfaces which can be used for evaporative desalination.[1][15]

- Self cleaning glass and Self cleaning textiles

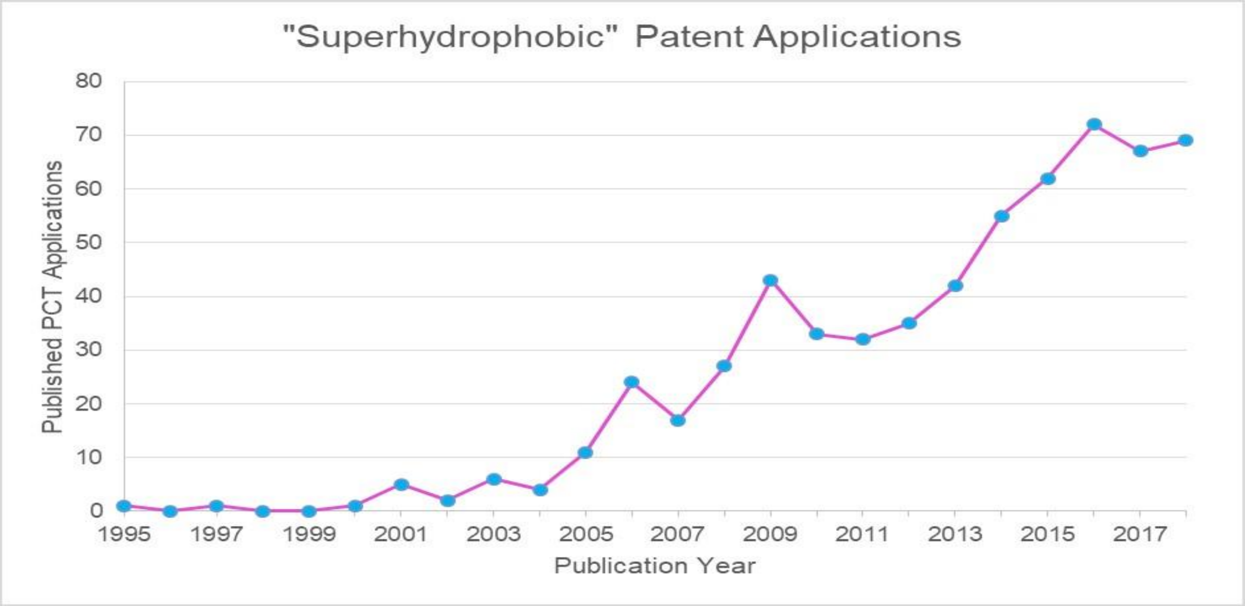
Such glass requires less of regular washing, scrubbing and polishing with chemical agents. Such glass can be prepared by techniques like plasma etching, chemical vapour deposition or based on photocatalysis[16] of organic impurities deposited on the glass surface by a catalyst layer, mostly TiO_2. The catalyst is activated by UV light and oxidizes the impurities on the surface. Another technique utilizes layer by layer technique to deposit silica nanoparticles of differing sizes on a glass substrate to obtain necessary degree of roughness that makes the surface superhydrophobic.[17]

- Other applications

Superhydrophobic paints are available commercially in several European markets. These paints are highly water and dirt repellent, UV stable with natural biocides. Superhydrophobic coatings are useful to monuments made up of marble and sandstones since, these coatings can prevent the damage done by acid rain.[18][19]

Global market

Global superhydrophobic coatings market is estimated to witness a CAGR of 34% during forecast of 2016-2024. Some of the important participants in the global market of superhydrophobic coatings are Beijing Neatrition Tech. Co Ltd., Tianhui Waterproof Mat Co Ltd., Drywired, Cytonix, Surfactis Technologies, Ultra Tech International Inc., Sherwin-Williams Company and Nippon Paints.[6][20]



Currently patent publications show that innovators are filling an increasing number of patent applications related to superhydrophobic technologies. The graph above shows the number of international patent applications published from 1995-2018. We can see a significant increase as every year passes[20].

Scientists at Rice University, University of Swansea and University of Bristol have developed a superhydrophobic nanomaterial which is inexpensive and non toxic. The hydrocarbon based material is a green replacement for costly, toxic fluorocarbons used for superhydrophobic materials. Aluminium oxide nanoparticles were modified with carboxylic acids that have highly branched hydrocarbon chains which induces roughness.

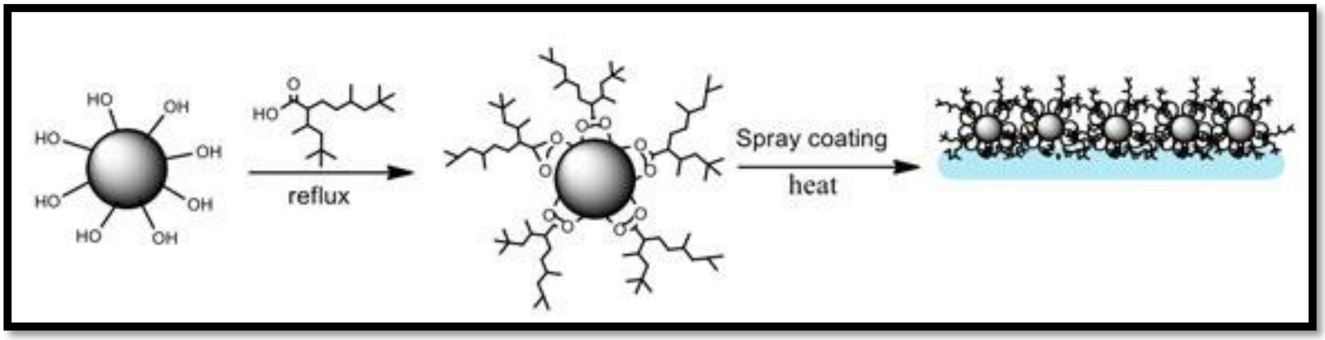


Fig.7. The spiky chains are the first line of defence against water making the surface rough.

Conclusion

In this literature review, basic definition of superhydrophobic nanomaterials and the theory behind superhydrophobicity is discussed. Also, recent advancements to modify these nanomaterials inorder to increase its durability, anti-icing properties and contact angle were seen. Since the superhydrophobic materials have novel properties like anti-adhesion, self cleaning, anti-corrosion, they have vast applications which are discussed in this review. Also the influence of superhydrophobic coatings on the global market was seen in the last section. Althogh, vast research has been done in this field, still efforts are being made to synthesize superhydrophobic coatings of high durability and less cost. Many of the superhydrophobic coatings are fluorine based which pose a major environmental issue. This needs a replacement with a more “greener” and non toxic coating material. Researchers also face challenges to sought the best fabrication method which is simple and versatile and can be carried out at various temperatures and environmental conditions.

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