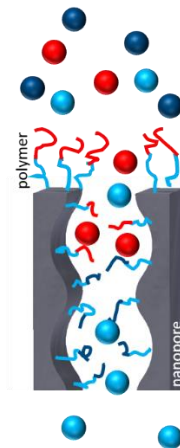


# Recent Trends in Nanopore Polymer Functionalization

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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.

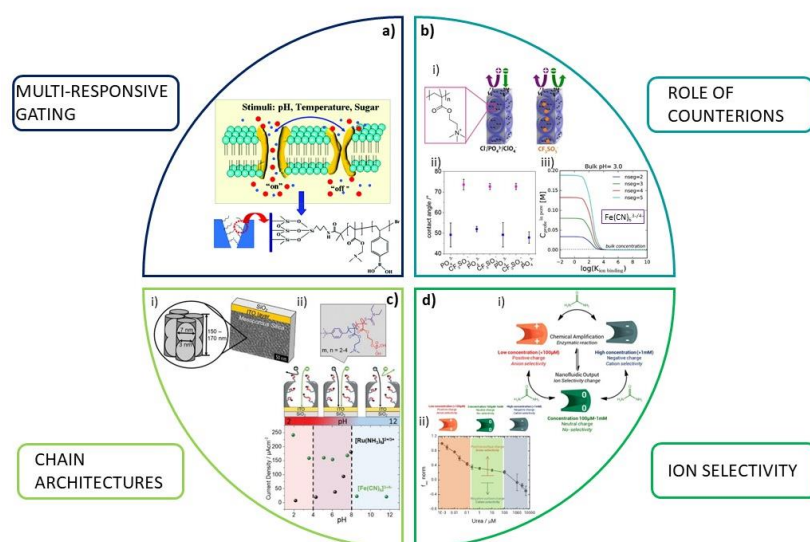
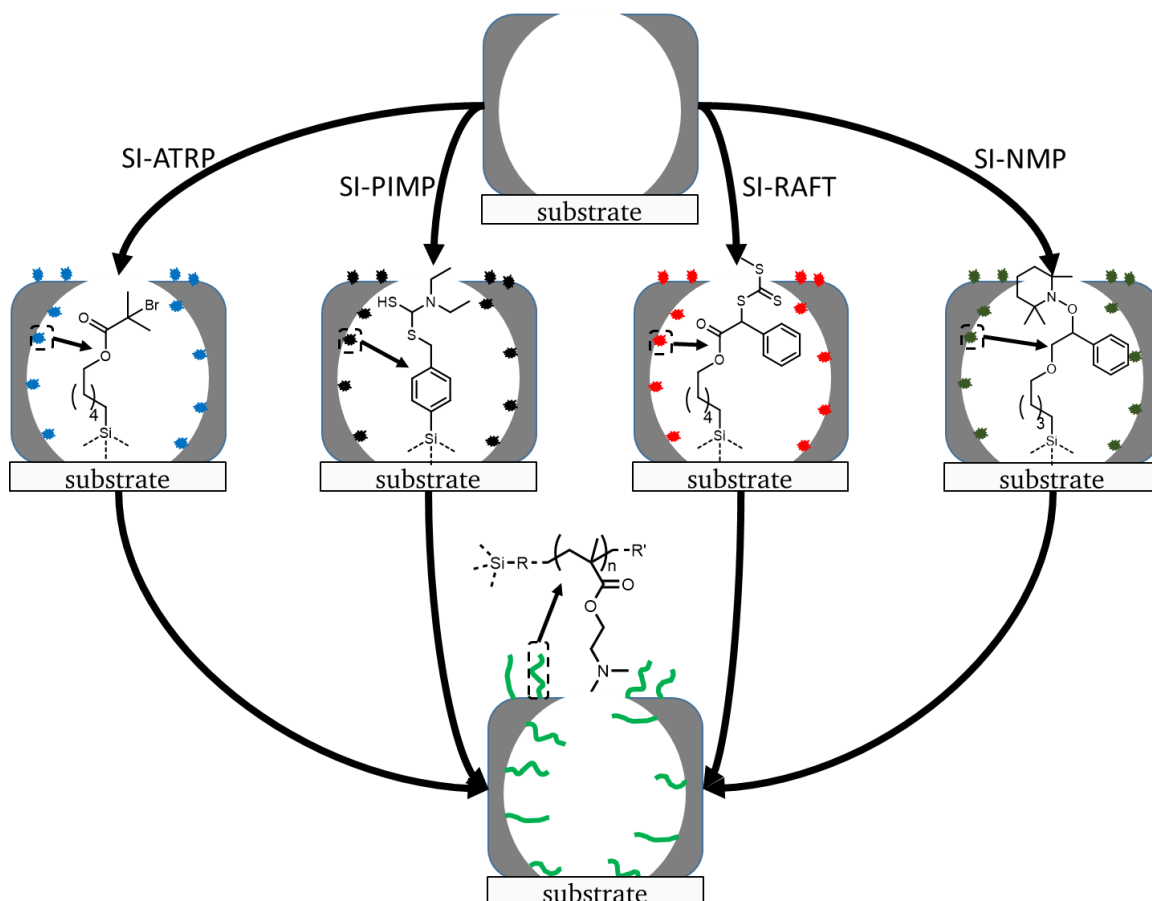


Figure 1: **a)** A triple-responsive nanofluidic diode under external stimuli including temperature, pH and sugar. The multi-responsive copolymer poly(*N,N*-dimethylamino ethyl methacrylate-*co*-4-vinyl benzene boric acid) (P(DMAEMA-*co*-VPBA)) was polymerized onto the interior surface of a single glass 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  $\text{PO}_4^{3-}$  and  $\text{ClO}_4^-$  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]<sup>\*</sup>, 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]<sup>\*</sup>, 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 ( $f_{\text{rec}}$ ) varying with urea concentration. Reprinted with permission from *Nano Lett.*, **2018**, 18, 3303–3310 [13]<sup>\*</sup>, 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] <sup>\*\*</sup> 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 FeBr<sub>3</sub> 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)ethyl-trimethylammonium 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]<sup>\*</sup> 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]<sup>\*</sup>). Based on these examples various Janus membranes demonstrating side-selective oil-water separation[77]<sup>\*</sup> 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

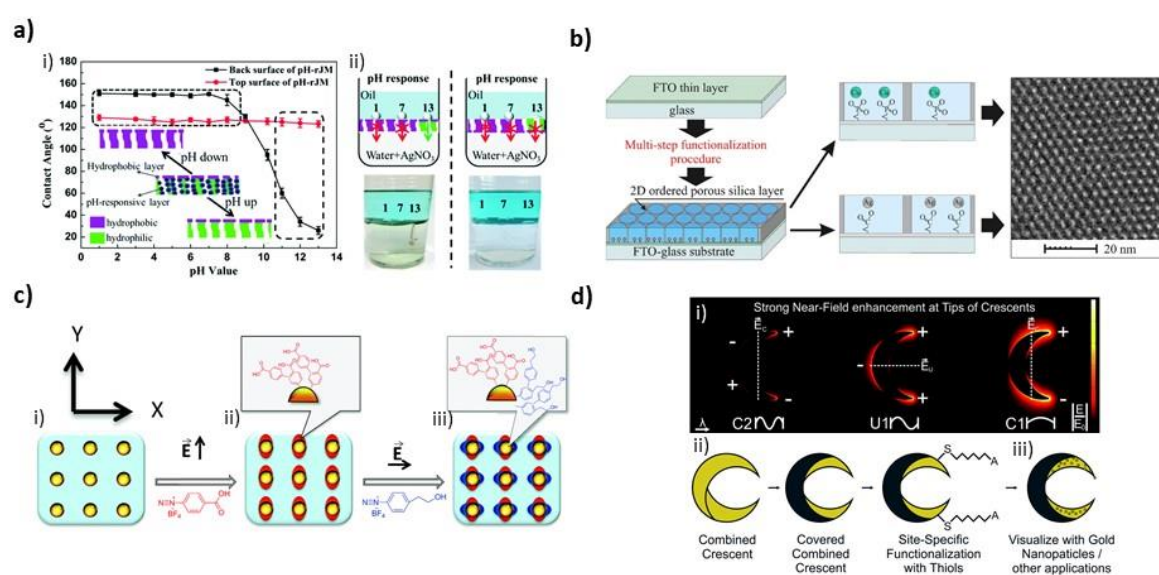


generation. As an example, *Bathfield et al.*[81] synthesized PEO-*b*-PNIPAM from a PEO macroinitiator and subsequent RAFT polymerization, and applied them as templates to produce thermosensitive drug-loaded OMS (silica-based ordered mesoporous materials). The mesoporosity of these materials was then 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.

### Acknowledgment

We thank Maria Ochs for providing literature and expertise with respect to ROMP in solution, on surfaces and in pores.

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