ABSTRACT: Alkyl silica membranes and wires were synthesized by a sol–gel method, which has the capacity to control the size of the particles or membranes by controlling the reactions. Trimethoxycetylsilane (C₈TMOS) was used as a chemical surfactant; poly(vinylpyrrolidone) (PVP) as an emulsifier, dissolved in butanol for emulsion; and tetraethylorthosilicate (TEOS) as a precursor and a source of silica. An assembly of silica wires was fabricated on glass and cotton substrates by the dip-coating technique. Porous membranes and silica wires were observed using scanning electron microscopy (SEM) images. The contact angles of all of the samples were in the range of 140°−154° as measured by ImageJ software, which confirmed the hydrophobic nature of the samples. The contact angle was increased by increasing the amount of the surfactant. Phase changes of silica wires and membranes were investigated by thermogravimetric analysis. Chemical bonds of the sample were studied using Fourier transform infrared (FTIR) spectroscopy. The band gap of silica nanowires was measured to be 3.8−3.4 eV using the UV−visible spectrum and decreased as compared to that of bulk silica. These silica-based porous membranes with enhanced transport properties can be used in filtration and separation techniques. This fabricated hybrid silica membrane showed ∼96% salt rejection within a permeation flux of 3.04 L/m² h.

INTRODUCTION

Membrane separation technology has developed rapidly over recent years because it is a low-cost and energy-efficient process compared to other filtration techniques. Silica membranes have good physical and chemical processes compared to other filtration techniques. Silica membranes have good physical and chemical properties with unique thermal and structural stabilities. Silica particles are very attractive additives and fillers for altering surface properties through functionalization. Initially, silica is hydrophilic due to the presence of silanol (Si−OH) groups on the surface of the particle. This hydrophilic additive destabilizes the dopant solution, thereby enhancing the viscosity and kinetic effect to promote the formation of highly modified porous membranes.

Silica membranes synthesized by the sol–gel method result in higher selectivity, controlled pore size, and a relatively thin (100 nm or less) separation layer, which is necessary to obtain high permeability. The two main routes in the sol–gel synthesis, the colloidal route and the polymeric route were, followed in membrane synthesis. Sol–gel is a facile technique that allows for a variety of binary, tertiary, and complex chemical compositions of ligands and networks resulting in organic and inorganic hybrid materials. Modification of ion exchange membranes with nanoparticles leads to significant changes in transport properties of membranes via pores and channel systems. Formation of nanoparticles into pores changes the pore size and volume, thus enhancing the transport of even smaller ions and molecules through hybrid membranes. Emerging membrane technologies are highly attractive for wastewater purification with higher efficiency. Membrane flux can be controlled by surface properties and the number and size of pores on the surface. The pore size formation is strongly affected by polymer-based solvent interactions, chain strength, arrangement, and entanglement that occur during initial phase changes through the reaction. Highly porous membranes can be developed mostly by incorporation of pores through hydrophilic polymeric additives such as poly(vinylpyrrolidone) (PVP), poly(ethylene glycol), etc. These additives destabilize the dope solution, which results in demixing, and thus promote the formation of highly porous membranes. Silica particles are more attractive additives as we can change their surface properties by functionalization. Inclusion of silica particles can significantly enhance the viscosity to increase the kinetic effect during phase changes. Addition of hydrophilic silica particles can increase the pore size, porosity, and wettability.

Very limited literature is available for the use of silica as an additive for membrane fabrication. This work explains the role of silica in upgrading the surface pore formation, size, and number.
performance of membranes. The wettability of fabricated silica wires was tested on various substrates such as glass and cotton fabrics. Agent concentration has a strong influence on the thermal properties of cotton fabric. Cotton fabric exhibited thermal degradation due to pyrolysis by two pathways: (i) the decomposition of the glycol units at low temperatures and (ii) the depolymerization of burning units into volatile products containing levoglucosan at high temperatures. The literature revealed the thermal stability of the thermal degradation and stability with density variations. The peak at 1659 cm⁻¹ is attributed to C=O stretching and that at 1462 cm⁻¹ is attributed to C–H stretching vibration of H₂O in the sample. The very feeble peak at 741 cm⁻¹ is due to the 

The results and discussion

FTIR Spectrum of the Samples. Fourier transform infrared (FTIR) spectroscopy was performed using an IRTracer-100 FTIR spectrometer in the 4000–400 cm⁻¹ range, and the resulting spectra are shown in Figure 1. The FTIR spectrum of the samples, as shown in Table 1, were characterized by various vibrations of structural units. Typically, the peak at 2933 cm⁻¹ and 2881 cm⁻¹ are assigned to the CH₃ symmetric and asymmetric stretching vibrations, respectively. The peak at 1659 cm⁻¹ is ascribed to the C=O stretching and that at 1462 cm⁻¹ is due to the C–H stretching vibration of H₂O in the sample, which is due to the fact that silica particles have a tendency to absorb water from the atmospheric air. The peak at 2958 and 2855 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibrations of the C–H group, respectively. The peak at 1659 cm⁻¹ is ascribed to the C=O stretching and that at 1462 cm⁻¹ is due to the C–H stretching vibration of H₂O in the sample, which is due to the fact that silica particles have a tendency to absorb water from the atmospheric air. The peak at 2958 and 2855 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibrations of the C–H group, respectively.

| Sample | FTIR Spectrum of the Samples. | FTIR Spectrum of the Samples. |
|--------|--------------------------------|--------------------------------|
| 10 μL  | SiO–H (symmetric)              | SiO–H (symmetric)              |
| 30 μL  | SiO–H (asymmetric)             | SiO–H (asymmetric)             |

Table 1. Characteristic Vibrational Frequencies (cm⁻¹) in FTIR Spectra of Hybrid Silica Wires (SiWs) Synthesized with Two Different Concentrations of Surfactant C₈TMOS, i.e., 10 and 30 μL

| no. | 10 μL | 30 μL | types of vibrations | structural units          |
|-----|-------|-------|---------------------|---------------------------|
| 1   | 3366  | 3366  | O–H stretching and   | H–O–H–H₂O and             |
|     |       |       | SiO–H               |                           |
| 2   | 2963  | 2963  | ν₁C=H               | –CH₂                      |
| 3   | 2933  | 2949  | ν₁C=H               | –CH₂                      |
| 4   | 2881  | 2881  | ν₁C=H               | –CH₂                      |
| 5   | 2168  | 2210  | C–C stretching      | C–C                       |
| 6   | 2115  | 2115  | a combination of hindered | H–O–H                  |
|     |       |       | rotation and O–H     | bending of water           |
| 7   | 1656  | 1656  | C =≡O stretching    | C≡O                       |
| 8   | 1422  |       | δ₁C=H               | Si=R                      |
| 9   | 1478  | 1380  | δ₁C=H               | –CH₂                      |
| 10  | 1297  | 1297  | δ₁C=H               | Si=R                      |
| 11  | 1219  | 1219  | CH₃ wagging vibrations | –CH₃                    |
| 12  | 1114  | 1114  | asymmetric vibrations of ν₁Si–O–Si | O–Si–O≡                 |
| 13  | 1048  |       | ν₁Si–O–Si (TO mode) | O–Si–O≡                  |
| 14  | 928   |       | ν₁Si–O              | Si–OH                    |
| 15  | 847   | 847   | ν₁Si–C              | Si=R                      |
| 16  | 1048, 732 |       | stretching          | Si–O–Si                  |
| 17  | 594   | 594   | (noise)             | SiO₂ defects              |
| 18  | 556   | 556   | (noise)             | SiO₂ defects              |

Figure 1. Comparison graph of FTIR spectra for samples prepared by 10 and 30 μL of trimethoxycycsilane.

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In an inert atmosphere under a flow of argon gas at a heating rate of 15 °C/min. Thermal properties such as weight loss at different temperatures were studied using the thermogravimetric analysis of samples shown in Figure 3. The TGA curve of samples prepared by 10 μL of C₈TMOS showed a weight loss of 13.4% at 288.9 °C corresponding to two endothermic peaks in the differential scanning calorimetry (DSC) curve at 132.8 and 193.8 °C, respectively. This initial weight loss is attributed to the evaporation of the solvent, i.e., ethanol.40 The same sample showed a further weight loss of 11.1% at 457.2 °C corresponding to exothermic peaks in the DSC curve at 516 °C. This later weight loss is due to the decomposition of the alkyl –CH₃ group.5

The TGA curve of samples prepared by 30 μL of C₈TMOS showed a weight loss of 12.5% up to 290.5 °C corresponding to endothermic peaks at 136.4 and 192 °C in the DSC curve. Then, a larger and rapid weight reduction of 38.8% was seen up to 497.6 °C corresponding to endothermic peaks at 316.7 and 454.8 °C in the DSC curve, which is attributed to the evaporation of the solvent, i.e., ethanol. Between 497.6 and 671 °C, there was only a slight decrease of 3.8% in weight, corresponding to an exothermic peak at 578.6 °C in the DSC curve, which is due to the decomposition of the alkyl –CH₃ group in the synthesized sample. An endothermic peak at 457.2 °C also showed the melting of the sample, indicating the change in its physical state from solid to liquid. The thermal stability of the sample is seen after 500 °C as depicted in Figure 2.

Contact Angle of Silica Nanomembranes. The prepared NW membranes were hydrophobic with a contact angle of 145° and 154° for 10 and 30 μL of trimethoxycyclotrisilane (C₈TMOS), respectively, as measured using a digital camera microscope (Figure 3a–c). This is because the C₈ group of the surfactant shielded the building blocks of the NW membrane. This revealed that the wettability of the membrane decreased because the contact angle increased. The increased amount of surfactant leads to superhydrophobicity and a decrease in wettability.

Contact Angle of Silica NWs on Glass Substrate. Silica NWs were coated on a glass slide with 10 and 30 μL of trimethoxycyclotrisilane (C₈TMOS) as the surfactant, presenting a contact angle of 140 and 153°, respectively, to confirm hydrophobicity (Figure 3c,d). Water droplets created a high-energy wall to form a liquid—solid boundary on the exterior surface. Moreover, the macropores in the networks of the NWs can set up air inside, providing an air pad to hang the drops of water. The increasing amount of surfactant increased the contact angle making the wires superhydrophobic.11

Contact Angle of Silica NWs on Cotton Fabric. The contact angle of silica nanowires on cotton fabric with 10 μL of trimethoxycyclotrisilane (C₈TMOS) as surfactant is 135°, confirming the hydrophobic property. The water-repellent ability of the coated surface can be credited to the result of nanosized silica particles and the hydrophobic characteristic of the alkyl silane agent, which in this case is the surfactant. The sample with 30 μL of trimethoxycyclotrisilane (C₈TMOS) as surfactant has a contact angle of 145°, which showed that by increasing the amount of surfactant the contact angle increases.

UV–Vis Spectroscopy. The UV–vis absorption spectrum of the prepared silica nanoparticles dispersed in ethanol was obtained using a U-2800 Hitachi UV–vis spectroscope.

The UV–vis spectrum of the sample synthesized with 10 μL of C₈TMOS represented a strong absorption peak at 276 nm, and the sample with 30 μL of C₈TMOS presented a peak at 280 nm, which is in the range of the absorption peak of silica nanoparticles as shown in Figure 4. These wavelengths showed that the prepared sample with 30 μL of C₈TMOS was red-shifted from 10 μL of C₈TMOS. The red shift indicated the increase in the size of the particles. On increasing the amount of surfactant, the value of absorbance increased. This is in accordance with Beer–Lambert’s law which states that the value of absorbance increases on increasing the concentration of nanoparticles in the solution.7

Band Gap. Using the Planck–Einstein equation, the relationship between band gap energy and wavelength is given as

$$E_g = h_v = h/c$$

In this equation, $E_g$ is the band gap energy in eV, $h$ is Planck’s constant, $v$ is the frequency, $c$ is the speed of light.8 The band gap can be calculated by plotting a graph between photon energy in eV and ($hv$). Using Tauc’s plot, the optical band
The band gap of SiO$_2$ with 10 and 30 $\mu$L of C$_8$TMOS was calculated to be 3.8 and 3.4 eV, respectively, as shown in Figure 5. The band gap was reduced because there was an increase in particle size, which predicted the size-dependent energy gap.

Morphological Analysis. Morphological analysis was performed using a Jeol SEM JSM-6480LV to visualize silica wires on various substrates and their self-assembly into membranes.

SEM of Silica NWs on Glass Substrate. Figure 6a,b shows the scanning electron microscopy (SEM) images of silica wires coated on glass substrate by dip-coating before and after sonication, Figure 6c,d, of silica suspension, respectively. A network of 3D superhydrophobic silica wires with a snakelike slim structure consisting of a less-bright Si core covered with a brighter silicon oxide shell was observed. The chemically inert Si oxide shell prohibited the lateral growth of Si wires; thus, their perpendicular growth resulted in the branched structure of the material as observed. The sample prepared using 30 $\mu$L of surfactant showed a more self-assembled porous structure of silica wires than that prepared using 10 $\mu$L. The more closely packed porous mesh of silica wires in the former sample, synthesized with a higher concentration of surfactant, resulted in a hierarchal surface ensuring the improved

Figure 3. Contact angle measurements for 10 and 30 $\mu$L of trimethoxysilylsilane (C$_8$TMOS) water droplets on substrates: (a) water droplet on silica membrane, (b, c) M10: 145° and M30: 154° on a membrane, (d, e) G10: 140° and G30: 153° for glass, and (f–h) C10: 135° and C30: 145°.

Figure 4. UV–vis absorption spectrum of silica nanomembranes with 10 and 30 $\mu$L of C$_8$TMOS.

Figure 5. Optical band gap spectrum of silica nanomembranes with (a) 10 $\mu$L and (b) 30 $\mu$L of C$_8$TMOS.
hydrophobicity as verified by water contact angle measurements of ∼140 and 153°. The SEM images of silica wires were obtained after the sonication process, resulting in tadpole-like 3D structures that were superhydrophobic.11

**SEM of Silica NWs on Cotton Fabric.** The morphology of cotton fabrics treated with silica wire samples synthesized with two different concentrations of 10 and 30 μL of surfactant trimethoxyoctylsilane (C₈TMOS), respectively, was observed using SEM images as shown in Figure 6e,f. The tiny particles of silica attached to fabric fibers contributed to the roughness, thus making the surface of the fabric more hydrophobic. The water repellency of the fabric was also evident by the contact angle measurement as discussed earlier. An increase in the concentration of surfactant can increase adsorption on cotton fabric and decrease the adhesion force, thus reducing the wetting ability of the fabric beyond the critical micelle concentration.12

**SEM of Silica Nanomembranes.** SEM images of hybrid silica membranes prepared using 10 and 30 μL of surfactant C₈TMOS revealed porous structures. These pores give rise to the hierarchal structure of the surface of the membranes and make them fairly rough by the arrangement of tiny air pockets within them, as shown in Figure 6g,h, thus contributing to superhydrophobicity.13 The closely packed porous network...
obtained by increasing the amount of surfactant (30 μL) resulted in a rougher surface and increased superhydrophobicity as confirmed by contact angle measurements. SEM images revealed the wirelike network of silica for C₈TMOS as compared to the scattered silica particles in SDS. Therefore, for further research, C₈TMOS was chosen as a closed network structure, and it was rough enough to achieve better hydrophobicity.

Silica Membrane Performance Test for Flux and MgSO₄ Rejection by Reverse Osmosis RO Filtration. The hybrid silica membrane prepared by 10 μL of surfactant trimethoxyoctylylsilane (C₈TMOS) showed 95.9% capability of MgSO₄ rejection at a permeate flux of 3.04 L/m² h whereas that prepared by 30 μL of surfactant resulted in a salt rejection capability of 96.8% with a 2.83 L/m² h permeate flux as performed by RO filtration plant (Hp 470 sterlith company deadend) in Georgia Institute of Technology. SEM images are shown in Figure 7.

The higher salt rejections were observed in the case of higher surfactant concentration (30 μL) as compared to the lower surfactant amount used in the synthesis of hybrid silica membranes. This is due to the fact that in the former case, a closely packed mesh of silica was formed in membranes due to the higher silica concentration, which caused smaller pores to be a hurdle to salt diffusion. However, poor flow dynamics consequently improved salt rejection resulting in a lower permeate flux of the prepared sample. This is due to hydrophobic membranes avoiding the diffusion of aqueous solution into the pores due to the difference in silica membrane pore sizes and those of salt molecules. 

## EXPERIMENTATION

### Synthesis of Silica Films on Glass and Fabric

In a typical synthesis, 2 g of PVP (C₆H₉NO) used as a precursor was dissolved in 20 mL of n-butanol. The mixture was stirred using a magnetic stirrer at 450–500 rpm for 10 min. Then, 2 mL of ethanol, 0.56 mL of distilled water, 1.36 mL of sodium citrate (Na₃C₆H₅O₇), and 0.4 mL of ammonia solution were added sequentially to the above solution. The mixture was poured into a Petri dish and dried in an oven at 45 °C for 3 min. Suspensions of both samples were made in ethanol having a silica concentration of 20 mg/mL. The silica films were coated on glass slides by the dip-coating technique. A glass slide of dimension 3 cm × 1 cm was hung between the clips of the dip coater. The glass slide was immersed in the suspension at a constant speed, i.e., 300 rpm. After soaking for about 10–12 s the suspension, the slide was then pulled out. On the glass slide, a thin layer of silica wires was deposited. The excess liquid was removed from the surface by shaking the glass slide for a few seconds. The mixture was shaken for 5 min immediately and left static for 22 h at 37 °C to grow silica wires (SiWs). The sample was then sonicated (D5A100-SK1-2.8L, V = 220 V, P = 100 W, 50 Hz) for 1 h and centrifuged (PLC-3, P = 220 V/50 Hz, 0.65 A) at 4500 rpm for 60 min to separate SiWs in a 15 mL centrifugation tube. The hybrid SiWs were washed with ethanol, air-dried for 2 days, and finally used to prepare a suspension of 20 mg/mL silica in ethanol. Samples denoted as S₁ and S₂ were obtained using two different amounts, i.e., 30 and 60 μL, of surfactant C₈TMOS by the above method. The silica films were coated on glass slides by the dip-coating method (as mentioned above) and cotton fabric by immersing the fabric in the final solution for 5 min with stirring and then drying in an oven at 80 °C for 3 min.

### Synthesis of Silica Membranes

Hybrid silica membranes were synthesized using the same method as that mentioned for silica films, with the only difference being that the amount of poly(vinylpyrrolidone) (PVP [C₆H₅NO3]) was doubled. PVP played the role of binding material for membrane function. Polymer blending demonstrates a wide range of properties such as water solubility, binding, high solubility, and good thermal resistance depending on pH, concentration, and density variations. The final solution was poured into a Petri dish and dried in an oven at 45 °C for 6 h, which resulted in very fine membranes. Schematics of the experiment are shown in Figure 8.

### Chemical Reactions

Sodium citrate was used as a stabilizing agent, and an ammonia solution was added to maintain the pH of the solution. When they both reacted due to the presence of hydrogen ions in water, the solution became acidic. Sodium citrate produced citric acid and then ammonium citrate was formed, which showed that no more hydrogen ions were present in the solution. 

**Preparation of Silica Nanoparticles.** Tetraethylorthosilicate (Si(O₂C₃H₇)₄) reacted with water to form silanol groups. The following chemical reactions are involved in preparation of silica nanoparticles. 

\[
\text{Si} (\text{OC}_3\text{H}_7)_4 + \text{H}_2\text{O} \rightarrow \text{Si(O}_3\text{C}_3\text{H}_7)_3\text{OH} + \text{C}_2\text{H}_5\text{OH}
\]

**Water Condensation:**
Alcohol Condensation:

\[
\text{Si} - \text{O} - \text{H} + \text{H} - \text{O} - \text{Si} \rightarrow \text{Si} - \text{O} - \text{Si} + \text{H}_2\text{O}
\]

The whole silica structure was made up of siloxane bridges (Si–O–Si) by the condensation/polymerization between the silanol groups or between ethoxy groups. The stages involved in the establishment of silica particles can be characterized by nucleation and growth.

The nucleated silica nanoparticles remained at the boundary of the droplets. The purpose of sodium citrate in the water droplets was to stabilize the hydrolyzed TEOS and to provide silica.

In the meantime, when in contact with simple water droplets, the trimethoxyoctylsilane C₈TMOS dissolved in the oil phase (n-butanol) and hydrolyzed into C₈Si(O−)₃. Prominently, C₈Si(O−)₃ had amphiphilic properties, i.e., it possesses both hydrophilic and lipophilic properties, with its hydrophilic Si(O−)₃ ion fronting the water phase and the C₈ tail toward the n-butanol solvent. The surface tension of the water droplet was reduced by interfacially arranged C₈Si(O−)₃ due to its role as a surfactant, which was in contact with the nucleated silica nanoparticles.

CONCLUSIONS

Silica particles were successfully synthesized in the presence of trimethoxyoctylsilane (C₈TMOS) as surfactant. The effect of different amounts of surfactant on the composition, morphology, and optical properties was studied in detail. The FTIR results confirmed the presence of alkyl groups on the silica surface at 2942–2168 cm⁻¹ and peaks from 1047 to 870 cm⁻¹ indicated the stretching vibrations of the Si–O–Si bond. Silica films and membranes showed hydrophobic and superhydrophobic characters within contact angles in the range of 140–154°. The contact angle was increased by increasing the amount of surfactant. This was evident for all samples coated on different substrates such as glass slides and cotton fabric and also for samples of the membrane. TGA and DSC analysis showed the weight loss at different temperatures, and thermal stability of both samples was attained after 500 °C. An
absorption peak at 276 and 280 nm and a band gap of 3.8 and 3.4 eV of 10 and 30 μL of C₆TOS, respectively, were observed. The absorption spectra were increased by increasing the amount of the surfactant as the particle size increased. The silica wires and membranes on the coating of the sample on glass slides and the porous structure of the membrane were evident. The prepared membranes were used to filter MgSO₄ solution, and the membrane prepared using 10 μL of C₆TOS showed a salt rejection capability of 95.9% and the membrane with 30 μL of C₆TOS had a salt rejection capability of 96.8%. It is estimated that the synthesized membranes can be used for application in water purification with accuracy, and these membranes can be made antibacterial for use in different fields of science and technology.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the support of laboratory facilities provided by Central Lab Lahore College for Women University, LCWU, Lahore, Pakistan; Polymer Engineering and Technology Department, Punjab University, Lahore, Pakistan; and Georgia Institute of Technology.

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