Inspired by the so-called “lotus effect” discovered in 1997, unusual water repellent surfaces have received immense interest in both fundamental research and realistic applications over the past decade. Naturally, water repellent plant leaves, such as Brassica oleracea, Eryngium ebracteatum, Nelumbo nucifera (lotus) and Colocasia esculenta, are covered with a layer of epicuticular waxes. These leaves exhibit a double-structured roughness, where submicrometric wax crystals cover a larger micrometric structure. Contact between such a surfaces and a water droplet generates repulsive forces that are sufficient to allow the water droplet to form a spherical shape and therefore to roll off the surface. Among various factors, surface energy and surface roughness are the dominant factors for the wettability. The surface energy affects the liquid-solid interface by influencing the attractive forces between the liquid and solid at the molecular scale. Surface morphology alteration at the micro-and/or nanoscale can allow for an air layer to be maintained in the space between the protrusions during liquid contact. Many scientists have made impressive efforts for the fabrication and understanding of superhydrophobic surfaces. Several technological approaches to altering the wetting-to-dewetting transition have been explored. An ideal superhydrophobic surface should exhibit not only high contact angle but also low sliding angle. Technologies related to water repellent coatings are important for suppressing chemical reactions and bonding formations between water and solid surfaces. Special attention has been focused on superhydrophobic surfaces as a result of a variety of practical applications, such as antibiofouling paints for boats, antisticking of snow (or ice) for antennas, self-cleaning of windshields, anti-rusting, and reduction of friction resistance and so forth.

Sol–gel technology makes it possible to produce silicate materials with properties that cannot be achieved by other techniques and to improve the properties of conventional materials. The sol-gel method is a novel procedure among solution reactions which is based on the preparation of macromolecular
network through the typical hydrolysis of metal alkoxide groups followed by the condensation of the silanols. The sol-gel method was applied to the fabrication of superhydrophobic surfaces by several groups. To obtain hydrophobic sol-gel coatings, usually, hydrophobic additives are mixed to a sol. The hydrophobic silica films are generally produced by two methods, co-precursor method and surface derivatization method.

As the synthesis of the hydrophobic silica films involves colloidal particle formation and condensation of these particles to form three-dimensional porous network, Chapter 1 describes some physico-chemical aspects of colloids. Also, this chapter includes fundamentals about forces between the colloidal particles and charge on the colloidal particles, shape of the colloidal particles, etc. Molecular kinetic properties of the colloidal particles and fundamentals regarding surface tension and surface energy have also been included in this chapter. Since the present thesis mainly deals with the hydrophobic silica films, the wetting phenomena and the related topics like surface tension and capillary force have been described in the Chapter 2. The other related topics like spreading parameter, Young’s equation, contact angle, contact angle hysteresis and surface treatments are also briefly described, in this chapter.

The properties of thin films depend on the method of deposition. The required properties and versatility can be obtained by choosing proper method of thin films deposition. Therefore, in Chapter 3, the basic concepts of dip, spin and spray deposition techniques have been discussed. The silica films have been characterized by Scanning Electron Microscope for the nanostructure analysis, Atomic Force Microscopy for the surface roughness measurement, Fourier Transform Infrared Spectroscopy (FT-IR), contact angle meter, etc. All these techniques have been described in this chapter with the relevant theory.

A water repellent behavior of the solid surfaces is one of the most important characteristics in both theoretical research and industrial applications. Surface modification with hydrophobic properties using the sol-gel method has been investigated during the recent years. The Chapter 4
describes the effect of the surface modifying agents on the hydrophobic behavior of the films. Optically transparent superhydrophobic silica films were synthesized at room temperature (27°C) using sol-gel process by a simple dip coating technique. The superhydrophobic coatings on glass substrates have been prepared under basic condition from the MTMS, CH$_3$OH, and H$_2$O in molar ratio of 1:10.56:4.16 respectively with 5M NH$_4$OH. Emphasis is given to the effect of the surface modifying agents on the hydrophobic behavior of the films. Methyl groups were introduced in the silica film by post-synthesis grafting from two solutions using trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDZ) silylating agents in hexane solvent, individually. The TMCS modified films exhibited a very high water contact angle (166±2°) in comparison to the HMDZ (138±2°) modified films, indicating the water repellent behavior of the surface. Higher surface modification was achieved via the TMCS post-treatment as compared to the HMDZ post-treatment.

The physico-chemical properties of TEOS based hydrophobic silica films using various co-precursors have been discussed in Chapter 5. The sol-gel method is a novel procedure among solution reactions which is based on the preparation of macromolecular network through the typical hydrolysis of metal alkoxide groups followed by the condensation of the silanols. The co-precursor sol-gel method is simple and less time consuming compared to the derivatization method. There are many reports available on the synthesis of TEOS based hydrophobic silica films by co-precursor method. The hydrophobic silica films were prepared using the isobutyl-trimethoxysilane (iso-BTMS), hexadecyltrimethoxysilane (HDTMS) and trimethylethoxysilane (TMES) as a co-precursor to lower the surface free energy of the coated substrate. The silica films prepared from iso-BTMS (A = 0.965), HDTMS (B = 22.9 x 10^{-2}) and TMES (C = 3.80) showed a static water contact angle of 140°, 125° and 130°, respectively and water sliding angle of 16°, 27° and 24°, respectively. All the modified silica films are strongly water repellent, optically transparent, adherent, thermally stable, and durable against humidity. The silica
films modified with different hydrophobic agents revealed to be effective for improving and maintaining film properties. By modification of silica sols with hydrophobic agents, sol-gel coatings could be prepared on glass substrate at room temperature owning to excellent water repellent properties.

Control on the wettability of solid state materials is a classical and key issue in surface engineering. Several researchers have reported that it is possible to combine excellent optical transmission with high water contact angles, however, only a few studies also report low contact angle hysteresis or a low sliding angle of water droplet. These later characteristics are required if a surface is to exhibit true self-cleaning properties. Sliding behavior of water drops on spin-deposited hydrophobic silica films have been described in Chapter 6. Optically transparent methyltriethoxysilane (MTES)-based silica films with water sliding angle as low as 9° were successfully prepared by two-step sol-gel co-precursor method. The emphasis is given to the effect of trimethylethoxysilane (TMES) as a co-precursor on water sliding behavior of silica films. The coating sol was prepared with molar ratio of methyltriethoxysilane (MTES), methanol (MeOH), acidic water (0.01M, oxalic acid) and basic water (12M, NH₄OH) kept constant at 1:12.73:3.58:3.58 respectively, and the molar ratio of TMES/MTES (M) was varied from 0 to 0.22. The static water contact angle as high as 120° and the water sliding angle as low as 9° was obtained by keeping the molar ratio (M) at 0.22. These films could find application as self-cleaning windshields of automobiles, in which a high transmission of visible light is desirable.

The uniform deposition is main requisite for superhydrophobic silica films. The spray pyrolysis deposition technique gives the uniform deposition over the substrate. Synthesis of superhydrophobic silica films by spray pyrolysis deposition technique have been described in Chapter 7. The silica films were spray deposited under basic condition from the MTMS, CH₃OH, and H₂O in molar ratio of 1:21.42:7.5 respectively with 3M NH₄OH. The MeOH/MTMS (M) molar ratio was varied from 10.71 to 21.42. The results indicate that it is possible to tailor the composition to modify the properties of
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these coatings such as surface morphology, hydrophobicity, wettability, adhesion. A very well spherical shaped silica particles with each having diameter typically ranges from 15 to 18 µm were obtained for the spray deposited silica films with molar ratio M = 21.42. Precise selection of precursor and sol–gel composition yielded coatings that were found to be uniform, transparent, adhesive, thermally stable, highly durable against humidity and water-repellent.

The nature of adhesive forces between water and hydrophobic materials has been a subject of great interest. Diverse methods to achieve a wettability modification of solid materials have been developed, including electrostatic, electrochemical, and photochemical modification, either permanent or reversible, in addition to the many methods based on radiation-induced damages. The influence of high energy electron irradiation (7 MeV) on wetting behavior of superhydrophobic silica films have been described in Chapter 8. The superhydrophobic silica films were prepared by a single step sol-gel process and surface derivatization method. The electron irradiation induces a structural change in the surface morphology. The porous surface morphology of pristine silica film is changed to compact morphology (pore fill up) due to high energy electron irradiation. The experiments showed a gradual decrease in static water contact angle (SWCA); whereas an abrupt increase in water sliding angle (WSA) of irradiated silica film. The water droplets easily roll off on the pristine silica films, whereas the water droplet does not slide on the irradiated silica film surface even when the surface is tilted vertically or turned upside down.

There is a current need for alternative coatings that can provide corrosion resistance to metals or alloy surfaces due to the environmental hazards posed by conventional coatings. The Chapter 9 enlights the synthesis of anticorrosive coatings on copper substrate. Methyltriethoxysilane (MTES) precursor is used to prepare hydrophobic coatings on copper substrate which not only provide improved adhesion but also act as a barrier protection layer for minimizing the permeability of corrosive species. The contact angle of the
water droplet on the bent (>90°) copper substrate was measured which shows the almost same contact angle as on the flat film. It is found that the coatings are effective at preventing corrosion of metal substrate. These films are more elastic as compared to TMOS-derived silica coatings and therefore do not undergo cracking. These coatings act as barrier layers for metal surfaces for preventing corrosion. The presence of organic groups also renders these materials hydrophobic making them impermeable to ions, moisture, and other hydrophilic species as compared to pristine sol–gel-derived silica coatings. Thus, by a judicious choice of the precursor, it is possible to impart desired properties to the final material such as adhesion, water-repellency, and hydrophobicity. Overall, the strategy presented herein may provide a generic approach for fabrication of protective coatings on different metallic surfaces.

The general conclusions drawn from these studies and the scope for the future work, in the field of superhydrophobic silica films, have been presented in Chapter 10.

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