Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Selective and ATP-driven transport of ions across supported membranes into nanoporous carriers using gramicidin A and ATP synthase†

Vitaliy Oliynyk [a]‡, Christian Mille [a,b]‡, Jovice B. S. Ng [a], Christoph von Ballmoos [c], Robert W. Corkery [b,d] and Lennart Bergström [a] *

[a] Department of Materials and Environmental Chemistry, 10691 Stockholm University, Stockholm, Sweden, [b] YKI, Institute for Surface Chemistry, Box 5607, 11486, Stockholm Sweden, [c] Department of Biochemistry and Biophysics, Stockholm University, Stockholm Sweden. [d] Department of Chemistry, Division of Physical Chemistry, KTH Royal Institute of Technology, Stockholm, Sweden.

‡ These authors contributed equally to this work.

1. Experimental Information

1.1 Synthesis of nanoporous silica particles

Polyethylene oxide hexadecyl ether, Brij 56 (Sigma-Aldrich), a nonionic surfactant, was used as the templating amphiphilic molecule, and tetraethoxysiloxane, TEOS (Purum >98%), was used as the silica source. Hydrochloric acid (HCl) (Normapur, VWR) and ethanol (99.7%, Solveco AB) were used as received. Millipore-grade water was used in all experiments. The precursor solution was prepared by mixing a solution consisting of 3.17 g of Brij 56 in 62 g of ethanol with a solution of 5.4 g of HCl (1 M) in 12 g of ethanol. TEOS (10.4 g) was added to the precursor solution and allowed to hydrolyze under vigorous stirring at room temperature for 20 min. The mesostructured nanoporous silica particles with spherical shape have been produced by an aerosol-assisted technique using a vibrating orifice aerosol generator (VOAG Model 3450, TSI Inc., USA), essentially following previously established procedures.[1,2] In short, the operation of the aerosol generator is based on the breakup of a cylindrical liquid jet by a vibrating orifice (10 μm) into uniform droplets. The precursor solution is forced through the vibrating orifice at constant speed using a syringe attached to a stepper motor. The generated droplets were injected axially from the vibrating orifice with a turbulent dispersion air jet (~15 cm^3/min) to suppress any coalescence of droplets followed by a greater volume of a laminar flow of dilution air (~5 L/min) into a vertical drying chamber (φ= 10 cm) where evaporation of solvents (essentially ethanol and water) takes place. The drying chamber is attached by a stainless steel tube (4 cm diameter) to a three-zone furnace held at 250 ºC (calibrated with thermocouples) where the silica particles are condensed before the particles are collected on a filter (Pall, A/D Glass fiber filter, with diameter 4.7 mm and pore size 3 μm). The collected mesostructured particles were calcined at 550 ºC for 4 h in air to remove the surfactant template.

1.2 Characterization of the monodisperse mesoporous spheres

The morphology of the particles was determined using scanning electron microscopy, JEOL 820 SEM, operating at 8-10 keV. The particles were thinly spread onto a carbon film supported on a brass stud and gold coated. The XRD patterns were obtained using a XPERT-PRO powder diffractometer (CuK_α radiation, λ = 1.5418 Å) over the range of 2θ = 1.0-6.0º. Porosity measurements were performed volumetrically using a Micromeritics ASAP 2020 analyzer. The samples were degassed at 150 ºC for 10 hours and data collection started typically at 77 K, following a program consisting of both an adsorption and desorption branch. The specific surface areas, SBET (m^2/g) were calculated using the Brunauer-Emmett-Teller (BET) model within the 0.05 – 0.15 p/pº relative pressure region. The pore volume, V_{pore} (cm^3/g), was estimated from the amount of N_2 adsorbed at a relative pressure around 0.99. The pore size distribution was calculated based on the non-local density functional theory (NLDFT) model.[3] The average particle diameter is determined from the average of 50 individual spheres from the SEM images (6.00 ± 0.2 μm). See Supporting Figure S3.

Characterization of mesoporous silica particles

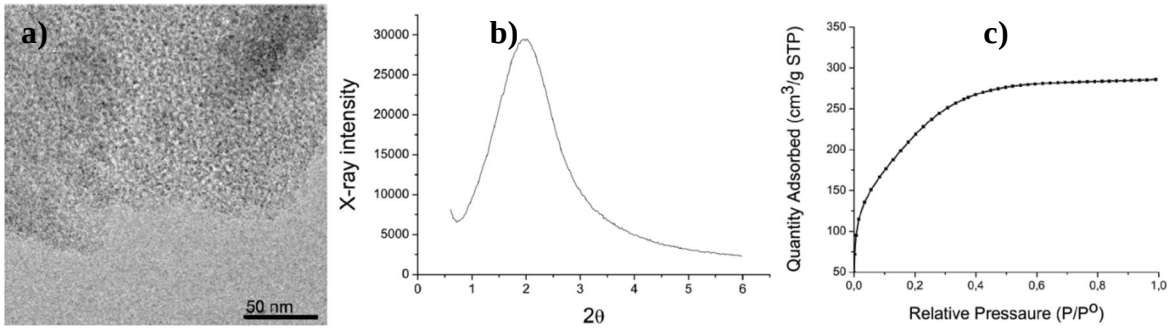

Fig. S1: Characterization of mesoporous silica particles. a) A representative transmission electron microscope image; b) the X-ray diffraction spectra; and c) the nitrogen isotherm of the calcined mesoporous particles.

CLSM scans of non-sealed particles before and after Na^+ uptake

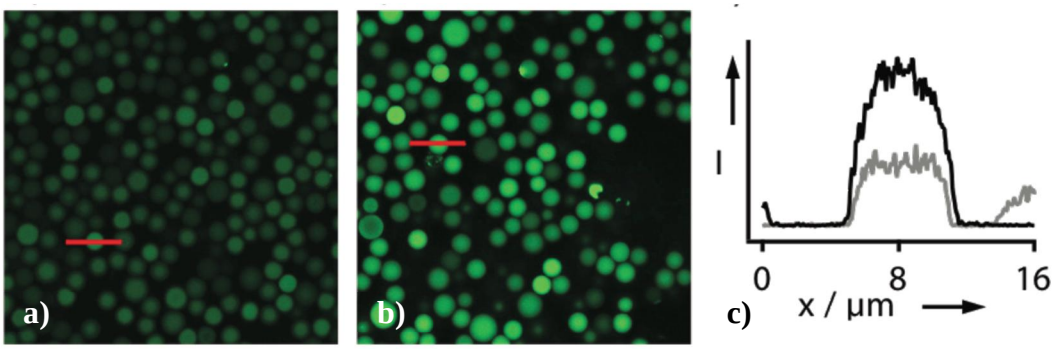

Fig. S2: CLSM scans of particles without lipid bilayers sealing before and after Na+ uptake. Images a) and b) corresponds to the two extreme cases of 0 mM and 100 mM of Na+ inside particles, respectively, preloaded with the same concentration of SG. Graph c) is an intensity plot across representative particles along red lines in a) and b).

CLSM images of the particles sealed with DLPC lipid bilayer without gramicidin A

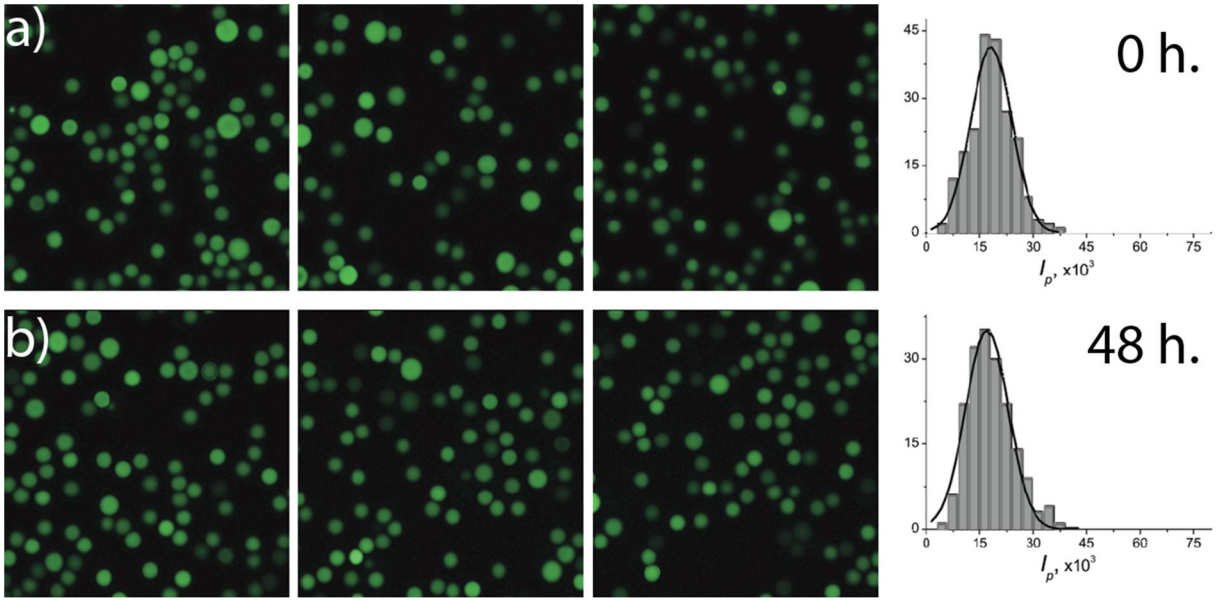

Fig. S3: CLSM images of mesoporous silica particles loaded with Sodium Green and sealed with DLPC lipid bilayer without gramicidin A. Panel shows three representative-CLSM images and the histograms of the integral intensity per particle a) before and b) 48 h. after injection of Na^+ to the outer bulk solution. CLSM images of optical sections at particles equator in each panel were recorded keeping the experimental conditions, microscope hardware and software settings identical.

References

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