

# MASTER RESEARCH PROJECT

---

Synthesis and characterization of zeolite A  
membranes for micro device applications

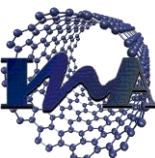
AUTHOR: TOSHIYUKI GHANI

SUPERVISOR :DR REYES MALLADA

ABSTRACT “In order to integrate zeolite membranes in micro devices, zeolite micro membranes were prepared on silicon grids to obtain self-supported membranes. The substrate was modified with PDDA, boehmite and different silanes to anchor the zeolite seeds for microwave secondary synthesis. The quality of the membranes was characterized by SEM to observe the effect of surface modification and synthesis parameters”.

## *Acknowledgement*

I would like to Thank Dr Reyes Mallada for her support and suggestions as my supervisor throughout the research, also I would like to thank Dr Pilar Pina, Dr Miguel Urbitzondo and Dr Ismael Pellejero for their help during the research project. I would like to thank Carlos for his help with extensive SEM sampling and EM3E committee for giving me the opportunity to be a part of the EM3E program. Also I appreciate all the help, suggestions, feedback and training given by all of my colleagues at Institute of Nanotechnology Aragon, Spain.



## DISCLAIMER

EN-This project has been funded with support from the European Commission. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

BG-Този проект е финансиран с подкрепата на Европейската комисия. Тази публикация отразява само личните виждания на нейния автор и от Комисията не може да бъде търсена отговорност за използването на съдържащата се в нея информация.

CS-Tento projekt byl realizován za finanční podpory Evropské unie. Za obsah publikací odpovídá výlučně autor. Publikace nereprezentují názory Evropské komise a Evropská komise neodpovídá za použití informací, jež jsou jejich obsahem.

DA-Dette projekt er finansieret med støtte fra Europa-Kommissionen. Denne publikation forpligter kun forfatteren, og Kommissionen kan ikke drages til ansvar for brug af oplysningerne heri.

DE- Dieses Projekt wurde mit Unterstützung der Europäischen Kommission finanziert. Die Verantwortung für den Inhalt dieser Veröffentlichung trägt allein der Verfasser; die Kommission haftet nicht für die weitere Verwendung der darin enthaltenen Angaben.

EL-Το σχέδιο αυτό χρηματοδοτήθηκε με την υποστήριξη της Ευρωπαϊκής Επιτροπής. Η παρούσα δημοσίευση δεσμεύει μόνο τον συντάκτη της και η Επιτροπή δεν ευθύνεται για τυχόν χρήση των πληροφοριών που περιέχονται σε αυτήν.

ES- El presente proyecto ha sido financiado con el apoyo de la Comisión Europea. Esta publicación es responsabilidad exclusiva de su autor. La Comisión no es responsable del uso que pueda hacerse de la información aquí difundida.

ET-Projekti on rahaliselt toetanud Euroopa Komisjon. Publikatsiooni sisu peegeldab autori seisukohti ja Euroopa Komisjon ei ole vastutav selles sisalduva informatsiooni kasutamise eest.

FI- Hanke on rahoitettu Euroopan komission tuella. Tästä julkaisusta (tiedotteesta) vastaa ainoastaan sen laatija, eikä komissio ole vastuussa siihen sisältyvien tietojen mahdollisesta käytöstä.

FR- Ce projet a été financé avec le soutien de la Commission européenne. Cette publication (communication) n'engage que son auteur et la Commission n'est pas responsable de l'usage qui pourrait être fait des informations qui y sont contenues.

GA- Maoiníodh an tionscadal seo le tacaíocht ón gCoimisiún Eorpach. Tuairimí an údair amháin atá san fhoilseachán [scéala] seo, agus ní bheidh an Coimisiún freagrach as aon úsáid a d'fhéadfaí a bhaint as an eolas atá ann.

HU- Az Európai Bizottság támogatást nyújtott ennek a projektnek a költségeihez. Ez a kiadvány (közlemény) a szerző nézeteit tükrözi, és az Európai Bizottság nem tehető felelőssé az abban foglaltak bárminemű felhasználásért.

IT- Il presente progetto è finanziato con il sostegno della Commissione europea. L'autore è il solo responsabile di questa pubblicazione (comunicazione) e la Commissione declina ogni responsabilità sull'uso che potrà essere fatto delle informazioni in essa contenute.

NL- Dit project werd gefinancierd met de steun van de Europese Commissie. De verantwoordelijkheid voor deze publicatie (mededeling) ligt uitsluitend bij de auteur; de Commissie kan niet aansprakelijk worden gesteld voor het gebruik van de informatie die erin is vervat.

LT- Šis projektas finansuojamas remiant Europos Komisijai. Šis leidinys [pranešimas] atspindi tik autoriaus požiūrį, todėl Komisija negali būti laikoma atsakinga už bet kokį jame pateikiamos informacijos naudojimą.

LV- Šis projekts tika finansēts ar Eiropas Komisijas atbalstu. Šī publikācija [paziņojums] atspoguļo vienīgi autora uzskatus, un Komisijai nevar uzlikt atbildību par tajā ietvertās informācijas jebkuru iespējamo izlietojumu.

MT- Dan il-proġett għe finanzjat bl-għajnuna tal-Kummissjoni Ewropea. Din il-publikazzjoni tirrifletti (Dan il-komunikat jirrifletti) l-opinjoni ta' l-awtur biss, u l-Kummissjoni ma tistax tinzamm responsabbli għal kull tip ta' uzu li jista' jsir mill-informazzjoni li tinsab fiha ( fih).

PL- Ten projekt został zrealizowany przy wsparciu finansowym Komisji Europejskiej. Projekt lub publikacja odzwierciedlają jedynie stanowisko ich autora i Komisja Europejska nie ponosi odpowiedzialności za umieszczoną w niej zawartość merytoryczną.

PT- Projecto financiado com o apoio da Comissão Europeia. A informação contida nesta publicação (comunicação) vincula exclusivamente o autor, não sendo a Comissão responsável pela utilização que dela possa ser feita.

RO- Acest proiect a fost finanțat cu sprijinul Comisiei Europene. Această publicație (comunicare) reflectă numai punctul de vedere al autorului și Comisia nu este responsabilă pentru eventuala utilizare a informațiilor pe care le conține.

SK-Tento projekt bol financovaný s podporou Európskej Komisie. Táto publikácia (dokument) reprezentuje výlučne názor autora a Komisia nezodpovedá za akékoľvek použitie informácií obsiahnutých v tejto publikácii (dokumente).

SL- Izvedba tega projekta je financirana s strani Evropske komisije. Vsebina publikacije (komunikacije) je izključno odgovornost avtorja in v nobenem primeru ne predstavlja stališč Evropske komisije.

SV- Projektet genomförs med ekonomiskt stöd från Europeiska kommissionen. För uppgifterna i denna publikation (som är ett meddelande) ansvarar endast upphovsmannen. Europeiska kommissionen tar inget ansvar för hur dessa uppgifter kan komma att användas

## List of figures

Figure 1: free standing membrane on silicon grid, .....	9
Figure 2: patterned membrane on silicon oxide wafer .....	9
Figure 3: steps for fabricating free standing membrane on silicon grids .....	10
Figure 4:: Zeolite A formation from tetrahedron(a), Sodalite cage (b), secondary building unit(c), zeolite A crystal(d,e) (3).....	11
Figure 5: Synthesis routes for zeolite membranes(6).....	12
Figure 6: Applications of zeolite films in micro scale applications (21) .....	16
Figure 7: The Knoevenagel condensation reaction between benzaldehyde and ethyl acetoacetate(28) .	17
Figure 8: Yeung`s work zeolite A membrane deposited in micro channels on silicon substrate(27) .....	18
Figure 9: SEM images of zeolite membrane on micro reactor walls (27) .....	18
Figure 10: micro channel fabrication on silicon substrate(37) .....	19
Figure 11: PDDA Molecule, schematic representation of PDDA layer on silicon oxide surface .....	21
Figure 12: left Boehmite structure, Right schematic representation of Boehmite layer on silicon oxide .	21
Figure 13: schematic of function of organo silane, (53) .....	22
Figure 14: left structure of trialkoxy-silanes, right APTES attachment on silicon oxide surface .....	22
Figure 15: left and right, complex mechanism of APTES orientation on silicon oxide .....	23
Figure 16: an ideal mechanism of APTES attachment on silicon oxide .....	24
Figure 17: Different modification of substrates for zeolite attachment(74) .....	25
Figure 18: left silicon oxide layer on silicon wafers; 4 inch wafer cut into small squares for synthesis.....	26
Figure 19: grid sizes description (a grid 1000_100) .....	27
Figure 20: Cross section of silicon grid.....	27
Figure 21: dip coating device .....	29
Figure 22: thermal expansion co-efficient of some zeolites(89) .....	31
Figure 23: Experimental setup for silanization process Left for small wafer, right for 3inch wafers. ....	33
Figure 24: TOP SEM image sizing data and Bottom DLS results for zeolite 4 .....	36
Figure 25: Silicon oxide without modification: seed concentration 1%,2% AND 3% SEM images of seeding left, right after 30 minute microwave synthesis.....	37
Figure 26: Silicon oxide without modification :seed concentration 3%,4% AND 5% SEM images of seeding left, right after 30 minute microwave synthesis.....	38
Figure 27: seeding and synthesis of PDDA modified surface using spin coating 1%, 2% and 3% seed concentration.....	42
Figure 28: seeding and synthesis of PDDA modified surface using spin coating 4%, 5% and 6% seed concentration.....	43
Figure 29: Effect of spin coating conditions.....	44
Figure 30: effect of PDDA solution mixed with zeolite seeds in water and spin coated .....	45
Figure 31: Dip coating of seeds on PDDA modified substrate .....	46
Figure 32: top Cross section of Boehmite and membrane layer, bottom microwave synthesis growth with time .....	48
Figure 33: Dip coating of Boehmite and zeolite seeds, seeding and synthesis .....	48

Figure 34: Spin coating of Boehmite and zeolite seeds. Followed by 30 minute synthesis ..... 49

Figure 35: SEM images of seeded Boehmite modified grids ..... 49

Figure 36: SEM images of Boehmite modified grids, evolution with time ..... 50

Figure 37: Boehmite 9% solution mixed with zeolite seeds 5% solution (1:1 ratio) spin coated ..... 51

Figure 38: different seeding solvents and seeding conditions on APTES modified support ..... 54

Figure 39: different concentration of APTES in toluene during surface modification 1mM, 6mM, 30mM ..... 55

Figure 40: different concentration of APTES in toluene during surface modification 50mM, 90mM, 120mM ..... 56

Figure 41: Evolution of thickness of membrane on APTES modified substrate ..... 57

Figure 42: Growth of membrane with synthesis time, ethanol seeded substrate ..... 57

Figure 43: Spin coating and dip coating sample on APTES modified substrates ..... 58

Figure 44: Samples for APTES modified substrates, tested under same conditions for reproducibility test ..... 59

Figure 45: Covalent linkage (epoxy-Amine) ..... 61

Figure 46: Covalent linkage using Halogen propyl -oxy silanes ..... 62

Figure 47: GRID PREPARATION ..... 71

### List of tables

Table 1: List of substrates used for zeolite A membrane synthesis(14) ..... 15

Table 2: cleaning procedure for silicon oxide substrates ..... 28

Table 5: Thermal expansion coefficient values ..... 31

Table 7: silanization process ..... 32

Table 3: zeolite seeds size data ..... 35

Table 4: list of PDDA experiments ..... 39

Table 6: Boehmite experiments ..... 47

Table 8: experiments performed for silanes ..... 53

## *TABLE OF CONTENT*

1.	OBJECTIVE OF THE PROJECT .....	9
2.	INTRODUCTION TO ZEOLITE MEMBRANES.....	11
2.1	Zeolite .....	11
2.2	Applications of zeolite membrane.....	11
2.3	Zeolite membrane synthesis.....	12
2.3.1	Microwave synthesis.....	13
2.4	Zeolite membranes in Microscale applications .....	16
2.5	Zeolite membrane synthesis on silicon substrates.....	19
2.6	Surface modification of silicon oxide substrate.....	20
2.6.1	Polydiallyldimethylammonium-chloride (PDDA) .....	20
2.6.2	Boehmite (aluminum oxide hydroxide / $\gamma$ -AlO(OH)).....	21
2.6.3	Silanization .....	21
3	EXPERIMENTAL .....	26
3.1	Materials .....	26
3.2	Silicon substrates .....	26
3.3	Preparation of zeolite A nanoparticles for seeding .....	28
3.4	Surface modification by PDDA solution .....	29
3.5	Surface modification by Boehmite solution .....	30
3.6	Surface modification by silanes .....	32
3.7	Preparing microwave synthesis solution .....	33
4	RESULTS AND DISCUSSION .....	35
4.1	Characterization of zeolite seeds.....	35
4.2	Seeding and synthesis on bare silicon oxide wafers.....	36
4.3	PDDA modified surface and synthesis .....	39
4.4	Boehmite surface modification and synthesis.....	47
4.5	Silanization surface modification and synthesis .....	52
5	Conclusion and future work suggestions.....	63
	References .....	65
	Appendix .....	68



## 1. OBJECTIVE OF THE PROJECT

The goal of this Final Master Project is to integrate zeolite membranes in micro devices. The zeolite micro membrane will be prepared in a silicon grid to obtain a self-supported membrane explained in figure 1. Alternatively zeolite layers on silicon wafers could be patterned for integration in a micro device as shown in figure 2.

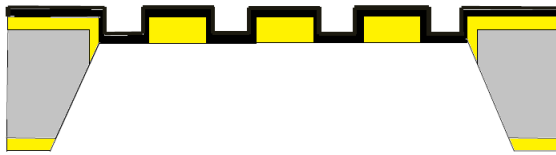


Figure 1: free standing membrane on silicon grid,

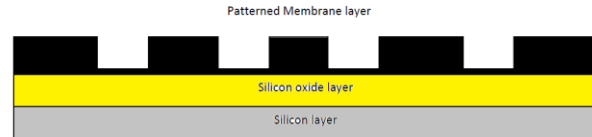


Figure 2: patterned membrane on silicon oxide wafer

To obtain the zeolite membrane; the secondary growth method that consists of two steps; seeding and hydrothermal synthesis will be applied. This method is well established for the synthesis of zeolite membranes and layers on porous supports such as alumina, stainless steel or cordierite. The goal is to develop a protocol for the secondary growth on silicon wafers. There are two main challenges, first compared to the traditional supports mentioned before, silicon wafers are flat surfaces, where the anchoring of the seeds will be difficult, and in this sense a proper surface modification to anchor the seeds will be necessary. Secondly silicon could be etched under the high alkalinity of the zeolite synthesis gel, to avoid this silicon oxide layers will be deposited and fast synthesis methods such as microwave heating will be employed.

The main objective is to combine a practical seeding approach with microwave synthesis. To achieve this; following tasks will be done (explained in figure 3).

- Synthesis of zeolite A nanocrystals
- Surface modification of silicon oxide surface
- Homogeneous seeding of modified surface
- Microwave synthesis of zeolite A layer

# Preparation of free standing membranes on silicon grids

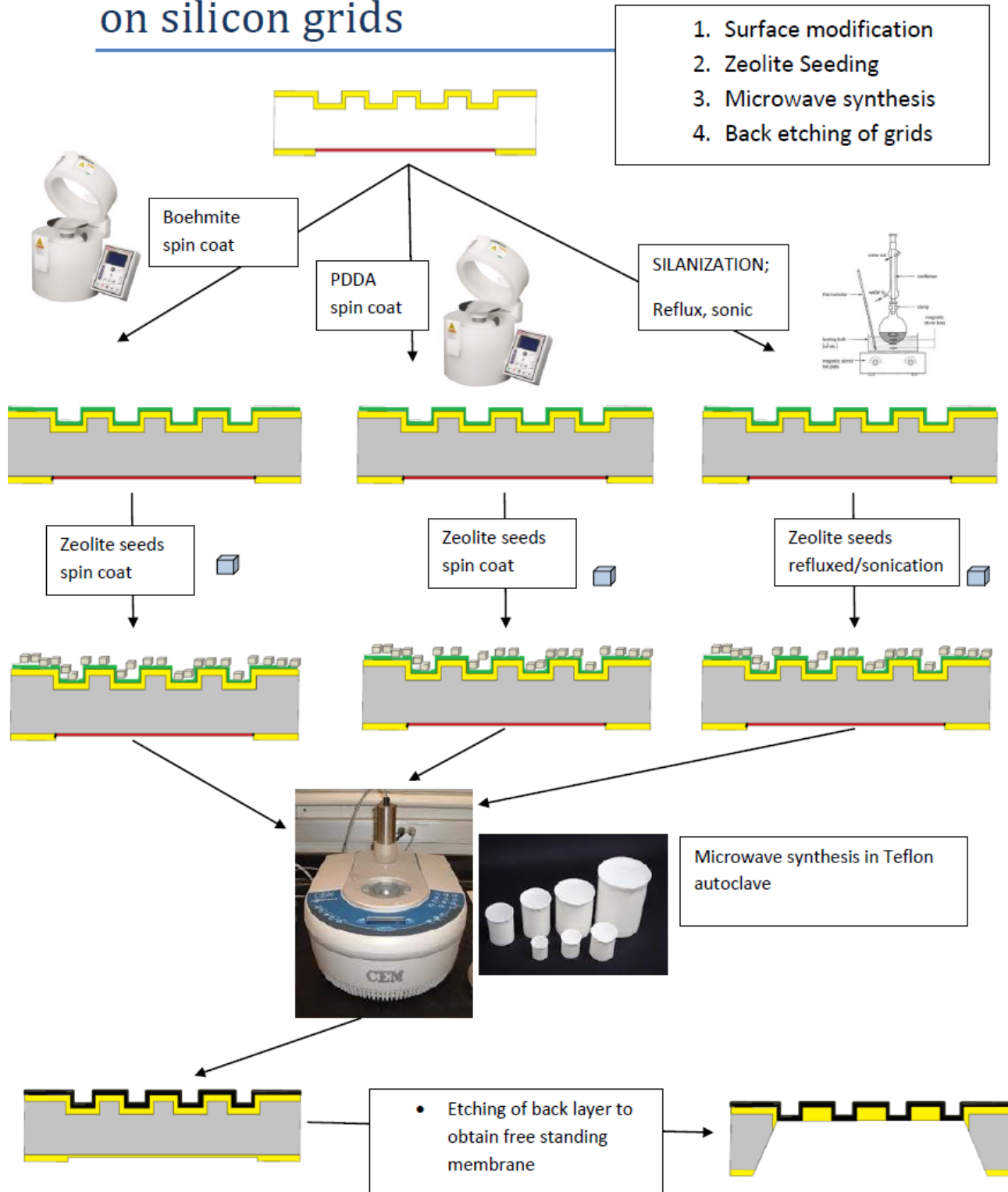
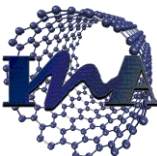


Figure 3: steps for fabricating free standing membrane on silicon grids



## 2. INTRODUCTION TO ZEOLITE MEMBRANES

### 2.1 Zeolite

Zeolites can be defined as “a porous crystal typically consisting of Si, Al, and O atoms”(1) also it can be defined as “a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions”(2). More detailed basic information on zeolites is in the appendix. Figure 4 explains the structure of zeolite A that will be used in this research.

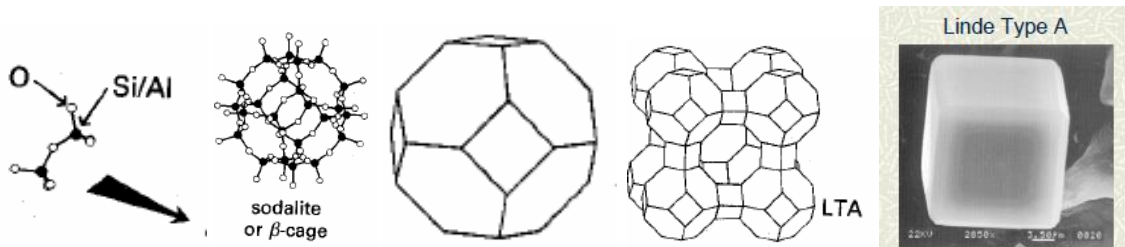
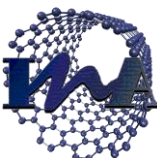


Figure 4:: Zeolite A formation from tetrahedron(a), Sodalite cage (b), secondary building unit(c), zeolite A crystal(d,e) (3)

### 2.2 Applications of zeolite membrane

Zeolites have been applied in many different industrial applications because of many advantages that owes to its unique structure. The inorganic materials have more durability in terms of high temperature resistance, high chemical resistance and higher strength compared to organic materials. Some of the applications based on the unique structure of zeolite are their use as ion exchangers and adsorbents because of the cation that balances the charge of the framework. So the higher the aluminum ratios in the framework the more cation are present to balance the charge and hence increasing the cation exchange capacity. Zeolites are also used as catalysts because the cation can be exchanged with acidic or basic ions. The catalytic property combined with well defined pore size ensures that selective catalysis takes place (2, 3). Other major applications use selective removal of molecules based on the pore size and the nature of the zeolite example dewatering of alcohol/water mixtures from azeotropic mixtures. Also one of the main application research areas for zeolites is green chemical processes, zeolites are being researched to improve the reaction by selective catalysis and removal of byproducts (1). The important research areas for zeolite in membrane applications include gas and separation, selective catalysis, reverse osmosis and chemical sensors. Recently the major disadvantage of zeolite application is high cost due to processing limitations(4).



### 2.3 Zeolite membrane synthesis

Zeolite membrane can be synthesized either by primary growth in which in-situ nucleation, crystallization and growth of zeolite membrane all takes place on the substrate as explained in figure 5. The substrate is placed in the zeolite synthesis solution and heated to desired temperature. The nucleation starts to take place on the surface and zeolite crystal growth takes place on the substrate till a membrane is formed(5). Nucleation is an important factor in this type of primary growth as many conditions needs to be precisely controlled so other zeolite structures or amorphous growth does not occur on the surface and cause defects in the membrane. The benefit of seeding free synthesis is that it requires less number of steps for membrane preparation but the limitation lies in slower processing and higher defects due to the possibility of amorphous and other morphology growth.

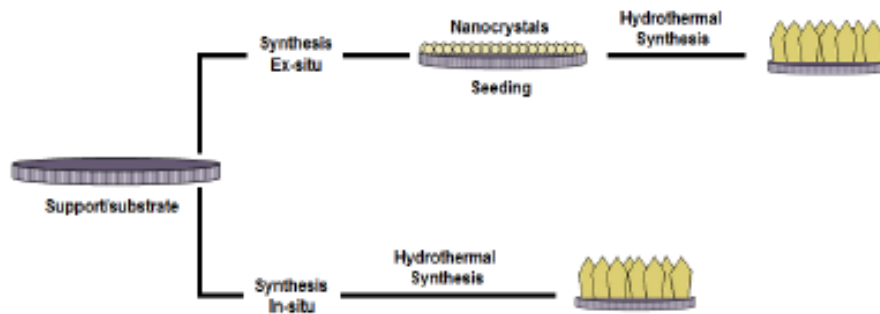


Figure 5: Synthesis routes for zeolite membranes(6)

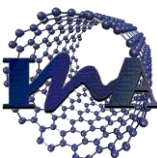
The second method is called seeding method or secondary synthesis of zeolite membrane, where first zeolite nanoparticles of desired zeolite is deposited on the surface and then the seeded substrate is placed into the zeolite synthesis solution, this removes the need for nucleation process and zeolite growth directly takes place due to epitaxial growth because of zeolite nano crystals present on the surface of the substrate(7, 8). We choose the seeding method to reduce the synthesis time as seeding-free synthesis would require more time which would cause excessive etching on our silicon substrate. So we use seeding synthesis method for our membrane synthesis.

The most common method of synthesis of zeolite A nanoparticles is by using structure directing agents or templating agents which provide the structural shape for the nutrients to grow on, trapping the SDA inside the growing zeolite particles(9). For synthesizing zeolite particles, the two main components of the synthesis gel are the silica and aluminum

sources which provide the nutrients. Proper selection of the precursors is important to obtain the required morphology of the nano particles. A study by Okubo(10) and his colleagues studied the effect of different silicon sources, they studied TEOS, Ludox AS30, TMA silicate. They concluded that there were differences in the initial particle size formed during the ageing process. They observed that with TEOS they obtained more rounded zeolites while Ludox AS30 provided more cubic structure and TMA silicate had more definitions in its micro structure. So in our synthesis we used colloidal silica Ludox AS-30 as our silica source as we want to synthesize cubic nano particles of zeolite A. Work by Round(11) showed that by using Aluminum isopropoxide instead of other aluminum sources like aluminum hydroxide and aluminum foil, they were able to get more well defined cubic crystals. Hence we use aluminum isopropoxide as our aluminum source in the synthesis solution. The structure directing agent for zeolite LTA and FAU crystals is Tetra-methyl-ammonium hydroxide, hence conditions need to be optimized to obtain one from the other during synthesis. The optimization of zeolite A crystal synthesis was performed based on various published articles which discuss, the ageing time, the temperature, sodium concentration on the yield, morphology and type of zeolite obtained by the hydrothermal synthesis. The solution is aged at room temperature to increase the nucleation in the solution, but research has shown that longer ageing of the synthesis solution of zeolite LTA leads to formation of FAU, so longer ageing will favor FAU growth(12). Our ageing time for the synthesis was 24 hours, although we can increase the ageing to increase nucleation in the solution, excessive ageing can cause FAU crystal formation in the solution along with zeolite A crystals. Mintova (12) in her experiments showed that Na<sup>+</sup> favors formation of LTA instead of FAU, so we add NaOH solution to promote the LTA crystallization. Generally temperature increases the nucleation and the growth rate of crystals, but growth has more exponential growth with increase in temperature, hence higher temperature would yield bigger crystals, so in order to obtain smaller crystals we synthesized our solution at 80C-90C to get smaller crystals with sufficient yield. A very detailed study on synthesis parameters for FAU and LTA phase selection has been carried out by Fan and his colleagues(13).

### 2.3.1 Microwave synthesis

Microwaves are electromagnetic waves with wavelength between 0.01m and 1m and frequency of 0.3 to 30Ghz. For industrial microwave equipments the frequency used is around 915 and 2450 Mhz and energy absorption of these waves by water is



maximum at this frequency. The interaction of dielectric material with microwaves is what leads to the dielectric heating, under the electric field of the microwaves the dielectric molecules try to orient themselves constantly under the changing field, but their movement is opposed by intramolecular friction and attraction causing the heating. Generally the materials can be classified into 3 groups based on how they interact with microwaves. 1. Which reflect the microwave most alloys and metals, 2. Materials which are transparent to microwaves like Teflon, quartz, glass, ceramic, 3. Materials which absorb microwaves like aqueous, polar solvents. There are many advantages of using microwaves faster heating, more efficient, heat can be introduced from an external source, selective heating, less gradient and instantaneous heating are some of the advantages of using microwave synthesis(14).

Microwave synthesis has been researched for use in batch and continuous synthesis for reactions to reduce energy wastage by selective heating of the chemicals instead of heating the whole system. Similarly microwave synthesis has been applied to zeolite membrane synthesis to reduce the synthesis generally which ranges from 10-20 hours to only a few hours or less by using microwave synthesis. Yang(14) has done a very detailed review of microwave synthesis used in zeolite membrane synthesis, they have covered a very broad review of application of microwaves for zeolite synthesis that can be seen in table 1, most of the synthesis is in the range of 10 min to 45mins at 90C. Tomsett(15, 16) conducted a very detailed review of microwave synthesis of nano porous materials which also includes zeolites, He also conducted a review later in which he describes detailed synthesis of zeolite with microwaves. Li(17) performed a seeding free zeolite a synthesis with microwaves on porous alumina support. Looking at these procedures we use 90c for all our microwave synthesis.

Table 1: List of substrates used for zeolite A membrane synthesis(14)

Substrate	Synthesis strategy	synthesis composition	Preparation procedure
		$\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$	
Copper and silicon wafer	In situ	3:1:2:200	120°C for 1 min followed by 100°C for 240 min
Alumina	Seeded	3:1:2:200	Heated to 90 °C in 1 min; held for 40 min
Al <sub>2</sub> O <sub>3</sub> modified	Seeded	3:1:2:200	Heated to 90 °C in 1 min; held for 45 min
Al <sub>2</sub> O <sub>3</sub>	sol gel	50:1:5:1000	
Alumina	Seeded	6:1:2:150	Fluxed at 90 °C for 25 min
Alumina	Seeded	3:1:2:150	Fluxed at 90 °C for 25 min
Alumina	In situ	3:1:0.85:200	Synthesis in microwave oven at 250 W for 20 min; dried in microwave oven at 120 W for 10 min
Alumina	In situ	50:1:5:1000	Aging at 50 °C for 7 h in air oven and then microwave synthesis at 90 °C for 25 min
Alumina	In situ	50:1:5:1000	Aging at 50 °C for 7 h in oven and then microwave synthesis at 90 °C for 35 min
Alumina	In situ	50:1:5:1000	MH: aging at 50 °C for 7 h in oven and then microwave synthesis at 90 °C for 25 min; CH: aging at 50 C for 7 h in oven and then conventional synthesis at 90°C for 3 h
Alumina	Seeded	50:1:5:1000	Heated to 90 °C in 60 s; held for 15 min
Alumina	Seeded	50:1:5:1000	Heated to 90 °C in 60 s; held for 15 min
Alumina	Seeded	50:1:5:1000	Heated to 90 °C in 60 s; held for 15 min

## 2.4 Zeolite membranes in Microscale applications

Apart from conventional large scale separation and synthesis a lot of focus is also based on micro scale applications ranging from sensors to micro reactors which utilize zeolite membrane in the micro scale for detection, catalysis, separation and adsorption. Previously our group from Institute of Nanotechnology of Aragon published a very detailed review on micro scale applications of zeolite membranes(18) and detail of some application is given in figure 6.

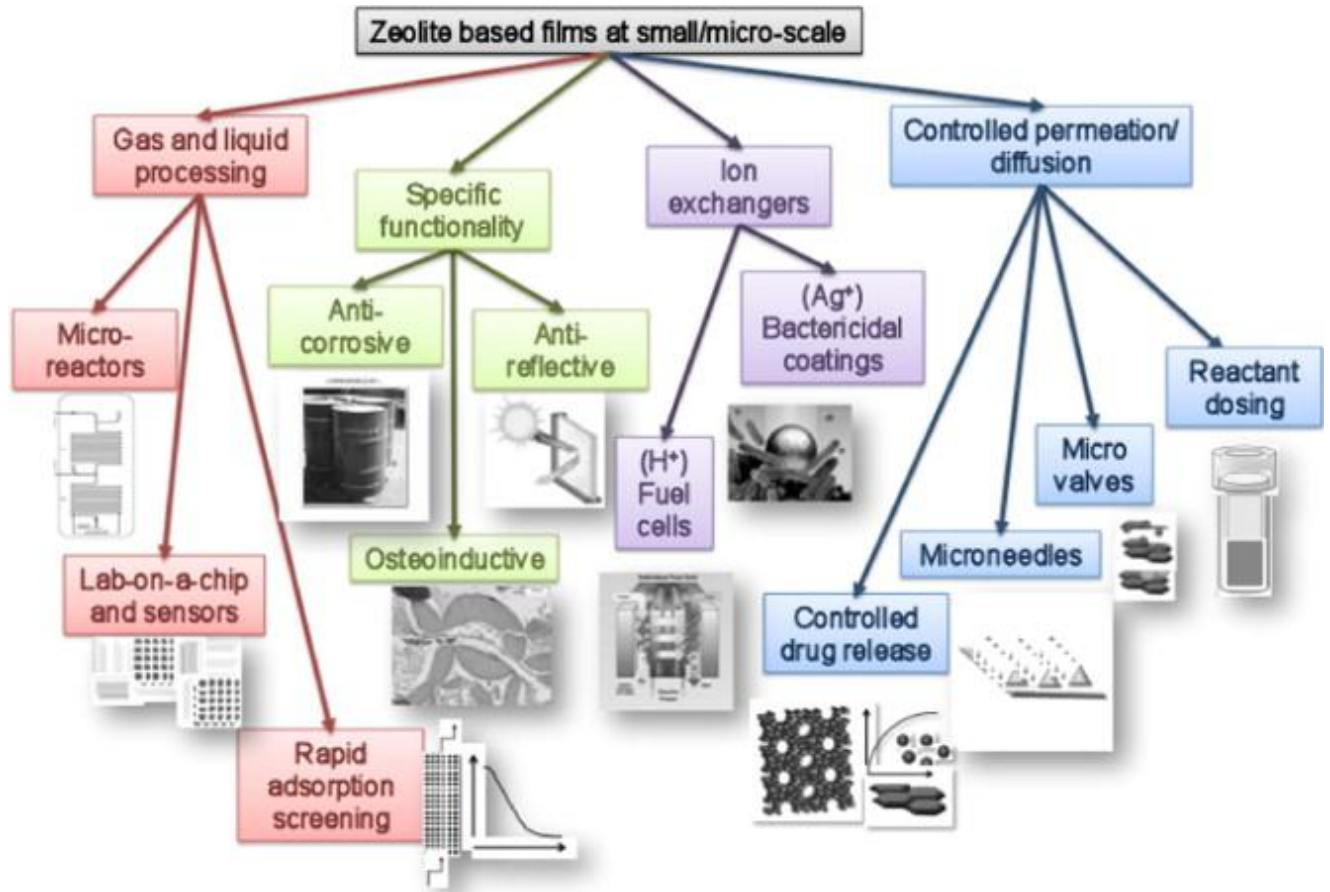


Figure 6: Applications of zeolite films in micro scale applications (21)

### Sensors

Zeolites have been applied in sensing devices to increase sensitivity and selectivity of detection of various molecules. There are many application reported in literature based on different mechanism from modification of traditional electrodes in liquid detection to modified cantilever in gas sensing. Some of the reasons for their functionality and use in sensors are based on its adsorption, high surface area, porosity, presence of mobile ions,



catalytic activity (19, 20). also a filter based on zeolite membrane have been previously proposed to act as a gas pre-filter(21). Zeolites have also been applied to improve conventional electrode sensors and are used to improve selectivity and sensitivity by modifying electrodes, they have been used in humidity sensors, ethanol sensors, NO, SO<sub>2</sub>, water sensing applications. They have also been used in cantilever based sensors where the cantilever acts as microbalance and can detect adsorption of specific components and hence has been applied to detect humidity based on this mechanism.(22) also gas sensors for explosive detection have been reported in literature based on zeolite material coating(23). More detailed information on zeolite based sensors are reported in the following sources which explain in detail the mechanism, fabrication and functionality of gas sensors based on Zeolites.(24, 25).

### Micro reactors

Process intensification and miniaturization is increasing for the goal to achieve more efficient reactions, to achieve higher conversion of reactants and to reduce the quantity of by products and to improve quality of the products. Zeolite membranes have been used as catalysts as a well as selective barriers for removal of products or harmful by products(18). In most cases the combined effect of selectivity and catalysis has improved many reactions of fine chemicals where selective catalysis is required to improve conversion and to reduce unwanted byproduct formation(4, 26). Other micro scale applications include use of zeolite membranes to remove volatile organic compounds from air and water and to recover catalysts from reactions(22). A detailed review of zeolite membrane reactors is described in the following publication by Kapteijn(27).

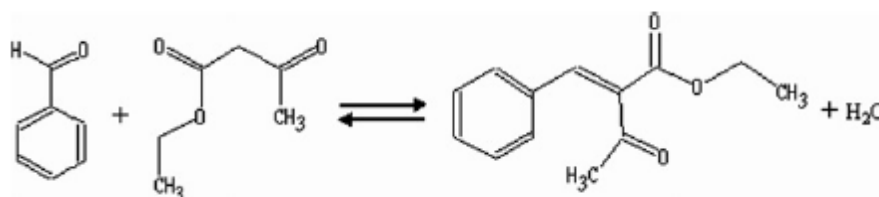


Figure 7: The Knoevenagel condensation reaction between benzaldehyde and ethyl acetoacetate(28)

Yeung and his colleagues have carried out extensive research in Knoevenagel reactions where 2 different layers of zeolite membranes are used in micro reactors for Knoevenagel reactions; one of the reactions is explained in figure 7. The first layer is used to remove water

which is the by product in the reaction and the 2nd layer acts as a selective catalyst only catalyzing the reactants as they are smaller in size to reach to the catalysts exchanged membranes as shown in figure 7 and 8. They etched different substrates silicon, stainless steel to design the micro channels and then using mercapto-3-propyltrimethoxysilane 50mM in ethanol for modifying the silicon substrate. Then they deposited the zeolite seeds using vacuum on the modified silicon, alumina or stainless steel substrate.

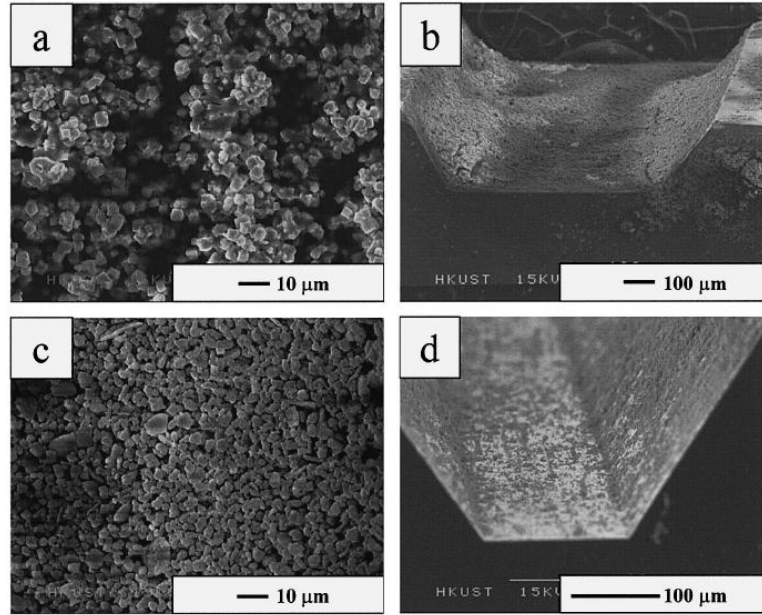


Figure 8: Yeung's work zeolite A membrane deposited in micro channels on silicon substrate(27)

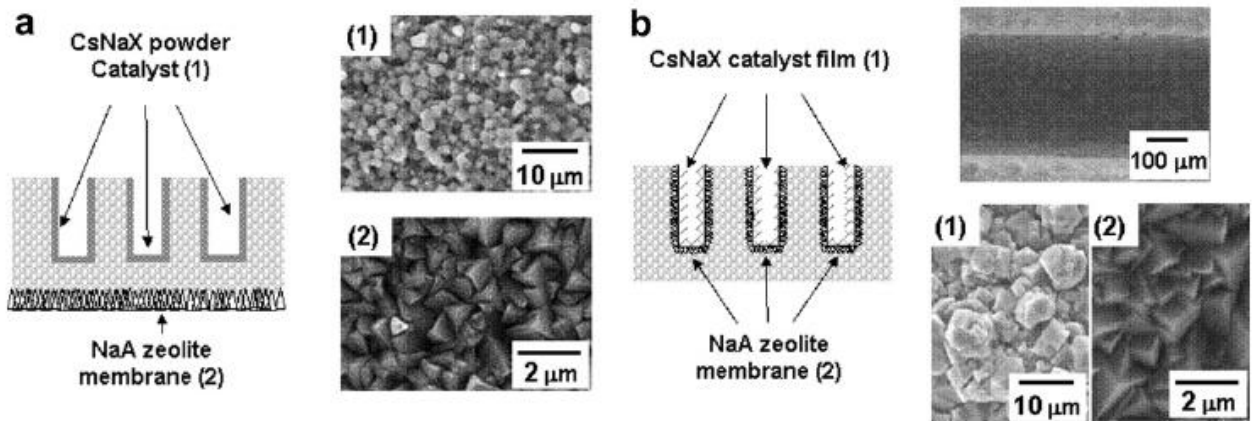


Figure 9: SEM images of zeolite membrane on micro reactor walls (27)

Yeung used zeolite A as the water removing membrane layer and zsm-5 exchanged with catalyst to perform the catalysis of the Knoevenagel reaction as explained in figure 9.

## 2.5 Zeolite membrane synthesis on silicon substrates

Many research has been published on zeolite membrane growth on various supports, most of the work is conducted on porous supports which provide structural support to the seeds and for the membrane to grow like porous alumina, porous stainless steel, porous ceramic supports and polymeric supports(29-33). Yang did an extensive review of microwave synthesis of zeolite and the table of supports used in microwave synthesis of zeolite LTA is listed in table 1. Our focus is to grow zeolite LTA membranes on flat nonporous support, previous works performed on flat surfaces include work by Frontera(34) where they modified silicon wafer with polyelectrolyte as mention in previous method by Decher(35), details of the modification were not published. Other work which included MFI zeolite membrane growth on silicon wafer is work by Mintova(36) where they tested the effect of different binders silica, TEOS and colloidal alumina as binder additives and different solvents and their effect on MFI membrane growth on silicon wafers. Yeung(37) applied zeolite A membrane for micro reactor application on silicon wafer with etched channels by using mercapto silane as the binder. Tsapatsis(38) tried different surface, seeding, zeolite modification and deposition on silicon wafers for zeolite A membranes he concluded that dip coating provided more close packing compared to spin coating, but spin coating provided more surface coverage, Tsapatsis also concluded that the electrostatic deposition did not create well intergrown membrane because the seed packing was too dense for the nutrients to go in the deposited seed. Ozburk and Akata(39) used e-beam lithography to pattern zeolite A nanoparticles on silicon wafers, they used IPA, toluene as solvents and they used ultrasound aided dip coating method, spin coating and direct attachment method previously reported by Yoon(40) and they concluded that Yoon`s method provided better result for making nano patterns of zeolite A nano crystals.

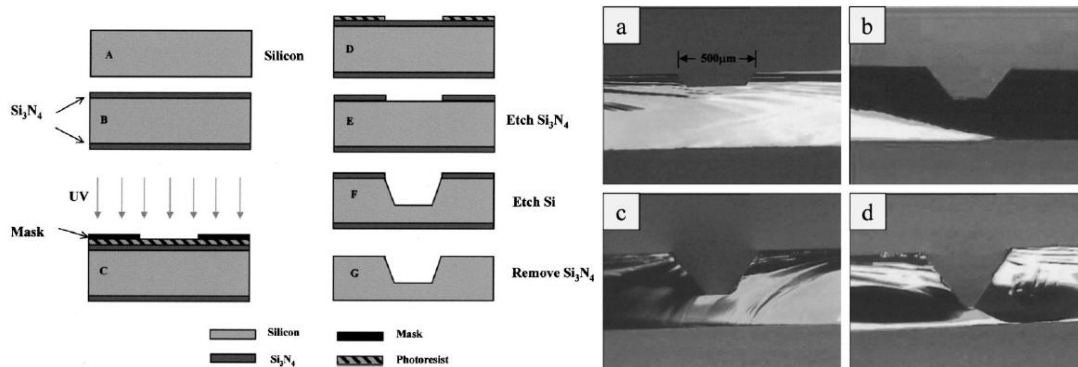


Figure 10: micro channel fabrication on silicon substrate(37)

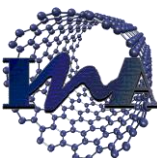
Most of Yeung`s work on micro reactor are on porous stainless steel or porous alumina substrates which are pre-etched with micro channels and then zeolite seeds are deposited followed by zeolite synthesis. Only one of his publication reports using silicon substrate of micro reactor application with zeolite membrane as shown in figure 10. He etched the channel pattern on the silicon using photolithography process; the silicon wafer was coated with a silicon nitride layer. KOH was used to etch the pattern. Silicalite seeding was performed using mercapto silanes and grown by traditional oven method for 110C at 24 hours.

## 2.6 Surface modification of silicon oxide substrate

Silicon oxide surface after cleaning has OH- groups on the surface making it hydrophilic and the OH- groups give the surface a negative charge. The zeolite A seed suspension have a negative charge in the solution, the similar charges cause repulsion and non-uniform seeding of zeolite crystals on silicon oxide surface. Different modifications were performed to attach zeolite seeds onto the silicon oxide surface. The important parameter for all coating is to ensure that the residual water is evaporated from the silicon surface by heating it above 100C; our samples were heated at 150C for more than 1 hour to remove water from the surface and to improve adhesion of modification and seeds.

### 2.6.1 Polydiallyldimethylammonium-chloride (PDDA)

Polydiallyldimethylammonium-chloride (polyDADMAC/PDDA) is a cationic polymer with a positive charge. It has been previously used to modify surfaces through self assembly of polymer to form monolayer and multilayer of opposite charge polymers. Caro used PDDA to modify porous alumina support to perform seeding free synthesis of zeolite A membrane, the positive charge attracted the nutrients onto the alumina surface modified by PDDA and was able to get better gas separation compared to untreated surface(41). Many other works of self assembly of PDDA on surfaces have been reported previously by Decher and also by Yang.(35, 42-44). Structure and attachment on silicon oxide surface is explained in figure 11.



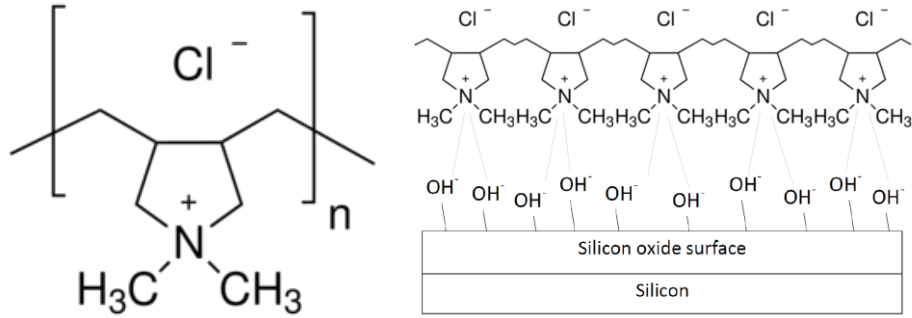


Figure 11: PDDA Molecule, schematic representation of PDDA layer on silicon oxide surface

### 2.6.2 Boehmite (aluminum oxide hydroxide / $\gamma$ -AlO(OH))

Boehmite is an aluminum oxide hydroxide ore and the reason to use Boehmite is to act as an aluminum source to feed the zeolite growth and also it has a low coefficient of thermal expansion, which helps reduce stress during processing and hence reducing cracks and defects during synthesis. Boehmite solution was spin coated 8 times because coverage was difficult during one spin coating process caused by repulsion between OH groups in Boehmite and silicon oxide layers. Preparation procedure for boehmite solution is reported in the annex. The structure of Boehmite is explained in figure 12.

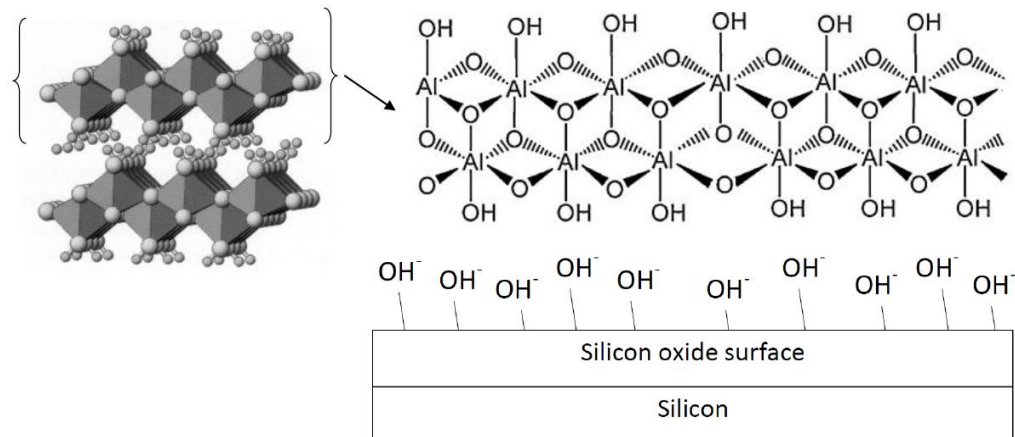


Figure 12: left Boehmite structure, Right schematic representation of Boehmite layer on silicon oxide

### 2.6.3 Silanization

Organo-silanes are molecules which contain a backbone of Si-C and have more than one functional group as shown in figure 13. Generally organo-functional alkoxy-silane are the most commonly used organo silanes as they alkoxy group reacts with hydroxyl (OH) groups on substrate and form covalent bond. There is another functional group for example

amine, ethoxy, halogen; alkyl group reacts with a different material. In this way the silanes are used as coupling agents to bind different materials like organic and inorganic materials, they are also used to modify surface characteristics, reducing agents, to functionalize surfaces and many other applications. It is widely used in rubber, glass fiber, composites, paints, inks, adhesives. (45-49)

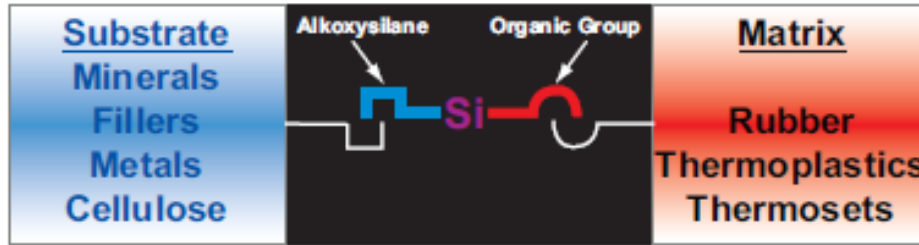


Figure 13: schematic of function of organo silane, (53)

In literature organo silanes have been used for improving metal adhesion on silicon substrate(50), modification of silica particles using different silanes(51), patterning of silicon oxide over silicon and using silane for gold patterning(52), modification of pores of porous silica membranes(53), nano patterning on silicon using silanes(54), using silane to apply dicarboxylic group on silicon surface(55). Below in figure 14 is a simple explanation of APTES and how it can interact with a silicon oxide surface.

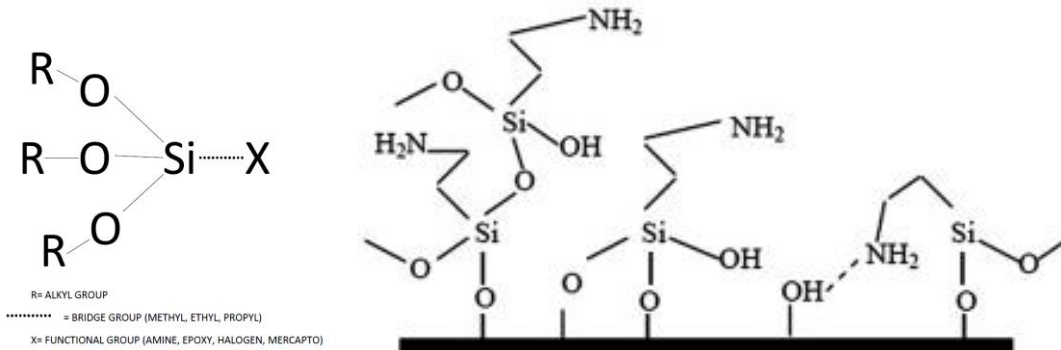
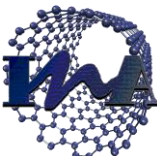


Figure 14: left structure of trialkoxy-silanes, right APTES attachment on silicon oxide surface

### Literature on silanization of surfaces

Up to date many works have been published to study the structure and reaction of organosilanes on silicon and silicon oxide surface. Some of the works include Vandenberg`s study on the structure of APTES on silicon oxide(56) where he did extensive study on effect of solvent, heat, time and different curing conditions, Manifar(57) studied in detail the effect on solvent on deposition Octadecyltrichlorosilane(OTS) on silicon



wafers, Hu(58) studied in detail the structure of MPTMS on silicon oxide and effect of water, concentration of silane and the surface of  $\text{SiO}_2$ . Petri(59) studied the assembly of APTES on silicon oxide by different characterization and then used the monolayer of silane to improve adhesion of Gold without using chromium which is used in conventional coating of silicon oxide with gold, Howarter(60) studied the deposition of APTES on silicon wafers and studied the effect of temperature. Zhang(61) studied the chemical vapor deposition of 3 different silanes including APTES and used a dye adsorption to test the density of amines and concluded that vapor phase deposition provides better monolayer coverage. Pasternack(62) studied the effect of solution temperature on APTES deposition on silicon oxide surfaces. Kim(63) studied the effect of post curing conditions on the structure and the stability of APTES on silicon oxide layers and found that curing does not have any significant effect on the silane structure. Zhu(64) performed a detailed literature review and experiments to obtain the best reproducibility and stability of different silanes on silicon wafers, and concluded the vapor phase deposition is more reproducible and ethoxy silanes are less effected by water concentration compared to methoxy silanes and hence are more reproducible. Gu(65) studied the deposition of APTES on silicon wafers and tested the effect of wear by friction on the APTES layer. Graf(66) experimented with the optimization of cleaning procedure for silicon wafers to be used for modification by silanes. Li(54) deposited APTES on silicon wafer using micro printing to form micro patterns by silanization. Kim(67) studied the effect of solvent Toluene and water on APTES deposited on silicon wafers by different characterization and concluded that Toluene deposition of APTES has more reactive surface amino groups compared to aqueous deposition. Wang(68) studied the effect of different vapor and liquid deposition technique on the formation of APTES silanization on glass slides.

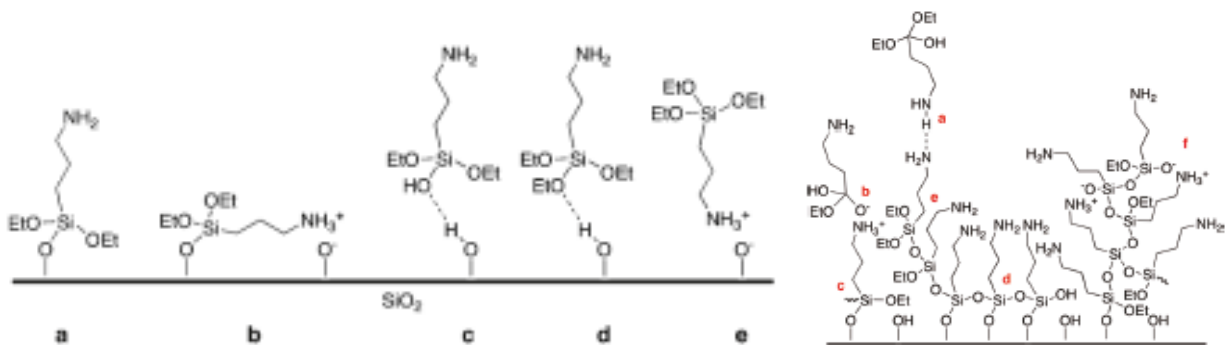
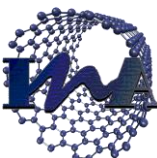


Figure 15: left and right, complex mechanism of APTES orientation on silicon oxide



All the work agrees on the fact that amount of water is the important parameter in silanization as excess water can cause self-polymerization of silanes while lack of water can cause poor coverage of the substrate. Other parameters include temperature; increase in temperature increases reactivity of the silanes and faster deposition of silane takes place at higher temperature. Another important parameter is silanization time, as with time the thickness and roughness of silane layer increases. So our main focus was to control water content by drying the silane system, and the substrate properly and uniformly to ensure reproducibility of the experiment.

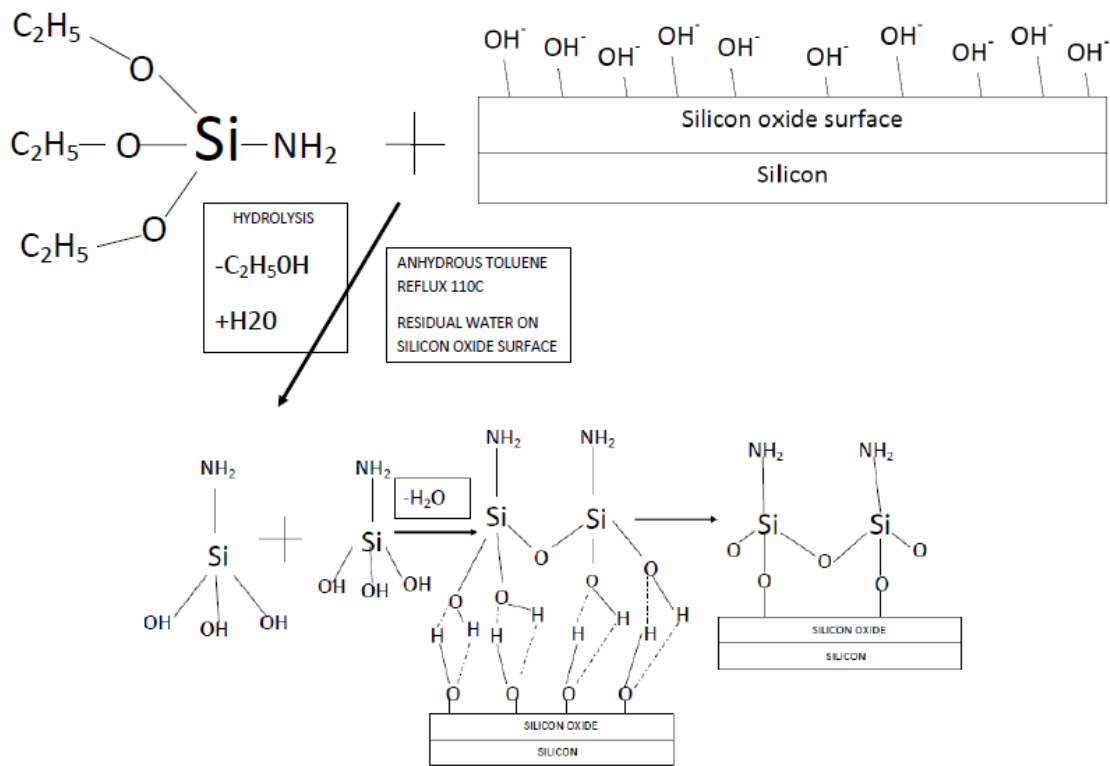


Figure 16: an ideal mechanism of APTES attachment on silicon oxide

### Silanization of substrates for zeolite membranes

Organo silanes have been previously used to modify substrates to attract zeolite nutrients from the synthesis solution to promote nucleation and growth and they have also been used to modify surface for seeding of Zeolites. Tsapatsis has modified zeolite seeds with APTES(38), Caro also extensively studied silanization of substrates for membrane growth which include APTES modified porous alumina support to grow zeolite FAU membrane without seeding(69), the seeding free synthesis of zeolite A membrane on porous alumina support using



CPTMS(70), Multilayer zeolite A synthesis on porous alumina support using APTES as interlayer(71), using APTES for seeding free zeolite A growth(72). Yoon has done extensive study of glass modification with silanes to bind zeolite seeds; he also explains various possible silanization processes to bind zeolites on substrates with hydroxyl groups one of them is explained in figure 17 (40), Zhang used silanes to attach zeolite catalysts on the stainless steel micro reactor channels(73). Yeung used 3-Mercapto-alkylmethoxysilane to attach zeolite A seeds on silicon, alumina and stainless steel substrates(37).

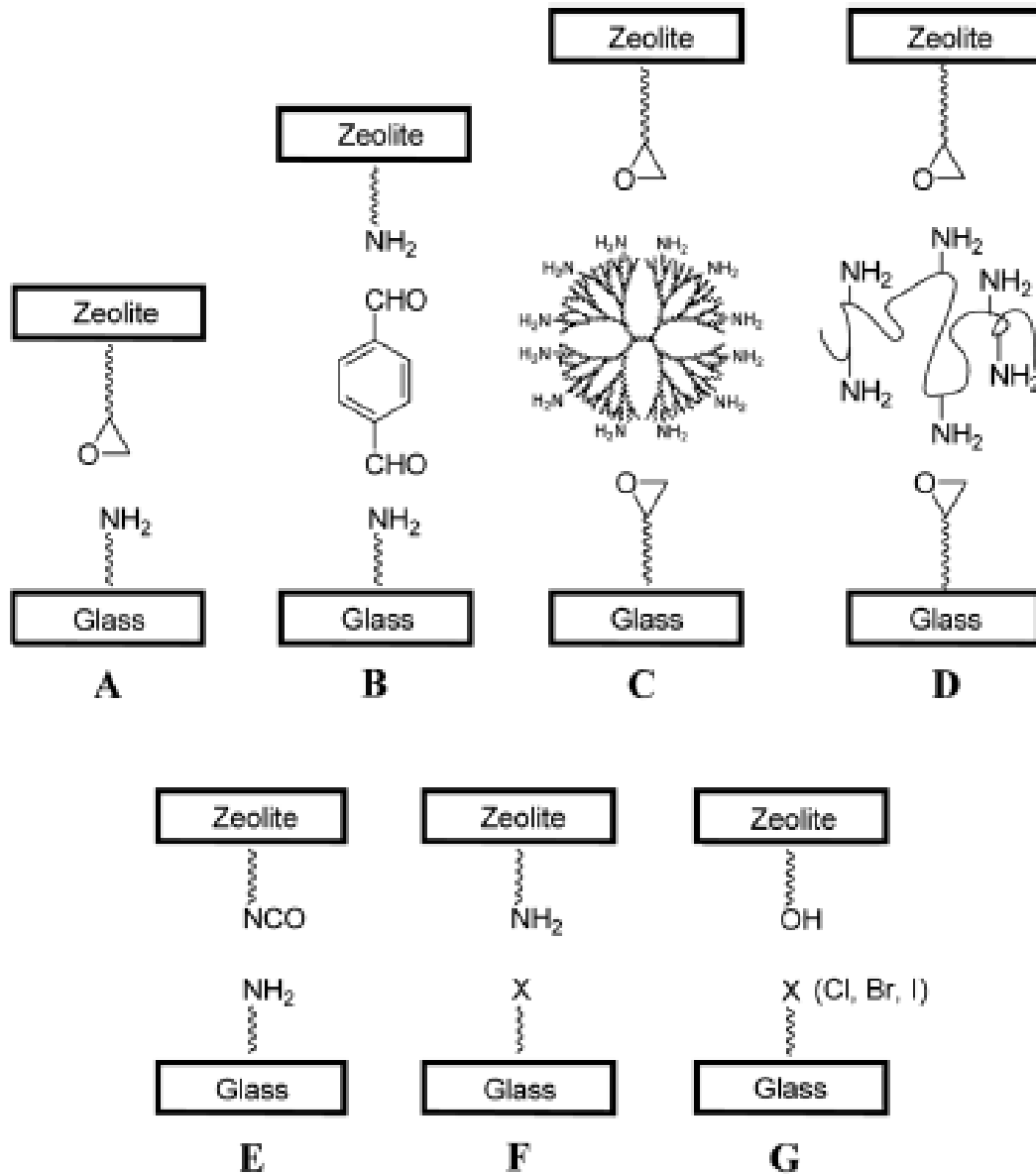


Figure 17: Different modification of substrates for zeolite attachment(74)

## 3 EXPERIMENTAL

### 3.1 Materials

The following chemicals 98% APTES(3-aminopropyltriethoxysilane), 98% APTMS(3-aminopropyltrimethoxysilane), 97% CPTMS(3-Chloro-tripropylmethoxysilane), 98% CPTES (3-Chlorotriethoxysilane), 95% IPTMS (3-IodoPropyltrimethoxysilane), 97% BPTMS (3-Bromotrimethoxysilane),  $\text{HNO}_3$ (67%),  $\text{H}_2\text{O}_2$  (30%),  $\text{H}_2\text{SO}_4$  (97%), Ethanol 99.7% (ANHYDROUS), Sodium silicate solution, Aluminum hydroxide, 98% Aluminum Isopropoxide, Acetone 99.9%, LUDOX AS-30 30% wt in  $\text{H}_2\text{O}$ , Sodium hydroxide Pellets 97%, Toluene Anhydrous 99.8% , Aluminum tri-sec-butoxide 97% , Poly DADMAC 20% wt in water, were purchased from sigma Aldrich. Silicon wafers and grids P type (100) with silicon oxide layer of 295nm were obtained from the institute of nanotechnology Aragon, Spain.

### 3.2 Silicon substrates

Silicon substrates with silicon oxide coating was chosen as the material support because of the well established silicon manufacturing technology in the semiconductor industry and silicon oxide layer to protect the silicon from etching from highly basic synthesis solution for the membrane synthesis

#### 3.2.1 Silicon wafers

The silicon wafers with silicon oxide layer used for the experiments were obtained from Institute of nanotechnology Aragon, Zaragoza, Spain with the specifications: P type (100) silicon wafers with silicon oxide layer of 285nm on top of 400 micron silicon wafer. The wafers were cut into squares of 15mm x 15mm shown in figure 18.

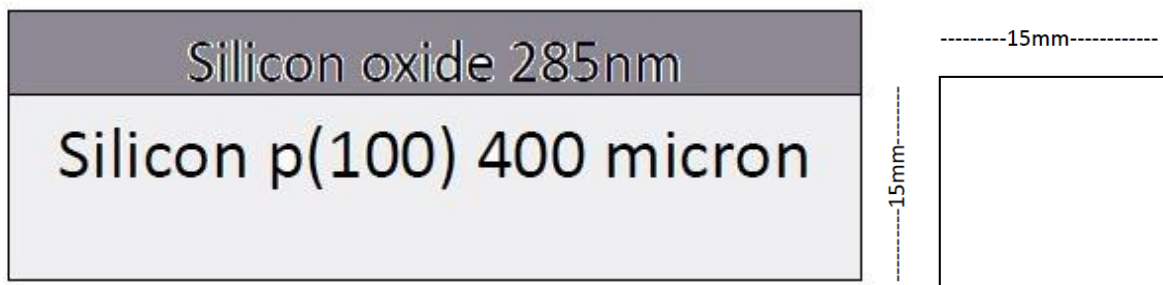


Figure 18: left silicon oxide layer on silicon wafers; 4 inch wafer cut into small squares for synthesis

### 3.2.2 Silicon grids

Silicon grids were also used in the experiment to study the effect of grid supports in order to fabricate free standing zeolite membranes on the silicon oxide grid. The grid size was 10mmX 10mm with different grid thicknesses. The grid size is explained in figure 19.

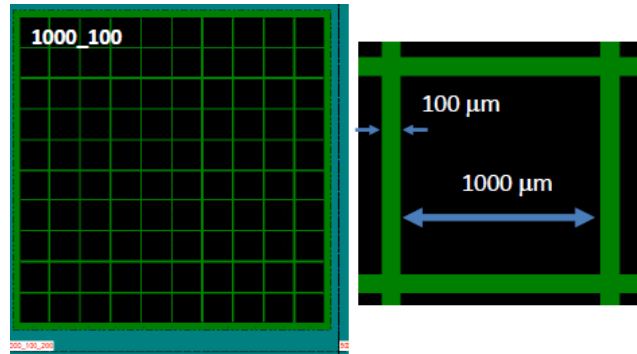


Figure 19: grid sizes description (a grid 1000\_100)

The grid were fabricated by Mesa institute for Nanotechnology, University of Twente by a procedure detailed in annex 5. Figure20 explains the cross section of our grids with 2micron layer of silicon oxide on the top part of grid while the on back side of the grid the silicon oxide layer is etched down to 285nm.

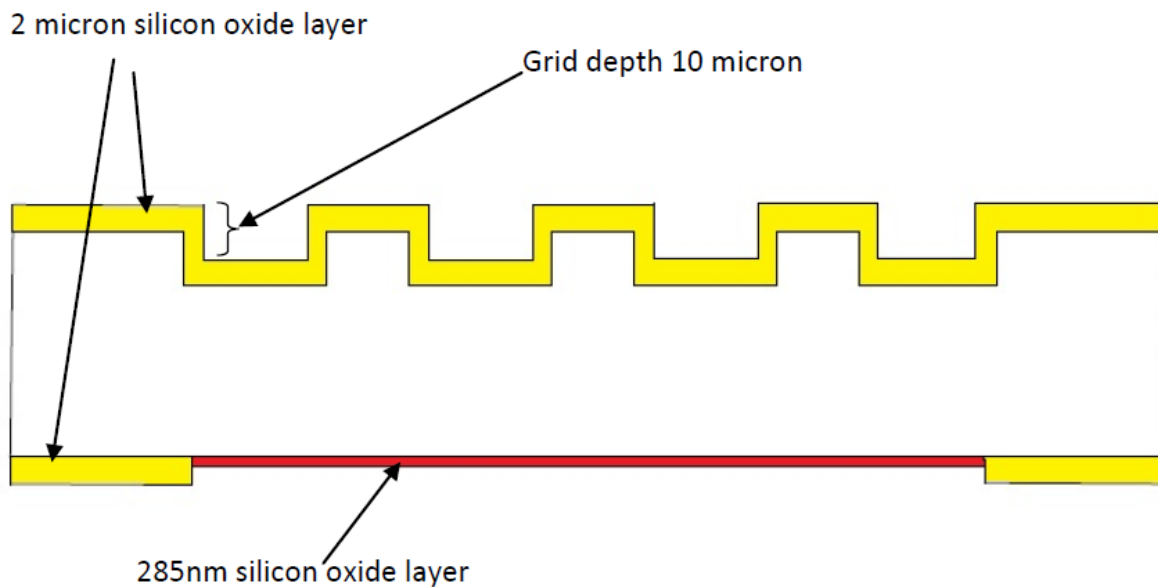


Figure 20: Cross section of silicon grid

### 3.2.3 Cleaning of silicon substrate

The cleaning procedure was prepared after reviewing many articles which used silicon and silicon oxide wafer for similar applications. Many publications have emphasized on the importance of cleaning to remove organic contaminants, metal particles, residues and to hydrolyze the surface with OH groups on the silicon oxide surface(75-88). Also a detailed study on Surface cleaning procedures for silanization gives a good comparison of different cleaning formulations(66). Based on these finding in the literature we developed our cleaning procedure explained in table2. The importance of cleaning can clearly be observed by testing two different samples, especially the Piranha solution which improves the wet ability of the silicon oxide surface by forming OH groups.

Table 2: cleaning procedure for silicon oxide substrates

	Silicon oxide cleaning procedure		
	Process	time(min)	Purpose
1	sonication in acetone	15min	remove protect films used during wafer cutting
2	sonication in ethanol	15min	remove organics and acetone residue
3	sonication in water	15min	remove water soluble residues
4	immersion in HNO <sub>3</sub> 67%	60min	to remove organics and metal contaminants
5	H <sub>2</sub> O wash		remove HNO <sub>3</sub> residue
6	nitrogen blow dry		dry water
7	immersion in piranha solution	60min	to hydroxylate the surface (OH groups formation)
	Ratio 7:3 H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O <sub>2</sub>		heated to 60-80 C when solution cools after 30mins
8	H <sub>2</sub> O wash		remove any residue of piranha solution
9	nitrogen blow dry		
10	dried on hot plate 150C		to remove moisture from substrate

### 3.3 Preparation of zeolite A nanoparticles for seeding

The synthesis composition ratio was 13.4 (TMA)<sub>2</sub>O: 0.3 Na<sub>2</sub>O:1.8 Al<sub>2</sub>O<sub>3</sub>: 11.25 SiO<sub>2</sub>:700 H<sub>2</sub>O. The silica source was prepared from mixing 12.8 g of Ludox AS30 and 11.36g distilled water. The aluminum source was prepared by mixing 39.76g water, 3.4 g of 1M sodium hydroxide, 28.4 g of TMAOH tetra-methyl-ammonium-hydroxide templating agent and

4.26g aluminum isopropoxide. The aluminum and silica solutions were mixed separately for 2 hours and then mixed slowly drop by drop, adding aluminum source in the silica source, then left for ageing with stirring under room temperature for 24 hours. The aged solution was then put in a flask and synthesis was performed in a Rota vapor at 80C for 15 hours. After the synthesis was completed the solution was centrifuged at 10,000 rpm for 30minutes and the supernatant was used again in the hydrothermal synthesis to recycle the solution to obtain from zeolite A nano crystals. The settled particles during the centrifuge were re-dispersed in water and sonicated to wash the solution to remove chemical material from the seed solution and centrifuged again at 10000 rpm for 30 minutes. This step was repeated 5 times and then the seed solution was finally dispersed again in water and sonicated to obtain zeolite A seed suspension in water. Synthesis conditions

### 3.4 Surface modification by PDDA solution

The poly-DADMAC solution was prepared by mixing 19.97 ml of water, 0.587gram of NaCl and 0.1 gram of PDDA 20wt% solution in water. The solution was filtered with a 0.5 micron syringe filter to remove any contaminants. Laurell WS400bz spin coater was used to spin coat PDDA solution on the silicon wafers. Dip coating device as shown in figure 21 was used to test dip coating of PDDA solution on the substrates.

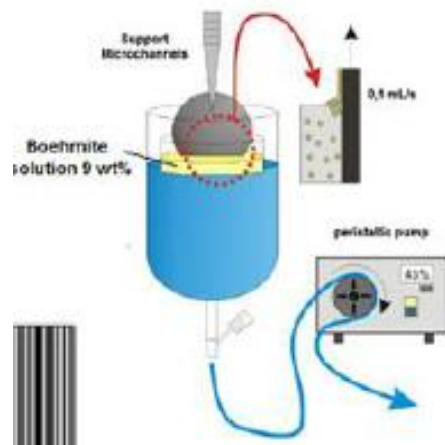


Figure 21: dip coating device

The normal spin coating condition used were the one reported by Castro(6)c 170rpm 1.5 minutes and 4000 rpm 1min, following the PDDA deposition the zeolite seeds in 2% wt suspension in water was spin coated at 100rpm 1 min and 3000 rpm 0.5 min. The observation was large depositions in some areas compared to other due to electrostatic forces because of the

surface modification which is similar to the finding of Tsapatsis as explained in section 2.5. So in order to improve seeding on this modified substrate we tried to use high speed spin coating of seeds at around 6000 RPM and also by introducing the seed solution drop by drop during the spinning process showing improved seeding. Apart from the spin coating process; we also tried dip coating method in order to try to improve the uniformity of the seeding process. Using dip coating device we coated PDDA layer and seeds on the substrate. We observed that the seeding was more packed and aligned in the dip coating process but the drawback was slower speed of the process.

During our experiments we observed that the viscosity of the seed solution and PDDA solution was low causing uneven wetting during the spin coating process. So in order to improve the distribution of seeds and PDDA on the substrate we tried to incorporate PDDA solution in the seeding solution, which increased the viscosity of the solution and also our objective was to suspend the zeolite seeds within the long chain polymers of PDDA. Different concentrations of PDDA were added in the seed solution 2%, 5% and 10% by volume of 20% PDDA solution in water and spin coated. The list of experiments performed for PDDA is listed in table 4.

### 3.5 Surface modification by Boehmite solution

Boehmite is used as an aluminum nutrient source to help speed up the zeolite growth and also to provide a reduced stress layer with a low coefficient of thermal expansion in order to reduce stress and crack formation; in table 5 are some thermal expansion coefficients of some materials. Also in figure 21 are some thermal expansion coefficients of zeolites. Since the difference of thermal expansion coefficient of the substrate and zeolite is high, it causes excessive stress during heating and cooling causing cracking. So Boehmite acts as a material whose thermal expansion coefficient lies in between the range of silicon wafer and zeolite, this helps reduce the thermal stress on the growing membrane. We used both spin coating and dip coating methods as previously studied by Castro(6) to optimize the deposition of Boehmite for zeolite A synthesis. The optimized parameters studied by Castro using spin coating is 100RPM 60 seconds and 3000RPM for 30 seconds and repeated 8 times to get uniform coating of Boehmite. Then the sample was dried at 200C for 2 hours, followed by seeding by 2% for 5 times at 100 RPM 30 seconds and 3000RPM 60 seconds. Then the sample was dried at 150C for 24 hour before synthesis. The drying is important to ensure that the

boehmite layer attaches to the silicon oxide layer. We also used the dip coating procedure reported by Castro which is dip coating 5 times of Boehmite, 2hr 200C heat treatment followed by, 5 times dip coating in zeolite suspension in water. In order to reduce the number of steps and reduce multiple spin coating and dip coating steps; we tried to incorporate Zeolite seeds in Boehmite solution and spin coated it once.

Table 3: Thermal expansion coefficient values

thermal expansion coefficient	$\alpha(10^{-6} m/m K)$
silicon nitride	3.3
alumina	5.4
aluminum	22.2
diamond	1.18
glass pyrex	4
silicon	3
silicon carbide	2.77
zeolite A wet	-40 to 50
zeolite A dry	-7 to 10

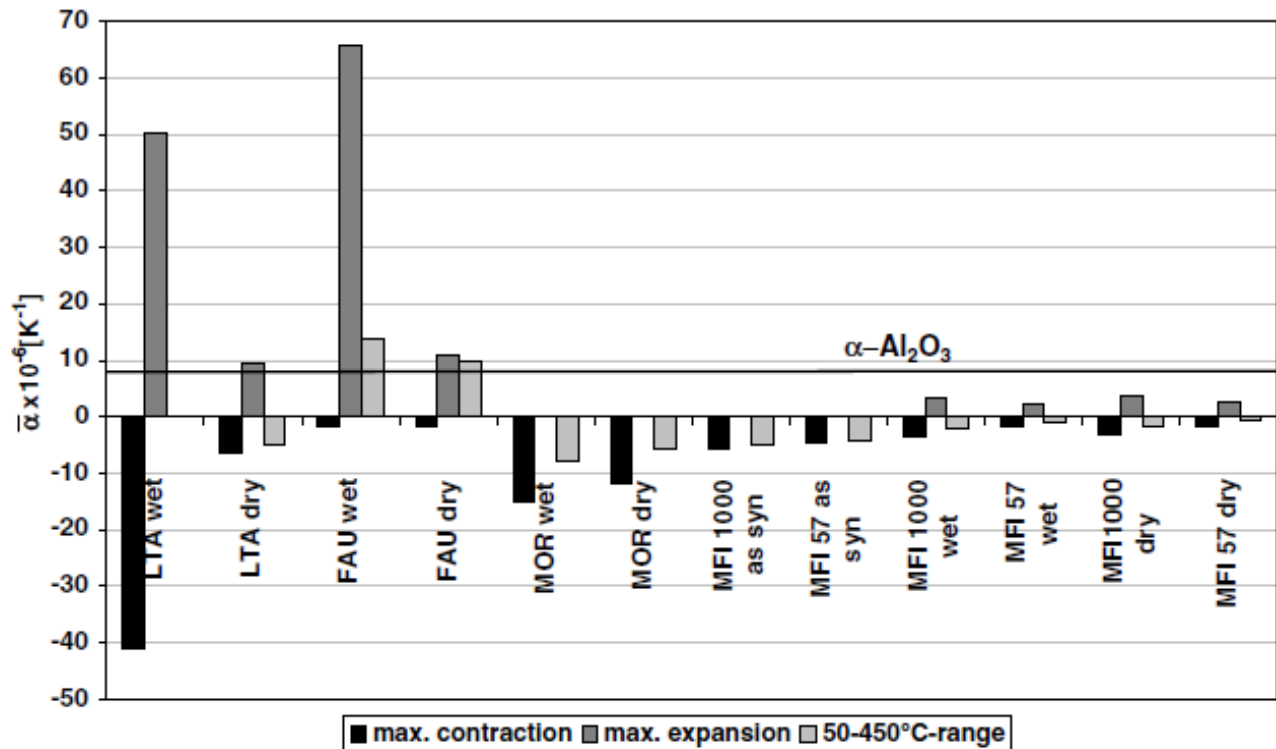


Figure 22: thermal expansion co-efficient of some zeolites(89)

### 3.6 Surface modification by silanes

For the preparation of silanization process, we dried the reflux chamber, the flasks and all other glassware in the oven at 150C over night to ensure no moisture is available on the surface. When the experiment is run, the glassware is taken out from the oven and the wafer on holder from the hot plate which is dried at 150C overnight is introduced into the hot reflux chamber and sealed with nitrogen flow. The chamber is purged for 30minutes before we introduce any solvents. Toluene is injected into the chamber using the syringe, and heated to the required reflux temperature. Finally the silane is added to the system. The solution is refluxed to the desired time, then solution is drained with the help of a syringe in the nitrogen environment, fresh toluene is added to wash the substrate, then drained, then for ethanol seeding procedure fresh absolute ethanol is added to clean the system twice and then finally zeolite seed suspension in ethanol is added and refluxed at 85C. Seeding is performed both under reflux of the solvent, sonication or a combination of both can be used. After seeding the sample, it is dried on a hot plate at 100-110C overnight to remove solvent. Table 7 explains the whole general process of silanization.

Table 4: silanization process

	Silanization process	Reason	Description
1	Complete drying of reflux system	To remove any moisture	150C dried overnight
2	silicon substrate drying	to remove moisture from surface	110-150c Hotplate
3	Substrate placed on a teflon holder	placed vertically in chamber	put nitrogen flow
4	venting	to remove atmosphere from chamber	N2 flow for 30minutes
5	Toluene added in the system	solvent	fixed amount (50ml)
6	System heated to reflux 110C	heat to increase reaction temperature	over stirrer/hot plate
7	Silane added	required conc and type silane added	silane addition
8	reflux	solution refluxed for required time	
9	draining solution	silane sol removed from chamber	
10	fresh toluene wash	to remove unreacted silane	wash
11	fresh ethanol wash X2	only for ethanol seeding	wash
12	addition of seed solution	reflux or sonication or combination	to attach seed to silane
13	wash	in the same solvent ( as used in seeding)	
14	dried 110c	remove solvent and cure	



Different silanes were used for the surface modification of silicon oxide wafers and grids. APTES was tested in great detail because of its stability and wide application in different silicon oxide modifications to attach different types of functional groups. We also used more reactive silanes capable of making covalent linkages as previously explained in the introduction section on silanes. We used Halogen based silanes to modify substrates and try to form covalent bonds between the modified substrate and our zeolite nano particles in order to try to improve anchoring of the zeolite seeds. In order to ensure reproducibility we used fixed volume of solvent for all experiments which was 50ml this is to ensure that the water content in the solvent is the same and we prepared samples in batches of two samples for each run.

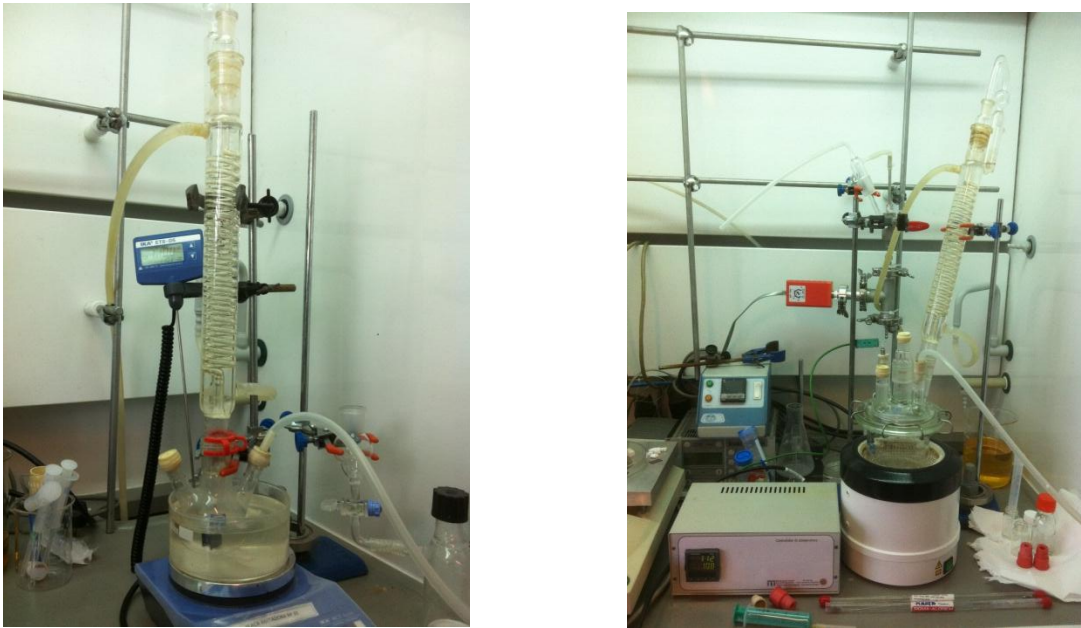


Figure 23: Experimental setup for silanization process Left for small wafer, right for 3inch wafers.

### 3.7 Preparing microwave synthesis solution

The gel composition for microwave synthesis has the molar ratio 1:1.8:7.2:108  $\text{Al}_2\text{O}_3$ :  $\text{SiO}_2$ :  $\text{NaOH}$ :  $\text{H}_2\text{O}$ . First the sodium silicate solution 30gm is mixed with 60gm of water and stirred. For aluminum source 17gm sodium hydroxide pellets and 17gm of water is stirred and heated between 50-70c and then 11.4 gram of aluminum hydroxide is added and stirred for 30minutes till it is dissolved into a transparent solution then 43.6 gm of water is added and stirred for at least 1 hour. Then drop by drop aluminum solution is added to silica solution under stirring. During the addition the PH of the silica solution becomes more basic

going to gelation of the solution we need to ensure the stirring is increased to make sure we prevent large aggregates. After the solution is completely mixed it is aged for at least 3 hours before use for microwave secondary synthesis of zeolite A membrane. In order to prevent the aggregates to get into the microwave synthesis solution, the aged solution was extruded through a syringe with a needle which breaks any large aggregates in the solution. The synthesis was carried out in a CEM microwave system using a fiber optic thermocouple to measure the reaction temperature and the maximum power setting used was 140watts. A Teflon autoclave was used for the synthesis to hold the sample and synthesis solution with a stirrer and the synthesis was carried out at 90C.(90, 91)

## 4 RESULTS AND DISCUSSION

### 4.1 Characterization of zeolite seeds

The characterization for the zeolite A seeds were conducted using the following equipment; the pH was tested using a pH meter EUTECH instruments model cyber scan pH2100, the particle size was analyzed using a DLS size analyzer Brookhaven instruments corporation 90Plus particle size analyzer and by using scanning electron microscope FEI instruments. The concentration of the zeolite A crystals was measured by using a microbalance Radwag Mya5/2Y. The zeolite seed data is give in table 5(molar mass of zeolite A-Na 2190g/mol).

Table 5: zeolite seeds size data

BATCH	AGEING TIME HOURS	SYNTHESIS TEMPERATURE C	SYNTHESIS TIME HOURS	DLS SIZE Nm	POLYDISPERSITY	SEM SIZE nm	ZETA POTEN Mv	PH	mass in grams	yield %
1	90	100	15	199.5±23	0.104	186±17.9	-37	10.2	1.896	86.5
2	20	95	15	129.5±19.5	0.036	127±21.3	-29	9.9	1.529	69.8
3	48	100	15	119.6±24.1	0.124	112±21.7	-33	10.4	1.78	81.2
4	30	90	22	95.3±6.2	0.048	97±9.1	-43	11.4	1.341	61.2
5	24	80	48	79±8.4	0.034	77.5±6.3	-49	9.9	0.978	44.6

We observed during our synthesis that ageing time significantly increases the yield. But at the same time it increases the size of the zeolite crystals. Also we observe that when the synthesis temperature is reduced we are able to obtain smaller crystal size but with lower yield. Hence to obtain smaller crystals with higher yield; we can age the solution longer, and synthesize at lower temperature to obtain the smallest size of zeolite A seeds with a suitable yield. We also observe good agreement between the DLS and SEM results for the zeolite particle sizing.

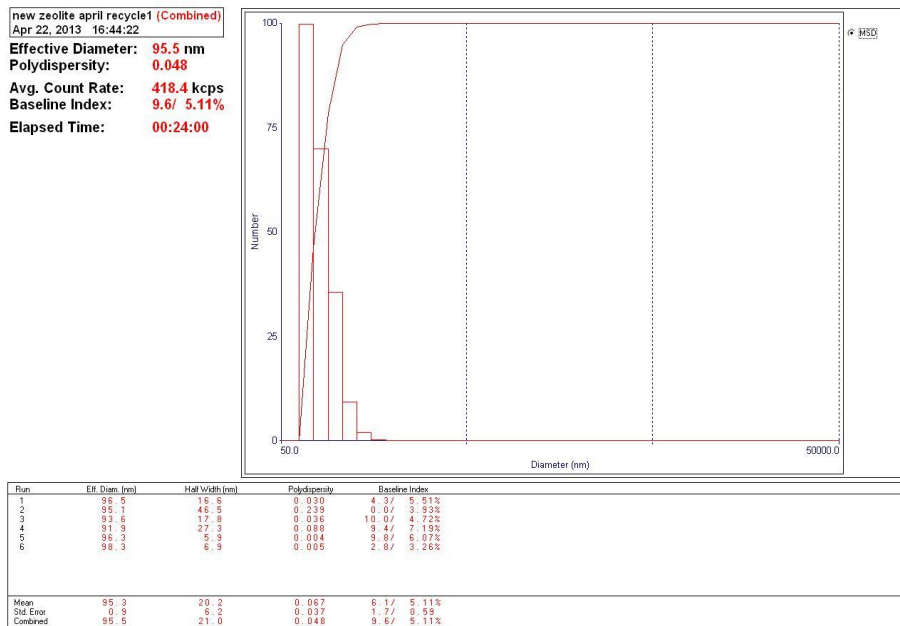
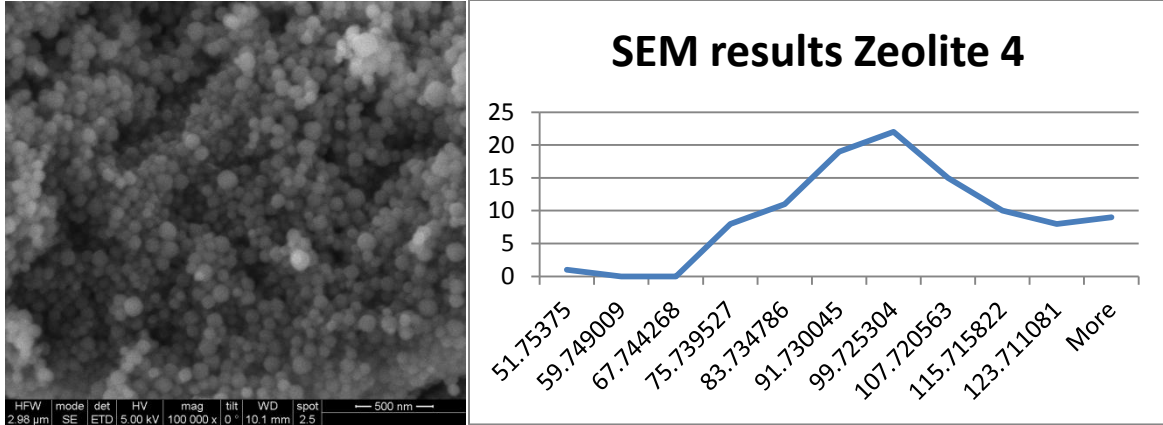
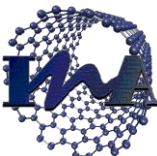


Figure 24: TOP SEM image sizing data and Bottom DLS results for zeolite 4

## 4.2 Seeding and synthesis on bare silicon oxide wafers

The zeolite seeds were spin coated at 100rpm 1 min and 3000 rpm 0.5 min. The seeding of bare silicon oxide wafers were performed at different seed concentrations and we can clearly see from the SEM images Figure 25 and 26 that the number of zeolite seeds increase with increasing concentration of seed solution, but due to similar charges and repulsion the coverage by the zeolite seeds was incomplete. Also this is further obvious after synthesis that most of the zeolite seeds on the surface are displaced during synthesis and do not take part in the membrane growth. Because of this we need to modify the surface to attract and possibly find ways to improve the membrane growth and attachment on the surface of silicon oxide wafers.



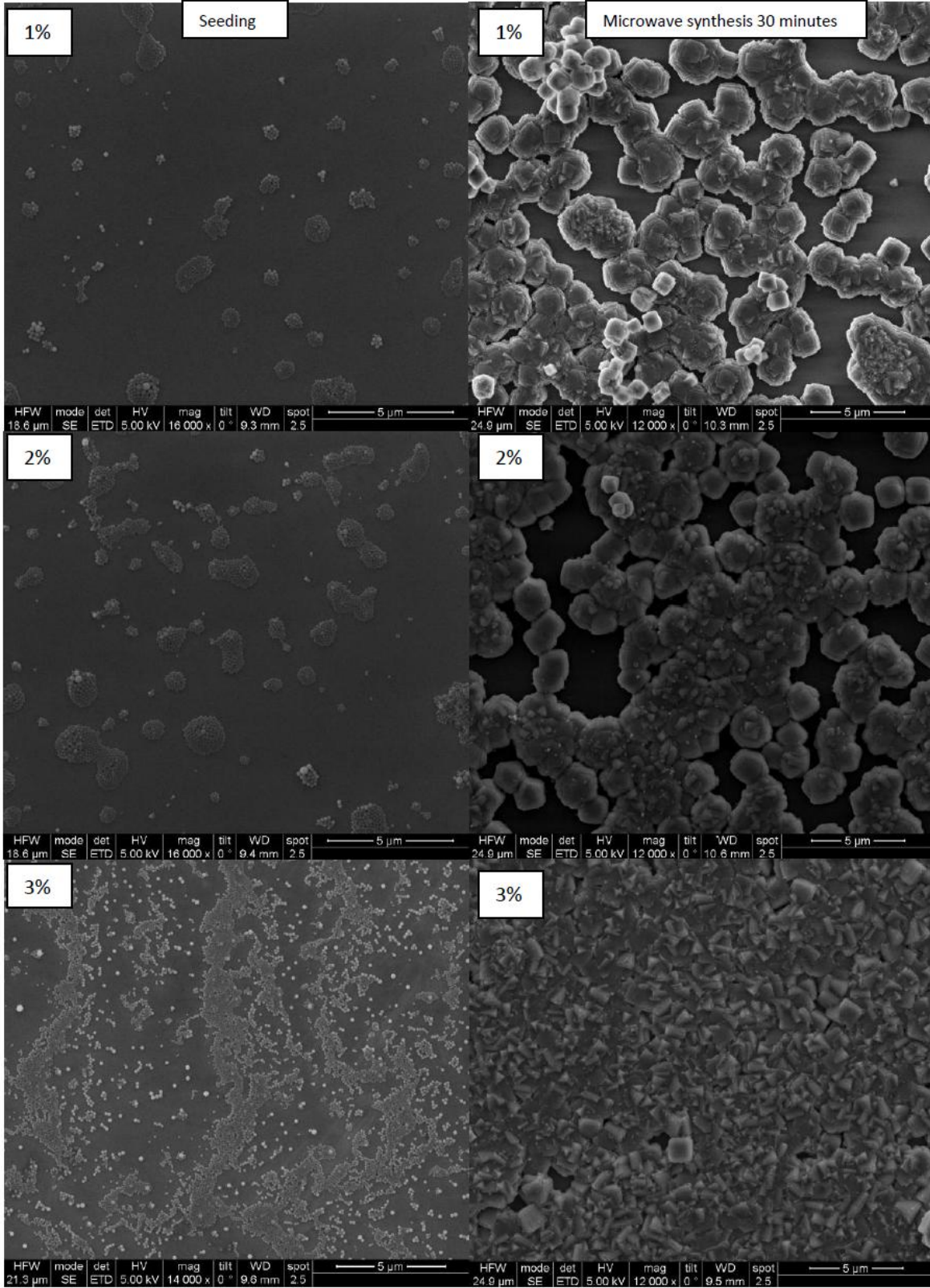


Figure 25: Silicon oxide without modification: seed concentration 1%,2% AND 3% SEM images of seeding left, right after 30 minute microwave synthesis

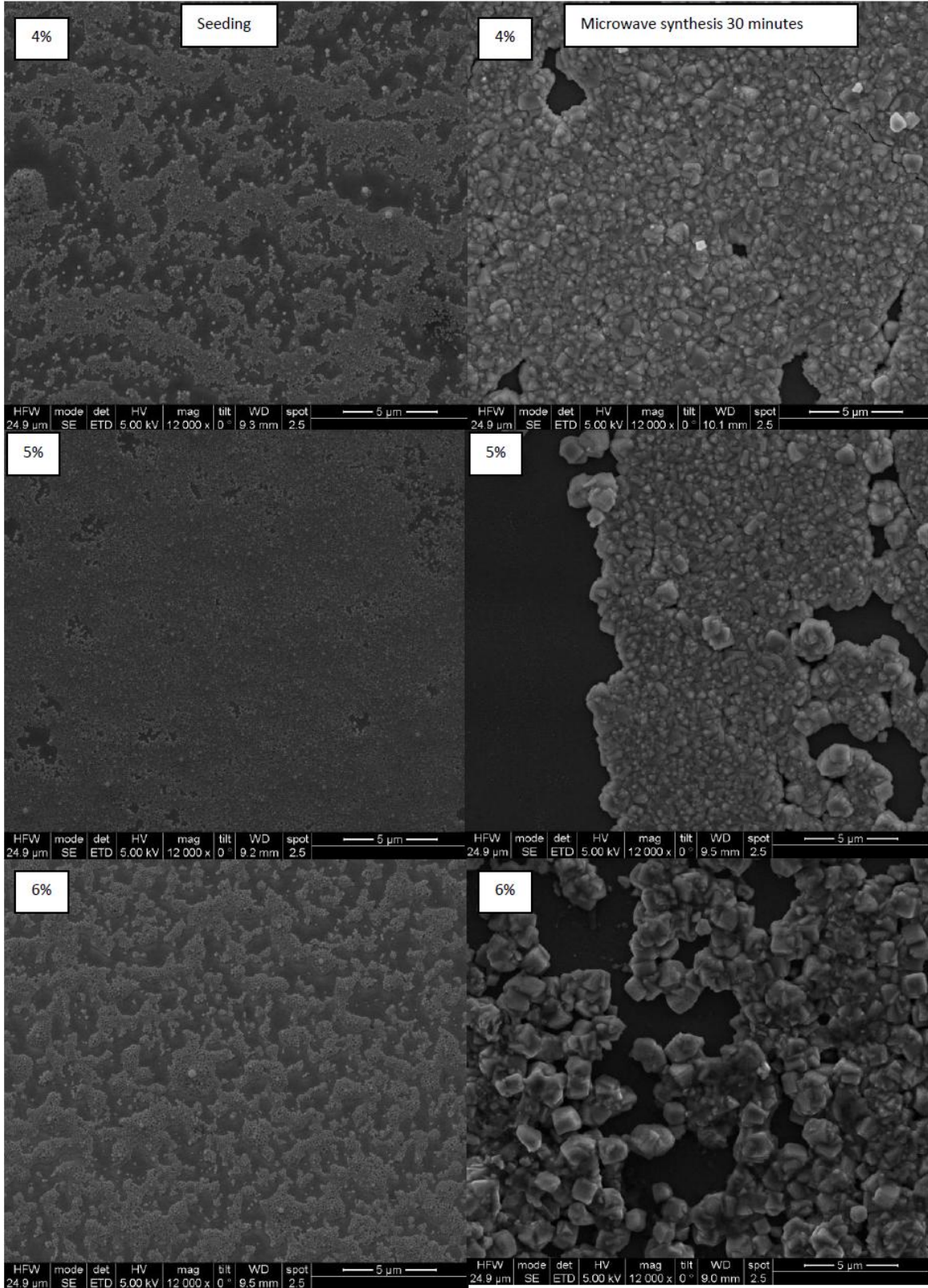


Figure 26: Silicon oxide without modification :seed concentration 3%,4% AND 5% SEM images of seeding left, right after 30 minute microwave synthesis

### 4.3 PDDA modified surface and synthesis

From the seeding images from figure 27 and 28 it is observed that the positively charged PDDA layer is attracting more zeolite seeds as seen in the SEM images. The insets in figure 27 and 28 show the zoomed out images for the synthesis sample. This increases the probability to attach seeds electrostatically to the substrate during synthesis. It is also observed that during synthesis we have well defined morphology which could be due to the fact that the PDDA attracts nutrients from the microwave synthesis solution. Seed concentration was varied from 1% to 6% using the spin conditions specified by Castro. We can clearly see that the thickness of seed deposition can be controlled by seed concentration, instead of multiple spin coating procedures.

Table 6: list of PDDA experiments

	PDDA experiments	Conditions	Results Figure
1	Effect of seed concentration	170rpm 1.5 minutes; 4000 rpm 1min PDDA; zeolite seeds in water at 100rpm 1 min and 3000 rpm 0.5 min Seed concentration 1-6%.(optimum 2%)	27, 28
2	Effect of spin coating conditions	Normal condition: 170rpm 1.5 minutes; 4000 rpm 1min PDDA; zeolite seeds in water at 100rpm 1 min and 3000 rpm 0.5 min 6000 rpm drop by drop PDDA; 6000 rpm drop by drop seed 2% normal PDDA; 6000rpm seeds drop by drop	29
3	Effect of PDDA in seed solution	300rpm 30 seconds ; 3000 rpm 1min concentration of PDDA (2%, 5%, 10% by vol of PDDA 20% solution ) in 2% seed solution	30
4	Comparison of dip coating and spin coating	dip coating 6 times PDDA solution; seed solution 2% 4 times	31

From the figure 27 and 28 we can observe that higher concentration of seeds causes more layers of seed deposition, after synthesis we observe that excessive seed deposition causes poor adhesion of the synthesized layer. This can be due to the fact that the top layer of deposited seed starts growing into the membrane blocking nutrients to the seed layer close to the substrate surface causing inadequate growth of zeolite seeds, which causes poor adhesion. According to the seed deposition effect we observed the best results for PDDA modified surface was obtained by using 2% seed concentration.

Another important observation was the uneven distribution of the zeolite seeds because of the electrostatic attraction of the zeolite seeds to the PDDA layer, as previously mentioned by Tsapatsis(38). The normal seeding conditions was 100rpm 1 min and 3000 rpm 0.5 min, this gives the zeolite seeds enough time to deposit on the substrate in multi layers and also unevenly. In order to provide better seeding we tried to deposit the seed at high revolutions and by dropping the seed solution on the spinning substrate, we called this process “drop by drop” process. As seen in figure 29. The spinning speed was 6000rpm for 1 minute and during the first 30 seconds 1ml of seed solution was deposited drop by drop on the spinning substrate. We also tried the same procedure for PDDA solution which is figure 29 a in which PDDA solution and seed solution were deposited by the drop by drop method and we can see that it did not have significant difference from figure 29 b which is only seeding with this procedure. So we conclude that the PDDA deposition is homogeneous during the normal spin coating process but the seeds due to electrostatic interaction deposit in many layers hence a high speed spin coat for seed solution is essential to deposit uniform seed layer.

Another approach was to reduce the number of spin coating steps and to improve the wet ability of the samples and to increase viscosity of the spin coated solution; we decided to incorporate PDDA solution in the seeding solution. The idea was to help incorporate the zeolite seeds within the polymer network that would help suspend the particles, increase the solution viscosity and also help improve the adhesion of the membrane by eliminating a boundary layer of PDDA between the silicon oxide and the membrane layer. From our results in figure 30, we observe some aggregates of zeolite seeds but the sample was fully covered with the PDDA seed solution. The main limitation that we see is during microwave synthesis, is that the PDDA coats the



zeolite seeds and prevents the nutrients from reaching them, causing slow and more rounded crystal growth.

Dip coating was also used to compare spin coating with other methods, we observed that dip coating (figure 31) had better packing density of the zeolite seeds. However the membrane after synthesis showed poor adhesion to the substrate. The observed average thickness of membrane growth on PDDA modified surface was around 1.5 microns for 30 minutes microwave synthesis, as seen in figure 31, we can see the different seeding techniques for the zeolite seeds, spin coating and dip coating and membrane after synthesis and washing procedure, we observe that spin coated samples had better membrane adhesion to the substrate compared to dip coated samples. Calcination was also used to remove excess PDDA from the surface and try to sinter the particles on the silicon oxide surface a similar technique is used by Aguado (92) to modify surface only by PDDA on a porous substrate.

PDDA MODIFIED SURFACE (SPIN COATING) SEEDING AND SYNTHESIS

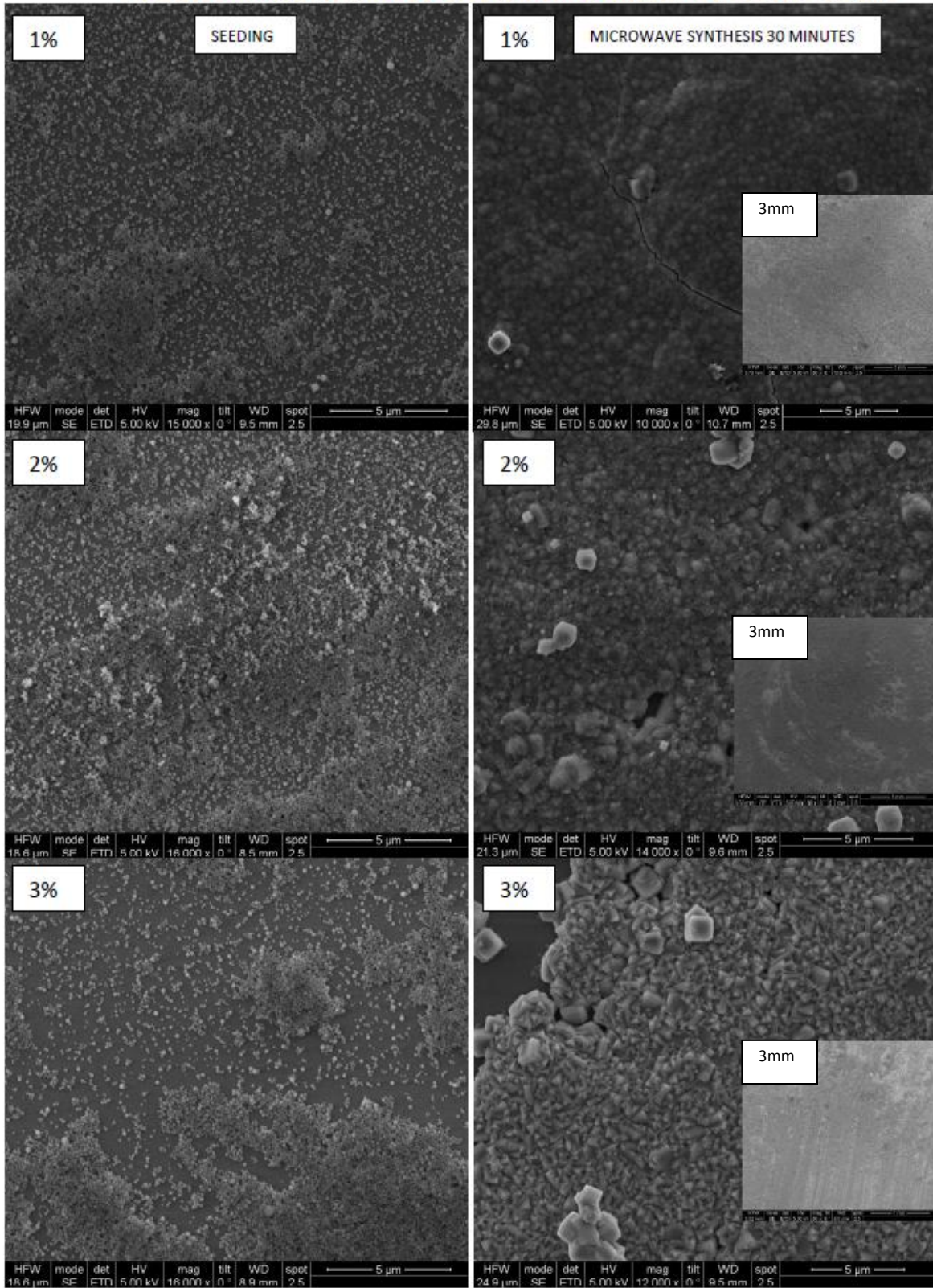


Figure 27: seeding and synthesis of PDDA modified surface using spin coating 1%, 2% and 3% seed concentration

PDDA modified surface (spin coating) seeding and synthesis

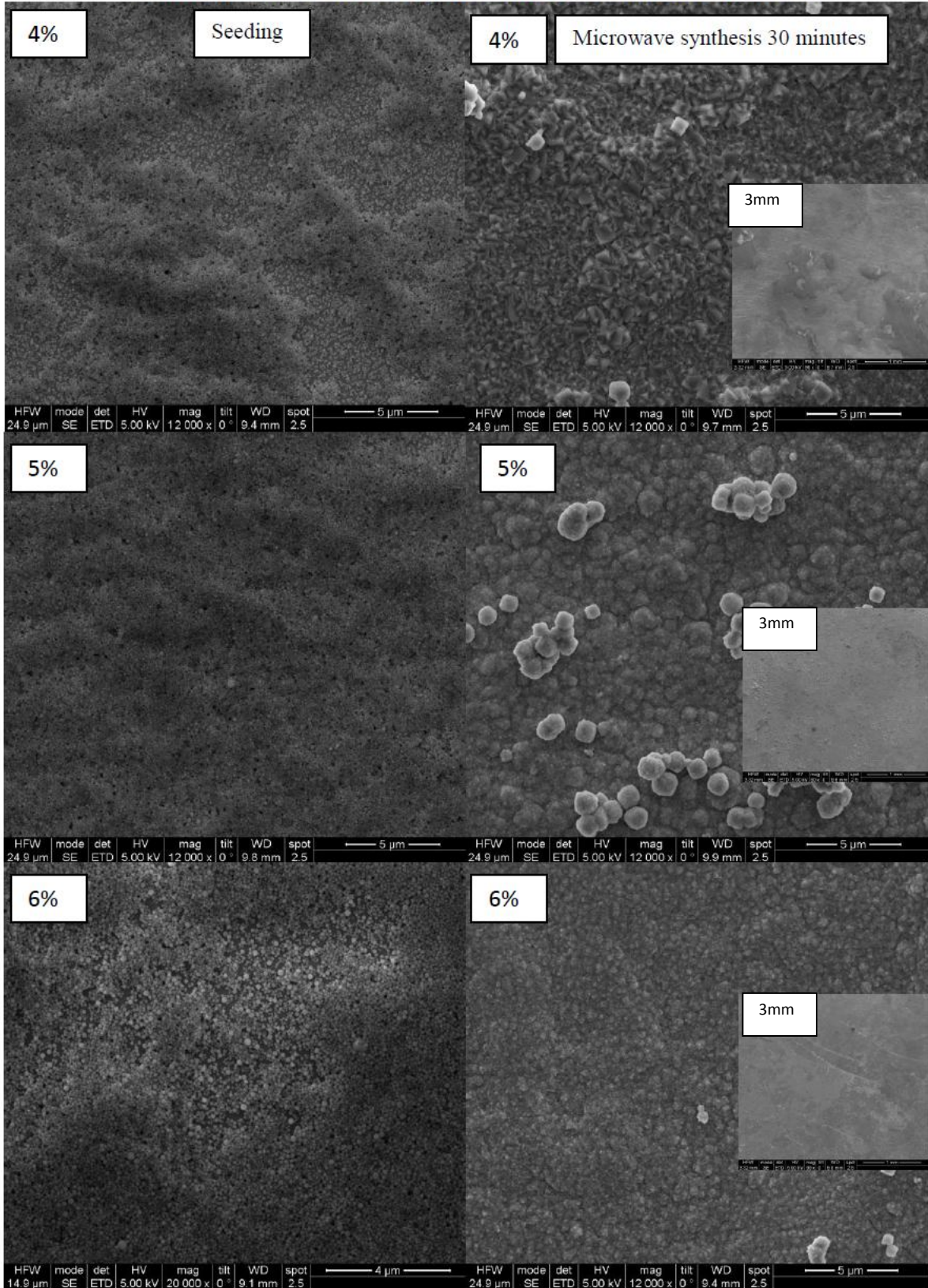


Figure 28: seeding and synthesis of PDDA modified surface using spin coating 4%, 5% and 6% seed concentration

*Effect of spin coating conditions on seeding*

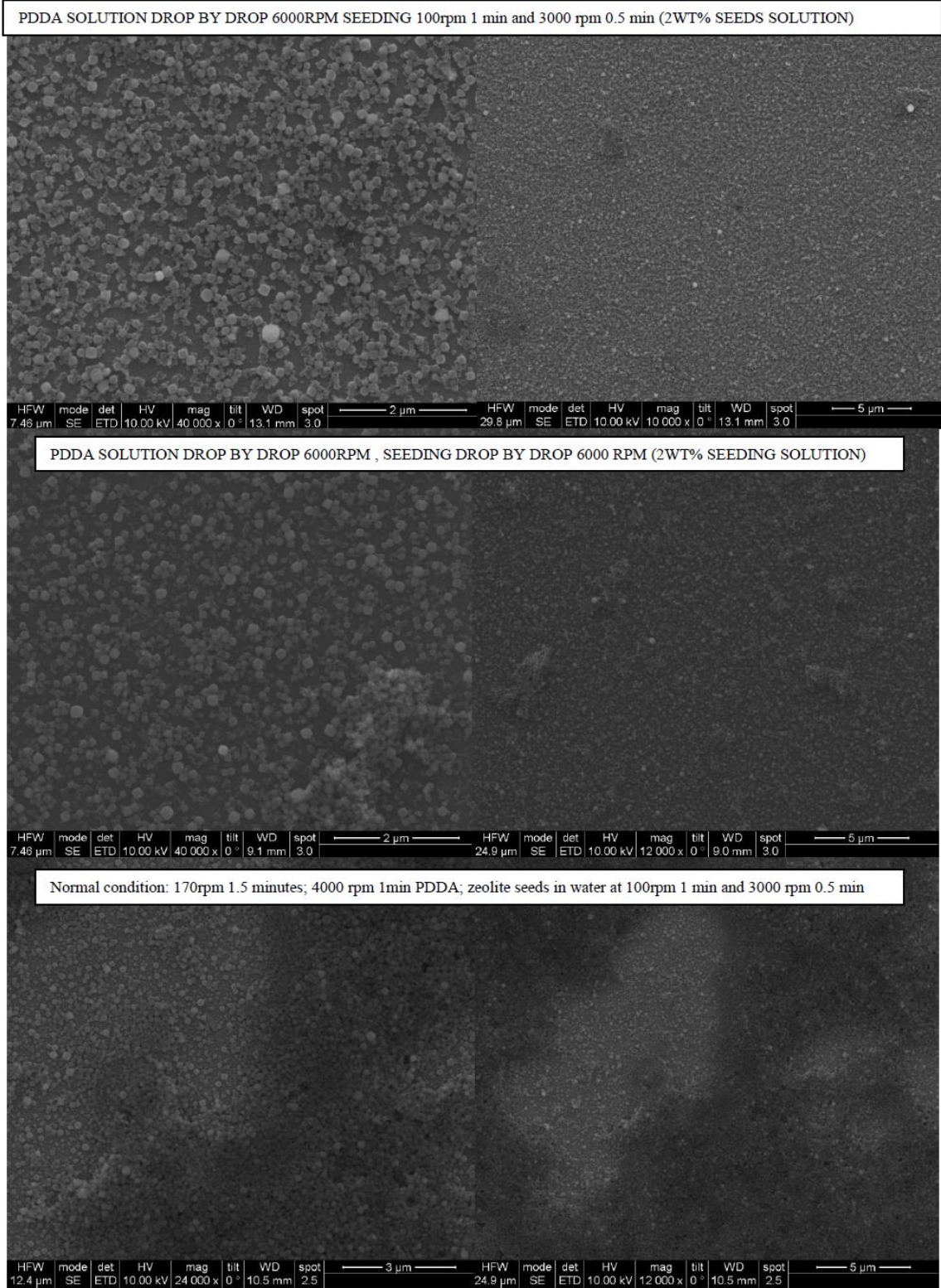
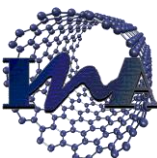


Figure 29: Effect of spin coating conditions



*Effect of PDDA modified zeolite seed solution*

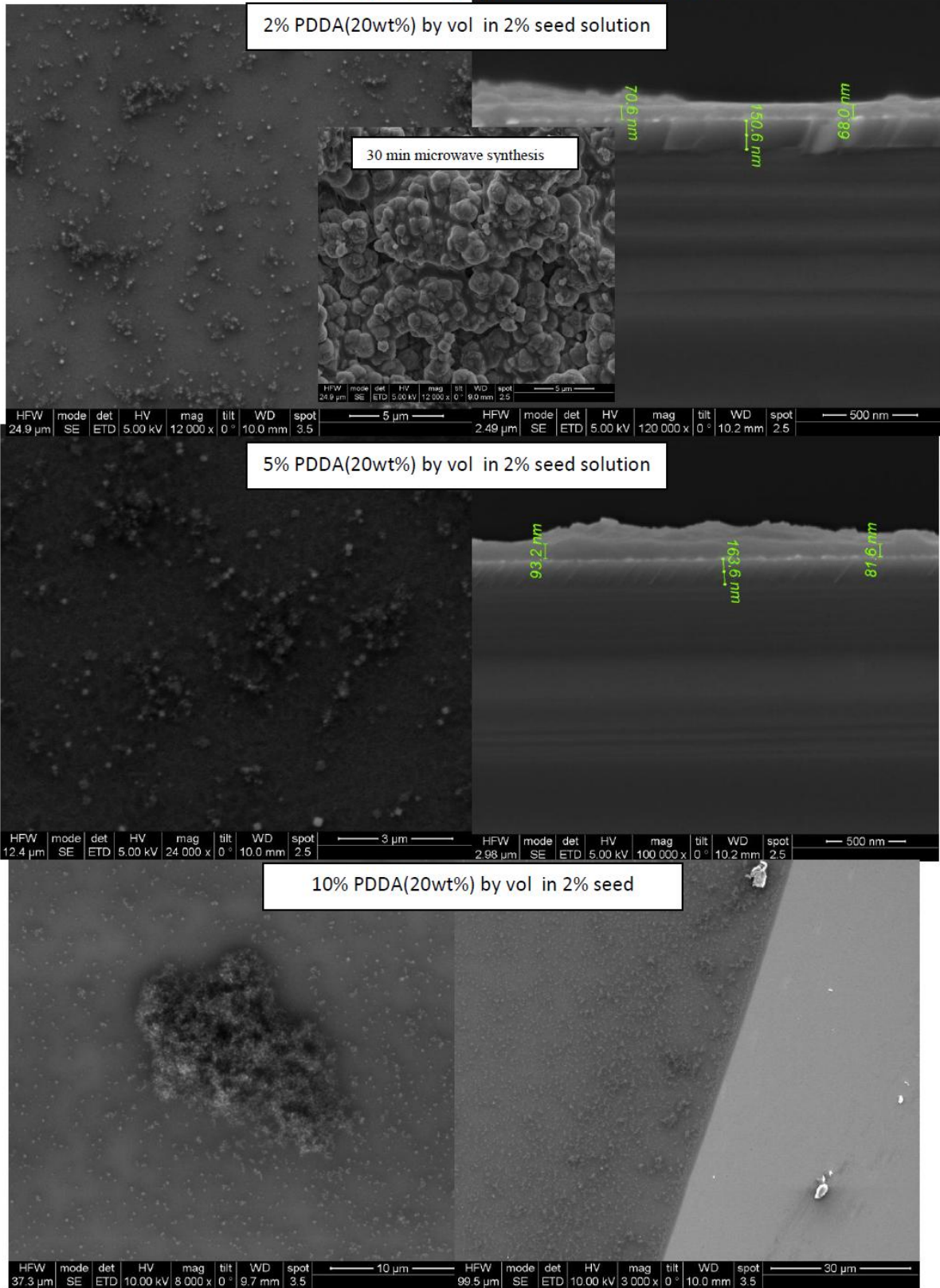


Figure 30: effect of PDDA solution mixed with zeolite seeds in water and spin coated

*Dip coating and synthesis PDDA solution*

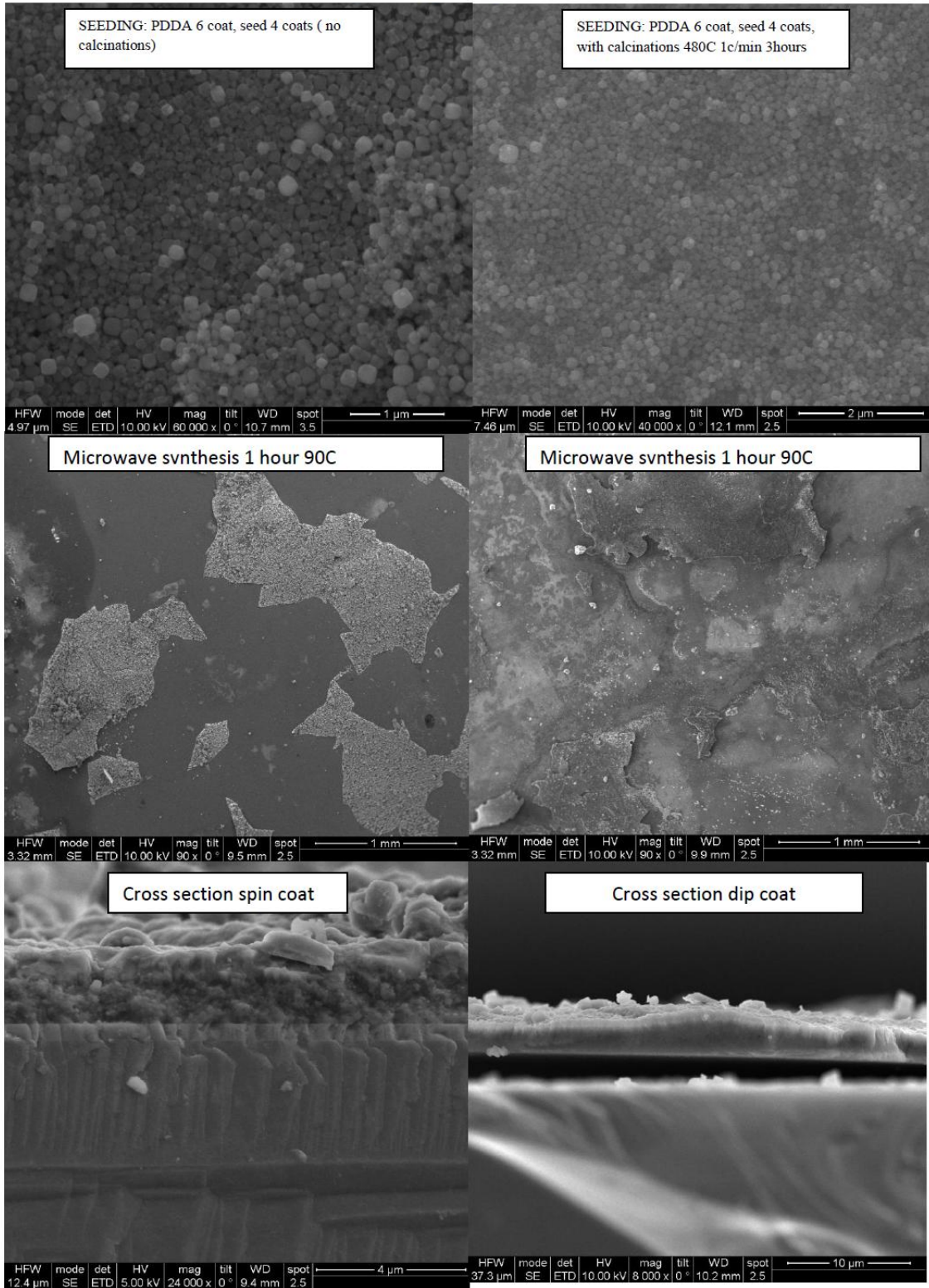


Figure 31: Dip coating of seeds on PDDA modified substrate

#### 4.4 Boehmite surface modification and synthesis

We used spin coating and dip coating to modify flat silicon surfaces with a Boehmite layer. Modification of flat silicon oxide surface with Boehmite produced fully covered membrane on the substrate but during the washing and cleaning process we observed the peeling of the membrane because of poor adhesion in some areas. The cleaning procedure consists of washing the substrate with distilled water followed by sonication for 15 second in distilled water.

In order to improve the adhesion and support the membrane we use silicon grids to provide the structural support. We observed that spin coating on grids caused variation in deposition of boehmite and seeding layer, causing more thickness on the edges as seen in figure 35, the edges of the windows have more deposition causing adhesion problems of the membrane after synthesis causing lift off during washing process. The layer of boehmite of the edges can clearly be observed in figure 32.

The observed thickness of 1 hour microwave synthesis on spin coated boehmite modified support was close to  $1.5 \pm 0.4$  microns, compared to 1.97 micron obtained after 14 hour oven synthesis of similar samples in the traditional oven synthesis technique (figure 32 and 36), where traditional oven synthesis utilizes a heated oven and the samples is heated by conventional heating in an autoclave.

Table 7: Boehmite experiments

	<b>Boehmite modification</b>	<b>Experiment</b>	<b>Substrate</b>	<b>Figure</b>
1	Effect of dip coat	dip coating 6 times, dry 200C 2hr, seeding 4 times	Wafer	30
2	Effect of spin coat	spin coat 8 times, 200C 2hr dry, seeding 5 times 100RPM 60 sec; 3000RPM 30 sec; seconds and 3000RPM 60 seconds. 8 times dried 200C for 2 hours seeding 2% 5 times at 100 RPM 30	Wafer	31
3	Boehmite in seed solution	50% Boehmite solution by vol(9% conc) in seed solution 5%	Wafer	34
4	Synthesis on grid different synthesis time	spin coat 8 times, seeding 5 times 30, 45 and 60 minutes microwave synthesis	Grid	30,31

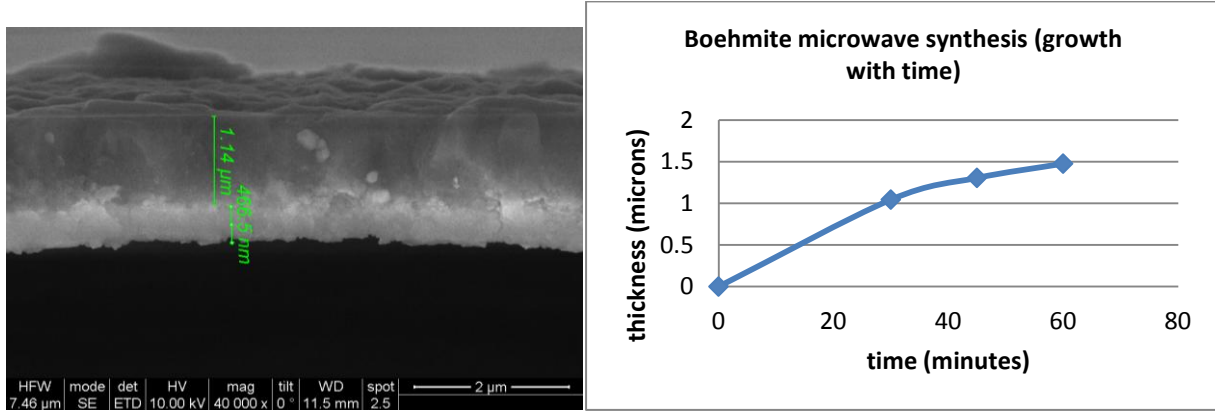


Figure 32: top Cross section of Boehmite and membrane layer, bottom microwave synthesis growth with time

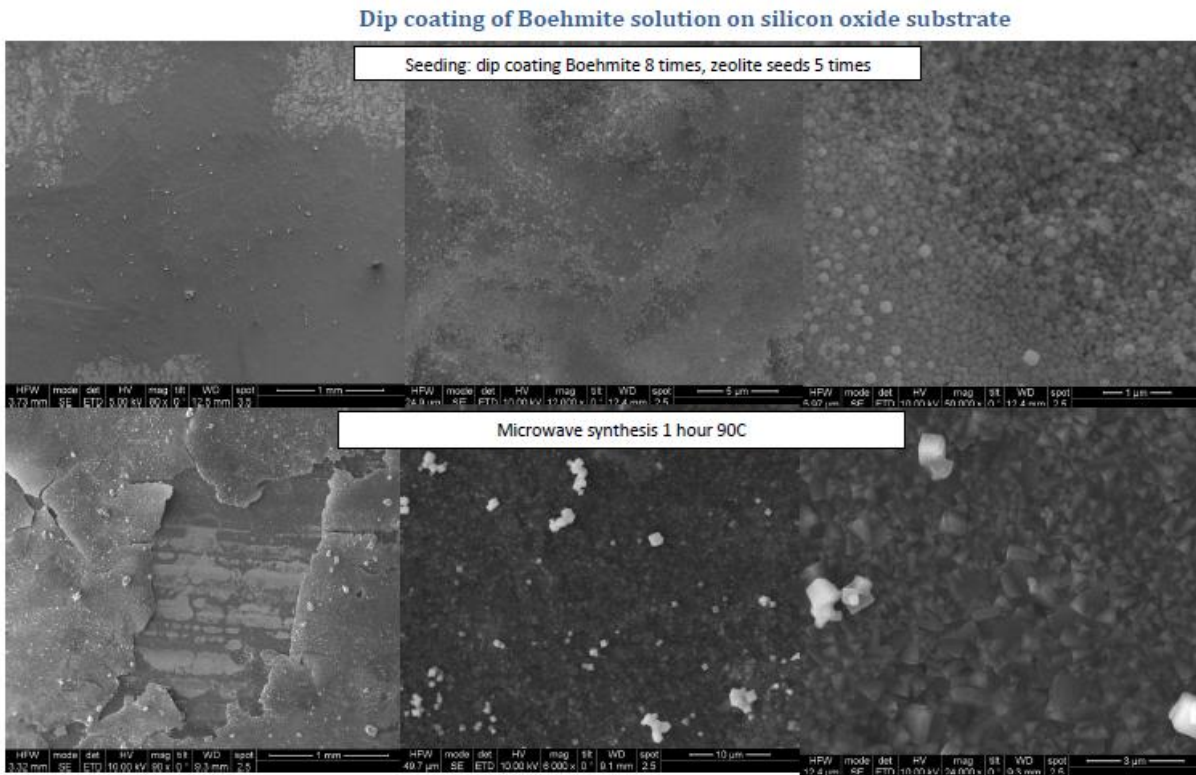


Figure 33: Dip coating of Boehmite and zeolite seeds, seeding and synthesis



Spin coating of Boehmite and zeolite seeds

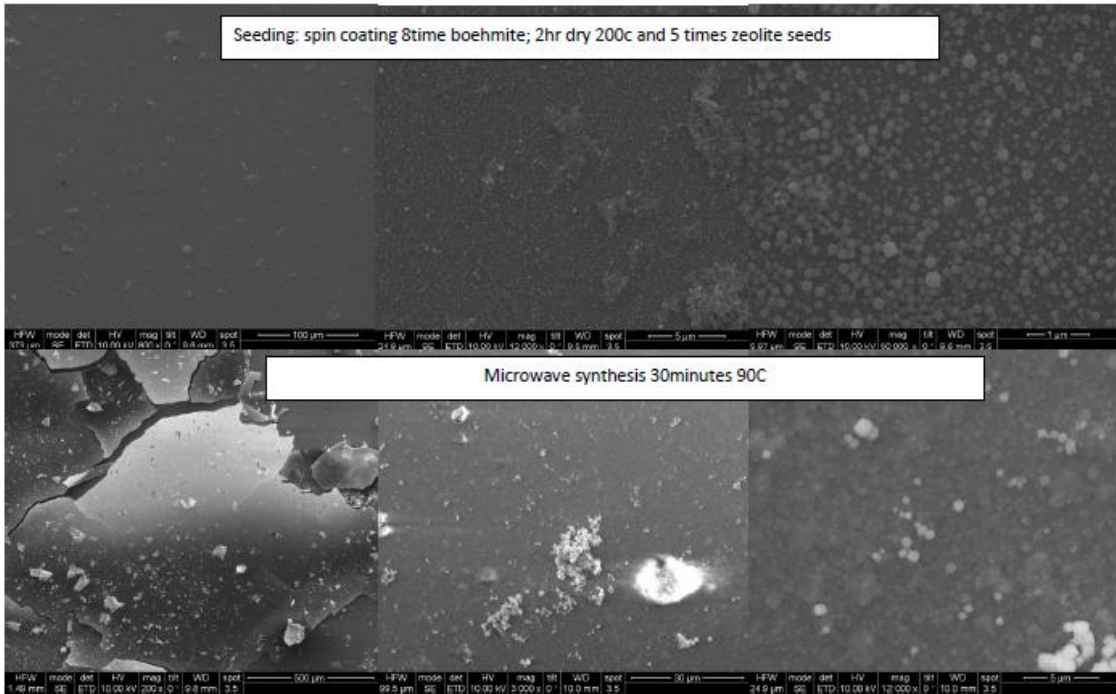


Figure 34: Spin coating of Boehmite and zeolite seeds. Followed by 30 minute synthesis  
Seeding of Boehmite modified silicon oxide supports

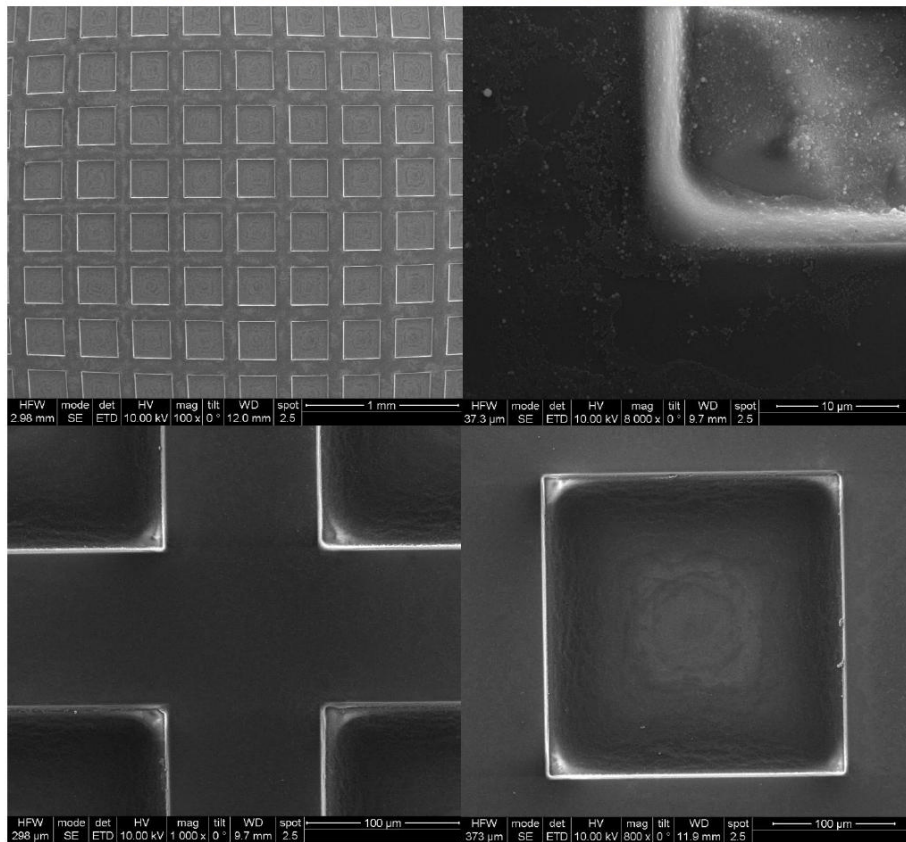


Figure 35: SEM images of seeded Boehmite modified grids



## Boehmite in zeolite seed suspension

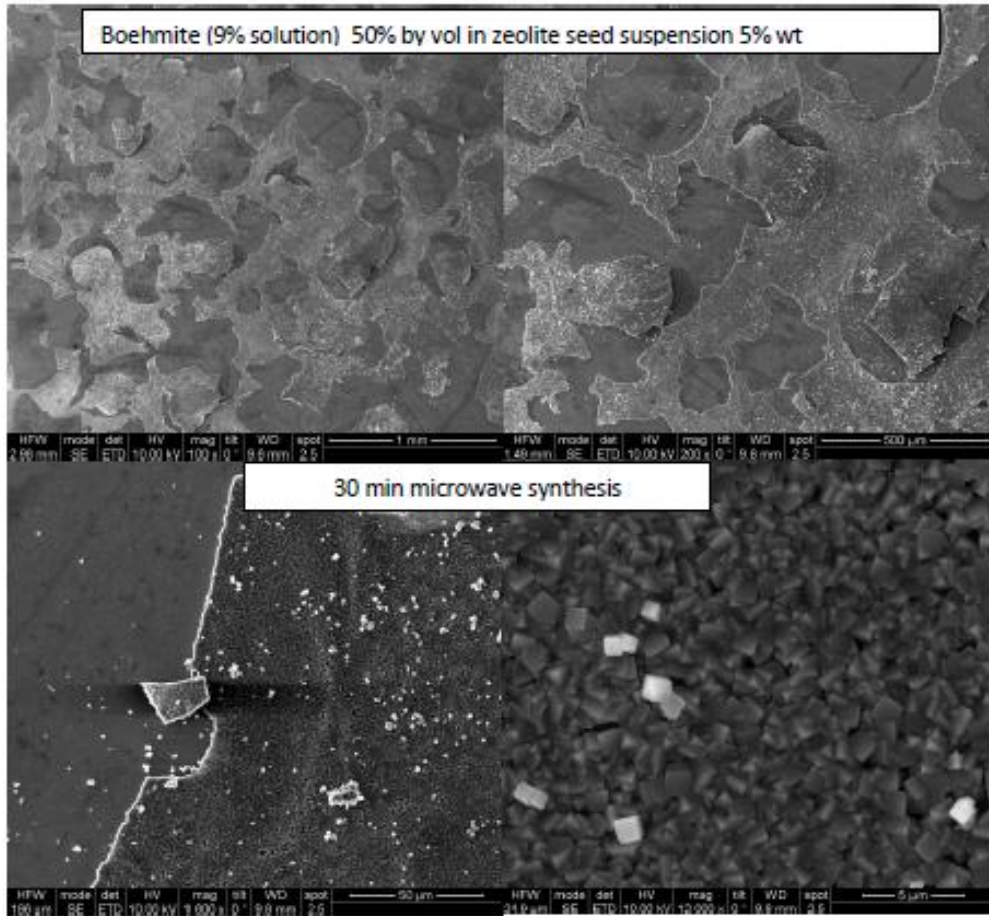


Figure 37: Boehmite 9% solution mixed with zeolite seeds 5% solution (1:1 ratio) spin coated

In order to incorporate the seeds and the Boehmite in one single step to cover the substrate and try to prevent the layer of remaining boehmite as seen in figure 32 to cause adhesion problems, we incorporated Boehmite and zeolite seeds in one solution. We observed increase in viscosity because of the change in pH, the boehmite solution has a pH of 3.5 while the seed solution has a pH of around 9-10. This pH changes causes either aggregation of zeolite seeds or the particles in the Boehmite solution causing the increase in viscosity. Due to the high viscosity the solution was spin coated at around 6000rpm for 1 min to help spread and reduce the deposited layer. After synthesis we observe good morphology but in some areas attachment was poor. Suggesting that uniform boehmite deposition is essential to obtain a defect free membrane using boehmite modification.

#### 4.5 Silanization surface modification and synthesis

Toluene was chosen as the solvent for silanization process as it has been reported in almost all of the silanization process using APTES as explained in section 2.6.3. Also experiments by Manifar(57) discuss various solvents and good results are observed from toluene as a solvent. In order to select the right conditions to test the effect of silane concentration, first we tested different seeding techniques using 120mM APTES. Figure 38 shows the results for different seeding solvent and different techniques for seeding including reflux, spin coating and dip coating on APTES modified support. Also a detailed comparison between spin and dip coated seeds on APTES modified surface is report in figure 43. We observed that since the seeds are more stable in ethanol suspension they seed the surface uniformly compared to toluene as in toluene we observe aggregates due to the drying process used to change the solvents. Although toluene is the solvent of choice, the seed stability is the problem that could be improved to improve seeding in toluene suspension. Because of these results we choose ethanol seed suspension as our seeding suspension to test the APTES concentration effect on seeding. Test for different APTES concentration on seeding was observed at 1,6, 30, 50, 90, 120 mM solution and the results are shown in figure 39 and 40. Since no major differences were observed we choose 120mM as our standard for all further experiments.

Grids were used to provide the structural support to try to fabricate a free standing defect free membrane. Variation of synthesis time was observed as seen in figure 42. And we can clearly observe the evolution of the membrane growth with time, it can also be seen that 30min is required to completely cover and obtain a defect free membrane. During our experiments we observed that reproducibility of the samples was a major limitation in silanization, as the variation in seeding and hence growth of the membrane was observed. To observe the reproducibility several samples on silicon oxide wafer and grid samples were conducted and are shown in figure 44. Our explanation for variation in the synthesis is that the moisture content is varying during silanization process, causing variation in the deposition of the silane layer causing changes in seeding. In order to further improve silanization and to obtain reproducibility we need to control the reaction and sample handling environment in a climate controlled glove box where humidity, temperature and atmosphere conditions can be reproduced.

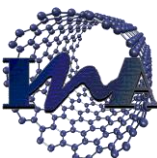


Table 8: experiments performed for silanes

	SILANIZATION experiment		Description	figure
1	effect of seeding solvent APTES	substrate	seeds in ethanol, toluene, APTES modified seeds in toluene, 120mM APTES	36
2	effect of spin coating of seeds  effect of dip coating of seeds  On APTES modified substrate	wafer	APTES 120mM, reflux 110c, 2 hour, spin coat 250rpm 30 sec, 2500 rpm 1min	36
3	effect of APTES concentration	grid	seeding in ethanol 1,6,30,50,90,120 mM concentration	37,38
4	effect of microwave synthesis time APTES	wafer	10,20,30 minutes cross sections	39 40
5	COVALENT LINKAGE  EPOXY+APTES	grid	120mM GPDMS substrate, 120mM APTES seeds in toluene and ethanol	45
6	effect of sonication  effect of relax	wafer	spin coat 250rpm, 30 sec 2500rpm 1min, sonication 5-30minutes	41

Comparison of different seeding solvents and conditions

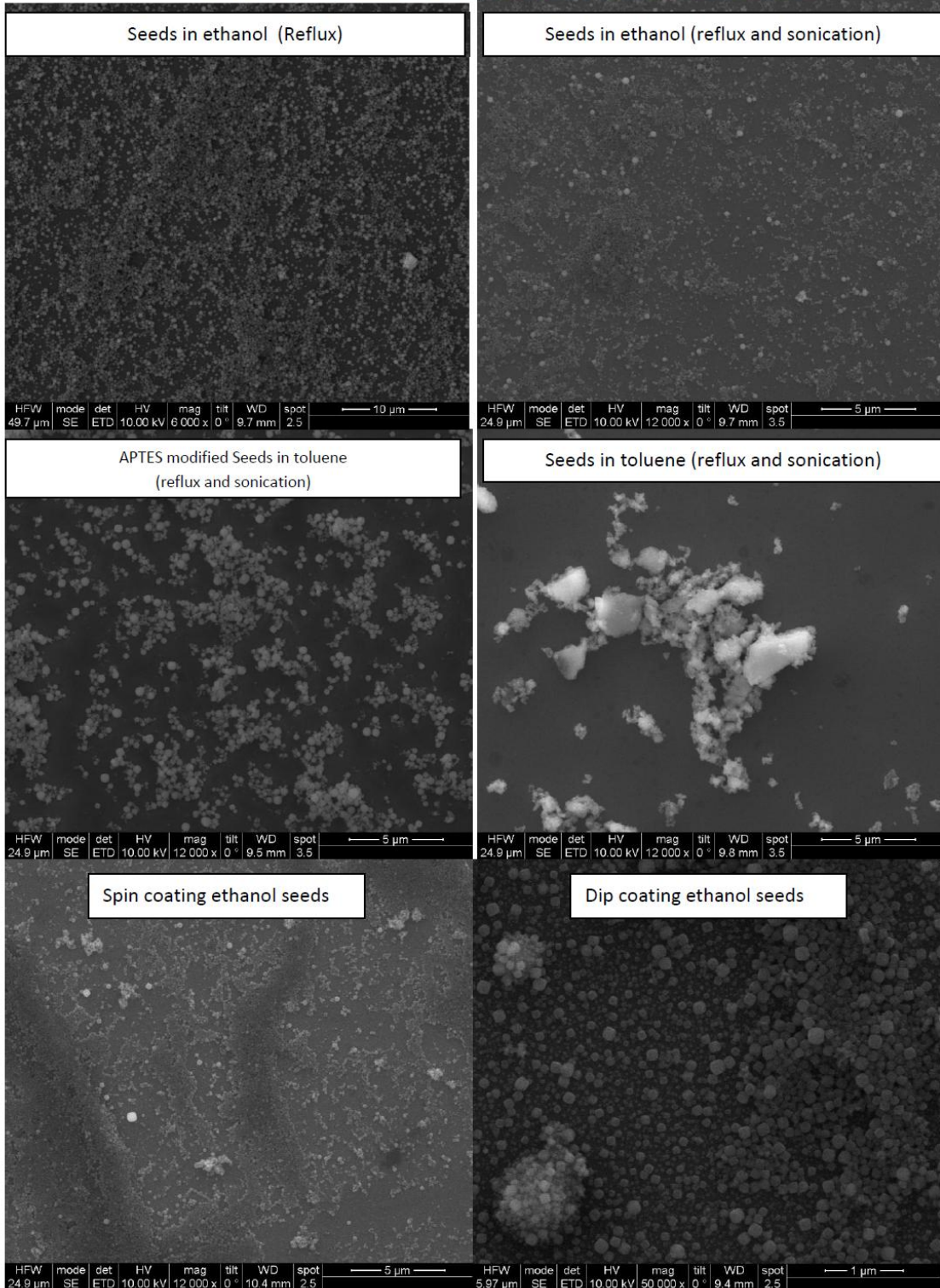


Figure 38: different seeding solvents and seeding conditions on APTES modified support

Effect of APTES concentration

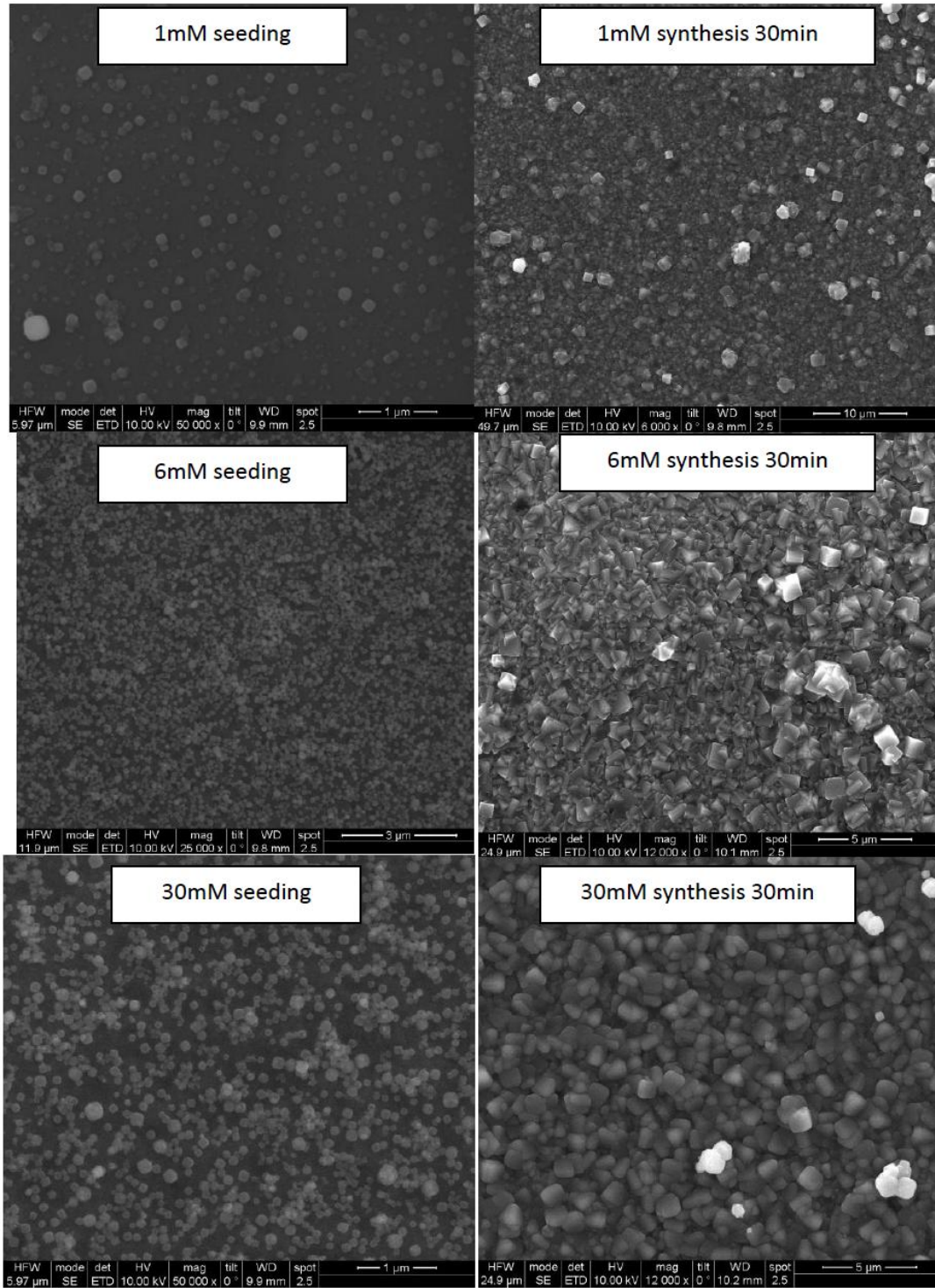


Figure 39: different concentration of APTES in toluene during surface modification 1mM, 6mM, 30mM

Effect of APTES concentration

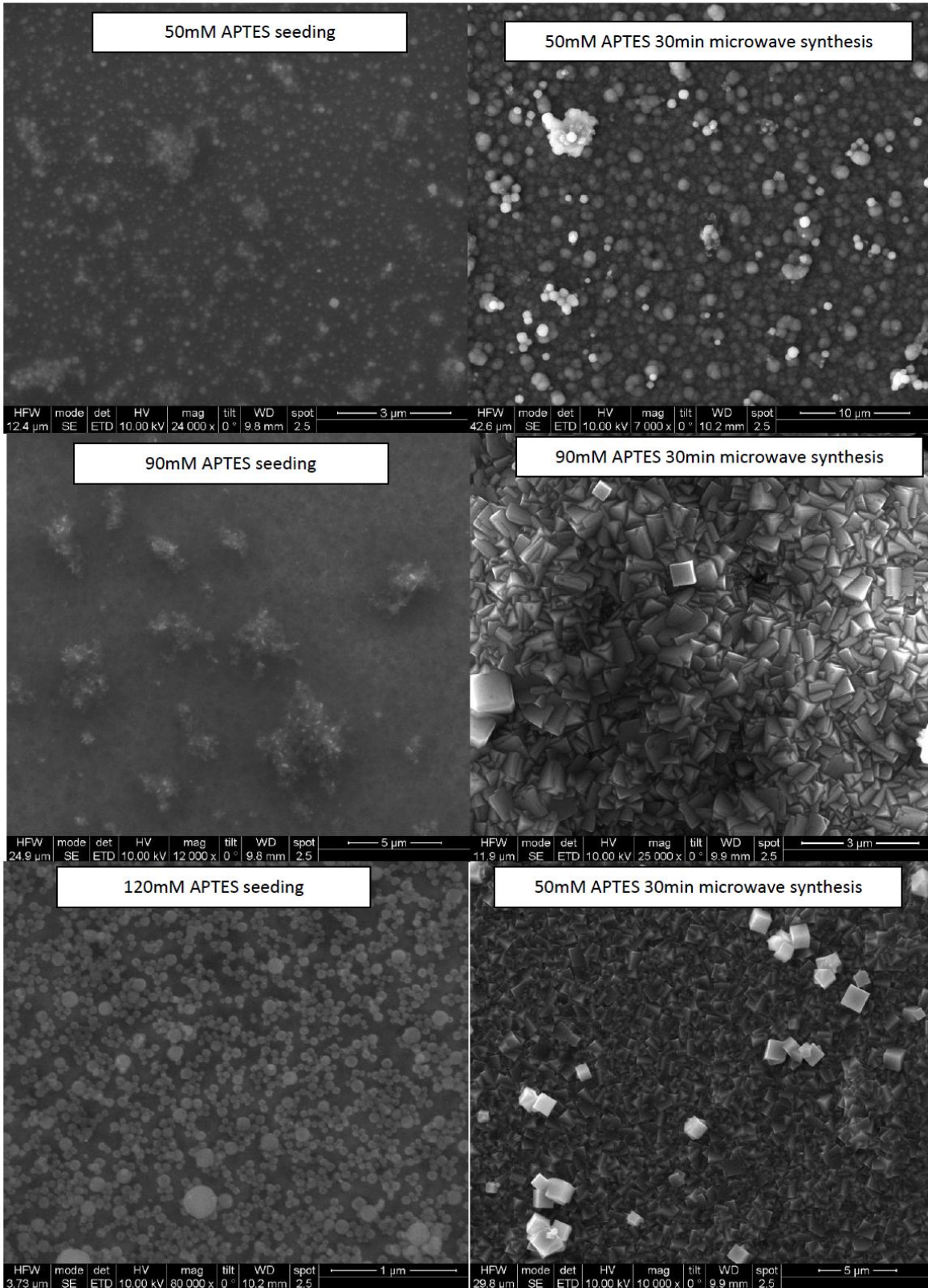


Figure 40: different concentration of APTES in toluene during surface modification 50mM, 90mM, 120mM



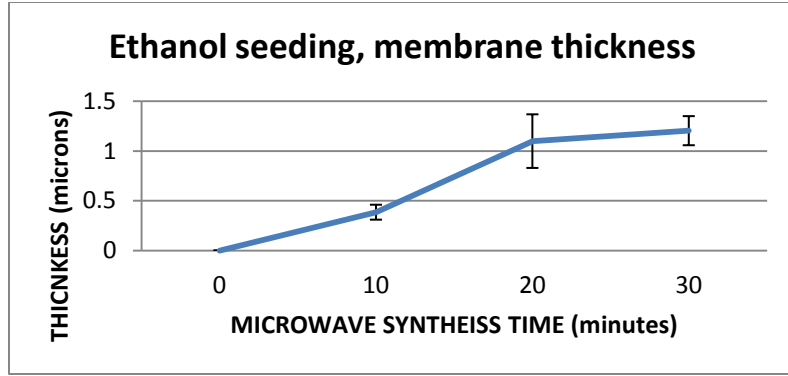


Figure 41: Evolution of thickness of membrane on APTES modified substrate

Growth of membrane APTES modified surface seeded in ethanol seed solution

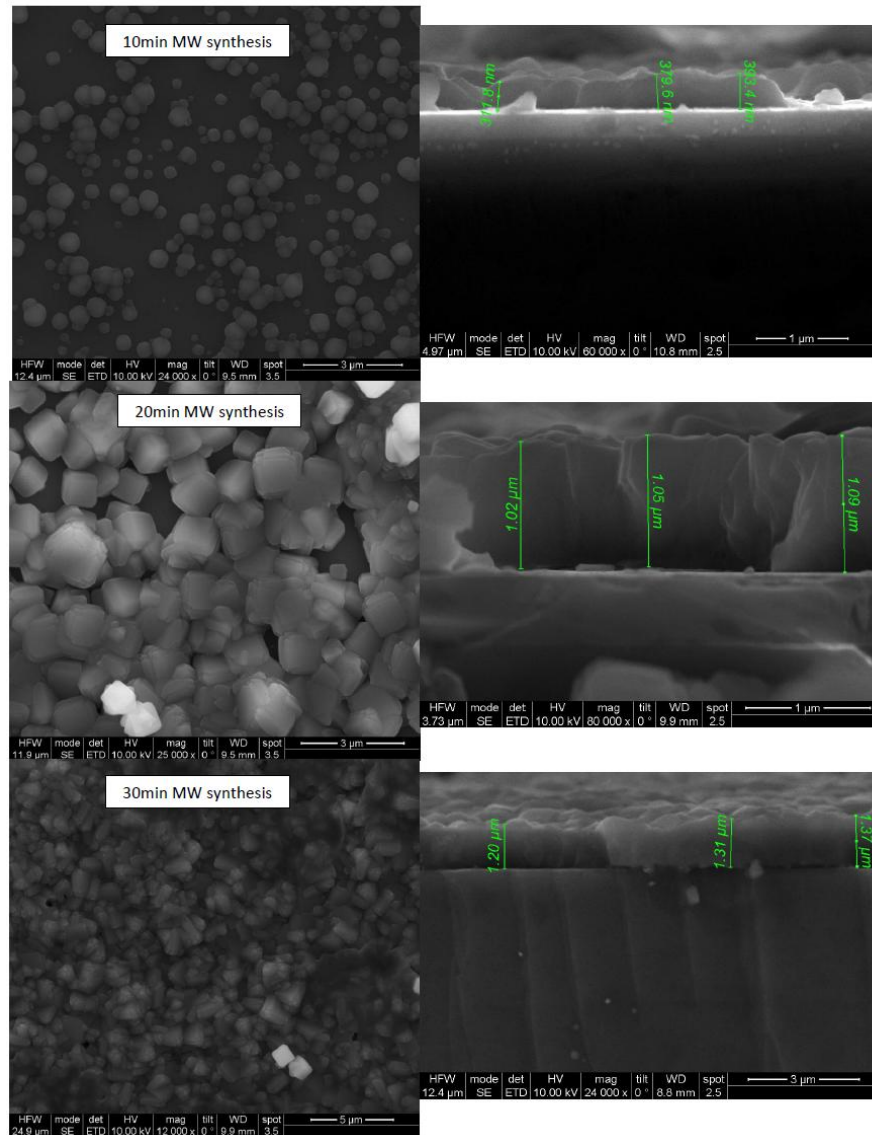


Figure 42: Growth of membrane with synthesis time, ethanol seeded substrate

## Dip coating and spin coating of zeolite seeds on APTES modified substrates

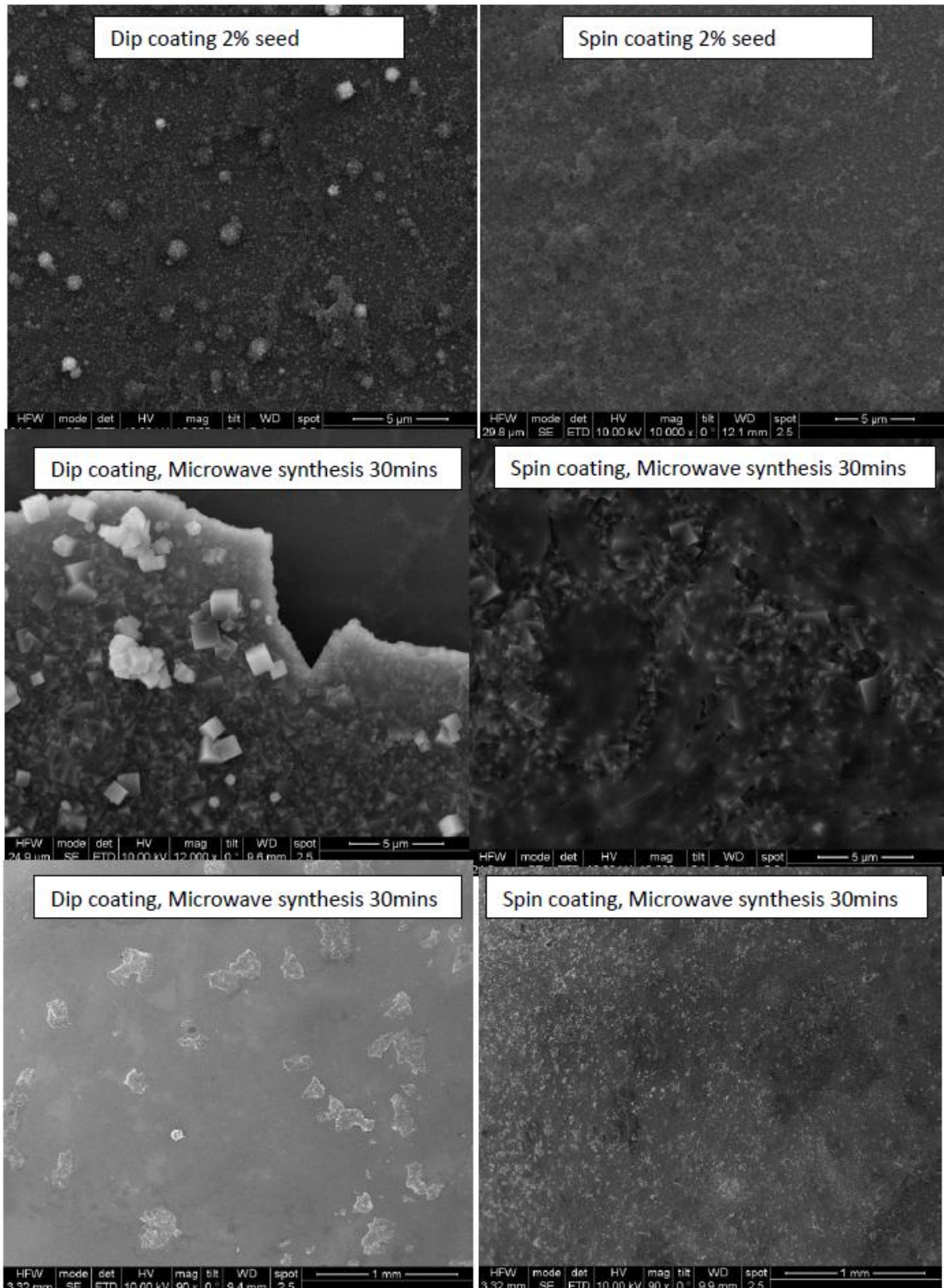


Figure 43: Spin coating and dip coating sample on APTES modified substrates

**REPRODUCIBILITY TEST: SAMPLES TESTED IN SAME CONDITIONS FOR APTES MODIFIED SUBSTRATES SEEDED IN ETHANOL(120mM AP特斯, SEEDING IN ETHANOL , 30MIN MICROWAVE SYNTHESIS)**

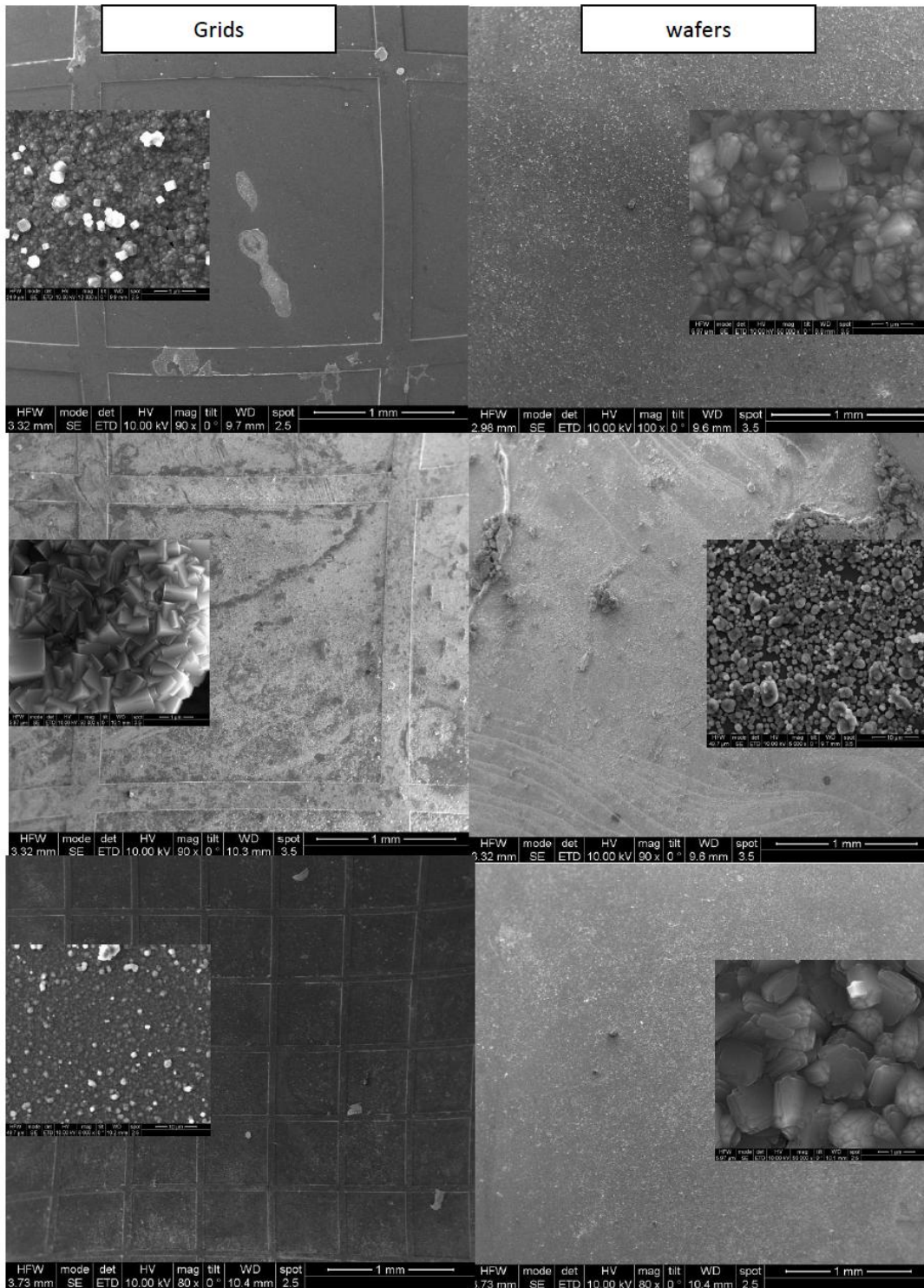
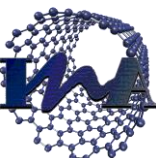


Figure 44: Samples for AP特斯 modified substrates, tested under same conditions for reproducibility test

## Covalent Linkage

Covalent linkage was also used to bond the zeolites to the substrate with covalent bonds; hence theoretically it should increase anchoring of the membrane during and after synthesis. Halogen based silanes were used and tested under the same conditions as used for APTES silanization and the results are in figure 46. Another covalent linking method is to modify the substrate with epoxy silanes and react it with amine group to form covalent links. We use GPDMS silane to modify our substrate and APTES to modify our zeolite seeds as seen in figure 45.



## COVALENT LINKAGE (EPOXY+ APTES)

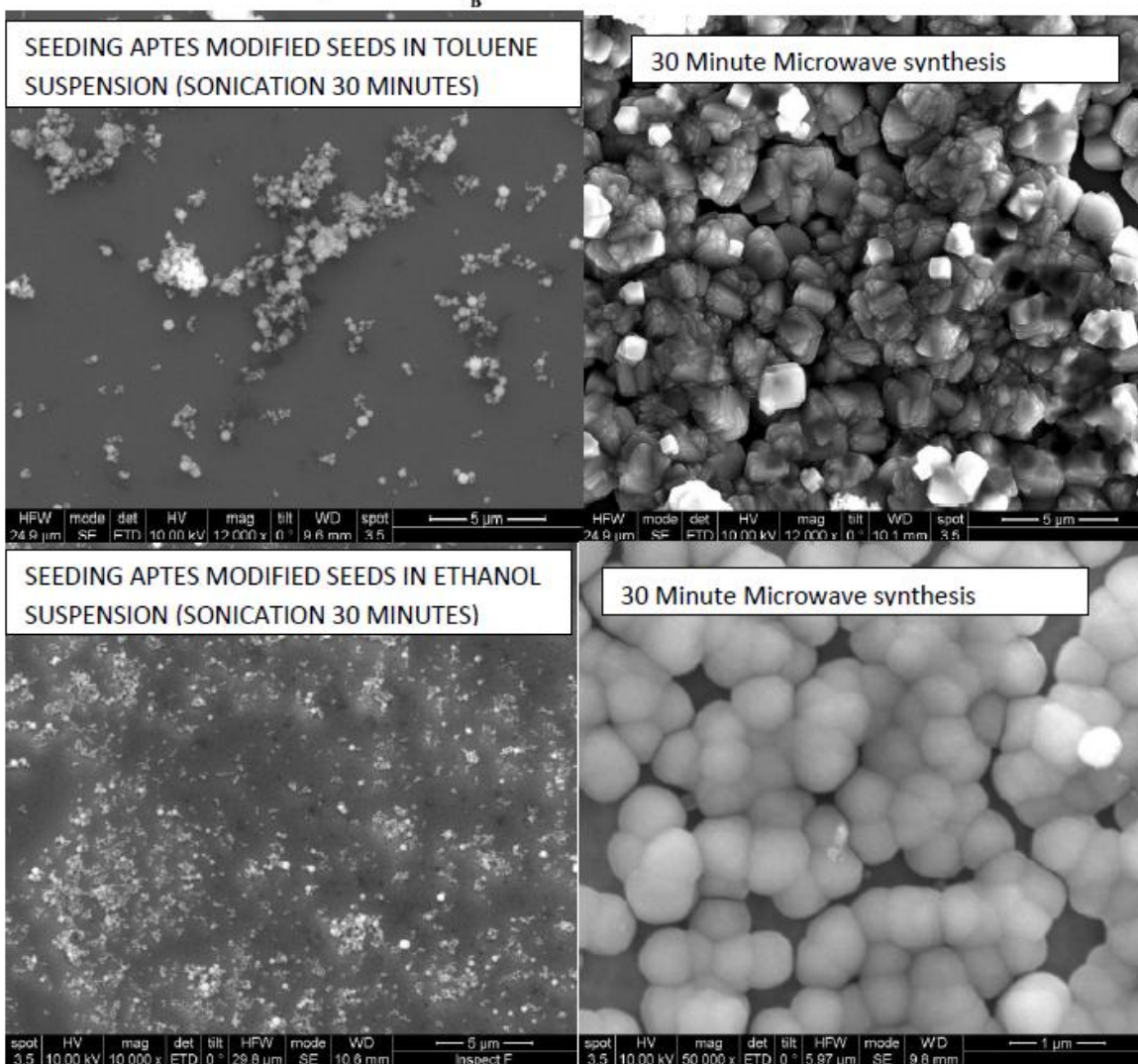
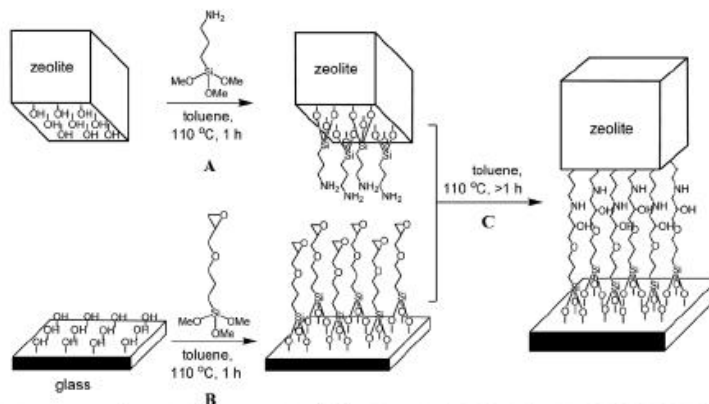


Figure 45: Covalent linkage (epoxy-Amine)

### Covalent bonding(halogen silanes)

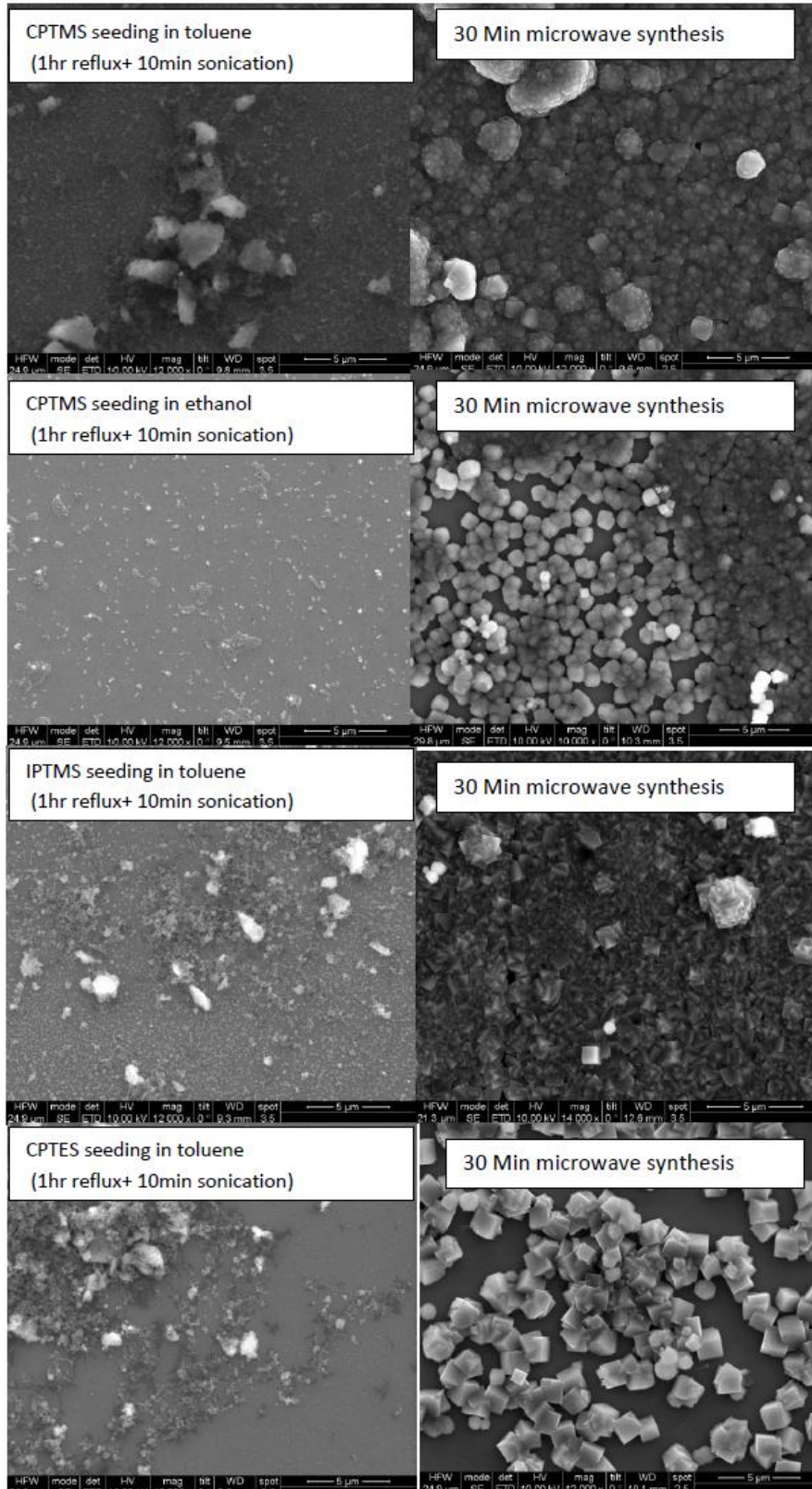


Figure 46: Covalent linkage using Halogen propyl -oxy silanes

## 5 Conclusion and future work suggestions

In this work the seeding conditions on flat or grids silicon oxide surfaces has been optimized using different strategies.

### *PDDA surface modification*

The best way to deposit homogeneously PDDA aqueous solution on the silicon oxide surface is to use sping coating at high speed, 6000rpm, adding the solution drop by drop. These conditions and a 2% wt of zeolite seeds are also optimum for deposition of zeolite seeds on the modified surface.

### *Boehmite deposition*

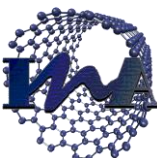
Although the boehmite layer helps to grow zeolite A membrane, the deposition of the boehmite solution, negatively charge, on the silicon oxide surface was difficult and the spin coating or dip coating should be repeated many times, 6 to 8 to get a good coverage. Furthermore the spin coating in the grids was uneven because to accumulation of material on the corners.

### *Surface silanization by APTES*

The silanization of the surface by covalent linkage using APTES solution in toluene was successful as previously reported. The second step, that comprises seeding of the modified APTES surface, could not be performed using high hydrophilic zeolite A and toluene solution. The seeding was successful using ZA seeds in ethanol solution under reflux and sonication getting a uniform distribution of the seeds on the surface.

The synthesis of seeded supports under microwave heating was highly reproducible and does not depend on the seeding strategy followed. The thickness of the layer could be controlled between 0.5 to 1.5 microns varying synthesis time from 10 to 60 minutes.

The main problem observed in this work is related to the detachment of the zeolite layer after the synthesis. The best results after sonication were observed in the case of the aptes modified surface layer where almost the whole membrane, 1 x 1cm remains. However there is still lack of reproducibility.



Future work is needed to improve adhesion of zeolite layer to the surface and reproducibility, several strategies are proposed:

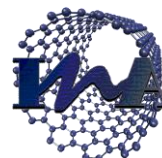
- The main limitation of all silanization process reproducibility could be due to change in moisture conditions. The silane handling and the sample handling should be performed under strictly controlled environment free of water. Also vapor phase deposition of silanes could be studied.
- Further studies in covalent linkage of zeolites to silane modified surface. For future work we suggest work on other silanes like ..... 1,2-Bis(triethoxysilyl)ethane which can be used as a linker between the silicon oxide surface and zeolite because of the presence of ethoxy groups at both ends of the silane.
- Increase the initial roughness of the surface.



## References

1. M. Niwa, N. Katada, K. Okumura, in *Characterization and Design of Zeolite Catalysts*. (Springer Berlin Heidelberg, 2010), vol. 141, pp. 1-8.
2. T. Maesen, in *Studies in Surface Science and Catalysis*, H. v. B. A. C. Jiří Čejka, S. Ferdi, Eds. (Elsevier, 2007), vol. Volume 168, pp. 1-12.
3. J. Weitkamp, M. Hunger, in *Studies in Surface Science and Catalysis*, H. v. B. A. C. Jiří Čejka, S. Ferdi, Eds. (Elsevier, 2007), vol. Volume 168, pp. 787-835.
4. T. M. Nenoff, J. Dong, in *Ordered Porous Solids*, V. Valentin, M. Svetlana, S. M. Michael TsapatsisA2 - Valentin Valtchev, T. Michael, Eds. (Elsevier, Amsterdam, 2009), pp. 365-386.
5. B. Subotić, J. Bronić, T. Antonić Jelić, in *Ordered Porous Solids*, V. Valentin, M. Svetlana, S. M. Michael TsapatsisA2 - Valentin Valtchev, T. Michael, Eds. (Elsevier, Amsterdam, 2009), pp. 127-185.
6. L. M. R. Castro, university of zaragoza (2013).
7. J. Caro, M. Noack, in *Advances in Nanoporous Materials*, E. Stefan, Ed. (Elsevier, 2010), vol. Volume 1, pp. 1-96.
8. A. Julbe, in *Studies in Surface Science and Catalysis*, H. v. B. A. C. Jiří Čejka, S. Ferdi, Eds. (Elsevier, 2007), vol. Volume 168, pp. 181-219.
9. A. W. Burton, S. I. Zones, in *Studies in Surface Science and Catalysis*, H. v. B. A. C. Jiří Čejka, S. Ferdi, Eds. (Elsevier, 2007), vol. Volume 168, pp. 137-179.
10. W. Fan *et al.*, *Microporous and Mesoporous Materials* **101**, 134 (2007).
11. C. I. Round, S. J. Hill, K. Latham, C. D. Williams, *Microporous Materials* **11**, 213 (1997).
12. S. Mintova, V. Valtchev, in *Studies in Surface Science and Catalysis*, G. P.-B. J. B. N. I. Kiricsi, H. G. Karge, Eds. (Elsevier, 1999), vol. Volume 125, pp. 141-148.
13. W. Fan, S. Shirato, F. Gao, M. Ogura, T. Okubo, *Microporous and Mesoporous Materials* **89**, 227 (2006).
14. Y. Li, W. Yang, *Journal of Membrane Science* **316**, 3 (2008).
15. G. A. Tompsett, W. C. Conner, K. S. Yngvesson, *ChemPhysChem* **7**, 296 (2006).
16. M. Gharibeh, G. A. Tompsett, K. S. Yngvesson, W. C. Conner, *The Journal of Physical Chemistry B* **113**, 8930 (2009/07/02, 2009).
17. Y. Li, H. Chen, J. Liu, W. Yang, *Journal of Membrane Science* **277**, 230 (2006).
18. M. P. Pina *et al.*, *Microporous and Mesoporous Materials* **144**, 19 (2011).
19. K. Sahner, G. Hagen, D. Schönauer, S. Reiß, R. Moos, *Solid State Ionics* **179**, 2416 (2008).
20. M. Vilaseca *et al.*, *Catalysis Today* **82**, 179 (2003).
21. O. Hugon, M. Sauvan, P. Benech, C. Pijolat, F. Lefebvre, *Sensors and Actuators B: Chemical* **67**, 235 (2000).
22. J. Coronas, J. Santamaria, *Chemical Engineering Science* **59**, 4879 (2004).
23. M. A. Urbiztondo *et al.*, *Sensors and Actuators B: Chemical* **137**, 608 (2009).
24. M. Urbiztondo, P. Pina, J. Santamaria, in *Ordered Porous Solids*, V. Valentin, M. Svetlana, S. M. Michael TsapatsisA2 - Valentin Valtchev, T. Michael, Eds. (Elsevier, Amsterdam, 2009), pp. 387-411.
25. S. Shivaji, M. Alan, in *Handbook of Zeolite Science and Technology*. (CRC Press, 2003).
26. M. Arruebo, R. Mallada, M. Pina, in *Handbook of Membrane Separations*. (CRC Press, 2008), pp. 269-323.
27. E. E. McLeary, J. C. Jansen, F. Kapteijn, *Microporous and Mesoporous Materials* **90**, 198 (2006).
28. W. N. Lau, K. L. Yeung, R. Martin-Aranda, *Microporous and Mesoporous Materials* **115**, 156 (2008).

29. L. Lai, J. Shao, Q. Ge, Z. Wang, Y. Yan, *Journal of Membrane Science* **409–410**, 318 (2012).
30. J. Li *et al.*, *Microporous and Mesoporous Materials* **160**, 10 (2012).
31. L. Li *et al.*, *Applied Catalysis A: General* **292**, 312 (2005).
32. K. Sato, K. Sugimoto, T. Nakane, *Journal of Membrane Science* **307**, 181 (2008).
33. J. Zah, H. M. Krieg, J. C. Breytenbach, *Microporous and Mesoporous Materials* **93**, 141 (2006).
34. P. Frontera, F. Crea, F. Testa, R. Aiello, *J Porous Mater* **14**, 325 (2007/09/01, 2007).
35. G. Decher, J. D. Hong, J. Schmitt, *Thin Solid Films* **210–211, Part 2**, 831 (1992).
36. L. Lakiss, I. Yordanov, G. Majano, T. Metzger, S. Mintova, *Thin Solid Films* **518**, 2241 (2010).
37. Y. S. S. Wan, J. L. H. Chau, A. Gavriilidis, K. L. Yeung, *Microporous and Mesoporous Materials* **42**, 157 (2001).
38. L. C. Boudreau, J. A. Kuck, M. Tsapatsis, *Journal of Membrane Science* **152**, 41 (1999).
39. S. Öztürk, B. Akata, *Microporous and Mesoporous Materials* **126**, 228 (2009).
40. J. S. Lee, J. H. Kim, Y. J. Lee, N. C. Jeong, K. B. Yoon, *Angewandte Chemie International Edition* **46**, 3087 (2007).
41. A. Huang, J. Caro, *Chemistry of Materials* **22**, 4353 (2010/08/10, 2010).
42. Y. Lvov, F. Essler, G. Decher, *The Journal of Physical Chemistry* **97**, 13773 (1993/12/01, 1993).
43. X. Yang, S. Johnson, J. Shi, T. Holesinger, B. Swanson, *Sensors and Actuators B: Chemical* **45**, 87 (1997).
44. G. Decher, M. Eckle, J. Schmitt, B. Struth, *Current Opinion in Colloid & Interface Science* **3**, 32 (1998).
45. T. W. Swaddle, in *Inorganic Chemistry - An Industrial and Environmental Perspective*. (Elsevier).
46. M. A. Brook. (John Wiley & Sons).
47. S. Ebnessajjad. (Elsevier).
48. M.-L. Abel, in *Handbook of Adhesion Technology*, L. M. da Silva, A. Öchsner, R. Adams, Eds. (Springer Berlin Heidelberg, 2011), pp. 237-258.
49. R. N. Rethon. (Smithers Rapra Technology).
50. M. B. Ali *et al.*, *Materials Science and Engineering: C* **28**, 628 (2008).
51. S. A. Kulkarni, S. B. Ogale, K. P. Vijayamohan, *Journal of Colloid and Interface Science* **318**, 372 (2008).
52. J. Zheng, Z. Zhu, H. Chen, Z. Liu, *Langmuir* **16**, 4409 (2000/05/01, 2000).
53. M. Ostwal, R. P. Singh, S. F. Dec, M. T. Lusk, J. D. Way, *Journal of Membrane Science* **369**, 139 (2011).
54. H. Li *et al.*, *Langmuir* **26**, 5603 (2010/04/20, 2009).
55. S. Demirci, T. Caykara, *Surface Science* **604**, 649 (2010).
56. E. T. Vandenberg *et al.*, *Journal of Colloid and Interface Science* **147**, 103 (1991).
57. T. Manifar, A. Rezaee, M. Sheikhzadeh, S. Mittler, *Applied Surface Science* **254**, 4611 (2008).
58. M. Hu, S. Noda, T. Okubo, Y. Yamaguchi, H. Komiyama, *Applied Surface Science* **181**, 307 (2001).
59. D. F. Siqueira Petri, G. Wenz, P. Schunk, T. Schimmel, *Langmuir* **15**, 4520 (1999/06/01, 1999).
60. J. A. Howarter, J. P. Youngblood, *Langmuir* **22**, 11142 (2006/12/01, 2006).
61. F. Zhang *et al.*, *Langmuir* **26**, 14648 (2010/09/21, 2010).
62. R. M. Pasternack, S. Rivillon Amy, Y. J. Chabal, *Langmuir* **24**, 12963 (2008/11/18, 2008).
63. J. Kim, P. Seidler, C. Fill, L. S. Wan, *Surface Science* **602**, 3323 (2008).
64. M. Zhu, M. Z. Lerum, W. Chen, *Langmuir* **28**, 416 (2012/01/10, 2011).
65. Q. Gu, X. Cheng, *Current Applied Physics* **8**, 583 (2008).
66. N. Graf *et al.*, *Surface and Interface Analysis* **40**, 180 (2008).
67. J. Kim, P. Seidler, L. S. Wan, C. Fill, *Journal of Colloid and Interface Science* **329**, 114 (2009).
68. W. Wang, M. W. Vaughn, *Scanning* **30**, 65 (2008).
69. A. Huang, N. Wang, J. Caro, *Journal of Membrane Science* **389**, 272 (2012).



70. A. Huang *et al.*, *Journal of Membrane Science* **437**, 57 (2013).
71. A. Huang, N. Wang, J. Caro, *Microporous and Mesoporous Materials* **164**, 294 (2012).
72. A. Huang, F. Liang, F. Steinbach, J. Caro, *Journal of Membrane Science* **350**, 5 (2010).
73. X. Zhang, E. S. Man Lai, R. Martin-Aranda, K. L. Yeung, *Applied Catalysis A: General* **261**, 109 (2004).
74. K. B. Yoon, *Bull. Korean Chem. Soc.* **27**, (2006).
75. A. Podolian *et al.*, *Solar Energy Materials and Solar Cells* **95**, 765 (2011).
76. G. W. Gale, R. J. Small, K. A. Reinhardt, in *Handbook of Silicon Wafer Cleaning Technology (Second Edition)*, A. R. Karen, K. Werner, Eds. (William Andrew Publishing, Norwich, NY, 2008), pp. 201-265.
77. W. Kern, in *Handbook of Silicon Wafer Cleaning Technology (Second Edition)*, A. R. Karen, K. Werner, Eds. (William Andrew Publishing, Norwich, NY, 2008), pp. 3-92.
78. Y. Han, D. Mayer, A. Offenhäusser, S. Ingebrandt, *Thin Solid Films* **510**, 175 (2006).
79. K. Qin, Y. Li, *Journal of Colloid and Interface Science* **261**, 569 (2003).
80. W. Kern, *Journal of The Electrochemical Society* **137**, 1887 (June 1, 1990, 1990).
81. K. A. Reinhardt, W. Kern. (William Andrew Publishing).
82. R. Kohli, K. L. Mittal. (William Andrew Publishing).
83. W. K. Shin, J. H. An, H. D. Jeong, *CIRP Annals - Manufacturing Technology* **60**, 579 (2011).
84. S. B. Awad, R. Nagarajan, in *Developments in Surface Contamination and Cleaning - Methods for Removal of Particle Contaminants*. (William Andrew Publishing, Oxford, 2010), pp. 225-280.
85. K. A. Reinhardt, in *Handbook of Silicon Wafer Cleaning Technology (Second Edition)*, A. R. Karen, K. Werner, Eds. (William Andrew Publishing, Norwich, NY, 2008), pp. 661-688.
86. P. M. Claesson, A. van der Wal, A. Fogden, in *Handbook for Cleaning/Decontamination of Surfaces*, J. Ingegärd, P. Somasundaran, Eds. (Elsevier Science B.V., Amsterdam, 2007), pp. 885-XXVI.
87. M. Chemla, S. Durand-Vidal, S. Zanna, S. Petitdidier, D. Levy, *Electrochimica Acta* **49**, 3545 (2004).
88. A. R. Martin, M. Baeyens, W. Hub, P. W. Mertens, B. O. Kolbesen, *Microelectronic Engineering* **45**, 197 (1999).
89. M. Noack, M. Schneider, A. Dittmar, G. Georgi, J. Caro, *Microporous and Mesoporous Materials* **117**, 10 (2009).
90. J. Forniés, university of zaragoza (2008).
91. S. Luances, university of zaragoza (2011).
92. S. Aguado, J. Gascon, D. Farrusseng, J. C. Jansen, F. Kapteijn, *Microporous and Mesoporous Materials* **146**, 69 (2011).
93. V. Sebastian, S. Irusta, R. Mallada, J. Santamaría, *Catalysis Today* **147**, **Supplement**, S10 (2009).
94. H. van Bekkum, H. W. Kouwenhoven, in *Studies in Surface Science and Catalysis*, H. v. B. A. C. Jiří Čejka, S. Ferdi, Eds. (Elsevier, 2007), vol. Volume 168, pp. 947-998.
95. M. S. Rigutto, R. van Veen, L. Huve, in *Studies in Surface Science and Catalysis*, H. v. B. A. C. Jiří Čejka, S. Ferdi, Eds. (Elsevier, 2007), vol. Volume 168, pp. 855-XXVI.
96. E. M. Flanigen, R. W. Broach, S. T. Wilson, in *Zeolites in Industrial Separation and Catalysis*. (Wiley-VCH Verlag GmbH & Co. KGaA, 2010), pp. 1-26.
97. T. C. Bowen, R. D. Noble, J. L. Falconer, *Journal of Membrane Science* **245**, 1 (2004).
98. W. N. Lau, K. L. Yeung, X. F. Zhang, R. Martin-Aranda, in *Studies in Surface Science and Catalysis*, Z. G. J. C. Ruren Xu, Y. Wenfu, Eds. (Elsevier, 2007), vol. Volume 170, pp. 1460-1465.
99. S. M. Lai, C. P. Ng, R. Martin-Aranda, K. L. Yeung, *Microporous and Mesoporous Materials* **66**, 239 (2003).
100. B. E. Yoldas, *American Ceramic Society Bulletin* **3**, 289 (1975).

## Appendix

### 1. Zeolites

Zeolites can be defined as Inorganic crystalline frameworks that consist of Silica ( $\text{SiO}_2$ ) and depending on the type of zeolite some Silicon( $\text{Si}^{4+}$ ) atoms are replaced by Aluminum ions ( $\text{Al}^{3+}$ ) in the framework giving the framework a negative overall charge which is balanced by a cation that is stay inside the porous cavity by electrostatic attraction to balance the charge, hence neutralizing and balancing the overall charge(2).

### 2. Applications of zeolites

#### 2.1 Gas separation

Gas separation is one of the largest researched areas for zeolite membrane application because of its potential to reduce separation and purification costs and is termed as green separation as the focus is to reduce energy and cost of separation and purification of gases. Some of the applications of Zeolites in gas separation are to remove water from gas streams, to remove trace amounts of impurity gases, to separate different bulk gases. The gas separation through zeolite membrane is based on 3 main mechanism, size exclusion, thermodynamic selectivity which is the preferential adsorption of some components over the other and kinetic selectivity which is the ability of some components to diffuse through pores(25)Hydrogen purification is also one of the major growth areas for future application of zeolite as much research is now focusing on renewable energy sources and significant research is being conducted on hydrogen fueled vehicles which will increase the need for hydrogen production and also improving the efficiency of the process. One of major hydrogen production is by steam reforming of light hydrocarbons and carbon dioxide is the major impurity in the hydrogen produced by this method. So improving  $\text{CO}_2$  removal by membranes is also an important area of research for gas separation(4). and selective oxidation of CO simulated in the hydrogen production from steam reforming process using zeolite/pt catalysts have been reported(93).

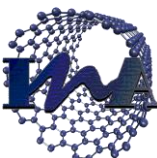
## 2.2 Liquid separation

Zeolite membranes are used for a wide variety of liquid/liquid separation, some of the main reasons for application of zeolite for liquid separation is lower energy requirements and hence lower cost and higher separation factors. One of the major areas of application and research is dehydration/drying using zeolite membranes to remove water from important industrial solvents like ethanol from their azeotropic mixtures and also from various other organic liquids. Another major area is of separating hydrocarbons from their isomers or byproducts, some examples are Isoprene which is used in artificial rubber production, isoprene needs to be purified from other similar hydrocarbons especially isoprene's azeotropic mixture with n-pentane. Another important industrial separation is p-xylene which is used in synthetic plastic manufacturing and needs to be purified from its isomers (p-xylene, o-xylene, m-xylene and ethylbenzene) and is an expensive purification process, Zeolites are being researched to reduce cost of purification. (4) Other applications in liquid separation include water removal from acid solutions requiring a stable membrane in highly acidic conditions which is fulfilled by zeolite membranes. Also organic pollutants can be removed from water using zeolite membranes. Another important organic separation is of methyl-tert-butyl ether, which is a fuel additive and needs to be purified from methanol impurities. [(26)] Detailed information on organic production and separation based on zeolites is described by Herman.(94, 95).

### 3. Zeolite LTA/ Zeolite A

Zeolite A is a low Si/Al ratio zeolite structure; it was first discovered by union carbide in 1950. The framework code for Zeolite A given by the International Zeolite Association is LTA (Linde Type A). Linde was division of the Union Carbide company that discovered this Zeolite. Si/Al ratio for zeolite A is around 1 to 1.5 and they are hydrophilic in nature. The general formula for Zeolite A is  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{H}_2\text{O}$ . The Zeolite A structure is a 4-4 structure of secondary building unit of sodalite or beta cage which is formed by the primary building block the tetrahedron which is combined in 4-4 oxygen ring pattern. This structure gives the highest cation exchange concentration to zeolite A and the optimum adsorption properties in terms of capacity and pore size.

It can be used to remove water from organic rich mixtures and also as catalyst. 70% of the total zeolite produced is Zeolite A and its main application is in detergents



where it acts as an ion exchanger.(96) There have been many lab scale applications of zeolite A micro membranes for sensor, liquid separation, gas separation applications in micro reactors, membranes and other applications. The only known industrial application of zeolite A membrane is in Ethanol dehydration to purify ethanol from the azeotropic mixture of ethanol and water. Mitsui engineering were the first to commercialize zeolite A membranes for industrial application in ethanol dehydration and other manufacturers are listed by Bowen in his publication(97). Another important application of zeolite A is in micro reactors where it is used as a selective barrier to remove water from reactions, micro reactor walls are lined with zeolite A where it can remove water or adsorb and desorb water in closed system, a lot of micro reactors lined with zeolite A membrane has been done by Yeung and his team.(28, 37, 73, 98, 99) . A detailed list of organic synthesis where Zeolites are used are listed in the following publications with numerous applications where zeolite A are used as water absorbers or catalysts and these can be further used in form of zeolite membranes in micro reactors for these chemical reactions(94).

#### **4. Boehmite solution preparation**

Boehmite preparation previously reported by Yoldas(100) was performed to obtain the required Boehmite solution. 100ml of distilled water is heated at 80C in a beaker with stirring closed from air with nitrogen purge to prevent moisture from air, 25ml of Aluminum-tri-sec-butoxide ( $\text{Al}[\text{OCH}(\text{CH}_3)\text{C}_2\text{H}_5]_3$ , 97 wt% Aldrich) is added from the nitrogen environment to prevent polymerization. After drop by drop addition of aluminum-tri-sec-butoxide is completed, the solution is stirred for 1 hour and the alcohol smell disappears indicating the hydrolysis of aluminum-tri-sec-butoxide is completed. Then temperature is raised to 90C and then 7ml of  $\text{HNO}_3$  of 1 MOLAR concentration added drop by drop. Then solution was transferred to Rota vapor equipment to age the sample at 90c for 24 hours and to prevent water evaporation during that time. The temperature was set to 90C at 80RPM. After the ageing of the solution is completed a 9% concentration of Boehmite solution is obtained. (after the synthesis the solution can be centrifuged at 3000rpm for 10 minutes to remove any big particles or it can be filtered).

## 5. Preparation of silicon grids

### Preparation of silicon grids

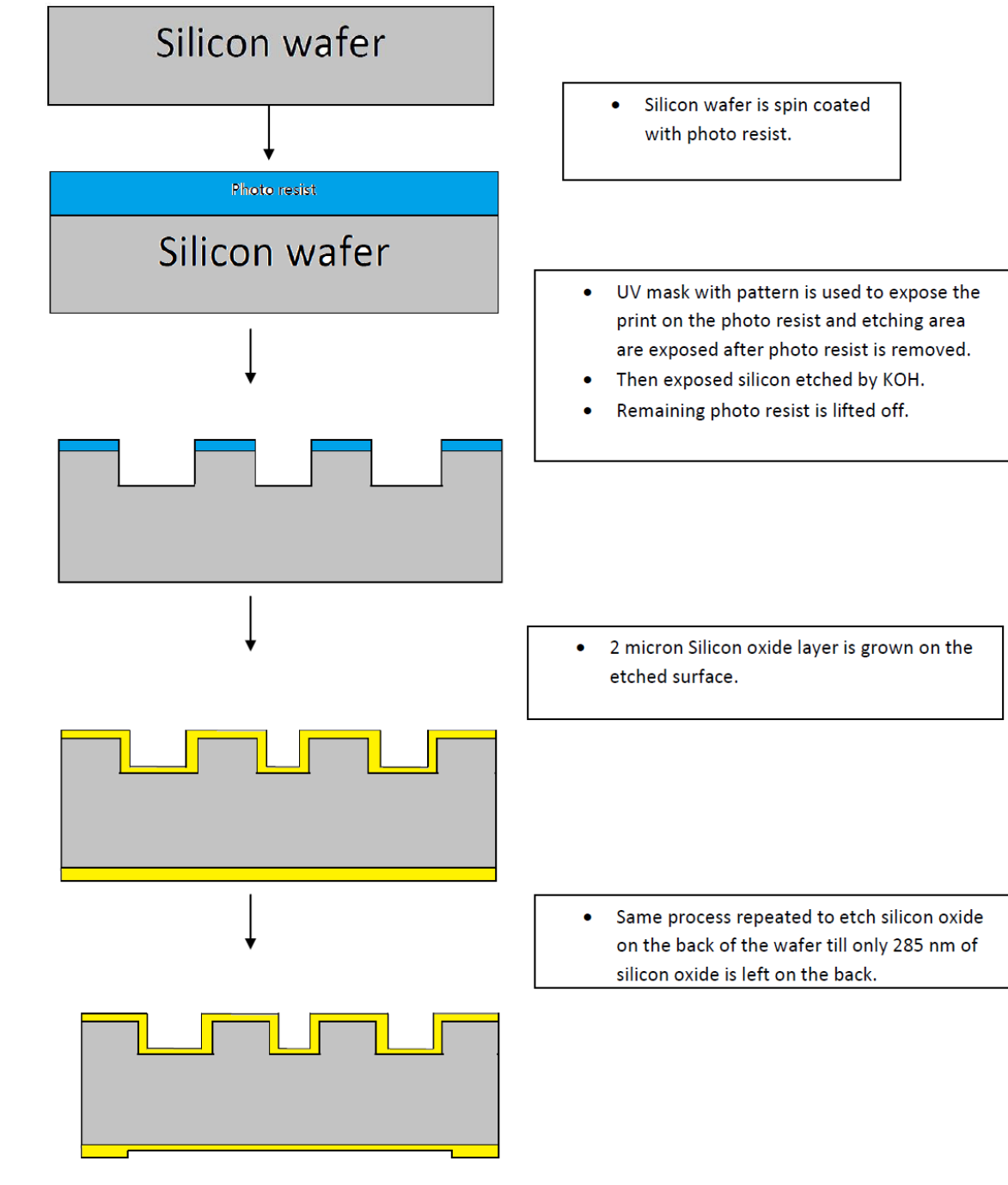


Figure 47: GRID PREPARATION