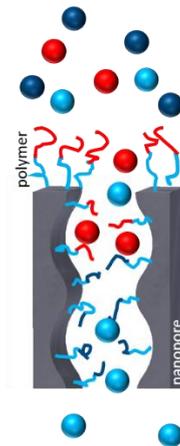


Recent Trends in Nanopore Polymer Functionalization

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Functional nanopores play an essential role in many biotechnological applications such as sensing, or drug delivery. Prominent examples are polymer functionalized ceramic or solid state nanopores. Intensive research efforts led to a plethora of polymer functionalized nanopores demonstrating gated molecular transport upon basically all common stimuli. Nevertheless, nature's biological pore transport precision is unreached. This can be, among others, ascribed to limits in design precision especially with respect to functionalization. Recent trends in polymer functionalized nanopores address the role of confinement and polymerization control, strategies towards more sustainable reaction conditions, such as visible light initiation, and strategies towards nanoscale local placement of polymer functionalization. Resulting nanopore performance reaching from multi-stimuli responsive and concerted release or transport, side selective separation and selective detection.



1. Introduction

Biological ion channels exhibit selective and spatiotemporal transport control. With this nature has set the unmatched standard for nanopore transport in terms of complexity, regulated selectivity, directional permeability, and temporal control. To advance biotechnology, e.g. drug delivery, sensing, or separation, nature's performance has to be implemented into robust technological nanopores[1-5]. This requires nanoporous materials with highly defined porous structure and precise functionalization. Within the last two decades a large portfolio of functional nanoporous materials has been explored. Examples are mesoporous silica, or ion track etched nanopores. The combination of these nanoporous materials with responsive

molecules, and above all responsive polymers, has led to a plethora of transport gating functional nanopores. Especially porous silica materials have been transformed into a diversity of functional hybrid materials and served to push the limits of polymer functionalization because of their versatile surface chemistry. Using responsive polymers all common stimuli, such as pH, temperature, light, or voltage have been demonstrated to gate molecular transport (Figure 1). Many reviews, including very recent ones[6-9], summarize achievements in functional nanopores, their transport characteristics, and application potential. In spite of many examples of switchable nanopores transport selectivity, spatiotemporal transport control, or transport direction remains a challenge but at the same time represents a key step towards complex nanosystem design and biotechnological applications. Both are a current driving force to advance precision of polymer functionalization in nanoporous materials which then become multi-stimuli responsive, multifunctional, and serve a specific application such as drug delivery or sensing even down to single molecule detection. At the same time polymerizations in nanopores itself are heavily investigated with respect to understanding confinement effects and to increase sustainability of synthesis procedures. In this review we highlight recent trends in polymer nanopore functionalization, which could help to further approach the precision level of transport control in nature and to design complex, multifunctional nanosystems for biotechnology.

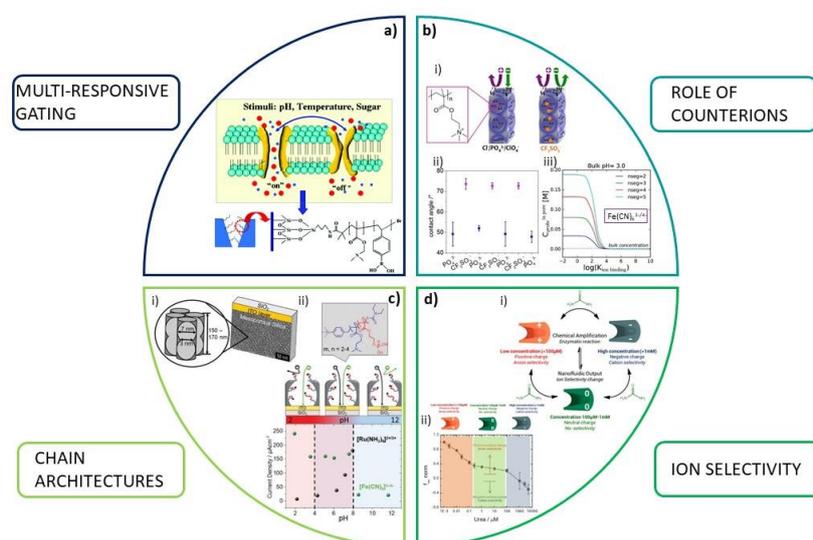


Figure 1: **a)** A triple-responsive nanofluidic diode under external stimuli including temperature, pH and sugar. The multi-responsive copolymer poly(*N,N*-dimethylamino ethyl methacrylate-*co*-4-vinyl benzene boric acid) (P(DMAEMA-*co*-VPBA)) was polymerized onto the interior surface of a single glass conical nanochannel and allows switching the nanochannel between high and low ion conducting states. Reprinted with permission from *Nanoscale*, **2017**, 9, 433 [10], Copyright (2017), American Chemical Society. **b)** (i) Effect of different counterions on the wetting and ionic transport in poly(2-(methacryloyloxy)ethyltrimethylammonium chloride)-functionalized silica mesopores. Ionic pore accessibility is strongly dependent on the counterion. (ii) Measuring contact angles on such modified mesoporous

silica thin films, a reversible switching of the advancing contact angle between PO_4^{3-} and ClO_4^- can be observed. (iii) Averaged in-pore concentration of $\text{Fe}(\text{CN})_6^{3-/4-}$ as a function of the log of the binding constant at pH 3, showing how to adjust the pores from positively charged when no ion binding occurs to negatively charged (from the deprotonation of surface silanol groups) when binding is strong. Reprinted with permission from *Langmuir*, **2018**, 34, 20, 5943-5953 [11]^{*}, Copyright (2018), American Chemical Society. **c)** (i) Responsive 2-dimethylamino)ethyl methacrylate)-*block*-2-methacryloyloxy)ethyl phosphate (DMAEMA-*b*-MEP)- functionalized mesoporous silica films show complex gating behavior. (ii) Measured ion permselectivity (of $\text{Fe}(\text{CN})_6^{3-/4-}$) of such modified silica films can be gradually adjusted from anion selective at acidic pH (red area) over an open state between approximately pH 4-8 to a cation selective nanopore at basic pH (blue area). Reprinted with permission from *Small*, **2019**, 15, 1902710 [12]^{*}, Copyright (2019), The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. **d)** Urea-dependent behavior of the PET/PAH/Ur (polyethylene terephthalate/poly(allylamine)/urease) modified nanochannel. (i) With increasing amount of urea in solution, the nanofluidic system shifts progressively from anion selectivity to cation selectivity, or from positive to negative rectifications, which can be shown by the (ii) rectification efficiencies (f_{rec}) varying with urea concentration. Reprinted with permission from *Nano Lett.*, **2018**, 18, 3303–3310 [13]^{*}, Copyright (2018), American Chemical Society.

2. Controlled Polymerization in Nanopores

Polymers carry multiple functions per surface anchor point and can be stimuli-responsive. This allows to induce time-dependent gating of nanopores based on changes in charge density, wettability, or ligand binding. Thereby nanopore filling, or polymer composition strongly determine the nanopore properties such as molecular transport. Highest polymer amount and nanopore filling control in nanopores has been achieved using grafting from polymerizations. In addition, control over polymer chain architecture has recently become accessible through surface-initiated controlled radical polymerizations (SI-CRP). With respect to detailed reviews on SI-CRP in solution and on surfaces we refer the interested reader to reviews by the group of Klok[14,15] ^{**} and further reviews on *Atom-Transfer Radical Polymerization* (ATRP)[16], *Reversible Addition Fragmentation Chain Transfer polymerization* (RAFT)[17] and *photo iniferter mediated polymerization* (PIMP) polymerizations[18]. The most important polymerization techniques applied in nanopores are ATRP, RAFT and PIMP (Fig. 2).

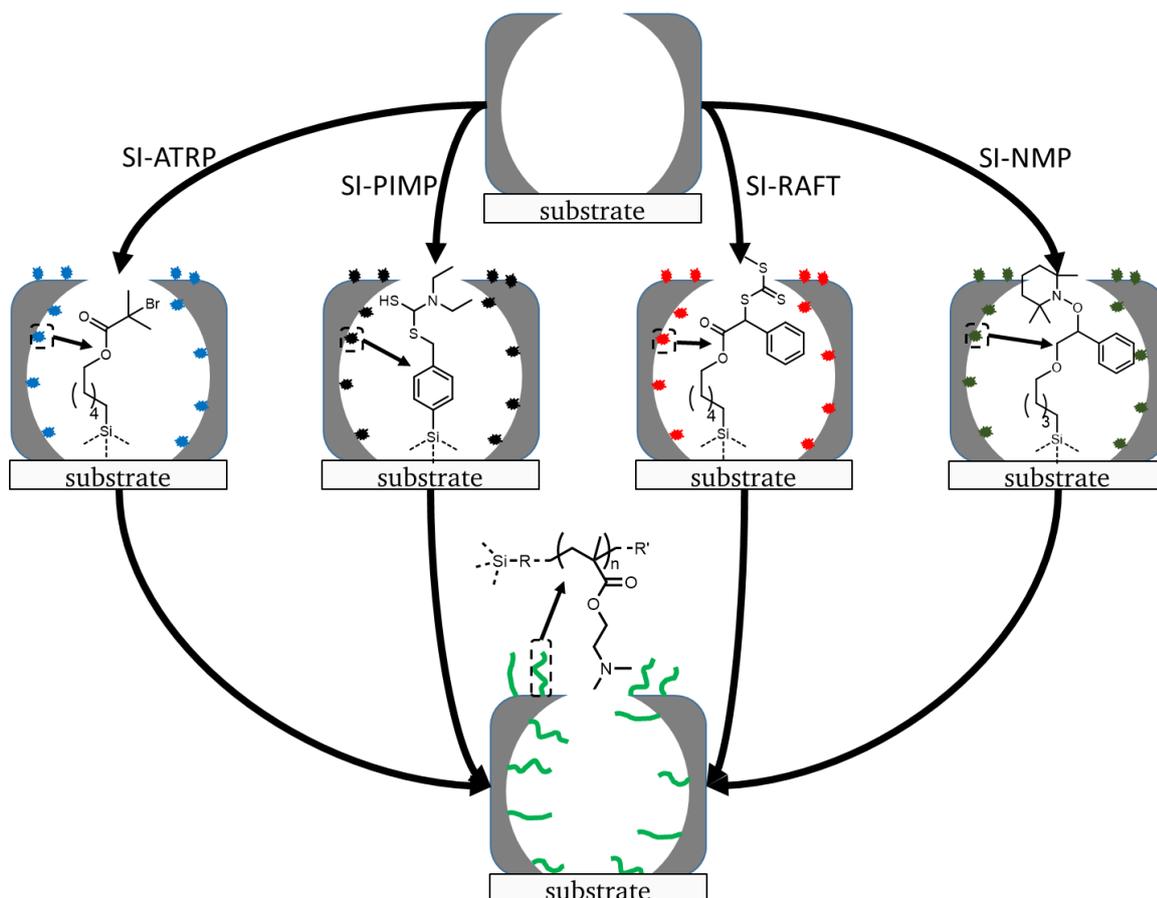


Figure 2. Schematic illustration of DMAEMA grafting from polymerization in a mesopore by SI-ATRP, SI-PIMP, SI-RAFT and SI-NMP (from left to right) at the pore wall. Polymerization control in ATRP is dependent on an activation-deactivation equilibrium depending on the presence of a transition metal complex and a dormant alkyl halide terminated polymer chain and monomers which all have to diffuse into the nanopore. The feature of PIMP polymerizations is that no further additives are needed since the iniferter is able to initiate the polymerization transFER the chains and TERminate (INI-FER-TER) the polymerization. The RAFT polymerization resembles mainly a conventional free radical polymerization with the addition of a *Chain Transfer Agent* (CTA), such as dithiocarbamate to enhance control. For a SI-RAFT either the initiator or the CTA can be attached to the surface. NMP uses a nitroxide radical to reversibly activate–deactivate the propagating polymer chain.

2.1 Surface Initiated Atom Transfer Radical Polymerization (SI-ATRP)

In the last years, different efforts turning SI-ATRP into a more environmentally friendly method are pursued. Since 2007[16] common Cu(0)-catalysts are used while performing the polymerization under ambient conditions. Yan *et al.* [19,20] * used this technique to polymerize poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) brushes on larger scale surfaces. Huang *et al.* [21] used photoATRP with FeBr₃ for surface modification of mesoporous silica. Even though SI-ATRP is widely used for many years in nanopores and has been systematically investigated in nanoporous silica[22] not every aspect is fully understood yet, especially regarding nanoconfinement with pore diameters below 15 nm. Regarding confinement effects

Chen et al. [23,24] showed that polymerization of styrene in mesoporous materials such as SBA-15 or MCM-41 lead to higher molecular weight, polydispersity, and glass transition temperature (T_g). Most recently, SI-ATRP has been employed to produce dual stimuli, pH and light responsive nanocarriers based on mesoporous silica particles[25]* or multi-stimuli responsive nanopores[10], low fouling nanoparticles with reduces cell uptake[26], and antimicrobial surfaces[27]. Polymer modification by SI-ATRP has also led to silica nanoparticles that are more salt tolerant and temperature stable[28], and a combination of MCM-41 mesoporous silica particles with polymer coated, silica covered magnetic nanoparticles was used to detect salmonella in milk samples[29]. That large scale production of polymer brush functionalized surfaces has been demonstrated by *Sato et al.* [30] * using a sol-gel based roll-to-roll or wire-bar coating process, which in combination with a technique developed by *Herzog et al.* [31]* can be transferred to nanoporous materials in the near future.

2.2 Surface Initiated Reversible Addition-Fragmentation Chain Transfer (SI-RAFT) and Photo Iniferter Mediated Polymerization (SI-PIMP)

For SI-RAFT and SI-PIMP numerous recent examples of nanopore and especially mesoporous silica functionalization are reported. A strong focus of current research is dedicated towards a better understanding of the surface-initiated polymerizations as well as to create more complex surfaces. *Zheng et al.* [32] grafted chloroprene to silica nanoparticles by SI-RAFT and demonstrated that even on particles surfaces SI-RAFT of chloroprene is slower than free RAFT polymerization. *Silies et al.* [11,33] * successfully polymerized 2-(methacryloyloxy)ethyltrimethylammonium chloride by SI-PIMP in silica mesopores (pore diameter <10 nm) while controlling pore filling. Investigating the influence of counter ions on ion transport and wetting, modulation of wetting from hydrophilic to hydrophobic and modulation of transport from closed to open nanopores was demonstrated. Using the same iniferter *Tom et al.* [12,34] ** achieved high pore filling degrees, successfully re-initiated the polymerizations and thus graft multi-stimuli responsive block-cooligomers in silica mesopores with a diameter of less than 10 nm. Interestingly, these mesopores do not show bipolar ion exclusion[12] as observed for zwitterionically charged nanopores[35,36]. *Chen et al.* [37,38] used light induced SI-RAFT to successfully graft zwitterionic and thermoresponsive monomers on fluorescent silica nanoparticles in the presence of oxygen. Although not surface initiated, *Xu et al.* [39]* used silica SBA-15 of pore sizes between 8-27 nm as micro-reactors for RAFT polymerizations and showed, that the spatial confinement leads to narrower molecular weight distributions. Magnetic mesoporous silica particles were modified with disulfide bonds by *Hegazy et al.* [40]* and the thermo responsive polymer poly(2-nitrobenzyl acrylate) via RAFT polymerization to create a dual stimuli drug release platform. *Wang et al.* [41] produces antimicrobial surfaces on

mesoporous silica by the formation of poly (3-acrylamidopropyl) trimethylammonium chloride brushes by SI-RAFT polymerizations.

2.3 Non Radical Controlled Surface Initiated Polymerizations

Other controlled polymerization techniques such as SI-Nitroxide-Mediated Polymerization (SI-NMP), ring-opening metathesis polymerization (ROMP) or ionic polymerization play only a minor role for nanopore functionalization especially regarding nanoporous silica. Although anionic polymerization has been applied to silica surfaces[42] the reactive nature of the silica surface hydroxyl groups, the remaining water traces and the synthetically demanding ionic polymerization offer no attractive alternative to SI-CRP techniques. ROMP on the other hand offers mild reaction conditions and can be used to generate block copolymers and complex polymer architectures on surfaces[43] but reaction control on surfaces remains limited. In addition, ROMP allows the synthesis of polymers which are inaccessible by radical polymerization, such as e.g. light-responsive spiropyran homopolymers. *Krohm et al.*[44] grafted norbornene-based polymers with a spiropyran- and spirooxazine side chain from mesoporous silica thin films using SI-ROMP. *Eder et al.*[45] used SI-ROMP in a *grafting-to* approach to combine norbornene-functionalized mesoporous silica with different derivatives of poly(ferrocene) using a Schrock-initiator.

3. Visible Light Induced Polymer Functionalization of Nanopores

Not only with respect to sustainable polymerization but as well regarding miniaturization and improved local resolution as well as for complex nanosystem design visible light induced polymerization is an emerging topic. Within the last years, most of the common polymerization techniques have been made visible light compatible. It has to be noted that visible light refers to a very broad wavelength range and even polymerizations initiated below 380 nm are sometimes categorized as visible light initiated. Here, we refer to visible light for wavelength larger than 380 nm. The majority of visible light polymerizations has been developed and optimized in solution.

3.1 Available Wavelengths for Visible Light Induced Polymerization

In solution, the probably most investigated visible light-initiated polymerization reaction is ATRP. Recent developments show ATRP initiation at 392 nm in aqueous solution using a copper catalyst[46]. The initiation wavelength has been further shifted to 464 nm by *Zhu* and coworkers[47] using $[\text{Ir}(\text{ppy})_3]$ as photoredox catalyst, the catalyst has been recycled after polymerization. Instead of recycling the catalyst *Yagci* and coworkers [48]* performed a metal-free ATRP with the use of perylene under irradiation of 400-500 nm. Besides ATRP, several

radical and ionic polymerizations are reported to be initiated by visible light. Recently, a radical-promoted cationic polymerization, initiated by 400-500 nm was achieved using an acylsilane photoinitiator at room temperature[49]. *Kaya et al.*[50] demonstrated free radical-promoted cationic polymerizations using organotellurium compounds in the presence of diphenyliodonium hexafluorophosphate initiated at 450 nm. Even ROMP initiated at 450-480 nm has been reported: *Boydston* and coworkers[51] used divinyl ether initiators and a photoredox catalyst to polymerize norbornene with blue light (450-480 nm). *Rovis* and coworkers[52]* reported a blue light controlled ROMP and photolithographic olefin metathesis polymerization (PLOMP) with 2,4,6-triphenylpyrylium tetrafluoroborate and $[\text{RuCl}_2(\text{CHPh})(\text{IMes})_2]$ as catalysts.

It has to be noted that only few examples demonstrate initiation at higher wavelength between 500 nm and 700 nm. Polymerization suitable for initiation in this wavelength range are for example a Photoinduced Electron Transfer (PET)-RAFT[53], which was used to polymerize *o*-nitrobenzyl methacrylate under irradiation of red (635 nm) and yellow (590 nm) light. Another example are dye-sensitized polymerizations, in which the wavelength is determined by choosing the dye e.g. to 660 nm using methylene blue. A significant number of visible light initiated polymerizations has been transferred to planar surfaces including RAFT[54-59] and ATRP [60-62].

3.2 Visible Light Induced Nanopore Functionalization

Functionalization of nanopores using visible light-initiated polymerizations is much less explored. To avoid scattering this requires sufficiently small pore-sizes or refractive index matching. The group of *Cai*[63] used the RAFT agent 4-cyano-4-(ethylsulfanylthiocarbonylsulfanyl)pentanoic acid (CEP) for a visible light mediated RAFT at 420 nm with polymerization-induced self-assembly to synthesize hydrogen-bonded pore-switchable cylindrical vesicles. Analyzing the polymer amount and pH-dependent porosity they show that nanotubes have a more sensitive switchable porosity as compared to vesicles. *Wei* and coworkers[37]** functionalized mesoporous silica nanoparticles with zwitterionic polymers using RAFT with CEP as RAFT agent at 480 nm. *Fan et al.*[64]** reported functionalized microcapsules, which impart a self-healing to hydrogels using a visible light induced PET-ATRP with rhodamine B as catalyst to functionalize porous carbon nanospheres with poly(4-vinylpyridine). *Ma et al.*[65] achieved a visible light (380 nm) induced SI-ATRP on SBA-15 using the photocatalyst 10-phenylphenothiazine (PTH). By functionalization with PMMA improved adsorption capacity for toluene could be observed. Recently, the group of *Silván*[66]** described a visible light assisted organosilane assembly (VLAO) on mesoporous silicon by irradiation with 700 nm. Visible light supports the surface oxidation of the

mesoporous silicon allowing a reaction with organosilanes (in this case 3-aminopropyltriethoxy-silane and 1*H*,1*H*,2*H*,2*H*-perfluorodecyl-triethoxy-silane). Functionalization of mesoporous silica thin films at wavelength between 400-700 nm was demonstrated using coinitiator (e.g. tertiary amine)/dye systems. This system is especially advantageous because it allows tuning the initiation wavelength by selecting suitable dyes. Polymerizations were successfully carried out at wavelength of 390 nm while using 2-chlorothioxanthone or with 660 nm while using methylene blue as dye[67].

4. Nanolocal Placement and Asymmetric Design of Functional Nanopores

Precise local functional placement on surfaces and especially in nanopores is expected to improve complex nanosystem design by allowing multifunctionality and locally controlled multiresponsivity, nanoscale gradients, or nanoscale pattern formation. To induce precise local placement of molecules and polymers into nanopores with ideally nanoscale precision functionalization technology beyond photolithography or soft lithography is required. Concerning planar surfaces and microchips *Rühe*[68]^{*} gives an overview on nanofabrication techniques.

4.1 Asymmetric design of nanoporous materials

Regarding nanopores already asymmetric shape in ion-track etched nanopores shows interesting diode like (side-selective) transport on a single nanopore level[69-71]. By introducing asymmetry into geometry (e.g. conical nanopores), but as well into functionalization, side-selective and multiresponsive, double-gated and multiresponsive ion transport has been demonstrated[68,72,73]. Interestingly, these activities have not been intensified within the last years. Instead, research on double- or multilayer membranes was strongly pursued. Prominent examples are Janus membranes and diode-like nanochannel membranes. *Jiang* and coworkers presented PET/PTFE-based Janus membranes for side-selective oil water separation (Fig. 3a)[74]^{**} as well as PSS (poly)styrenesulfonate)/AAO (anodic alumina oxide)- and kaolinite-based Janus membranes for selective ion transport in the context of osmotic-energy based energy conversion[75,76] ([75]^{*}). Based on these examples various Janus membranes demonstrating side-selective oil-water separation[77]^{*} and osmosis transport[78]^{**} have been developed within the last two years. Functionalizing only the outer planar surface of mesoporous films allows to investigate the interplay of orthogonally functionalized layers. As a recent example PNIPAM-capped mesoporous thin films have been equipped with thermosensitive cation-selectivity based on such concerted function[79]. Further developments discuss in-situ functionalized mesoporous silica[80]^{**} for multilayer film

generation. As an example, *Bathfield et al.*[81] synthesized PEO-*b*-PNIPAM from a PEO macroinitiator and subsequent RAFT polymerization, and applied them as templates to produce thermosensitive drug-loaded OMS (silica-based ordered mesoporous materials). The mesoporosity of these materials was then created by water washing below the LCST of PNIPAM. The approach of local in-situ functionalization in combination with printing processes[31] bares great potential for model system design to understand nanopore performance in hierarchical materials. Understanding the role of nanopores and their distribution within hierarchical materials is essential to understand material function as has been demonstrated for paper wetting and paper based fluidics by *Nau et al.*[82]*. Blocking fiber swelling and nanopore accessibility using a thin silica coating results in side selective oil-/water permeation.

4.2 Nanoscale local functionalization

Besides multilayer Janus membrane generation and ion-track etched single pore functionalization material deposition and resulting orthogonal surface chemistry has been used as well recently to achieve local resolution. One recent example is the synthesis of an ordered, vertically aligned mesoporous silica thin film with propyl-copper-phosphonate or propyl-silver-carbonate groups localized exclusively at the pores bottom (Fig. 3b)[83]**. Going beyond double layer formation nanolocal placement of polymers into nanopores with high precision is an ongoing challenge. Nanoscale local functionalization on surfaces has been achieved e.g. by dip-pen-lithography and two-photon lithography. While dip-pen lithography remains limited to monolayers, and is time-consuming, scanning near-field optical microscopy (SNOM) and beam-pen lithography, in combination with two-photon polymerizations or cross-linking reactions, incorporate challenges, such as writing speed, difficulty controlling the amount of light and the development of suitable polymerization systems, but could potentially be combined with nanoporous materials and especially films. Another very promising concept to confine nanopore functionalization and polymerization to the nanoscale, and thus below the diffraction limit, is the use of localized near fields such as surface plasmons[84]. Pioneering work by *Kreiter*[84,85] and *Soppera*[86], exploiting the excitation of locally enhanced optical near-field of silver nanoparticles achieving a sub-10 nm optical resolution of photopolymerization at metal nanoparticles using visible light. Thereby the required polymerization wavelength which is determined by the near-field generating metal and usually is located within the visible or even infrared wavelength range remains a challenge but recently becomes accessible. The first example of surface plasmon-induced polymerization with mesoporous silica thin films was presented by *Herzog et al.*[87] still not showing nanolocal control. Nevertheless, these films provide polymer controlled ionic permselectivity. Structured chemical surface functionalization

with nanoscale local resolution was demonstrated by *Nguyen et al.*[88] through aryl film grafting covalently bonded on gold nanostripes. Additionally, using polarized light for plasmon excitation allows regioselective multifunctionalization of gold nanodisks (Fig. 3c)[89]**. By exploiting the strong near-field enhancement at the tips of crescent-shaped nanostructures, they were site-selectively modified (Fig. 3d)[90]**. These recent advances in precise, nanoscale arrangement of functionalizations can be expected to be transferred to nanopores in the near future.

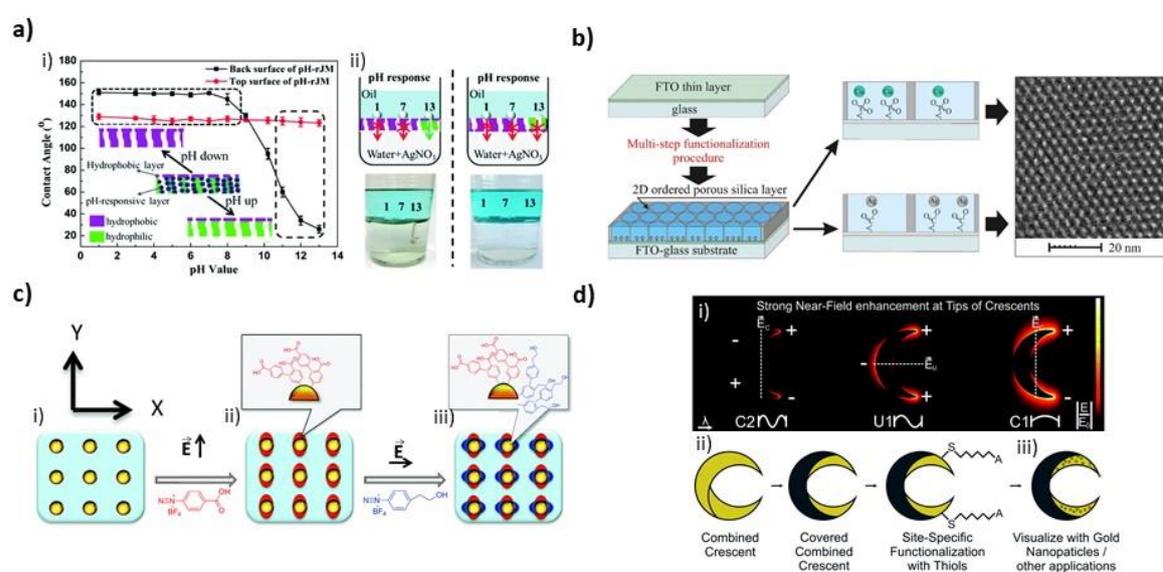


Figure 3. a) pH responsive Janus membrane realizing selective permeation of water droplets in oil. (i) pH dependent water contact angle at the top and the bottom of the Janus membrane. (ii) Illustrations and photographs confirming selective, pH dependent permeation of water droplets (pH = 1, 7, 13. left); water droplets with different pH values were blocked after inverting the pH responsive Janus membrane (right). Reprinted with permission from *Nanoscale Horiz.*, **2018**, 3, 53-57 [74], Copyright (2017), The Royal Society of Chemistry. b) Multi-step synthesized ordered porous silica thin layer with vertically aligned pores containing copper and silver ion binding groups exclusively at the pores bottom. Reprinted with permission from *Microporous and Mesoporous Materials*, **2019**, 274, 356-362 [83], Copyright (2018), Elsevier. c) Nanolocal multifunctionalization of gold nanodisks under irradiation with polarized light. (i) The nanostructures were incubated in an aqueous solution of carboxyphenyl diazonium salt and (ii) irradiated with a polarized laser in y-direction, followed by (iii) incubating those nanostructures in an aqueous solution of hydroxyethyl phenyl diazonium salt under laser irradiation in x-direction. Reprinted with permission from *Nanoscale Horiz.*, **2018**, 3, 53-57 [89], Copyright (2018), The Royal Society of Chemistry. d) Nanolocal functionalization in the regions of plasmon enhancement of gold nanocrescents. (i) Nanocrescents can evoke the fundamental dipole resonance (C1), the first order resonance (U1) and the second order resonance (C2). (ii) First, a combined crescent with extended contour *via* two gold deposition steps is produced. Subsequently, the nanocrescents are partially covered by evaporating a blocking layer. Finally, the structure can be functionalized with thiols, which exclusively binds to the free gold surface. (iii) The successful site-specific functionalization is demonstrated by electrostatically adsorb gold nanoparticles. Reprinted with permission from *Nanoscale Adv.*, **2020**, Advance Article [90], Copyright (2020), The Royal Society of Chemistry.

Conclusion

Responsive polymer functionalized nanopores have made first steps towards nature inspired nanopore performance accessible and hold promise for the design of complex nanosystems in the context of biotechnology. Functionalization concepts have been demonstrated to enable transport gating upon basically all common stimuli, gradual transport control, side selective transport in Janus membranes, and concerted transport control in double layer architectures. Recent developments in nanopore polymer functionalization focus on more sustainable functionalization, e.g. using visible light, enhanced control and understanding of confinement effects as well as precise local placement of polymers into nanopores. Functional asymmetry is envisioned to transform side selective transport into precisely directed, selective transport. These activities will not only result in new synthesis technologies, but as well push the development of complex nanosystems and alongside this, enable and improve technologies such as drug delivery, sensing, water management or energy conversion.

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References

1. Castillo RR, Lozano D, Gonzalez B, Manzano M, Izquierdo-Barba I, Vallet-Regi M: **Advances in mesoporous silica nanoparticles for targeted stimuli-responsive drug delivery: an update.** *Expert Opin Drug Deliv* 2019, **16**:415-439.
2. Wang Y, Sun S, Zhang Z, Shi D: **Nanomaterials for Cancer Precision Medicine.** *Adv Mater* 2018, **30**:1705660.
3. Knežević NŽ, Gadjanski I, Durand J-O: **Magnetic nanoarchitectures for cancer sensing, imaging and therapy.** *Journal of Materials Chemistry B* 2019, **7**:9-23.
4. Nasir T, Herzog G, Hebrant M, Despas C, Liu L, Walcarius A: **Mesoporous Silica Thin Films for Improved Electrochemical Detection of Paraquat.** *ACS Sens* 2018, **3**:484-493.
5. Zhang H, Tian Y, Jiang L: **Fundamental studies and practical applications of bio-inspired smart solid-state nanopores and nanochannels.** *Nano Today* 2016, **11**:61-81.
6. Fu L, Zhai J: **Biomimetic stimuli-responsive nanochannels and their applications.** *Electrophoresis* 2019, **40**:2058-2074.
7. Zhu Z, Wang D, Tian Y, Jiang L: **Ion/Molecule Transportation in Nanopores and Nanochannels: From Critical Principles to Diverse Functions.** *J Am Chem Soc* 2019, **141**:8658-8669.
8. Perez-Mitta G, Toimil-Molares ME, Trautmann C, Marmisolle WA, Azzaroni O: **Molecular Design of Solid-State Nanopores: Fundamental Concepts and Applications.** *Adv Mater* 2019, **31**:e1901483.
9. Zhang Z, Huang X, Qian Y, Chen W, Wen L, Jiang L: **Engineering Smart Nanofluidic Systems for Artificial Ion Channels and Ion Pumps: From Single-Pore to Multichannel Membranes.** *Adv Mater* 2019:1904351.
10. Zheng YB, Zhao S, Cao SH, Cai SL, Cai XH, Li YQ: **A temperature, pH and sugar triple-stimuli-responsive nanofluidic diode.** *Nanoscale* 2017, **9**:433-439.

11. Silies L, Gonzalez Solveyra E, Szeleifer I, Andrieu-Brunsen A: **Insights into the Role of Counterions on Polyelectrolyte-Modified Nanopore Accessibility.** *Langmuir* 2018, **34**:5943-5953.

This study considers external influences on nanopores, which is extremely important in real applications.

12. Brilmayer R, Hess C, Andrieu-Brunsen A: **Influence of Chain Architecture on Nanopore Accessibility in Polyelectrolyte Block-Co-Oligomer Functionalized Mesopores.** *Small* 2019:1902710.

This study represents the first systematic investigation of block-co-polymer/oligomer synthesis and resulting transport in nanopores.

13. Perez-Mitta G, Peinetti AS, Cortez ML, Toimil-Molares ME, Trautmann C, Azzaroni O: **Highly Sensitive Biosensing with Solid-State Nanopores Displaying Enzymatically Reconfigurable Rectification Properties.** *Nano Lett* 2018, **18**:3303-3310.

This study is an example of bioinspired smart nanopores and demonstrating the versatility of nanopore application in sensing.

14. Zoppe JO, Ataman NC, Mocny P, Wang J, Moraes J, Klok HA: **Surface-Initiated Controlled Radical Polymerization: State-of-the-Art, Opportunities, and Challenges in Surface and Interface Engineering with Polymer Brushes.** *Chem Rev* 2017, **117**:1105-1318.

This review provides in depth information on the state of SI-CRP with all basic informations.

15. Badoux M, Billung M, Klok H-A: **Polymer brush interfaces for protein biosensing prepared by surface-initiated controlled radical polymerization.** *Polymer Chemistry* 2019, **10**:2925-2951.

This review provides in depth information on the state of SI-CRP with all basic informations.

16. Matyjaszewski K, Dong H, Jakubowski W, Pietrasik J, Kusumo A: **Grafting from surfaces for "everyone": ARGET ATRP in the presence of air.** *Langmuir* 2007, **23**:4528-4531.

17. Christopher BK, P. DT, A. HJP, H. SM, Philipp V, Michael W: **RAFTing down under: Tales of missing radicals, fancy architectures, and mysterious holes.** *Journal of Polymer Science Part A: Polymer Chemistry* 2003, **41**:365-375.

18. Otsu T: **Iniferter concept and living radical polymerization.** *Journal of Polymer Science Part A: Polymer Chemistry* 2000, **38**:2121-2136.

19. Yan W, Fantin M, Spencer ND, Matyjaszewski K, Benetti EM: **Translating Surface-Initiated Atom Transfer Radical Polymerization into Technology: The Mechanism of Cu(0)-Mediated SI-ATRP under Environmental Conditions.** *ACS Macro Letters* 2019, **8**:865-870.

20. Yan W, Fantin M, Ramakrishna S, Spencer ND, Matyjaszewski K, Benetti EM: **Growing Polymer Brushes from a Variety of Substrates under Ambient Conditions by Cu(0)-Mediated Surface-Initiated ATRP.** *ACS Appl Mater Interfaces* 2019, **11**:27470-27477.

This studies (Ref 19 and 20) explore SI-ATRP aiming for its use in technical applications.

21. Huang L, Liu M, Mao L, Huang Q, Huang H, Zeng G, Tian J, Wen Y, Zhang X, Wei Y: **A facile FeBr₃ based photoATRP for surface modification of mesoporous silica nanoparticles for controlled delivery cisplatin.** *Applied Surface Science* 2018, **434**:204-210.

22. Kruk M: **Surface-Initiated Controlled Radical Polymerization in Ordered Mesoporous Silicas.** *Israel Journal of Chemistry* 2012, **52**:246-255.

23. Chen M, Qin L, Wei Y, Liu Y, Zhang F: **Confinement effect of mesoporous silica reactors on electron transfer atom transfer radical polymerization of styrene.** *Journal of Porous Materials* 2018, **26**:7-17.

24. Chen M, Qin L, Liu Y, Zhang F: **Controllable preparation of polymer brushes from mesoporous silica SBA-15 via surface-initiated ARGET ATRP.** *Microporous and Mesoporous Materials* 2018, **263**:158-164.

25. Wang C, Isaacson SG, Wang Y, Lionti K, Volksen W, Magbitang TP, Chowdhury M, Priestley RD, Dubois G, Dauskardt RH: **Surface Chemical Functionalization to Achieve**

Extreme Levels of Molecular Confinement in Hybrid Nanocomposites. *Advanced Functional Materials* 2019, **29**.

This study is an interesting example for the versatility of nanopore-polymer combinations for complex system design.

26. Encinas N, Angulo M, Astorga C, Colilla M, Izquierdo-Barba I, Vallet-Regi M: **Mixed-charge pseudo-zwitterionic mesoporous silica nanoparticles with low-fouling and reduced cell uptake properties.** *Acta Biomater* 2019, **84**:317-327.

27. Oh YJ, Khan ES, Campo AD, Hinterdorfer P, Li B: **Nanoscale Characteristics and Antimicrobial Properties of (SI-ATRP)-Seeded Polymer Brush Surfaces.** *ACS Appl Mater Interfaces* 2019, **11**:29312-29319.

28. Ma L, Luo P, He Y, Zhang L, Fan Y, Jiang Z: **Ultra-Stable Silica Nanoparticles as Nano-Plugging Additive for Shale Exploitation in Harsh Environments.** *Nanomaterials* 2019, **9**.

29. Bayramoglu G, Ozalp VC, Dincbal U, Arica MY: **Fast and Sensitive Detection of Salmonella in Milk Samples Using Aptamer-Functionalized Magnetic Silica Solid Phase and MCM-41-Aptamer Gate System.** *ACS Biomaterials Science & Engineering* 2018, **4**:1437-1444.

30. Sato T, Dunderdale GJ, Urata C, Hozumi A: **Sol-Gel Preparation of Initiator Layers for Surface-Initiated ATRP: Large-Scale Formation of Polymer Brushes Is Not a Dream.** *Macromolecules* 2018, **51**:10065-10073.

This study explores the scalability of polymer functionalization in mesoporous materials by SI-ATRP, which is needed for technological applications

31. Herzog N, Brilmayer R, Stanzel M, Kalyta A, Spiehl D, Dörsam E, Hess C, Andrieu-Brunsen A: **Gravure printing for mesoporous film preparation.** *RSC Advances* 2019, **9**:23570-23578.

This study explores the scalability of mesoporous film preparation using gravure printing which is relevant for fast and defined multilayer formation.

32. Zheng Y, Abbas ZM, Sarkar A, Marsh Z, Stefik M, Benicewicz BC: **Surface-initiated reversible addition-fragmentation chain transfer polymerization of chloroprene and mechanical properties of matrix-free polychloroprene nanocomposites.** *Polymer* 2018, **135**:193-199.

33. Silies L, Didzoleit H, Hess C, Stühn B, Andrieu-Brunsen A: **Mesoporous Thin Films, Zwitterionic Monomers, and Iniferter-Initiated Polymerization: Polymerization in a Confined Space.** *Chemistry of Materials* 2015, **27**:1971-1981.

34. Tom J, Brilmayer R, Schmidt J, Andrieu-Brunsen A: **Optimisation of Surface-Initiated Photoiniferter-Mediated Polymerisation under Confinement, and the Formation of Block Copolymers in Mesoporous Films.** *Polymers* 2017, **9**:539.

This study presents the first block-co-oligomer formation by reinitiation in nanopores sub 10 nm.

35. Silies L, Andrieu-Brunsen A: **Programming Ionic Pore Accessibility in Zwitterionic Polymer Modified Nanopores.** *Langmuir* 2018, **34**:807-816.

36. Calvo A, Yameen B, Williams FJ, Soler-Illia GJ, Azzaroni O: **Mesoporous films and polymer brushes helping each other to modulate ionic transport in nanoconfined environments. An interesting example of synergism in functional hybrid assemblies.** *J Am Chem Soc* 2009, **131**:10866-10868.

37. Chen J, Liu M, Huang L, Huang H, Wan Q, Tian J, Wen Y, Deng F, Zhang X, Wei Y: **Preparation of zwitterionic polymers functionalized fluorescent mesoporous silica nanoparticles through photoinduced surface initiated RAFT polymerization in the presence of oxygen.** *Journal of the Taiwan Institute of Chemical Engineers* 2018, **91**:570-577.

This study provides one of the very few examples of (complex) nanopore functionalization using visible light.

38. Chen J, Liu M, Huang H, Deng F, Mao L, Wen Y, Huang L, Tian J, Zhang X, Wei Y: **Facile preparation of thermoresponsive fluorescent silica nanoparticles based composites through the oxygen tolerance light-induced RAFT polymerization.** *Journal of Molecular Liquids* 2018, **259**:179-185.

39. Xu X, Zeng Y, Yu C, Zhang F: **Controlled RAFT polymerization of MMA in confined space of various pore sizes of SBA-15.** *Journal of Porous Materials* 2019.

This study explores the use of mesoporous silica particles as microreactors for RAFT polymerizations.

40. Hegazy M, Zhou P, Rahoui N, Wu GY, Taloub N, Lin YP, Huang X, Huang YD: **A facile design of smart silica nanocarriers via surface-initiated RAFT polymerization as a dual-stimuli drug release platform.** *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 2019, **581**.

This study is an interesting example for complex system design, using RAFT polymerization to create a dual stimuli responsive drug release platform.

41. Wang Y, Yin M, Lin X, Li L, Li Z, Ren X, Sun Y: **Tailored synthesis of polymer-brush-grafted mesoporous silicas with N-halamine and quaternary ammonium groups for antimicrobial applications.** *J Colloid Interface Sci* 2019, **533**:604-611.

42. Kim CJ, Sondergeld K, Mazurowski M, Gallei M, Rehahn M, Spehr T, Frielinghaus H, Stühn B: **Synthesis and characterization of polystyrene chains on the surface of silica nanoparticles: comparison of SANS, SAXS, and DLS results.** *Colloid and Polymer Science* 2013, **291**:2087-2099.

43. Cao E, Pichavant L, Prouzet E, Héroguez V: **The formation and study of poly(ethylene oxide)-poly(norbornene) block-copolymers on the surface of titanium-dioxide particles: a novel approach towards application of si-ROMP to larger surface modification.** *Polymer Chemistry* 2016, **7**:2751-2758.

44. Krohm F, Kind J, Savka R, Alcaraz Janßen M, Herold D, Plenio H, Thiele CM, Andrieu-Brunsen A: **Photochromic spiropyran- and spirooxazine-homopolymers in mesoporous thin films by surface initiated ROMP.** *Journal of Materials Chemistry C* 2016, **4**:4067-4076.

45. Eder K, Reichel E, Schottenberger H, Huber CG, Buchmeiser MR: **Alkyne Metathesis Graft Polymerization: Synthesis of Poly(ferricinium)-Based Silica Supports for Anion-Exchange Chromatography of Oligonucleotides.** *Macromolecules* 2001, **34**:4334-4341.

46. Pan X, Malhotra N, Simakova A, Wang Z, Konkolewicz D, Matyjaszewski K: **Photoinduced Atom Transfer Radical Polymerization with ppm-Level Cu Catalyst by Visible Light in Aqueous Media.** *Journal of the American Chemical Society* 2015, **137**:15430-15433.

47. Liu X, Ni Y, Wu J, Jiang H, Zhang Z, Zhang L, Cheng Z, Zhu X: **A sustainable photocontrolled ATRP strategy: facile separation and recycling of a visible-light-mediated catalyst fac-[Ir(ppy)₃].** *Polymer Chemistry* 2018, **9**:584-592.

48. Aydogan C, Yilmaz G, Yagci Y: **Synthesis of Hyperbranched Polymers by Photoinduced Metal-Free ATRP.** *Macromolecules* 2017, **50**:9115-9120.

This study provides a recent example for the development of environmentally friendly polymerization.

49. Sari E, Mitterbauer M, Liska R, Yagci Y: **Visible light induced free radical promoted cationic polymerization using acylsilanes.** *Progress in Organic Coatings* 2019, **132**:139-143.

50. Kaya K, Seba M, Fujita T, Yamago S, Yagci Y: **Visible light-induced free radical promoted cationic polymerization using organotellurium compounds.** *Polymer Chemistry* 2018, **9**:5639-5643.

51. Lu P, Alrashdi NM, Boydston AJ: **Bidirectional metal-free ROMP from difunctional organic initiators.** *Journal of Polymer Science Part A: Polymer Chemistry* 2017, **55**:2977-2982.

52. Theunissen C, Ashley MA, Rovis T: **Visible-Light-Controlled Ruthenium-Catalyzed Olefin Metathesis**. *Journal of the American Chemical Society* 2019, **141**:6791-6796.

This study presents an interesting new synthesis strategy by merging olefin metathesis and photoredox catalysis.

53. Bagheri A, Yeow J, Arandiyana H, Xu J, Boyer C, Lim M: **Polymerization of a Photocleavable Monomer Using Visible Light**. *Macromolecular Rapid Communications* 2016, **37**:905-910.

54. Li M, Fromel M, Ranaweera D, Rocha S, Boyer C, Pester CW: **SI-PET-RAFT: Surface-Initiated Photoinduced Electron Transfer-Reversible Addition-Fragmentation Chain Transfer Polymerization**. *ACS Macro Letters* 2019, **8**:374-380.

55. Seo SE, Discekici EH, Zhang Y, Bates CM, Hawker CJ: **Surface-initiated PET-RAFT polymerization under metal-free and ambient conditions using enzyme degassing**. *Journal of Polymer Science Part A: Polymer Chemistry* 2019.

56. Bagheri A, Arandiyana H, Adnan NNM, Boyer C, Lim M: **Controlled Direct Growth of Polymer Shell on Upconversion Nanoparticle Surface via Visible Light Regulated Polymerization**. *Macromolecules* 2017, **50**:7137-7147.

57. Tucker BS, Coughlin ML, Figg CA, Sumerlin BS: **Grafting-From Proteins Using Metal-Free PET-RAFT Polymerizations under Mild Visible-Light Irradiation**. *ACS Macro Letters* 2017, **6**:452-457.

58. Li X, Ye S, Huang Y, Li JL, Cai T: **Precise growth of polymer brushes on silica-based nanocomposites via visible-light-regulated controlled radical polymerization**. *Journal of Materials Chemistry A* 2019, **7**:6173-6179.

59. Bagheri A, Sadreiarhami Z, Adnan NNM, Boyer C, Lim M: **Surface functionalization of upconversion nanoparticles using visible light-mediated polymerization**. *Polymer* 2018, **151**:6-14.

60. Yang Y, Liu X, Ye G, Zhu S, Wang Z, Huo X, Matyjaszewski K, Lu Y, Chen J: **Metal-Free Photoinduced Electron Transfer-Atom Transfer Radical Polymerization Integrated with Bioinspired Polydopamine Chemistry as a Green Strategy for Surface Engineering of Magnetic Nanoparticles**. *ACS Applied Materials & Interfaces* 2017, **9**:13637-13646.

61. Discekici EH, Pester CW, Treat NJ, Lawrence J, Mattson KM, Narupai B, Toumayan EP, Luo Y, McGrath AJ, Clark PG, et al.: **Simple Benchtop Approach to Polymer Brush Nanostructures Using Visible-Light-Mediated Metal-Free Atom Transfer Radical Polymerization**. *ACS Macro Letters* 2016, **5**:258-262.

62. Ma A, Zhang J, Wang N, Bai L, Chen H, Wang W, Yang H, Yang L, Niu Y, Wei D: **Surface-Initiated Metal-Free Photoinduced ATRP of 4-Vinylpyridine from SiO₂ via Visible Light Photocatalysis for Self-Healing Hydrogels**. *Industrial & Engineering Chemistry Research* 2018, **57**:17417-17429.

63. Gao P, Cao H, Ding Y, Cai M, Cui Z, Lu X, Cai Y: **Synthesis of Hydrogen-Bonded Pore-Switchable Cylindrical Vesicles via Visible-Light-Mediated RAFT Room-Temperature Aqueous Dispersion Polymerization**. *ACS Macro Letters* 2016, **5**:1327-1331.

64. Fan D, Wang G, Ma A, Wang W, Chen H, Bai L, Yang H, Wei D, Yang L: **Surface Engineering of Porous Carbon for Self-Healing Nanocomposite Hydrogels by Mussel-Inspired Chemistry and PET-ATRP**. *ACS Applied Materials & Interfaces* 2019, **11**:38126-38135.

This study is one of the first examples transferring environmentally friendly ATRP with visible light to controlled surface functionalization of porous carbon.

65. Ma L, Li N, Zhu J, Chen X: **Visible Light-Induced Metal Free Surface Initiated Atom Transfer Radical Polymerization of Methyl Methacrylate on SBA-15**. *Polymers* 2017, **9**:58.

66. Rodriguez C, Muñoz Noval A, Torres-Costa V, Ceccone G, Manso Silván M: **Visible Light Assisted Organosilane Assembly on Mesoporous Silicon Films and Particles**. *Materials* 2019, **12**:131.

This study is an interesting example of advanced pore functionalization by using visible light.

67. Herzog N, Kind J, Hess C, Andrieu-Brunsen A: **Surface plasmon & visible light for polymer functionalization of mesopores and manipulation of ionic permselectivity.** *Chemical Communications* 2015, **51**:11697-11700.

68. R  he J: **And There Was Light: Prospects for the Creation of Micro- and Nanostructures through Maskless Photolithography.** *ACS Nano* 2017, **11**:8537-8541.

This review provides an overview of nanofabrication processes.

69. Huang X, Kong X-Y, Wen L, Jiang L: **Bioinspired Ionic Diodes: From Unipolar to Bipolar.** *Advanced Functional Materials* 2018, **28**.

70. Zhang H, Tian Y, Jiang L: **From symmetric to asymmetric design of bio-inspired smart single nanochannels.** *Chem Commun (Camb)* 2013, **49**:10048-10063.

71. Hou X, Zhang H, Jiang L: **Building bio-inspired artificial functional nanochannels: from symmetric to asymmetric modification.** *Angew Chem Int Ed Engl* 2012, **51**:5296-5307.

72. Ermis M, Antmen E, Hasirci V: **Micro and Nanofabrication methods to control cell-substrate interactions and cell behavior: A review from the tissue engineering perspective.** *Bioact Mater* 2018, **3**:355-369.

73. Zhou H, Guo Z: **Superwetting Janus membranes: focusing on unidirectional transport behaviors and multiple applications.** *Journal of Materials Chemistry A* 2019, **7**:12921-12950.

74. Wang Z, Yang X, Cheng Z, Liu Y, Shao L, Jiang L: **Simply realizing "water diode" Janus membranes for multifunctional smart applications.** *Materials Horizons* 2017, **4**:701-708.

This study represents the first prominent example of Janus membranes, which allow pH-switchable side-selective oil-water separation.

75. Sui X, Zhang Z, Li C, Gao L, Zhao Y, Yang L, Wen L, Jiang L: **Engineered Nanochannel Membranes with Diode-like Behavior for Energy Conversion over a Wide pH Range.** *ACS Appl Mater Interfaces* 2019, **11**:23815-23821.

This study demonstrates the applicability of local and hierarchical nanoporous material design for energy conversion.

76. Cheng H, Zhou Y, Feng Y, Geng W, Liu Q, Guo W, Jiang L: **Electrokinetic Energy Conversion in Self-Assembled 2D Nanofluidic Channels with Janus Nanobuilding Blocks.** *Adv Mater* 2017, **29**.

77. Yang J, Li H-N, Chen Z-X, He A, Zhong Q-Z, Xu Z-K: **Janus membranes with controllable asymmetric configurations for highly efficient separation of oil-in-water emulsions.** *Journal of Materials Chemistry A* 2019, **7**:7907-7917.

In this study novel demulsification-type Janus membranes with controllable asymmetric configurations lead to high separation efficiency.

78. Zhou S, Xiong Z, Liu F, Lin H, Wang J, Li T, Han Q, Fang Q: **Novel Janus membrane with unprecedented osmosis transport performance.** *Journal of Materials Chemistry A* 2019, **7**:632-638.

This study represents a novel Janus membrane with unprecedented osmotic water permeability and nearly complete salt rejection through asymmetrical porous structure and wettability design.

79. Schmidt S, Alberti S, Vana P, Soler-Illia G, Azzaroni O: **Thermosensitive Cation-Selective Mesochannels: PNIPAM-Capped Mesoporous Thin Films as Bioinspired Interfacial Architectures with Concerted Functions.** *Chemistry* 2017, **23**:14500-14506.

80. Tom JC, Appel C, Andrieu-Brunsen A: **Fabrication and in situ functionalisation of mesoporous silica films by the physical entrapment of functional and responsive block copolymer structuring agents.** *Soft Matter* 2019, **15**:8077-8083.

This study presents an innovative and simple design of multilayered porous systems with different stimuli-responsive functions via in-situ functionalization.

81. Bathfield M, Reboul J, Cacciaguerra T, Lacroix-Desmazes P, Gérardin C: **Thermosensitive and Drug-Loaded Ordered Mesoporous Silica: A Direct and Effective Synthesis Using PEO-b-PNIPAM Block Copolymers**. *Chemistry of Materials* 2016, **28**:3374-3384.
82. Nau M, Herzog N, Schmidt J, Meckel T, Andrieu-Brunsen A, Biesalski M: **Janus-Type Hybrid Paper Membranes**. *Advanced Materials Interfaces* 2019, **6**.

In this study, the combination of nanopores and their distribution within hierarchical materials realized novel side-selective permeation properties.

83. Laskowski Ł, Laskowska M, Dulski M, Zubko M, Jelonkiewicz J, Perzanowski M, Vila N, Walcarius A: **Multi-step functionalization procedure for fabrication of vertically aligned mesoporous silica thin films with metal-containing molecules localized at the pores bottom**. *Microporous and Mesoporous Materials* 2019, **274**:356-362.

This study belongs to the first examples demonstrating local placement of functional units into nanopores which is an essential requirement for complex system design and transport control therein.

84. Dostert KH, Alvarez M, Koynov K, del Campo A, Butt HJ, Kreiter M: **Near field guided chemical nanopatterning**. *Langmuir* 2012, **28**:3699-3703.

85. Álvarez M, Best A, Unger A, Alonso JM, del Campo A, Schmelzeisen M, Koynov K, Kreiter M: **Near-Field Lithography by Two-Photon Induced Photocleavage of Organic Monolayers**. *Advanced Functional Materials* 2010, **20**:4265-4272.

86. Deeb C, Ecoffet C, Bachelot R, Plain J, Bouhelier A, Soppera O: **Plasmon-based free-radical photopolymerization: effect of diffusion on nanolithography processes**. *J Am Chem Soc* 2011, **133**:10535-10542.

87. Herzog N, Kind J, Hess C, Andrieu-Brunsen A: **Surface plasmon & visible light for polymer functionalization of mesopores and manipulation of ionic permselectivity**. *Chem Commun (Camb)* 2015, **51**:11697-11700.

88. Nguyen M, Lamouri A, Salameh C, Levi G, Grand J, Boubekur-Lecaque L, Mangeney C, Felidj N: **Plasmon-mediated chemical surface functionalization at the nanoscale**. *Nanoscale* 2016, **8**:8633-8640.

89. Tijnelyte I, Kherbouche I, Gam-Derouich S, Nguyen M, Lidgi-Guigui N, de la Chapelle ML, Lamouri A, Lévi G, Aubard J, Chevillot-Biraud A, et al.: **Multi-functionalization of lithographically designed gold nanodisks by plasmon-mediated reduction of aryl diazonium salts**. *Nanoscale Horizons* 2018, **3**:53-57.

This study realized precise local multifunctionalization of gold nanodisks using near-field methods.

90. Goerlitzer ESA, Speichermann LE, Mirza TA, Mohammadi R, Vogel N: **Addressing the plasmonic hotspot region by site-specific functionalization of nanostructures**. *Nanoscale Advances* 2020.

In this study further advancements regarding precise, nanoscale arrangement of functionalization of crescent-shaped nanostructures are presented.