B.Tech Project Report on

SELF-ASSEMBLY OF SILICA NANOPARTICLES ON GLASS SURFACE

For partial fulfilment of the requirements for the degree of

Bachelor of Technology

In

Chemical Engineering

Submitted by:

Utkarsh Singh

Roll No. 111CH0088

Under the guidance of:

Dr. Santanu Paria

Department of Chemical Engineering

National Institute of Technology Rourkela

Rourkela-769008

2015

Department of Chemical Engineering
National Institute of Technology Rourkela
Rourkela-769008, Odisha

CERTIFICATE

This is to certify that the project report titled "**Self-Assembly of Silica Nanoparticles on Glass Surface**" submitted by **Utkarsh Singh (111CH0088)** in partial fulfilment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance.

To best of my knowledge, the content embodied in this thesis has not been submitted to any other university or institute for the award of any degree.

Date: 10/05/2015

Place: NIT Rourkela

Dr. Santanu Paria
Department of Chemical Engineering,
National Institute of Technology Rourkela
Rourkela - 769008

ACKNOWLEDGEMENT

I would like to convey my gratitude to my supervisor Prof. (Dr.) Santanu Paria for his careful guidance throughout the research project work. His constant motivation and constructive criticism helped in imbibing in me an interest in research.

I would also like to extend my gratitude to the Head of the Department, Prof. (Dr.) Pradip Rath for his careful supervision and management of the undergraduate project work.

My heartfelt thanks go to the post-graduate students and doctoral fellows in Interfaces and Nanomaterials Laboratory, especially Nainsi Saxena for helping me in getting acquainted with the instruments in the lab. The association of people in the lab will stay with me throughout my career. I also thank my class friends for helping me in some form or the other during my project work.

I would like to thank my parents and family members blessing me throughout my stay at NIT Rourkela.

Date: 10/05/2015 **Utkarsh Singh**

Place: NIT Rourkela **Roll No. 111CH0088**

Department of Chemical Engineering

National Institute of Technology Rourkela

Rourkela-769008

CONTENTS

Certificate…….… ii

Acknowledgement……..... iii

Abstract……..... vi

List of Figures…….. vii

Nomenclature……ix

1. Introduction

1.1 Self-Assembly……2

1.2 Types of Self-Assembly……...……..2

1.3 Applications of Self-Assembly……..……2

1.4 Hydrophilicity and Superhydrophilicity……..…….3

1.5 Layer-by-Layer Assembly……...…..3

1.6 Present Scenario and Future Applicability……...…….3

2. Literature Review

2.1 Introduction……6

2.2 Synthesis of Silica Nanoparticles……...6

2.3 Superhydrophilicity and Layer-by-Layer Assembly……..7

3. Synthesis of Silica Nanoparticles

3.1 Introduction……12

3.2 Materials and Methods…….…….……12

3.3 Results and Discussion……...13

4. Self-Assembly of Silica Nanoparticles and their Layer-by-Layer Coating on a Glass Surface

4.1 Introduction……..……16

4.2 Materials and Methods……...16

4.2.1 Preparation of Silica Nanoparticle and CMCNa Template.....17

4.2.2 LbL Dip Coating of PDDA and Silica Nanoparticles……...17

4.2.3 LbL Dip Coating of PDDA and Solution "D"……. 18

4.3 Results and Discussion……...…18

4.3.1 Evaporation-Induced Self-Assembly of CMCNa and Oxalic Acid (Solution "D")……..18

4.3.2 Sessile Drop of SiO_2 Nanoparticles and Solution "D"……...19

4.3.3 LbL Dip Coating of PDDA and SiO_2 Nanoparticles……..20

4.3.4 LbL Dip Coating of PDDA and SiO_2 Nanoparticles-CMCNa Template.....21

(a) Images from Optical Microscope……21

(b) Images from Scanning Electron Microscope (SEM)…..22

4.3.5 Contact Angle Measurements on Dip-Coated Slides…..……22

(a) Contact Angle with $(PDDA/SiO_2)_{10}$ Coating……..22

(b) Contact Angle with $(PDDA/D5)_{10}$ Coating…….23

5. Conclusions…...……26

References…….28

ABSTRACT

In this work, silica nanoparticles were synthesised using Stöber Method. Compared to other synthesis techniques like, Stöber Method is regarded as one of the simplest and most effective route for silica nanoparticle synthesis. Low temperature stabilises the nanosilica suspension, and low ratio of NH_3/TEOS avoids coagulation of particles.

These nanoparticles (average size less than 1 μm) were self-assembled on a glass surface using sodium carboxymethyl cellulose (CMCNa) and oxalic acid template. The silica nanoparticle self-assembly was validated by the observed fractal-pattern in a sessile drop. For preparing superhydrophilic film, sequential adsorption (layer-by-layer coating) of a polyelectrolyte and silica nanoparticle suspension on the surface was done for appropriate number of cycles. Layer-by-Layer assembly is an economical, easy and a fast technique for coating of substrates with alternate layers. It is known that superhydrophilicity (and superhydrophobicity) increases with increase in surface roughness. By this technique, two different coatings with equal number of depositions were created – one consisting of polyelectrolyte and silica nanoparticles and other consisting of polyelectrolyte and silica nanoparticle with sodium carboxymethyl cellulose and oxalic acid. Contact angle measurement done on these two coating validated the superhydrophilic property of the films. The second-type coating had a lower contact angle (less than 10°) while the first-type coating had a contact angle slightly greater than 10°.

Key words: self-assembly; Stöber Method; silica nanoparticles; superhydrophilic; layer-by-layer; sodium carboxymethyl cellulose

LIST OF FIGURES

Figure 2.1 SEM images of a sample of silica spheres in, (a) ethanol-ethyl ester system, and (b) ethanol-pentyl ester system…….……..7

Figure 2.2 (a) TEM image of SiO_2 nanoparticles, (b) Schematic of the fabrication procedure……...….8

Figure 2.3 Schematic of the multilayer film showing the three main assembly blocks…….……9

Figure 2.4 Image of a glass slide coated with transparent, superhydrophobic multilayer film……...…9

Figure 2.5 Schematic illustration of fabrication of AR coatings on quartz and silicon substrate……10

Figure 2.6 (a) SEM image of the superhydrophobic AR coating. (b)Magnified view of SiO_2 particles in (a). (c) The cross-sectional SEM image of the superhydrophobic AR coating. (d) & (e) Shapes of water droplets (4 μl) on top of the superhydrophobic AR coatings……...…10

Figure 3.1 SEM images of synthesised silica nanoparticles. Scales: (a) 5μm, (b) 3μm, (c) 500 nm, (d) 5μm…….……14

Figure 3.2 Particle size v/s Intensity (%) from DLS analysis……..……..14

Figure 4.1 Schematic diagram of LbL for $(PDDA/SiO_2)_6$ coating……18

Figure 4.2 Tree-like fractal pattern by EISA of solution "D", with scales (a) 500 μm, (b) 50 μm…….……18

Figure 4.3 Fractal pattern with SiO_2 nanoparticles and solution "D" (before calcination) for the two volume ratios, with scales (a) 50 μm, (b) 50 μm, (c) 500 μm, (d) 50 μm……19

Figure 4.4 Fractal pattern with SiO_2 nanoparticles and solution "D" (after calcination) for the two volume ratios, with scales (a) 50 μm,(b)50 μm,(c)200 μm, (d) 50 μm…….…...….20

Figure 4.5 SEM images of $(PDDA/SiO_2)_n$,(a) n=1,(b) n=4,(c)n=4(magnified),(d)n=5....20

Figure 4.6 Optical Microscope images of $(PDDA/D5)_3$ coatings before calcination, with scales (a) 200 μm (b) 50 μm……...21

Figure 4.7 Optical Microscope image of $(PDDA/D5)_5$ coating after calcination, scale 50 μm…….……..…21

Figure 4.8 SEM images of $(PDDA/SiO_2)_3$ coating after calcination, with scales (a) 5μm (b) 10 μm……...…...22

Figure 4.9 Contact angle on uncoated plane slide, (a) 44.4° (Left CA), 42.4° (Right CA). Contact angle on $(PDDA/SiO_2)_{10}$, (b) 8.9° (Left CA), 13.4° (Right CA) (c) 18.2° (Left CA), 16.9° (Right CA) (d) 16.1° (Left CA, right CA).……..…….23

Figure 4.10 Contact angle on uncoated plane slide, (a) 42.8° (Left CA), 42.0° (Right CA). Contact angle on $(PDDA/D5)_{10}$ slides, (b) 6.7° (Left CA), 6.7° (Right CA) (c) 8.9° (Left CA), 8.4° (Right CA), (d) 7.3° (Left CA), 8.7° (Right CA)..……24

NOMENCLATURE

AR	Anti-reflective
CVD	Chemical Vapor Deposition
EISA	Evaporation-Induced Self-assembly
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
LbL	Layer-by-Layer
WCA	Water contact angle
DLS	Dynamic Light Scattering
Solution "D"	A solution of 0.4 wt% CMCNa, 40 mM oxalic acid, and deionised water
D5	A 1:5 volume ratio of diluted silica nanoparticle solution (1:10 in ethanol) and solution "D"
$(PDDA/SiO_2)_n$	"n" number of alternate deposition of PDDA and silica nanoparticle cycle deposited by dip coating
$(PDDA/D5)_n$	"n" number of alternate deposition of PDDA and silica nanoparticle with CMCNa template by dip coating

CHAPTER 1

INTRODUCTION

1 INTRODUCTION

1.1 Self-Assembly

Self-assembly is defined as the spontaneous organisation of individual components into an ordered structure without human intervention. Self-assembly is the process where components spontaneously organize or assemble into more complex objects, typically by bouncing around in a solution or gas phase until a stable structure of minimum energy is reached. These processes are common throughout nature and technology, involving components from the molecular to planetary scales, under appropriate conditions. Various forces exist which are responsible for self-assembly, *viz.*, molecular interactions, electrostatic interaction, hydrogen bonding, hydrophobic forces, dispersion forces, etc. Factors responsible for, and affecting, self-assembly are temperature, reactant concentration and ratios, solution condition (pH), substrate property, drop size, time, etc. In recent years, self-assembly has evolved into various other sub-groups such as Aerial Assembly, Fluid Assembly, Fluid Crystallization, Bio-molecular Self-Assembly, Autonomous mass-assembly, Chiral Self-Assembly, Self-Assembly Line.

1.2 Types of Self-Assembly

Based on methods of fabrication self-assembly is classified as (i) Top-down approach, and (ii) Bottom-up approach. Based on energy consideration, it can be classified as (i) Static self-assembly, and (ii) Dynamic self-assembly. In static self-assembly there is no energy dissipation during the entire assembly process. Examples of static self-assembly includes formation of globular proteins and molecular crystals. In case of dynamic self-assembly, there is a constant dissipation of energy by the system, such as in a tissue, a school of fish. Further, based on the sizes of self-assembling particles, it may be classified into Atomic Self-Assembly, Molecular Self-Assembly, Colloidal Self-Assembly, Biological Self-Assembly, and Interfacial Self-Assembly. Surface modified silica nanoparticles are classified as molecular self-assembled structure.

1.3 Applications of Self-Assembly

The idea of a self-assembled, minimum energy and stable structure has attracted considerable attention. In recent times, self-assembly has evolved into a span encompassing multifarious applications, both on a research and an industrial scale. It is believed to have a great potential

in materials and condensed matter science. It has applications in crystallisation (at all scales), nanoscience and technology, robotics and manufacturing, microelectronics, etc.

1.4 Hydrophilicity and Superhydrophilicity

The term "superhydrophilicity" was first used in the year 2000 being derived as an extension to the term "superhydrophobicity". A variety of different definitions of hydrophilic and hydrophobic surfaces are used by the scientific community. A hydrophilic surface has a strong affinity towards water whereas a hydrophobic surface repels water. Hydrophilic surface possesses a water contact angle (WCA) less than 90° while a hydrophobic surface has WCA exceeding 90°. Moreover, a superhydrophilic surface has WCA lower than 10° while a superhydrophobic surface has a WCA higher than 150°. Both these properties can be attributed to the surface roughness and topography of the surface. Almost all natural materials are hydrophilic in nature.

1.5 Layer-by-Layer Assembly

Layer-by-Layer (LbL) assembly is a cost-effective and simple technique to alternatively deposit oppositely charged layers of desired material. The alternate deposition is done till the required thickness of film is achieved. This method provides a higher degree of control over film thickness compared to other techniques. Other advantages of LbL includes – use of aqueous solution, making it more convenient than other techniques; ability for deposition on curved surfaces; cost-effectiveness and potential of large-scale production. Literatures have shown the possibility of manipulating thickness as low as 1 nm by LbL technique.

1.6 Present Scenario and Future Applicability

As discussed earlier, almost all natural materials are hydrophilic in nature. It is therefore possible to replicate hydrophilic properties in artificial materials. Wide variety of materials are already available in the market whose design is based on superhydrophilic phenomenon. Biotechnology and Biomedical Engineering are two of the fastest developing fields in modern-day science and engineering. One of the primary applications of these is in human health. Biocompatible scaffolds, devices and implants for in-vivo use require hydrophilicity and superhydrophilicity as essential phenomena in the host environment. Other uses of superhydrophilic coatings include anti-fogging screens (in cars, mirrors, windows, etc.), microfluidic devices in electronics, anti-fouling coatings in heat transfer and mass transfer operation, etc. A unique application of superhydrophilic films can be exploited by converting

them into superhydrophobic films by depositing the former with a hydrophobic layer. Although, in the present scenario, huge applications of superhydrophobic films have been well researched and reviewed, there is an increasing emphasis on potential applications of superhydrophilic films in other areas.

CHAPTER 2

LITERATURE REVIEW

2 LITERATURE REVIEW

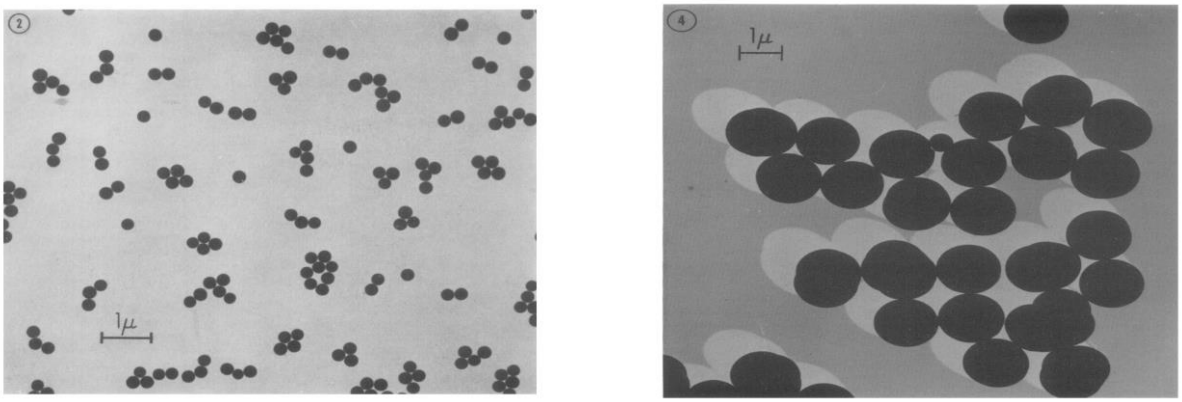
2.1 Introduction

Silica nanoparticles are of promising application in emerging areas of technology and research because of the varied applications that they have. Silica particles obtained from natural sources, like sand, contain metal impurities and are therefore unsuitable for advanced scientific research and industrial application [1]. Mesoporous silica is a mesoporous form of silica, the most common types being MCM-41 and SBA-15.

Self-assembly is defined as the spontaneous organisation of individual components into an ordered structure without human intervention. Much of the work in the field of self-assembly has been done on molecular level, but self-assembly at nano level to micro level provides better control over reaction conditions [2]. In fact, as the size of assembling particles increases, more reaction parameters can be varied to analyse the self-assembly.

2.2 Synthesis of Silica Nanoparticles

The first pioneering work in nanosilica synthesis was done by Stöber et al. [3] in that they used alkyl silicates in various alcoholic solvents, *viz*, methanol, ethanol, *n*-propanol and *n*-butanol in ammonia resulting in particles in 0.05-2 μ range. Particles were grown under various conditions by using different component concentration and several alcohols or alcohol mixture or solvents. They compared the reaction rates with tetramethyl ester and tetrapentyl ester and observed that the former gave fastest rate (less than 1 min.) with smallest sized particle (less than 0.2 μ) while reaction with the latter gave slowest rate but big particles. Ammonia apparently influenced the morphology, and created spherical particles whenever it was present during the reaction. Reaction rate was found to be fastest with methanol while n-butanol resulted in slowest rate but with wide-size distribution. Further, a volume ratio methanol:butanol of 1:1 resulted in more uniform larger particles. An increase in ammonia concentration up to 8M resulted in larger particles. By varying the water concentration, maximum particle size was obtained at 6M while different ester concentration between 0.02 and 0.5M had no significant influence on particle size. The reactions were carried out under isothermal condition (22°C).



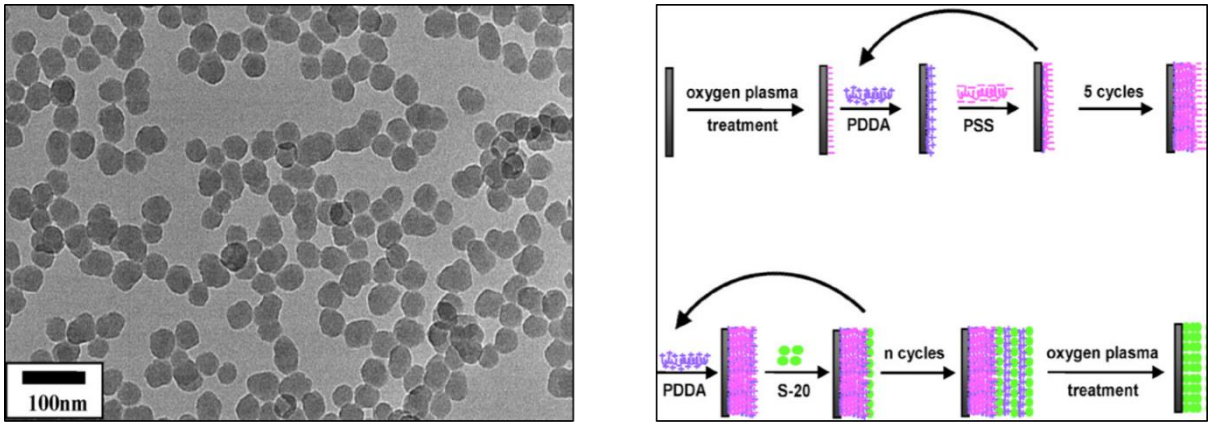
(a) (b)

Figure 2.1: SEM images of a sample of silica spheres in, (a) ethanol-ethyl ester system, and (b) ethanol-pentyl ester system. [3]

Silica particles in the size range of tens–hundreds nanometers by using microemulsions method [4]. Although, reverse microemulsion produces particles with higher average monodispersity (particularly in the size range of 30-60 nm) compared to Stöber Method, its main drawback is high cost and the difficulty in adequate removal of surfactant in the final product . Synthesis by Stöber Method leads to formation of monodispersed spherical particles under mild reaction conditions, and it is regarded as the simplest and the most effective route for nanoparticle synthesis [5].

2.3 Superhydrophilicity and Layer-by-Layer Assembly

Superhydrophilic and AR (anti-reflective) silica nanoparticle coating was fabricated on poly (methyl methacrylate) (PMMA) via LbL assembly of PDDA and SiO_2 suspension followed by oxygen plasma treatment [6]. Prior to (PDDA/SiO_2) coating, a primer layer comprising alternatively-deposited PDDA and PSS was coated. Firstly, monodisperse silica nanoparticles (ca. 20nm) were synthesised by Stöber Method. The adsorption of alternate layers of PDDA and SiO_2 suspension depends on a trade-off between the electrostatic attraction between PDDA and SiO_2, and repulsion between similar PDDA and SiO_2. The obtained coating was highly transparent with a transmittance as high as 99% before oxygen plasma treatment and 98.5% after oxygen plasma treatment. The WCA reached below 5° in 0.5 seconds after oxygen plasma treatment using water droplets of 1 μl. Surface morphology of the coating and structure of the nanoparticles was observed by SEM and TEM.



(a) (b)

Figure 2.2: (a) TEM image of SiO_2 nanoparticles, (b) Schematic of the fabrication procedure. [6]

In another work, two differently sized silica nanoparticles (20 nm and 50 nm) were synthesised for developing transparent superhydrophilic films using Layer-By-Layer coating process wherein sequential adsorption of silica nanoparticle and poly (allylamine hydrochloride) was performed on a glass surface. The authors prepared three main layers on the glass surface [7]. These three layers were the adhesion layer, body layer, and the top layer. The bottom most layer comprised binder and poly (allylamine hydrochloride) while the other two layers comprised mixture of silica nanoparticle and poly (allylamine hydrochloride). The final film was made superhydrophobic by CVD of silane. It was observed that as the number of mixed nanoparticle bilayers was increased, both the advancing and receding contact angle increased. Moreover, after the CVD was done, multilayer films with 20 or more bilayers exhibited superhydrophobic properties (contact angle greater than 150° and low contact angle hysteresis). An increase in this number to 40 showed nearly same superhydrophobic properties. Various properties were measured, namely thickness (nm), refractive Index, *rms* thickness, advancing CA (before and after silane treatment), receding CA (after silane treatment). Their study suggested that a trade-off exists between transparency and superhydrophobicity. By controlling the placement and level of aggregation of the differently sized nanoparticles within the resultant multilayer thin film, it is possible to optimise the level of roughness to achieve superhydrophobic behaviour with limited light scattering.

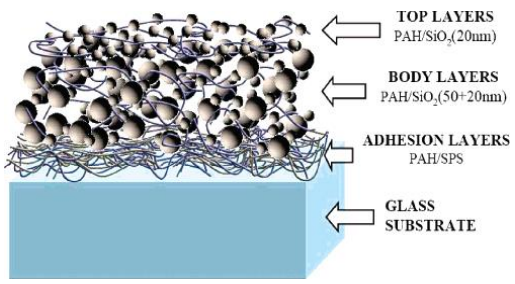


Figure 2.3: Schematic of the multilayer film showing the three main assembly blocks. [7]

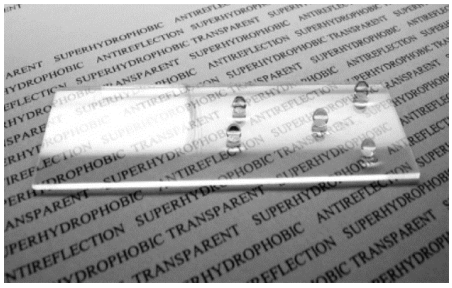


Figure 2.4: Image of a glass slide coated with transparent, superhydrophobic multilayer films. [7]

Superhydrophobic films using a simpler procedure, as discussed above were developed. In this work, mesoporous silica nanoparticle (ca. 70-90 nm in size) of non-spherical morphology were synthesised using cetyltrimethylammonium bromide (CTAB) as surfactant and TEOS as precursor and Ibuprofen as co-surfactant [8]. The particles were coated on a glass surface by Layer-by-Layer technique. The obtained coating was antireflective and superhydrophilic which was subsequently converted to antireflective and superhydrophobic (sliding angle less than 1°) coating. While micrometer-scale roughness and mesopores of silica nanoparticles affect both superhydrophilicity and superhydrophobicity, self-cleaning property can be achieved by a low water droplet sliding angle (less than 10°) on the coated substrate [9]. In the above literatures, no one explained assembly of silica nanoparticles through spin-coating. We will try to further explore this work by studying EISA behaviour of metal nano-particles on this surface and its application.

A 400-nm thick superhydrophobic AR (anti-reflective) coating on a quartz and silicon substrate in near infrared region (NIR) by LbL deposition was prepared followed by CVD of fluoroalkylsilane 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS) [9]. Firstly, the SiO_2 nanoparticles were synthesised by Modified Stöber method. Then, on a quartz/silicon substrate, LbL deposition of (PDDA/SiO_2) multilayer film was done, followed by LbL deposition of (PDDA/sodium silicate) multilayer film. Finally, the film was surface-modified by fluorination treatment (CVD of POTS). The as-fabricated superhydrophobic AR coating was also found to prevent water absorption when used in an environment of high humidity. They studied the dependence of water contact angle on the number of cycle depositions. With the deposition cycle increasing, transmittance increased accordingly. The unique superhydrophobicity property of obtained film (WCA of 154°) is credited to a two-level hierarchical rough structure.

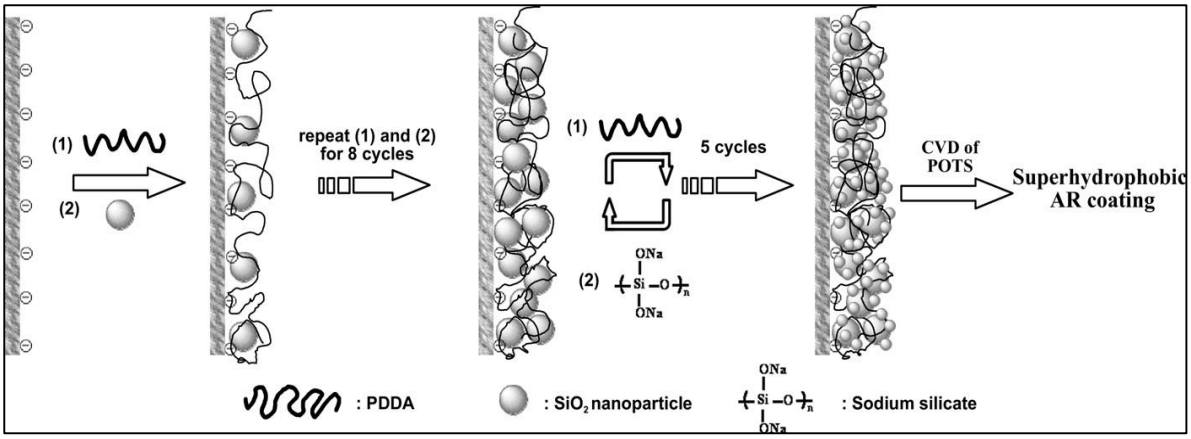


Figure 2.5: Schematic illustration of fabrication of AR coatings on quartz and silicon substrate. [9]

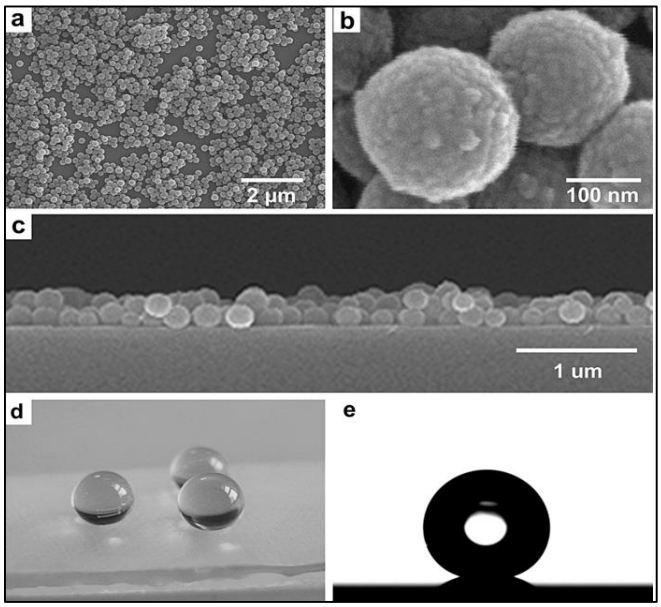


Figure 2.6: (a) SEM image of the superhydrophobic AR coating. (b)Magnified view of SiO_2 particles in (a). (c) The cross-sectional SEM image of the superhydrophobic AR coating. (d) & (e) Shapes of water droplets (4 μl) on top of the superhydrophobic AR coatings. [9]

Effect of UV radiation on hydrophilicity and transparency of TiO_2 coated glass slide has also been studied. It was found that water droplets on the TiO_2 coated glass slide, initially stored in dark, formed lens cap. Upon illumination with UV radiation, complete wetting took place [10].

CHAPTER 3

SYNTHESIS OF SILICA NANOPARTICLES

3 SYNTHESIS OF SILICA NANOPARTICLES

3.1 Introduction

Materials such as silica exhibit unusual absorption properties, along with useful thermal, mechanical and optical properties. Natural silica contains metal impurities which makes it unsuitable for advanced scientific and industrial use, thus making it essential to synthesise silica artificially. Some of the techniques for silica nanoparticle synthesis are Reverse Microemulsion, Flame Synthesis, and Sol-gel method. Among these, Sol-Gel method is widely used due to its ability to control particle size and distribution by carefully controlling the reaction parameters. The famous Stöber Method is a sol-gel method for synthesising monodisperse silica nanoparticles under mild reaction conditions, and it is considered as one of the most effective route for silica nanoparticles synthesis. Stöber Method involves synthesis of spherical and monodispersed silica particles by hydrolyses and condensation of Tetraethyl orthosilicate (TEOS) in aqueous alcohol in the presence of ammonia as catalyst. An optimal condition for Stöber Method would result in smallest, homogeneous, and monodispersed nanoparticles.

3.2 Materials and Methods

Chemical used in the synthesis of silica nanoparticles were: Tetraethyl orthosilicate (TEOS) (99%, Sigma Aldrich), aqueous ammonia (25%, Sigma Aldrich), absolute ethanol (99.5%, Sigma Aldrich). Deionised water was used for all the experiments. Some of the instruments used during synthesis were: Bath Ultrasonicator (Elmasonic PH 10), Probe Ultrasonicator (Sonics), Magnetic Stirrer and Heater (IKA® ICT Basic), Air Oven (Reico), Optical Microscope (Leica), etc. The size of nanoparticles were determined by SEM (Geol).

Tetraethyl orthosilicate, ethanol and aqueous ammonia were used as obtained from the supplier. Firstly, certain amount of ethanol, aqueous ammonia and deionised water were mixed in a reaction container. The mixture was then stirred in a magnetic stirrer (IKA® ICT Basic) for 3 hours. Three minutes after stirring was started, a known volume of tetramethyl orthosilicate was added drop wise into the reaction container. This ensured uniform mixing of

tetraethyl orthosilicate in the mixture. The average particle size was determined from DLS analysis, and surface morphology was observed by SEM. The experiment was carried out at room temperature (27°C), and all the vessels were cleaned with water under sonication at 37 and 60 kHz before using.

3.3 Results and Discussion

The clear solution turned showed turbidity ten minutes after drop wise addition of Tetramethyl orthosilicate to the mixture of ethanol, aqueous ammonia and water. This was due to the condensation reaction. The solution was completely turbid after 3 hours of stirring.

Following reactions take place during the synthesis –

$$Si(C_2H_5O)_4 + H_2O \xrightarrow{\text{Hydrolysis}} Si(OC_2H_5)OH + C_2H_5OH \ldots\ldots\ldots(1)$$

$$(OR)_3 - Si - OH + OH - Si - (OR)_3 \xrightarrow{\text{Water condensation}} (OR)_3 - Si - O - Si - (RO)_3 + H_2O \ldots\ldots\ldots(2)$$

$$(OR)_3 - Si - OC_2H_5 + HO - Si - (RO)_3 \xrightarrow{\text{Alcohol condensation}} (OR)_3 - Si - O - Si - (RO)_3 + C_2H_5OH \ldots(3)$$

Tetraethyl orthosilicate hydrolyses to form silanol, $Si(OC_2H_5)OH$. The silanol molecules condense among themselves and/or with the ethoxy groups to form siloxane bridges which form the basis of the nanoparticle structure.

Following observations were made:

i. Low temperature stabilises the solution.
ii. Hydrolysis of TEOS is accelerated by increasing the ammonia and water concentration till a maximum limit. After this, the hydrolysis rate starts decreasing.
iii. Low ratio of NH_3/TEOS avoids the coagulation of particles.

The surface morphology of the particle was determined by Scanning Electron Microscopy. Particles were chiefly spherical in shape which can be seen in the subsequent figure.

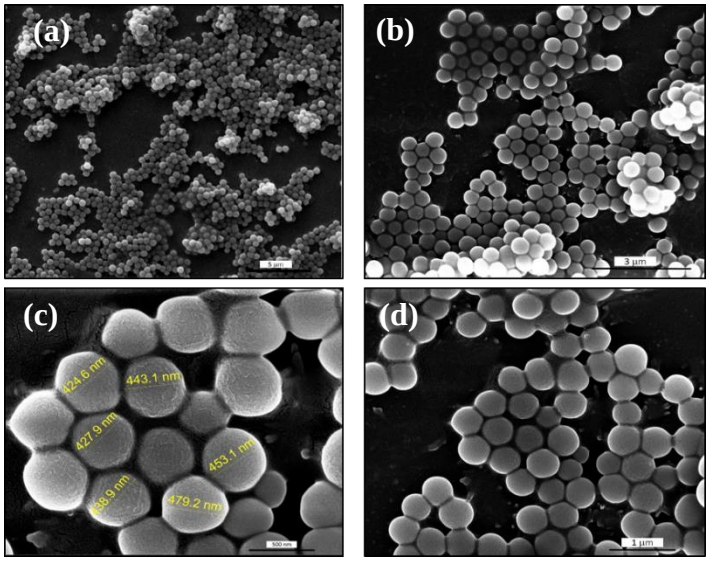


Figure 3.1: SEM images of synthesised silica nanoparticles. Scales: (a) 5µm, (b) 3µm, (c) 500 nm, (d) 5µm.

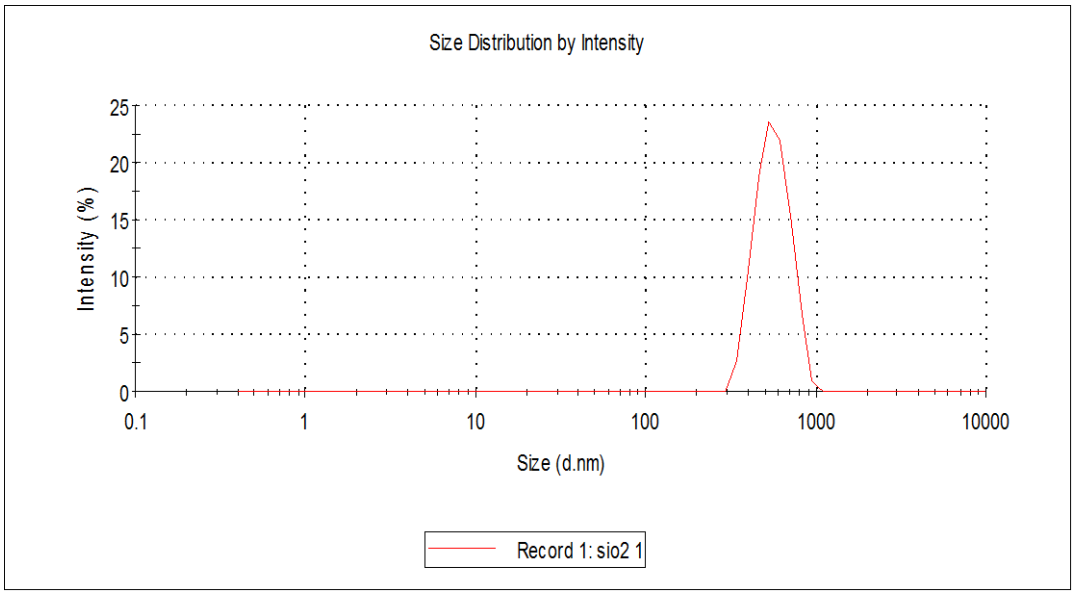


Figure 3.2: Particle size v/s Intensity (%) from DLS analysis.

From Dynamic Light Scattering (DLS), it was found that maximum detectable particle size of 955.4 nm were lowest in intensity (0.9%) while lowest detectable particle size had intensity of 2.7%. It was also observed that particles with the highest mean intensity (23.6%) were of size 531.2 nm.

CHAPTER 4

SELF-ASSEMBLY OF SILICA NANOPARTICLES AND THEIR LAYER-BY-LAYER COATING ON A GLASS SURFACE

4 SELF-ASSEMBLY OF SILICA NANOPARTICLES AND THEIR LAYER-BY-LAYER COATING ON A GLASS SURFACE

4.1 Introduction

Compared to other techniques like spin coating, spray coating and electrospinning, layer-by-layer coating is considered as one of the easy and cost-effective techniques to coat thin films. As stated earlier, surface thickness as low as 1 nm can be achieved by LbL coating. It has several advantages over other techniques: (i) coating can be carried out at low temperature which makes it useful for coating polymers that are non-resistant to high temperature, (ii) it utilises aqueous solution which makes it more convenient than other coating techniques, and (iii) it is comparatively faster than many coating techniques.

Self-assembly of silica nanoparticles has applications in sensors, membranes, catalyst supports, and low dielectric films. Well-ordered arrays of silica nanoparticles, known as self-assembled layers (SEMs), can be obtained by evaporation-induced self-assembly of silica nanoparticles. Two-dimensional self-assemblies of silica nanoparticles with a surface coverage of almost 100% has been previously obtained under appropriate conditions. The arraying order of SiO_2 nanoparticles is found to be independent of type of substrate, pH and size regularity of particles.

4.2 Materials and Methods

The following chemicals were used: Poly (diallyl dimethyl ammonium chloride) (PDDA) (20 wt%, Sigma Aldrich), sodium carboxymethyl cellulose (0.9 wt %, Sigma Aldrich), oxalic acid (100mM, Sigma Aldrich). Deionised water was used in all the experiments. Some of the instruments used were: Contact Angle Measurement System (Dataphysics), Optical microscope (Leica), Muffle Furnace (Testing Instruments Mfg. Co. Ltd., India), Heating Dry Bath (Genetix), Scanning Electron Microscope (Geol), and micro-syringe (Hamilton).

All the glass slides were initially cleaned with isopropanol to remove dirt and then rinsed with deionized water and dried in air oven to remove existent moisture. All the prepared precursors were sonicated for 5 minutes before use.

4.2.1 Preparation of Silica nanoparticle and CMCNa template

Stock solution of sodium carboxymethyl cellulose (0.9 wt%), oxalic acid (100 mM) were available. A known volume of oxalic acid and deionised water were blended in a magnetic stirrer with a constant drop wise addition of known volume of sodium carboxymethyl cellulose in the reaction vessel. As the sodium carboxymethyl cellulose was highly viscous, the stirring was continued for 30 minutes to ensure proper mixing of the components. The volume ratio was taken to ensure 0.4 wt% of CMCNa, 40 mM of oxalic acid in the final solution. This solution, henceforth is named "D".

The silica nanoparticle solution obtained in the previous chapter was diluted with ethanol in 1:10 volume ratio. A solution, denoted by "D5", was prepared by mixing this diluted nanosilica suspension with solution "D" in 1:5 volume ratio.

4.2.2 LbL Dip Coating of PDDA and Silica Nanoparticles

Layer-by-Layer assembly of PDDA and nanosilica suspension for appropriate number of cycles was done on a glass surface by alternatively dip coating the glass slide in PDDA and silica suspension. The following procedure was followed for dip coating. A clean glass slide was first dipped in PDDA (20 wt%) for 5 minutes. The glass slide was then shaken in deionized water for 2 minutes followed by 1 minute rinsing period. It was then dried in air oven for few minutes to ensure removal of excess polyelectrolyte from glass slide. The PDDA coated glass slide was then dipped in SiO_2 suspension for 10 minutes. The coated slide (named $(PDDA/SiO_2)_1$) was then dried in heating air bath for 1 hour. Similar procedure was followed for 10 number of cycles. The obtained slide was thus denoted by $(PDDA/SiO_2)_{10}$ where the subscript "10" denotes 10 number of cycles.

The $(PDDA/SiO_2)_{10}$ was observed under optical microscope. It was then calcinated in a muffle furnace at 900°F to remove all the polyelectrolyte from the film. Further, SEM and contact angle measurement was done for observing the surface morphology and studying contact angle, respectively.

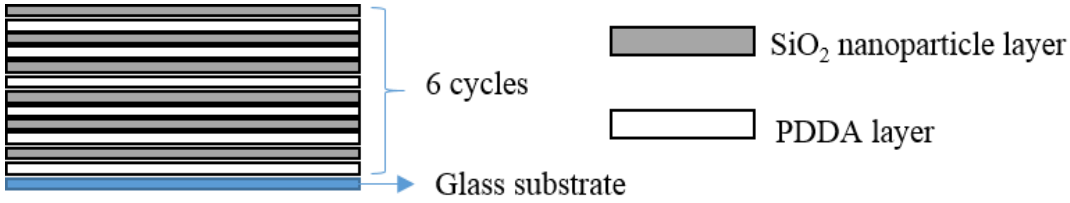


Figure 4.1: Schematic diagram of LbL for $(PDDA/SiO_2)_6$ coating.

4.2.3 LbL Dip Coating of PDDA and Solution "D"

Similar procedure as discussed in the above section was followed for LbL assembly of PDDA and "D5" solution. The final coated slide for 10 number of cycles was denoted by $(PDDA/D5)_{10}$.

The coated slide was first observed under optical microscope to observe the self-assembled fractal pattern formed by CMCNa and oxalic acid along with silica nanoparticles. It was then calcinated, initially at 500°F, to remove all the CMCNa and then at 900°F to remove polyelectrolyte from the film. It was followed by SEM analysis and contact angle measurement.

4.3 Results and Discussion

4.3.1 Evaporation-Induced Self-Assembly of CMCNa and Oxalic Acid (Solution "D")

When a drop of solution "D" was dried and observed under optical microscope, fractal, tree-like pattern was formed. These patterns, as discussed in the subsequent sections, form the template for the assembly of silica nanoparticles. Following images depict the fractal patterns:

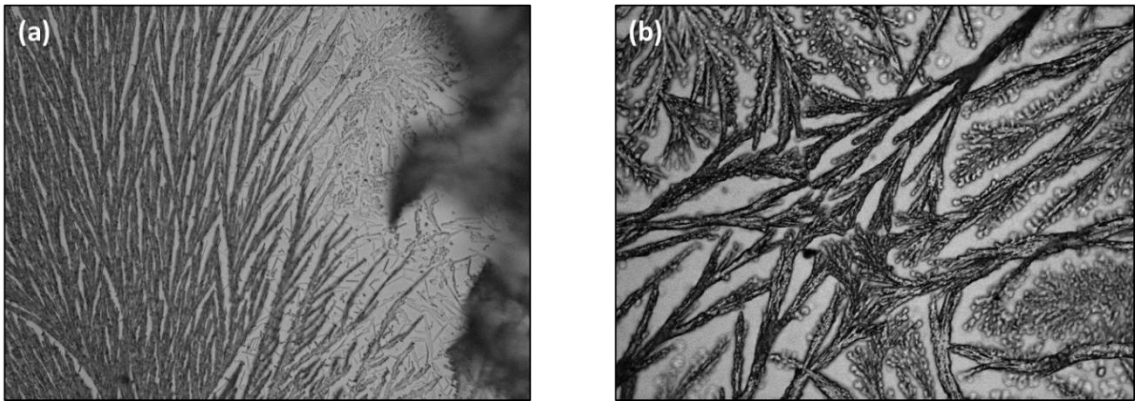


Figure 4.2: Tree-like, fractal pattern by EISA of solution "D," with scales (a) 500 μm (b) 50 μm.

4.3.2 Sessile Drop of SiO_2 Nanoparticles and Solution "D"

Sessile drops of various volume ratios – 1:2, 1:3, 1:5, 2:5, 3:5, 1:7 of silica nanoparticles and solution "D" were observed under optical microscope. According to observations, best results were obtained for volume ratios of 1:5 and 2:5. Following images clearly depict adherence of silica nanoparticles with the fractal pattern even after CMCNa was removed by calcination.

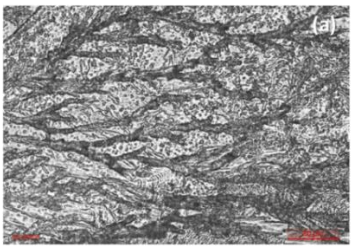
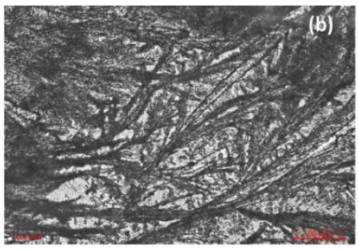
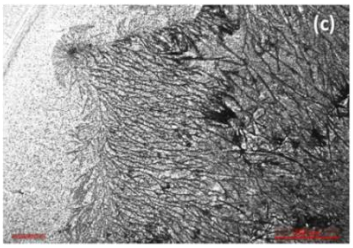
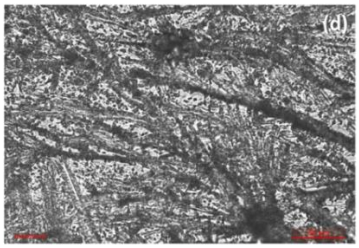
Volume Ratio	Fractal pattern with SiO_2 nanoparticles and Solution "D" (before calcination)	
1:5		
2:5		

Figure 4.3: Fractal pattern with SiO_2 nanoparticles and solution "D" (before calcination) for the two volume ratios, with scales (a) 50 µm, (b) 50 µm, (c) 500 µm, (d) 50 µm.

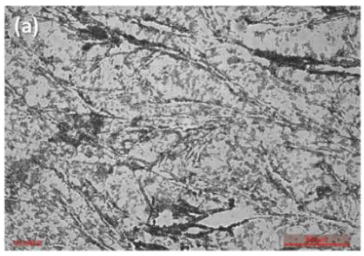
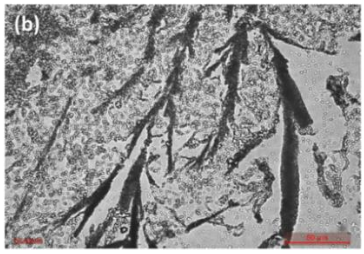
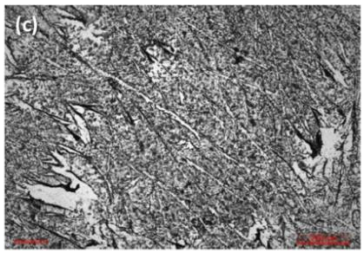
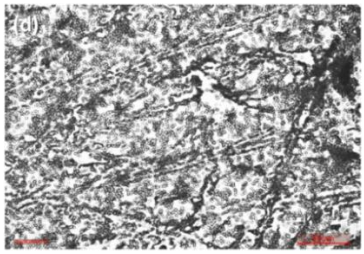
Volume Ratio	Fractal pattern with SiO_2 nanoparticles and Solution "D" (after calcination)	
1:5		
2:5		

Figure 4.4: Fractal pattern with SiO_2 nanoparticles and solution "D" (after calcination) for the two volume ratios, with scales (a) 50 µm, (b) 50 µm, (c)200 µm, (d) 50 µm.

4.3.3 LbL Dip Coating of PDDA and SiO_2 Nanoparticles

Since PDDA is a polycation, it is electrostatically attracted to the oppositely charged layer of silica nanoparticles. This lead to layer-by-layer deposition of PDDA and silica nanoparticles and a stable film. Adherence of the nanoparticles with the film was evident from the fact that the areal number density of particles increased with deposition cycles.

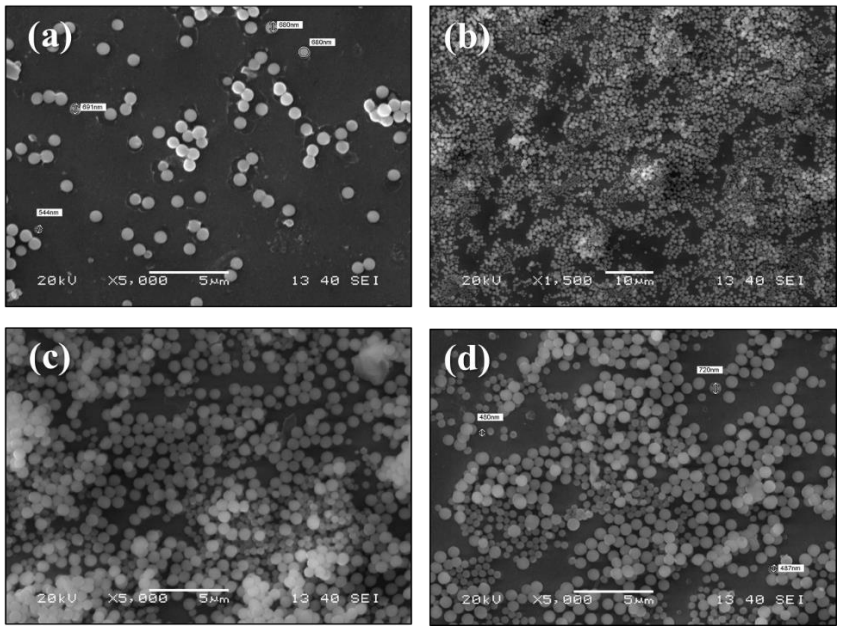


Figure 4.5: SEM images of (PDDA/SiO_2), (a) n=1, (b) n=4, (c) n=4 (magnified), (d) n=5.

4.3.4 LbL Dip Coating of PDDA and SiO_2 Nanoparticles-CMCNa Template

(a) Optical Microscopic Analysis

Similar to the results obtained in evaporation-induced self-assembly of sessile drops, the dip-coated glass slides displayed tree-like fractal pattern. The intensity and of these patterns increased with the deposition cycles. Silica particles clearly adhered to the fractal pattern, forming a self-assembled pattern among themselves. Before calcination, the nanoparticles adhered to the CMCNa on the glass slides. These particles retained the assembled pattern even after the CMCNa pattern was removed by calcination at 500°F.

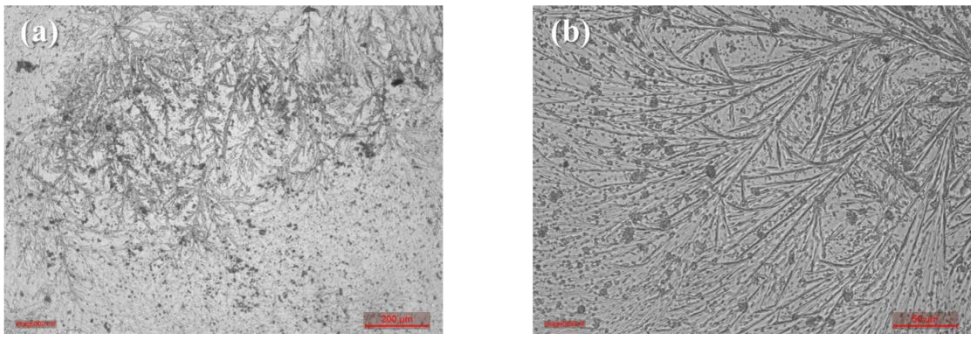


Figure 4.6: Optical Microscopic images of $(PDDA/D5)_3$ coatings before calcination, with scales (a) 200 μm (b)50 μm.

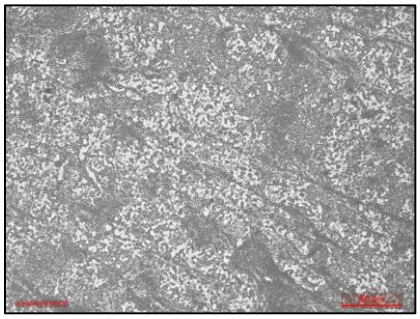


Figure 4.7: Optical Microscopic image of $(PDDA/D5)_5$ coating after calcination, scale 50 μm.

(b) Scanning Electron Microscopic Analysis

Images from SEM validated the fact that particles retained the self-assembled pattern even after calcination of the film, although lumps of nanoparticles could also be seen near the fractal pattern. Previous literatures have shown that self-assembled structure are more stable. This was validated by dipping the coatings in water after 5 days. The coatings were found to be stable even which was later confirmed by observing the film under optical microscope.

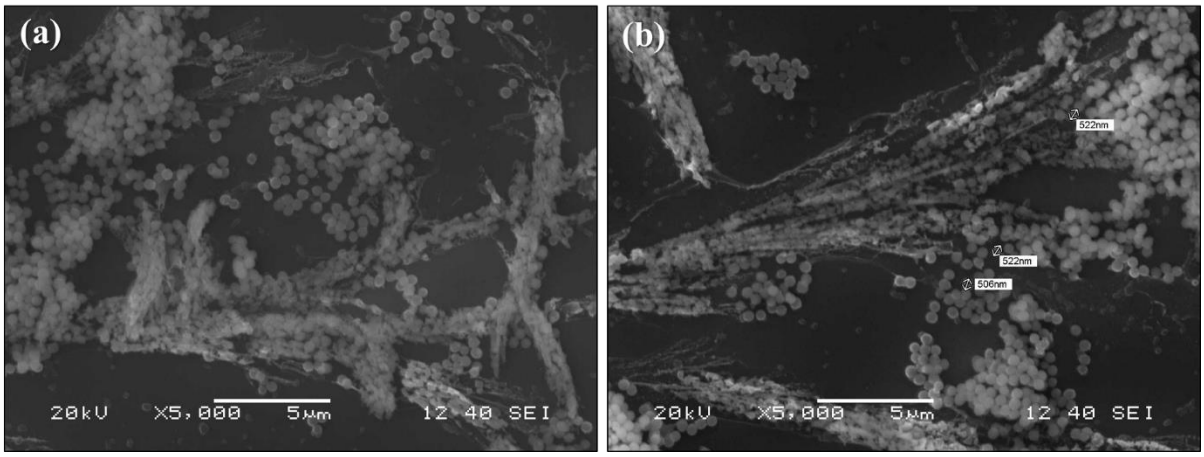


Figure 4.8: SEM images of $(PDDA/SiO_2)_3$ after calcination, with scales (a) 5µm (b) 10 µm.

4.3.5 Contact Angle Measurements on Dip-Coated slides

For superhydrophilicity, micro- and nano-level surface roughness is essential. Thus, more number of cycles of dip coating should result in lower contact angle. The contact angle obtained for both cases – $(PDDA/SiO_2)_n$ and $(PDDA/D5)_n$ were quite satisfactory.

a) Contact Angle with $(PDDA/SiO_2)_{10}$ Coating

Compared to the solution "D" coated film (discussed in the subsequent section), the $(PDDA/SiO_2)_{10}$ film exhibited near-superhydrophilic contact angle which was slightly greater than 10°. Moreover, water droplet suspended by the micro-syringe immediately wetted the film as soon as it came in contact with it. Low contact angle can also be achieved by using smaller sized nanoparticles which increases the roughness at the micro- and nano-scale.

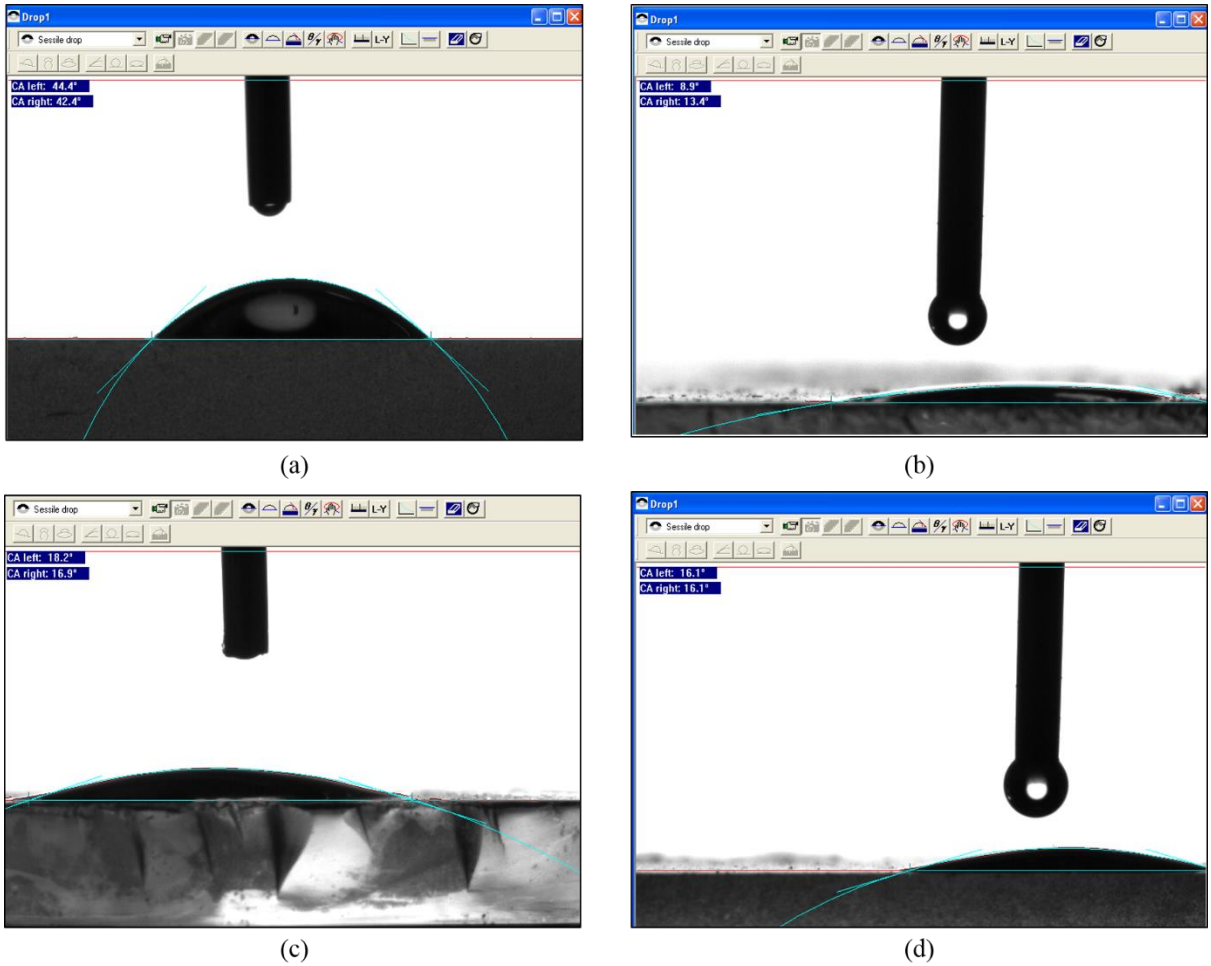


Figure 4.9: Contact angle on uncoated plane slide, (a) 44.4° (Left CA), 42.4° (Right CA).Contact angle on $(PDDA/SiO_2)_{10}$, (b) 8.9° (Left CA), 13.4° (Right CA) (c) 18.2° (Left CA), 16.9° (Right CA) (d) 16.1° (Left CA, right CA).

b) Contact Angle with $(PDDA/D5)_{10}$ Coating

It was observed that superhydrophilic contact angles (less than 10°) were exhibit by the $(PDDA/D5)_{10}$ coated film at various locations on the surface. Similar to $(PDDA/SiO_2)_{10}$, the drop immediately wetted the film as soon as it came in contact with the film after being released by the micro-syringe. Superhydrophilic property was exhibited in less than a second.

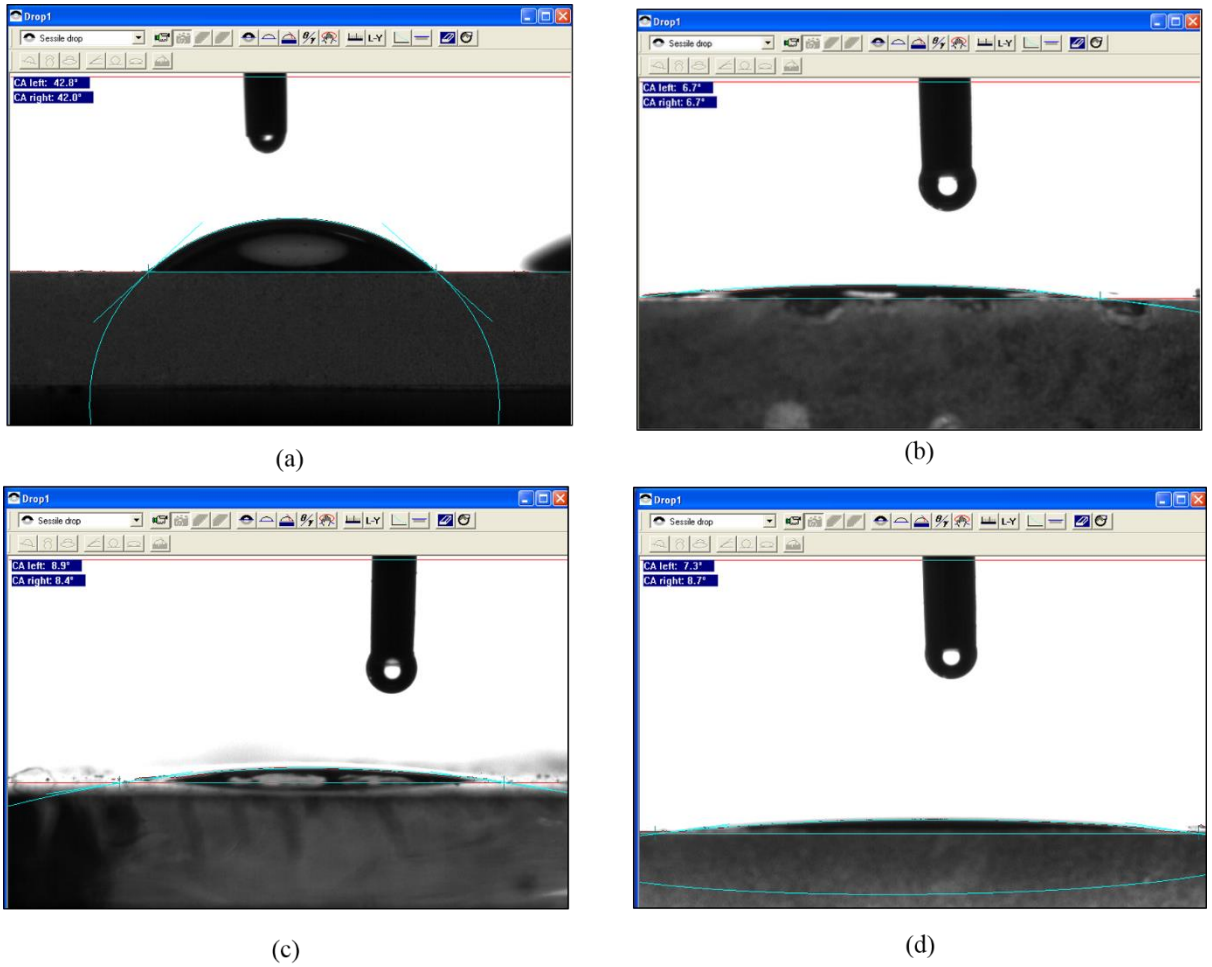


Figure 4.10: Contact angle on uncoated plane slide, (a) 42.8° (Left CA), 42.0° (Right CA). Contact angle on $(PDDA/D5)_{10}$ slides, (b) 6.7° (Left CA), 6.7° (Right CA) (c) 8.9° (Left CA), 8.4° (Right CA), (d) 7.3° (Left CA), 8.7° (Right CA).

The assembly on a substrate by layer-by-layer technique has proven to be an easy and cost-effective route for coating films to nanometer level. As observed, the glass slide coated $(PDDA/D5)_{10}$ coating exhibited superhydrophilic property with contact angle as low as 6.7°. It may be inferred that on increasing the surface roughness by reducing the nanosilica particle size and/or by increasing the number of deposition cycle will lead to lesser contact angle, which may approach 0°. Using multilayer coatings comprising dual sized nanoparticles also leads to increased surface roughness.

CHAPTER 5

CONCLUSIONS

5. CONCLUSIONS

Compared to top-down approach, bottom-up approach for self-assembly offers higher flexibility to manipulate the parameters during the self-assembly process. This was shown by the Stöber Method where by careful control of reactant concentration and reaction parameters lead to an optimal particle size. Reduction in size of silica nanoparticles can be achieved by using ammonium salts of bromine, iodine and chlorine. This will increase the superhydrophilicity of silica nanoparticle-coated films.

The self-assembled structure of silica nanoparticles along the sodium carboxymethyl cellulose – oxalic acid template is more stable than only-silica nanoparticle-coated glass surface as these structures reach a minimum energy level after the spontaneous ordered arrangement brought out by evaporation-induced self-assembly. Superhydrophobicity and superhydrophilicity two of the most researched topics in material science and engineering because of the varied potential applications that they possess. It has thus become essential to analyse the physics behind these surfaces – the ability of a surface to either allow liquid penetration or liquid suspension. Much research and review work on hydrophobicity and superhydrophobicity has been done, but superhydrophilicity still continues to be a relatively younger concept. One of the possible reasons for this may be that superhydrophilic films can be subsequently converted into superhydrophobic films by deposition of a hydrophobic layer. This conversion has been carried out by many researchers because of the immense applications that superhydrophobicity has shown in the recent past.

REFERENCES

REFERENCES

[1] I.A. Rahman and P. Vejayakumaran, "Synthesis of Silica Nanoparticles by Sol-Gel: Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites—A Review", *J. Nanomaterial*, 2012 (2012), 1-15

[2] M. W. George and B. Mila, "Beyond molecules: Self-assembly of mesoscopic and macroscopic components", *Perspective*, 99 (2002), 4769-4764.

[3] W. Stöber, A. Fink, E. Bohn, "Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range", *J. Colloid Interface* Sci. 26 (1968), 62–69.

[4] M.P. Pileni, "The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals", *Nat. Mater.*, 2 (2003), 145-150.

[5] X. D. Wang, Z. X. Shen, T. San, X. B. Cheng, M. F. Li, L. Y. Chen, Z. S. Wanga, "Preparation of spherical silica particles by Stöber process with high concentration of tetra-ethyl-orthosilicate", *J. Colloid Interface Sci.*, 341 (2010), 23-29.

[6] Z. Geng, J. He, and L. Xu, "Fabrication of superhydrophilic and antireflective silica coatings on poly (methyl methacrylate) substrates", *Materials Research Bulletin*, 47 (2012), 1562-1567.

[7] J. Bravo, L. Zhai, Z. Wu, R. E. Cohen, and M. F. Rubner, "Transparent Superhydrophobic Films Based on Silica Nanoparticles", *Langmuir***,** 23 (2007), 7293-7298.

[8] X. Li, X. Du, and J. He, "Self-Cleaning Antireflective Coatings Assembled from Peculiar Mesoporous Silica Nanoparticles", *Langmuir*, 26 (2010), 13528–13534.

[9] L. Zhang, Y. Li, J. Sun, and J. Shen, "Layer-by-layer fabrication of broad-band superhydrophobic antireflection coatings in near-infrared region", *J. Colloid Interface Sci.*, 319 (2008), 302-308.

[10] J. Drelich, E. Chibowski, D. D. Mengb and K. Terpilowski, "Hydrophilic and Superhydrophilic Surfaces and materials", *Soft Matter*, 7 (2011), 9804-9828.