

## Support Information

# Perspectives on Surface Functionalization of Polymeric Membranes with Metal and Metal-Oxide Nanoparticles for Water/Wastewater Treatment

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**Table S1.** Productions and Typical Usages of Common Metal and Metal-Oxide NPs (Joo and Zhao, 2017)

NPs	Productions (ton/year)	Application
TiO <sub>2</sub>	3,000	Cosmetics, paints and coatings, plastics, consumer electronics, filters, cleaning agents
Ag	N/A	Antibacterial agents
ZnO	550	Cosmetics, plastics, polymers, paints and coatings
Al <sub>2</sub> O <sub>3</sub>	55 (AlO <sub>x</sub> )	Batteries, fire protection, grinding, metal- and bio-sorption, paints
Fe <sub>2</sub> O <sub>3</sub>	55 (FeO <sub>x</sub> )	Concrete additive, biomedical applications
Mn <sub>2</sub> O <sub>3</sub>	N/A	Catalyst
ZrO <sub>2</sub>	N/A	Bio-medical applications as component of bio-ceramic implants
Fe <sub>3</sub> O <sub>4</sub>	55 (FeO <sub>x</sub> )	Bio-chemical assays, contaminant removal, bio-manipulation

**Table S2.** The Outline Information of Polymerization Techniques Commonly Used for Membrane Surface Coating (Miller et al., 2017)

Technique	Membrane type	Advantage	Disadvantage
UV-induced polymerization	MF, UF	Rapid, simple polymerization	May damage membrane and reduce rejection rate
Chemical-induced small molecule coupling	MF, UF, NF, RO	Permanent polymerization to membrane surface	May require several synthetic steps
Chemically induced polymerization	MF, UF, NF, RO	Permanent polymerization to membrane surface; may increase rejection rate	May decrease water permeability
Plasma polymerization	MF, UF, NF, RO	Rapid polymerization; applicable to many membranes	Require plasma reactor; aggressive treatment may damage membrane
Plasma-induced graft polymerization	MF, UF, NF, RO	Simple polymerization; applicable to many membranes	Require plasma reactor; aggressive treatment may damage membrane
Corona discharge-induced polymerization	MF, UF	Rapid, simple polymerization; applicable to many membranes	Require corona discharge reactor; aggressive treatment may damage membrane

**Table S3.** Summary of the Performance of Polymeric Membranes before and after Surface Modification with Ag NPs

Membrane	Filtration type	Material	Modifica-tion method	Contact angle		Permeate flux		Surface charge		Rejection rate		Antibac-te-rial perfor-mance	TMP	Applica-tion	Refere-rence
				Before	After	Before	After	Before	After	Before	After				
Ag-coated TFC membrane	RO	AgNO <sub>3</sub> , NH <sub>4</sub> OH, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>2</sub> O	Chemical reduction	-	-	0.3 m <sup>3</sup> /m <sup>2</sup> day	0.8 m <sup>3</sup> /m <sup>2</sup> day	-	-	50%	99%	-	800 psi	TDS removal	Yang et al., 2009
Ag/MWNTs coated PAN hollow fiber membrane	UF	EDA	Self-assembly	76.5°	79.9°	117 L/m <sup>2</sup> h bar	193 L/m <sup>2</sup> h bar	-	-	-	-	Decreased ~ 80-fold of live <i>E. coli</i> in reject water	2.0 bar	Filtration bacterial water (10 <sup>6</sup> cfu/ml)	Guna-wan et al., 2011
PEI-Ag NP (MWCO: functionalized PSF membrane	UF	PEI, Ag NPs	Oxygen plasma treatment followed by post-synthesis grafting	68°	40°	75 L/m <sup>2</sup> h bar	30 L/m <sup>2</sup> h bar	-20 mV	10 mV	92 %	96%	Over 94% of inactivation rates within 1 h	95 kDa PEO solutes	Mauter et al., 2011	
PES membrane	MF	Poly(styrene-sulfonate) (PSS), PDADMAC, Ag NPs	Polyelectrolyte multilayer coating	25.4 ± 3.73°	22.1 ± 2.3°	Drop 23%	Drop 8%	-2.96 ± 0.68 mV	-51.8 ± 0.4 mV	-	-	Almost no living cells on surface after 2 h filtration	69 kPa	Water filtration with and <i>E. coli</i> (10 <sup>6</sup> cfu/mL)	Diagne et al., 2012
Ag-Am-PES membrane	UF (MWCO: 150 kDa)	Acrylamide (AM), AgNO <sub>3</sub> , NH <sub>4</sub> OH	Photografting polymerization followed by in-situ reduction	90°	40°	200 L/m <sup>2</sup> h bar	150 L/m <sup>2</sup> h bar	-	-	20%	90%	99.999% on membrane surface	0.1 Mpa	BSA filtration	Sawada et al., 2012
Ag/PVDF-g-PAA composite membrane	-	PAA, AgNO <sub>3</sub> , NaBH <sub>4</sub>	Physisorbed free radical PAA grafting followed by in-situ reduction	82.6 ± 1.5°	48.5 ± 1.2°	100 L/m <sup>2</sup> h	90 L/m <sup>2</sup> h	-	-	-	-	-	0.1 MPa	BSA filtration	Li et al., 2013
Ag-PVDF membrane	MF (pore size: 0.06 μm)	Thiol-modified P(E-b-EO), Ag NPs	Covalent self-assembly	-	-	1,742 L/m <sup>2</sup> h ± 35	1,768 L/m <sup>2</sup> h ± 37	-	-	-	-	Decrease 52 % of irreversible fouling	1 bar	Water filtration with <i>E. coli</i>	Park et al., 2013
TFC-S-AgNPs membrane	RO	Cysteamine, Ag NPs	Covalent self-suspension assembly	56.7 ± 2.2°	32.9 ± 0.7°	49.8 ± 1.7 L/m <sup>2</sup> h	69.4 ± 0.3 L/m <sup>2</sup> h	-	-	95.9 ± 0.6%	93.6 ± 0.2%	0.5 mm inhibition zone	300 psi	NaCl rejection	Yin et al., 2013
Ag/MWN Ts coated PAN membrane	UF	Ag/MWNTs	Vacuum deposited	-	-	99 L/m <sup>2</sup> h bar	236 L/m <sup>2</sup> h bar	-	-	-	-	-	-	<i>E. coli</i> removal (10 <sup>6</sup> cfu/mL)	Yoose-fi et al., 2013
Ag-PEGylated dendrimer TFC membrane	FO	PEG, MEA AgNO <sub>3</sub>	Surface chemical grafting followed by light induced reduction	68°	50°	1.7 L/m <sup>2</sup> h bar	1.8 L/m <sup>2</sup> h bar	-70 mV	120 mV	96%	96%	Live bacteria on surface decreased from 6.5% to 0.01%	10 bar	NaCl rejection	Zhang et al., 2013

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Membrane	Filtration type	Material	Modifica-tion method	Contact angle		Permeate flux		Surface charge		Rejection rate		Antibac-te-rial perfor-mance	TMP	Applica-tion	Refere-rence
				Before	After	Before	After	Before	After	Before	After				
Ag-NPs modified TFC membrane	RO	AgNO <sub>3</sub> , NaBH <sub>4</sub>	In-situ formation	-	-	2.41 ± 0.14 L/m <sup>2</sup> h bar	2.12 ± 0.2 L/m <sup>2</sup> h bar	-	-	98.85 ± 0.26%	98.85 ± 0.3%	Decrease 90.7 ± 3.8% live bacteria with 2 h	-	Salt rejection	Ben-Sasson et al., 2014
Woven fabric membrane	MF	AgNO <sub>3</sub> , NaBH <sub>4</sub>	In-situ formation	-	-	114 ± 14 L/m <sup>2</sup> h	183 ± 60 L/m <sup>2</sup> h	-	-	84 ~ 91%	100% -	-	2,250 Pa	Treat-ment of water (25 ~ 770 cfu/ mL E coli)	Mecha and Pillay, 2014
PEG-Ag immobilized PES membrane (0.09 um)	UF	PANCMA, AgNO <sub>3</sub> , PEG	Thermal grafting	62.6 ± 3.7°	15.3 ± 1.2°	513 L/m <sup>2</sup> h	702 L/m <sup>2</sup> h	-	-	95%	97%	2.5 mm width inhibition zone	0.4 bar	TOC removal	Prince et al., 2014
TFC membrane	RO	PAA, PEI, Ag NPs	Layer-by-layer (LBL) Ag NP self-assembly	66°	25°	Drop by 20 ~ 30%	-	-	-	-	Increase about 20% inactivation on surface within 1 h	> 95%	-	NaCl rejection	Rahaman et al., 2014
TFC membrane	FO	NaOH, AgNO <sub>3</sub>	In-situ formation	-	-	1 L/m <sup>2</sup> h bar	1.5 L/m <sup>2</sup> h bar	-	-	97%	95%	No visible bacterial on surface after 3 days	1 bar	NaCl rejection	Liu et al., 2015
TFC-S-BioAg membrane	NF	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>2</sub> -SH, biogenic Ag NPs	Covalent self-assembly	42.5 ± 2.2°	37.0 ± 4.5°	13.24 L/m <sup>2</sup> h	17.39 L/m <sup>2</sup> h	-	-	86.89 ± 2.10%	87.03 ± 0.99%	Almost no living cells on surface in 8 h	0.35 MPa	Na <sub>2</sub> SO <sub>4</sub> rejection	Liu et al., 2015b
TFC membrane	RO	Ar plasma, 1-vinyl imidazole (VIm), Ag NPs	Plasma polymerization followed by self-assembly	-	-	40 L/m <sup>2</sup> h	10 L/m <sup>2</sup> h	-	-	97.8 ± 0.5%	95.8 ± 0.4%	342 μm inhibition zone	15 bar	NaCl rejection	Reis et al., 2015
TFC membrane	FO	Cysteamine solution, GO/Ag NPs	Covalent bonding	55°	24°	1.5 L/m <sup>2</sup> h bar	1.4 L/m <sup>2</sup> h bar	-	-	-	-	96% inactivation on surface within 1 h	-	NaCl rejection	Soroush et al., 2015
AgNP/PE Ms-polysulfone (PSU) membranes	MF (pore size: 0.2 μm)	Ag NPs, PEMs	Ag NP deposition by suction filtration followed by LBL assembly	-	-	-	-	-	-	-	-	Reversibility of bacterial deposition to over 90%	-	-	Tang et al., 2015
Polysulfone (PSU) membrane	-	Dopamine, AgNO <sub>3</sub>	Bioinspire d PDA film followed by in-situ formation of Ag NPs by light induced reduction	70°	25°	-	-	-	-	-	-	99% inactivation of bacteria attached to the surface	-	-	Tang et al., 2015b

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Membrane	Filtration type	Material	Modifica-tion method	Contact angle		Permeate flux		Surface charge		Rejection rate		Antibac-te-rial perfor-mance	TMP	Applica-tion	Refere-rence
				Before	After	Before	After	Before	After	Before	After				
Ag NPs-APES composite membrane	-	SnCl <sub>2</sub> ·2H <sub>2</sub> O, NaI, HCl, AgNO <sub>3</sub> , NaBH <sub>4</sub>	Amination followed by in-situ formation	-	-	-	-	-	-	-	-	5.5 mm width zone around	-	-	Haider et al., 2016
Ag NPs-PDA/PSf membrane	UF	PDA, Ag(NH <sub>3</sub> ) <sub>2</sub> OH, PVP and glucose	PDA deposition and Ag NPs in-situ reduction	76°	48 ~ 52°	40 L/m <sup>2</sup> h	70 L/m <sup>2</sup> h	-	-	80%	83%	~100% after 2 h contact	0.20 MPa	BSA rejection	Huang et al., 2016
TFC membrane	FO	Dopamine, AgNO <sub>3</sub>	Dopamine self-polymerization followed by Ag in-situ formation	68.4 ± 1.9°	28.5 ± 4.6°	17.49 ± 0.42 L/m <sup>2</sup> h	13.31 ± 0.95 L/m <sup>2</sup> h	-	-	-	-	Decreased 94.4 ± 2.3% of attached live <i>E. coli</i> on surface	-	NaCl rejection	Liu and Hu, 2016
(NF90-PVA-Ag NPs) modified membranes	NF	PVA, AgNO <sub>3</sub>	PVA cross-linking followed by Ag heating in-situ formation	-	-	30.5 L/m <sup>2</sup> h	23.8 L/m <sup>2</sup> h	-	-	98.8%	99.6%	Decreased 99% live <i>E. coli</i> on surface	0.6 MPa	Na <sub>2</sub> SO <sub>4</sub> solution	Zhang et al., 2016
TA-Fe-PEI/Ag-modified TFC membrane	RO	Tannic acid (TA), ferric ion, PEI	In-situ reduction	54.3 ± 3.8°	30.8 ± 3.2°	2.95 bar	3.41 bar	-	-	98.95 ± 0.15%	99.18 ± 0.06%	Increase about 85% within 1.5 h	-	Salt rejection	Dong et al., 2017
TFC-GOAg membrane	FO	EDC, N-hydroxysuccinimide (NHS), GOAg NPs	Chemically cross-linking (NHS), GOAg NPs	38.1 ± 1.9°	33.8 ± 6.2°	12 L/m <sup>2</sup> h	15 L/m <sup>2</sup> h	-	-	-	-	Decreased > 80% of live <i>Pseudomonas aeruginosa</i> on surface	-	NaCl solutions	Faria et al., 2017
PES membrane	UF	PSBMA/poly(sodium acrylate), AgNO <sub>3</sub> , NaBH <sub>4</sub>	UV light-initiated crosslinking copolymerization followed by in-situ reduction	78.3°	40°	27.4 mL/m <sup>2</sup> h	20.5 mL/m <sup>2</sup> h	-	-	91.3%	93.4%	Strong antibacterial ability for more than 5 weeks	-	BSA rejection	He et al., 2017
PSBMA-Ag TFC membrane	FO	SBMA, AgNO <sub>3</sub> , NaBH <sub>4</sub>	Atom transfer radical polymerization (ATRP) followed by in-situ Ag reduction	74° ± 10°	21° ± 7°	16.8 L/m <sup>2</sup> h	18.4 L/m <sup>2</sup> h	-	-	-	-	95% inactivation rates for 3 h	-	-	Liu et al., 2017

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Membrane	Filtration type	Material	Modifica-tion method	Contact angle		Permeate flux		Surface charge		Rejection rate		Antibac-te-rial perfor-mance	TMP	Applica-tion	Reference
				Before	After	Before	After	Before	After	Before	After				
Ag NPs grafted TFC membranes	FO	BSA/Ag NPs	Layer-by-layer interfacial polymerization	69.7 $\pm$ 5.7°	87.4 $\pm$ 2.1°	28.3 $\pm$ 1.7 L/m <sup>2</sup> h	30.2 $\pm$ 0.8 L/m <sup>2</sup> h	-45 mV	-35 mV	-	-	Decreased > 96.4% of live <i>E. coli</i> on surface	-	-	Liu et al., 2017
Ag/SiO <sub>2</sub> -PVDF membrane	-	KOH, KMnO <sub>4</sub> , NaHSO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , TMC, Ag/SiO <sub>2</sub> NPs	Chemical treatment followed by self-assembly	81.6°	34.4°	115.1 L/m <sup>2</sup> h	550 L/m <sup>2</sup> h	-	-	82%	78%	Clear inhibition zone	0.1 MPa	BSA rejection	Pan et al., 2017
Ag(0)-zeolite coated TFC membrane	NF90	Dopamine, zeolite NPs, AgNO <sub>3</sub> , NaBH <sub>4</sub>	Thermal induced PDA/zeolite coating followed by in-situ reduction	40°	5°	2.78 $\times$ 10 <sup>-11</sup> m/s Pa	2.5 $\times$ 10 <sup>-11</sup> m/s Pa	-	-	-	-	Surface inactivation rate of ~70% on day 17	150 psi	-	Wu et al., 2017
M-PDA/-PEI-SBMA-Ag PES membrane	-	PEI, SBMA, Co-PDA, AgNO <sub>3</sub>	Co-polymerization followed by in-situ Ag NPs formation	77.6°	58°	-	-	-20 mV	-10 mV	-	-	Clear inhibition zone	-	-	Xie et al., 2017
Ag-GO coated PVDF membranes (pore size: 0.22 μm)	MF	-	Pressure-ized filtration	89.45°	81.55°	380 L/m <sup>2</sup> h	348.8 L/m <sup>2</sup> h	-	-	82%	80%	Decreased > 94.7% of live <i>E. coli</i> on surface after filtration	7 kPa	Turbidity	Ko et al., 2018
PAUI-Ag TFC RO membrane	RO	AgNO <sub>3</sub>	-	-	-	34 L/m <sup>2</sup> h	21.5 L/m <sup>2</sup> h	-	-	92%	92%	90% antibacterial efficiency	1.55 MPa	NaCl rejection	Liu et al., 2018
PSF membrane	UF	mPEG-SH, AgNO <sub>3</sub> , Dopamine	In-situ reduction	75°	70°	Drop 14%	-20.8 $\pm$ 1.5 mV	-12.9 $\pm$ 1.6 mV	42%	58%	Decreased > 96.8% of live <i>E. coli</i> on surface	1.0 bar	BSA rejection	Qi et al., 2018	
ZTFC-Ag TFC membrane	FO	1,4-Bis(3-aminopropyl)-piperazine, 3-bromo-propionic acid, AgNO <sub>3</sub> , NaBH <sub>4</sub>	Second interfacial polymerization of zwitterion acid, AgNO <sub>3</sub> , followed by in-situ reduction	72°	33°	4.92 h	2.26 h	-	-	96%	96%	> 96% antimicrobial efficiency, exposure to <i>E. coli</i> for 2 h	0.6 MPa	NaCl rejection	Qiu and He, 2018
Casein-coated Ag NPs CA membranes	UF	Cyste-amine, Ag NPs	Chemical treatment followed by self-assembly	59.6°	60°	7.6 $\pm$ 0.4 L/m <sup>2</sup> h	5.8 $\pm$ 0.6 L/m <sup>2</sup> h	-	-	12.4 $\pm$ 3.5%	32.4 $\pm$ 3.9%	Reasonable drop in live cells on surface in 48 h filtration	4.14 bar	Salt rejections	Sprick et al., 2018

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				Before	After	Before	After	Before	After	Before	After				
PES/PEI- SBMA/OS A-n-Ag membrane	UF	SBMA, PEI, oxidized sodium alginate, AgNO <sub>3</sub> , NaBH <sub>4</sub>	Layer-by-layer coating followed by in-situ reduction	64°	30°	-	-	-18 mV	0 mV	-	-	Almost no living cells on surface in 96 h test	-	-	Xie et al., 2018
Polyimide - PEI/Ag- SBMA membrane	-	PEI, AgNO <sub>3</sub> , NaBH <sub>4</sub> , SBMA	In-situ Ag reduction followed by SBMA grafting through UV radiation	45°	30°	1.4 L/m <sup>2</sup> h	31.4 L/m <sup>2</sup> h	-	-	-	-	0.5 bar	DTAB dodecyl trimethyl ammonium bromide	Zhang et al., 2018	
CA membrane	UF	DA, Tris phosphate, AgNO <sub>3</sub>	PDA coating followed by in-situ Ag NPs immobilization	76.4°	55.8°	24.7 L/m <sup>2</sup> h	113.1 L/m <sup>2</sup> h	-	-	82%	94.1% Clear inhibition zone	414 kPa	BSA rejection	Sarawathi et al., 2019	
COO- zwitterion modified Ag TFC membrane	NF	DEDA, PS aqueous solution, AgNO <sub>3</sub> , NaCl	Chemical treatment followed by in-situ formation	-	-	25 L/m <sup>2</sup> h	35 L/m <sup>2</sup> h	-35 mV	-45.3 mV	90%	95% 93.1% of reduction	0.2 MPa	Na <sub>2</sub> SO <sub>4</sub>	Yi et al., 2019	
AgNPs@Z IF-8 hybrid crystals modified PES membrane	NF (pore size: 0.22 μm)	DA, AgNPs@ZIF	PDA coating followed by self-assembly	69.8°	57.8°	~50 L/m <sup>2</sup> h	~300 L/m <sup>2</sup> h	-	-	~5%	~80% Over 90 % less than that of control membranes	0.2 MPa	BSA rejection	Feng et al., 2021	