Electronic Supporting Information

Robust transparent mesoporous silica membranes as matrices for colorimetric sensors

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Materials and methods

Preparation of mesoporous silica membranes Mesostructured silica membranes were synthesized by self-assembly of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer Pluronic™ F127 (Sigma-Aldrich), according to a method described previously.[1] In brief, 8.2 g of tetraethoxysilane (Sigma-Aldrich) in 12 ml of ethanol was hydrolyzed with 0.007 g of HCl (Fisher Scientific) and 3.6 g of water. After 1 h stirring, the solution was mixed with a 20-ml block-copolymer ethanolic solution (F127/TEOS molar ratios between 0.004 and 0.010) and further stirred for 2 h. The mesostructured silica membranes were prepared by casting the solution in polystyrene Petri dishes. The membranes were dried under ambient conditions for 1-4 days to evaporate the solvent and to achieve high degrees of silica crosslinking. The resultant membranes were cut into desired shapes and detached from the polystyrene Petri dishes to yield free-standing mesostructured silica membranes with thicknesses between 100-250 μm.

Various post-synthesis treatments were performed on the as-synthesized free-standing mesostructured silica membranes to strengthen the silica frameworks without inducing micro- or macroscale cracking. For the hydrothermal treatment, as-synthesized membranes were immersed in de-ionized water at 80 °C for 1 day. For the thermal treatment, as-synthesized membranes were heated in an oven at 120 °C for 2 days. For the water-vapor treatment, as-synthesized membranes were placed in a closed container with a water reservoir, and the container was kept at 80 °C for 2 days. Mesostructured silica membranes prepared without and with post-synthesis treatments were sequentially calcined at

550 °C in air for 12 h to remove the triblock copolymer structure-directing species and thereby generate porosity.

Dithizone functionalization of mesoporous silica membranes Transparent mesoporous silica membranes were functionalized with dithizone to yield colorimetric sensing capability (e.g., Pb^{2+} ion), as reported by Balaji *et al.*[2] Mesoporous silica membranes prepared with a 0.0078 F127/TEOS molar ratio were immersed in a 0.05-M dithizone (Sigma-Aldrich) ethanolic solution contained in a glass vial. After ultra-sonication for 30 min, the vial was kept at 40 °C for 2 h for homogeneous incorporation of dithizone. Dithizone-grafted mesoporous silica membranes prepared with longer ultra-sonication times did not yield noticeable differences in optical densities, indicating the absence of significant dithizone-loading gradients across the membranes. This is consistent with the small size of the dithizone molecules, relative to the uniform ~8-nm mean diameter of the mesopores. After cooling, the membranes were filtered, and excess dithizone solution on the membranes was removed with Kimwipes™. The dithizone-containing mesoporous silica membranes were then dried at 40 °C under vacuum.

For comparison, conventional mesoporous silica powder was also synthesized and grafted with dithizone. Mesoporous silica powder materials were synthesized as reported by Zhao *et al.*[3] and mixed with an ethanolic 0.05 M dithizone solution. After ultra-sonication for 30 min, the vial was kept at 40 °C for 2 h for homogeneous incorporation of dithizone. Excess dithizone solution was removed from mesoporous silica powder materials by vacuum filtering. The resulting dithizone-containing mesoporous silica powder materials were dried at 40 °C under vacuum.

Differences in the light-absorption properties of dithizone-grafted mesoporous silica membranes and powder materials upon formation of dithizone-Pb^{2+} complexes were used to detect Pb^{2+} ions in aqueous solutions.[2] 50 mg of dithizone-grafted mesoporous silica membranes were immersed in 200 ml of a pH 7 3-(N-morpholino)propanesulfonic-acid (MOPS, Sigma-Aldrich) aqueous buffer solution (0.2 M) containing various concentrations of Pb^{2+} ions (0-1000 ppb) for 1 day. For such dilute Pb^{2+} species (e.g., 20 ppb), a detection time of 1 day was required to observe significant color changes of dithizone-grafted mesoporous silica membranes. This relatively long overall time is based on the buildup of sufficient quantities of Pb^{2+}-dithizone complexes to register sufficient signal. The optical response upon binding of Pb^{2+} to the dithizone moieties is very rapid (ca. ns), as governed by intrinsic photophysical processes that are not significantly affected by grafting onto the silica membranes. (For example, the lifetime of the excited state for a similar mercury-dithizone complex has been reported to be on the order of 100 ps by Paci, et al., *J. Photochem. Photobiol., A* **2000,** *137*, 141.) The slow rate of formation of Pb^{2+}-dithizone complexes is limited principally by the time required for sufficient quantities of Pb^{2+} ions in the dilute bulk solutions to diffuse to the external membrane surfaces and to diffuse and adsorb in the internal mesopores, driven by the minute concentration gradients and against entropic factors that promote dispersal of the Pb^{2+} in the bulk solution. Bulk diffusion (e.g., 9.2×10^{-6} cm^2/s for 0.135-mM Pb^{2+} ions in aqueous solution, as reported by Kariuki and Dewald, *Electroanalysis* **1996**, *8*, 307) or intramembrane diffusion are both relatively fast relative to 1 day and are thus not expected to contribute significantly to the time required to obtain adequate signal sensitivity. Rather, the inherently low Pb^{2+} concentrations in the bulk solutions are principally responsible for the long detection times. In general, for small molecules, sensing selectivity is expected to be governed by the choice of the colorimetric sensor species, rather than the properties of the mesoporous silica membranes. For comparison, 12.5 mg of dithizone-grafted mesoporous silica powder materials were mixed with 50 ml of a pH 7 aqueous buffer solution (MOPS, 0.2 M) without and with 1-ppm Pb^{2+} ions for 10 min.

Characterization Mesostructure orderings of mesoporous silica membranes were investigated by using small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). SAXS patterns were collected to investigate the long-range ordering of mesoporous silica membranes on a home-built diffractometer with XENOCS Genix 50W X-ray microsource (K_α Cu anode, 1.54 Å) and Bruker HI-STAR multiwire area detector. 2D X-ray diffraction patterns were recorded for the different mesostructured silica membranes and converted into 1D patterns by azimuthal integration. Short-range ordering was characterized by TEM images that were acquired on an FEI Titan™ G2 microscope operating at 200 kV. The mesoporous silica membranes were gently ground into powders and dispersed in ethanol. After 30-min ultra-sonication, the dispersions were deposited on copper grids with carbon supports and dried under ambient condition.

The porosities of the mesoporous silica membranes were determined by nitrogen sorption and pycnometry analyses. Nitrogen sorption isotherms at 77 K were acquired on a Micromeritics Tristar™ 3000 instrument. Gently ground mesoporous silica membranes were dried at 120 °C under N_2 flow overnight by using Micromeritics FlowPrep™ before the measurements. Surface areas and pore size distributions of mesoporous silica membranes were calculated from N_2 adsorption isotherm curves by using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses, respectively. Closed porosities of mesoporous silica membranes were determined, based on densities measured by using a Micromeritics Pyc1330™ pycnometer or by using He gas, and compared to apparent densities of identical membranes measured using N_2 gas. Volume fractions of closed mesopores that are not accessible to N_2 molecules were calculated based on the differences between the density and the apparent density of the respective membrane materials. For the low loadings of dithizone used in this study (~1 nmol in a 1 cm^2 x 120-μm membrane), the reduction of available surface area of the mesoporous silica upon grafting of dithizone is not significant.

The mechanical robustnesses of the mesoporous silica membranes were assessed by measuring their hardnesses using a Hysitron™ Triboindenter with a Berkovich tip. Tip-area function for a Berkovich tip was calibrated with fused silica. Load-depth profiles for mesoporous silica membranes prepared with different treatments were acquired with maximum loads that yielded ~180 nm contact depths. Hardnesses were calculated from the initial slopes of unloading load-depth curves.

Quantitative solid-state single-pulse ^{29}Si NMR spectra were acquired on a Bruker AVANCE-300 NMR spectrometer with a wide-bore 7-Tesla magnet at 59.62 MHz under magic angle spinning (MAS) condition. Measurements were performed at room temperature with a spinning rate of 7 kHz. ^{29}Si chemical shifts were referenced to tetramethylsilane (TMS) using tetrakis(trimethylsilyl)silane

$[(CH_3)_3Si]_4Si$ as a secondary standard. All ^{29}Si spectra were acquired under simultaneous high-power proton decoupling with the Small Phase INcremental ALteration pulse scheme using 64 steps (SPINAL-64) with a 100 kHz ^{1}H decoupling field.

UV/Visible transmission spectra were acquired for mesoporous silica membranes without and with functional species (e.g., dithizone) to assess colorimetric properties by using Shimadzu UV3600 UV-Vis-NIR Spectrometer. 1 or 5-pieces membranes were taped on the sample holder, and their spectra were acquired from 750 nm to 350 nm in transmission mode, which were enabled by the high transparencies of the membranes, even with colorimetric functional species. For dithizone-functionalized mesoporous silica powder materials, glass cuvettes with 1-mm path length were packed with the samples to be measured in a transmission mode.

Figures and Tables

Table S1. Relative percentages of ^{29}Si moieties for mesostructured silica membranes prepared with different post-synthesis treatments.

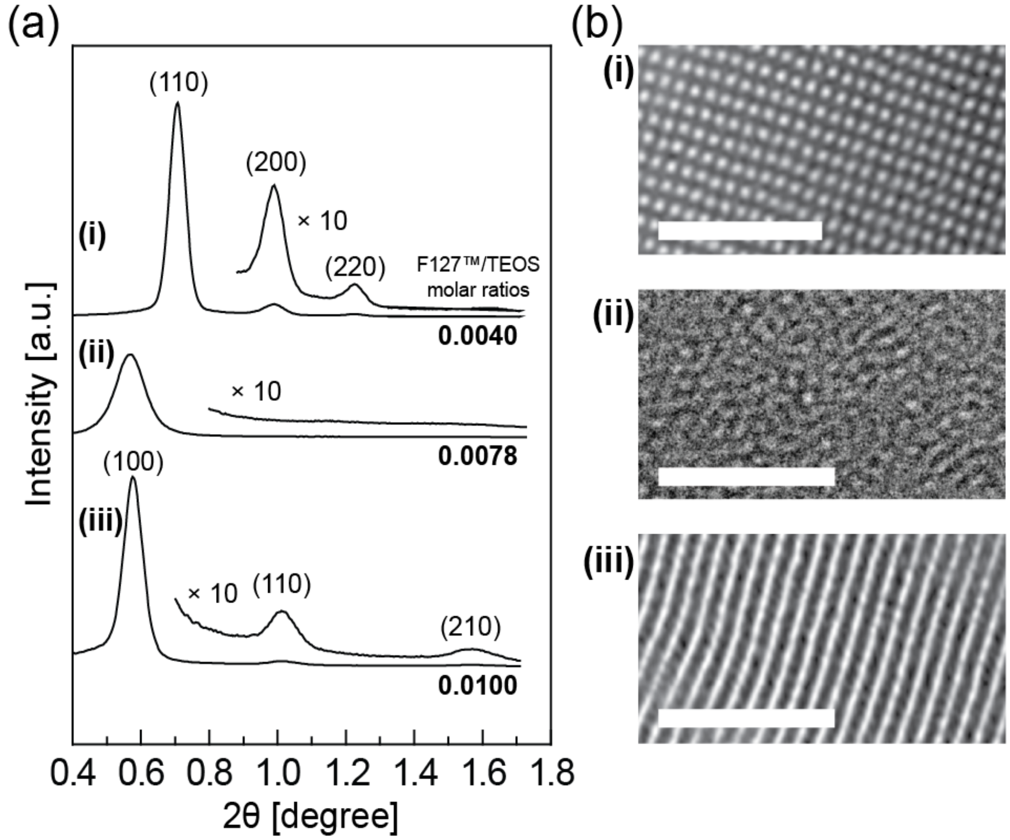
Membrane treatment	Relative percentages of ^{29}Si moieties[a]		
	Q^2	Q^3	Q^4
No treatment	13 %	50 %	37 %
Calcination	5 %	8 %	87 %
Heat-treatment	9 %	52 %	39 %
Hydrothermal-treatment	2 %	16 %	82 %
Water-vapor treatment	5 %	37 %	58 %

[a] The relative percentages of ^{29}Si moieties for each membrane were established from quantitative solid-state single-pulse ^{29}Si MAS NMR spectra. Overlapping ^{29}Si signals for mesoporous silica membranes were deconvoluted into three Gaussian peaks centered at -91, -101, and -110 ppm, which correspond to Q^2, Q^3, and Q^4 ^{29}Si species, respectively. (Q^n represents four-coordinate ^{29}Si atoms that are covalently bonded to *n* nearest Si atoms through bridging oxygen atoms, where *n* is an integer that varies from 0 to 4).

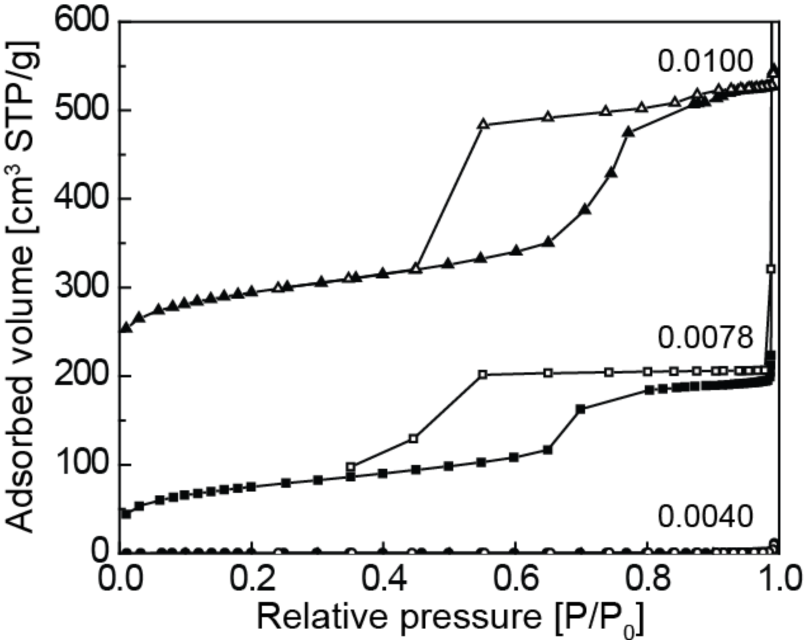
Table S2. Hardnesses of mesostructured silica membranes prepared with different treatments.

Membrane treatment	Hardness (GPa)[a]
No treatment	0.18
water-vapor treatment	0.50
Calcination (550 °C)	5.4
water-vapor treatment and subsequent calcination (550 °C)	2.3

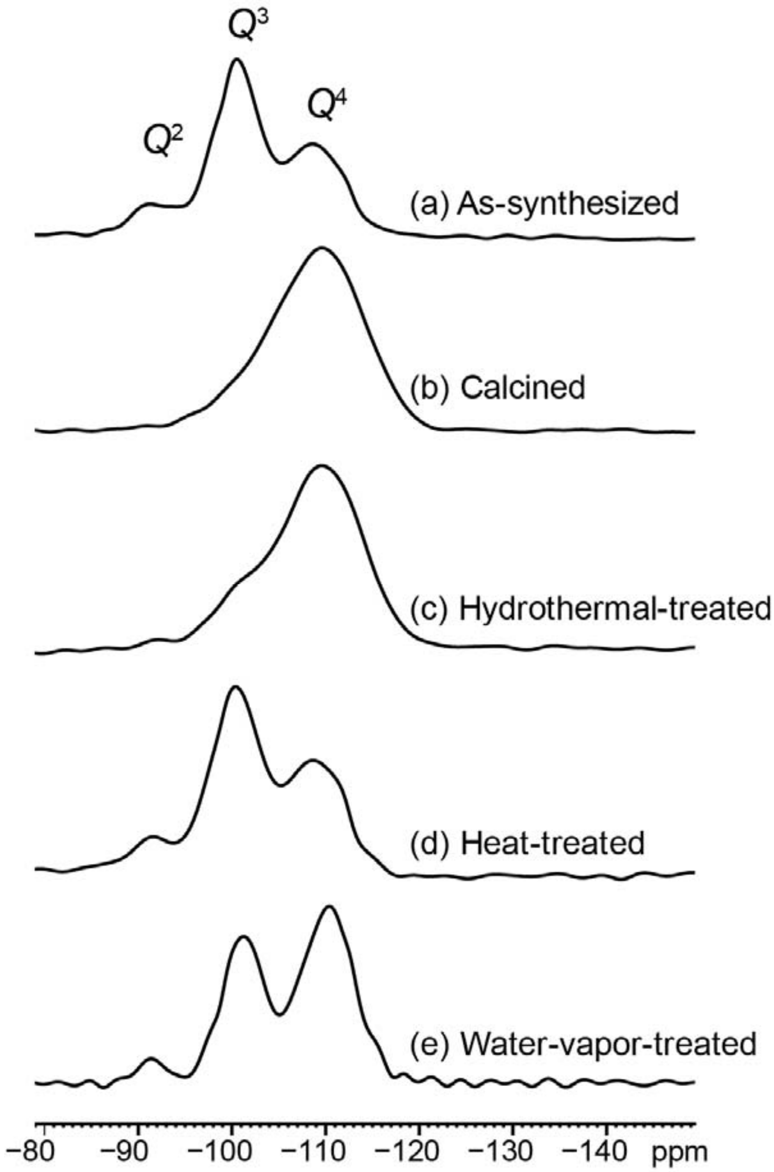
[a] Hardnesses of mesostructured silica membranes prepared with no treatment, with water-vapor treatment, after calcination (550 °C in air) without treatment, and after water-vapor treatment and subsequent calcination (550 °C in air). The hardness values were calculated from the initial slopes of unloading load-depth profiles acquired from nano-indentation measurements with a Berkovich tip. Maximum loadings were determined to yield ~180 nm contact depths (0.2, 0.5, 2, and 4 μN, respectively).



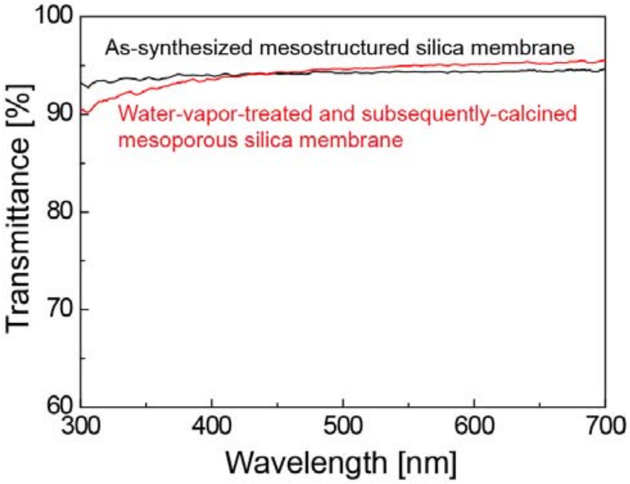
Supporting information Figure S1. (a) SAXS patterns and (b) representative high-resolution transmission electron microscopy (HR-TEM) images of as-synthesized mesostructured silica membranes prepared with (i) 0.0040, (ii) 0.0078, or (iii) 0.0100 F127/TEOS molar ratios. Scale bars represent 100 nm. The mesostructured silica membrane prepared with a F127/TEOS molar ratio of 0.004 yields distinct SAXS reflections at 2θ values of 0.71, 0.99, and 1.23°, which can be assigned to the (110), (200), and (220) reflections of the *Im3m* cubic structure with a lattice parameter of 17.5 nm.[3] A highly ordered cubic structure with large domain sizes (>1 µm) is also observed in the accompanying HR-TEM image. As the F127/TEOS mol ratio was increased higher than 0.0064 (e.g., 0.0078), the membranes yielded no high-order reflections, which establish the absence of long-range mesostructural ordering. This is corroborated by the accompanying HR-TEM image of the material, which shows sphere-like pores with a relatively low extent of overall mesostructural order. By comparison, when the F127/TEOS molar ratio was increased to 0.01, the membrane exhibits SAXS reflections at 2θ values of 0.57°, 1.04°, and 1.58° that are indexable to a hexagonal *P3mm* structure with a lattice parameter of 17.8 nm.[3] The HR-TEM image of the membrane reveals highly-ordered cylindrical pores of the 2D hexagonal structure viewed normal to their axes. Heterogeneities in the mesostructural ordering of the membranes are thought to arise from non-uniform drying, which is typically difficult to control over the entire membrane.



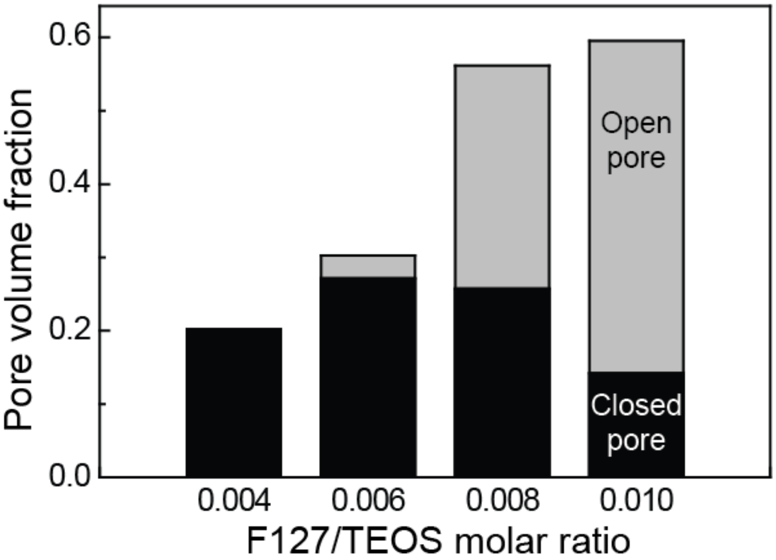
Supporting information Figure S2. N_2 sorption isotherms acquired at 77 K for calcined mesoporous silica membranes prepared with F127/TEOS molar ratios of (a) 0.0040, (b) 0.0078, or (c) 0.0100. For clarity of presentation, the isotherm for the mesoporous silica membrane synthesized with a F127/TEOS molar ratio of 0.008 has been translated along the vertical axis by 200 cm^3/g. Interestingly, mesoporous silica membranes prepared with a F127/TEOS mol ratio of 0.004 yield adsorb little N_2 over the entire pressure range, which reflects a material with very low surface area. SAXS patterns of the same membranes in Fig. S1a show three distinct reflections, which indicate mesostructural ordering was maintained during calcination and suggests that spherical pores of the membranes were closed during calcination and therefore not accessible to N_2 molecules. By comparison, mesoporous silica membranes prepared with F127/TEOS mol ratios of 0.0078 and 0.008 exhibit Type-IV isotherms with H2 hysteresis,[4] which indicate high mesoporosities accessible to N_2 molecules. H2-type hysteresis of the mesoporous silica membrane with a F127/TEOS mol ratio of 0.008 suggests that the membrane has a significant fraction of spherical pores that were also observed in HR-TEM.



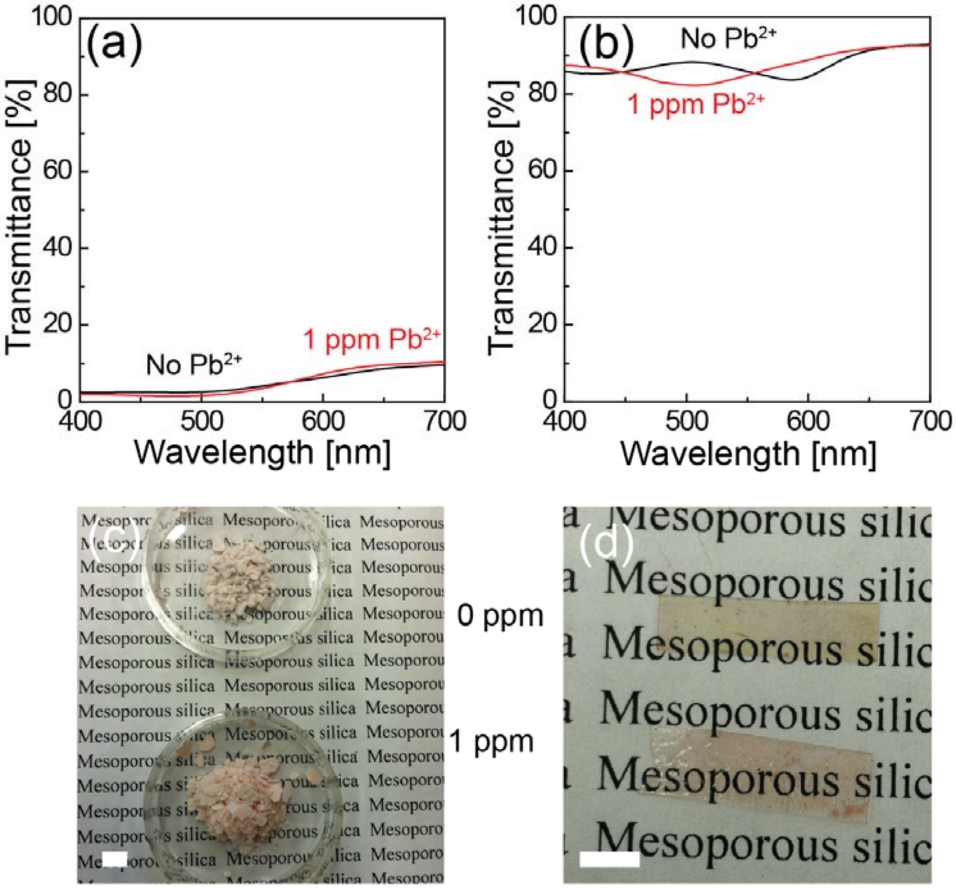
Supporting information Figure S3. Solid-state single-pulse ^{29}Si MAS NMR spectra of (a) as-synthesized, (b) calcined, (c) heat-treated, (d) hydrothermally-treated, and (e) water-vapor-treated mesostructured silica membranes synthesized under otherwise identical conditions with a F127/TEOS molar ratio of 0.004. Solid-state single-pulse ^{29}Si MAS NMR spectroscopy enables quantitative detection for the amount of ^{29}Si atoms that have distinct local electron densities. All spectra exhibit inhomogeneously-broaden signals, which are centered at isotropic chemical shifts of -91, -101, and -110 ppm that are assigned to four-coordinated ^{29}Si atoms that are covalently bonded through bridging oxygen atoms to 2, 3, or 4 neighboring Si atoms, designated Q^2, Q^3, and Q^4, respectively.[5] The relative percentage of each moiety was calculated by deconvoluting the signals into three Gaussian peaks, as summarized in Table S1. The as-synthesized mesostructured silica membrane without any post-synthesis treatment contained significant fractions of Q^2 and Q^3 moieties (13% and 50%, respectively). The low content of fully-condensed Q^4 ^{29}Si species (37%) establishes the relatively low extent of silica cross-linking in this membrane material. Hydrothermal treatment increases the extent of silica cross-linking in the membrane, as established by high-content of Q^4 ^{29}Si moieties (82%), although this material exhibited significant membrane cracking. While both heat treatment and water-vapor treatment yield membranes that are not cracked, heat treatment yields only 39% of Q^4 ^{29}Si moieties in the membrane, which is less than the Q^3 species (52%). By comparison, water-vapor treatment (which is distinguished from hydrothermal treatment by exposure to much lower concentrations of water) results in high Q^4 content (60%) in the membrane, while also being sufficient to prevent micro-cracks or mesopore closure.



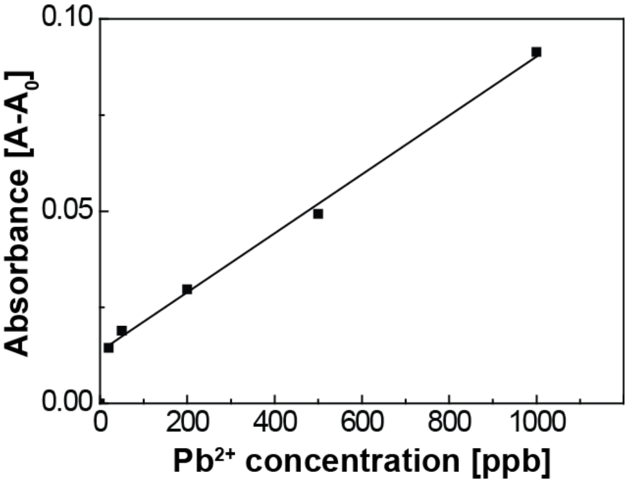
Supporting information Figure S4. Visible-light transmission spectra acquired for an as-synthesized mesostructured silica membrane (~150 μm thickness) and a water-vapor-treated and subsequently calcined mesoporous silica membrane (~120 μm thickness).



Supporting information Figure S5. Closed- and open-pore volume fractions for calcined mesoporous silica membranes prepared with F127/TEOS molar ratios of 0.004, 0.006, 0.008 or 0.010. Closed- and open-mesopore volume fractions in this work were determined based on accessibility for N_2 molecules by using pycnometery and N_2 sorption measurements.



Supporting information Figure S6. (a,b) UV/Vis transmittance and (c,d) images of dithizone-grafted (a,c) mesoporous silica powder and (b,d) transparent membranes (~120 µm thickness) exposed to pH-7 buffer without and with 1-ppm Pb^{2+} ions. Scale bars represent 5 mm.



Supporting information Figure S7. Absorbance changes at 505 nm for 5-piece overlaid dithizone-functionalized transparent mesoporous silica membranes upon exposure to pH-7 buffer solutions containing 0-1000 ppb Pb^{2+} ions. A_0 represents the absorbance at 505 nm for 5-piece stacked dithizone-functionalized transparent mesoporous silica membranes exposed to pH-7 buffer solution containing no Pb^{2+} ions.

Reference

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