

Supplementary material

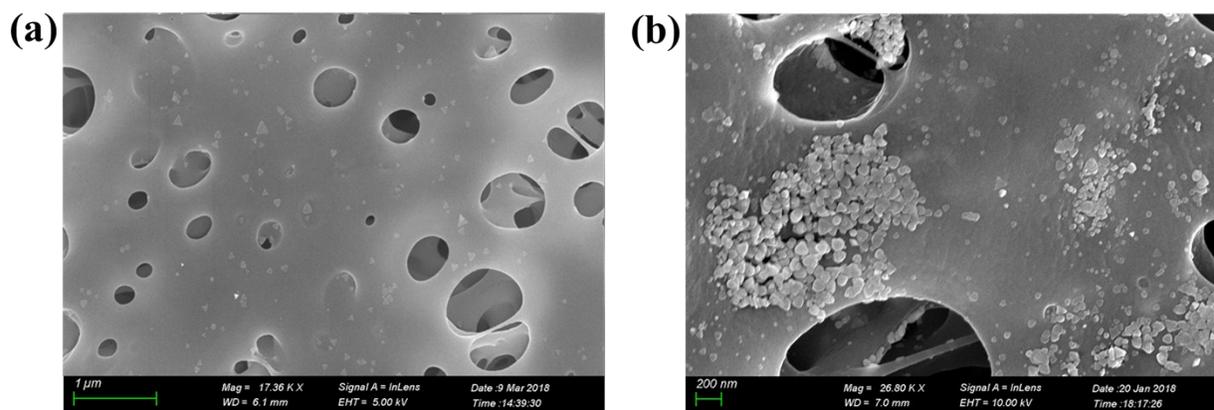


Fig. 1. Membranes modified with variant TSNP wt.%, resulting in poor membrane coverage (a) membrane modified with 0.5 Ag wt.% (b) membrane modified with 3.5 Ag wt.%

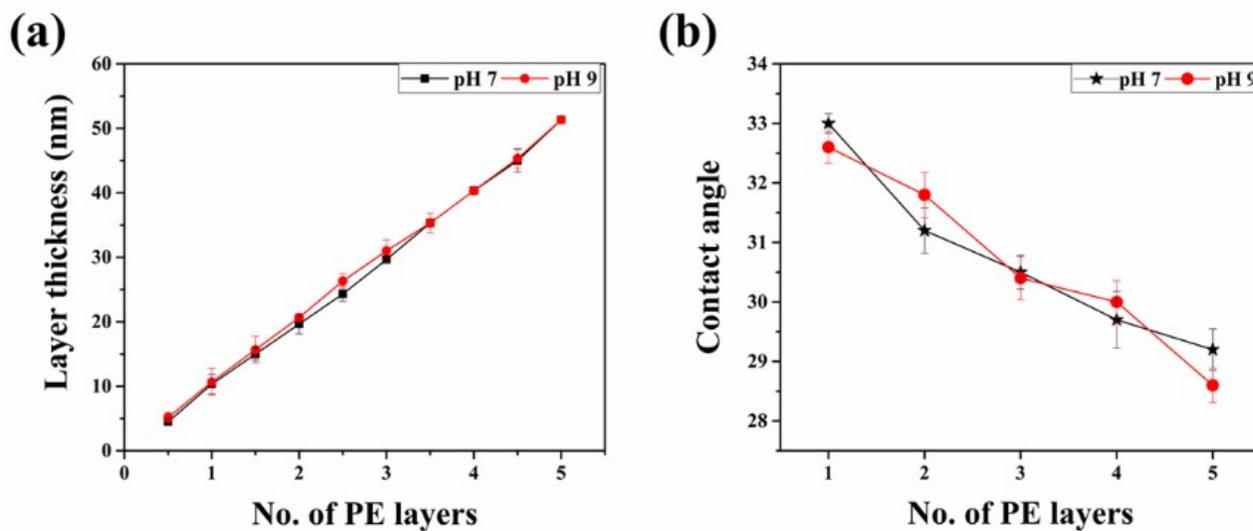


Fig. 2. Ellipsometric result of LBL membrane modification with polyelectrolytes. (a) represents the number of layers with resultant thickness at different pH values (b) illustrates the contact angle reduction with increased in number of polyelectrolyte (PE) layers

Note 1

Layer by layer PE deposition was employed to increase the charged density of the membranes for maximum nanoparticles (NP) anchorage and to provide charge repulsion between membrane surface and bacteria, PE layers were deposited to 5 bilayers. Since the charge of strong polyelectrolytes is not pH dependent, it can be incurred that the structure of all films formed using strong polyelectrolytes pair (PDADMAC/PSS) should be identical. PE layers were formed at 2 different pH values (pH 7, pH 9). The pH of the solution was adjusted by using HCL and NaOH. As expected, the results showed that PE layers thickness is not pH dependent. The thickness of layers depositing followed the constant pattern of average 5 nm thickness upon each PE layer deposition. Similar pH independent trend was observed for contact angle measurements upon 5 bilayers deposition. Contact angle decreased upon increasing PE layers.

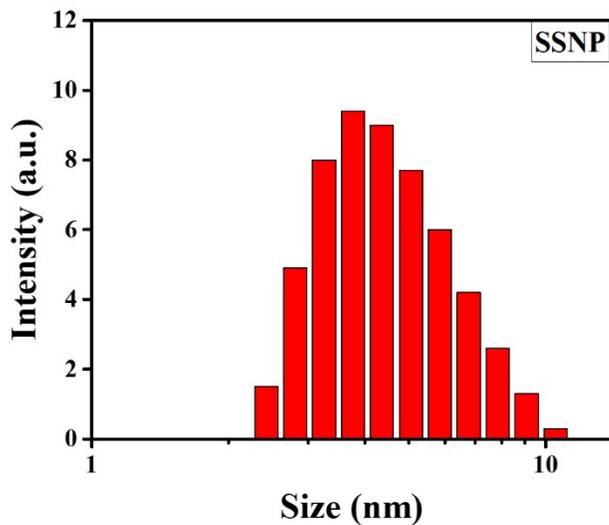


Fig 3. DLS size distribution of spherical silver nanoparticles (SSNP)

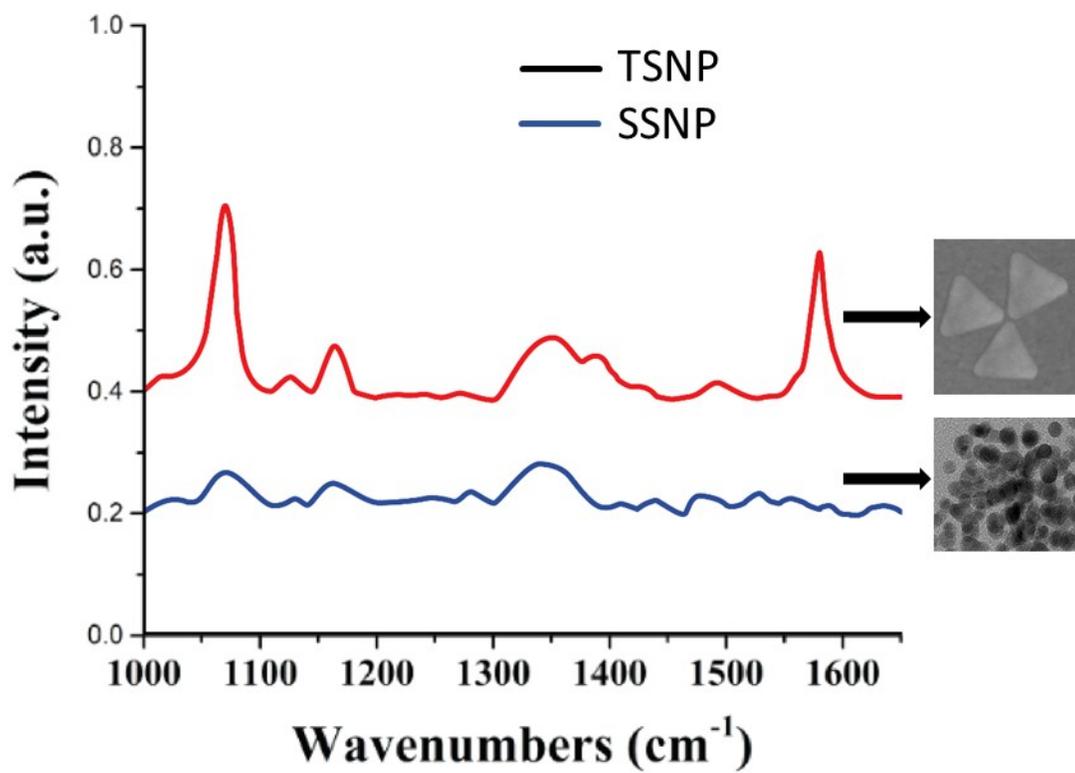


Fig.4. Raman spectra of self-assembled TSNP and SSNP with accumulation time of 10 s, illustrating the strong electric field enhancement achieved through the plasmonic self-assembly of TSNP forming “hot spots” in comparison to SSNP. The samples were prepared by drying concentrated solution of the nanoparticles with 4-MBA (0.5 mM) on a silicon wafer. The measurements were taken by using QE 65 Pro spectrometer.

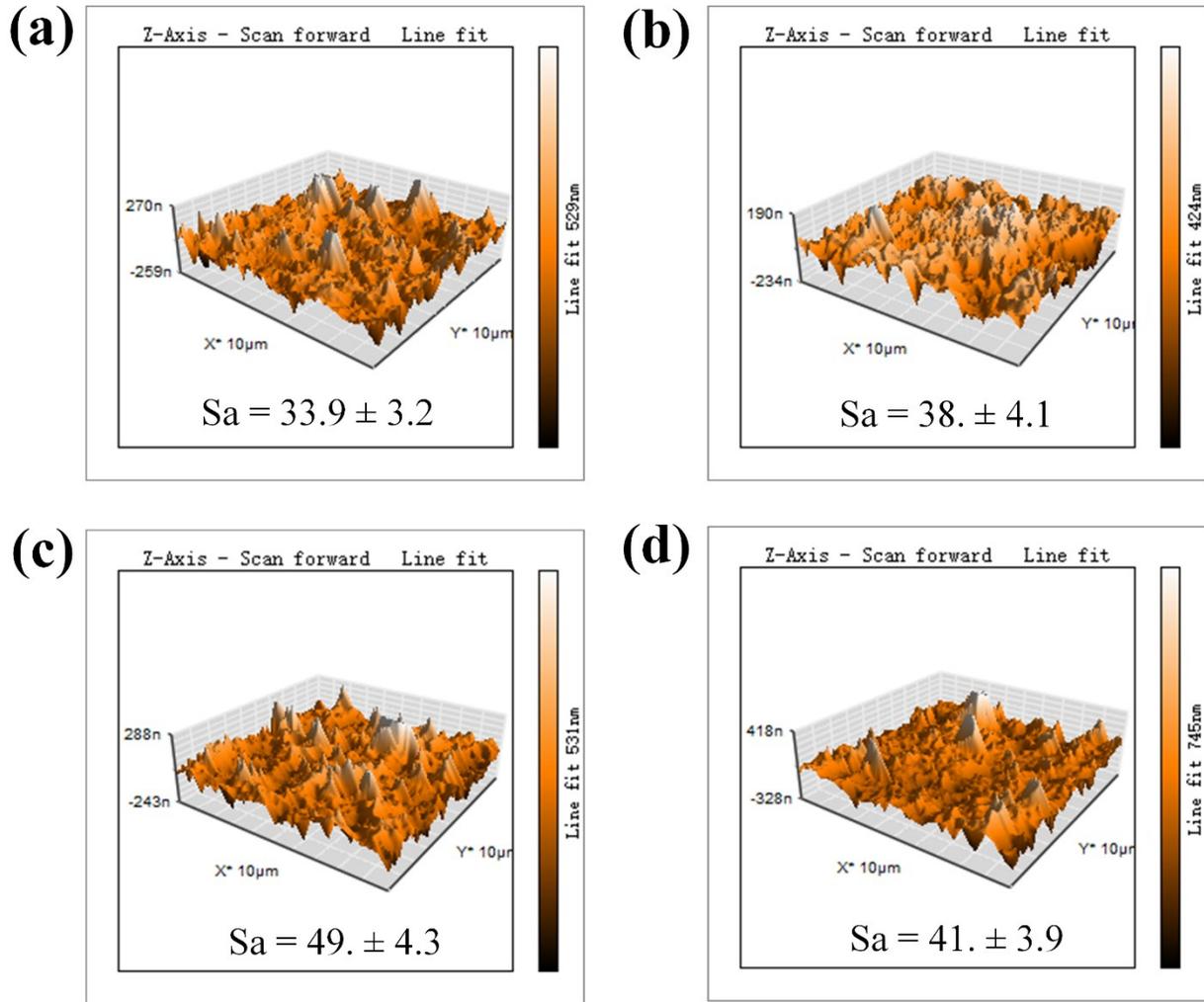


Fig. 5. AFM images of the unmodified and modified membranes illustrating their surface roughness (a) PES virgin membrane (b) PE-modified membrane (c) PE-SSNP2 membrane (d) PE-TSNP2 membrane. Results obtained are the average of three separate areas of three separate samples for each membrane type. Sa mean value is represented in nano meters (nm)

Table 1

Membrane surface characterization and filtration data of the membrane modified with PE and 2 wt.%, 30 nm size of spherical silver nanoparticles and (30 nm PE-SSNP2)

Characterization	~30 nm PE-SSNP2
Contact angle (deg.)	34 ± 1.42
ζ potential (mV)	-49 ± 0.12
Antibacterial performance	89%
Anti-adhesion performance	76 ± 2.6%
Initial flux (L m⁻² h⁻¹)	
Biofouling	103 ± 1.6
Organic fouling	96.3 ± 2.2
Bio-organic fouling	90 ± 1.9
Flux recovery rate (%)	
Biofouling	87%
Organic fouling	83%
Bio-organic fouling	79%

Note 2**Action mechanism of AgNP against microbes**

Silver nanoparticles can interact with the bacterial cell described by various studies through several ways. The primary action of the silver NP is the direct adhesion of the nanoparticle to the bacterial surface. High surface to volume ratio of the nanoparticles enables them to make strong contact with the bacterial surface, hindering the membrane properties. Surface zeta potential of silver NP plays a vital role in the bacterial attachment [1]. Extremely small size of silver nanoparticles increases the lethality by allowing them to penetrate into the bacterial cell. Particles size smaller than 5 nm is found to be easily transported through the cell membrane, resulting in DNA damage by interfering with DNA replication process which subsequently decreases the number of cells over time [2]. The release of silver ions is considered the most effective killing tool in the arsenal of silver nanoparticles. Ag⁺ ions interact with sulphur-containing proteins in the bacterial cell wall. Silver ions also found to be responsible for denaturing of ribosomes and compromising ATP production by hindering enzymes and proteins essential for Krebs cycle. Furthermore, the generation of reactive oxygen species (ROS) by silver ions can cause permanent damage to DNA molecules [3].

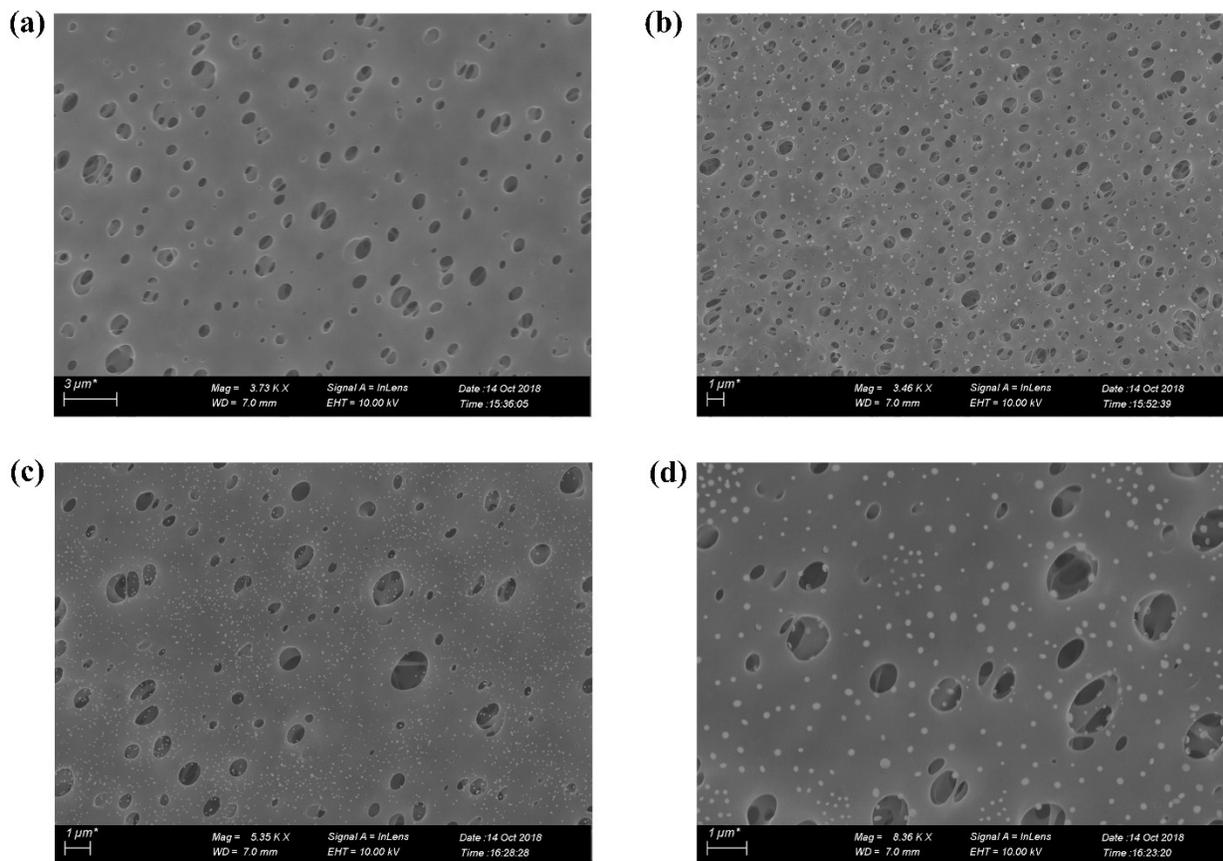


Fig. 6. SEM images of the membranes (a) Virgin PES microfiltration membrane (b) PE-TSNP2 membrane (c) PE-SSNP2 membrane with AgNP size ranging from 4-6 nm (d) PE-SSNP2 membrane modified with AgNP of average size 30 nm.

References

- [1] Chwalibog, E. Sawosz, A. Hotowy, J. Szeliga, S. Mitura, K. Mitura, M. Grodzik, P. Orłowski, A. Sokolowska, Visualization of interaction between inorganic nanoparticles and bacteria or fungi, *Int. J. Nanomedicine* 5 (2010) 1085-1094
- [2] I. Sondi, B. Salopek-Sondi, Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria, *J. Colloid Interface. Sci.* 275 (2004) 177-182
- [3] H.-J. Park, J.Y. Kim, J. Kim, J.-H. Lee, J.-S. Hahn, M.B. Gu, J. Yoon, Silver-ion-mediated reactive oxygen species generation affecting bactericidal activity, *Water Res.* 43 (2009) 1027-1032.