Title: Scalable manufacturing of ZnO and TiO2 based biofouling-resistant nanostructured membranes for water purification

Context of the PhD grant:

This PhD grant is associated with the chair of excellence of the nanoscience foundation awarded to Professor Daeyeon Lee (UPenn).

Context and position of the project on the international scale

Access to clean water is not assured for major swathes of humanity. In the last century, demand grew at twice the rate of the population. The United Nation as well as the US National Academy of Engineering has indeed identified providing access to clean water as one of the Grand Challenges of the 21st century. In the Malthusian catastrophe, nearly one-fifth of the world's population lack access to clean water and a quarter of the population faces economic water shortages [1]. Membrane separations are promising alternatives to thermal separations for production of clean water because of their scalability and energy efficiency [2]. Water treatment reverse osmosis membranes have been implemented in some parts of the world (e.g., Israel) to give solutions to a small region, proving that membrane technology will play a major role in solving the water issue globally [3]. Although numerous advances in membrane technologies have been made, there are outstanding challenges that impede their widespread adoption across the world. We have identified three problems that could potentially be addressed by advances in nanoscience and technology:

1. Membrane separation is often limited by the trade-off between selectivity and permeability. Membranes that are very permeable (i.e., that give high flux) are not very selective and vice versa [4, 5].
2. Biofouling and growth of biofilms (attachment and proliferation of bacteria on surfaces) significantly compromise the performance of these membranes and cause major health hazards [6, 7].
3. Many membranes suffer from long-term stability/durability issues under prolonged usage. The membranes inevitably have to be cleaned periodically to remove biofilms and other contaminants. Chlorine-based bleach, which is the most common and effective agent, significantly damages the structural integrity of the membranes, compromising their durability [8].

Recent advances in nanostructured membranes present a versatile approach to overcoming challenges associated with trade-off between permeability and selectivity and achieving highly efficient water purification while preventing biofouling on the membrane surfaces [4, 5]. Previous studies have shown that nanoparticle-incorporated films and membranes can be used for antibacterial applications as well as efficient water purification [9]. For example, TiO_2 nanoparticle-incorporated films have shown to exhibit excellent antibacterial properties [10]. Incorporation of silica nanoparticles in polymer matrix led to fabrication of separation membranes with simultaneous enhancement of permeability and selectivity [4, 5, 11].

Unfortunately, most current methods to generate such nanostructured coatings and membranes are suitable only for lab-scale production owing to complicated fabrication steps. A critical bottleneck is the lack of robust methods to enable the cost-effective/large-scale fabrication of nanostructured membranes while maintaining the precise control over their nanoscale structures. Such membranes are typically fabricated by incorporation of nanoparticles directly into the polymer solutions for membrane formation [12]. This approach is challenging due to unfavorable interactions between the polymers and nanoparticles that drive nanoparticle aggregation, compromising the membrane structure and properties [13].

It is thus critical to develop means to fabricate nanostructured composite membranes with properties designed for specific applications and with high durability in challenging conditions based on scalable methods. We propose to develop heat- or solvent-driven infiltration of polymers into the interstices of nanoparticle/nanowire packings (capillary rise infiltration (CaRI) [14, 15] and solvent-driven infiltration of polymers (SIP) [16]) and solvent transfer-induced phase separation (STRIPS) of nanoparticle-containing ternary solutions to enable the scalable fabrication of nanocomposite membranes [17, 18].

Scientific Objectives: Scalable Nanomanufacturing of Nanostructured Membranes for Clean Water

The main objectives of this PhD thesis will be to transform the manufacturing of nanostructured composite membranes to enable their production in a scalable process suitable for large scale, low-cost manufacturing. Along the way, the PhD student will isolate key features required to maintain the advantages of these membranes, and potentially amending the process parameters of the membrane synthesis to retain key features while reducing cost and complication. The main aspects of this project are:

1. Development of nanostructured composite membranes with ZnO nanowires or TiO_2 nanoparticles, based on polymer infiltration. To achieve this objective, we aim to understand the infiltration of polymer into the interstices between nanoparticles/nanowires via capillary rise infiltration (CaRI) or solvent-driven infiltration of polymers (SIP).

2. Development of nanostructured hollow fiber membranes with dense coatings of photocatalytic nanoparticles or photopolymerizable inorganic materials (i.e, TiO_2 photoresist) via STRIPS. Membranes will be manufactured with photocatalytic nanomaterials (i.e., TiO_2 or ZnO) to impart photocatalytic activity for anti-biofouling and self-cleaning membrane fabrications.

3. In collaboration with a postdoctoral researcher, the separation performance and antibacterial/antifouling properties of membranes will be tested. Formation of biofilms and adhesion of bacteria on membranes surfaces under flowing or quiescent conditions will be investigated as a function of the structure, surface roughness, composition and wettability of our membranes under UV (photocatalytic conditions) or in dark conditions. Water purification performance of nanostructured membranes as well as their durability will be investigated.

Starting date: before October the 1th.

Contact: David Riassetto : David.Riassetto@grenoble-inp.fr
Daeyeon Lee : daeyeon@seas.upenn.edu

Laboratories and researchers:

LMGP: D. Riassetto, M. Langlet, C. Ternon http://www.lmgp.grenoble-inp.fr/
University of Pennsylvania (UPenn): D. Lee http://www.seas.upenn.edu/~leegroup/people.html
LEPMI : L. Flandin http://lepmi.grenoble-inp.fr/
LiPhy: S. Lecuyer https://www-liphy.ujf-grenoble.fr/
ILL: G. Fragneto, P. Gutfreund https://www.ill.eu/fr/

References

[1] Nations U. Water Scarcity | International Decade for Action 'Water for Life' 2005-2015". UNDP; 2006.
[2] Sholl DS, Lively RP. Seven chemical separations: to change the world: purifying mixtures without using heat would lower global energy use, emissions and pollution--and open up new routes to resources. Nature 2016;532:435-438.
[3] Greenlee LF, Lawler DF, Freeman BD, Marrot B, Moulin P. Reverse osmosis desalination: water sources, technology, and today's challenges. Water research 2009;43:2317-2348.
[4] Merkel TC, Freeman BD, Spontak RJ, He Z, Pinnau I, Meakin P, Hill AJ. Ultrapermeable, Reverse-Selective Nanocomposite Membranes. Science 2002;296:519-522.
[5] Robeson LM. The upper bound revisited. Journal of Membrane Science 2008;320:390-400.
[6] Nguyen T, Roddick FA, Fan L. Biofouling of water treatment membranes: a review of the underlying causes, monitoring techniques and control measures. Membranes 2012;2:804-840.
[7] Zodrow K, Brunet L, Mahendra S, Li D, Zhang A, Li Q, Alvarez PJ. Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal. Water research 2009;43:715-723.
[8] Glater J, Hong S-k, Elimelech M. The search for a chlorine-resistant reverse osmosis membrane. Desalination 1994;95:325-345.
[9] He L, Riassetto D, Bouvier P, Rapenne L, Chaix-Pluchery O, Stambouli V, Langlet M. Controlled growth of silver nanoparticles through a chemically assisted photocatalytic reduction process for SERS substrate applications. J Photochem Photobiol A: Chem 2014;277:1-11.
[10] Messaoud M, Chadeau E, Brunon C, Ballet T, Rappenne L, Roussel F, Leonard D, Oulahal N, Langlet M. Photocatalytic generation of silver nanoparticles and application to the antibacterial functionalization of textile fabrics. J Photochem Photobiol A: Chem 2010;215:147-156.
[11] Chan EP, Mulhearn WD, Huang YR, Lee JH, Lee D, Stafford CM. Tailoring the Permselectivity of Water Desalination Membranes via Nanoparticle Assembly. Langmuir 2014;30:611-616.
[12] Yin J, Deng B. Polymer-matrix nanocomposite membranes for water treatment. Journal of Membrane Science 2015;479:256-275.
[13] Soroko I, Livingston A. Impact of TiO 2 nanoparticles on morphology and performance of crosslinked polyimide organic solvent nanofiltration (OSN) membranes. Journal of Membrane Science 2009;343:189-198.
[14] Hor JL, Jiang Y, Ring DJ, Riggleman RA, Turner KT, Lee D. Nanoporous Polymer-Infiltrated Nanoparticle Films with Uniform or Graded Porosity via Undersaturated Capillary Rise Infiltration. ACS Nano 2017;11:3229-3236.
[15] Huang Y-R, Jiang Y, Hor JL, Gupta R, Zhang L, Stebe KJ, Feng G, Turner KT, Lee D. Polymer nanocomposite films with extremely high nanoparticle loadings via capillary rise infiltration (CaRI). Nanoscale 2015;7:798-805.
[16] Manohar N, Stebe KJ, Lee D. Solvent-driven Infiltration of Polymers into Nanoparticle Films. ACS Macro Letters under review.
[17] Haase MF, Stebe KJ, Lee D. Continuous Fabrication of Hierarchical and Asymmetric Bijel Microparticles, Fibers, and Membranes by Solvent Transfer-Induced Phase Separation (STRIPS). Advanced Materials 2015;27:7065-7071.
[18] Haase MF, Sharifi-Mood N, Lee D, Stebe KJ. In Situ Mechanical Testing of Nanostructured Bijel Fibers. ACS Nano 2016;10:6338-6344.