

Size-selective molecular transport through silica colloidal nanopores

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Supplementary Information

Materials. Ammonium hydroxide (28-30% as NH_3 , EMD Chemicals, Inc.), tetrabutylammonium hydroxide (40% wt solution in water, Sigma-Aldrich), chloroform (ACS grade, VWR International), methanol (HPLC grade, Mallinckrodt), nitric acid (68-70%, ACS-grade, EMD Chemicals, Inc.), tetraethylorthosilicate (99.999+%, Alfa Aesar), ethanol (200 proof, ACS-grade, Pharmacopaper), PAMAM dendrimer 1,4-diaminobutane core, amidoamine surface, generation 1 (20% wt solution in methanol, Dendritic Nanotechnologies Inc.), PAMAM dendrimer 1,4-diaminobutane core, amidoamine surface, generation 2 (20% wt solution in methanol, Dendritic Nanotechnologies Inc.), PAMAM dendrimer 1,4-diaminobutane core, amidoamine surface, generation 3 (20% wt solution in methanol, Aldrich), PAMAM dendrimer 1,4-diaminobutane core, amidoamine surface, generation 4 (10% wt solution in methanol, Dendritic Nanotechnologies Inc.), PAMAM dendrimer 1,4-diaminobutane core, amidoamine surface, generation 5 (10% wt solution in methanol, Aldrich), Rhodamine B isothiocyanate (mixed isomers, Sigma) were all used as received. Millipore water ($18 \text{ M}\Omega\cdot\text{cm}$) used in all experiments was obtained from a Barnstead "E-pure" water purification system. Acetonitrile (HPLC grade, VWR Scientific) was freshly distilled from calcium hydride. TLC was performed using Silica gel 60 F_{254} on aluminium sheets (EMD Chemicals, Inc.). Dialyses were performed using Slide-A-Lyzer dialysis cassettes (2,000 MWCO, Thermo Scientific). Scanning electron microscopy (SEM) images were obtained using either a Hitachi S3000-N or an FEI NanoNova instrument. UV/Vis measurements were performed using an Ocean Optics USB2000 or USB4000 instrument. A Branson 1510 sonicator was used for all sonications. A Clay Adams Compact II Centrifuge (3200 rpm, Becton Dickinson) was used for all centrifugations. A Fisher Scientific Isotemp Programmable Muffle Furnace (Model 650) was used for all sintering purposes.

Preparation of 350 nm-diameter silica spheres. All silica spheres were prepared according to modifications of previously reported procedures.¹ All glassware was cleaned with Millipore water prior to use. A batch of silica spheres is made by mixing 500.0 mL of an ethanolic solution containing TEOS (51.4 mL, 0.20 mol) with 500.0 mL of an ethanolic solution containing NH_4OH (70.0 mL, 1.1 mol) and water (257 g, 14.3 mol). These two solutions are poured simultaneously in a 2 L Erlenmeyer flask and vigorously stirred. The resulting mixture has final concentrations of 0.2 M TEOS, 1.1 M NH_3 and 17.0 M H_2O . The onset of turbidity after a short while indicates the start of silica sphere formation. After 24 h, the mixture is then poured into 15 mL centrifuge tubes (Corning) and centrifuged for 10 minutes. The supernatant is discarded, leaving the spheres as pellets at the bottom of the centrifuge tubes. Purification of the spheres is achieved by a repetitive cycle of suspending the spheres via sonication for 10 minutes followed by centrifugation for 10 minutes in a gradient series of 10 mL supernatant: 100% water, 25% ethanol, 50% ethanol, 75% ethanol (twice) and finally 100% ethanol. After the final rinsing, the supernatant is decanted and the silica spheres air-dried overnight. The dried spheres are then pre-shrunk by transferring to a Petri dish (breaking any large aggregates with a spatula) and placing in a furnace programmed to heat the spheres for 4 h at 600°C (desired temperature achieved at a heating rate of 20 °C/min).² SEM images are taken of the spheres and the size is determined from 100 individually measured spheres to be $346 \pm 15 \text{ nm}$ in diameter.

Preparation of 230 nm-diameter silica spheres. A batch of smaller size silica spheres was also prepared and pre-shrunk as outlined above. The final concentrations of the reagents were 0.2 M TEOS (51.4 mL, 0.20 mol), 0.4 M NH_3 (26.78 mL, 0.4 mol) and 16.0 M H_2O (288 g, 16.0 mol) in an ethanolic reaction solution of total volume of 1.0 L. The reaction mixture was stirred vigorously for 24 hours at room temperature. SEM images of the spheres were taken and the diameters determined from 100 individually measured silica spheres in each sample to be $261 \pm 20 \text{ nm}$ and $231 \pm 20 \text{ nm}$ before and after preshrinking, respectively.

Preparation of 430 nm-diameter silica spheres. A batch of larger size silica spheres was also prepared and pre-shrunk using a modification of the procedure above. The final concentrations of the reagents were 0.2 M TEOS (51.4 mL, 0.20 mol), 4.0 M NH_3 (267.8 mL, 4.0 mol) and 5.0 M H_2O (90 g, 5.0 mol) in an ethanolic reaction solution of total volume of 1.0 L. The reaction mixture was stirred vigorously and its temperature maintained at 10°C for 6 h. SEM images of the spheres were taken and the diameters determined from 100 individually measured silica spheres in each sample to be $432 \pm 27 \text{ nm}$ and $427 \pm 29 \text{ nm}$ before and after preshrinking, respectively.

¹ (a) W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62-69; (b) W. Wang, B. Gu, L. Liang and W. Hamilton, *J. Phys. Chem. B*, 2003, **107**, 3400-3404.

² (a) T. V. Le, E. E. Ross, T. R. C. Velarde, M. A. Legg and M. J. Wirth, *Langmuir*, 2007, **23**, 8554-8559; (b) A. A. Chabanov, Y. Jun and D. J. Norris, *Appl. Phys. Lett.*, 2004, **84**, 3573-3575; (c) S. Zheng, E. Ross, M. A. Legg and M. J. Wirth, *J. Am. Chem. Soc.*, 2006, **128**, 9016-9017.

Preparation of as-sintered nano-frits.³

The nano-frits were prepared by a vertical deposition onto a glass substrate of ~12 wt% colloidal solutions of pre-shrunk silica spheres in ethanol. The resulting membranes were then gently lifted from the substrate and sintered in a furnace for 12 h at 1050°C (desired temperature achieved at a heating rate of 20°C/min).² The sintered silica colloidal membranes

were noticeably much more robust and durable, making handling easier. SEM images of these nano-frits were taken to give average diameters of 252 ± 10 nm, 100 ± 6 nm and 362 ± 27 nm, respectively in the order of description above, as measured from 100 individual spheres in each colloidal membrane. The thickness of each colloidal membrane was measured with a Vernier caliper at six different points throughout the piece. To make as-sintered frits, the pieces were then sandwiched between two PTFE washers (5.0 mm inner diameter, 14.0 mm outer diameter and 1.0 mm thickness, Small Parts, Inc.) with Loctite Hysol 0151 Epoxy (Fig. 1S). Nano-frits constructed as such were allowed to cure for at least 24 h prior to use for diffusion experiments.

Preparation of rehydroxylated nano-frits. Hydroxyl groups were reintroduced onto the surfaces of the colloidal membranes by immersing

the pieces in an aqueous pH 9.5 solution of tetrabutylammonium hydroxide (in a polyethylene bottle) maintained at 60°C for 24 h in an oil bath.^{2a} The rehydroxylated pieces were then washed with Millipore water, 1 M nitric acid, methanol, Millipore water and acetonitrile consecutively. The air-dried pieces were then made into nano-frits in the same manner as above.

Modification of Dendrimers. PAMAM dendrimers of generations 1 to 5 were used as received and dye-labeled with Rhodamine B isothiocyanate according to the following procedure. The dye was initially dissolved in not more than 2.00 mL of absolute ethanol. Dissolution was performed by stirring under an inert atmosphere (e.g. under N₂ gas). An aliquot of the dendrimer was then added and allowed to react for 1 h at room temperature. The dendrimers were found to react nearly stoichiometrically with the reactive isothiocyanate group on the dye. The resultant ratio of dye per dendrimer molecule ranged from 2 to 6, as evaluated by UV-Vis absorbance measurements at 546 nm (determined λ_{max} with measured $\epsilon = 52,829 \text{ M}^{-1} \text{ cm}^{-1}$ from prepared standard solutions of the dye). The success of the reaction was confirmed by TLC analysis (mobile phase, CHCl₃/MeOH/H₂O in a 70:30:4 v/v/v ratio).⁴ The dye-labeled PAMAM had an R_f value of 0 while the excess dye is observed at R_f close to 1. Dye-labeled dendrimers were purified via dialysis. The reaction mixture was placed in a Slide-A-Lyzer dialysis cassette with a 3-mL volume capacity and 2,000 MW cutoff and dialyzed overnight with stirring against 400 mL of deionized water. The dialysis bath was changed three times.

Diffusion measurements through nano-frits. Diffusion experiments through the colloidal membranes were performed by placing a nano-frit between two connected 1-cm quartz cuvettes (Fig. 2S). The feed cell contained 4.00 mL of an aqueous dye-labeled dendrimer solution while the reservoir cell contained 4.00 mL of deionized water. The nano-frit was placed between two Kalrez o-rings to guard against leaking, and the whole assembly was then secured with a clamp. Each cell was covered with Parafilm to prevent eventual evaporation, and the contents of both cells continually stirred. The reservoir cell was placed between two fiber optic cables and was initially blanked. The flux was monitored by recording the absorbance at 546 nm in the reservoir cell for at least 18 h. Data points were acquired every 150 s with an initial delay of 150 s. Prior to using a nano-frit for a new trial, it was immersed in deionized water for at least two days and the water was replaced occasionally to ensure removal of any previous probe molecule from within the colloidal membrane. All measurements were repeated in triplicate.

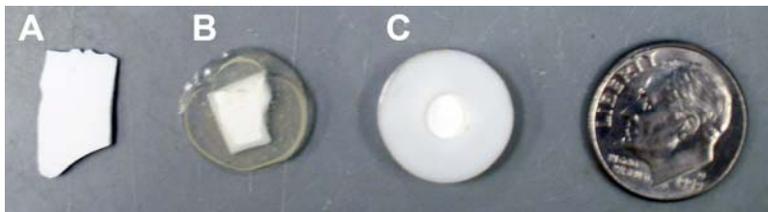


Fig. 1S A sintered colloidal crystal (A) as made and (B) embedded in epoxy. (C) A membrane constructed by sandwiching a sintered colloidal crystal embedded in epoxy between a pair of PTFE washers (a dime is included for size comparison).

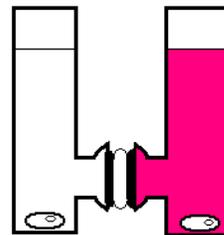


Fig. 2S Diffusion experiment set-up. The absorbance at the reservoir cell (left) is monitored at 546 nm as the species diffuse from the feed cell (right).

³ A. K. Bohaty, J. J. Smith and I. Zharov, *Langmuir* 2009, **25**, 3096.

⁴ D. A. Schlapak, N. Saucedo-Zeni, G. Latini, H. J. Gruber, P. Mesquida, Y. Samotskaya, M. Hohage, F. Cacialli and S. Howorka, *Langmuir*, 2007, **23**, 8916-8924.