

ORGANICALLY MODIFIED SILICA BASED NANOMATERIALS FOR FUNCTIONAL SURFACES

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August, 2012

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ABSTRACT

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Organically modified silicas (ormosils) are unique materials due to their combined properties achieved from organics and inorganics. Ormosils contain at least one non-hydrolysable organic groups which results in a decrease of rigid Si-O-Si bonds, introducing a flexible character. Therefore, ormosils exhibit both flexibility of organics and atmospheric stability of inorganics. Organic group determines the functionalities of ormosils, thus their properties can be adjusted by choice of appropriate organic modification. Ormosils can be easily prepared in mild conditions of sol-gel technique, and can be applied on different surfaces by low cost and simple techniques.

In this thesis, we prepared superhydrophobic-superhydrophilic, antireflective-antifogging, anticorrosion and antiicing (ice retarding) functional surfaces using organically modified silica and its nano-composites in thin film form. Methyltrimethoxysilane (MTMS) is used in the synthesis of all films due to its intrinsically hydrophobic nature. This monomer is found to enable porous film formation without any modifications at ambient temperature and pressure. Superhydrophobic ormosil aerogel films with water contact angles reaching 179.9° and porosity of 86 % have been prepared using phase separated colloidal suspensions of MTMS, which exhibited flexibility, thermal stability and superhydrophilic transition after annealing at 600°C . Antireflective films with high mechanical stability are prepared from co-condensation of MTMS with tetraethylorthosilicate monomer, which exhibited transmission as high as 99.6 % with flexibility and transition to antifogging after annealing at 600°C . Anticorrosion films for glass surfaces have been prepared by encapsulation of ZnO and ZrO₂ nanoparticles to yield nano-composites of porous and nonporous ormosil films, which resulted in four times less corrosion compared to bare glass and acts as a barrier layer for

corrosion of glass substrates against alkaline corrosion. In formation of antiicing coatings various combinations of ormosil films mentioned are used and correlation between contact angle, stability of contact angle against cooling, surface roughness and freezing times are investigated. Compared to bare glass, freezing times are increased two order of magnitudes.

Keywords: Nanomaterials, functional surfaces, ormosil, thin film, aerogel, sol-gel, anticorrosion, antiicing, superhydrophobic, antireflective.

ÖZET

FONKSİYONEL YÜZEYLER İÇİN ORGANİK OLARAK MODİFİYE EDİLMİŞ SİLİKA NANOMALZEMELER

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Organik olarak modifiye edilmiş silikalar (ormosiller) organik ve inorganiklerin birleşimi özelliklerinden dolayı eşsiz malzemelerdir. Ormosiller içeriklerinde sert Si-O-Si bağlarında azalma sağlayan, esnek karakter kazandıran en az bir hidrolize olmayan organik grup bulundurlar. Böylece ormosiller hem organiklerin esnekliğini hem de inorganiklerin dayanıklılığını gösterirler. Organik grup ormosilin fonksiyonunu belirler, böylece uygun organik modifikasyonlarla özellikleri ayarlanabilir. Ormosiller kolayca sol-jel tekniğinin ılıman koşullarında hazırlanabilirler ve değişik yüzeylere düşük maliyetli ve basit tekniklerle uygulanabilirler.

Bu tezde süperhidrofilik-süperhidrofobik, ışığı geri yansıtmayan-buğulanmayan, korozyon önleyici ve buzlanma önleyici (geciktirici) fonksiyonel kaplamalar, ormosil'ler ve ince film formundaki nano-kompozitleri kullanılarak hazırlanmıştır. Metiltrimetoksisilan (MTMS) içsel hidrofobik doğasından dolayı bütün filmlerin sentezinde kullanılmıştır. Bu monomer herhangi bir yüzey modifikasyonuna gerek duyulmadan, normal sıcaklık ve basınçta gözenekli film oluşmasını sağlamaktadır. Su temas açıları 179.9° 'ye ulaşan ve gözenekliliği % 86 olan, esneklik, termal dayanımı yüksek, 600°C 'de fırınlandıktan sonra süperhidrofilliğe geçiş yapma özelliğine sahip süperhidrofobik ormosil aerogel incefilmler faz ayrışması olmuş MTMS koloidal süspansiyonlarından hazırlanmıştır. Yüksek mekanik dayanımı olan, % 99.6 kadar yüksek ışık geçirgenliğine sahip, esnek ve 600°C 'den sonra buğulanmama özelliğine geçiş yapan ışığı geri yansıtmayan filmler MTMS ve tetraetilortosilikat'ın birlikte jelleşmesiyle elde edilmiştir. Cama kıyasla dört kat daha az korozyona uğrayıp korozyona karşı bariyer görevi görerek cam substratı alkalın korozyonundan koruyan cam için korozyon önleyici filmler

ZnO ve ZrO₂ nanoparçacıklarının gözenekli ve gözeneksiz ormosil film nanokompozitlerinin hazırlanmasıyla oluşturulmuştur. Buzlanma geciktirici kaplamaların hazırlanmasında şimdiye kadar bahsedilen ormosil filmlerin değişik kombinasyonları kullanılmıştır ve temas açısı, temas açısının soğutma karşısında dayanıklılığı, yüzey pürüzlülüğü ve donma zamanları arasındaki bağıntı incelenmiştir. Donma süresi boş camla kıyaslandığında ormosil kaplamalarda yüz kattan fazla artış gözlemlenmiştir.

Anahtar sözcükler: Nanomalzemeler, fonksiyonel yüzeyler, ormosil, aerogel, sol-jel, korozyon önleyici, buzlanma önleyici, süperhidrofobik, ışığı geri yansıtmayan.

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Dedicated to my lovely
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Chapter 1

INTRODUCTION

Improvements in science and technology have changed the perspective of scientists to the materials. It is realized that as the size of a material goes down to nanometer scale, the properties of the material drastically change. This change stems from increasing surface area compared to bulk which exhibits different properties due to its different energy. Thus surfaces started to become even more important.

Surfaces of substrates which are modified or enhanced in some properties in order to provide an extra functionality are called as functional surfaces. These kind of surfaces can be achieved either by changing the surface topography or chemistry of the substrate itself or by coating the substrate with another material which provides the functionality [1, 2]. Superhydrophobic (extremely water repellent), antireflective, antifogging, antiicing, self cleaning, antibacterial, antibiofouling and sensing surfaces are most commonly used functional surfaces [3, 4, 5, 6, 7]. Superhydrophobic surfaces are important for many industrial applications like self-cleaning surfaces including stain-resistant textiles, self-cleaning traffic indicators, prevention of accumulation of snow on the antennas and windows; reducing the friction on the ship hulls and for prevention of bio-fouling [1, 8, 9]. Antireflective surfaces are commonly used in solar cells, display screens, optical filters, windows and eye-wears to eliminate reflection losses [10, 11, 12]. Antifogging surfaces are based on superhydrophilicity (extremely water liking).

They are commonly used on glasses and mirrors to prevent fog formation, and they also provide self-cleaning to the surfaces they are coated but by a different mechanism compared to superhydrophobic surfaces [13, 14, 15]. Antiicing surfaces are crucial for wind turbines and aerospace industry in addition to other application fields like antennas in order to increase efficiency and decrease damage generated by ice accretion [16, 17, 18]. Self-cleaning surfaces are especially important where it is hard to reach and the surface is sensitive to chemical cleaning agents or scrubbing like solar concentrators and optical lenses [4, 19, 20]. In addition these surfaces help to eliminate the cleaning costs. Sensing surfaces are preferred because of their low cost and their fast responses against chemicals due to their high surface area compared to bulk materials [21, 22, 23]. Anticorrosion surfaces are especially important for prevention of aqueous corrosion on both glasses and metal surfaces which have tendency to oxidize.

In this thesis, we combined extreme properties of aerogels with ormosils in order to obtain functional thin film coatings. We preferred to use methyltrimethoxysilane (MTMS) precursor, which has three hydrolysable groups and a hydrophobic ($-\text{CH}_3$) group which makes it suitable for construction of ambient pressure dried ormosil aerogels. For obtaining ormosil thin films we initially prepared colloidal suspensions, from ultrasonically breaking of ormosil gels by dilution with appropriate solvent. Finally obtained colloidal suspension containing porous ormosil nanoparticles were deposited on almost any surface by spin, spray or dip coating techniques. Using this method we successfully prepared flexible superhydrophobic films which can be transformed into superhydrophilic, flexible and mechanically stable antireflective films which can also be converted to antifogging films.

In addition we prepared nano-composite thin films using porous and non-porous ormosil structures for encapsulation of ZnO and ZrO_2 nanoparticles, which are used for providing anticorrosion against alkaline solutions. Four times less corrosion is achieved using ormosil nano-composite thin films.

Finally, ice retardation properties of ormosil films with roughness values varying from 0.8 nm to 120 nm and contact angles varying from 30.3° to 179.9° have

been investigated for several films. Based on the findings of these results we investigated the properties dominating on the determination of freezing times.

This thesis is organized as follows: in Chapter 2 we provide theoretical preliminaries that are necessary for development and understanding of thesis work, addressing the terms and concepts like hydrophobicity, antireflection, corrosion and icing. Chapter 3 provides detailed instrumental techniques used for analysis of the structures synthesized. In chapter 4, we present our works on synthesis and characterization of highly transparent, flexible and thermally stable ormosil aerogel thin films. Their change form superhydrophobic to superhydrophilic is investigated in detail. Chapter 5 presents preparation and characterization of flexible, mechanically stable and antireflective ormosil thin films. The control mechanisms on thickness and porosity are visualized. Moreover, their transition to antifogging in addition to antireflection by annealing is characterized. In Chapter 6, preparation of nanoparticle embedded ormosil nano-composite films are prepared and their anticorrosion characteristics are examined against alkaline corrosion for glass substrates. In chapter 7, antiicing properties of ormosil films with contact angles and roughness varying from high to low are examined and compared to bare glass, two order of magnitudes enhancement in freezing time is observed. Chapter 8 we conclude the subjects investigated and give potential application areas.

Chapter 2

THEORETICAL BACKGROUND OF FUNCTIONAL SURFACES

2.1 Sol-Gel Chemistry of Silica

Sol is the colloidal suspension of solid particles freely moving inside the liquid, where gel is the macroscopically extended version of these particles, linked each other throughout the solution [24]. As the name implies, sol-gel technique is based on the formation of an initial sol which have possible sites for cross linking, then formation of a gel using this colloidal suspension. As silicon is one of the most abundant materials in nature, sol-gel chemistry of silicates are investigated in detail. There are examples of naturally occurring silicate gels as in case in opal, which is composed of amorphous silica particles glued by silicate gel [25]. Silicate gels are obtained by hydrolysis and condensation reactions of silicate monomers. Most commonly used silicate monomers are tetraalkoxysilane precursors such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) [26]. There are three reaction types in silicates in the functional group level as shown in Figure 2.1.

As reactions given in Figure 2.1 indicate, it is possible to obtain silicate gels in the absence of catalysts. On the other hand, without a catalyst hydrolysis rate is very low, and it is not possible to fully hydrolyze the precursors. Similarly, for

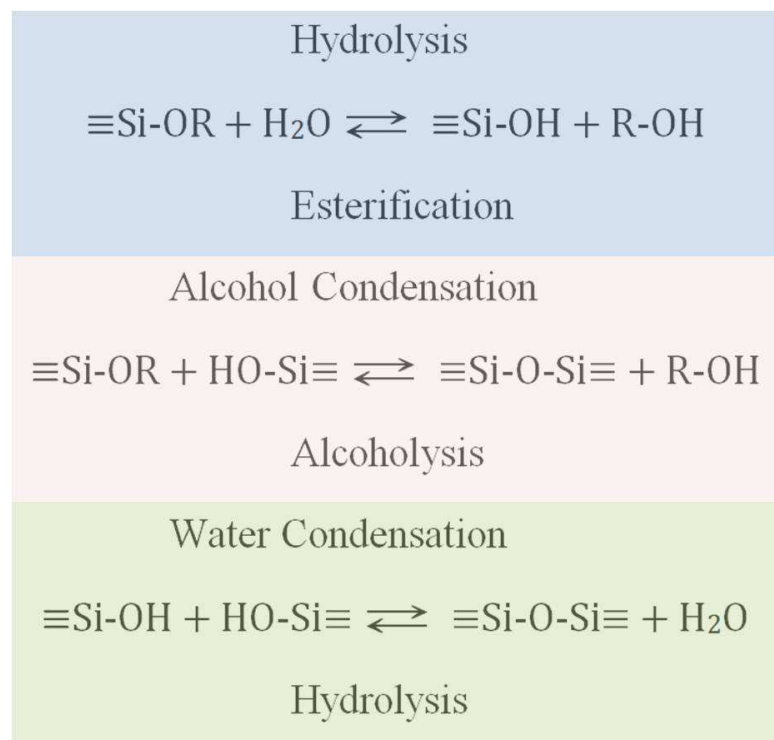


Figure 2.1: Main reaction types observed for silicates.

complete condensation elevated temperatures would be required. Thus acids or bases are used for catalyzing hydrolysis and condensation of silicates [24].

2.1.1 Acid Catalysed Hydrolysis

In acid catalyzed hydrolysis of alkoxysilanes, initially an alkoxide group is protonated. Protonation results in withdrawal of electron density from silicon, enabling it to be attacked by water molecules present in the environment. Back side attack of water results in reduction of positive charge on protonated alkoxide. Reaction takes place with leaving of the alcohol and inversion of the tetrahedron of silica as shown in Figure 2.2. Mineral acids, acetic acid, hydrofluoric acid and potassium fluoride are highly used for hydrolysis of silicates due to their fast and effective reactions [24, 27].

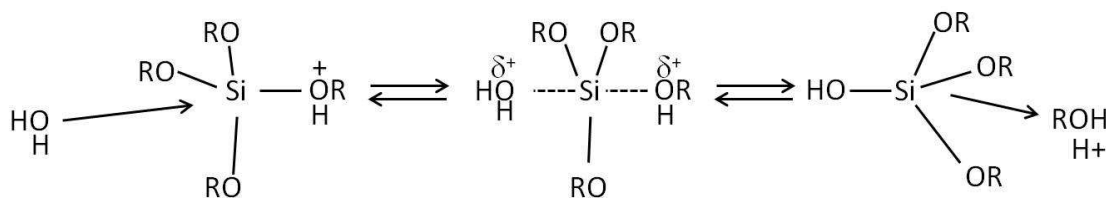


Figure 2.2: Acid catalysed hydrolysis mechanism for alkoxysilanes.

2.1.2 Base Catalyzed Hydrolysis

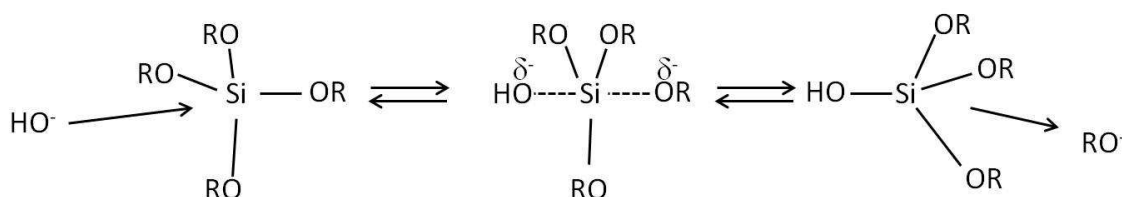


Figure 2.3: Base catalysed hydrolysis mechanism for alkoxysilanes.

Under basic conditions, free hydroxyl ions rapidly form inside the reaction mixture which can attack the silicon atom from back side. Hydroxyl replaces alkoxide anion with inversion of the tetrahedron of silica, as given schematically in Figure 2.3. Potassium hydroxide, ammonium hydroxide and amines are commonly used for this purpose [28].

2.1.3 Acid Catalyzed Condensation

Acid catalyzed condensation reaction is initiated with formation of a protonated silanol, of which silicon becomes more electrophilic. Higher electrophilicity makes silicon of protonated silanol more susceptible to nucleophilic attacks by neutral silanols. Reaction between electrophilic and neutral silanol ends with formation of Si-O-Si bridge and hydronium ion, Figure 2.4

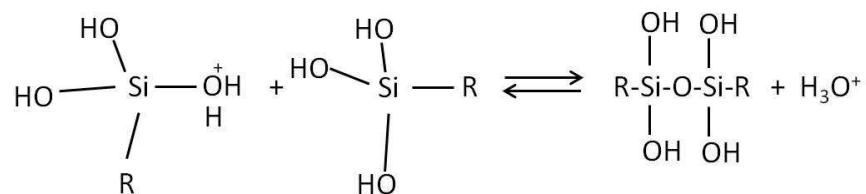


Figure 2.4: Acid catalysed condensation mechanism for alkoxysilanes.

2.1.4 Base Catalyzed Condensation

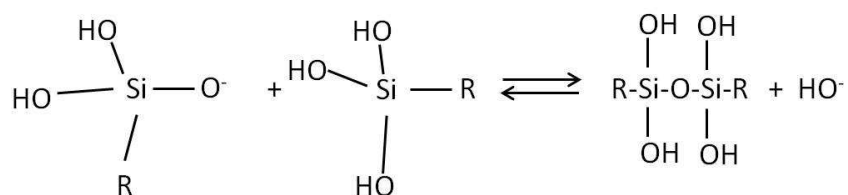


Figure 2.5: Acid catalysed condensation mechanism for alkoxysilanes.

Most widely accepted base catalyzed condensation mechanism is based on the attack of a deprotonated silanol to a neutral silanol. After binding of the negatively charged oxygen of the charged silanol, a hydroxyl group is kicked out from the initially neutral silanol and Si-O-Si bridge is formed.

2.1.5 Gelation and Aging

Gelation takes place with the condensation reactions. As the number of Si-O-Si bonds increases and the domain size of these condensed molecules increases, the viscosity of the reaction mixture increases. When the size of cross linked molecules reaches all solution, the gel is formed. Gel can be defined as a continuous, linked solid network filled with liquid. The instance at which the last bond is formed is called as the gel point, but it is not easily measurable [24, 29]. Bond

formation inside the gel continues even after the gel point as a result of motions, rotations inside the gel; enabling formation of new bonds between species in close proximity. In addition, tiny moving sol particles can also attach themselves to the gel network. This time duration of additional condensation is called as aging, which changes the final properties of the formed gel network due to continuing condensation and hydrolysis reactions taking place [24].

2.2 Aerogels

Most of the functional surfaces either require designed surface roughness or porosity. Silica aerogels are the lightest solids ever synthesized due to their extremely porous structure [30]. The high porosity is a result of the three dimensional structure of aerogels which is composed of SiO_2 nanospheres of a few nanometers in diameter surrounded by macro and meso-pores [31]. The open structure provides aerogels with some extreme properties such as high porosity (up to 99.9 %), high surface area ($1200 \text{ m}^2/\text{g}$), low density (0.003 g/cm^3), low thermal conductivity (0.005 W/mK) and very low index of refraction (1.01) [32, 33, 34, 35, 36]. Potential applications of aerogel films are varied from being dielectric in integrated-circuits to corrosion inhibition, humidity sensors and antireflection coatings [37, 38, 39]. Synthesis of aerogels are mainly based on three steps: gel preparation, gel aging and drying of the gel [40]. During the drying step, because of the high surface tension formed at the vapor-liquid interface inside the pores, the silica network can collapse. In order to prevent collapsing of the network, supercritical drying is applied using either the solvent of the gel or liquid CO_2 . Recently, ambient pressure methods have been established. These techniques require either modification of gel with hydrophobic groups or additional washing and aging steps to strengthen the gel network in order to minimize the capillary tension and additional condensation induced shrinkage [41, 42]. This phenomenon is known to be the spring-back effect, because during drying the gel structure initially shrinks along the drying line, then springs back to a level close to its initial volume [42]. Modification steps required at ambient drying method

for obtaining spring back can be eliminated by using alkyltrialkoxysilane precursors with hydrophobic functional groups. It is reported that ambient pressure dried silica aerogels can be synthesized using methyltrimethoxysilane monomer without applying surface modifications due to its hydrophobic nature [43].

2.3 Organically Modified Silicas (ORMOSILs)

There are many different methods used to prepare functional surfaces, but among the materials used organically modified silicas (ormosils or organosilica hybrids) have superior properties compared to inorganic silica based materials and fully organic materials. As the name implies ormosils are silicas which contain one or more non-hydrolysable organic groups. The organic moiety that silica monomers contain results a decrease in the number of rigid Si-O-Si bonds and introduces a flexible character to the structure. Thus ormosils have unique properties such as flexibility and atmospheric stability which cannot be afforded neither by organics nor inorganics alone. More over their physical and chemical properties can be tuned by varying the organic groups of the silica monomers [44]. Organic groups can further be used to adjust the surface properties such as polarity, hydrophobicity, and catalytic, optical and electronic activities [45, 46, 47].

Ormosils can be easily obtained under mild conditions using sol-gel techniques and for preparation of functional surfaces they can be applied to substrates using simple techniques like spin, dip or spray coating techniques which enables large area fabrication. On the other hand most of the functional surfaces are obtained using chemical vapor deposition, layer by layer deposition, plasma etching, electrospinning and lithographic methods which are time, capital and energy consuming [11, 48, 49, 50, 51, 52, 53, 54].

2.4 Superhydrophobicity-Superhydrophilicity

In Greek hydro means water and phobos means fear, thus hydrophobicity means water repellant. Behaviors of solid surfaces against liquids are defined according to the contact angle of liquid when it is suspended over the solid surface. When the applied liquid is water, this angle is defined to be water contact angle, which is formed between three phase boundary; where liquid, solid and gas intersect as illustrated in Figure 2.6. If the contact angle is higher than 150° and sliding angle is smaller than 10° , then the surface is called to be superhydrophobic where surfaces with contact angle smaller than 10° are encountered as superhydrophilic [8].

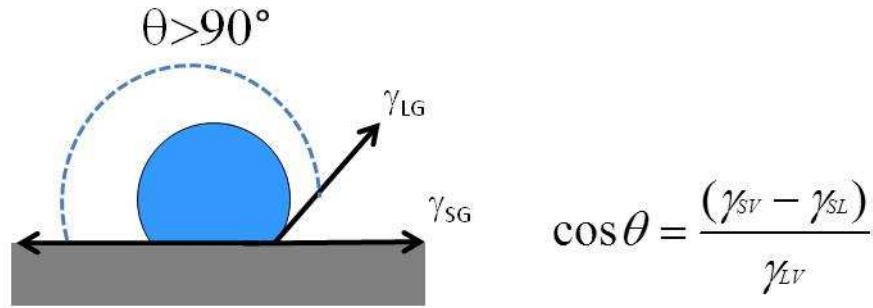


Figure 2.6: Illustration of relation between contact angle and surface tensions and Young's equation.

Even though Aristotle, Archimedes, and Galileo mentioned wetting phenomenon, Thomas Young is the person who defined the contact angle [55]. According to Young's equation given in Figure 2.6 contact angle, given as θ is directly related to surface tensions between solid-vapor (γ_{SV}), solid-liquid (γ_{SL}) and liquid-vapor (γ_{LV}) [56]. However this equation is not valid for rough surfaces as it does not include any roughness parameter where roughness enhances hydrophobicity in high extent. It is not possible to obtain a surface with water contact angle higher than 120° without introducing roughness to the surface [57, 58]. Rough surfaces are categorized according to filling behavior of water between the protrusions on the surface, given in Figure 2.7. If the water fills the

space between protrusions Wenzel equation needs to be used where contact angle is defined as θ' and r is the roughness factor - the ratio of actual area to the geometrically projected area [58]. If there is trapped air between water droplet and protrusions than Cassie-Baxter equation is applied which uses θ'' for definition of contact angle and φ as the surface fraction of the solid [59].

$$\cos \theta' = r \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right) = r \cos \theta, \cos \theta'' = \varphi \left[\left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right) + 1 \right] \quad (2.1)$$

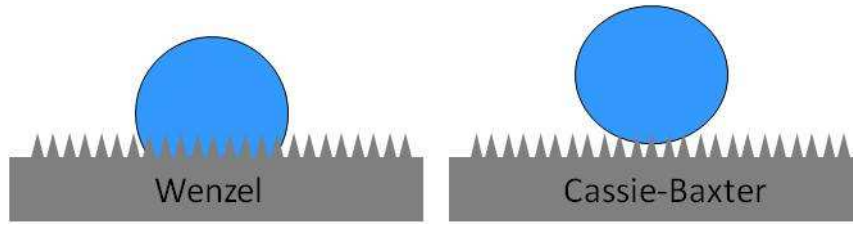


Figure 2.7: Schematic representation of two different types of filling behavior of water on protrusions.

There are many examples of hydrophobic surfaces in nature which inspired humans for production of such surfaces especially due to their self cleaning property. Lotus is a very well known superhydrophobic plant existing in nature [60]. It is composed of micrometer and nanometer scaled patches, coated with a hydrophobic wax secreted by plant. Wax on the surface decreases the surface energy to provide hydrophobicity where dual scale roughness enhances hydrophobicity providing the surface superhydrophobicity [61].

Superhydrophobic and superhydrophilic surfaces both find applications in self-cleaning with different mechanisms. In a superhydrophilic surface, the drop covers the surface of the substrate as a film while sliding off it. During this sliding motion the moving film removes the dirt from the surface. However, in a superhydrophobic surface the droplet forms a spherical shape and while rolling on the surface it also removes the dirt particles which stick on its surface [62]. In addition to self cleaning, superhydrophobic surfaces are important for production of stain resistant textiles, prevention of snow accumulation on outdoor antennas,

windows and traffic lamps, where superhydrophilic surfaces are important for obtaining antifogging property which is crucial especially for surgical applications, optical devices, fog free mirrors and eyewear.

2.5 Antireflection

Reflection can be defined as change in the direction of light beam when it encounters an interface between two different media with different refractive indices, and return into the medium from which it originated. It is undesirable because reflection limits the performance of optical devices as the intensity decreases especially in solar cells, optical lenses and detectors [63]. Thus in order to prevent reflection losses antireflective coatings are tried to be developed. Antireflective structures are also present in nature. Cornea of moth and some butterflies contains some pillar like structures which reduce reflection and increase sensitivity even in the dark [64]. There are many different approaches used for preparation of antireflective surfaces where some are based on mimicking the examples from nature. There are mainly four different approaches used for obtaining antireflective surfaces, which are summarized in Figure 2.8 [65].

As the reflection results due to difference in the refractive indices, first strategy that can be applied is using a material which has refractive index in between the indices of two mediums; air and substrate. As shown in Figure 2.8 (a), the minimum reflection from the surface is obtained when the index of the film (n_1) is chosen as $n_1 = \sqrt{n_2 n_0}$ where n_0 and n_2 are refractive indices of the first and second medium respectively. In this method it is also important to provide destructive interference between the beams reflected from the interfaces of first medium to film and film to second medium. This condition is provided when the thickness of the antireflective film is equal to $\lambda/4$ where λ is the wavelength of the incident beam, thus reflected beams from coating and substrate surfaces destructively interfere due to $\lambda/2$ phase difference. When the glass is the substrate of interest the optimum value of refractive index is approximately 1.22 for monolayer coatings. Normally materials with such low refractive indices are not

present. In order to decrease refractive index, porosity needs to be introduced into the material [66]. The amount of the porosity introduced into the material can be calculated using equation:

$$\pi = \frac{n_N - n_D}{n_N - n_A} \quad (2.2)$$

where π is percent porosity, n_N , n_D and n_A are refractive indices of nonporous film and porous film from same material, and air respectively [37]. Instead of using a single layer with a constant refractive index, a material with gradually decreasing refractive index would result in better antireflective effect. Another method shown in Figure 2.8 (c) is using different coatings on top of each other in order to provide graded index structure. In this method the top layer has the lowest refractive index and as the layer gets closer to the surface its refractive index increases. Graded structure provides antireflection in a broad band of wavelengths where homogeneous monolayer structure (Figure 2.8(a)) works with highest efficiency for a narrow spectrum.

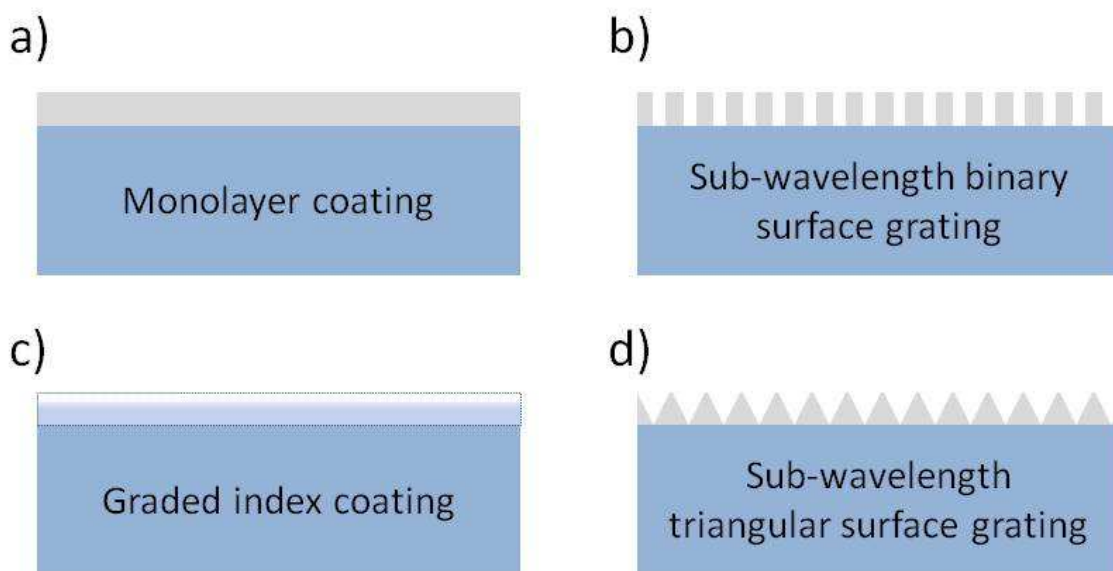


Figure 2.8: Schematic representation of different techniques used for preparation of antireflective surfaces.

Antireflective surfaces can also be obtained just by patterning the surfaces in order to introduce some air gaps to decrease effective refractive index on the surface of the substrate, Figure 2.8(b). Such patterns can be easily obtained using photolithography or ICP etching techniques. Similar to structure obtained in Figure 2.8 (a), these structures also work most efficiently in a small range of wavelengths. Broad band antireflection graded index structures can be obtained by generation of bigger the air gaps on the outer surface and smaller gap as you go deeper in the material, Figure 2.8 (d). Such graded index patterns can be obtained using reactive ion etching (RIE) or glancing angle deposition techniques [67, 68].

Antireflective films can be easily obtained on rigid and durable commonly used substrates like glass and silicon by glancing angle deposition, reactive ion etching, patterning, phase separation of polymers [61, 63, 65, 66]. However, current technology requires production of antireflective surfaces on flexible substrates.

2.6 Anticorrosion for Glass Substrates

Silicate glasses are highly used in household, storage, cookware, windows and many different applications due to its properties such as long term stability compared to most other materials, easy production, low cost and fine appearance. Even though silicate glasses are resistive against many chemicals, they can corrode simply by exposure of water. Furthermore, silicate glasses are known to be hydrophilic, which makes them attract water even from the humidity of the atmosphere. The water layer spreading on top of the glass causes corrosion on glass by various mechanisms. One of these mechanisms is based on diffusion of hydroxonium ions, present on the water layer, into the glass network and ion exchange between the protons and alkali network modifiers such as sodium ions leaving behind silanol groups [69]. This is an example of acidic corrosion observed on glass. Especially hydrofluoric acid and hot concentrated phosphoric acid are known to corrode silicate glass effectively. Another type of corrosion on

glass is based on high alkaline ion concentration, where this causes the dissolution of silicate itself [70]. This is the most common reason of corrosion of glasses because alkaline corrosion acts at a constant rate without reaching saturation and as the temperature increases its rate of dissolution also increases [71]. Even though the corrosion rate is low at ambient conditions, in long term corrosion due to humidity causes an undesired, opaque appearance on glass surface, as shown in Figure 2.9 [72].



Figure 2.9: A photograph of window glass after long term corrosion by water.

Schematic representation of dissolution and corrosion mechanism of sodium silicate glasses in the presence of water is shown in Figure 2.10, including the chemical changes taking place [73]. In the first case instantaneous establishment of electrochemical equilibrium takes place, which enables ion exchange between the sodium inside the sub-surface and hydrogen in the solution phases, shown in case 2. Case 3 summarizes the fast transportation of sodium and hydrogen ions, and molecular water over the sub-surface zone to solution phase. In case 4, initially formed silanol groups condensate in order to form a gel network, where in case 5 an opposite reaction takes place resulting in dissolution of silica structure [74].

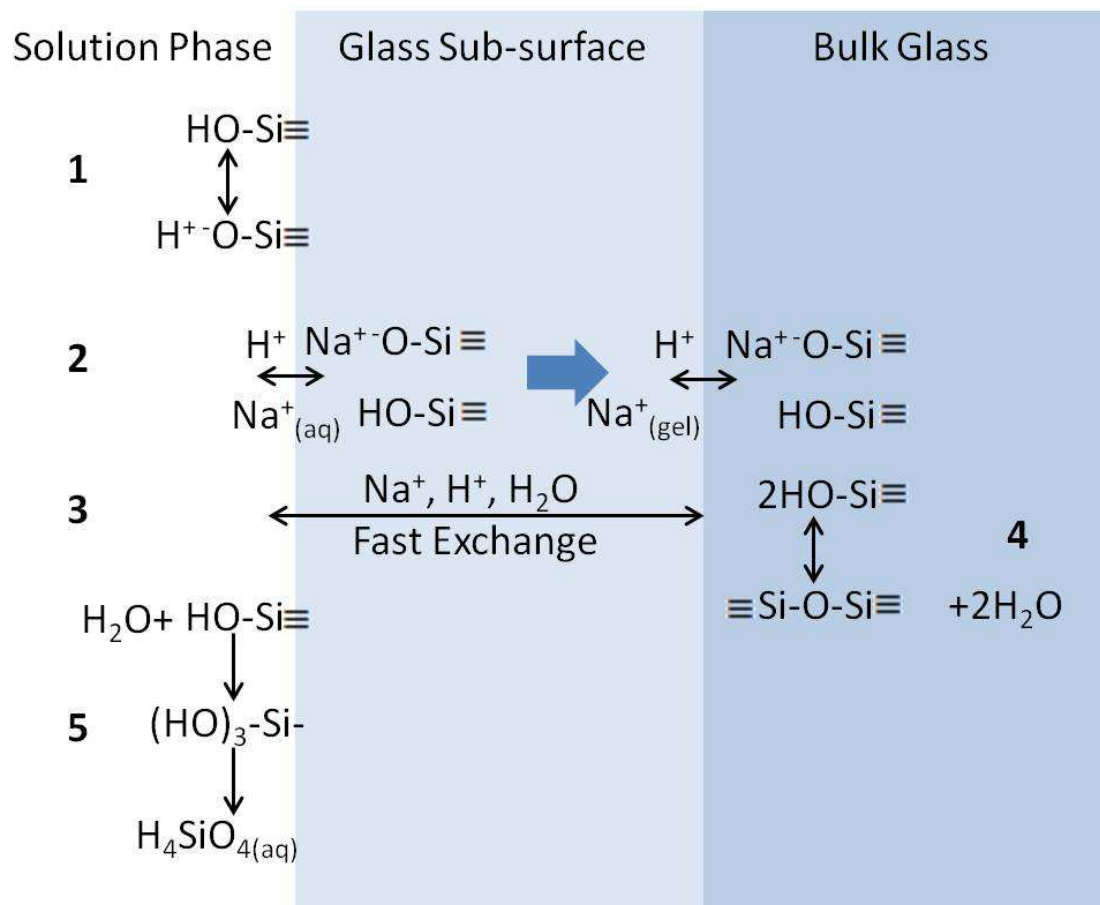


Figure 2.10: Schematic representation of corrosion mechanism on sodium silicate glasses.

In industry, most of the glass produced is in the flat glass form, which is the common window glass. Once produced, reaching of the products to the consumer can take 1-2 years depending on the demand. It is known that these warehouses do not provide well proof from humidity, thus glasses can get corroded even before being sold. Never the less, they also get exposed to humidity when they are sold. In addition to flat glasses, fiber glasses used as reinforcing materials in cement are also exposed to alkaline environments, which also need protection. In order to overcome corrosion of glass, there are several techniques. Dealkalization is the most common technique used to prevent corrosion of glass surfaces. In this technique, alkali ions are removed from the outermost layer of the glass by

chemical treatment. Thus the layer which has lack of alkali ions, act as a barrier layer for diffusion of other ions from the bulk of the material. This method requires use of elevated temperatures (650 °C or higher) and sulfur or fluorine containing compounds [74]. Due to its high cost, this technique is not preferred for flat glass applications. Another way of protecting silicate glasses against corrosion is using corrosion inhibition films. Materials such as titanium dioxide and zirconium dioxide are known to be resistive against alkaline corrosion and are used for thin film production by incorporation into silica structure [75]. ZnO is also shown to be corrosion resistant for steel in salty water when incorporated into epoxy coating, which is also a candidate for production of anticorrosive thin films for glass substrates [76].

2.7 Antiicing Surfaces

Ice formation is an important problem especially in cold regions due to its undesired results such as higher energy consumption, serious risk of falling on aircrafts, damages in power transmission lines, decreasing efficiency of wind turbines [77]. There are mainly three types of icing mechanism: in cloud icing, precipitation and frost [18]. Former one takes place when a supercooled water droplet meets a cold surface which has temperature below freezing point (0 °C). In the case of precipitation, as the name implies, initially precipitated particles like snow or rain hit the surface below freezing point. On the other hand frost is direct formation of ice on solid surface by solidification of water vapour up on impact.

In order to obtain a better understanding of the icing, one needs to investigate the thermodynamic equilibrium of ice formation. As water is cooled down from its freezing temperature, formation of solid phase becomes thermodynamically favourable because free energy of solid is smaller than free energy of liquid below freezing temperature. However, formation of solid nuclei inside the liquid requires generation of a solid surface. Thus there will be a positive free energy related to formation of this new area of solid, which acts as a barrier to the formation of solid nuclei [78]. Inside the liquid which is cooled under its freezing point, nuclei

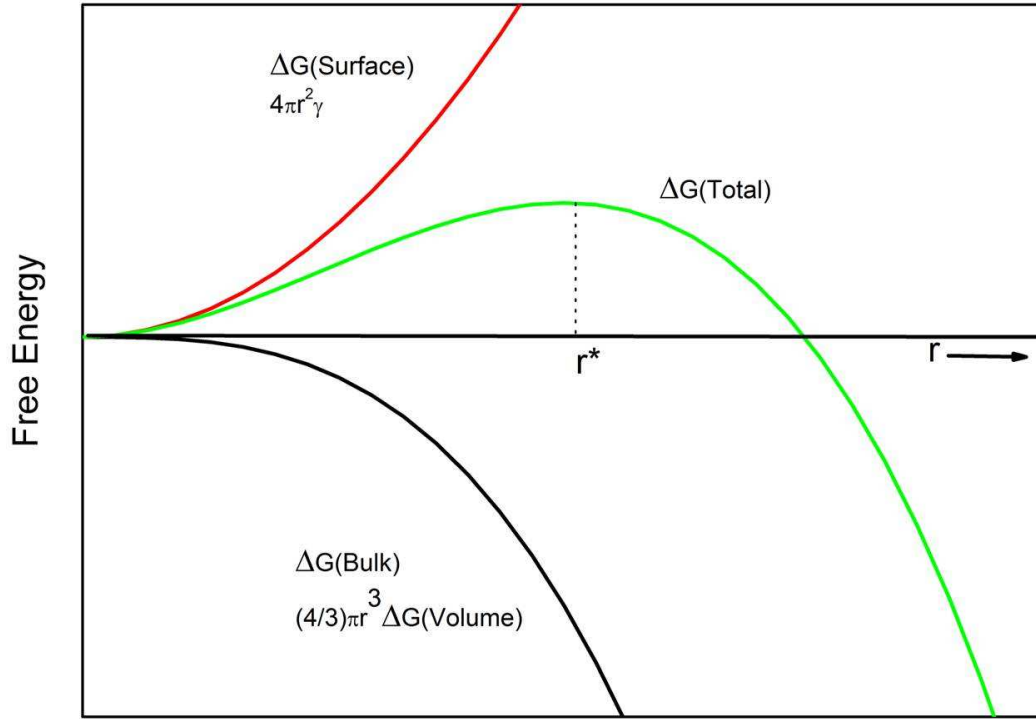


Figure 2.11: Energy diagram showing the formation of a homogeneous nucleation site as a function of its radius.

instantaneously form and disappear due to random addition and subtraction of atoms. If the size of these nuclei reaches r^* (critical size of nucleation), then it continues growing, because after critical size of nucleation the energy barrier due to formation of a new surface is exceeded. The free energy of formation of a solid nucleus inside the liquid is shown in Figure 2.11 with green line. Free energy required for formation of a new surface is given in red and formation of a solid volume is in black. The amount of extra cooling from the freezing temperature of a liquid is defined as supercooling. In order to find actual homogeneous nucleation, gravitation free conditions are applied to small volumes of liquids and the supercooling required for freezing is determined. It is reported the water freezes at around -37°C under this conditions [79].

As we keep liquids in containers, we do not observe such high amount of supercooling. The walls of containers act as heterogeneous nucleation sites for

liquids, for which the energy barrier is much smaller. During the formation of solid-container interface, initially existing liquid-container interface is destructed, which results in energy release. Free energy change required for homogeneous nucleation is given by

$$\Delta G_{homo} = -\frac{4}{3}\pi r^3 \Delta G_B + 4\pi r^2 \gamma_{SL} \quad (2.3)$$

where r is the radius of nucleus, ΔG_B is difference in free energies of liquid and solid at that temperature and γ_{SL} is the surface tension between solid and liquid. On the other hand, free energy required for heterogeneous nucleation is given by

$$\Delta G_{hetero} = \Delta G_{homo} f(\theta) \quad (2.4)$$

where $f(\theta)$ is a function of contact angle (θ) given by

$$f(\theta) = \frac{1}{2} - \frac{3}{4}\cos(\theta) + \frac{1}{4}\cos^3(\theta) \quad (2.5)$$

thus the barrier energy of the heterogeneous nucleation is directly related to the contact angle of the liquid on the container surface [77].

Formation of ice on a surface can be prevented either using energy consuming active methods like resistance heating, blowing hot air or by passive methods like application of antiicing coatings [80]. It is not possible to completely prevent formation of ice; however by application of suitable coatings the freezing time can be elongated. Elongated freezing time increases the probability of removal of the drop from the surface before freezing. One strategy is using superhydrophobic surfaces as antiicing coatings. Contact angle dependent function given for heterogeneous nucleation indicates that, as the contact angle increases, the nucleation barrier also increases. However this term is independent of the roughness, which can also affect freezing acting as a dislocation. Most of the available literature

points that superhydrophobic coatings act as ice retarders, where some debate on the affect of roughness and contact angle [75, 81, 82, 83, 84, 85].

Chapter 3

EXPERIMENTAL

3.1 Sample Characterization

3.1.1 Scanning Electron Microscopy (SEM)

Microstructural observations of the thin films were carried out using an environmental scanning electron microscope and a scanning electron microscope; E-SEM, Quanta 200F, FEI and NanoSEM, Nova, FEI on ultra-high resolution mode with a Helix detector respectively. In both, low vacuum conditions are used without application of any conductive coatings in order to directly observe the surfaces, operated at 5mm separation with 5 kV and around 0.98 Torr.

3.1.2 Transmission Electron Microscopy (TEM)

The skeletal and porous structure of the ormosil colloids, sizes and the structure of nanoparticles were visualized by bright-field images with a transmission electron microscope; TEM, Tecnai G2 F30, FEI operated at 200 kV. TEM samples are prepared by placing a drop of colloidal suspension used for film preparation on holey carbon coated copper grid or by scratching an already prepared film and

dispensing it in ethanol onto grid.

3.1.3 Atomic Force Microscopy (AFM)

The surface roughness and the topography of the films prepared on glass substrates were analysed using an atomic force microscope; AFM, XE-100E, PSIA in non-contact mode.

3.1.4 Contact Angle Measurement System (CAM)

A contact angle meter, OCA 30, Dataphysics, was used to measure the water contact angles of the prepared surfaces. Water droplets of 4 μL volume were used and normal fitting is applied for contact angles smaller than 120° where Laplace-Young fitting was applied for highly hydrophobic samples.

Temperature dependent contact angle measurements were performed using CCD camera of the CAM system in corporation to homemade cooling system composed of two Peltier coolers placed on each other, both with the cold side up. In addition, these coolers are placed on top of an aluminum cooling plate with two computer fanners. A multi-input temperature controller is used for adjusting the temperature and temperature is controlled with help of a small thermocouple, placed in contact with examined sample by using a heat conducting silicon paste. Same system is also used for freezing time measurements by adjusting the temperature to -10°C .

3.1.5 Ellipsometric Measurements

Thickness and spectroscopic refractive index measurements were obtained by an Ellipsometer, V-Vase, J. A. Woollam. The measurements are performed in the range of 400 to 1200 nm. The experimental results were fitted by using Cauchy



Figure 3.1: Home-made temperature controlled cooling system.

model as:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (3.1)$$

where, n is refractive index, A (dimensionless), B (μm^2) and C (μm^4) are Cauchy parameters.

3.1.6 UV-Visible Spectroscopy

UV-vis spectroscopy is used for monitoring the transmittance of the prepared films on glass and cellulose acetate substrates and for monitoring the corrosion of the substrates. UV-Vis spectra were recorded using Varian Carry100 spectrophotometer between the 300 and 800 nm in transmission mode.

3.1.7 X-ray Photoelectron Spectroscopy (XPS)

Chemical analysis of the surface was performed using X-ray photoelectron spectroscopy (XPS), K-Alpha, Thermo Scientific. XPS measurements were performed on the slightly etched (clean) surfaces of the examined surfaces. The data was collected at survey mode while flood gun was operating in order to prevent charging of the surfaces.

3.1.8 Thermal Gravimetric Analysis (TGA)

Detailed chemical analyses were performed using thermal gravimetric analysis (TGA), Q500, TA Instruments. TGA measures the weight of the sample under constant heating. This way, the change on the weight of the sample can be investigated on the basis of temperature, enabling to observe decompositions. Measurements are conducted under the flow of oxygen.

3.1.9 Differential Scanning Calorimetry (DSC)

Phase and chemical changes in the samples were monitored using differential scanning calorimeter (DSC), Q2000, TA Instruments. Sample is placed in an aluminum crucible and placed into instrument together with an empty crucible. Device measures how much energy is required to increase the temperature of both crucibles 1 °C using the empty crucible as reference. This way, changes in the heat capacity are monitored as a function of temperature.

3.1.10 X-Ray Diffractometer (XRD)

X-ray diffractometer (XRD) Xpert Pro MPD, Panalitical is used for examining the crystallinity of the synthesized ZnO and ZrO₂ nanoparticles.

3.1.11 Fourier Transform Infrared Spectroscopy (FTIR)

Functional groups were on the prepared samples were characterized using a Fourier transform infrared spectrometer (FTIR), Vertex 70, Bruker. The FTIR measurement samples are prepared by dispersing small portions of synthesized films into KBr and preparation of pellets by compression under high pressure. Bare KBr pellets are used for baseline measurements.

3.1.12 Mechanical Stability Tests

Mechanical stability of the prepared samples were tested using different techniques as water dripping, adhesive tape testing and pencil hardness (scratching) tests [86, 87, 88, 89, 90]. In water dripping test films were placed with an inclination of 45° and 30 cm apart from a source of tap water. Then water droplets of approximately 100 μ L start to fall at a rate of one drop per second at least for 24 h. After the test, the change in the film can be monitored by SEM, CAM or transmission measurements.

In adhesive tape test a piece of tape is pressed on the coated surface with a force around 10 kPa, and then peeled off. The stability of the film on the substrate surface is monitored comparing the amount of the film initially on the substrate and after the test.

Pencil hardness test is performed by scratching the films with approximately 1 MPa of pressures with pencils of varying hardnesses in the range of 6H to 8B. The formation of scratches is then monitored using SEM.

Chapter 4

SYNTHESIS AND CHARACTERIZATION OF HIGHLY TRANSPARENT, FLEXIBLE, AND THERMALLY STABLE SUPERHYDROPHOBIC ORMOSIL AEROGEL THIN FILMS

Superhydrophobic surfaces with water contact angles larger than 150° and sliding angles smaller than 10° have many potential applications. These fields of applications are both related to their stability against water and moisture, and dirt due to self cleaning properties [8, 9]. It is known that for obtaining superhydrophobicity or superhydrophilicity, surface needs to have low surface energy in addition to high surface roughness [58]. Fluorocarbons are known to have low surface energy values, where lowest surface energy is measured for regularly aligned hexagonal $-\text{CF}_3$ surfaces is 6.7 mJ/m^2 [57]. Without surface roughness maximum achievable contact angle cannot exceed 120° [58]. Nature has combined low surface energy and high roughness in lotus leaf. Lotus leaves are combined of micrometer and

nanometer-scaled patches coated by 1 nm thick hydrophobic layer [4]. High surface roughness due to dual scale roughness enables trapping of air below the water droplets, which helps the rolling of droplets easily, resulting in well designed superhydrophobic surfaces. Superhydrophobic films established up to now are mainly based on methylchlorosilanes, fluoroalkylsilanes, SiO_2 nanoparticles embedded into polymers, binary polymer brushes, ZnO nanorods [91, 92, 93, 94, 95]. On the other hand, aerogel structures are suitable candidates for rough film production due to their highly porous structure. Even though aerogel production is mainly done by critical point drying (at elevated temperatures and pressures), recently ambient pressure drying techniques are developed by modification of the gel structure in order to minimize capillary tension [42, 43]. Ormosils are known to exhibit superior properties compared to both organics and inorganics such as long term atmospheric stability and flexibility. Furthermore it is possible to tune the physical properties of ormosils by changing the organic functional groups [44]. Several ormosil superhydrophobic films have been reported up to date using electrospinning, vapor deposition and co-condensation techniques, where some have lack of transparency, some does not have good porosity and thickness control, and some needs pre- or post treatments [56, 96, 97, 98, 99].

In this chapter, we report synthesis and characterization of highly transparent, flexible and thermally stable ormosil aerogel thin films using methyltrimethoxysilane (MTMS) precursor using sol gel technique [100]. Ormosil films are obtained without any surface modifications as a result of intrinsically hydrophobic nature of monomer. Produced aerogel thin films contain both micrometer and nanometer scaled roughness similar to lotus leaves, allowing air to be trapped between the water droplet and the film surface. The film transparency is an important issue in terms of its technological applications. Although roughness enhances superhydrophobicity, it diminishes the transparency when it is higher than 100 nm resulting in the scattering of light [8]. Even though MTMS precursor results in opaque gels, the produced thin films are highly transparent. Superhydrophobic samples are observed to exhibit self cleaning properties. They can be easily cleaned simply by rinsing with water after contamination with nanoparticles. The contact

angle of the prepared films can be tuned by annealing in the range from superhydrophobicity to superhydrophilicity with water contact angles smaller than 5° . During the change through superhydrophilic character, the transparency of the films further increases with decreasing surface roughness due to change of skeletal structure from ormosil to silica.

4.1 Synthesis of Ormosil Aerogel Thin Films

For the production of superhydrophobic ormosil aerogel thin films methyltrimethoxysilane monomer is used for its nonhydrolyzable, functional methyl group. Reaction is proceeded through two steps, acid catalyzed hydrolysis and base catalyzed condensation mechanism. Methyltrimethoxysilane (MTMS), methanol, oxalic acid, and ammonium hydroxide (26 %) were used as purchased. Initially 1 mL of MTMS is dissolved in 9.74 mL methanol (for obtaining 1:35 mol fraction of MTMS: methanol, for 1:25 and 1:15 fractions 6.96 and 4.17 mL methanol is used respectively). 0.5 mL 0.001 M oxalic acid solution was added into reaction mixture and stirred for 30 min. After hydrolysis at ambient temperature for 24 h, 0.4 mL ammonium hydroxide solution dissolved in 0.21 mL water is slowly added in to reaction mixture and further stirred for 15 minutes. With addition of base, condensation reactions starts and gel forms within 24 hours of rest. The obtained gel is further aged for 24 hours, thus gelation and aging takes 2 days.

Thin films are obtained by ultrasonically breaking the gel structure, using a liquid homogenizer, into colloidal nanoparticles [42] and diluting the suspension. 10 mL of methanol is used for dilution as it is the reaction solvent, and gel is sonicated at 20 W power for 45 s. Obtained colloidal suspensions are suitable for dip, spin and spray coating techniques. For obtaining homogeneous and controllable thickness values, we preferentially used spin coating at 2000 rpm for 45 s.

The prepared films are named as the number in the abbreviation (Me35-a) indicating the mol fraction of methanol and the letter following the dash indicating

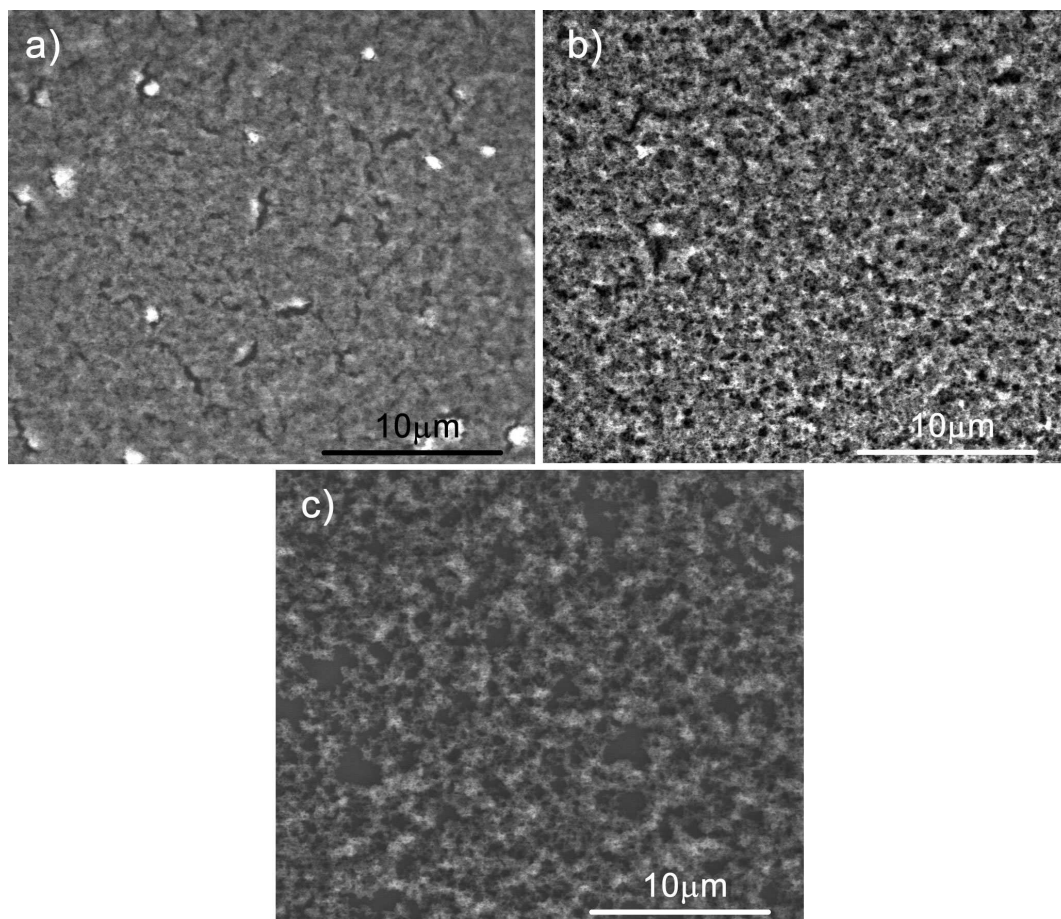


Figure 4.1: SEM images of a) Me15-a, b) Me25-a, and c) Me35-a showing the effect of changing methanol ratio on the porosity.

the heat treatment condition. In order to change physical and chemical properties of the films, thermal annealing is applied. Letter a stands for asprepared film, b and c for 450 and 600 °C annealing for 1 h durations.

4.2 Characterization of Thin Films

Surface morphologies of asprepared ormosil aerogel thin films with three different methanol fractions (15, 25 and 3) are investigated using SEM, Figure 4.1. SEM

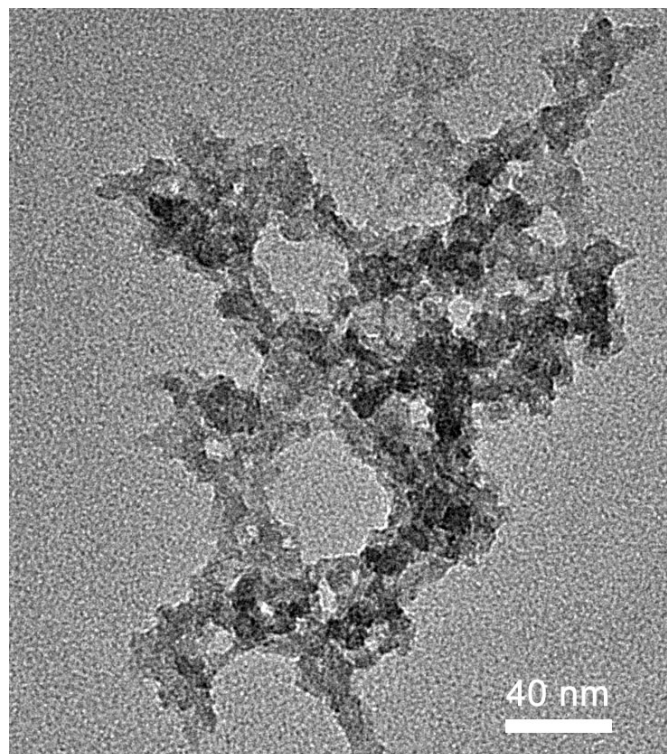


Figure 4.2: TEM micrograph of Me25 film visualizing the silica network with pores.

micrographs reveal that all films are composed of highly porous structure. On the other hand, comparison of films indicates that gel prepared with lower fraction of methanol, Me15 (Figure 4.1-a)), has a denser structure with smaller pores, where Me35 has more micrometer sized holes (Figure 4.1-c)). As expected Me25 exhibits an intermediate pore character (Figure 4.1-b)) compared to Me15 and Me35.

Skeletal structure of the Me25-a is visualized using TEM micrograph, given in Figure 4.2. It is seen that the aerogel structure is composed of approximately 20 nm sized ormosil clusters, interconnected to each other and surrounded by pores. Films are composed from interconnection of sub-micrometer sized clusters, obtained from sonication of gel structure.

Use of superhydrophobic coatings in window glass or solar cells requires these

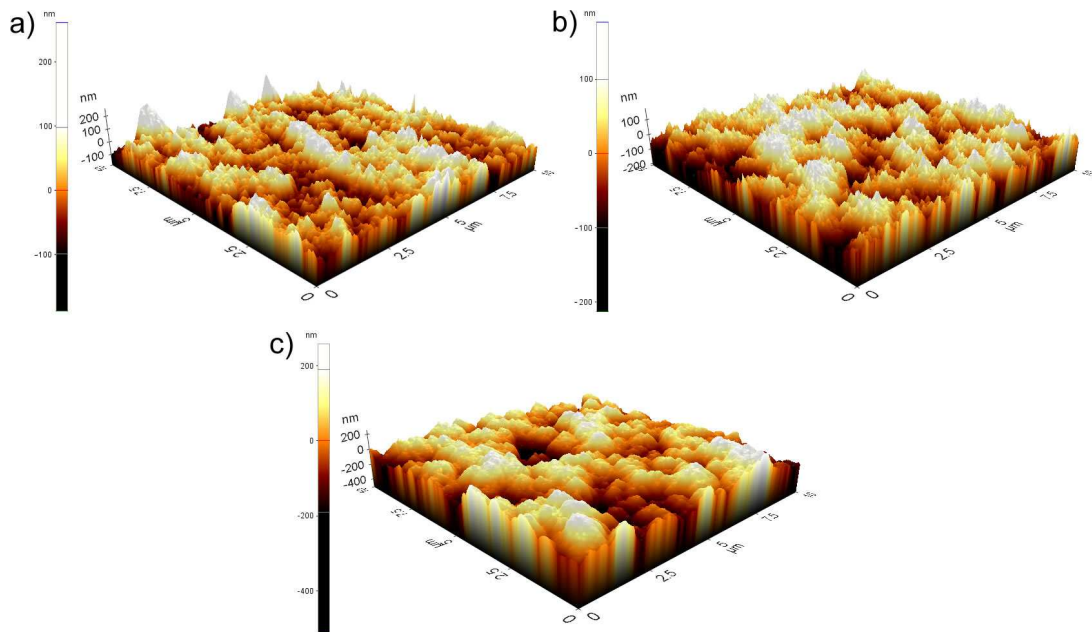


Figure 4.3: 3D AFM images of a) Me15-a, b) Me25-a, and c) Me35-a showing the affect of porosity on roughness.

coatings to be transparent. Both SEM images and TEM micrographs reveal that films are highly porous with pore sizes varying from nanometers to micrometer scale, which would result in high surface roughness required for superhydrophobicity. However, high surface roughness enhancing the superhydrophobicity lowers the transparency by scattering the light, when the roughness is higher than 100 nm [8, 12]. Surface topography of the films is investigated using AFM technique. $10 \times 10 \mu\text{m}^2$ regions scanned at non-contact mode are shown in Figure 4.3. From AFM images, it can be seen that all films have high roughness. Average surface roughness measurements have also been obtained from AFM measurements. Average surface roughness of asprepared Me15 and Me25 have been found to be around 40 nm, where this value is around 120 nm for Me35 film.

MTMS monomer is known to result in superhydrophobic and flexible bulk aerogels when supercritical drying is applied due to hydrophobic methyl groups present in the monomer which are directed through the surface [101]. In this work, we also used MTMS aerogel network structure with high enough porosity

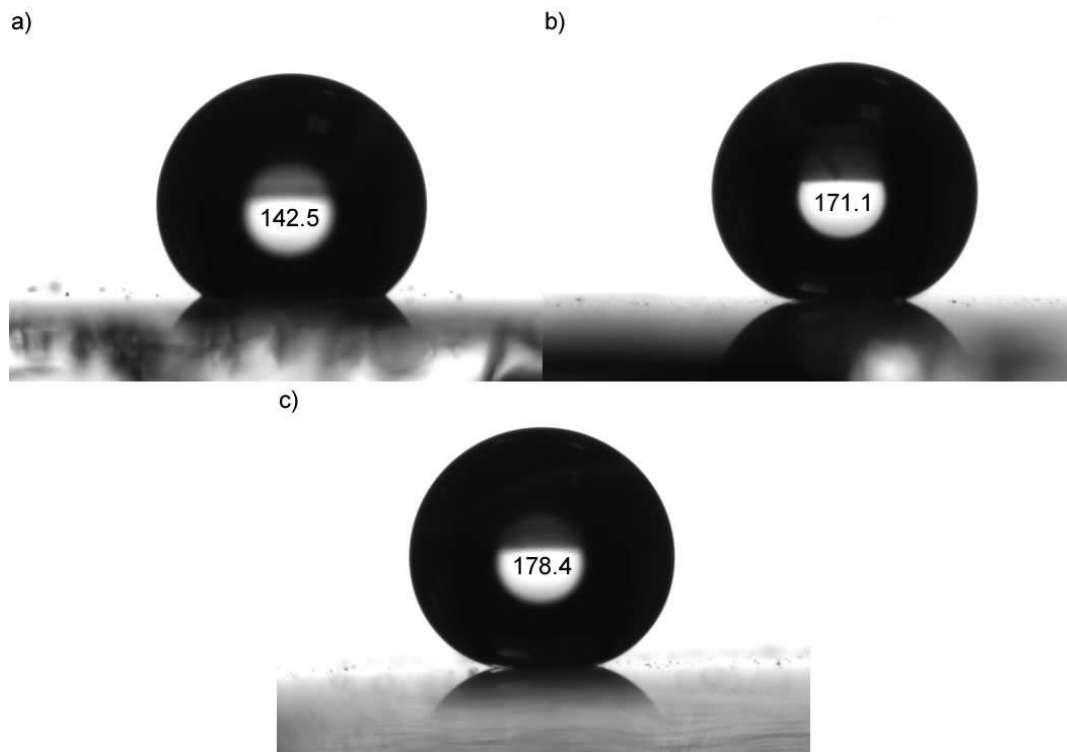


Figure 4.4: Photographs of a) Me15-a, b) Me25-a, and c) Me35-a taken during contact angle measurements showing how water stands on each surface, with measured values written inside the drops.

and roughness, in thin film form. In order to examine how water droplet stands on the surface, we used a contact angle measuring system. Sessile drop technique is applied. Water droplets of $4\ \mu\text{L}$ volume are dispensed onto surfaces and contact angles were measured. Photographs taken during contact angle measurements are shown in Figure 4.4. Contact angle of the films are found to increase with increasing fraction of the methanol used in the gel synthesis. Average contact angle of Me15-a is found to be 142.5° , where this value is 171.1° for Me25-a and 178.4° for Me35-5 where increases up to 179.9° after annealing. Based on the combined evaluation of SEM and contact angle measurements, it can be said that increasing macroporosity results in superhydrophobicity.

Optical transmission of the ormosil aerogel films coated on glass substrates has

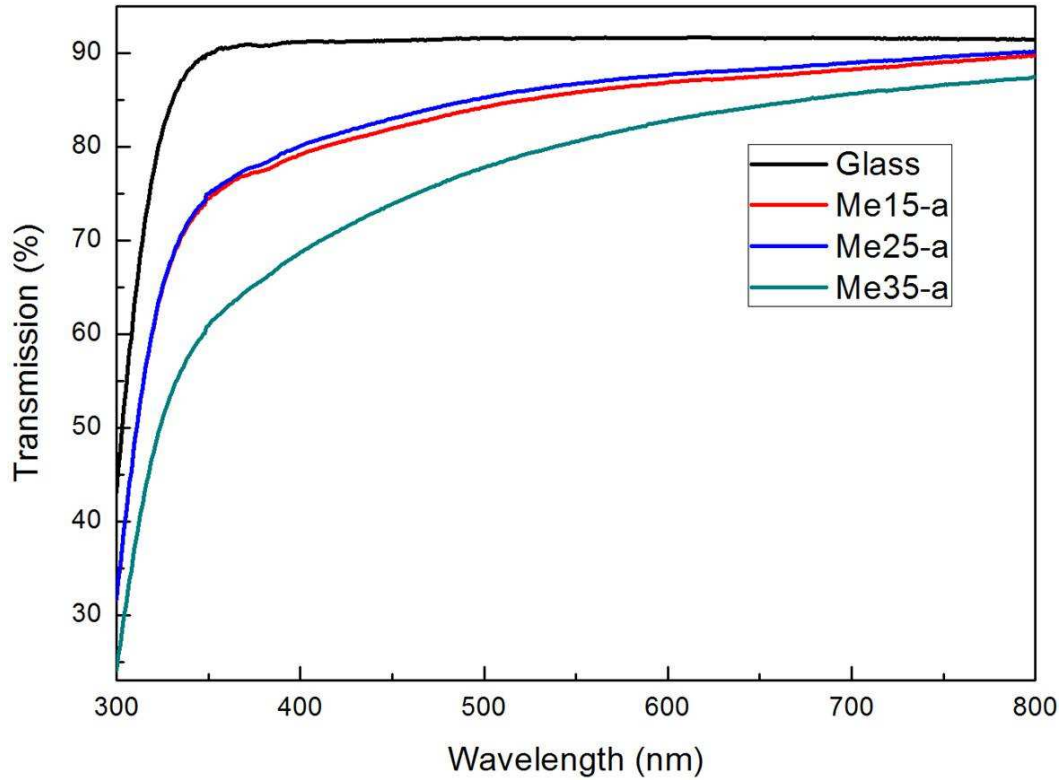


Figure 4.5: Transmission measurements of as prepared Me15 (red), Me25 (blue) and Me35 (green) with comparison to bare glass.

been measured using UV-vis spectrophotometer, given in Figure 4.5 in comparison to uncoated glass substrate. All films are found to be highly transparent but due to higher surface roughness, Me35-a exhibits lower transparency compared to Me15-a and Me25-a as expected.

Porosity of the films are monitored using TEM, SEM and AFM techniques, but for obtaining a quantitative analysis of the fraction of porosity, we used ellipsometric refractive index measurements. For calculation of porosity we used the equation [34]:

$$\pi = \frac{1.399 - n_D}{1.399 - n_A} \quad (4.1)$$

where π is the porosity, 1.399 is the refractive index of the nonporous film obtained from MTMS, n_D is the measured refractive index and n_A is the refractive

Table 4.1: Affect of composition and annealing conditions on physical properties such as contact angle, roughness, refractive index and porosity.

Film	Contact Angle ($^{\circ}$)	Roughness (nm)	Refractive Index	Porosity (%)
Me15-a	142.5 ± 1	39	1.16	60
Me15-b	170.4 ± 4.3	51	1.09	78
Me25-a	171.1 ± 2	41	1.16	59
Me25-b	164.8 ± 3.2	40	1.09	78
Me35-a	178.4 ± 1.5	120	1.10	75
Me35-b	179.5 ± 0.4	86	1.08	80
Me35-c	< 5	67	1.05	88

index of the air. Refractive index values of Me15-a and Me25-a are found to be 1.16, where it is found to be 1.10 for Me35-a indicating higher porosity of Me35 films. Porosity values for asprepared films are found to be 60 % for Me15 and 59 % for 25 films, where it is 75 % for Me35. Thicknesses of the asprepared films are also measured to be 550, 800 and 680 nm respectively for Me15, Me25 and Me35 using an ellipsometer.

Physical properties of the ormosil aerogel thin films are summarized in Table 4.1 based on their contact angles, roughness, refractive indices and porosity. Based on the evaluation of asprepared films (Me15-a, Me25-a and Me35-a), it can be concluded that lower mol fraction of methanol containing gels results in films with closer packing and lower porosity in addition to smaller average roughness. Similarly, contact angle is found to increase with increasing methanol fraction.

Annealing at 450 $^{\circ}$ C for 1h results in decrease in refractive indices with enhancement in porosity for all samples (Me15-b, Me25-b and Me35-b). This change is related to removal of some unreacted species trapped inside the gel structure during the heat treatment. In addition roughness is observed to generally decrease and contact angles increase due to removal of unreacted silanol groups during annealing at 450 $^{\circ}$ C [102]. Me35-b is found to exhibit contact angles as high as 179.9 $^{\circ}$. On the other hand, when it is annealed at 600 $^{\circ}$ C for 1h it becomes a superhydrophilic surface with water contact angles smaller than 5 $^{\circ}$.

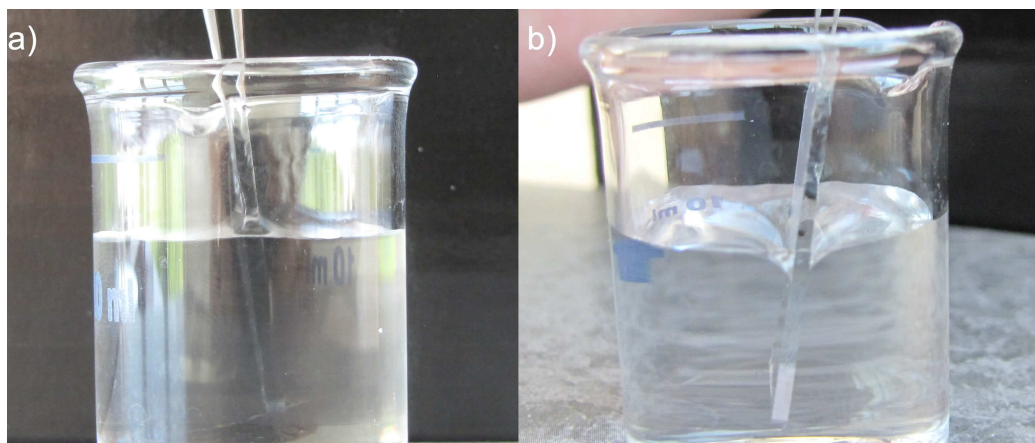


Figure 4.6: Photographs of a) bare glass dripped into water in comparison with, b) Me35-a coated glass.

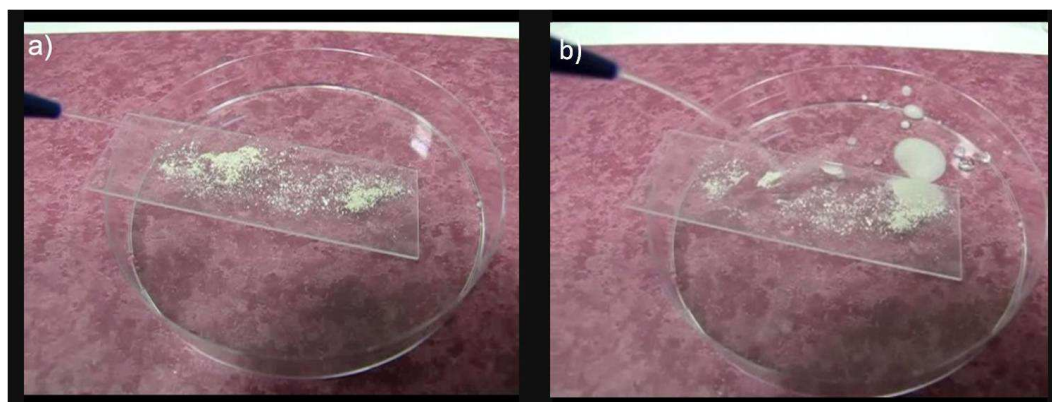


Figure 4.7: Photographs of Me35-a film indicating the self-cleaning property a) before water pouring, and b) after cleaning with water for less than 1 s.

Table 4.2: Water contact angles and sliding angles for Me35 coated different substrates, which exhibited superhydrophobicity upon coating.

Substrate	Contact Angles (°C)	Sliding Angles (°C)
Polyethersulfone	156.0 ± 3.3	3.8
Polysulfone	156.2 ± 2.9	2.3
Polyvinylidene fluoride	156.7 ± 3.3	2.3
Wood	170.1 ± 9.7	1.5
Wall tile	167.6 ± 4.2	2.3
Aluminum slab	172.8 ± 6.8	2.3
Cotton cloth	157.6 ± 4.9	3.1
Glass	178.4 ± 1.5	0.7

This drastic change results from decomposition of surface methyl groups, and their replacement by hydrophilic hydroxyl groups.

As Me35 exhibits the highest contact angles with superhydrophobic property, we investigated it in more detail. In order to visualize extreme water repellency of Me35-a it is dripped into a beaker full of water, Figure 4.6-b. For comparison, photograph of bare glass dipped into water is also taken, Figure 4.6-a. When bare glass is dipped, due to its hydrophilic character a concave meniscus forms between the water and the walls of the glass substrate. On the other hand, when Me35-a coated glass sample is dipped into water, a convex meniscus forms due to water repelling property of the superhydrophobic film. Air, trapped on the protrusions, can be easily seen on the film surface during dripping into the water, which minimizes the interaction between water and coating.

Self cleaning property of Me35-a film has been visualized by contaminating it with ZrO_2 nanoparticles. Water is poured onto the contaminated film surface with the help of a wash bottle. It is seen that water droplets touching the film surface removes the dirt while bouncing back from surface due to extreme water repellency of the ormosil aerogel coating, shown in Figure 4.7. First instances of water pouring are shown in Figure 4.7-a. While there are ZrO_2 powders initially at that region, with in a second those particles are seen bouncing from surface

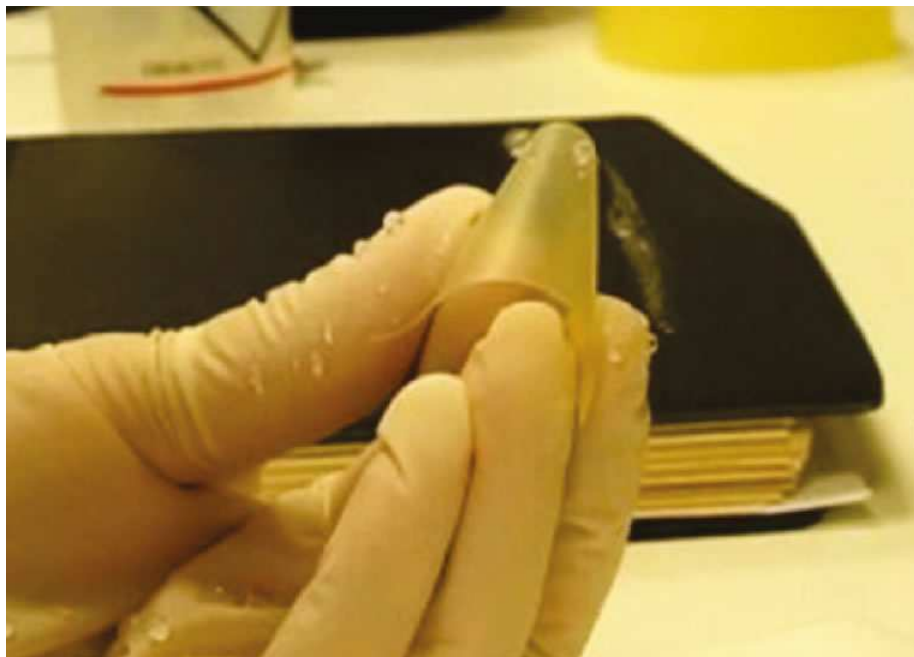


Figure 4.8: Rolling water droplets from Me35 coated polyethersulfone sample even when the film is bent.

inside the water droplets in Figure 4.7-b. After exposure to water droplets for 6 s, all particles were cleaned from superhydrophobic ormosil aerogel coated glass substrate. Sliding angle of the water droplets from Me35-a is found to be as small as 0.7° , which enables easily removal of striking water droplets.

Superhydrophobic aerogel ormosil thin films prepared in this work are suitable for many different surfaces including flexible substrates. Less cross-linked polymerization of ormosil compared to silica, due to presence of nonhydrolyzable methyl groups, provides flexibility to the skeletal structure. Me35 film is applied on many different surfaces including wall tiles, polymers, cotton and wood. It is found to exhibit superhydrophobicity in all substrates with sliding angles smaller than 4° , given in Table 4.2.

Superhydrophobic ormosil aerogel thin films coated on flexible substrates are found to preserve their superhydrophobic character even when the films are bent.

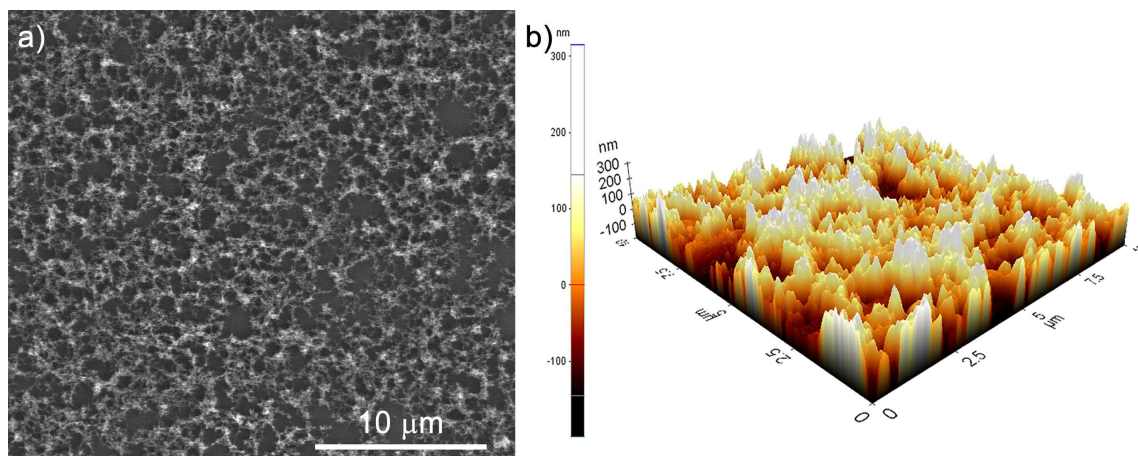


Figure 4.9: SEM image of Me35-c, and b) AFM image of Me35-c showing the effect of annealing at 600 °C for 1h.

Figure 4.8 shows how easily water droplets slide off the coated polyethersulfone sample, indicating the films are both flexible and superhydrophobic.

Affect of thermal annealing on physical and chemical structure of Me35 film is investigated in detail. SEM image of Me35-c (shown in Figure 4.9) reveal that, compared to asprepared Me35 film, the skeletal structure gets thinner. The size of the pores increase and the substrate surface becomes more apparent as a result of removal of the organic functional groups due to high temperature annealing. AFM results also indicate the thinning of aerogel structure after annealing. The average roughness decreases to 67 nm, where before annealing this value was 120 nm. Moreover, the large silica domains observed in Me35-a are absent in Me35-c due to removal of organic groups initially present all over the silica structure.

Based on the SEM images and AFM topography measurements, we expected the removal of methyl groups after annealing at 600 °C for 1 h. In order to check the validity of this assumption, we conducted some experiments. We obtained FTIR measurements from both Me35-a and Me35-c as shown in Figure 4.10. All peaks are assigned according to literature [2]. Intensity of the band around 3500 cm^{-1} observed for Me35-a diminishes for Me35-c which is an indication of C-H bonds. Moreover, bands around 1250 and 750 cm^{-1} are also very low in intensity

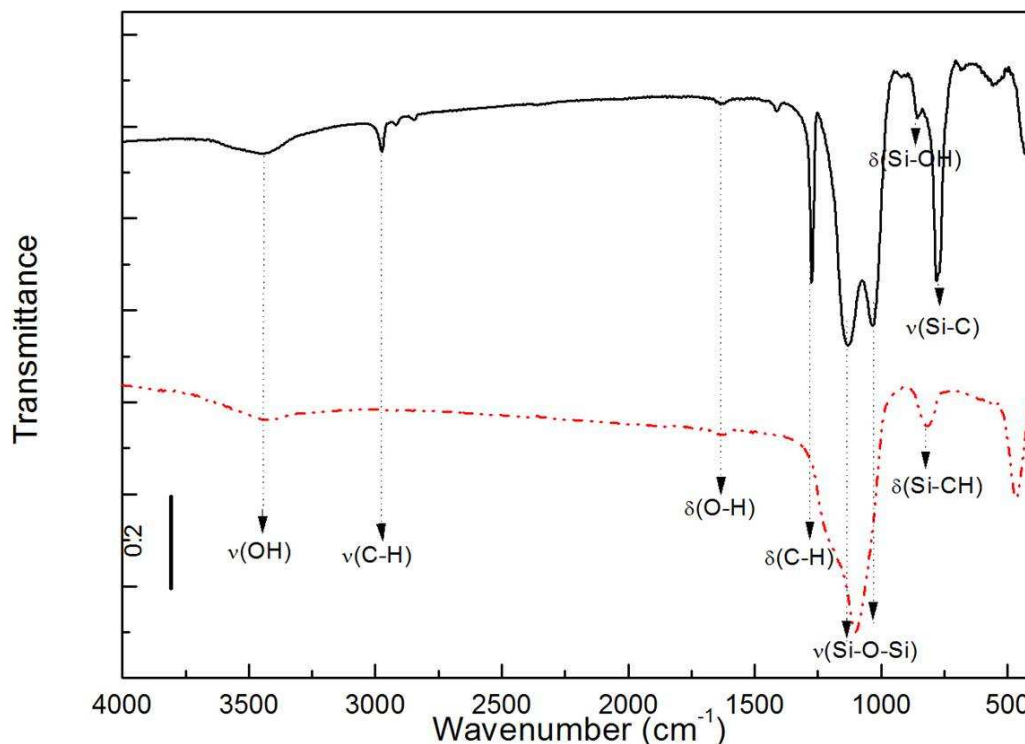


Figure 4.10: FTIR measurements of Me35-a and Me35-c indicating the decomposition of methyl groups after annealing at 600 °C for 1h.

for Me35-c compared to asprepared sample indicating removal of methyl groups. In addition, weak shoulder around 900 cm^{-1} observed in Me35-a is attributed to Si-OH bond, which is an indication of incomplete condensation of the gel structure.

In order to observe the decomposition conditions, DSC and TGA measurements are recorded for Me35 sample, Figure 4.11. In both measurements temperature ramp of 10 °C/min is used. A sealed pan is used in DSC measurement under nitrogen flow, where oxygen purge gas is preferred in TGA measurement for providing oxidation during decomposition. Both experiments indicate that decomposition starts after 300 °C. An exothermic reaction starts after 300 °C and continues up to 550 °C which is the maximum operation temperature we could achieve with aluminum pan. As platinum pan is used for TGA, we could

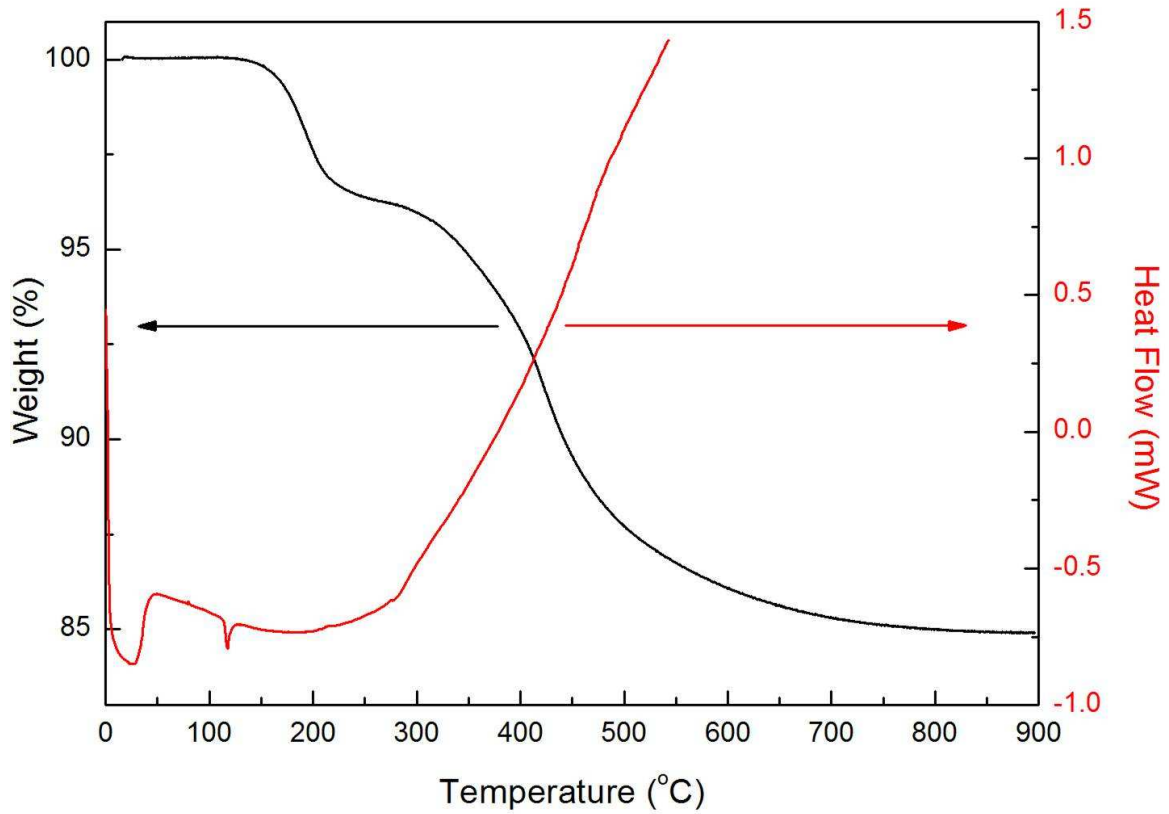


Figure 4.11: DSC and TGA measurements of Me35 sample for determination of decomposition conditions of methyl groups.

continue this measurement up to 900 °C. TGA measurement is further used for determination of the molecular formula of the ormosil aerogel structure. FTIR measurements (presence of Si-OH stretching vibration at 900 cm^{-1}) indicated that gel structure was incompletely condensed. Molecular formula of resulting incomplete condensation product is expected to be $\text{CH}_3\text{SiO}_{1.5-n}(\text{OH})_{2n}$, where it is expected to become SiO_2 after complete oxidation up to 900 °C under oxygen flow. We use the formula:

$$M = \frac{M_{\text{SiO}_2}}{81.5\%}, \quad (4.2)$$

Where M is the molecular weight of incomplete condensation product, M_{SiO_2}

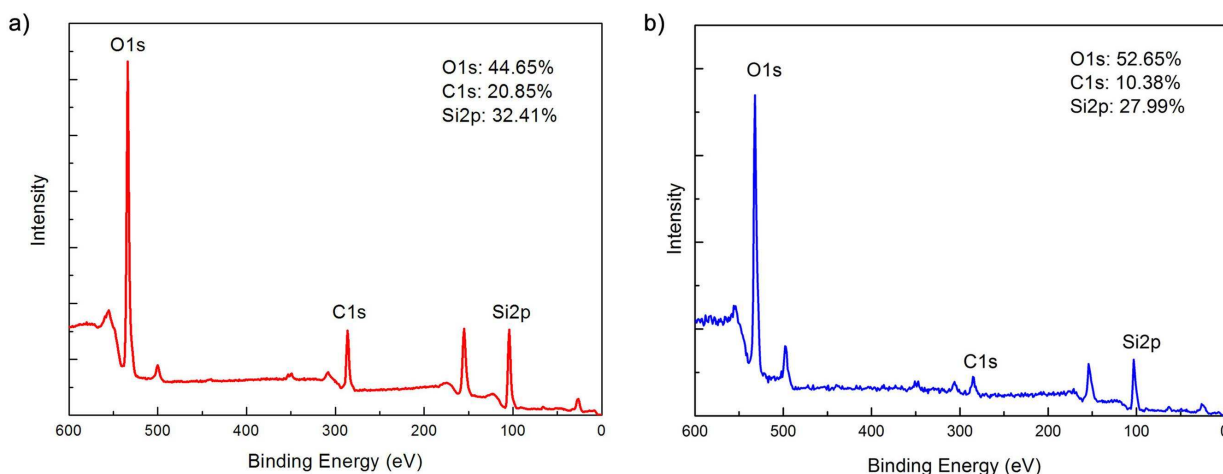


Figure 4.12: XPS results obtained from a) Me35-a and b) Me35-c indicating replacement of surface methyl groups by hydroxyls due to annealing at 600 °C.

is the molecular weight of SiO_2 , and 84.9 is the percentage of the solid remaining after calcinations. From this equation, we calculated the molecular formula of the gel structure as $\text{CH}_3\text{SiO}_{1.29}(\text{OH})_{0.42}$, where n value is 0.21.

During the thermal annealing, the replacement of methyl groups by oxidation is also demonstrated using XPS measurements, Figure 4.12. For Me35-a sample carbon content is found to be 20.85 % and oxygen percent is found to be 44.65 %. After annealing at 600 °C for 1h, these numbers become 10.38 and 52.65 % respectively. Indicating cleavage of hydrophobic Si-CH₃ bonds and replacement by hydroxyls which are hydrophilic. Due to high surface roughness of 67 nm measured by AFM, hydrophilicity is also enhanced and Me35-c film acts as superhydrophilic with water contact angle smaller than 5°, shown in Figure 4.13.

Transition of films from superhydrophobic to superhydrophilic is investigated in detail by monitoring the contact angles during application of various annealing temperatures for 1 h durations and varying the annealing durations at 600 °C, shown in Figure 4.14. Hydrophobic to hydrophilic transition temperatures are reported to be around 260 to 480 °C for bulk aerogels [101, 103, 104], and 500 °C for thin films obtained using MTMS monomer [2], where this temperature reaches

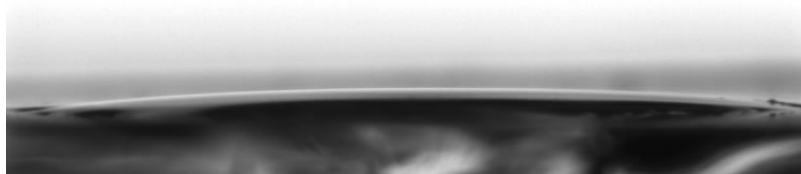


Figure 4.13: Photograph of 4 μL water droplet on Me35-c indicating superhydrophilic behavior with contact angle smaller than 5° .

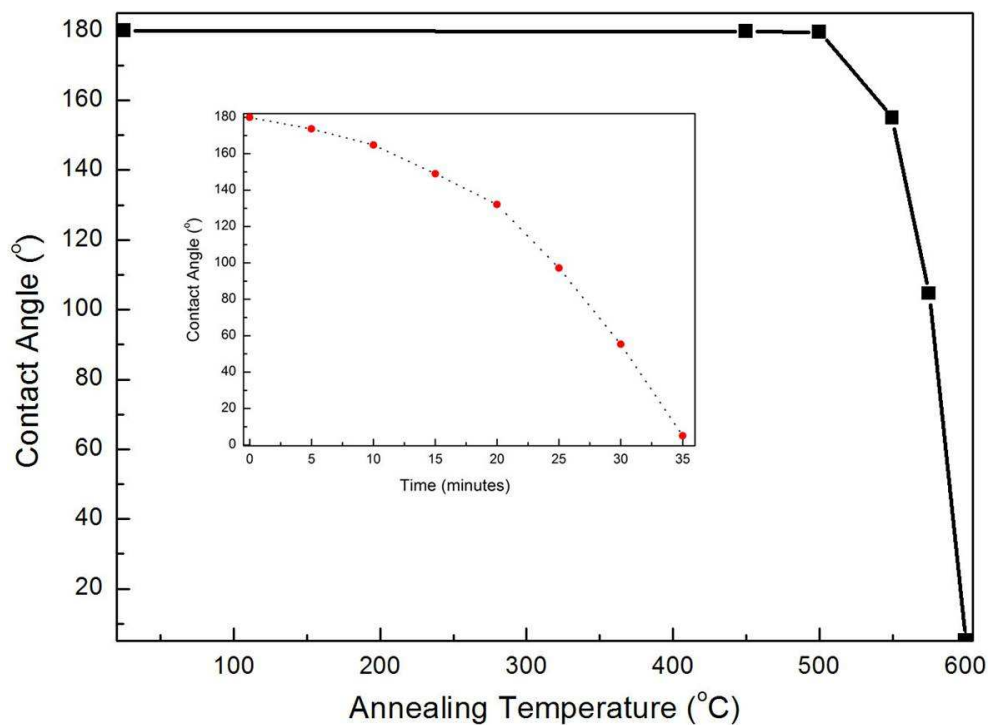


Figure 4.14: Change of contact angle as a function of annealing temperature for 1 h annealing durations, and as a function of annealing duration at 600 $^\circ\text{C}$ given as inset.

700 °C for methyltriethoxy silane monomer [96]. In our study, we observed that the contact angle remains unaffected up to annealing temperature of 500 °C, which shows that the ormosil aerogel thin films are thermally stable. For higher temperatures, contact angle start to continuously decrease, and finally after annealing at 600 °C, films become superhydrophilic. The time dependence of the contact angle during annealing at 600 °C is given in inset of Figure 4.14. This experiment indicates that complete transition to superhydrophilic takes 35 minutes. During this transition contact angle gradually decreases. The continuous change in contact angle dependent on the annealing temperature and duration indicates that ormosil aerogel thin film structures can be used for obtaining surfaces with desired contact angles by adjusting the annealing conditions.

During annealing, in addition to contact angle changes, transmittance and refractive indices of the films also changes due to removal of unreacted species and oxidation of methyl groups. Figure 4.15-a shows the photographs of Me35-a, Me35-b and Me35-c from left to right (as prepared, 450 °C 1 h annealed and 600 °C 1 h annealed respectively). From the photograph it is clearly seen that as annealing increases the transmittance. Transmission graph of these films also verifies this change in transparency due to annealing, Figure 4.15-b. Me35-c has been observed to be as transparent as bare glass. Moreover, it slightly exceeds the transmittance of bare glass for wavelengths larger than 600 nm exhibiting antireflective properties. For simplicity only Me15-c and Me35-c are shown here, but similar to Me15-c, transmittance of Me25-c exhibits better antireflective properties compared to Me35-c. This increase in transmittance following annealing can also be attributed to elimination of back reflections due to decreasing reflective index values after annealing in addition to decreasing surface roughness values and decreased scattering.

As indicated in Table 4.1 ormosil aerogels prepared using MTMS monomer by two step route at ambient conditions can be used as a trapping medium due to their high porosity. As reaction conditions and drying do not require elevated temperatures, it is possible to add organic molecules into the porous system. We have used a similar wet bench composition ormosil aerogel structure with 1:15:4.8 fractions of MTMS: Methanol: water which results in formation of hydrophobic

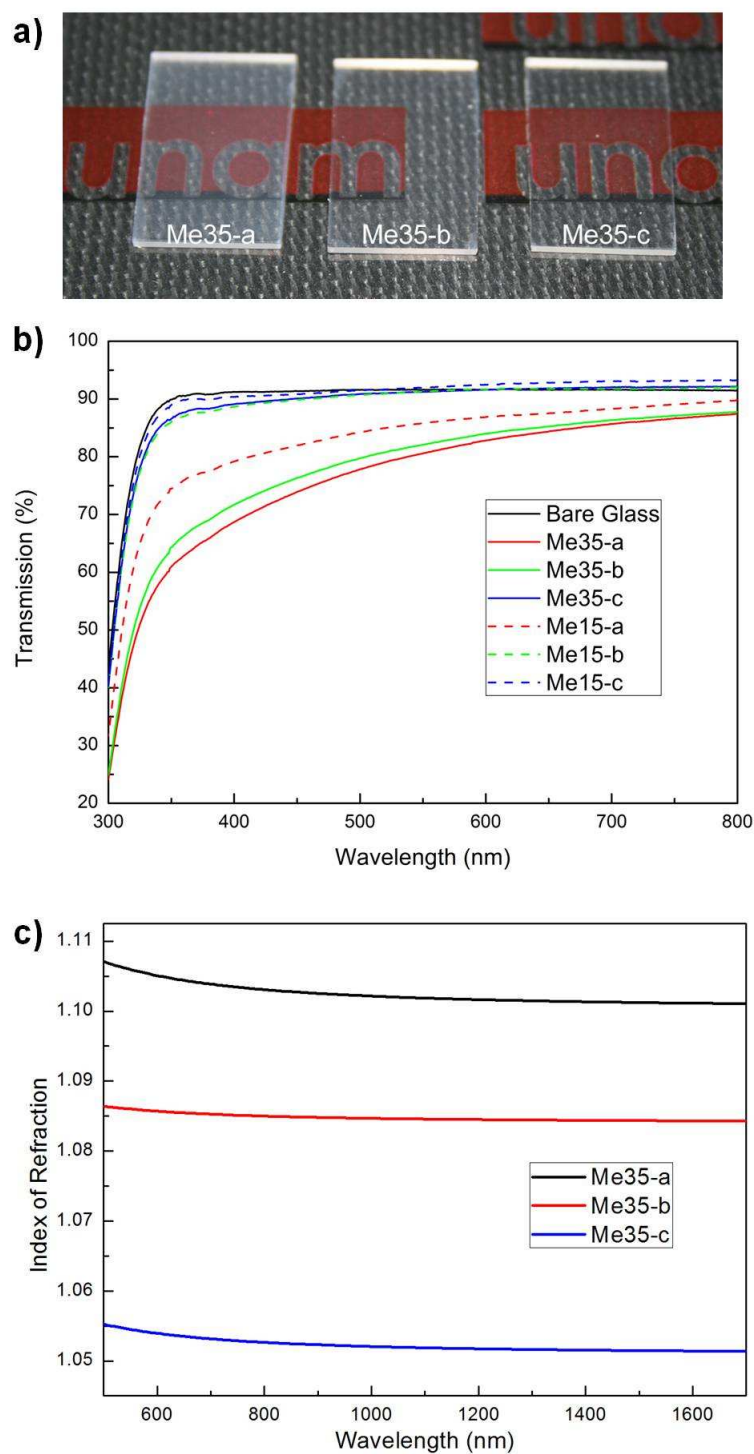


Figure 4.15: a) Photographs of Me35-a, Me35-b and Me35-c from left to right indicating the enhancement in transparency as a result of annealing. b) Transmission graph of Me35-a, Me35-b and Me35-c and Me15-a, Me15-b and Me15-c showing the increase in transmittance, and c) wavelength dependent refractive index measurements of Me35-a, Me35-b and Me35-c samples.

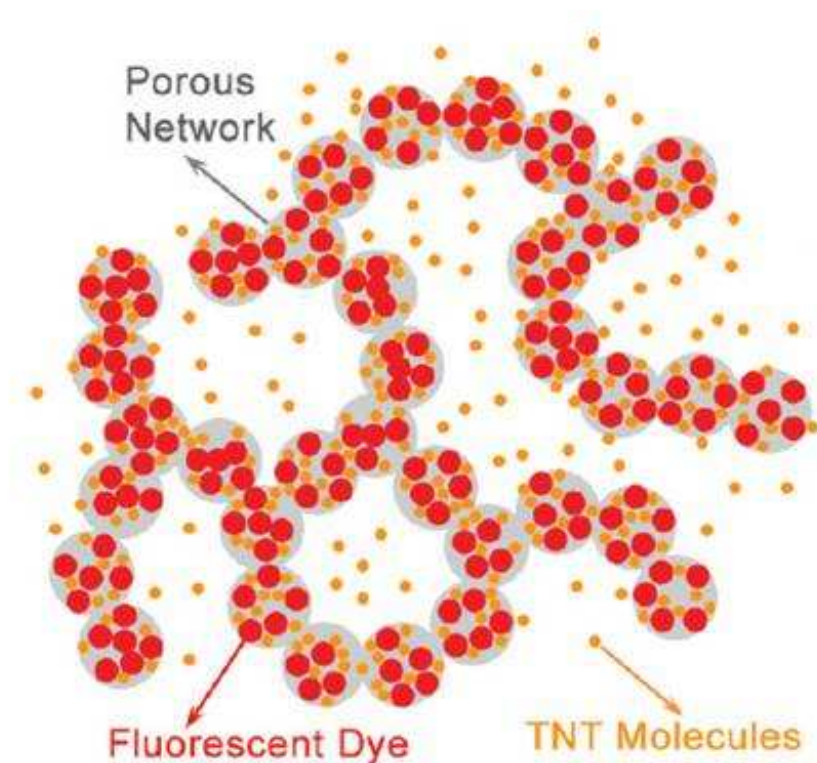


Figure 4.16: Schematic representation of dye molecules encapsulated into aerogel structure, interacting with the TNT molecules present in air.

structure where the fraction of 1:35:8 was used for preparation of superhydrophobic films [105]. Meso-tetrakis-p-carboxyphenylporphyrin (TCPPH2) dye is added into reaction mixture right after addition of base for catalyzing condensation reaction. Dye encapsulated ormosil aerogel structure is prepared for use in explosive (TNT) detection, due to changes observed in the fluorescence of dye molecules in the presence of TNT. Ormosil structure is intended to act as a scaffold for dye, increasing its area of interaction due to its highly porous structure. Normally similar structures have been prepared using mesoporous films, prepared by using surfactant molecules, which needs to be removed after the generation of pores [106]. During these washing steps, if the dopant (dye in this case) is not chemically bonded to the porous network, leakages can take place, where chemically bonding is another time and effort consuming problem [107, 108, 109].

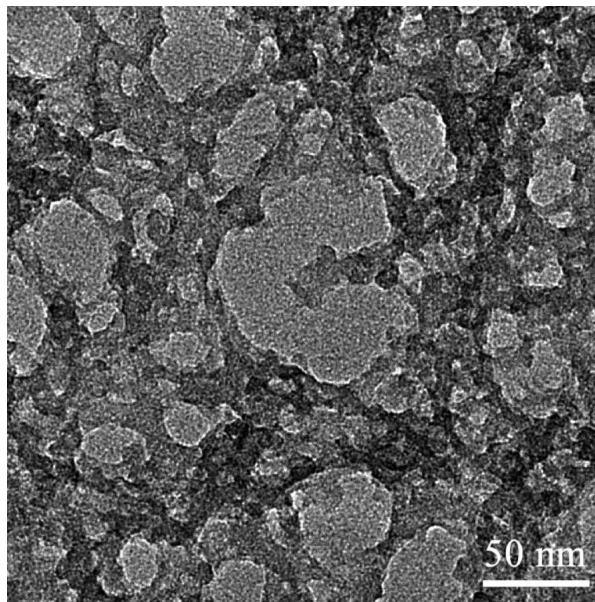


Figure 4.17: TEM image of porphyrin dye encapsulated ormosil thin film, showing the high nanoporosity.

In addition to being template free, ormosil films also has the advantage of being hydrophobic, which provides them long term atmospheric stability. In this work the dye is physically encapsulated into the network simply by dissolving inside the reaction solvent. As the mechanism is free of washing steps, it is a one pot approach, fluorescent ormosil thin films with porosity as high as 73.7 % are simply achieved. Figure 4.16 shows the schematic representation of dye molecules encapsulated inside porous ormosil aerogel thin film. High porosity of the film enables entrance of the TNT molecules present in the environment into the close proximity of the dye molecules present on the film surface. This way, TNT molecules can bind to dye molecules resulting in the quenching of the fluorescence due to electron transfer from electron rich porphyrin dye to electron withdrawing nitro aromatic ring.

Highly porous structure which enables fast detection of the analyte molecules is shown in Figure 4.17. Porphyrin molecule is found to be physically unaffected after encapsulation based on the UV-vis and fluorescence measurements. The

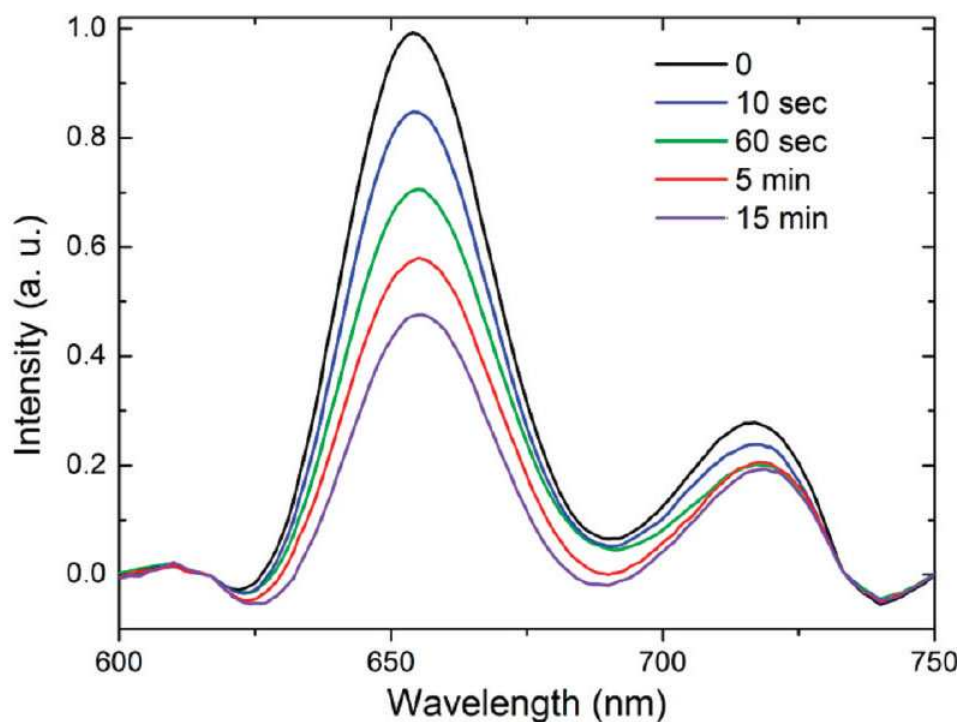


Figure 4.18: Time dependent fluorescence quenching experiment on porphyrin encapsulated ormosil.

absorption band of dye molecule corresponds to 420 nm, which is exactly at the same position when dye is inside ormosil network. Moreover, fluorescence emission peak is observed to be at 650 nm for both dye in ethanol and dye in ormosil thin film, indicating that obtained thin film structure is suitable for TNT detection.

For examination of hybrid ormosil films fluorescence quenching experiments are conducted by placing films to saturated TNT atmosphere. This is provided by placing small amount of TNT with a piece of cotton into a closed vial and keeping at room temperature over night. Prepared films are found to react very fast to the presence of TNT molecules. When we compare the fluorescence intensity of the film before interaction with the analyte, even 10 s of exposure results in 8.6 % quenching in fluorescence. This number becomes 28.2 % in 60 s and 50 % in 900 s. Same experiment is also repeated using dinitro toluene (DNT) as the analyte

molecule, which has a similar structure to TNT. In the first instance it behaves comparable to TNT with quenching efficiencies of 10.3 % in 10 s and 20.6 % in 60 s. However, in long term it stays around 30 % after 900 s exposure, indicating higher binding efficiency of TNT with the dye.

Chapter 5

SYNTHESIS AND CHARACTERIZATION OF FLEXIBLE, MECHANICALLY STABLE ANTIREFLECTIVE COATINGS FROM ORMOSIL COLLOIDS

Antireflective coatings have high technological importance due to their application fields such as solar cells, display screens and optical lenses, where reflection losses are the limiting factor for higher efficiencies [10, 11, 12] . It is possible to use many different techniques for fabrication of antireflective coatings, such as use of monolayer coatings, graded index coatings, binary and triangular grating structures [65]. Even though, graded index structure and triangular grating structures can provide antireflection in broad band, other two are much easily processed. Moreover, easiest among these strategies is application of a monolayer coating with constant refractive index. When the glass is chosen as substrate, optimum index of refraction for an antireflective coating should be 1.22 according to Fresnel equation with a thickness of $\lambda/4$ [110]. Homogeneous materials with such low refractive index do not exist, thus in order to obtain this low refractive index values, air needs to be introduced into materials in form of pores [10]. Moreover, sizes of the pores should be small enough to eliminate Rayleigh scattering.

Thus nanoporous films need to be used which have been prepared up to date by techniques such as sol-gel [111, 112, 113], chemical vapour deposition [48], phase separation in polymers [63, 114], layer by layer deposition [10, 49]. However, most of these coatings are deposited on rigid substrates and lack of flexibility in addition to being high cost and energy consuming. On the other hand low cost and flexible antireflective coatings would be very desirable for flexible electronics and photovoltaic applications.

In this chapter, we report a facile method for preparation of flexible nanoporous ormosil thin films with antireflection property and high mechanical stability at ambient conditions [115]. It is known that methyltrimethoxysilane (MTMS) monomer can result in formation of cyclic, cage-like structures of methylsilsesquioxane due to phase separation [101, 116, 117]. Phase separation can be eliminated either using surfactant molecules [117], non-alcoholic polar solvents like dimethyl sulfoxide [118], or using a co-monomer which does not contain any organic groups [119]. In this work we used tetraethylorthosilicate (TEOS) as co-monomer for obtaining transparent ormosil gels. Prepared gels are ultrasonically broken into ormosil colloidal particles which yield antireflective films. Colloidal suspensions are successfully applied to glass and cellulose acetate substrates, and they are found to be flexible with preserving their antireflectivity after many cycles of bending. Thickness and porosity of the films can be tuned changing the dilution amount during sonication and changing the fraction of co-monomers. The adhesion of the films to the glass substrates are tested by adhesive tape test and their mechanical stability is tested by water dripping and pencil hardness tests. Films are found to be highly stable against bending, water dripping and adhesive tape tests. Moreover, antireflective films are found to exhibit antifogging properties after annealing at 600 °C in addition to antireflection properties.

5.1 Synthesis of Antireflective Ormosil Thin Films

Antireflective ormosil thin films have been prepared using co-condensation of tetraethylorthosilicate (TEOS) and MTMS monomers by using slightly modified two step acid-base catalyzed sol gel route [43]. Similar to preparation of super-hydrophobic ormosil aerogel structures, initially x mL ($0 \leq x \leq 1$) of TEOS and $1x$ mL of MTMS were dissolved in 9.74 mL of methanol. Following the addition of 0.5 mL of 10 mM aqueous oxalic acid solution the reaction mixture was stirred for 30 min and left for hydrolysis for 24 h at room temperature. Following the hydrolysis, 0.40 mL of ammonium hydroxide (26 %) and 0.21 mL of water were added drop wise into the reaction mixture in order to catalyze the condensation. The gelation times vary depending on the TEOS fraction and increasing TEOS fraction results in prolonged gelation times. Following gelation, all films were aged for 2 days in order to strengthen gel network.

Aged gels were diluted with 15 mL methanol and ultrasonically homogenized using liquid homogenizer probe for 45 to 75 s at 20 W power. Obtained colloidal suspension was spin coated on cleaned glass, silicon, cellulose acetate substrates at 2000 rpm for 45 s. In order to obtain better antireflection, films were preferentially applied on both sides. Before application to the second side, films were either left to dry at ambient conditions overnight or at vacuum oven at 50 °C for 15 min.

Films are named according to their TEOS fraction. T25 means 25 volume percent TEOS and 75 volume percent MTMS containing film, where T100 means 100% TEOS containing film.

5.2 Characterization of Thin Films

Surface morphology of the films is characterized using SEM technique. 10,000 and 150,000 magnified SEM images for T0, T25, T60, T80 and T100 films with scale bars of 10 μ m and 500 nm are shown in Figure 5.1. These images clearly

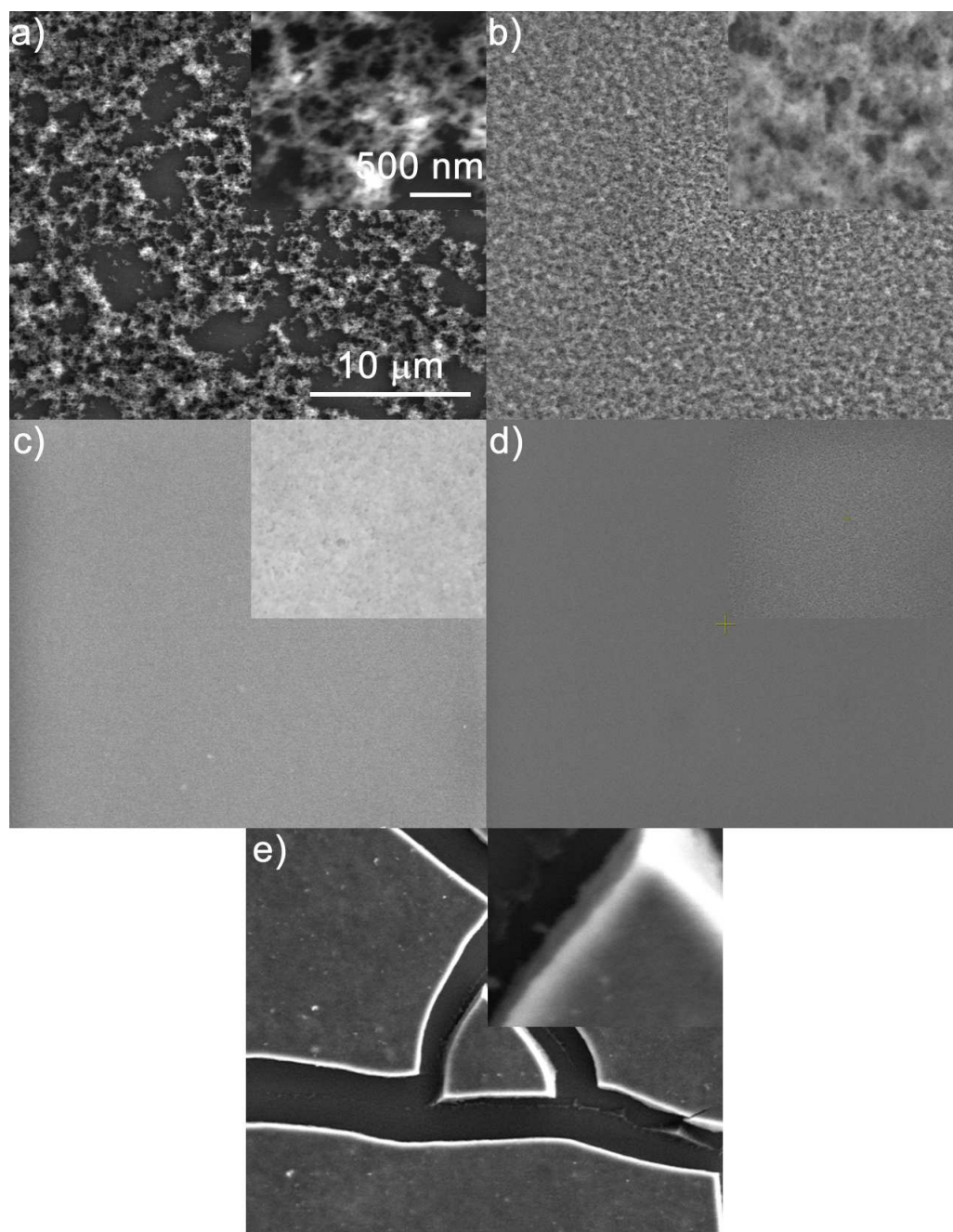


Figure 5.1: SEM images of a) T0, b) T25, c) T60, d) T80 and e) T100 films, showing the decrease in pore sizes with increasing TEOS fraction.

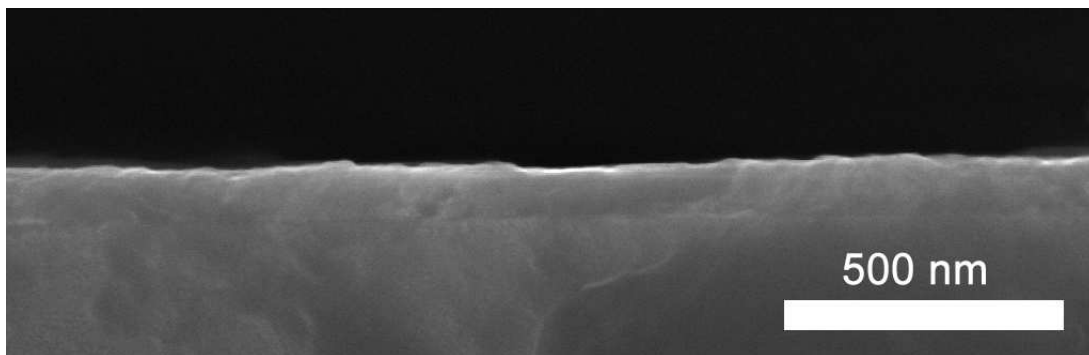


Figure 5.2: Cross sectional SEM image of T60 film on silicon substrate with thickness around 100 nm.

reveal that as the TEOS fraction increases, the micrometer sized pores disappear. Thus more uniform films are obtained with better surface coverage.

Both high and low magnification SEM images of T0 film indicate that there are large pores and when these areas come close, they result in a few micrometer diameters uncoated regions on the substrate. On the other hand, with addition of 25 % TEOS, T25 film has all pores smaller than 100 nm, which results in better surface coverage. As the fraction of TEOS further increased, pore size distribution is seen to be more uniform with decreasing pore sizes. T60 film is found to have smaller pores than T25, where T80 film has even smaller pores than T60. One reason of this smaller and more uniform pore formation can be attributed formation of smaller domains with increasing TEOS fraction. On the other hand, methyl group of MTMS is the functional group which provides spring-back and flexible character to the ormosil structure. Thus, an optimum amount of MTMS needs to be used for obtaining porous and uniform film formation. T100 is shown in Figure 5.1-e which is composed of pure TEOS monomer. It does not seem to contain any pores, because it does not contain any hydrophobic functional groups which can eliminate capillary tension during drying. More over it is only composed of rigid Si-O-Si bonds and does not have any flexibility. It is seen to be shrunk and cracked because of these reasons, where T80 film is porous and uniform.

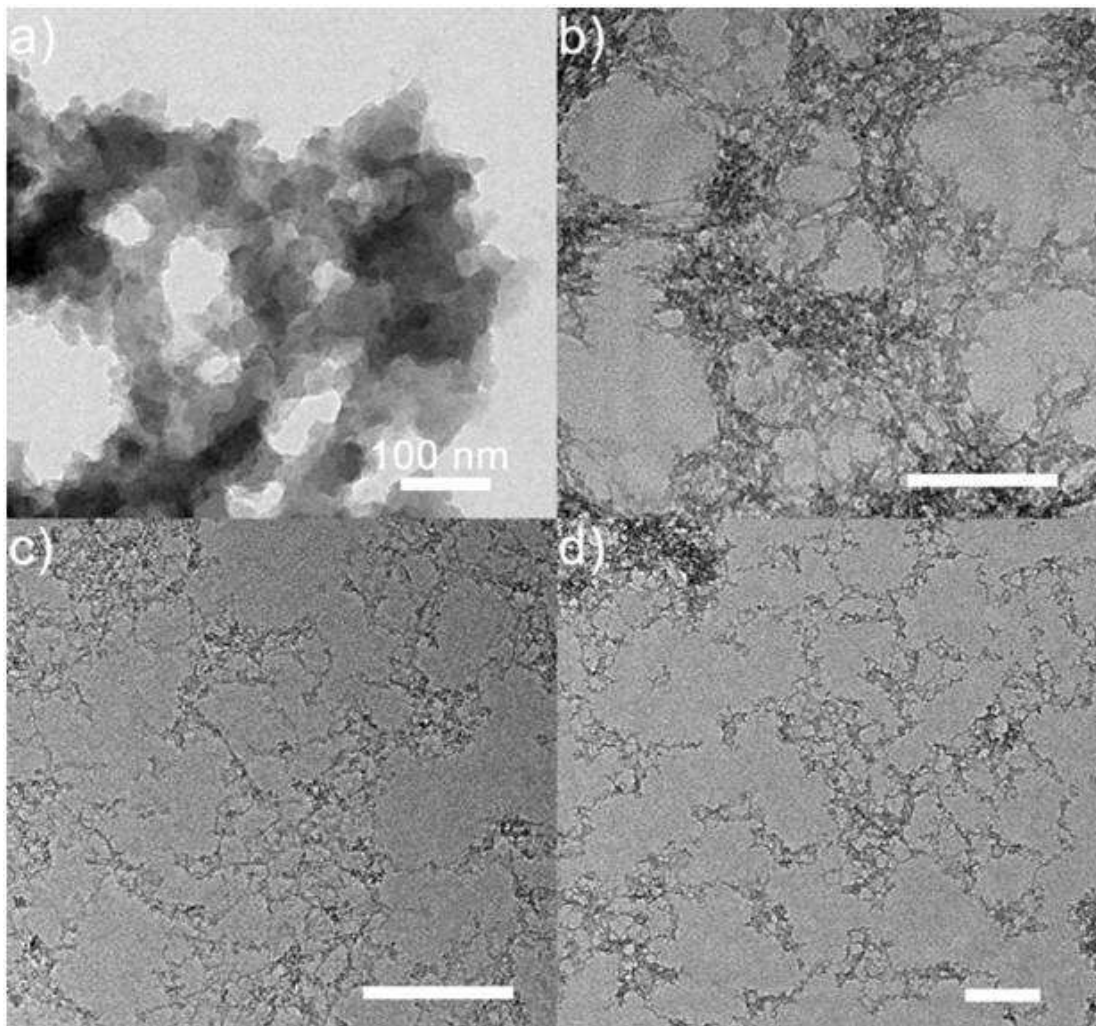


Figure 5.3: TEM micrographs of a) T0, b) T25, c) T60, and d) T80 films, showing the skeletal structures getting thinner with increasing fraction of TEOS, with scale bars of 100 nm.

Cross sectional SEM images are used for the determination of homogeneity of the film thickness. For this purpose T60 film is coated onto a silicon wafer for minimizing charging as we do not apply any conductive coatings before imaging. In order to provide a continuous and undamaged crack like cut we initially immerse coated substrate into liquid nitrogen for a few minutes, then hit onto the substrate. A cross sectional SEM image of T60 is shown in Figure 5.2. Film is seen to have a thickness of 100 nm. The film thickness seems to be uniform all over the film.

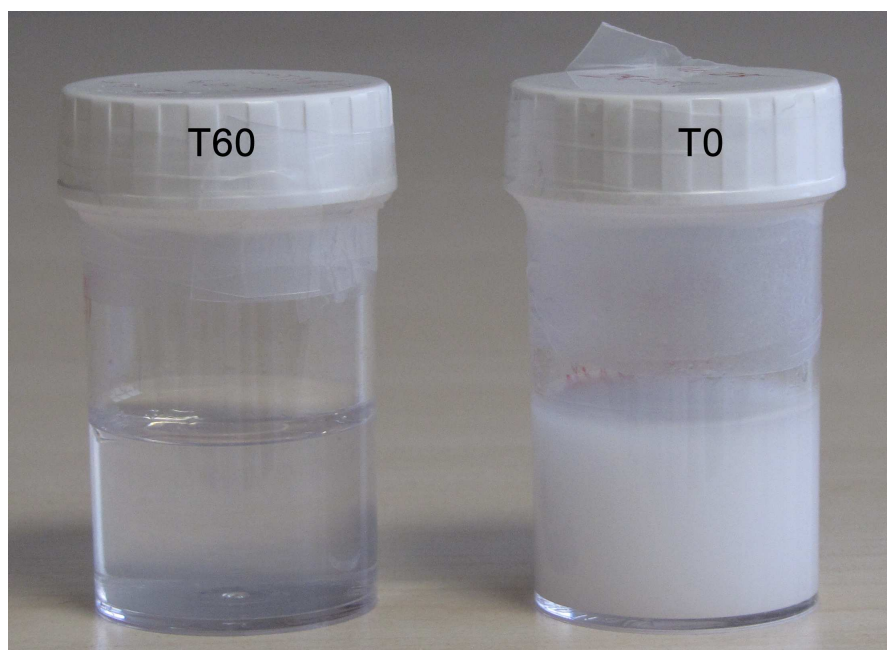


Figure 5.4: Photographs of T60 and T0 gel indicating the phase separation free, transparent gel formation for hybrid compositions.

Skeletal structures of ormosil films have been investigated using TEM technique. Samples are prepared using colloidal suspensions used for film preparation, Figure 5.3. T0 film is seen to be composed of silica domains of approximately 20 nm in diameter, surrounded by pores with various sizes. On the other hand T25 is composed of domains smaller than 10 nm. T25 has much thinner skeletal structure compared to T0 and as the fraction of TEOS increases to 80 % (T80), domain sizes decrease with decreasing pore sizes. Moreover, as estimated from

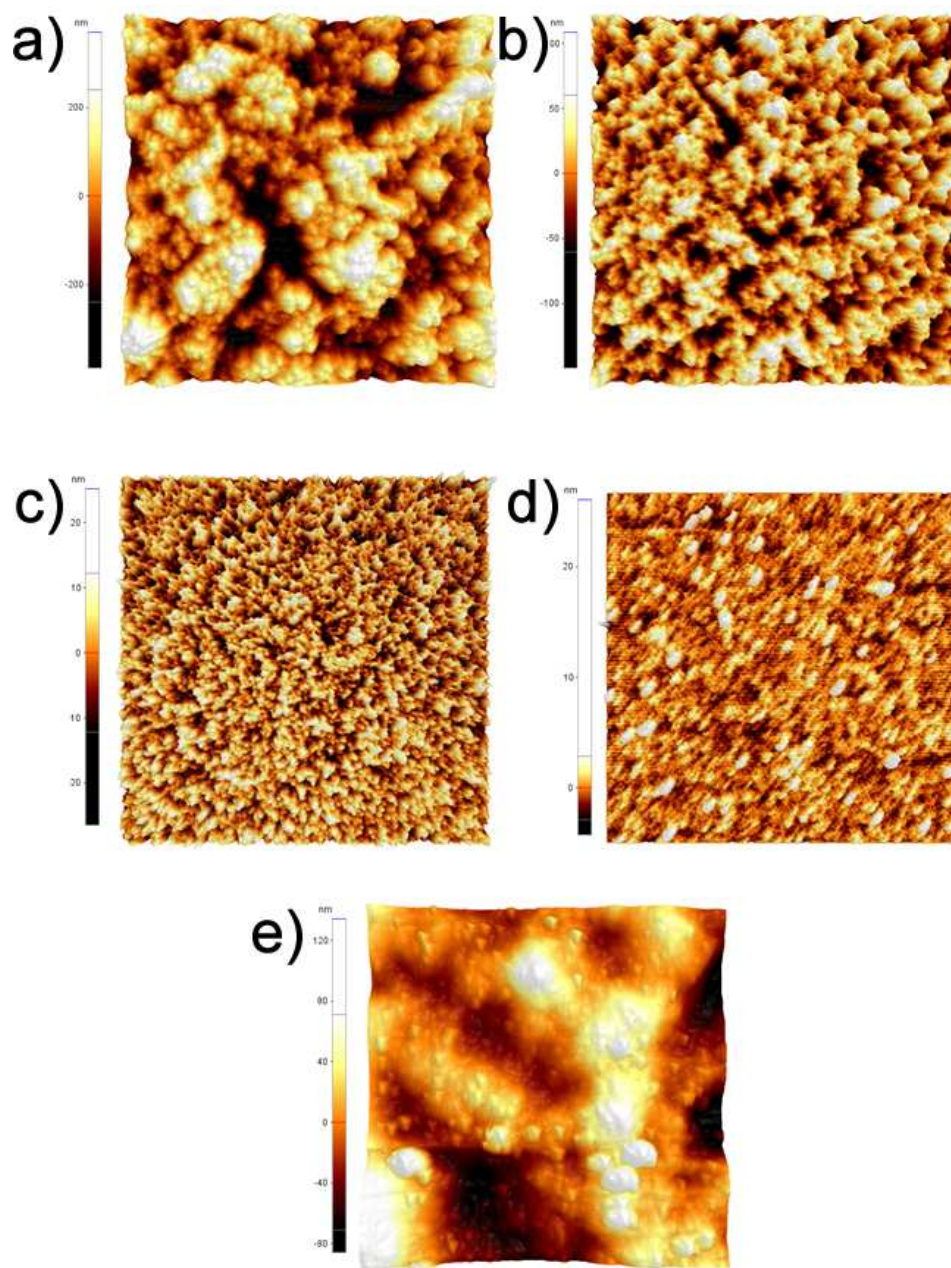


Figure 5.5: AFM images of a) T0, b) T25, c) T60, d) T80, and e) T100 films indicating hybrid films have better surface coverage with uniform pore size distribution, where T0 has pore distribution over a wide range and T100 is nonporous.

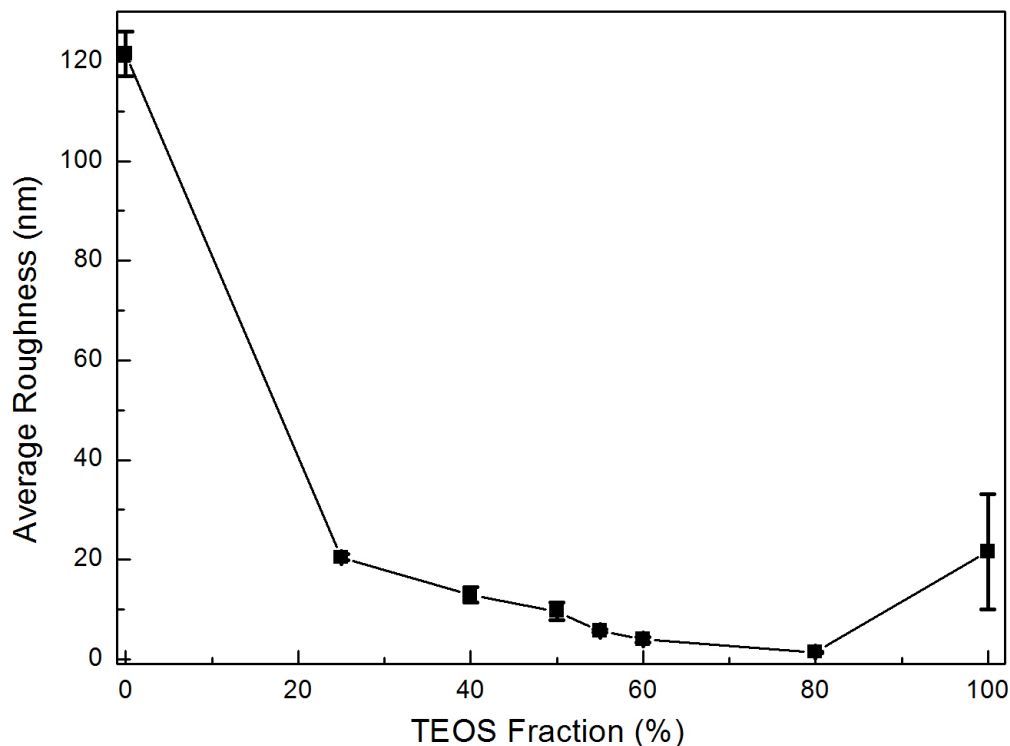


Figure 5.6: Plot showing change in average roughness of the films with respect to changing TEOS fractions.

SEM images, pore size distribution gets narrower, which would result in formation of more homogeneous films with smaller roughness values.

Photographs of T60 and T0 gels are shown in Figure 5.4. T60 gel containing 60 % TEOS is completely transparent, where T0 gel, composed of 100 % MTMS is opaque due to phase separation of methylsilsesquioxane species. Even though the T0 gel is opaque, thin films obtained from colloidal suspensions of it are highly transparent with transmittance of 80 % at 600 nm. As phase separation in hybrid films is prevented, they result in formation of antireflective films. We observed that addition of 25 % TEOS results in highly transparent gels but after

40 %, completely transparent gels are obtained.

Surface topography of the prepared films is investigated using AFM technique, Figure 5.5. AFM images obtained from $10 \times 10 \mu\text{m}^2$ regions are in accordance with the results obtained from SEM and TEM, indicating that TEOS-MTMS hybrids result in more uniform film formation compared to bare TEOS or bare MTMS. While there are larger domains and uncoated regions visible for T0 (Figure 5.5-a), the domain sizes decrease for increasing TEOS ratios and surface coverage becomes better with lower height differences between adjacent domains. Similar to T0, T100 is also been found to be highly rough, but with lack of pores due to their collapse during drying.

Surface roughness values are evaluated by taking the average of 3 different $10 \times 10 \mu\text{m}^2$ regions scans of AFM in non-contact mode. In order to obtain antireflection surface roughness needs to be kept under 50 nm for prevention of scattering. As a result of decreasing pore sizes and fine surface coverage observed in SEM images, hybrid films are expected to have low surface roughness values. Plot of average surface roughness vs. TEOS fraction is given in Figure 5.6. It is seen that while the average roughness of T0 is 122 nm, this value falls down to 20.4 nm with addition of only 25 % TEOS. With increasing fraction of TEOS average roughness continuously falls down to 1.4 nm for T80 film. For hybrid films with such low roughness, scattering due to roughness can be ignored. On the other hand, T100 film has higher roughness compared to hybrid film due to its shrunk and cracked structure.

Refractive index values of films are measured using spectroscopic ellipsometry technique, and porosity of the films are calculated on the basis of refractive index-porosity relation which uses comparison of nonporous films from same composition to the porous films [34]. Results obtained for hybrid films with TEOS fractions varying between 25 to 80 % are shown in Figure 5.7. Expected on the evaluation of SEM and TEM images, as fraction of TEOS increases index of refraction almost linearly decreases. Refractive index of the films can be tuned in the range of 1.17 to 1.23 by changing the TEOS fraction with porosity varying

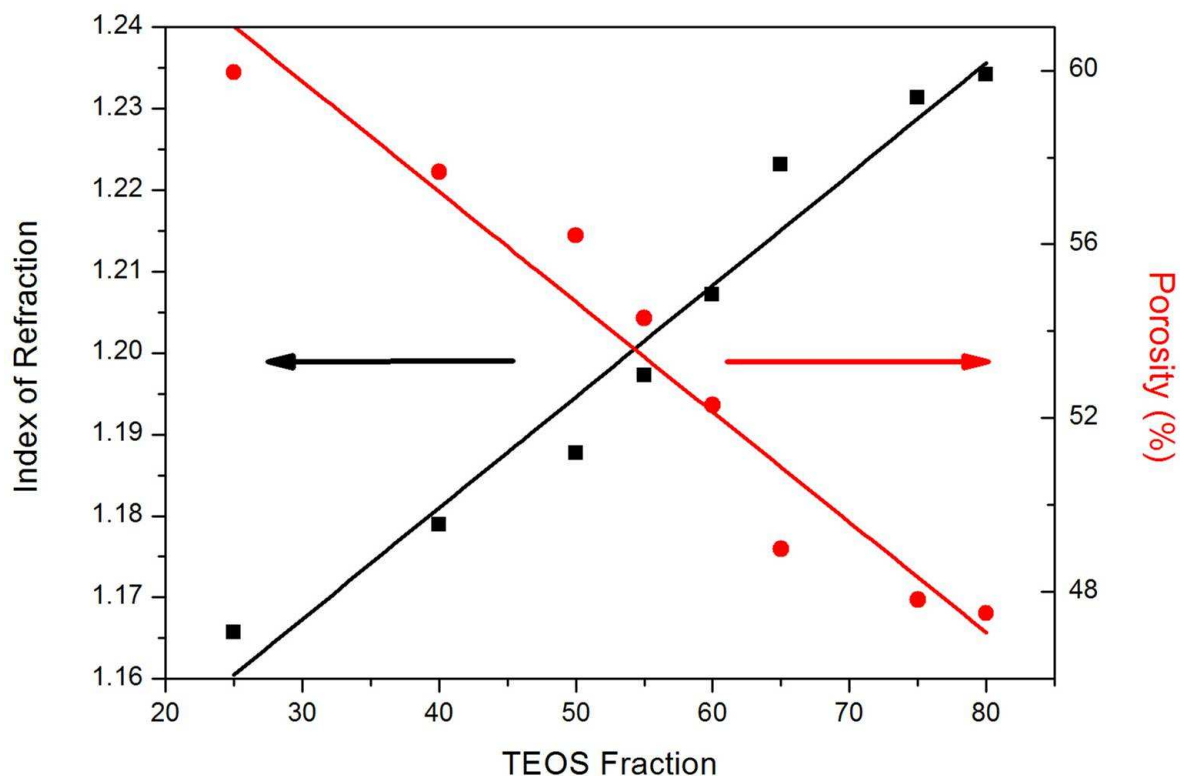


Figure 5.7: Plot of index of refraction and percent porosity with respect to TEOS fraction, indicating increasing TEOS fraction results in decreasing porosity.

from 60 to 48 %. As TEOS fraction increases, hydrophilic nature increases, flexibility and hydrophobicity which provides spring back are reduced. Thus tendency of pores collapse increases, which results in lower porosity. However, only 20 % MTMS containing T80 film is found to have significant porosity (48 %), where T100 film is shrunk and nonporous.

Transmission graphs of hybrid films coated on both sides of the glass substrates with comparison to T0, T100 and bare glass are given in Figure 5.8. As expected from their low roughness and refractive index values, all hybrid films exhibited antireflective properties. In order to get maximum transmission in the visible region, the thicknesses of the films are adjusted to be around 125 nm, which will be discussed later. Even though, T25 (shown in red) is also antireflective, T60 and T80 exhibits better antireflection properties. For T80 (shown

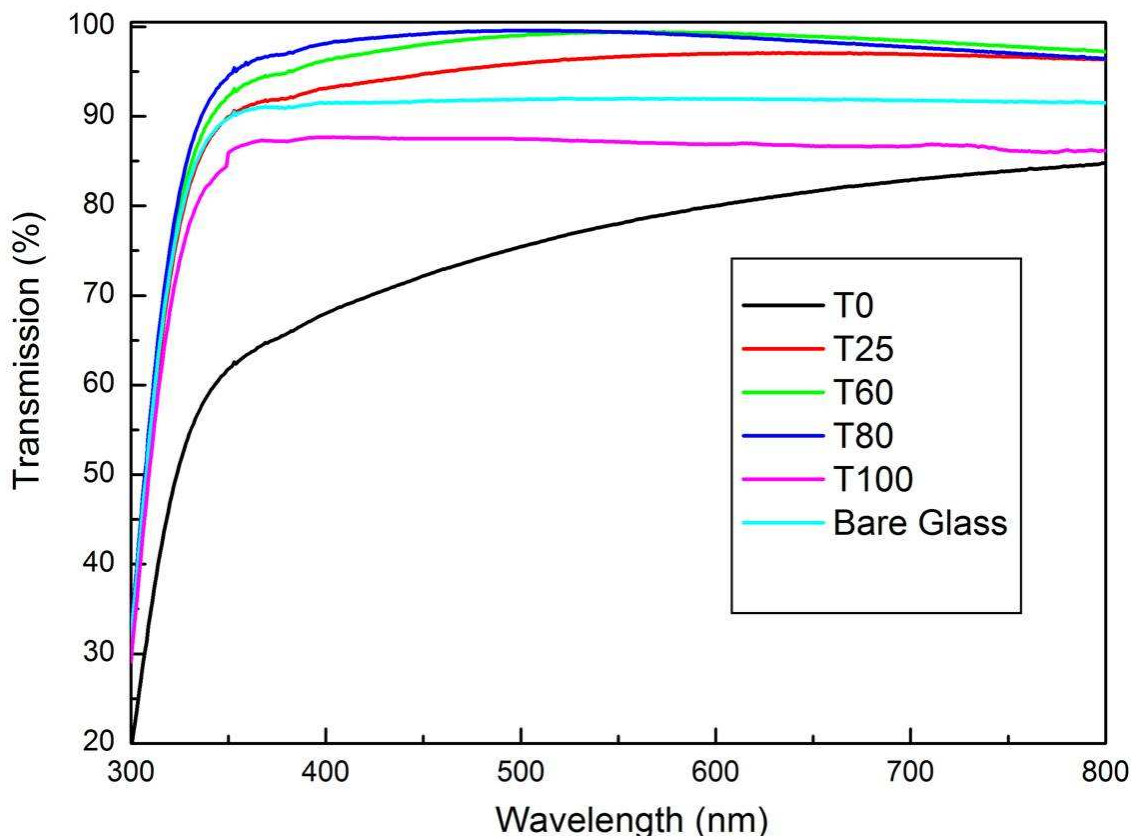


Figure 5.8: Transmission graph of T0, T25, T60, T80 and T100 films with comparison with bare glass showing the antireflection property of hybrid films.

in blue), maximum transmittance of 99.58 % is observed at 510 nm, where this value is 99.43 % for T60 (shown in green) observed at 550 nm. T100 and T0 are found to have lower transmittance compared to bare glass because of their non-uniform or cracked surface which scatters light.

As the best antireflection properties are observed for T60 and T80 films and there is no significant difference in their transmission values, we preferred to continue the detailed analysis of films using T60 because it is expected to exhibit more flexible character and higher porosity. It is mentioned before that porous MTMS ormosil films have flexible character. In order to examine whether TEOS-MTMS hybrid films have flexibility, we applied these films on flexible cellulose

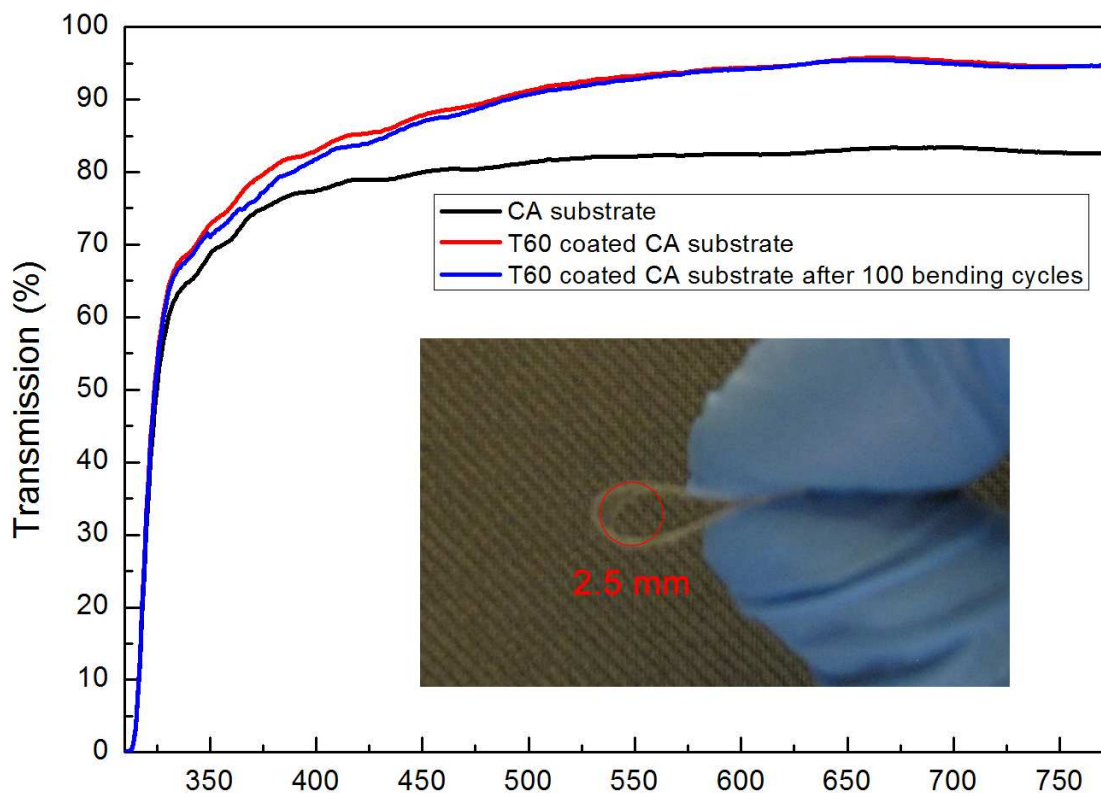


Figure 5.9: Transmission measurements of double side T60 coated cellulose acetate substrate before and after 100 bending cycles with a bending diameter of 2.5 mm. inset shows the bent CA substrate.

acetate (CA) substrates. Then transmission measurements are conducted before and after bending the samples. CA substrate can be bent up to a diameter of 2.5 mm, and for further bending plastic deformation takes place inside the polymer substrate, so the T60 coated CA substrates are bent up this limit cyclically for 100 times for flexibility test, shown in Figure 5.9. Bare CA substrate has a transmission around 80 %, where T60 coated substrate exhibits around 95 % transmission. Moreover, after 100 cycles of bending, the transmission of the coated substrate does not significantly change. Similar results have been obtained for T0, T25 and T80 films, not shown here. As T60 is found to be flexible, it is expected that T0 and T25 would also be flexible because their organic functionality providing monomer fractions are higher than T60, which provides flexibility. However, T80,



Figure 5.10: Photographs of hybrid ormosil coated and bare CA substrates visualizing antireflective property of coatings.

which has smaller fraction of MTMS compared to T60, is also found to be flexible according to bending tests. This indicates that even 20 % MTMS can provide both spring back effect and flexible character to TEOS-MTMS hybrid ormosil films.

Photographs of T60 coated and bare CA substrates are given in Figure 5.10 taken under ambient day light. It is clearly seen that bare CA substrate highly reflects incident light, thus acts as a semi opaque sample by preventing the transmittance of the light to the colored Bayindir Group logo underneath. On the other hand, coated substrate does not reflect the light, thus logo can be clearly seen.

Film thickness plays a crucial role in light transmission, because maximum light transmission is obtained for thickness of $\lambda/4$, where λ is the wavelength. Thus, in order to adjust the desired wavelength of maximum transmission, one needs to adjust the film thickness. For this purpose, we changed the amount of solvent used for dilution just before sonication from 5 mL to 20 mL with increments of 2.5 mL each time. Following each dilution, suspension is sonicated for additional 5 s for providing homogeneous dilution. Change in thickness with

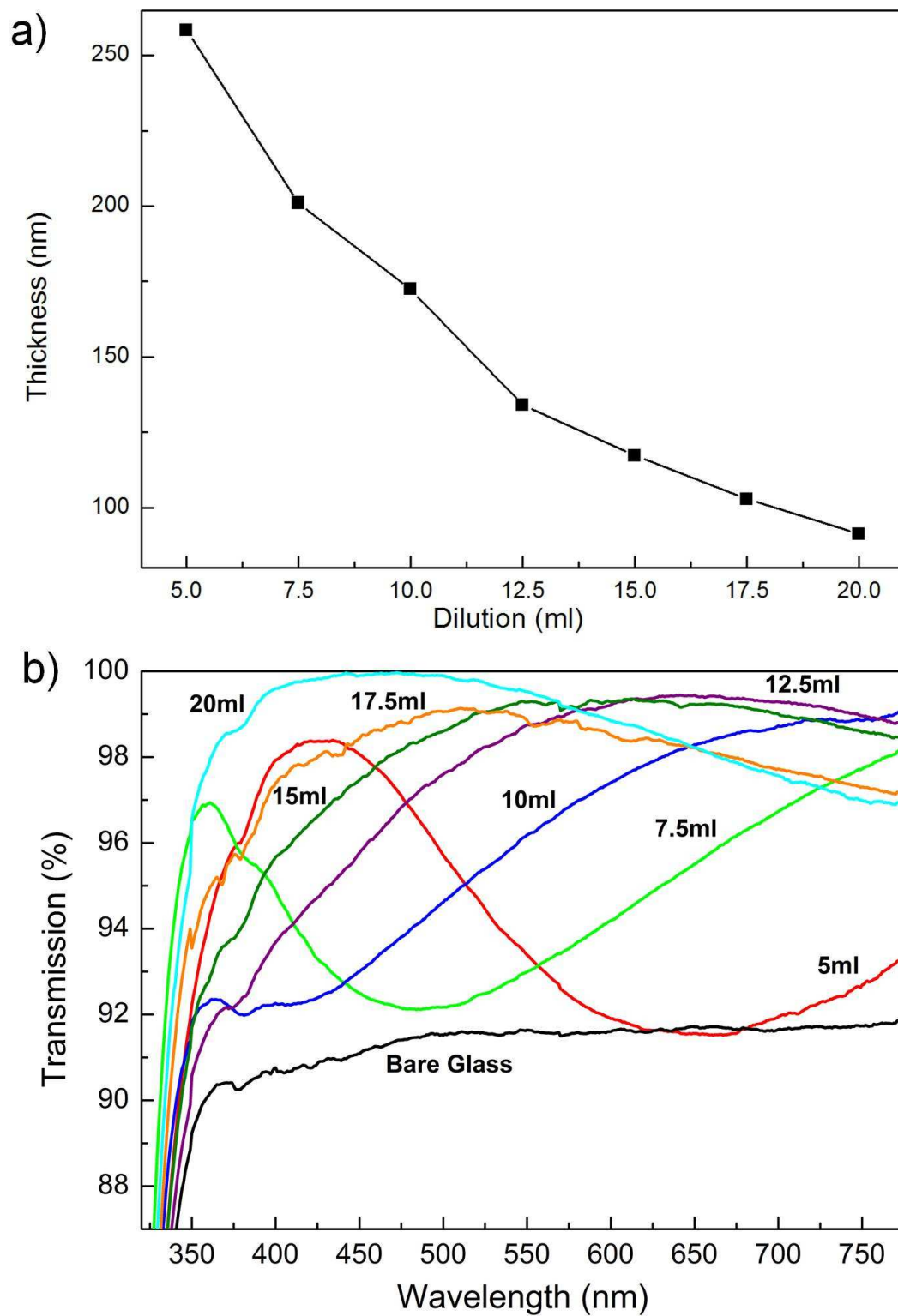


Figure 5.11: For T60 film a) change of thickness with respect to dilution amount, b) change in transmission according to dilution.

respect to dilution volume graph is given in Figure 5.11-a. Figure 5.11 clearly shows that with every dilution film thickness almost linearly decreases. While the thickness of 5 mL diluted film was measured to be 260 nm, this value reaches 90 nm after 20 mL dilution. This graphic can be used for obtaining a desired film thickness in the range of 260 to 90 nm. The change of transmittance with respect to changing dilution graph is given in Figure 5.11-b. This graph indicates that T60 film for all dilution amounts exhibits antireflective property. Moreover, maximum transmission shifts to lower wavelengths with increasing dilution of the colloidal suspension. The maximum point of 5 mL diluted film is in infra-red region, but for 7.5 mL diluted T60, this value is around 800 nm, where for 20 mL diluted film it is around 450 nm.

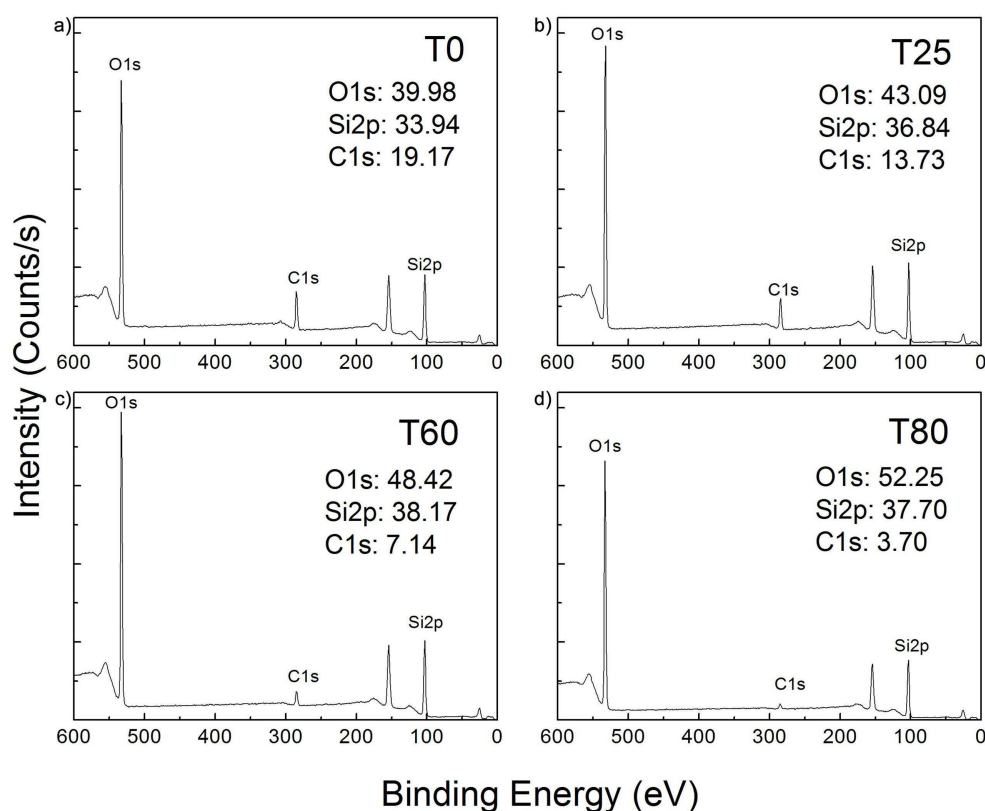


Figure 5.12: XPS results of a) T0, b) T25, c) T60 and d) T80 for monitoring change in organic content.

Chemical compositions of prepared films are investigated using XPS technique by scanning relative ratios of oxygen, carbon and silicon. With increasing ratio of TEOS from 0 to 80 %, fraction of carbon atoms are found to decrease from 19.17 to 3.70 % with oxygen fraction increasing from 39.98 to 52.25 % due to replacement of nonhydrolysable methyl containing MTMS with TEOS, given in Figure 5.12.

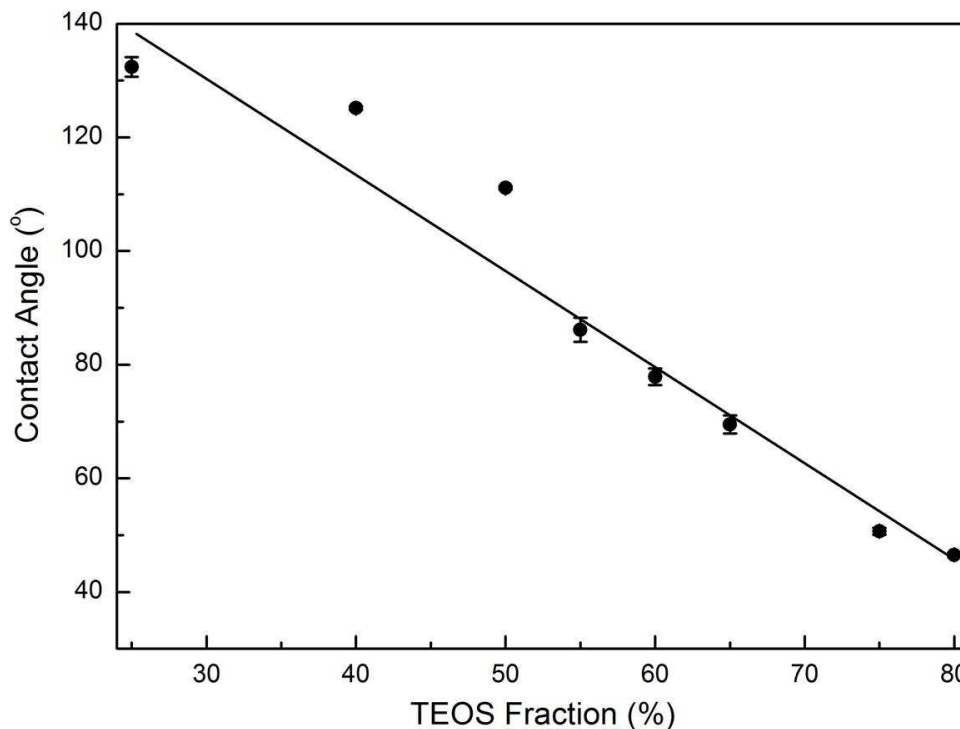


Figure 5.13: Change of contact angle with respect to TEOS fraction, indicating the increase in hydrophilicity with increasing TEOS.

Water contact angles observed for hybrid films are plot against their TEOS fractions are shown in Figure 5.13. As expected, this graph shows that the contact angles decrease with increasing TEOS ratios used for gel preparation. This change in contact angle is found to be almost linear for hybrid films. It varies between 140° to 40° for hybrid films, where it is measured to be 178.4° for T0 and 23.3° for T100, indicating the it is related to presence of surface methyl groups.

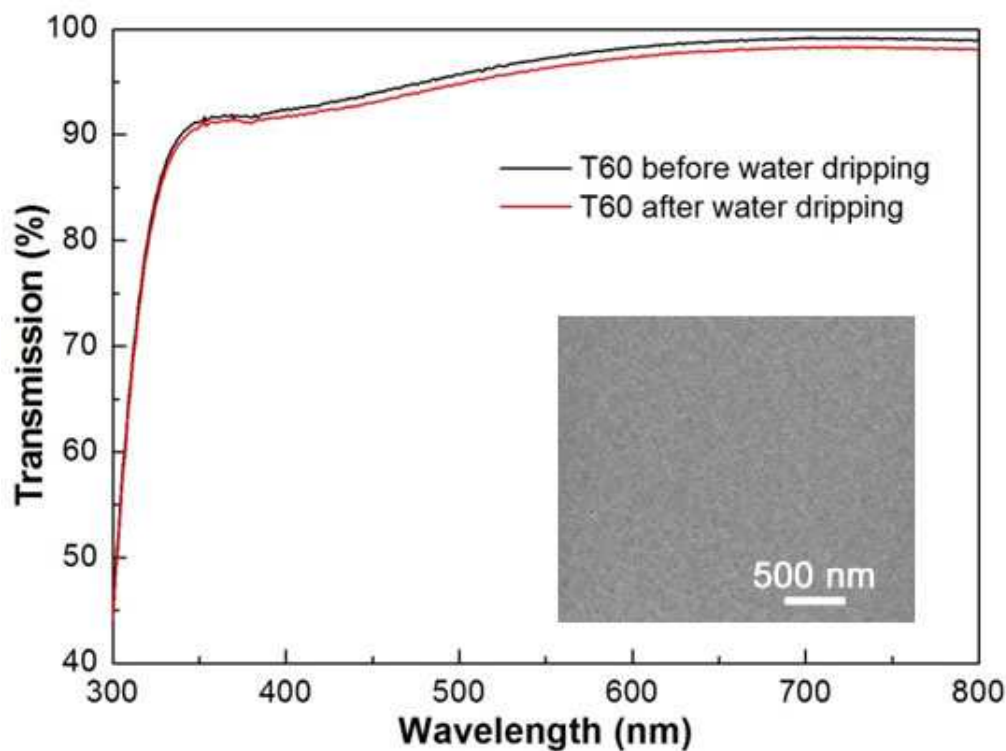


Figure 5.14: Transmission plots of T60 before (black line) and after (red line) 90 h of water dripping indicating that the film is mechanically stable.

For testing the mechanical stability of T60 film water dripping, pencil hardness and adhesive tape tests have been applied. In water dripping test, tap water droplets were falling from 30 cm to the 45° inclined coated substrate surface for 90 h. Transmission of the film is measured before and after water dripping test and we observed that only 0.9 % decrease after approximately 324,000 droplets (Figure 5.14). This result indicates that the film is mechanically highly stable. SEM image given in Figure 5.14 as inset also indicates that after excessive water dripping, porous morphology of the film remains unaffected. Similar results are obtained for other hybrid films with slight decrease in transmission after 24 h water dripping under same conditions.

For testing the adhesion of the porous film, adhesive tape test is performed. In this test a scotch tape is pressed on T60 coated glass surface by applying

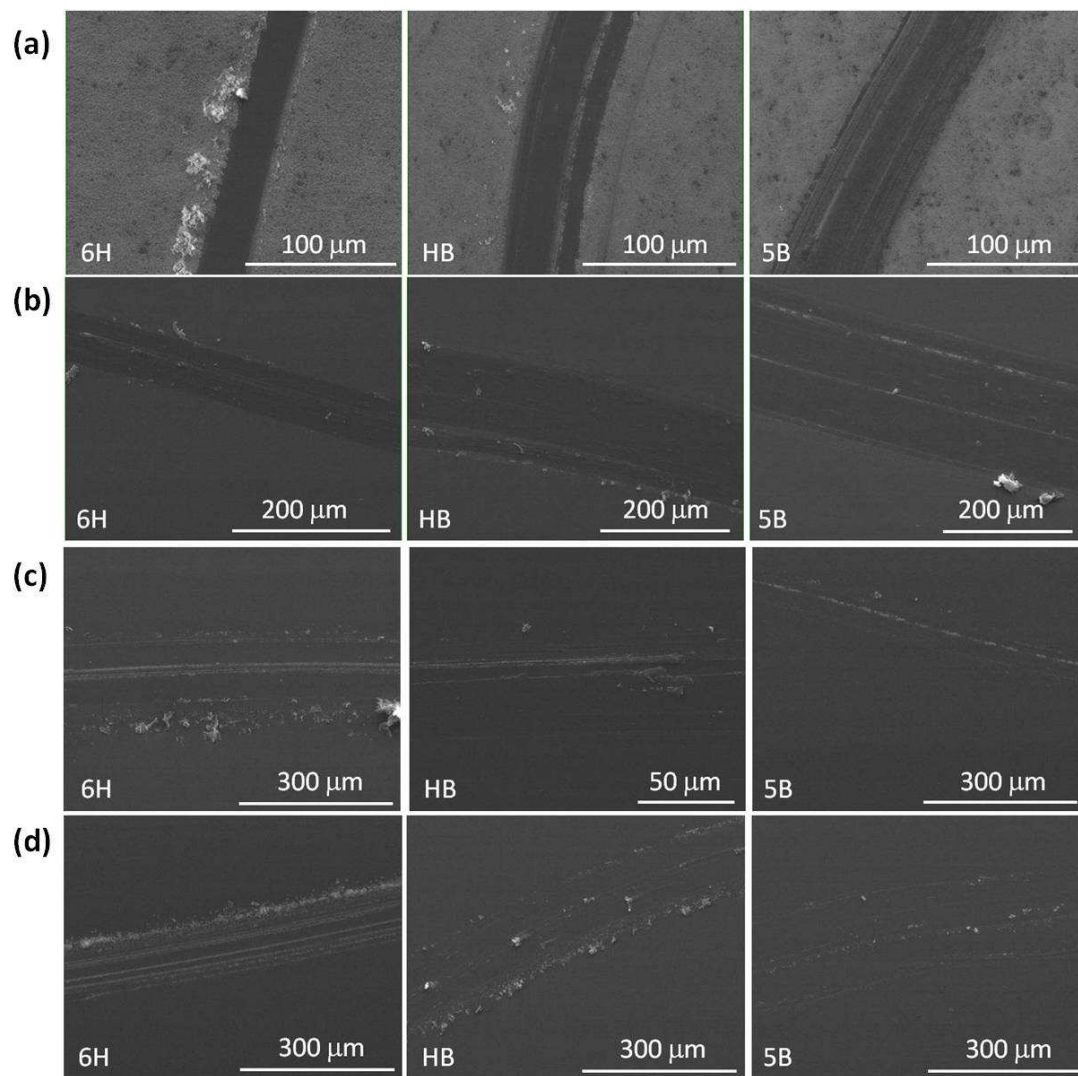


Figure 5.15: SEM images of a) T0, b) T25, c) T60 and d) T80 films after scratching with 6H, HB and 5B hardness pencils.

approximately 10 kPa pressure. During removal from the tape from film surface we observed adhesive material of the tape to remain on the coating. This indicates that adhesion between the coating and the glass substrate is stronger than the adhesion between the adhesive material and the tape.

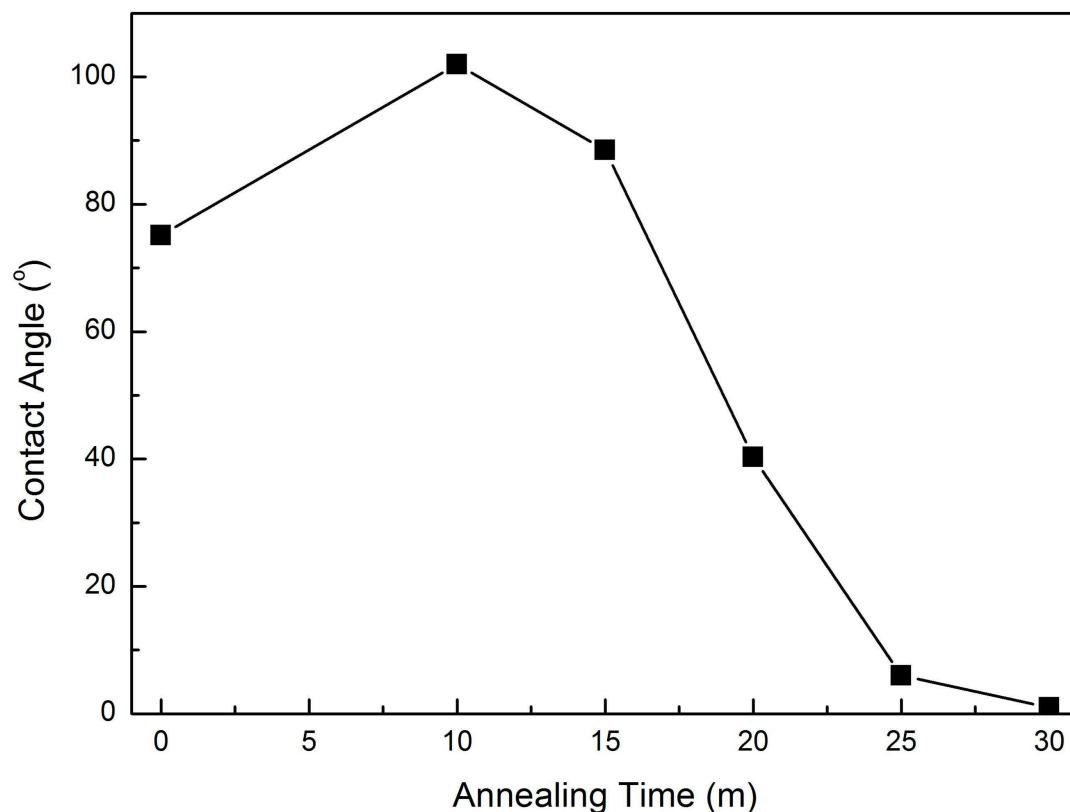


Figure 5.16: Affect of annealing at 600 °C for 5 min durations on contact angle of T60 film, which ends up with transition to superhydrophilic.

Scratching resistance of the films were determined using pencils with harnesses varying from 6H to 8B by application of approximately 1 MPa pressure. Scratch formation is observed by taking SEM images of films after tests, shown in Figure 5.15. These images reveal that as the fraction of TEOS increases, the amount of removed material during scratching decreases due to increasing hardness with increasing inorganic fraction. Moreover, for T60 and T80 films, no scratch formation is observed for scratching by 8B pencil. Scratch tests indicate that ormosil

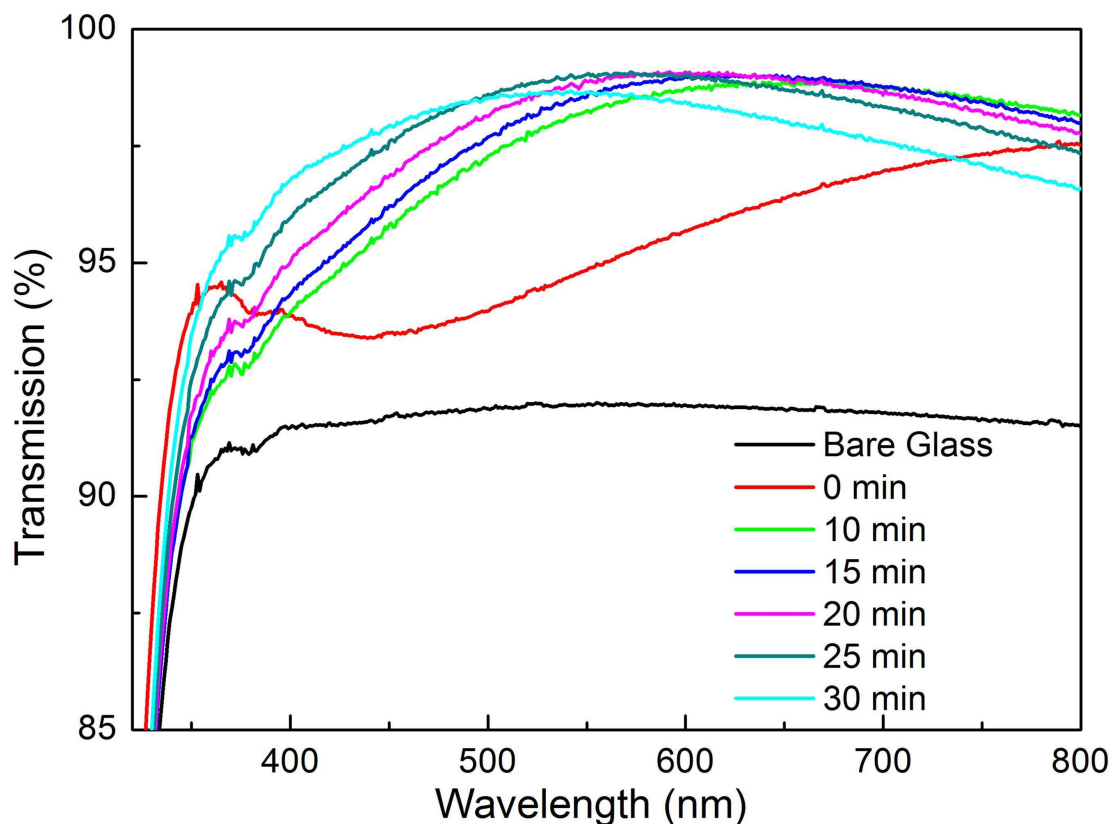


Figure 5.17: Transmission plot of thick T60 film during transition to superhydrophilic with increasing antireflectivity.

films are not resistant for scratching even though they are mechanically stable with good adhesion.

Similar to superhydrophobic films we prepared and described in detail before, hybrid films also exhibit transition to superhydrophilic after annealing at 600 °C [100]. This change is monitored using contact angle measurements, shown in Figure 5.16. T60 film is placed to oven preheated to 600 °C and its contact angle is measured before and after each annealing steps of 5 min durations. Initial contact angle is found to be around 75°. After annealing for 5 min, this value increases to the level of 100° due to removal of unreacted species [118]. After this point, it continuously decreases and at the end of 35 minutes, film becomes

superhydrophilic with contact angle reaching 0° .

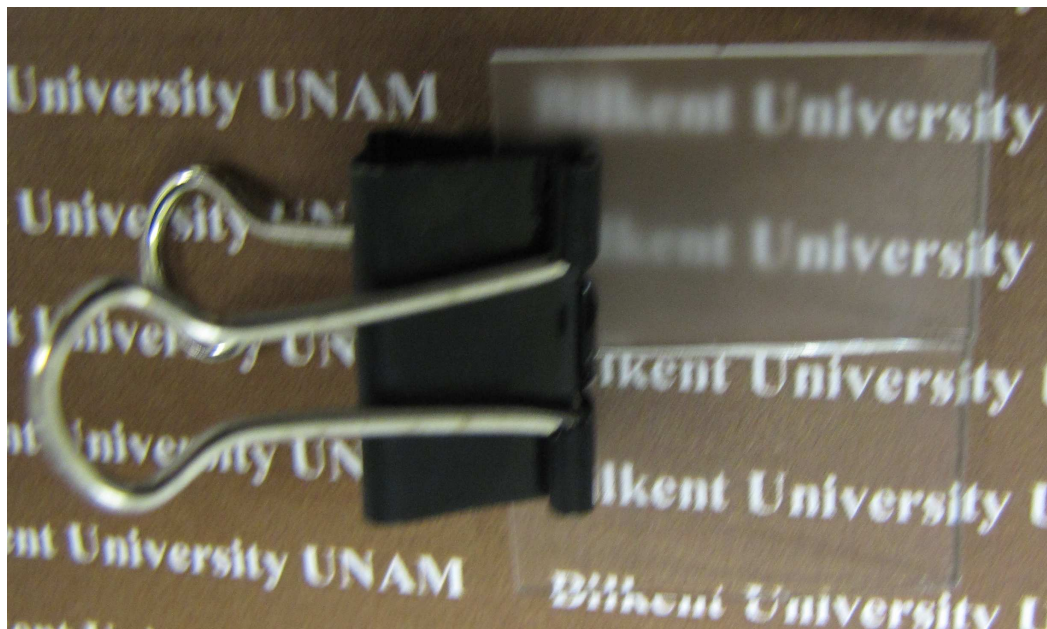


Figure 5.18: Photograph showing the antifogging property of superhydrophilic antireflective T60 film annealed at 600°C .

During transition from normal contact angles to superhydrophilic, film remains antireflective with increasing transmission values. This change in transmittance is shown in Figure 5.17. Considering the decreases in the film thickness during annealing, we used a thick T60 film with thickness around 200 nm, which gives transmission maximum in infrared region. With increasing annealing durations, it is observed that the maximum shifts to lower wavelengths. After annealing for 30 min, maximum point reaches to 550 nm corresponding to an approximate thickness of 135 nm.

Superhydrophilic film is observed to exhibit antifogging properties as shown in Figure 5.18. Superhydrophilic film on glass and bare glass substrate are placed into freezer at -20°C for 5 min until they reach equilibrium. When they are removed from freezer to room temperature, a thin layer of fog is observed to form on bare glass due to condensation of water vapor on cold surface. This results in a translucent appearance on bare glass (Figure 5.18, glass on top). On the other

hand, no fog formation is observed on superhydrophilic antireflective film (Figure 5.18, glass on bottom). A similar fogging test is performed by placing these two samples inside a stream of water vapor. Again no fog formation is observed for antireflective superhydrophilic film, where fog formation existed on bare glass. Anti fogging property is achieved on superhydrophilic antireflective films due to their extreme water spreading property. Instead of forming islands, water forms a thin film on glass, thus translucent appearance does not form.

Chapter 6

SYNTHESIS AND CHARACTERIZATION OF ZnO AND ZrO_2 ENCAPSULATED ORMOSIL NANO-COMPOSITES AS TRANSPARENT ANTICORROSION COATINGS ON GLASS SUBSTRATES

Silicate glasses are commonly used in many different applications due to their easy processing, low price, long term durability and silica itself being one of the most abundant materials in earth [69]. Despite of corroding in highly corrosive mediums such as presence of hydrofluoric acid, hot phosphoric acid and high alkaline concentrations glass is known to resist most of the acids [69, 70]. Nevertheless, when glass is exposed to simply water, it starts to corrode [75]. Due to its hydrophilic nature glass attracts water molecules onto its surface, facilitating corrosion. Corrosion of glass in the presence of water mainly takes place due to ion exchange between the hydroxonium ions present in water and alkaline network modifiers, leaving behind silanol groups and increasing the pH of the surrounding water [69].

In literature, there are publications related to acid and base corrosion mechanisms for glass [70, 120, 121], where some indicate that after some corrosion due to densification of the glass structure resulting in pore closure would end up corrosion [122]. Based on the generation of a barrier layer to diffusion of ions which cause corrosion, dealkalization technique is developed, which requires use of elevated temperatures in the presence of sulfur or fluorine containing compounds [73]. Due to high cost and corrosive working conditions, dealkalization is not a preferred option for commonly used window glass type flat glass applications. For such glasses most suitable anticorrosion technique would be use of simple coatings. Up to date many different anticorrosion coatings have been developed against aqueous corrosion either for metals or for glasses. Application of ormosils by simple sol-gel techniques is applied as one option [123], where some used hydrophobic [124] and superhydrophobic ormosils for this purpose [38]. It is known that silica coatings act as barrier layer to corrosion and some elements such as ceria [125], zirconia [126, 127], titania [74, 128], and ZnO [76] have been used as corrosion inhibitors in different surrounding media.

In this work, we prepared transparent ormosil thin film nano-composites by encapsulation of ZnO and ZrO₂ into porous and nonporous matrices. Porous and nonporous silica films are prepared using methyltrimethoxysilane (MTMS) monomer, and both films result in antireflection properties before addition of ZnO and ZrO₂ nanoparticles. When composite films are prepared, transmittance of the films is decreased compared to bare films due to increasing effective refractive index increase. However films still exhibited high transparency, where some nano-composite films exhibited antireflection. Corrosion characteristics of the prepared films are measured using UV-vis spectrometer in transmission mode. The transmission values of films before and after corrosion are compared. Moreover, surface morphologies of the films are controlled before and after corrosion using SEM technique. These anticorrosion films are developed for providing anticorrosion to flat glasses before they reach consumer, only during storing period. Thus films are designed to be cleanable easily with a piece of paper towel. The transmission graphs and SEM and AFM images are also recorded for cleaned films for this purpose. We observed that both ZnO and ZrO₂ containing ormosil

nano-composite films exhibit anticorrosion.

6.1 Synthesis of Porous Ormosil Films

Porous ormosil thin films used for production of anticorrosive and antiicing surfaces are prepared using MTMS monomer. It is known that use of MTMS results in phase separated, cyclic and cage like particles of methylsilsesquioxane (MSQ); which causes an opaque appearance in the absence of template directing agents [117]. However, we have shown that instead of using alcohols, use of dimethyl sulfoxide (DMSO) results in transparent MTMS based gels [118]. For the preparation of porous ormosil films, 1 mL of MTMS was dissolved in 2 mL DMSO and 0.5 mL of 10 mM oxalic acid solution was slowly added into the reaction mixture and stirred for 30 min. As the solvent amount is small, enough hydrolysis is achieved during 30 min stirring period. Following hydrolysis, 0.45 mL ammonium hydroxide, 0.20 mL water dissolved in 5 mL DMSO was slowly added to silica solution and further stirred for 15 min. Gel formation takes place within an hour. Obtained gels were washed 4 times with methanol to prevent over condensation. In each washing, solvent was kept for minimum of 6 h. Washed gels were diluted with 10 mL methanol, sonicated for 45 s at 20 W, and applied by spin coating as usual.

6.2 Synthesis of Nonporous Ormosil Films

Nonporous ormosil films are used both to see the effect of porosity on the corrosion and the effect of roughness on antiicing films. For preparation of nonporous ormosil films 2 mL MTMS was dissolved in 2 mL ethanol 0.2 mL water and 5 μ l (37% HCl solution), and stirred at 60 °C for 90 min. Then 0.4 mL 0.1M HCl solution and 0.35 mL water was added into reaction mixture at room temperature, and further stirred for 15 min. Finally sol was aged at 60 °C for 15 min prior to application by spin coating.

6.3 Synthesis of ZnO Nanoparticles

Firstly ZnO nanoparticles are synthesized starting from zincacetate dihydrate according to literature [129]. Zincacetate dihydrate (0.55 g) is dissolved in 25 mL boiling ethanol. As soon as it forms a white precipitate of zincacetate, it is cooled to 0 °C. Lithiumhydroxide (0.145 g) dissolved in 25 mL ethanol and cooled to 0 °C is dropwise added into zincacetate solution. The total addition time for lithiumhydroxide solution exceeds 1 hour in order to prevent temperature increase, which can lead to production of bigger particles. Resulting ZnO particles are finely crystalline and all are smaller than 3 nm. ZnO nanoparticles containing solution is kept at 0 °C until used. ZnO nanoparticles are added into porous films with its reaction solution during dilution as the dilution solvent, before sonication. Similarly, they are added into nonporous films as dilution solvent.

6.4 Synthesis of ZrO₂ Nanoparticles

ZrO₂ nanoparticles were prepared according to slightly modified previously reported procedure [130]. 1.18 g of ZrCl₄ was dissolved by slowly addition into 25 mL water containing 0.20 mL of HCl solution (37 %) placed in ice bath in order to eliminate overheating. This mixture is drop wise added to 20 mL ammonium hydroxide solution (25 %) dissolved in 20 mL water, again placed in an ice bath to prevent excessive growth of the nucleating ZrO₂ nanoparticles. The resulting particles are found to be amorphous, but they can be transformed into crystalline by annealing at 500 °C for 1 h. These particles were washed 3 times with methanol using centrifuge at 18,000 rpm for 20 min in order to remove chlorine ions present in the reaction solution. Then some were resuspended by using ultrasonic probe, and some were dried and grinded for annealing for crystallization at 500 °C, and regrinded following annealing. Both amorphous particles in methanol and crystalline solid particles were used in porous and nonporous film production.

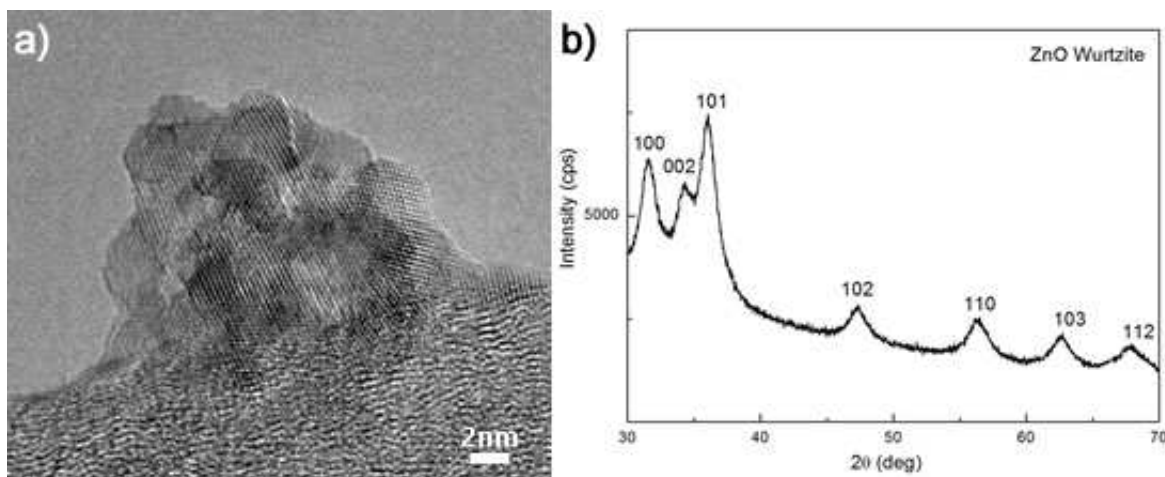


Figure 6.1: TEM micrograph showing particle sizes and crystallinity, and b) XRD plot of ZnO nanoparticles indicating Wurtzite structure.

6.5 Characterization of ZnO Containing Nano-Composites

ZnO nanoparticles were prepared in ethanol as mentioned above and were found to be so small that they cannot be isolated from solvent by centrifugation indicating that their particle sizes are very small. ZnO nanoparticles are visualized by TEM micrograph shown in Figure 6.1-a. The particles are observed to be finely crystalline with diameters smaller than 5 nm. Crystallinity of the particles is also controlled using XRD technique, given as Figure 6.1-b. Particles are found to be in wurtzite structure. Peaks are assigned according to literature [131, 132].

In order to simplify, firstly we investigated the porous ZnO containing ormosil nano-composites. Table 6.1 indicates the refractive index values and thicknesses of porous films prepared for anticorrosion. Both refractive index and thickness measurement have been conducted using spectroscopic ellipsometry. In the abbreviation used “PF” stands for porous film and “NPF” for nonporous film. Initial letters before “PF” and “NPF” stand for the composite materials added into porous film with “B” denoting bare and “Zn” denoting ZnO. As expected films

Table 6.1: Table of refractive index and thickness for ZnO containing and bare porous and nonporous films.

Sample	Refractive Index	Thickness (nm)
BPF	1.126	347
BNPF	1.403	1068
ZnPF	1.409	454
ZnNPF	1.490	1092

which contain nanoparticles have higher refractive index values compared to bare films due to high refractive index of ZnO (approximately 2.0).

Surface morphology of the films is investigated using SEM for high and low magnifications, shown in Figure 6.2. BPF is seen to have highly porous structure clearly seen from high magnification SEM image (Figure 6.2-a), and uniform surface coverage (Figure 6.2-b). Porous structure is not clearly seen for ZnPF (Figure 6.2-c,d). BNPF and ZnNPF do not seem to differ from each other morphologically from SEM images. Both exhibit uniform surface coverage.

Films corrosion stability is tested against 1 M NaOH at 60 °C which results in a faster corrosion compared to room temperature [132]. After measuring the transmittance, films are placed into closed vials containing 10 mL 1 M NaOH and placed into preheated oven. In each experiment one piece of bare glass is also placed into NaOH at same conditions for comparison. Corrosion test results of BPF and ZnPF are shown in Figure 6.3. Transmission measurements obtained before corrosion are given in solid lines, where ones after corrosion test for 24 h are shown in dashed lines. It is clearly seen that porous ormosil films provide some anticorrosion, on the other hand, it does not seem to result from the presence of the ZnO nanoparticles. Both ZnPF and BPF have same transmission after corrosion, indicating that presence of ZnO nanoparticles inside porous film cannot provide any corrosion prevention.

Same corrosion test is applied to BNPF and ZnNPF as shown in Figure 6.4. Even though, nonporous film has a denser structure compared to porous film, it is

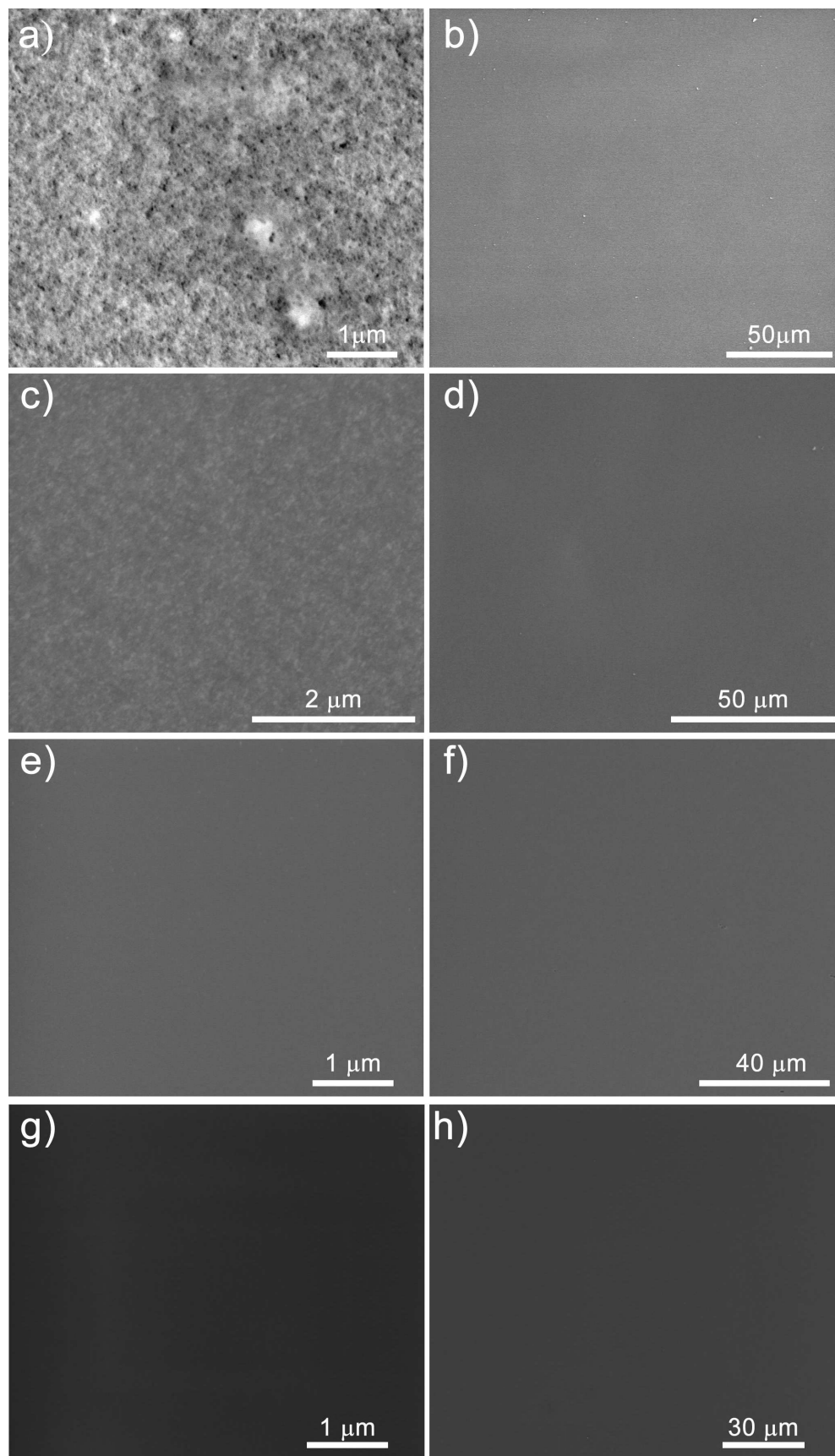


Figure 6.2: SEM images of a-b) BPF, c-d) ZnPF, e-f) BNPF, and g-h) ZnNPF.

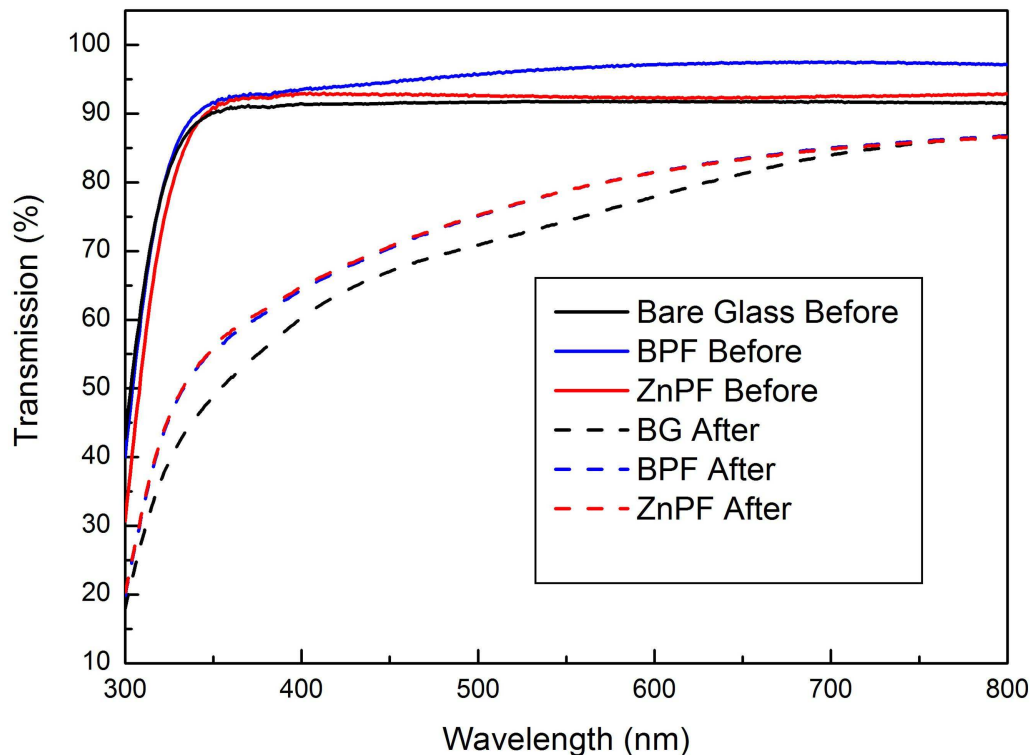


Figure 6.3: Transmission measurements of BPF and ZnPF before and after corrosion indicating some protection resulting from porous film.

seen that neither BNPF or ZnNPF cannot provide any corrosion protection. They are observed to have transmission at the same level with corroded glass, again indicating that addition of ZnO nanoparticles does not have any anticorrosion effect.

Considering that NPFs were used as soon as they were prepared and could not have enough time for polymerization, we applied the same test on BNPF and ZnNPF after annealing them at 450 °C for 1h, which further increases the densification of films. Figure 6.5 shows the transmission graphs of corrosion test results. After annealing, ZnNPF (red dashed line) exhibited almost 10 % enhanced transmission following the corrosion for 24 h. Anticorrosion observed after annealing of ZnNPF can be result of increasing crystallinity. On the other hand, bare glass and BNPF had very close transmission values where bare glass

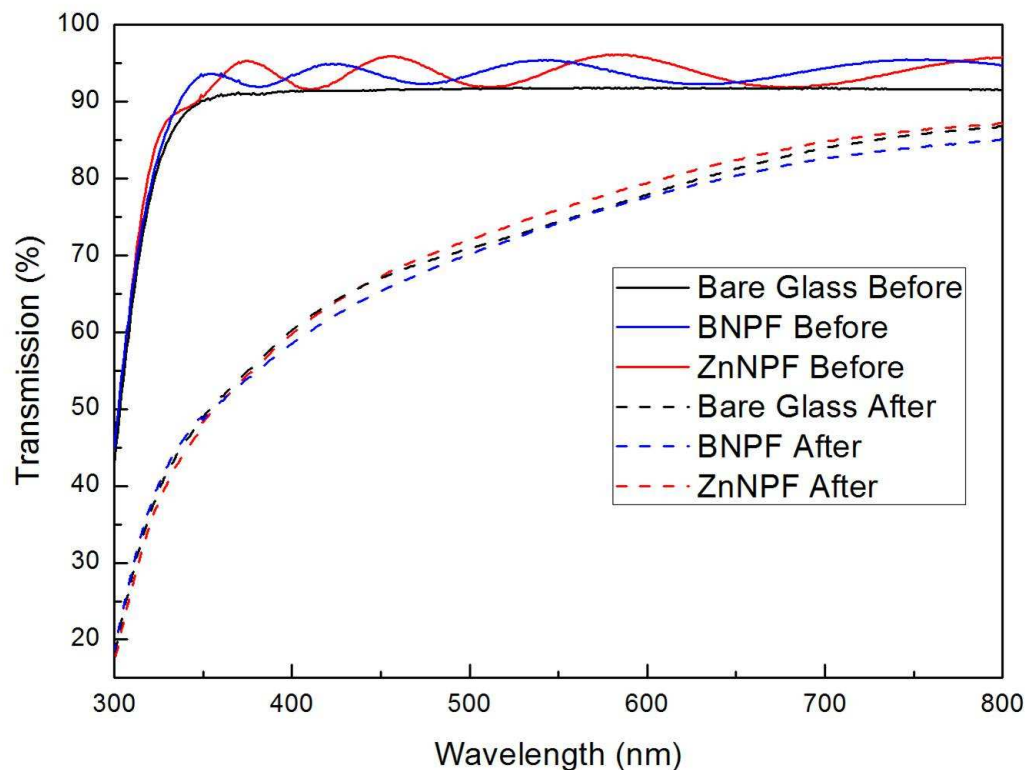


Figure 6.4: Transmission measurement showing the results of corrosion tests on ZnNPF and BNPF with comparison to bare glass.

after corrosion (black dashed line) had slightly higher transmission.

The effect of corrosion on films is visualized taking SEM images of 24 h corroded bare glass, ZnPF and ZnNPF, shown in Figure 6.6 a-b, c-d and e-f respectively. Flake like structures are seen on bare glass. Similar structures are reported on bare glass after solvothermal treatment with water at 180 °C for 10 h [133]. In ZnPF, flake like structures are seen but there are also cloud like regions, probably due to highly etched porous structure. After corrosion, ZnNPF annealed at 450 °C for 1 h seems to have pores. On the other hand, it is clearly seen that there are much less density of flake like corrosion products on the surface of this film.

As mentioned before these anticorrosive films are intended to be cleaned at the end of storage period. With this aim we removed the prepared films from

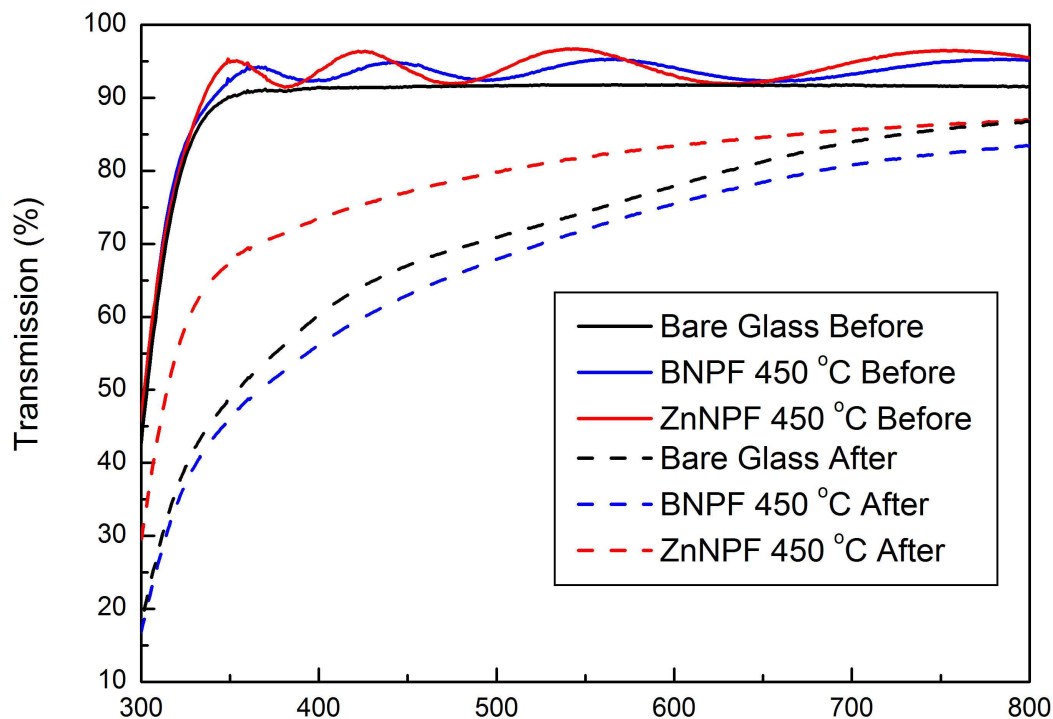


Figure 6.5: Transmission measurements showing the results of corrosion tests on 450 °C 1h annealed ZnNPF and BNPF with comparison to bare glass, indicating that annealed ZnNPF nano-composite can provide some extend of anticorrosion.

the surface of glass substrates in order to see if there is any corrosion on glass itself. Similarly we cleaned the corroded region of the corroded bare glass and compared this with ormosil coating applied surfaces. SEM images of corroded and cleaned glass ZnPF, BPF and BNPF are shown in Figure 6.7. In bare glass corroded interface cannot be removed by mechanical cleaning completely. On the other hand corroded regions are completely removed from ormosil coating applied surfaces. In porous films, besides the corroded region, coating itself is also completely removed, where on BNPF only corroded region is completely removed. Some of the NPF is still seem to remain on the surface even after cleaning due to its enhanced adhesion. Same morphology is seen for ZnNPF, thus it is not shown.

Transmission graphs of corroded and cleaned films are given in Figure 6.8,

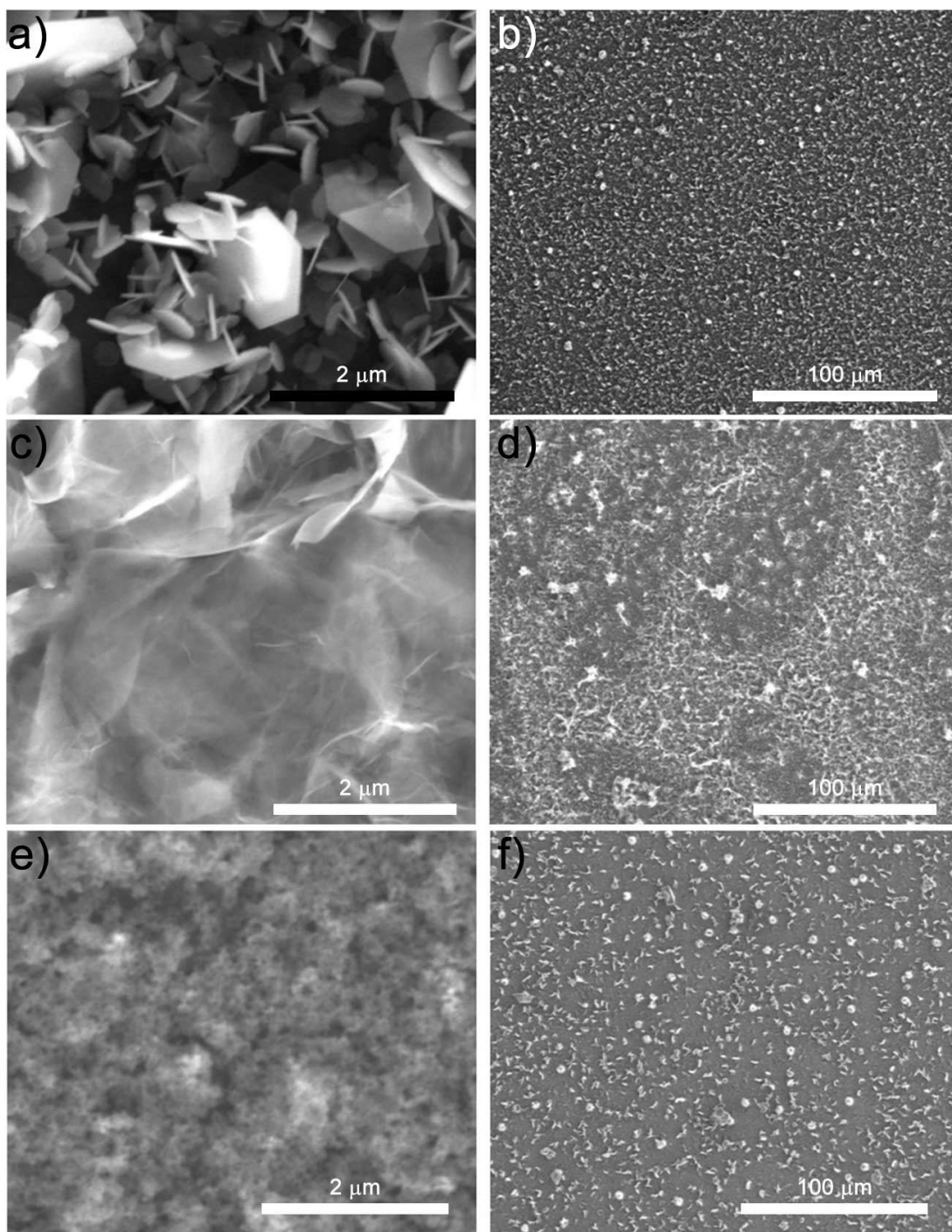


Figure 6.6: SEM images of 24 h corroded a-b) bare glass, c-d) ZnPF, and e-f) ZnNPF annealed 450 °C for 1h.

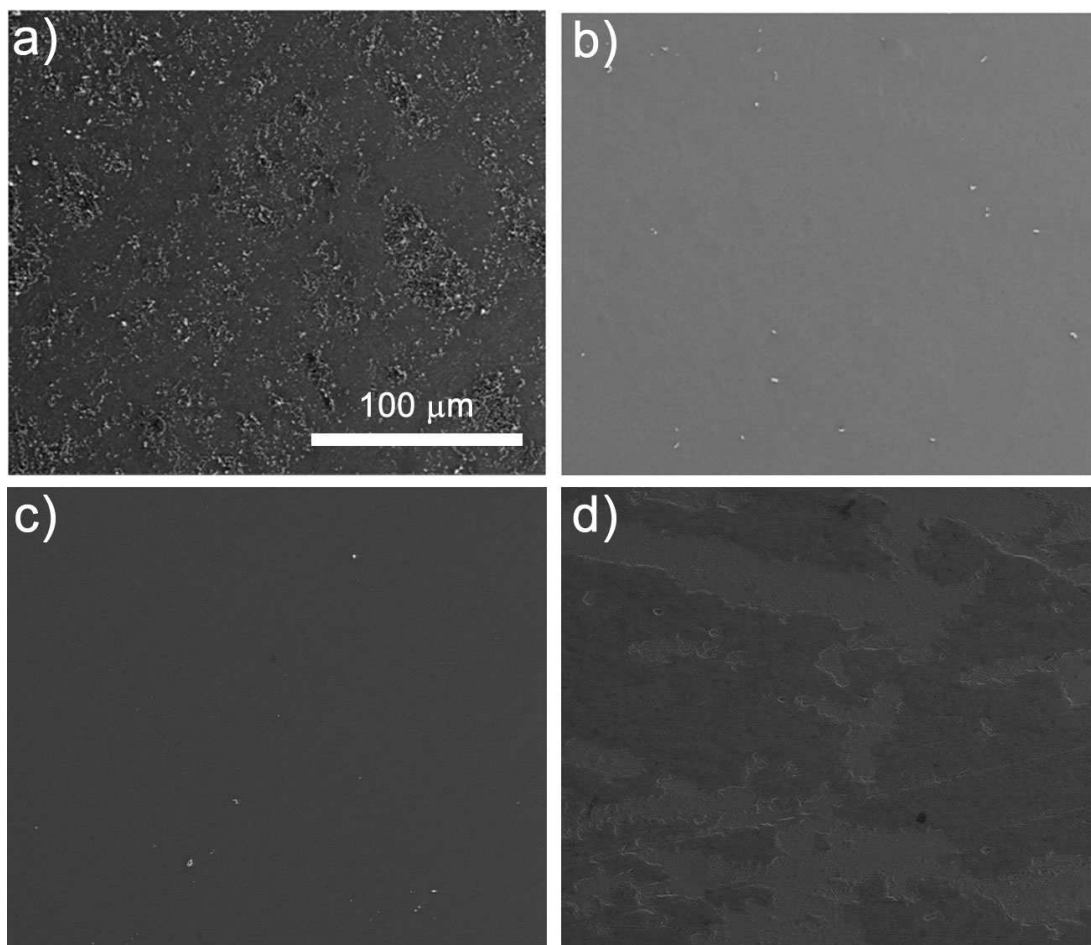


Figure 6.7: SEM images of corroded and cleaned a) bare glass, b) ZnPF, c) BPF and d) BNPF indicating that ormosil nano-composites can protect the glass substrates from corrosion.

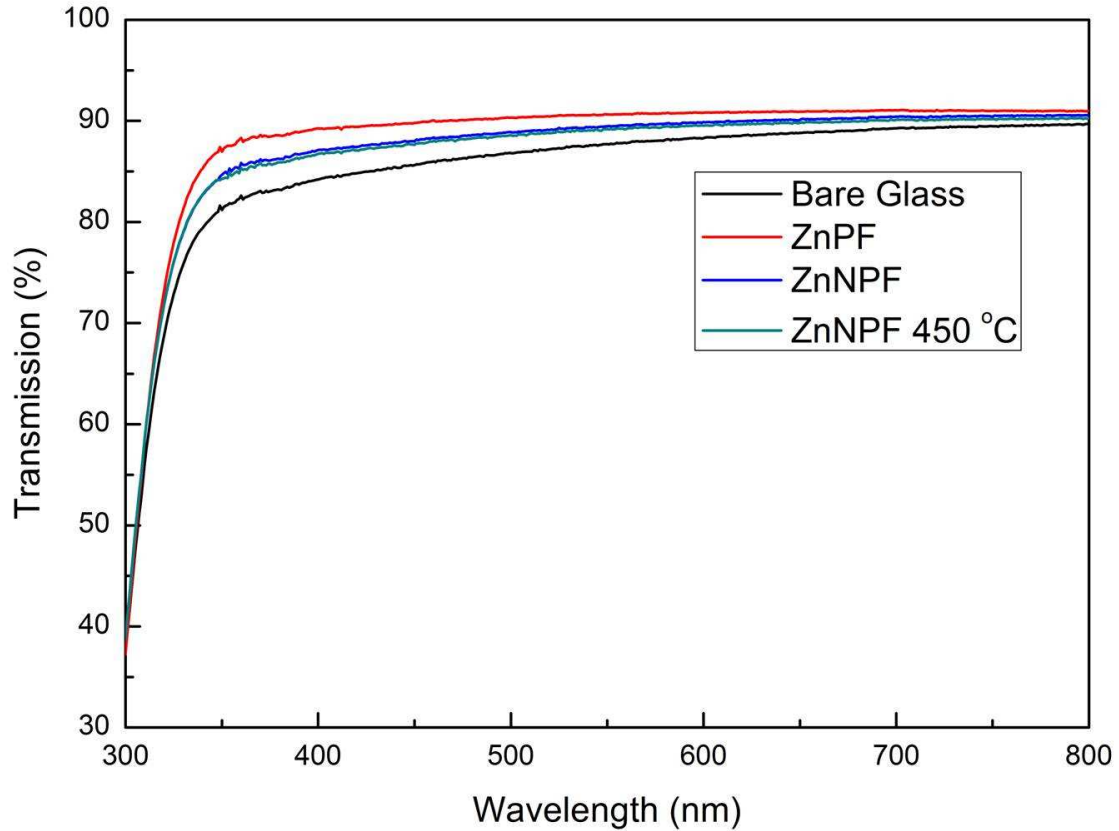


Figure 6.8: Transmission graphs of 24 h corroded and cleaned films, indicating that ormosil films provide glass substrate from corrosion.

which are in accordance with SEM images. It is seen that after cleaning, bare glass cannot retain its initial transmittance. On the other hand, ormosil coated samples can provide better transparency after corrosion and cleaning, indicating the corrosion takes place only on the ormosil film surfaces, not on the glass itself. It was published before that anticorrosion coatings of Ti_5Si_3 structure had a corrosion rate of 0.33 nm/min, according to which 475 nm of film should be corroded in 24 h [128]. On the other hand, thickness of both BPF and ZnPF are smaller than this value, indicating that corrosion in our ormosil films is slower.

Surface topography of the films are characterized using AFM after corrosion and cleaning, shown in Figure 6.9. In bare glass, remaining corroded regions

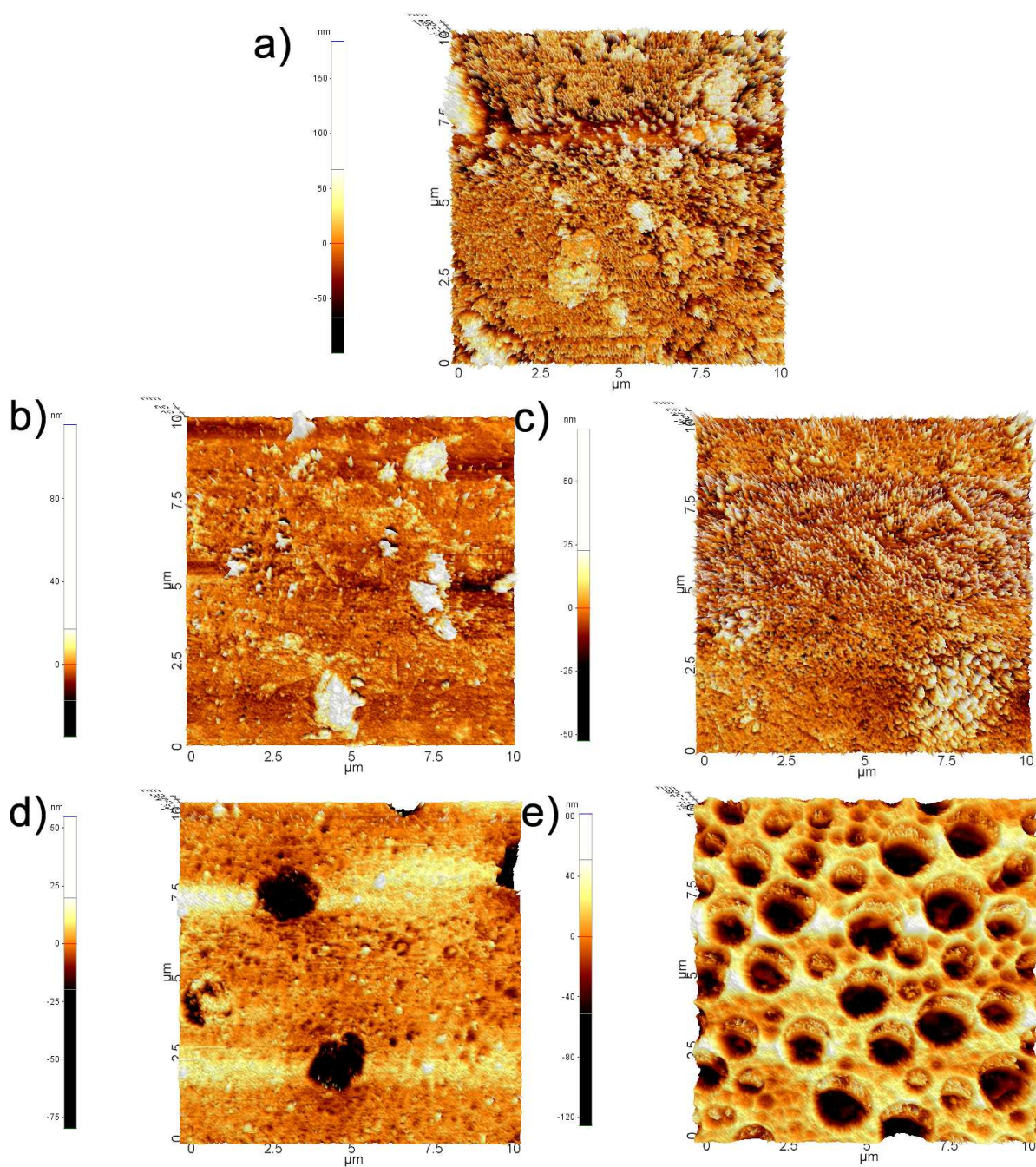


Figure 6.9: AFM images of corroded and cleaned films, indicating corroded layer is removed from ormosil film coated glass substrates.

Table 6.2: Table of roughness values of ZnO loaded and bare porous and non-porous films, obtained from $10 \times 10 \mu\text{m}^2$ regions.

Sample	Roughness Before Corrosion (nm)	Roughness After Corrosion and Cleaning (nm)
Bare Glass	0.68	26.5
BPF	4.8	5.06
ZnPF	118.6	8.33
BNPF	0.80	6.64
ZnNPF	7.57	16.7

are seen, where in ormosil films only some remaining coating is visible. The amount of remaining film is higher in case of BNPF and ZnNPF (Figure 6.9 d and e respectively). The average roughness values are also measured for both asprepared films and for corroded and cleaned films as shown in Table 6.2. This table indicates that for bare glass, roughness is enhanced almost 40 times. For porous films, there is no such enhancement, where roughness of ZnPF is decreased a lot after removal of film. Enhancement is also seen for nonporous films, due to strong adhesion of the film to the surface, which causes partially removal of film from glass substrate.

6.6 Characterization of ZrO_2 Containing Nano-Composites

ZrO_2 nanoparticles are prepared in aqueous solution. After synthesis, described above, particles are washed 3 times with methanol. TEM technique is used for determination of particle sizes and crystallinity. Figure 6.10-a shows the TEM images of ZrO_2 nanoparticles which are interconnected to each other. As seen, particles are found to be amorphous in asprepared form. In order to crystallize, they are annealed at 500°C for 1 h. Plot of XRD measurement, given in Figure 6.10-b, indicate that after annealing ZrO_2 nanoparticles become crystalline. All reflections in XRD plot are assigned according to literature [130].

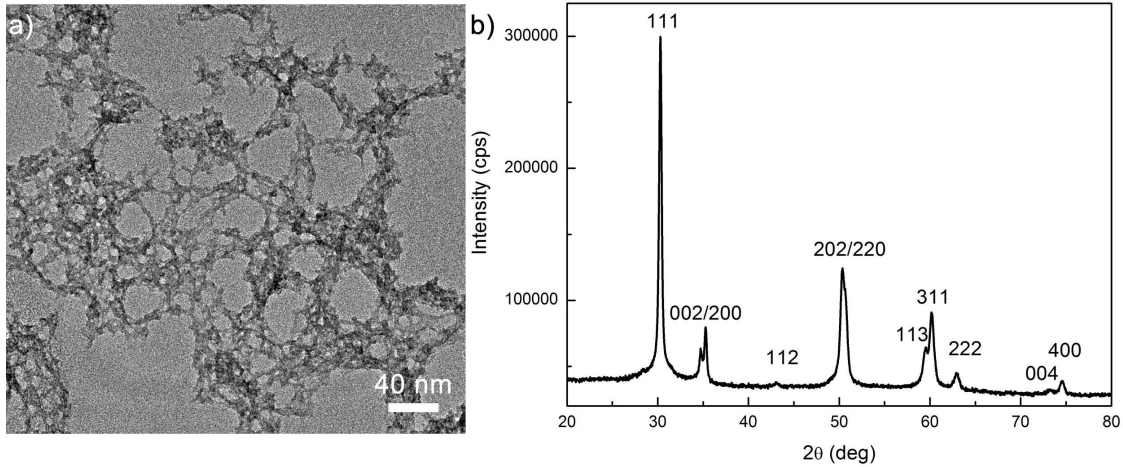


Figure 6.10: TEM image of aerogel like interconnected ZrO₂ nanoparticles in amorphous state, b) XRD plot of crystalline ZrO₂ nanoparticles obtained by annealing at 500 °C for 1h.

Table 6.3: Table showing refractive index and thickness values of ZrPF and ZrNPF.

Sample	Refractive Index	Thickness (nm)
ZrPF	1.138	346
ZrNPF	1.403	1211

Table 6.3 shows the refractive index and thickness values measured for ZrO₂ ormosil nanocomposite structures. Thickness of ZrPF is found to be almost same to BPF due to its addition after several washing cycles, and it is seen to increase the refractive index of the porous film from 1.126 to 1.138. ZrNPF have slightly higher thickness compared to BNPF, which had thickness of 1092 nm, expected to be due to increasing viscosity after addition of nanoparticles. On the other hand, refractive index of ZrNPF is found to be almost same with BNPF due to agglomeration of particles inside film.

Surface morphology of ZrO₂ containing nanocomposites are investigated using SEM, shown in Figure 6.11. Even though ZrO₂ particles have been added into

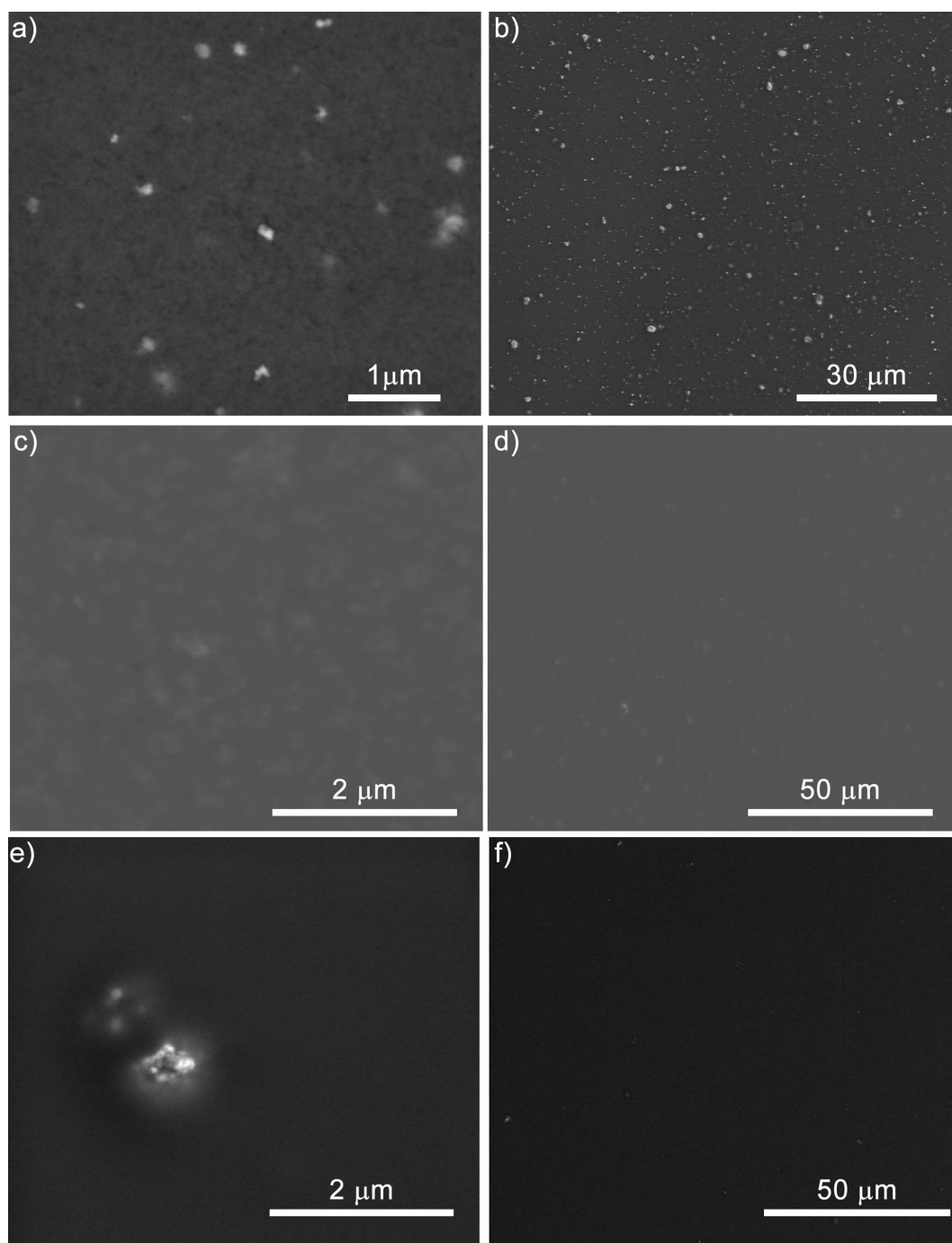


Figure 6.11: SEM images of a-b) ZrPF, c-d) ZrNPFamp, and e-f) ZrNPFxtl indicating that particle distribution is better in NPF.

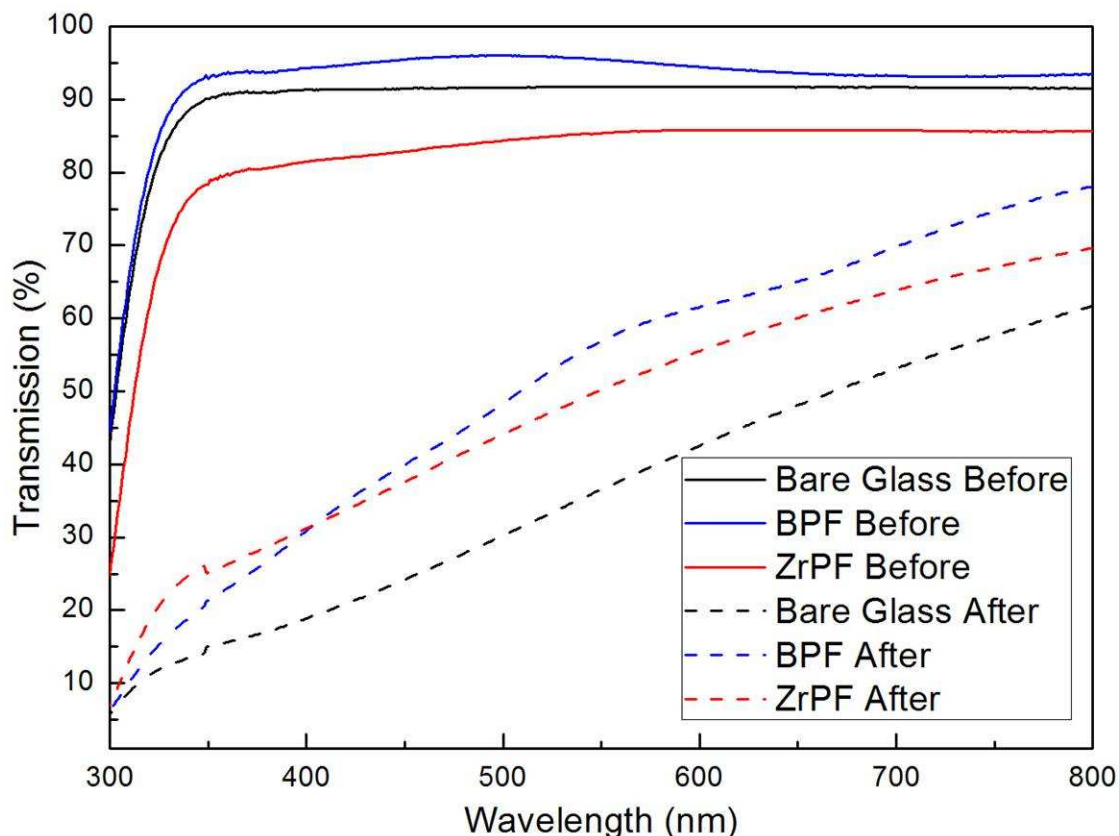


Figure 6.12: Transmission measurements of BPF (blue lines) and ZrPF (red line) with comparison to bare glass for before (solid lines) and after (dashed lines) cases.

porous film structure only as dilution solvent in crystalline phase, it has been added into nonporous film structure both in amorphous and crystalline forms. These samples have been named as ZrNPFamp and ZrNPFxtl respectively. SEM images reveal that ZrO_2 particles are not well distributed in porous film. They remain in forms of clusters as seen from both high and low magnification images. Contrary to ZrPF, ZrNPFamp seem to have a homogeneous distribution of particles over the film. On the other hand, ZrNPFxtl also has non uniform particle distribution as can be seen from high magnification image, where similar clusters are not apparent in lower magnification images.

Prepared ZrO_2 -ormosil nano-composite films are corroded for 48 h, and as for

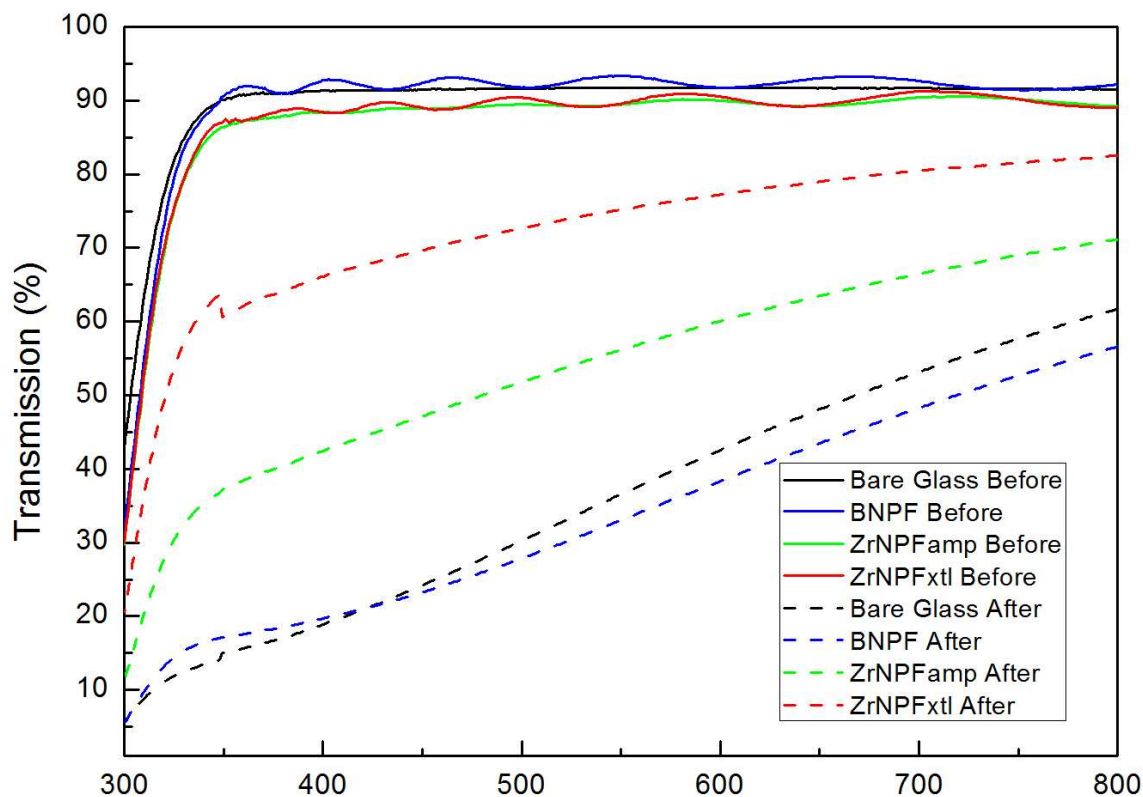


Figure 6.13: Transmission measurements of BNPF (blue lines), ZrNPFamp (green line) and ZrNPFxtl (red line) with comparison to bare glass for before (solid lines) and after (dashed lines) cases.

films containing ZnO nanoparticles, changes in film are initially monitored using transmission measurements. Corrosion test results obtained for porous films in comparison to bare glass are given in Figure 6.12. As the graph indicates, both BPF and ZrPF have higher transmittance (approximately 10 %) compared to bare glass after corrosion tests. On the other hand, transmittance of ZnPF and BPF is decreased a lot in order to be considered as anticorrosion films.

Corrosion test results for BNPF, ZrNPFamp, and ZrNPFxtl are given in Figure 6.13. Even though BNP has lower transmission values after corrosion compared to bare glass, nano-composite films are seen to exhibit much higher transmission values compared to corroded bare glass. When initial transmittance

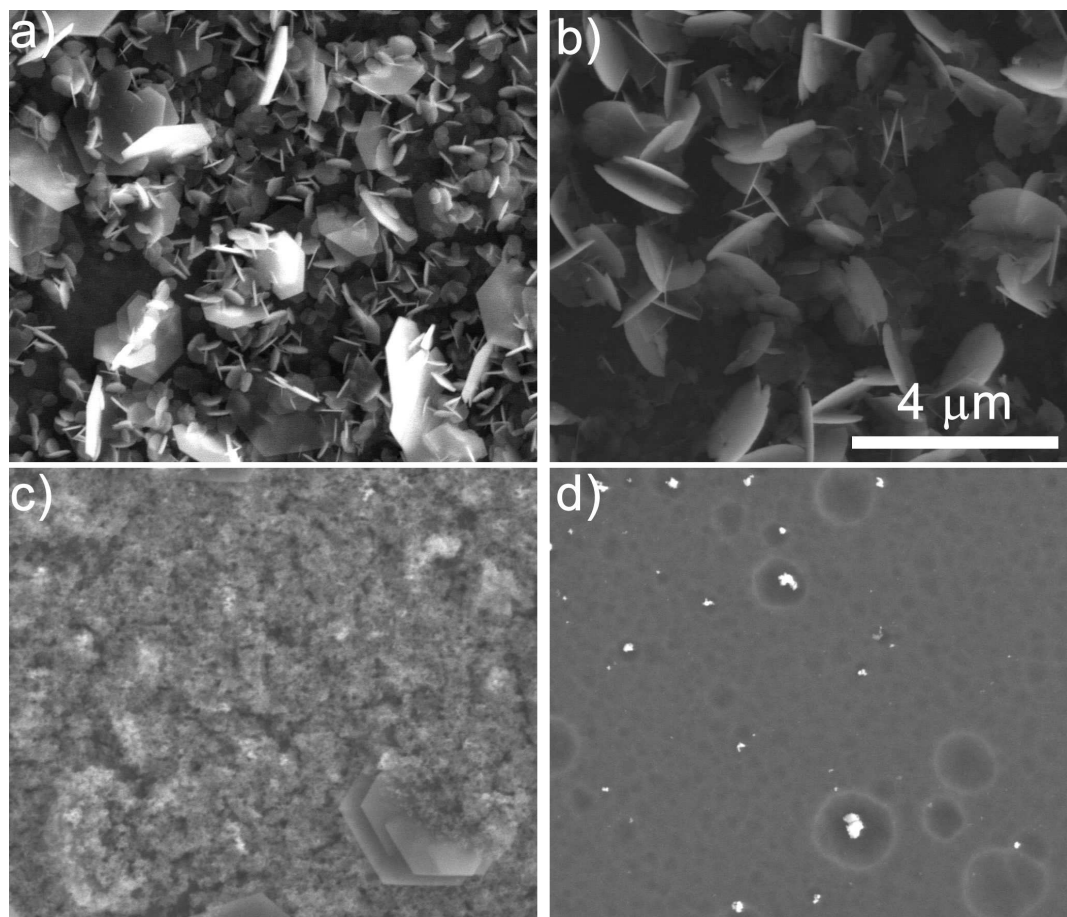


Figure 6.14: SEM images of a) bare glass, b) ZrPF, c) ZrNPFamp and, d) ZrNPFxtl, indicating that nano-composite films of nonporous structure are corroded less. Scale bar is the same and $4\text{ }\mu\text{m}$ for each image.

and final transmittance (transmittance after corrosion) are compared, transmittance of bare glass decreases 53.40 % where these values are 33.08 % for ZrNPFamp and 14.47 % for ZrMPFxtl. Even though, though these films were intended to be used only for storage, with such low corrosion after 48 h 1M NaOH at $60\text{ }^{\circ}\text{C}$, these films are candidates to be used as permanent anticorrosion coatings for glass substrates.

In addition to transmission measurements, SEM images of these samples are also taken, shown in Figure 6.14. Again corroded bare glass is given as Figure

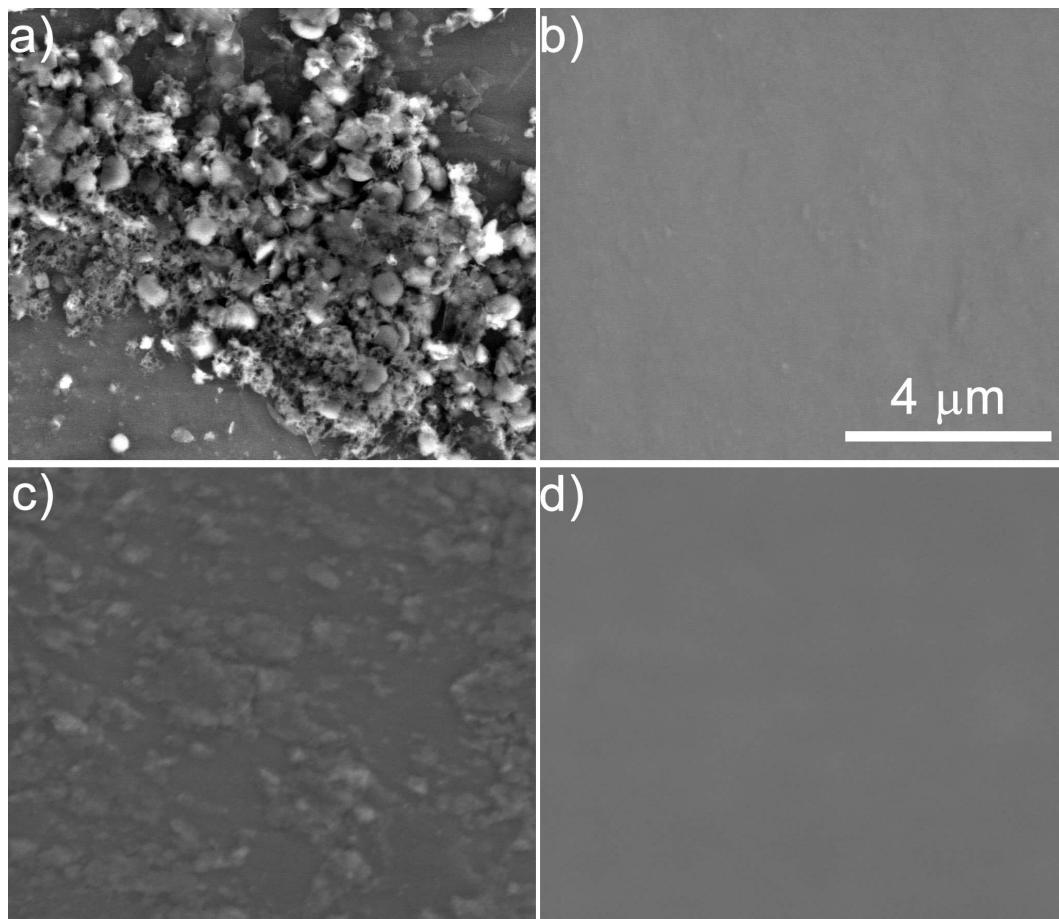


Figure 6.15: SEM images of corroded and cleaned a) bare glass, b) ZrPF, c) ZrNPFamp, and d) ZrNPFxtl with scale bar of $4\text{ }\mu\text{m}$ for each image.

6.14-a for comparison to other films. It is seen that flake like corrosion products are present on the surface of ZrPF, which indicates that porous film cannot resist to this much corrosion and starts to decompose itself. On the other hand, ZrNPFs are seen to corrode much less. Even though the surface of ZrNPFamp seem to become porous after 48 h corrosion, surface of ZrNPFxtl is only very little effected from corrosion.

As mentioned before these films are intended to be removed before selling to consumers, thus we removed the films by simply rubbing by paper towel. SEM images taken after cleaning are given in Figure 6.15. These images indicate that

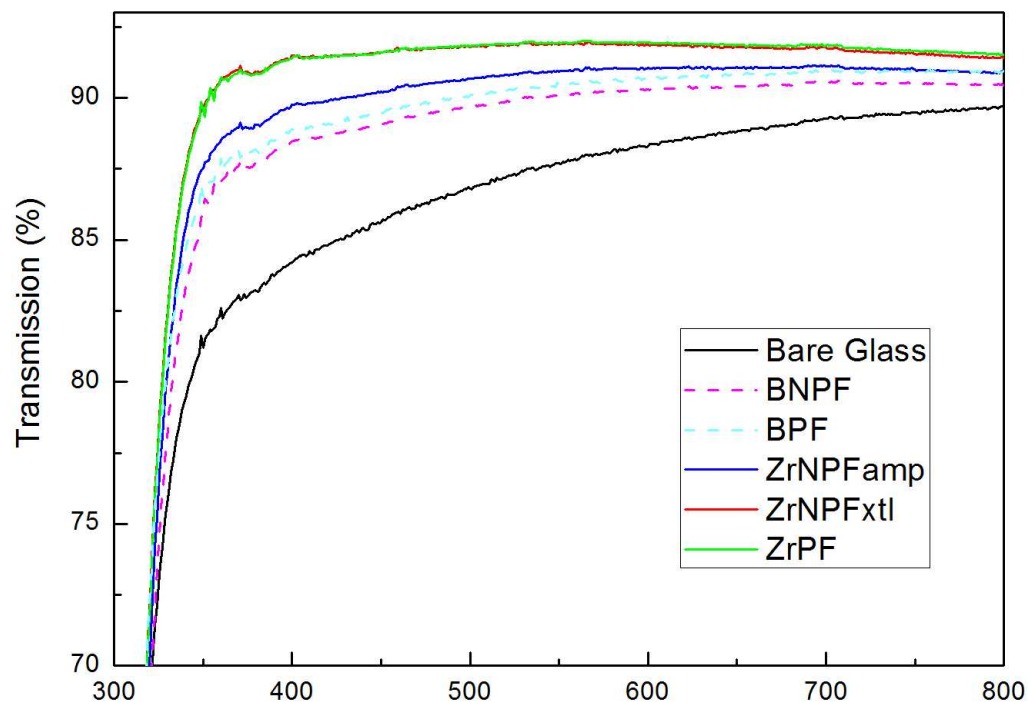


Figure 6.16: Transmission graph of 48 h corroded and cleaned ZrO_2 containing and bare porous and nonporous films.

for all ormosil nanocomposite films, corrosion remains on the film surface and cannot go deep inside the glass substrate. So that after removal of the films, no corrosion products are present on the surface for these films. On the other hand, surface of glass contains corrosion products which cannot be removed that easily. There are also some remaining species on the surface of ZrNPFamp, but considering their structure, we believe that is the remaining nonporous film.

Transmission graph of corroded and cleaned films are given in Figure 6.16 for comparison with SEM images obtained from corroded and cleaned films (Figure 6.15). Transmission result seems to be in good correlation with findings of SEM. According to SEM images, ZrPF and ZrNPFxtl have the cleanest surface after corrosion, thus in transmission measurements they exhibited the highest values. They have the same transmittance. ZrNPFamp has the second greatest

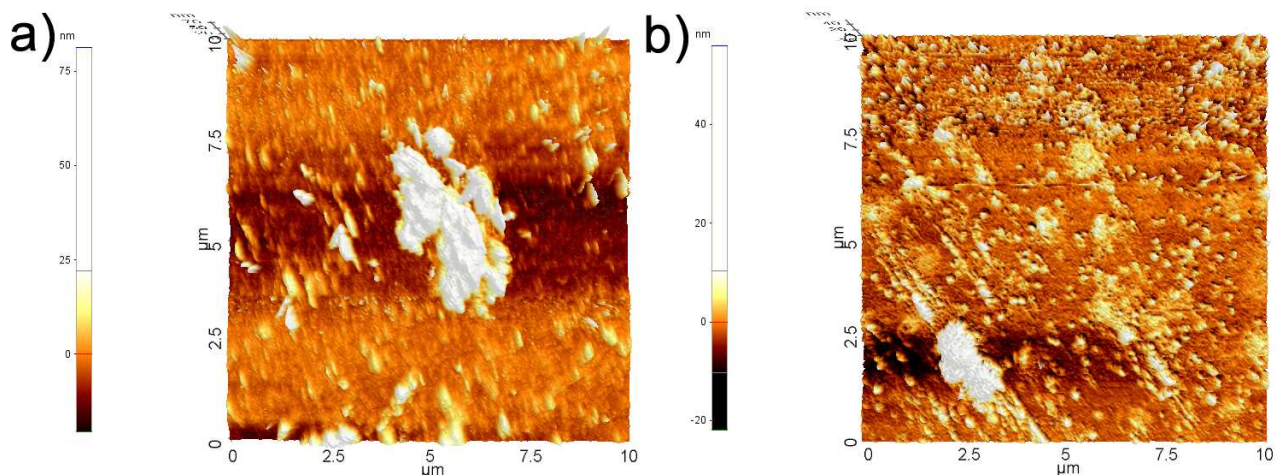


Figure 6.17: AFM images of corroded and cleaned a) ZrPF and b) ZrNPFxtl.

transmittance after these two films, and the worst is found to be bare glass indicating ZrO_2 -ormosil nano-composites also provide anticorrosion when they are cleaned. Moreover, as observed, ZrNPFxtl can be used as a permanent coating for anticorrosion purposes.

Surface topography of corroded and annealed ZrPF and ZrNPFxtl are also examined using AFM technique, shown in Figure 6.17. these images indicate that nonporous film has a lower surface roughness after cleaning with 2.53 nm where it was 1.80 nm before corrossion tests. On the other hand porous nano-composite has roughness of 7.07 nm after corrosion and cleanin, where it was 32.4 nm before corrosion. The average roughness for bare glass was found to be 26.5 nm, which is much higher than ormosil nano-composites.

Chapter 7

CHARACTERIZATION OF ANTIICING PROPERTIES OF ORMOSIL COATINGS WITH DIFFERENT WETTING PROPERTIES AND VARIOUS ROUGHNESS VALUES

Ice accretion on surfaces is most of the time is undesirable, especially on movable parts but it can also has effect on stationary parts during its freezing, due to expansion in volume [77]. However, the results on movable parts can be more drastic. When ice forms on the blades of helicopters, it can cause it to fall. Formation of ice on blades of wind turbines can cause formation of ice stalactites randomly breaking and moving like a bullet due to speed of turbine in addition to decreasing efficiency of the turbine. Because of similar reasons, people tried to overcome this problem. There are two types of approaches for prevention of ice accretion; active and passive methods [80]. In active methods all the time some energy is consumed for resistive heating or blowing hot air in addition to ice sensors. On the other hand, in passive methods, a coating is applied to the substrate which retards ice formation and decreases the total amount of accretion.

Due to lower cost and easier handling passive methods are preferred [134].

Most of the passive methods are based on use of superhydrophobic films [83, 134, 135, 136], where some compared hydrophobic coatings with superhydrophobic [77, 137, 138], some indicating that roughness should be high [80, 139, 140], and some saying that low roughness is better [84]. Moreover, there is a study characterizing the physicochemical properties of some organosilicates which can affect the ice formation such as wettability and heat conductivity [141].

In this study we prepared 13 ormosil thin films, each with different contact angles, roughness. Contact angles of these films are also measured as a function of temperature, and it is observed that each film has a different contact angle change profile in addition to having different roughness and contact angle. Freezing times are measured by placing a 5 μ L water droplet on the substrates, placed on the temperature controlled cooling system and cooling to -10 °C. Used homemade system works in -11 to -8 °C range when set to -10 °C. Laboratory temperature during experiments was 25 °C and humidity was 41 %. Heat conducting paste is used for better heat transfer between the components and the thermocouple. We investigated the correlation between the freezing times and the variables. Bare glass is also used as a comparison sample to ormosil coatings.

7.1 Characterization Ormosil Films in Terms of Ice Retardation

It is not possible to prevent freezing completely but due to reduced interaction between the surface and the liquid droplet which retards the heterogeneous nucleation, ice formation duration can be elongated. Table 7.1 summarizes the properties of each film in terms of contact angle (CA), change in contact angle, surface roughness and average freezing time (FT) in addition to standard deviation (STD) in freezing time. Bare glass is named as 1. As it is too complicated to characterize this many samples with this much variables at once we will compare affects of each variables in turn.

Table 7.1: Table of contact angle values, change in contact angle during cooling from 20 to -10 °C, average surface roughness, average freezing time, and standard deviation in freezing time.

Sample	C. A. at 20 °C (°)	C. A. Change(°)	Roughness (nm)	Freezing Time (s)	STD in Freezing Time (s)
1	23.2	2.6	0.481	38	3.6
2	111.7	11.2	4.8	236	42
3	179.9	75.2	120	295	35
4	140.1	23.4	83.18	349	43
5	179.7	55.2	90.94	520	66
6	147.2	25.5	85.9	500	45
7	87.2	1	0.8	488	108
8	31.4	3.5	4.11	59	8.5
9	79.9	7.6	30.88	137	9.0
10	75	12.6	11.74	135	22
11	30.3	3.7	1.51	64	7.2
12	82.6	4.2	7.57	531	146
13	79.3	2	0.9	370	20
14	179.6	57.3	97.47	419	60

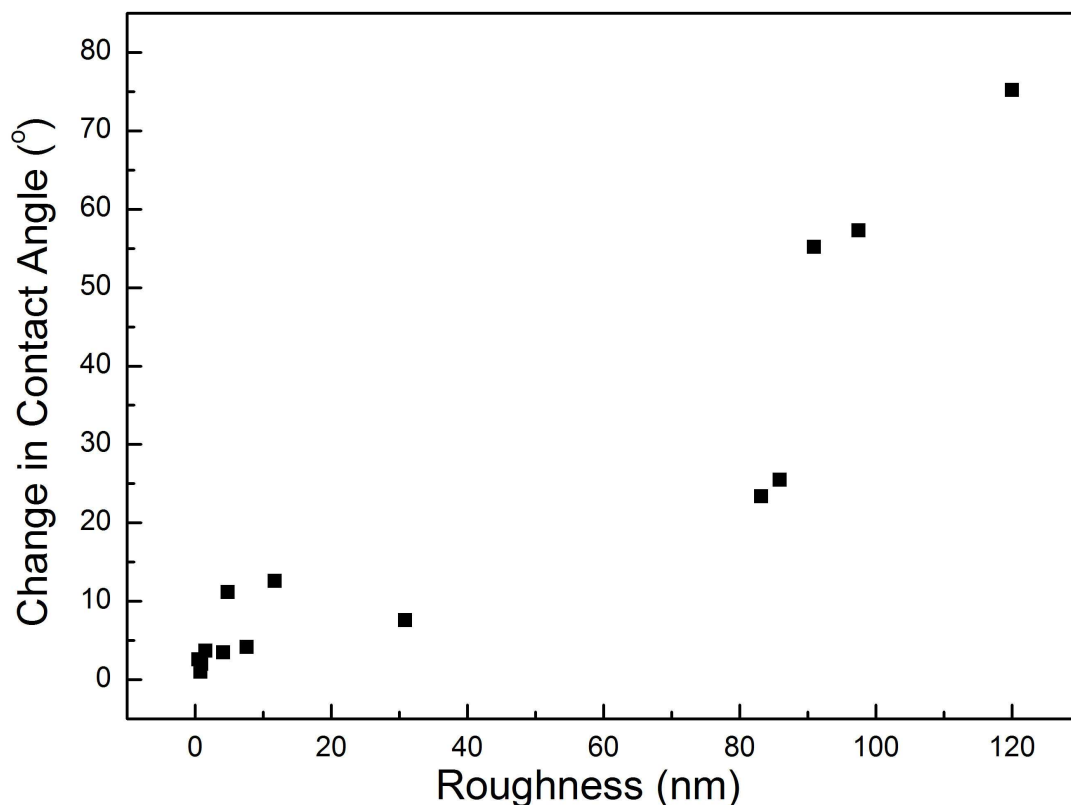


Figure 7.1: Effect of roughness on the change in contact angles during cooling to -10°C from room temperature.

During freezing experiments we observed that, as the temperature decreases, the observed contact angle also decreases. This behavior is also reported before and attributed to oscillations of micro and nanostructures [77, 142]. Figure 7.1 shows the change in contact angle during cooling with respect to roughness. It is seen that for roughness values smaller than 30 nm CA change does not exceed 15° . On the other hand, for roughness higher than 100 nm, this value reaches 75° . It can be said that CA change is directly related to surface roughness.

The dependence of contact angle on roughness for antiicing ormosil films is visualized in Figure 7.2. In this graph in addition to contact angle values measured, the drop in CA is also indicated using error bars. It is clearly seen that for

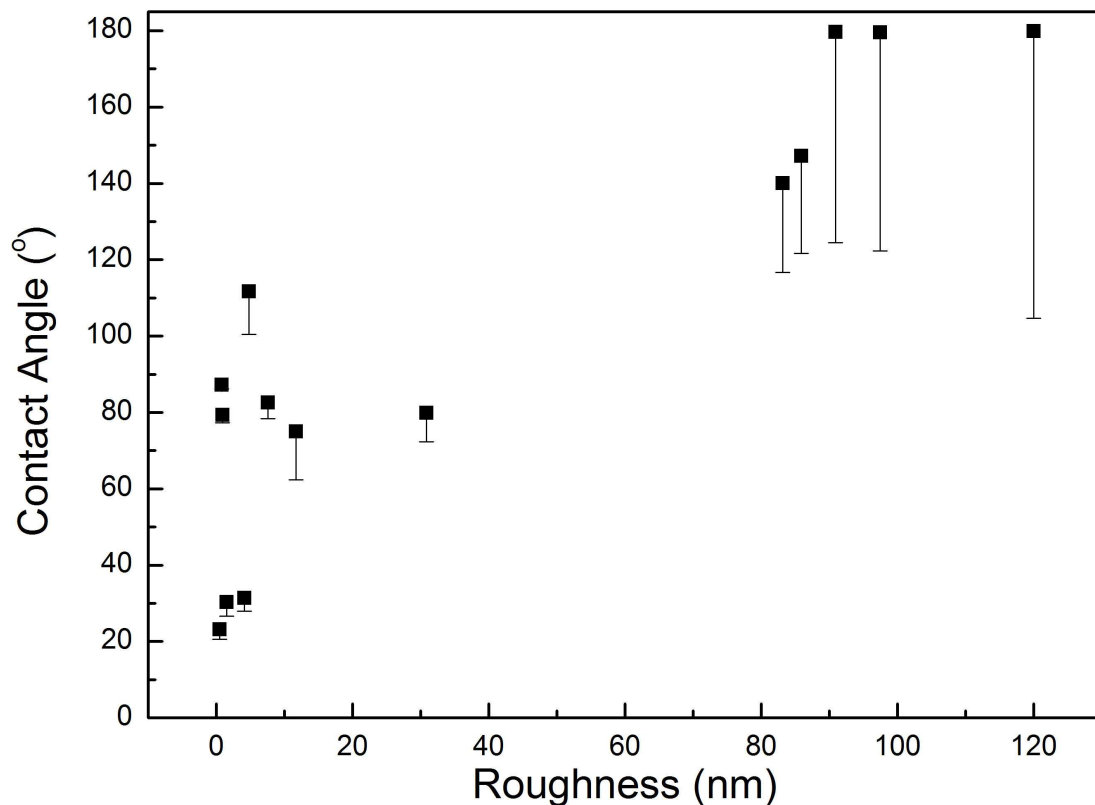


Figure 7.2: Plot of contact angle with respect to surface roughness, indicating that roughness is crucial for high water repellency.

roughness values smaller than 40 nm, highest achieved contact angle is 120°. As mentioned in literature, contact angle is found to be a function of roughness [57] and for obtaining high contact angles, thus superhydrophobicity, surface needs to be rough. Moreover, this graph also indicates that all films with high contact angles, high hydrophobicity, will exhibit high contact angle changes during cooling for freezing experiments.

Freezing experiments have been conducted by placing 5 μL volume of water to inspected samples and cooling system to -10 °C. the chronometer is started as the temperature falls to 0 °C, and experiment is ended as soon as the formation of point tip is observed, which is an indicator of complete freezing of the droplet [142]. Figure 7.3 shows the freezing process of a liquid droplet placed on

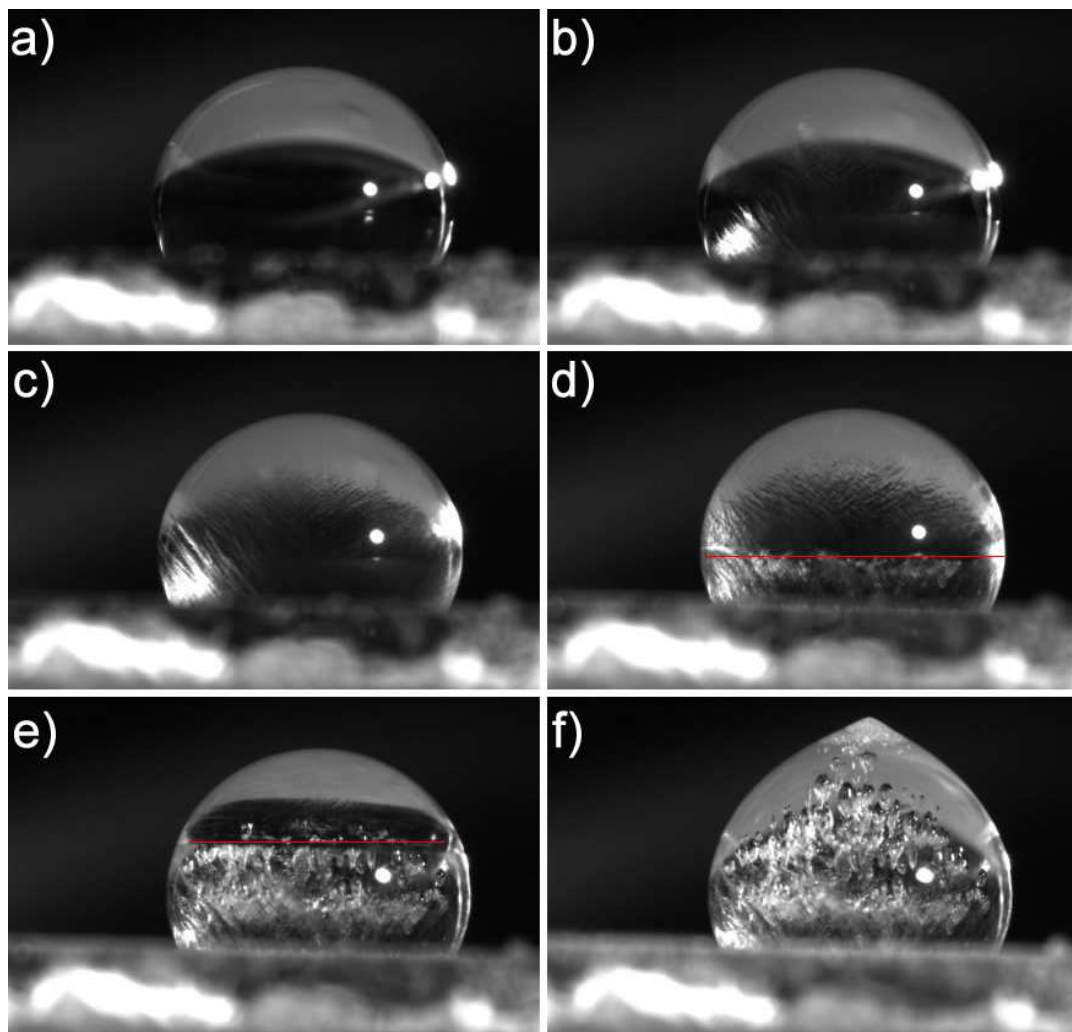


Figure 7.3: Freezing period of a water droplet on ormosil sample during continuous cooling at $-10\text{ }^{\circ}\text{C}$.

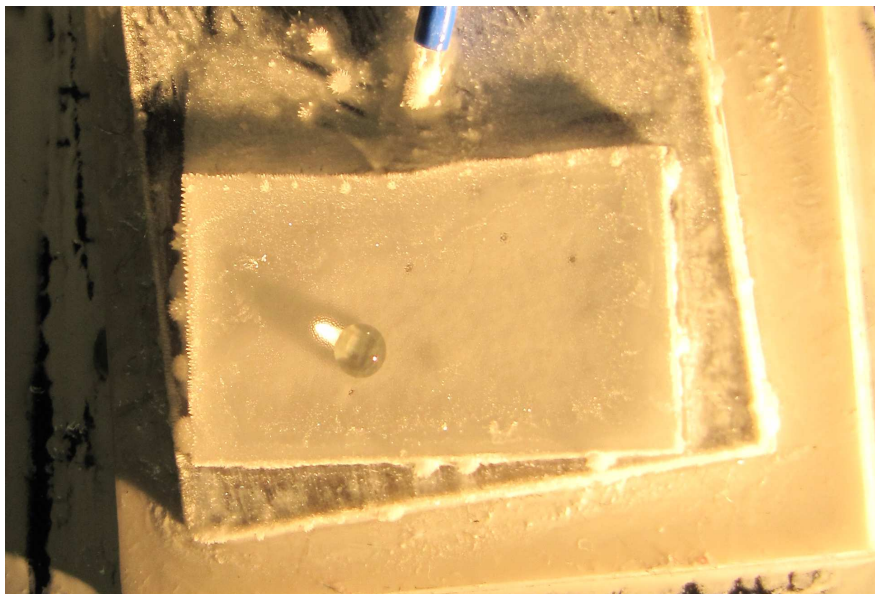


Figure 7.4: Photograph showing ice formation starting from side walls, through the center of the film.

an ormosil sample. In Figure 7.3-a ice formation is not started yet. In Figure 7.3-b, ice starts to form from the bottom, indicating the nucleation is heterogeneous. These ice shell covers all over the droplet with in a second. Freezing line is clearly seen in Figure 7.3-d, indicated with red line, and ice growth continues with movement of ice line through the top of the sample. Icing finishes when the tip, seen in Figure 7.3-f. When there is no surface around the liquid, from which it can nucleate to solidify by replacing liquid-surface interface, homogeneous nucleation takes place, which has a higher barrier for formation. Homogeneous nucleation temperatures are determined by levitation technique, and for water these condition is found to be around $-37\text{ }^{\circ}\text{C}$ and takes around 300 s [79].

During icing experiment with in first a few minutes, ice formation starts from the sides of the glass substrate, which are in contact with the conductive paste. Photograph shown in Figure 7.4 is taken after 6 minutes of cooling to $-10\text{ }^{\circ}\text{C}$. During this period ice started to form from sides, and continuously move to the center of the film. Ice crystals are apparent on the cut sides of glass substrate.

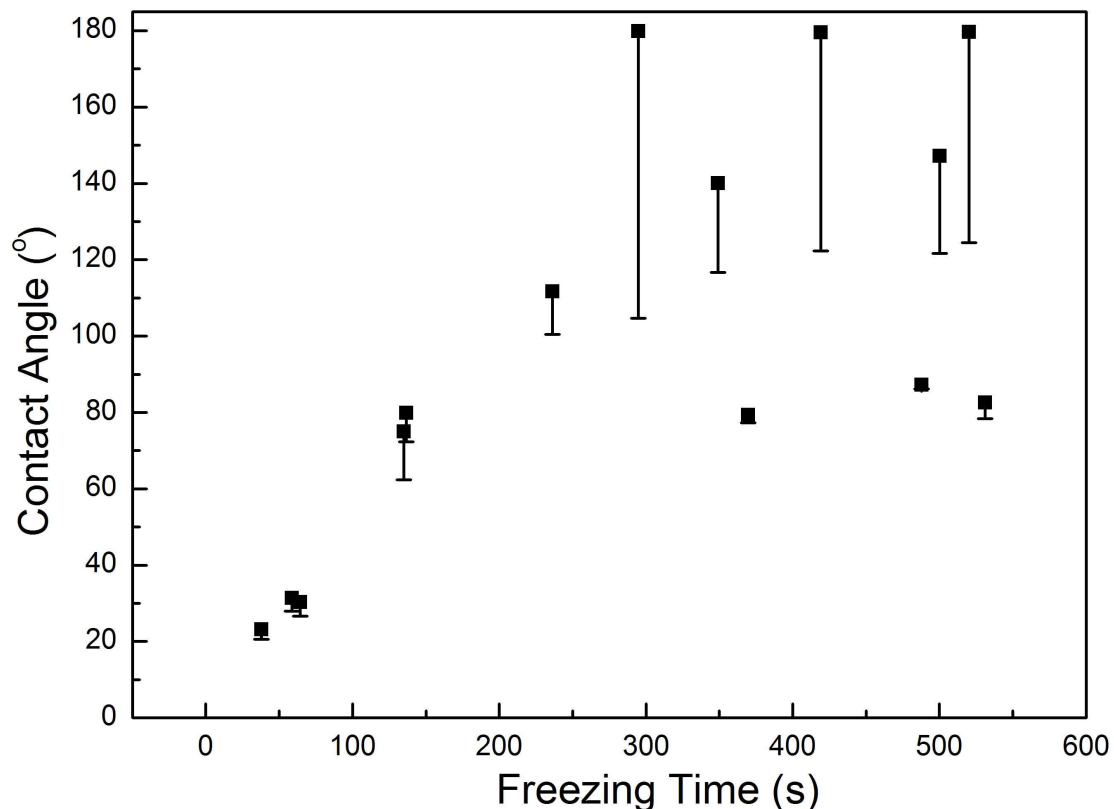


Figure 7.5: Plot of contact angle with respect to freezing time, including the contact angle change values as a result of cooling.

These moving ice line also moves the oil of the conductive paste through the center, so that for accurate measurements, icing tests are done by placing drops to the center of films.

In order to see whether there is any relation between contact angle and freezing durations, we plotted these two against each other, as shown in Figure 7.5. Changes in contact angles during cooling are also indicated with error bars. Graph indicates that all hydrophobic films have larger freezing times than 250 s, where this value is only 38 s for bare glass. Moreover, for superhydrophobic samples, freezing times exceed 300 s. On the other hand, films with contact angle around 80° , and based on the error bars with low roughness are also found to have as high freezing times as superhydrophobic samples.

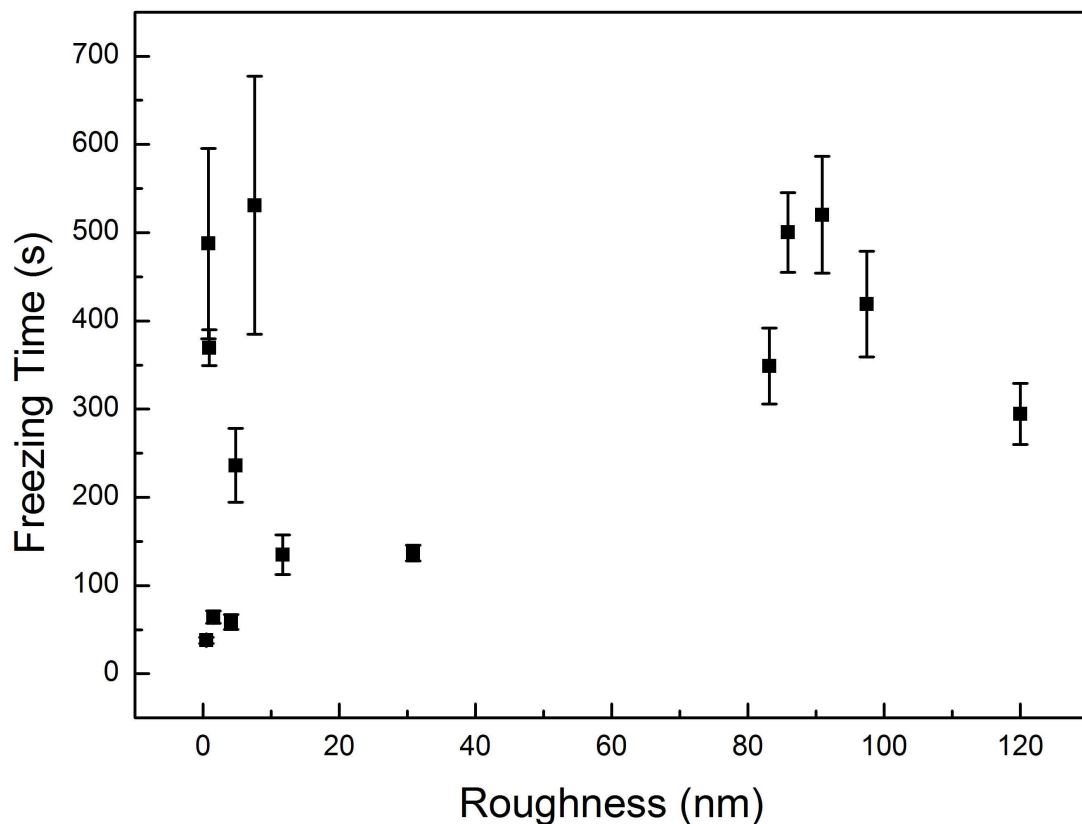


Figure 7.6: Graph of freezing time with standard deviations with respect to average surface roughness.

In order to see, direct relation between freezing time and average surface roughness, a plot of these two parameters with standard deviation of freezing times is given in Figure 7.6. This graph indicates that there is no direct correlation between the freezing time and surface roughness. Both high roughness and low roughness samples are seen to exhibit high freezing times. On the other hand, highest freezing time is achieved for low surface roughness samples, with high fluctuations of the freezing times, where standard deviation observed for high roughness and high freezing time observed samples are smaller compared to low roughness and high freezing time samples.

For investigation of three different parameters simultaneously, we plotted

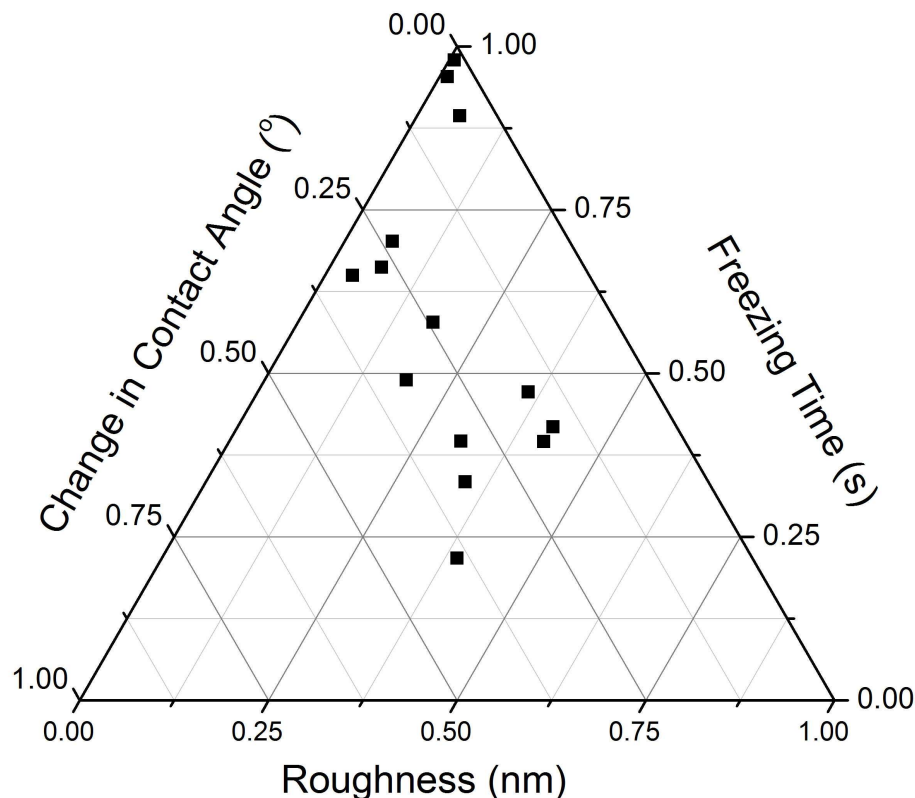


Figure 7.7: Ternary diagram of roughness, freezing time and contact angle change.

ternary diagram of roughness, freezing time and contact angle change due to cooling, shown in Figure 7.7. This graph indicates that films with smaller changes in contact angles have highest freezing times. In addition, lower roughness results in elongated freezing durations. Similarly, Figure 7.8 also indicates that highest freezing times are achieved for films with low roughness and moderate contact angle values.

For sample with contact angle of 82.6° and roughness of 7.57 nm we observed the highest freezing time of 746 s , with average freezing time of 531 s . In literature, freezing time of 515 s at 10°C [77] and 520 s at -8°C [83] are reported in addition to 7720 s at -10°C [139] all on superhydrophobic and rough surfaces. The fluctuations on the freezing times can be a result of damage formation after freezing. In all of our hydrophobic and superhydrophobic samples, due to their

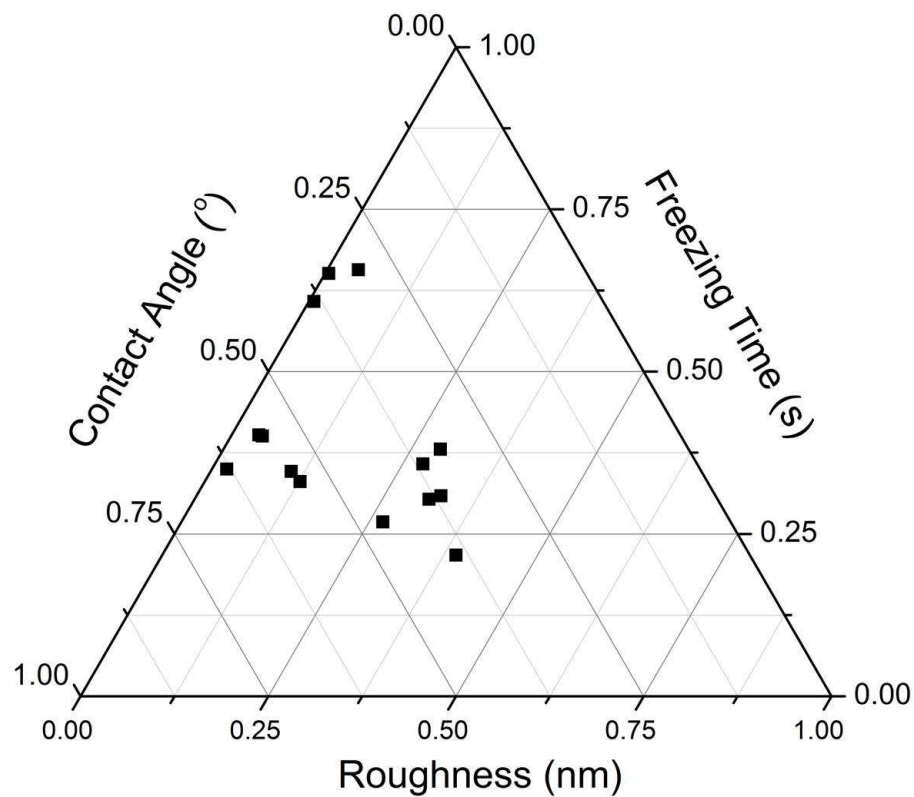


Figure 7.8: Ternary diagram of roughness, freezing time and contact angle.

highly porous and rough surface structure we observed damage on the surface after freezing and melting. Damage forms due to low adhesion of the coatings on the glass and the stress caused during freezing expansion of ice. Similar damages are also reported in the literature [83, 85].

Chapter 8

CONCLUSIONS

In this work, we have prepared four different types of functional surfaces: Superhydrophobic-superhydrophilic, antireflective-antifogging, anticorrosion and finally antiicing (ice retarding) using organically modified silica.

In the first part, we have successfully prepared ormosil aerogel superhydrophobic thin films with high transparency and flexibility. Thin films are obtained from colloidal suspensions of ormosil aerogel structures prepared in methanol without any surface modifications, simply by using intrinsically hydrophobic methyltrimethoxysilane monomer. Obtained ormosil dispersions offer easy handling and good reproducibility for production of superhydrophobic thin films on large areas with simple coating methods like dip, spin and spray coatings. Furthermore, these superhydrophobic films applicable to almost every substrate without the need of any pretreatments to the substrate. The films on flexible substrates are found to exhibit superhydrophobic behavior even when the substrate is highly bent, indicating that films are also flexible as a result of the ormosil network.

As-prepared ormosil aerogel thin films have contact angles as high as 179.9° and low sliding angles smaller than 5° , as a result of dual scale roughness. The hydrophobicity of the films is found to be stable up to 500°C , above which contact angle values gradually decrease and finally reach superhydrophilic region ($\lambda < 5^\circ$)

at 600 °C. As-prepared films are highly transparent with transmittance reaching 87.6 % at 650 nm. Furthermore, transmission can be improved by calcinations (up to 92.1 % at 650 nm after annealing at 600 °C).

This simple, large area, and low-cost fabrication method of superhydrophobic ormosil aerogel thin films make them suitable for application fields including solar cells, waterproof textiles, flexible electronics, and lab on papers as transparent and flexible self-cleaning coatings.

In the second part, we prepared flexible anti reflective coatings from hybrid ormosil colloids which are prepared from co-condensation of methyltrimethoxysilane and tetraethylorthosilicate monomers. We observed that the methyltrimethoxysilane monomer provides flexibility and porosity to the coatings; where, tetraethylorthosilicate monomer provides transparency, thickness uniformity and a smooth surface, while decreasing the porosity. The porosity of these hybrid ormosil coatings can be adjusted by simply changing the monomer ratio. Moreover, the thickness of the coatings can be controlled by adjusting the colloid concentration.

The nanoporous and uniform ormosil coatings reveal anti reflective properties both on glass and cellulose acetate substrates. The anti effective films on flexible cellulose acetate substrates retain their anti reflective properties even after 100 excessive bending cycles; without a significant change in transmission. It is shown that the films on glass substrates are stable against excessive water dripping and there is strong adhesion between the films and substrates. In addition, antireflective coatings on glass substrates are found to exhibit antifogging properties after annealing at 600 °C.

This facile and low-cost fabrication method of flexible and mechanically stable AR and antifogging coatings makes them also suitable for several application fields including solar cells, flexible electronics, and optical devices.

In the third part of this thesis, we prepared and characterized ZnO and ZrO₂ encapsulated ormosil nano-composites for obtaining transparent anticorrosion coatings for glass surfaces. For this purpose both porous and nonporous ormosil film structures have been examined. Films are corroded by placing into

10 mL of 1 M NaOH solutions placed at 60 °C. Corrosion is monitored using transmission results, in addition to that SEM images are used for observing the level of surface morphology changes. These anticorrosion coatings were intended to be used only for prevention due to humidity during long storage periods for flat glasses. Thus, after inspection of corrosion amount, films are removed from substrate surfaces by mechanical cleaning by a piece of paper towel. The results indicated the ZnO-nonporous ormosil film can provide some corrosion resistance when used without cleaning as a permanent coating after annealing at 450 °C for 1 h, which is seen to enhance crystallinity of ZnO nanoparticles. Similarly, amorphous ZrO₂ nanoparticle encapsulated nonporous coating has been observed to have slightly higher anticorrosion compared to ZnO containing film. On the other hand, crystalline ZrO₂ nanoparticle encapsulated nonporous coating has been observed to exhibit 4 times less corrosion compared to bare glass. Indicating that it can be used as a permanent coating for glass surface. Moreover, after cleaning following the corrosion, all coatings have been observed to provide better transmission values compared to corroded and cleaned bare glass. This finding indicates that ormosil films act as a barrier layer preventing the corrosion of glass substrate underneath, thus if are going to be removed afterward, all ormosil films prepared in this study can be used as anticorrosion films for glass surfaces.

In the fourth and the last part of this thesis, we investigated the icing properties of ormosil films with different wetting characteristics and surface roughness values. These two factors are mentioned to be the most effective parameters in the freezing times. For comparison, we used a bare glass sample which has a contact angle of 23.3°, roughness of 0.48 nm and freezing time of 38 s. The lowest freezing time observed from ormosil films was around 59 s which had a contact angle of 31.4° and roughness of 4.11 nm. We used films with contact angles varying from 179.9° to 31.4° and roughness varying from 120 to 0.8 nm for ormosil films. Our results indicate that films with moderate contact angles and low roughness and stable (little changing) contact angles with respect to temperature result in highest freezing temperatures reaching 746 s which is observed for sample with contact angle of 82.6° and roughness of 7.57 nm. Such passive ice retardation surfaces can be applied to blades of helicopters, airplanes and wind turbines, in

addition to antennas.

Our achievements indicate that use of ormosils paves the way for preparation of different functional coatings, some with multifunctionality at ambient temperature and pressures without using surfactant molecules. More over, due to mild conditions of sol-gel technique, they can be applied to flexible and organic substrates like polymer films and cloths, with ease of application to large area.

Bibliography

- [1] H. Y. Erbil, A. L. Demirel, Y. Avci, and O. Mert, “Transformation of a simple plastic into a superhydrophobic surface,” *Science*, vol. 229, p. 1377, 2003.
- [2] R. Chen, X. Zhang, Z. Su, R. Gong, X. Ge, H. Zhang, and C. Wang, “Perfectly hydrophobic silicone nanofiber coatings: preparation from methyltrialkoxysilanes and use as water-collecting substrate,” *J. Phys. Chem. C*, vol. 113, p. 8350, 2009.
- [3] Y. Zhang, Y. Chen, L. Shi, J. Lib, and Z. Guo, “Recent progress of double-structural and functional materials with special wettability,” *J. Mater. Chem.*, vol. 22, p. 799, 2012.
- [4] P. Gould, “Smart, clean surfaces,” *Materials Today*, vol. 6, p. 44, 2003.
- [5] B. A. Akgun, A. W. Wren, C. Durucan, M. R. Towler, and N. P. Mellott, “Solgel derived silver-incorporated titania thin films on glass: bactericidal and photocatalytic activity,” *J Sol-Gel Sci Techn.*, vol. 59, p. 228, 2011.
- [6] S. Schilp, A. Rosenhahn, M. E. Pettitt, J. Bowen, M. E. Callow, J. A. Callow, and M. Grunze, “Physicochemical properties of (ethylene glycol)-containing self-assembled monolayers relevant for protein and algal cell resistance,” *Langmuir*, vol. 25, p. 10077, 2009.
- [7] R. T. Bronson, D. J. Michaelis, R. D. Lamb, G. A. Hussein, P. B. Farnsworth, M. R. Linford, R. M. Izatt, J. S. Bradshaw, and P. B. Savage,

- “Efficient immobilization of a cadmium chemosensor in a thin film: generation of a cadmium sensor prototype,” *Organic Letters*, vol. 7, p. 1105, 2005.
- [8] Q. F. Xu, J. N. Wang, and K. D. Sanderson, “Organic-inorganic composite nanocoatings with superhydrophobicity, good transparency, and thermal stability,” *ACS Nano*, vol. 4, p. 2201, 2010.
- [9] X.-M. Li, D. Reinhoudt, and M. Crego-Calama, “What do we need for a superhydrophobic surface? a review on the recent progress in the preparation of superhydrophobic surfaces,” *Chem. Soc. Rev.*, vol. 36, p. 1350, 2007.
- [10] L. Zhang, Z.-A. Qiao, M. Zheng, Q. Huo, and J. Sun, “Rapid and substrate-independent layer-by-layer fabrication of antireflection- and antifogging-integrated coatings,” *J. Mater. Chem.*, vol. 20, p. 6125, 2010.
- [11] M. Faustini, L. Nicole, C. Boissiere, P. Innocenzi, C. Sanchez, and D. Grosso, “Hydrophobic, antireflective, self-cleaning, and antifogging sol-gel coatings: an example of multifunctional nanostructured materials for photovoltaic cells,” *Chem. Mater.*, vol. 22, p. 4406, 2010.
- [12] H. Yabu and M. Shimomura, “Single-step fabrication of transparent superhydrophobic porous polymer films,” *Chem. Mater.*, vol. 17, p. 5231, 2005.
- [13] F. C. Cebeci, Z. Wu, L. Zhai, R. E. Cohen, and M. F. Rubner, “Nanoporosity-driven superhydrophilicity: a means to create multifunctional antifogging coatings,” *Langmuir*, vol. 22, p. 2856, 2006.
- [14] L. Zhang, Y. Li, J. Sun, and J. Shen, “Mechanically stable antireflection and antifogging coatings fabricated by the layer-by-layer deposition process and postcalcination,” *Langmuir*, vol. 24, p. 10851, 2008.
- [15] J. A. Howarter and J. P. Youngblood, “Self-cleaning and next generation anti-fog surfaces and coatings,” *Macromol. Rapid Commun.*, vol. 29, p. 455, 2008.
- [16] I. A. Ryzhkin and V. F. Petrenko, “Physical mechanisms responsible for ice adhesion,” *J. Phys. Chem. B*, vol. 101, p. 6267, 1997.

- [17] A. Alizadeh, M. Yamada, W. S. R. Li, S. Otta, S. Zhong, L. Ge, A. Dhinjwala, K. R. Conway, V. Bahadur, A. J. Vinciguerra, B. Stephens, and M. L. Blohm, "Dynamics of ice nucleation on water repellent surfaces," *Langmuir*, vol. 28, p. 3180, 2012.
- [18] O. Parent and A. Ilinca, "Anti-icing and de-icing techniques for wind turbines: Critical review," *Cold Regions Science and Technology*, vol. 65, p. 88, 2011.
- [19] L. K. Verma, M. Sakhuja, J. Son, A. Danner, H. Yang, H. C. Zeng, and C. S. Bhatia, "Self-cleaning and antireflective packaging glass for solar modules," *Renewable Energy*, vol. 36, p. 2489, 2011.
- [20] X.-T. Zhang, O. Sato, M. Taguchi, Y. Einaga, T. Murakami, and A. Fujishima, "Self-cleaning particle coating with antireflection properties," *Chem. Mater.*, vol. 15, p. 696, 2005.
- [21] Z. Sun, L. Jin, S. Zhang, W. Shi, M. Pu, M. Wei, D. G. Evans, and X. Duan, "An optical sensor based on h-acid/layered double hydroxide composite film for the selective detection of mercury ion," *Analytica Chimica Acta*, vol. 702, p. 95, 2011.
- [22] D. T. McQuade, A. E. Pullen, and T. M. Swager, "Conjugated polymer-based chemical sensors," *Chem. Rev.*, vol. 100, p. 2537, 2000.
- [23] B. Adhikari and S. Majumdar, "Polymers in sensor applications," *Prog. Polym. Sci.*, vol. 29, p. 699, 2004.
- [24] C. J. Brinker and G. W. Scherer, *Sol-Gel Sci.* Elsevier, 1990.
- [25] J. D. Mackenzie, *Ultra Structure Processing of Glasses, Ceramics, and Composites*. Wiley, 1984.
- [26] Q. Y. Zhang, J. Wang, G. Wu, J. Shen, and S. Buddhudu, "Interference coating by hydrophobic aerogel-like SiO_2 thin films," *Matter. Chem. Phys.*, vol. 72, p. 56, 2001.

- [27] D. Grosso, A. R. Balkenende, P. A. Albouy, M. Lavergne, L. Mazerollese, and F. Babonneau, "Highly oriented 3d-hexagonal silica thin films produced with cetyltrimethylammonium bromide," *J. Mater. Chem.*, vol. 10, p. 2085, 2000.
- [28] M. G. Voronkov, V. P. Mileshekevich, and Y. A. Yuzhelevski, *The Siloxane Bond*. New York, 1978.
- [29] L. L. Hench and J. K. West, "The sol-gel process," *Chem. Rev.*, vol. 90, p. 33, 1990.
- [30] S. S. Kistler, "Coherent expanded aerogels and jellies," *Nature*, vol. 127, p. 741, 1931.
- [31] D. W. Schaefer, C. J. Brinker, D. Richter, B. Farago, and B. Frick, "Dynamics of weakly connected solids: Silica aerogels," *Phys. Rev. Lett.*, vol. 64, p. 2316, 1990.
- [32] L. W. Hrubesh, "Aerogels - the worlds lightest solids," *Chem. Ind.*, vol. 24, p. 824, 1990.
- [33] J. Fricke, "Aerogels highly tenuous solids with fascinating properties," *J. Non-cryst. Solids*, vol. 100, p. 169, 1988.
- [34] G. S. Kim, S. H. Hyun, and H. H. Park, "Synthesis of low-dielectric silica aerogel films by ambient drying," *J. Am. Chem. Soc.*, vol. 84, p. 453, 2001.
- [35] J. C. E. Carraher, "General topics: silica aerogels-properties and uses," *Polym. News*, vol. 30, p. 386, 2005.
- [36] T. Tsutsui, M. Yahiro, H. Yokogawa, K. Kawano, and M. Yokoyama, "Doubling coupling-out efficiency in organic light-emitting devices using a thin silica aerogel layer," *Adv. Mater.*, vol. 13, p. 1149, 2001.
- [37] G. S. Kim and S. H. Hyun, "Synthesis and characterization of silica aerogel films for inter-metal dielectrics via ambient drying," *Thin Solid Films*, vol. 460, p. 190, 2004.

- [38] P. M. Barkhudarov, P. B. Shah, E. B. Watkins, D. A. Doshi, and C. J. Brinker, "Corrosion inhibition using superhydrophobic films," *Corrosion Science*, vol. 50, p. 897, 2008.
- [39] C. T. Wang, C. L. Wu, I. C. Chen, and Y. H. Huang, "Humidity sensors based on silica nanoparticle aerogel thin films," *Sensors and Actuators B*, vol. 107, p. 402, 2005.
- [40] M. H. A. A. S. Dorcheh, "Silica aerogel; synthesis, properties and characterization," *J. Mat. Proc. Tech.*, vol. 199, p. 16, 2008.
- [41] M. A. Einarsrud, S. Haereid, and V. Wittwer, "Some thermal and optical properties of a new transparent silica xerogelmaterial with low density," *Solar Energy Mater. Solar Cells*, vol. 31, p. 341, 1993.
- [42] S. S. Prakash, C. J. Brinker, A. J. Hurd, and S. M. Rao, "Silica aerogel films at ambient pressure via surface derivatization and reversible drying shrinkage," *Nature*, vol. 374, p. 439, 1995.
- [43] S. D. Bhagat, C. S. Oh, Y. H. Kim, Y. S. Ahn, and J. G. Yeo, "Methyltrimethoxysilane based monolithic silica aerogels via ambient pressure drying," *Microporous and mesoporous Materials*, vol. 100, p. 350, 2007.
- [44] M. Pagliaro, R. Ciriminna, and G. Palmisano, "Silica-based hybrid coatings," *J. Mater. Chem.*, vol. 19, p. 3116, 2009.
- [45] K. Moller and T. Bein, "Inclusion chemistry in periodic mesoporous hosts," *Chem. Mater.*, vol. 10, p. 2950, 1998.
- [46] A. Stein, B. J. Melde, and R. C. Schroden, "Hybrid inorganic-organic mesoporous silicates-nanosopic reactors coming of age," *Adv. Mater.*, vol. 12, p. 1403, 2000.
- [47] A. Sayari and S. Hamoudi, "Periodic mesoporous silica-based organic-inorganic nanocomposite materials," *Chem. Mater.*, vol. 13, p. 3151, 2001.
- [48] J. Xiong, S. N. Das, B. Shin, J. P. Kar, J. H. Choi, and J. M. Myoung, "Biomimetic hierarchical zno structure with superhydrophobic and antireflective properties," *J. Colloid Interface Sci.*, vol. 350, p. 344, 2010.

- [49] P. Podsiadlo, L. Sui, Y. Elkasabi, P. Burgardt, J. Lee, A. Miryala, W. Kusumaatmaja, M. R. Carman, M. Shtein, J. Kieffer, J. Lahann, and N. A. Kotov, "Layer-by-layer assembled films of cellulose nanowires with antireflective properties," *Langmuir*, vol. 23, p. 7901, 2007.
- [50] J.-C. Hsu, P. W. Wang, Y.-H. Lin, H.-L. Chen, Y.-Y. Chen, Y.-D. Yao, and J.-C. Yu, "Anti-reflective effect of transparent polymer by plasma treatment with end-hall ion source and optical coating," *Opt. Rev.*, vol. 17, p. 553, 2010.
- [51] M. Ma, R. M. Hill, J. L. Lowery, S. V. Fridrikh, and G. C. Rutledge, "Electrospun poly(styrene-block-dimethylsiloxane) block copolymer fibers exhibiting superhydrophobicity," *Langmuir*, vol. 21, p. 5549, 2005.
- [52] Y. Zhu, J. Zhang, Y. Zheng, Z. Huang, L. Feng, and L. Jiang, "Stable, superhydrophobic, and conductive polyaniline/polystyrene films for corrosive environments," *Adv. Funct. Mater.*, vol. 16, p. 568, 2006.
- [53] G. McHale, S. Aqil, N. J. Shirtcliffe, M. I. Newton, and H. Y. Erbil, "Analysis of droplet evaporation on a superhydrophobic surface," *Langmuir*, vol. 21, p. 11053, 2005.
- [54] C. Sanchez, B. Julian, P. Belleville, and M. Popall, "Applications of hybrid organic-inorganic nanocomposites," *J. Mater. Chem.*, vol. 15, p. 3559, 2005.
- [55] L. Gao and T. J. McCarthy, "Wetting and superhydrophobicity," *Langmuir*, vol. 25, p. 14100, 2009.
- [56] Z. Yoshimitsu, A. Nakajima, T. Watanabe, and K. Hashimoto, "Effects of surface structure on the hydrophobicity and sliding behavior of water droplets," *Langmuir*, vol. 18, p. 5818, 2002.
- [57] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, and Y. Ueda, "The lowest surface free energy based on cf_3 alignment," *Langmuir*, vol. 15, p. 4321, 1999.

- [58] M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto, and T. Watanabe, "Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces," *Langmuir*, vol. 16, p. 5754.
- [59] E. Martines, K. Seunarine, H. Morgan, N. Gadegaard, and C. D. W. Wilkinson, "Superhydrophobicity and superhydrophilicity of regular nanopatterns," *Nano Lett.*, vol. 5, p. 2097, 2005.
- [60] A. Marmur, "The lotus effect: superhydrophobicity and metastability," *Langmuir*, vol. 20, p. 3517, 2004.
- [61] N. Shirtcliffe, G. McHale, M. Newton, G. Chabrol, and C. Perry, "Dual-scale roughness produces unusually water repellent surfaces," *Adv. Mater.*, vol. 16, p. 1929, 2004.
- [62] R. Blossey, "Self-cleaning surfaces - virtual realities," *Nature Mater.*, vol. 2, p. 301, 2003.
- [63] S. Walheim, E. Schaffer, J. Mlynek, and U. Steiner, "Nanophase-separated polymer films as high-performance antireflection coatings," *Science*, vol. 283, p. 520, 1999.
- [64] Y. Li, J. Zhang, and B. Yang, "Antireflective surfaces based on biomimetic nanopillared arrays," *Nano Today*, vol. 5, p. 117, 2010.
- [65] B. Paivanranta, P. K. Sahoo, E. Tocce, V. Auzelyte, Y. Ekinici, H. H. Solak, C.-C. Liu, K. O. Stuen, P. F. Nealey, and C. David, "Nanofabrication of broad-band antireflective surfaces using self-assembly of block copolymers," *ACS Nano*, vol. 5, p. 1860, 2011.
- [66] L. Zhang, Y. Li, J. Sun, and J. Shen, "Layer-by-layer fabrication of broad-band superhydrophobic antireflection coatings in near-infrared region," *J. of Colloid Science*, vol. 319, p. 302, 2008.
- [67] Y. Li, J. Zhang, S. Zhu, H. Dong, F. Jia, Z. Wang, Z. Sun, L. Zhang, Y. Li, H. Li, W. Xu, and B. Yang, "Biomimetic surfaces for high-performance optics," *Adv. Mater.*, vol. 21, p. 4731, 2009.

- [68] S. R. Kennedy and M. J. Brett, "Porous broadband antireflection coating by glancing angle deposition," *Applied Optics*, vol. 42, p. 4573, 2003.
- [69] T. Geisler, A. Janssen, D. Scheiter, T. Stephan, J. Berndt, and A. Putnis, "Aqueous corrosion of borosilicate glass under acidic conditions: A new corrosion mechanism," *Journal of Non-Crystalline Solids*, vol. 356, p. 1458, 2010.
- [70] H. Roggendorf, F., and J. T. Syrowatka, "Corrosion of sodium silicate glasses in aqueous solutions- influence of ph," *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, vol. 51, p. 318, 2010.
- [71] R. Conradt, "Chemical durability of oxide glasses in aqueous solutions: A review," *J. Am. Ceram. Soc.*, vol. 91, p. 728, 2008.
- [72] <http://corrosion doctors.org/Household/Glass.htm>.
- [73] D. E. Clark, C. G. Pantano, and L. L. Hench, *Corrosion of glass*. Books for Industry, 1979.
- [74] J. Cheng, W. Liang, Y. Hu, Q. Chen, and G. Frischat, "Development of a new alkali resistant coating," *Journal of Sol-Gel Science and Technology*, vol. 27, p. 309, 2003.
- [75] A. Maddalena, M. Guglielmi, V. Gottardi, and A. Raccanelli, "Interactions with portland cement paste of glass fibres coated by the sol-gel method," *J. Non-Cryst. Solids*, vol. 82, p. 356, 1986.
- [76] B. Ramezanzadeh and M. Attar, "Studying the corrosion resistance and hydrolytic degradation of an epoxy coating containing zno nanoparticles," *Materials Chemistry and Physics*, vol. 130, p. 1208, 2011.
- [77] M. He, J. Wang, H. Li, X. Jin, J. Wang, B. Liu, and Y. Song, "Super-hydrophobic film retards frost formation," *soft matter*, vol. 6, p. 2396, 2010.
- [78] J. D. Verhoeven, *Fundamentals of Physical Metallurgy*. 1975.

- [79] P. Stockel, H. Vortisch, T. Leisner, and H. Baumgartel, “Homogeneous nucleation of supercooled liquid water in levitated microdroplets,” *J. Molecular Liq.*, vol. 96, p. 153, 2002.
- [80] R. Menini, Z. Ghalimi, and M. Farzaneh, “Highly resistant icephobic coatings on aluminum alloys,” , *Cold Regions Science and Technology*, vol. 65, p. 65, 2011.
- [81] L. Cao, A. K. Jones, V. K. Sikka, J. Wu, and D. Gao, “Anti-icing superhydrophobic coatings,” *Langmuir*, vol. 25, p. 12444, 2009.
- [82] H. J. Lee, “Design and development of anti-icing textile surfaces,” *J. Mater. Sci.*, vol. 47, p. 5114, 2012.
- [83] H. Wang, G. He, and Q. Tian, “Effects of nano-fluorocarbon coating on icing,” *Applied Surface Science*, vol. 258, p. 7219, 2012.
- [84] S. Jung, M. Dorrestijn, D. Raps, A. Das, and C. M. Megaridis, “Are superhydrophobic surfaces best for icephobicity,” *Langmuir*, vol. 27, p. 3059, 2011.
- [85] S. A. Kulinich, S. Farhadi, K. Nose, and X. W. Du, “Superhydrophobic surfaces: Are they really ice-repellent,” *Langmuir*, vol. 27, p. 25, 2009.
- [86] Y. Li, F. Liu, and J. Sun, “A facile layer-by-layer deposition process for the fabrication of highly transparent superhydrophobic coatings,” *Chem. Commun.*, vol. 19, p. 2730, 2009.
- [87] X. Deng, L. Mammen, Y. Zhao, P. Lellig, K. Mullen, C. Li, H. J. Butt, and D. Vollmer, “Transparent, thermally stable and mechanically robust superhydrophobic surfaces made from porous silica capsules,” *Adv. Mater.*, vol. 23, p. 2962, 2011.
- [88] H. Jiang, W. Zhao, C. Li, and Y. Wang, “Nanoporous films with designable porosity prepared with binary polymer latexes,” *Soft Matter*, vol. 7, p. 2817, 2011.

- [89] D. K. Hwang, J. H. Moon, and Y. G. Shul, "Scratch resistant and transparent uv-protective coating on polycarbonate," *J. Sol-Gel Sci. Technol.*, vol. 26, p. 783, 2003.
- [90] Z. Chen, L. Y. L. Wu, E. Chwa, and O. Tham, "Scratch resistance of brittle thin films on compliant substrates," *Mater. Sci. Eng. A*, vol. 493, p. 292, 2008.
- [91] L. Gao and T. J. McCarthy, "A perfectly hydrophobic surface," *J. Am. Chem. Soc.*, vol. 128, p. 9052, 2006.
- [92] A. Nakajima, K. Hashimoto, T. Watanabe, K. Takai, G. Yamauchi, and A. Fujishima, "Transparent superhydrophobic thin films with self-cleaning properties," *Langmuir*, vol. 16, p. 7044, 2000.
- [93] J. Bravo, L. Zhai, Z. Wu, R. E. Cohen, and M. F. Rubner, "Transparent superhydrophobic films based on silica nanoparticles," *Langmuir*, vol. 23, p. 7292, 2007.
- [94] P. Uhlmann, L. Ionov, N. Houbenov, M. Nitschke, K. Grundke, M. Motornov, S. Minko, and M. Stamm, "Surface functionalization by smart coatings: Stimuli-responsive binary polymer brushes," *Organic Coatings*, vol. 55, p. 168, 2006.
- [95] C. Xu, M. Kim, J. Chun, and D. E. Kim, "The selectively manipulated growth of crystalline zno nanostructures," *Nanotechnology*, vol. 16, p. 2104, 2005.
- [96] H. S. Lim, J. H. Baek, K. Park, H. S. Shin, J. Kim, and J. H. Cho, "Multi-functional hybrid fabrics with thermally stable superhydrophobicity," *Adv. Mater.*, vol. 22, p. 2138, 2010.
- [97] G. R. J. Artus, S. Jung, J. Zimmermann, H. P. Gautschi, K. Marquardt, and S. Seeger, "Silicone nanofilaments and their application as superhydrophobic coatings," *Adv. Mater.*, vol. 18, p. 2758, 2006.

- [98] A. V. Rao, S. S. Latthe, D. Y. Nadargi, H. Hirashima, and V. J. Ganesan, "Preparation of mtms based transparent superhydrophobic silica films by solgel method," *Colloid Interface Sci.*, vol. 332, p. 484, 2009.
- [99] M. M. Kulkarni, R. Bandyopadhyaya, and A. Sharma, "Janus silica film with hydrophobic and hydrophilic surfaces grown at an oilwater interface," *J. Mater. Chem.*, vol. 18, p. 1021, 2008.
- [100] H. Budunoglu, A. Yildirim, M. O. Guler, and M. Bayindir, "Highly transparent, flexible, and thermally stable superhydrophobic ormosil aerogel thin films," *ACS Appl. Mater. Interfaces*, vol. 3, p. 539, 2011.
- [101] A. V. Rao, S. D. Bhagat, H. Hirashima, and G. M. Pajonk, "Synthesis of flexible silica aerogels using methyltrimethoxysilane (mtms) precursor," *J. Coll. Interf. Sci.*, vol. 300, p. 279, 2006.
- [102] L. T. Zhuravlev, "Concentration of hydroxyl groups on the surface of amorphous silicas," *Langmuir*, vol. 3, p. 316, 1987.
- [103] N. J. Schirtcliffe, G. McHale, M. I. Newton, C. C. Perry, and P. Roach, "Porous materials show superhydrophobic to superhydrophilic switching," *Chem. Commun.*, vol. 25, p. 3135, 2005.
- [104] A. V. Rao, M. M. Kulkarni, D. Amalnerkar, and T. Seth, "Superhydrophobic silica aerogels based on methyltrimethoxysilane precursor," *J. Non-Cryst. Sol.*, vol. 330, p. 187, 2003.
- [105] A. Yildirim, H. Budunoglu, H. Deniz, M. O. Guler, and M. Bayindir, "Template-free synthesis of organically modified silica mesoporous thin films for tnt sensing," *ACS App. Mater. Interf.*, vol. 2, p. 2892, 2010.
- [106] S. Tao, G. Li, and H. Zhu, "Metalloporphyrins as sensing elements for the rapid detection of trace tnt vapor," *J. Mater. Chem.*, vol. 16, p. 4521, 2006.
- [107] N. Leventis and I. A. Elder, "Durable modification of silica aerogel monoliths with fluorescent 2,7-diazapyrenium moieties. sensing oxygen near the speed of open-air diffusion," *Chem. Mater.*, vol. 11, p. 2837, 1999.

- [108] F. S. Rodenbusch, L. F. Campo, S. Rigacci, and V. Stefani, "A new esipt fluorescent dye-doped silica aerogel," *AerogelMacromol. Symp.*, vol. 229, p. 188, 2005.
- [109] I. A. E. J. Y. A. D. C. S.-L. N. Leventis, A. M. Rawashdeh, "Synthesis and characterization of ru(ii) tris(1,10-phenanthroline)-electron acceptor dyads incorporating the 4-benzoyl-n-methylpyridinium cation or n-benzyl-n'-methyl-viologen. improving the dynamic range, sensitivity and response time of sol-gel based optical oxygen sensors," *Chem. Mater.*, vol. 16, p. 1493, 2004.
- [110] X. Li, J. P. Gao, L. J. Xue, and Y. C. Han, "Porous polymer films with gradient-refractive-index structure for broadband and omnidirectional antireflection coatings," *Adv. Funct. Mater.*, vol. 20, p. 259, 2010.
- [111] A. L. Penard, T. Gacoin, and J. P. Boilot, "Functionalized solgel coatings for optical applications," *Acc. Chem. Res.*, vol. 40, p. 895, 2007.
- [112] P. Nostell, A. Roos, and B. Karlsson, "Optical and mechanical properties of sol-gel antireflective films for solar energy applications," *Thin Solid Films*, vol. 351, p. 170, 1999.
- [113] W. Shimizu and Y. Murakami, "Microporous silica thin films with low refractive indices and high youngs modulus," *ACS Appl. Mater. Interfaces*, vol. 2, p. 3128, 2010.
- [114] J. Hiller, J. D. Mendelsohn, and M. F. Rubner, "Reversibly erasable nanoporous anti-reflection coatings from polyelectrolyte multilayers," *Nature Mater.*, vol. 1, p. 59, 2002.
- [115] H. Budunoglu, A. Yildirim, and M. Bayindir, "Flexible and mechanically stable antireflective coatings from nanoporous organically modified silica colloids," *J. Mater. Chem.*, vol. 22, p. 9671, 2012.
- [116] H. Dong, R. F. Reidy, and J. D. Brennan, "Shrinkage and springback behavior of methylsilsesquioxanes prepared by an acid/base two-step processing procedure," *Chem. Mater.*, vol. 17, p. 6012, 2005.

- [117] K. Kanamori, M. Aizawa, K. Nakanishi, and T. Hanada, "New transparent methylsilsesquioxane aerogels and xerogels with improved mechanical properties," *Adv. Mater.*, vol. 19, p. 1589, 2007.
- [118] A. Yildirim, H. Budunogl, M. Yaman, M. O. Guler, and M. Bayindir, "Template free preparation of nanoporous organically modified silica thin films on flexible substrates," *J. Mater. Chem.*, vol. 21, p. 14830, 2011.
- [119] L. Martin, J. O. Osso, S. Ricart, A. Roig, O. Garcia, and R. Sastre, "Organo-modified silica aerogels and implications for material hydrophobicity and mechanical properties," *J. Mater. Chem.*, vol. 18, p. 207, 2008.
- [120] F. Iacopi, C. Elia, T. Fournier, F. Sinapi, and Y. Travaly, "Stress corrosion of organosilicate glass films in aqueous environments: Role of ph," *J. Mater. Res.*, vol. 23, p. 862, 2008.
- [121] T. V. Antropova, "Kinetics of corrosion of the alkali borosilicate glasses in acid solutions," *Journal of Non-Crystalline Solids*, vol. 345, p. 270, 2004.
- [122] C. Cailleteau, F. Angeli, F. Devreux, S. Gin, J. Jestin, P. Jollivet, and O. Spalla, "Insight into silicate-glass corrosion mechanisms," *nature Mater.*, vol. 7, p. 978, 2008.
- [123] D. Wang and G. P. Bierwagen, "Solgel coatings on metals for corrosion protection," *Progress in Organic Coatings*, vol. 64, p. 327, 2008.
- [124] B. C. Dave, X. Hu, Y. Devaraj, and S. K. Dhali, "Solgel-derived corrosion-protection coatings," *Journal of Sol-Gel Science and Technology*, vol. 32, p. 143, 2004.
- [125] A. Pepe, M. Aparicio, S. Cere, and A. Duran, "Preparation and characterization of cerium doped silica solgel coatings on glass and aluminum substrates," *Journal of Non-Crystalline Solids*, vol. 348, p. 162, 2004.
- [126] L. V.-Castro, J. M.-Vivar, and R. M.-Serna, "Porous $\text{SiO}_2\text{TiO}_2\text{ZrO}_2$ obtained from polymeric systems prepared by the solgel process," *Journal of Porous Materials*, vol. 8, p. 303, 2001.

- [127] W. Boysen, A. Frattini, N. Pellegrini, and O. Sanctis, "Protective coatings on copper prepared by solgel for industrial applications," *Surface and Coatings Technology*, vol. 122, p. 14, 1999.
- [128] Z. Ren, Y. Huang, M. Shen, C. Song, W. Weng, G. Han, N. Ma, and P. Du, "Electrical and corrosion properties of the Ti_5Si_3 thin films coated on glass substrate by APCVD method," *Journal of Non-Crystalline Solids*, vol. 357, p. 2802, 2011.
- [129] E. A. Meulen Kamp, "Synthesis and growth of ZnO nanoparticles," *J. Phys. Chem. B*, vol. 102, p. 5566, 1998.
- [130] F. C. M. Woudenberg, W. F. C. Sager, J. E. Elshof, and H. Verweij, "Nanostructured dense ZrO_2 thin films from nanoparticles obtained by emulsion precipitation," *J. Am. Ceram. Soc.*, vol. 87, p. 1430, 2004.
- [131] L. Spanhel and M. A. Anderson, "Semiconductor clusters in the sol-gel process: Quantized aggregation, gelation, and crystal growth in concentrated ZnO colloids," *J. Am. Chem. Soc.*, vol. 113, p. 2826, 1991.
- [132] W. G. Beier and G. H. Frischat, "Thin $\text{SiO}_2\text{-TiO}_2\text{-ZrO}_2$ films from alkoxide solutions," *J. Non-Cryst. Solids*, vol. 100, p. 531, 1988.
- [133] X. Liu and J. He, "One-step hydrothermal creation of hierarchical microstructures toward superhydrophilic and superhydrophobic surfaces," *Langmuir*, vol. 25, p. 11822, 2009.
- [134] L. Yin, Q. Xia, J. Xue, S. Yang, Q. Wang, and Q. Chen, "In situ investigation of ice formation on surfaces with representative wettability," *Applied Surface Science*, vol. 256, p. 6764, 2010.
- [135] C. Antonini, M. Innocenti, T. Horn, M. Marengo, and A. Amirfazli, "Understanding the effect of superhydrophobic coatings on energy reduction in anti-icing systems," *Cold Regions Science and Technology*, vol. 67, p. 58, 2011.
- [136] S. Kulinich and M. Farzaneh, "Ice adhesion on super-hydrophobic surfaces," *Applied Surface Science*, vol. 255, p. 8153, 2009.

- [137] F. Wang, C. Li, Y. Lv, F. Lv, and Y. Du, “Ice accretion on superhydrophobic aluminum surfaces under low-temperature conditions,” *Cold Regions Science and Technology*, vol. 62, p. 29, 2010.
- [138] K. K. Varanasi, T. Deng, J. D. Smith, M. Hsu, and N. Bhate, “Frost formation and ice adhesion on superhydrophobic surfaces,” *Appl. Phys. Lett.*, vol. 97, p. 234102, 2010.
- [139] P. Guo, Y. Zheng, M. Wen, C. Song, Y. Lin, and L. Jiang, “Icephobic/anti-icing properties of micro/nanostructured surfaces,” *Adv. Mater.*, vol. 24, p. 2642, 2012.
- [140] R. Jafari, R. Menini, and M. Farzaneh, “Superhydrophobic and icephobic surfaces prepared by rf-sputtered polytetrafluoroethylene coatings,” *Applied Surface Science*, vol. 257, p. 1540, 2010.
- [141] S. V. Chuppina, “Anti-icing gradient organosilicate coatings,” *Glass Physics and Chemistry*, vol. 33, p. 502, 2007.
- [142] A. Hashmi, A. Strauss, and J. Xu, “Freezing of a liquid marble,” *Langmuir*, vol. in press.